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THE SYNTHESIS AND PROPERTIES OF
RIGID TRANSPARENT POLYURETHANE ELASTOMERS

by

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DEDICATION

This entire work up to the peak of my educational career is respectively dedicated to:

my father, Mr Nagarbhai N. Panchal
and mother, Mrs Kamuben N. Panchal.

Their continuous encouragement and patience along with my brothers, sisters and in particular my wife, Aruna, whose prayers and perseverance have transformed my ambition into a reality.

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ABSTRACT

Transparent polyurethanes have been synthesised producing flexible to rigid polymers. Thermoplastic polyurethanes as well as thermoset (crosslinked) polyurethanes have been made. The syntheses of these elastomers were all based on polycaprolactone polyols of differing molecular weight, and functionality; the thermoset polyurethanes were synthesised with triols and tetra-ols. Several diisocyanates were used, but most work concentrated on 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI or Desmodur W); others included isophorone diisocyanate (IPDI) 1,4-cyclohexane diisocyanate (CHDI), para-phenylene diisocyanate (PPDI) and 2,2,4-(2,4,4-) and trimethyl-hexamethylene diisocyanate (TMDI). The synthesis method varied with the diisocyanate and crosslinking system used.

The approach was to make a series of polyurethanes over the range flexible to rigid; this was accomplished by synthesising polymers with varying polyol molecular weights (soft segment content) and block ratios (hard segment content). Observations of physical properties gave values for modulus, ultimate tensile strength, elongation at break and hardness; some of the polyurethanes were found to have good impact and ballistic performance.

Investigation of the effect of different chemical constituents on the properties was carried out by way of thermal analysis techniques such as Dynamic Mechanical Thermal Analysis (DMTA) and Differential Scanning Calorimetry (DSC). X-ray and infra-red (IR) techniques were also used to elucidate the reasons for transparency in the polymers. The long term stability of these polymers is also important and the systems used were especially chosen to maximise retention of physical properties and transparency.

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CHAPTER 1

1A.1 ANCIENT ARMOUR

The earliest basic form of protection evolved from using furs and skins for clothing as well as protective materials against injury. The Assyrians (1100-600 BC), the Persians (500 BC), the Greeks (8-6 BC) followed by the Romans brought about the use of metallic armour for both the soldier and the horse. Mail armour called 'byrnie' or 'ring woven corselet' was used by the Saxons in 640 AD. By 1200 AD, the Normans were using a full suit of mail called 'haubeck' and by 1400 AD complete armour was available. By the 16th century the armour was improved for strength and by the following century was getting too heavy, such that an unhorsed knight in battle was easy prey. Personal armour worn by knights represented the ultimate development of early armour, and due to its weight, discomfort and reduction in mobility, it disappeared almost entirely from the battle scene. Use of animals (e.g. horses) became obsolete. The history of armour has been well documented, a few of many references [1-3] are given.

1A.2 MODERN ARMOUR

Ancient armour showed excellent craftsmanship in design but lacked a thorough approach to protection of the individual soldier. Since the turn of the century ballistic evaluation of armour has been approached more realistically by simulation of service conditions of attack. This has, however, been a continuously changing problem for all services because of the new specialised weapons and materials which are introduced constantly in modern warfare.

The essential need in modern warfare is to have an effective threat analysis. Armour is expensive and before decisions are made it is

necessary not only to define the ballistic characteristics of the wounding agents, but also the relative likelihood or frequency of these agents being encountered and the relative exposures of the body. An analysis is important from data collected on wounds in battle casualties for the types of injuries (eye, head or other) sustained with the protection and armoury used in the battle. The analysis would give information regarding which parts of the body require protection and what changes in armour design are needed to improve protection. Another area of concern is the effectiveness of the armour, this involves ensuring that protective devices do not pose too great a barrier to efficient accomplishment of the wearer's mission. The aim being more protection, lighter weight and greater flexibility. Many references can be found, two are given [4-5].

1A.3 TRANSPARENT ARMOUR

Development of transparent armour is important and receiving more attention as tasks required of military and civilian personnel need materials which are transparent and impact resistant. Military use is varied, including windshields for aircraft and ground vehicles, goggles, visors etc. In the civilian sector, workers in a variety of disciplines are required to use impact resistant goggles, visors, shields etc such as laboratory personnel, police, riot control personnel etc. Transparency is limited to the visual range of those wavelengths of light responsive to the eye. Impact resistance in terms of armour applications has to do with the ability of a given material to stop or defeat impacting missiles of varying shapes, sizes, velocities and energies.

In the general field of optics, inorganic glasses and organic plastics are prime materials, and throughout the years glasses have remained the premier optical materials. The use of plastics in optical applications is by comparison relatively new, plastics have the advantage of being easily formed into intricate shapes and can be polished to high quality glass optics at far less cost. In terms of armour application the energy absorbing mechanisms of plastics

offer advantages over glass. Glass shattering is an obvious hazard and plastics can be designed not to shatter or in combination with glass inhibit the shattering of glass.

Plastics can also be toughened and improved ballistically by several techniques, originally developed for non-transparent armour applications. The addition of a rubbery second phase to a glassy polymeric matrix forming a copolymer is one such approach. If the rubber particle size is smaller than the wavelength of light, optical clarity and insignificant hazing should be achievable. This would effectively eliminate the scattering of light at the interface between the two phases. Matching indices of refraction of two materials will also result in reduced light scattering and resultant transparency or optical homogeneity [6-7]. Lamination of dissimilar materials with retention of optical clarity is another option that could be used for improved ballistic resistance.

Army material which provides both the required visibility and the ballistic protection is termed 'Transparent Armour'. This combination of optimum visibility and resistance to projectile penetration has been a difficult item to develop, largely because of the inherent incompatibility of these properties in available materials.

The development of transparent armour up to just after World War II usually consisted of 'safety' or 'bullet proof' glass, which was two or more panels of glass laminated with a thin flexible plastic interlayer. It is well known that glass-plastic armour has improved ballistic protection than that obtainable with the same weight and thickness of safety glass. Ofner [8] published a literature survey on 'Transparent Armour' containing 133 references which include the topics: glass, plastics, glass-plastics, single crystal ceramics, dynamic properties of polymers, vision blocks, military handbooks and drawings.

1A.3.1 Face Visors

The earliest ballistic protective visors for the face consisted of metallic materials perforated by slots or holes to permit vision. Such a system detracts severely from the visual awareness of the wearer and in jobs like Explosive Ordnance Disposal can be a positive danger to him. The present combat soldier can be provided with armour covering the top and back of the head, neck, thorax, abdomen and pelvic area. The only vulnerable area left exposed, if we accept that wounds to the arms and legs are not usually incapacitating, is the face. Protection of the face is important not only because of the vulnerability of the eyes but also because a fragment penetrating the face may well enter the brain.

Suitable materials must have a high degree of visual transparency, exhibit stable optical properties, be impact and scratch resistant, and be light weight and rigid. These must also be capable of fabrication into curved visor screens giving little or no optical distortion, if they are to provide a wide unobstructed field of view and cover the whole face. Plastic materials are most desired as they have high impact resistance to small velocity missiles, being lighter, more transparent and more resistant to accumulation of water vapour on their surfaces. The main disadvantage of plastics is its susceptibility to scratching.

1A.4 TRANSPARENT POLYMERS

Natural and most synthetic rubbers can be fabricated into thin sheets with a fair degree of transparency, the refractive indices of the fillers and rubbers must be similar [9-11]. Such rubbers often become opaque when stretched and do not recover when the stress is relaxed. A further disadvantage of many transparent rubbers is that they are coloured. Transparent material presently known with sufficient high impact strength to be used as riot protective visors and shields is bisphenol A polycarbonate, which also has a worthwhile level of ballistic resistance. The trade names are

'Makrolon' manufactured by Bayer, Germany and 'Lexan' by General Electric Plastics BV Holland. The disadvantage of polycarbonate is that its optical clarity is readily degraded by surface abrasion and its susceptibility to stress cracking in a variety of solvents. A wide variety of transparent or semi-transparent polymers have been proposed as suitable alternatives to polycarbonate, but in most cases they suffer from poorer impact properties, cold cracking defects or slowly lose plasticiser.

Acrylic materials ('Perspex', 'Oraglass' etc) have been extensively used as optical and personnel protective devices, but suffer some brittle fracture on ballistic impact, which can be a serious threat to personnel. Polycarbonate eliminates the brittle fracture problem, and also has a slight ballistic advantage over poly (methylmethacrylate) but shows poor resistance to abrasion and cleaning solvents.

1A.5 COMPOSITE ARMOUR AND VISOR MATERIALS

A number of armours consisting of a polycarbonate sheet as a back face and a harder material as the front face have been evaluated [12]. Polymethylmethacrylate (PMMA) was the principal material used for the front face, being rather harder than polycarbonate, yet still easy to form a fracture on the front face thus spreading the load on the back face over a large area [13] on ballistic impact of thick sections.

Early work carried out with PMMA and polycarbonate in contact showed unbonding of the laminate to occur, the effects of an airgap and of various adhesives/interlayer systems were later also studied [12]. The initial attraction of an interlayer is that it removes misting problems caused by moisture getting into the airgap between the front and back faces, but there is also evidence [14] that ballistic performance can be improved by an interlayer. Interlayers used included 'Twinstick' a double sided transparent adhesive tape and

'Lexgrip' an adhesive recommended for sticking 'Lexan' but both these tapes degrade the optical quality of the composite.

Being a harder material, one would expect glass to be a more satisfactory front face than PMMA and tests [12] were carried out using Sodalime glass (Pilkington Bros Ltd) and borosilicate glass (Corning 7740) with Twinstick as a bonding agent. The problem of using glass in visors is likely to be one of forming it to the same curvature as the polycarbonate backing. Tests show that both the glass/polycarbonate armours are significantly better than PMMA/polycarbonate, but there is insufficient data to support a choice between the two types of glass.

A number of so called armoured glasses are commercially available. Three of these have been tested [12], two consisted of alternate layers of glass and polycarbonate with an unknown adhesive and the third ('Armourglas') consisted of sheets of glass bonded together. All three were poor even by the standards of polycarbonate alone, indicating there is little merit in using glass alone or in alternate plies with polycarbonate.

In 1976 a variety of coatings, taken from studies (see [15-16]) on helicopter windshield materials, on polycarbonate were evaluated by the US Army. These materials were compared to cellulose butyrate, the standard material then used for the sun, wind and dust goggles. The results of this study and other available data indicated polycarbonate to be the material of choice. Since it has optical clarity and good ballistic properties at thicknesses acceptable for optical goggles, and it can be coated to provide a measure of scratch resistance without loss of its ballistic properties.

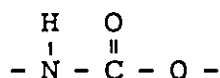
Early work on transparent block copolyurethanes was carried out at the Army Centre in Watertown, USA [17] and also at PERME (Propellants, Explosives, Rocket Motor Establishment) at Waltham Abbey [18-19]. The ballistic results were good and in some cases comparable to polycarbonate at the same thickness. Polyurethanes

have therefore been found to represent one of the few classes of transparent polymers which approach the performance of polycarbonate.

1B.1 POLYURETHANES - INTRODUCTION

Polyurethanes are a family of materials which can be formulated to produce a range of products from hard to soft, solid to low density foams. Their versatility and outstanding properties find use in a wide variety of commercial materials [20] in many forms including films, foams, fibres, plastics, surface coatings and elastomers. Most notable amongst their properties are excellent abrasion resistance, good low temperature flexibility, high modulus and impact strength.

The term polyurethane is one of convenience rather than accuracy as they are not derived by polymerising a monomer 'urethane' molecule, nor are they always polymers containing primarily urethane groups. Polyurethanes [21] include those polymers that contain a significant number of urethane groups, regardless of what the rest of the molecule may be. The polymers are characterised by the urethane linkage:



although other groups such as ester, ether, urea, biuret, allophanate, amide etc may also be present in the polymer molecule.

1B.2 HISTORY AND GROWTH OF POLYURETHANES

There has been a marked increase, since 1950 (Figure 1B.2.1) of the use of polyurethane chemicals amounting to three million tonnes being sold by 1987. Polyurethane chemicals have a great many diverse end uses, with about 75% (Figure 1B.2.2) being used for flexible and rigid foams. As polyurethanes are generally expensive

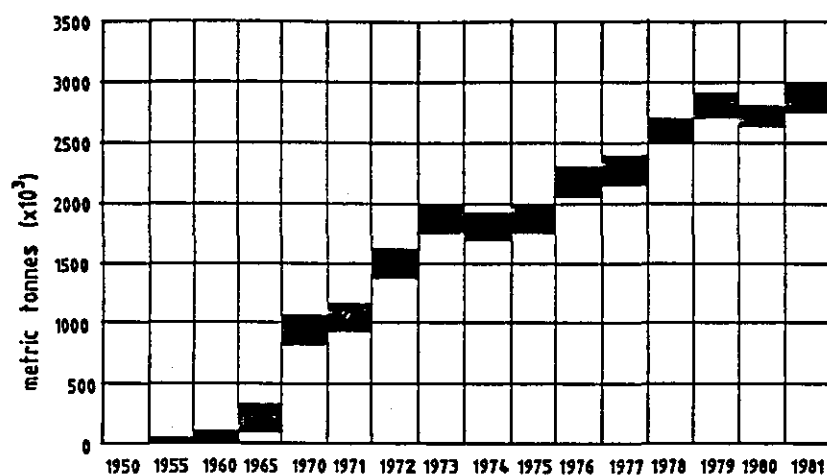


FIGURE 1B.2.1: GROWTH OF POLYURETHANES

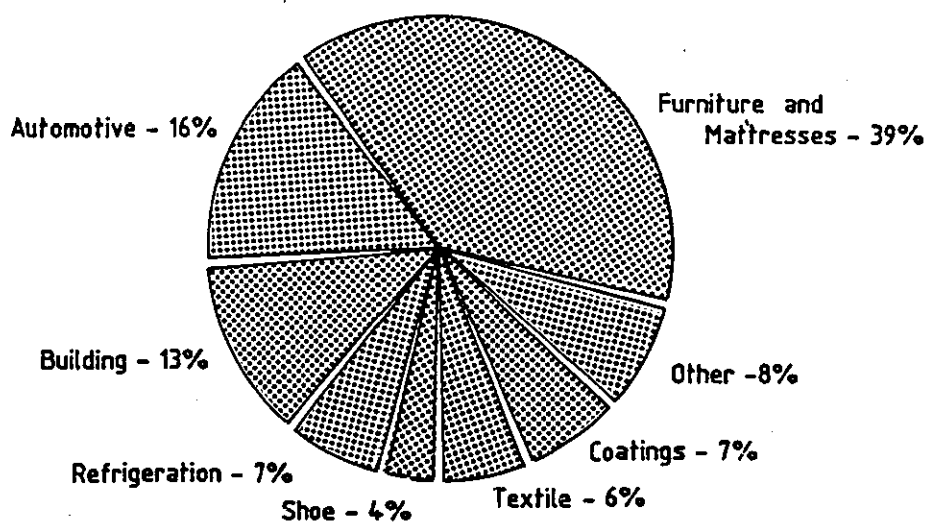


FIGURE 1B2.2: WORLD CONSUMPTION OF POLYURETHANES - 1981

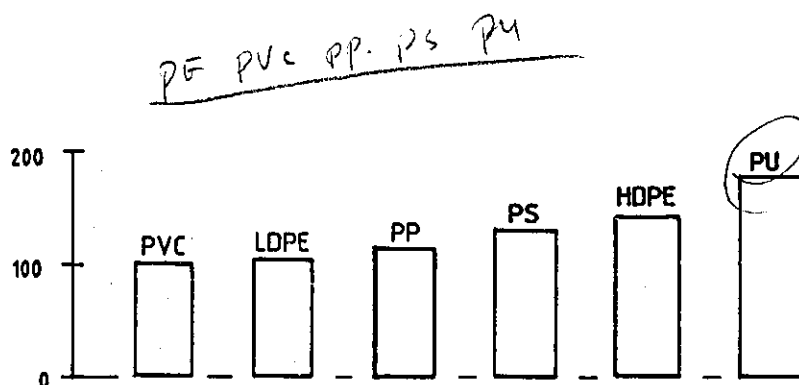


FIGURE 1B2.3: COST INDICES OF POLYURETHANES - JANUARY 1983
AVERAGE GERMAN PRICES

(Figure 1B.2.3) they do not compete with the bulk commodity thermoplastic polymers.

The investigation of urethanes (originally by Wurtz and Hofman [22]) leading to their commercialisation began with work from Professor Otto Bayer [23] and co-workers at I.G. Farbenindustrie A.G. (Leverkusen), Germany in 1937. A patent [24] was later published covering the basic principles of the processes involved. The interest in the potential of the diisocyanate reaction grew, with development of the 'I' Gummi class of materials in the mid 1940s [25] and the 'Vulkollan' castable elastomers by 1952.

In the late 1940s, Bayer AG and Henecke AG worked together to produce a continuous process for flexible foam. Later ICI, Du Pont, Union Carbide, Shell Chemicals Ltd, Dow Chemicals and others also marketed a wide range of polyurethane products. Many inventions and developments have been made, a few are listed below:

1. 1955-1960:

Thermoplastic polyurethanes, invented, tin/amine catalyst developed, hot cure mouldings of flexible foams

2. 1960-1965:

Rigid foam blowing by chlorofluorocarbons, lamination processes developed for rigid foams

3. 1965-1970:

Isocyanurate rigid foams, microcellular car bumpers, shoe solings and RIM developed

4. 1970-1980:

Flat block flexible foam processes, RIM and RRIM processes and applications developed, MDI moulded flexible foams.

New developments are still occurring, such as the recent new 'Vertifoam' process, which produces foam in a vertical direction [26] as opposed to conventional horizontal processes. Worldwide polyurethane consumption is predicted [27] to increase by 4% per year, mainly in MDI based systems. The highest growth rate is expected in the elastomer area [28] due to the projected growth in RIM-type mouldings. Despite the increased demand, capacities for isocyanate and polyether polyols will not be fully utilised. The expected increase of major isocyanates (MDI and TDI) with polyether polyols is shown in Figure 1B.2.4.

Polyurethanes are certainly the most developed reactive processing chemical systems available today and chemical suppliers are able to define suitable products for many major industrial sectors. The physical, mechanical and processing properties of the polyurethanes are still being developed in several applications sectors, one such recent development is transparent polyurethanes. Although it has certainly come of age, the polyurethane industry is still far from being mature.

1B.3 TRANSPARENT POLYURETHANES AND SOME USES

Commercial applications of transparent polyurethanes have only recently been found, mainly in aircraft canopies, laminates, visors and coatings etc. In some applications, polyurethanes have replaced polycarbonate which is vulnerable to surface damage by abrasion, erosion, weather, chemical solvents and cannot be easily polished. The urethanes have excellent thermal stability, hydrolytic stability, adhesion and are resistant to weather, abrasion and are now commonly used as surface coating of polycarbonate aircraft canopies [29].

A considerable amount of data has been obtained on helicopter and aircraft windshields (such as found in [17,30 and 31]) by the US Army at Watertown, MA. The most prevalent problems are abrasion, loss of transparency, spallation and being vulnerable to small arms

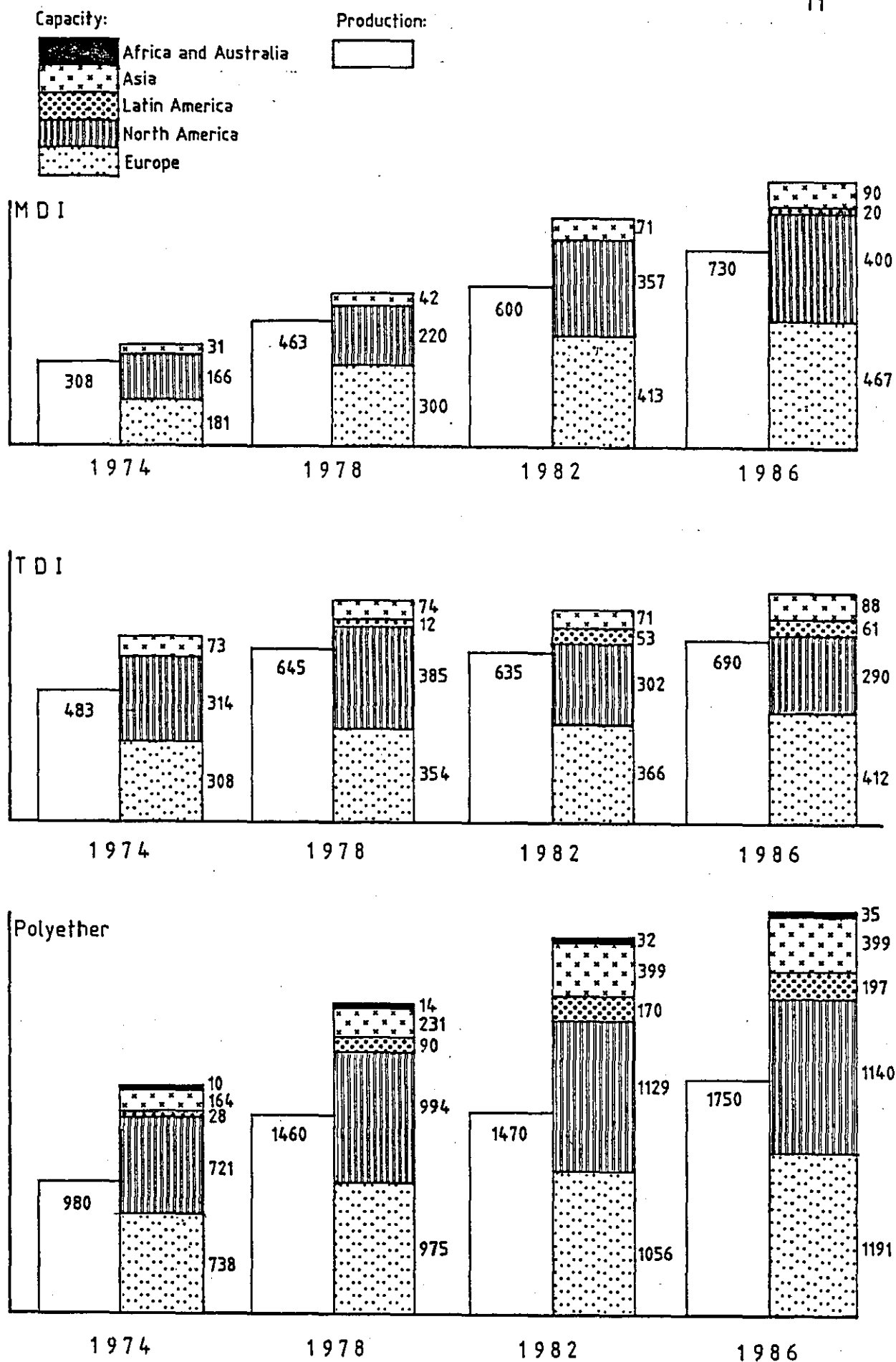


FIG. 1B2 . 4 . Capacities by region and world population, 1000 tons.

projectiles and shrapnel. Abrasion is a problem arising from windshield wiper action and the impact of sand and gravel thrown up by the rotor blades. Acrylic windshields have deficiencies resulting from the brittle behaviour on ballistic impact causing radial cracking which degrades the optical clarity and may produce backspall which can prove dangerous to persons inside.

Spallation plays an important role in the impact process as displayed in the property of brittleness and has been described [32] essentially as fracture away from impact. The suppression of spallation is a powerful method of increasing impact resistance. A solution would be the substitution to a material which fails in a ductile fashion.

A series of commercial acrylics, polyurethanes and polycarbonates, singly and as composites with and without coatings have been studied and reported [33]. It was found that chemically strengthened glass provides the most abrasion resistant surface while unprotected polycarbonate is the poorest. Spallation is not significantly affected by hard surface coatings when applied to one side or both sides, but a ductile failure mode can change to a brittle failure if the coating becomes too thick. Spallation of polyurethane and polycarbonate materials when impacted consisted of a 'closed hole', due to ductile failure, resulting in optically clear materials as compared to acrylics which suffer clarity problems caused by spallation.

A series of experiments to evaluate the ballistic performance of transparent urethane block copolymers compared to polycarbonate were carried out by A F Wilde and others [17,30,31,34]. They synthesised polyurethanes based on 2,4-TDI, polytetramethylene oxide (PTMO of 1000 and 2000 M.wt) and 1,4-BD. It was observed that higher cure temperature, longer room temperature cure, higher block ratio and lower PTMO M.wts gave harder, more rigid and transparent specimens with improved ballistic performance. These materials gave good ballistic performance, but modifications are required for

improvements as compared to polycarbonate giving the best combination of properties in terms of ballistic performance and optical clarity.

The ballistic performance is characterised in terms of a quantity called the ' V_{50} ' which is defined and experimentally determined in a standard way [35]. The V_{50} limit velocity is an estimate of the mean velocity at which an average 50% of the (standard) projectiles striking the target will defeat it. A defeat occurs when there is a through hole in the target which allows the projectile to pass through it.

Security glazing of vehicles has brought a mini-boom due to armed robberies, riots and terrorism. Bullet stopping glass laminates are thick and heavy. As laminates of plastic and glass are available, the requirements are optical clarity, sufficient adhesion to glass to prevent splinters flying around and enough impact strength to withstand occupants being thrown against the laminate during a crash. In addition the laminate should have sufficient edge stability which would prevent water from penetrating the edges causing discolouration and delamination.

These include glass/polycarbonate and glass/acrylic laminates. A recent development is a laminate interlayer of an optically clear adhesive film of modified aliphatic thermoplastic polyurethane (Figure 1B.3.1 [36]) having less than 2% haze. This laminate interlayer not only solves the problem of bonding to both plastic and glass, but has enough 'give' to accommodate the difference in thermal expansion. Exterior lamination of specially designed aliphatic films can contribute additional scratch resistance and durability. For equal bullet stopping power, the glass/polycarbonate laminate weighs only 40 to 50% as much as glass and is proportionally thinner.

Some earlier polyurethane interlayers for laminated safety glass suffer from one or more drawbacks which makes them unsuitable [37]. This data shows the poor optical properties obtained with polyurethane interlayers of other isocyanate systems. The preferred system is a cycloaliphatic diisocyanate (H_{12} MDI) with poly 1,4-butylene adipate and 1,4-BD. The substitution to polyoxytetramethylene glycol (polyether) results in an unacceptable hazy level in the laminate.

Glass laminates in the most part are made by using polyvinyl butyral (PVB) in sheet form as the interlayer material, produced by using high temperature and pressure laminating techniques which are difficult and cumbersome. PVB is unsatisfactory for laminating glass to polycarbonate. The laminated structure based on the conventional plasticised PVB develops stress cracks in the polycarbonate in a short time and optical clarity soon drops below permissible levels. These difficulties can be overcome by an easily handled resinous polyurethane [38] which provides a laminate of suitable properties.

The consumption of PVB as an interlayer in automotive safety glass is estimated at being 50 million pounds per year. There is a constant drive to produce safer windshields and new concepts in their design can now be considered with modified polyurethanes; less weight through thinner glass while retaining structural and safety properties are now achievable. Polyurethanes will continue to be an important factor in aircraft and land transportation. A new approach is to retain the PVB interlayer and add an inner layer of polyurethane (Figure 1B.3.1). The new structure known as the 'laceration windshield' [39], uses the polyurethane's strength both to prevent penetration and to act as a shield from the broken glass. Another version uses a single ply of glass with an inner layer of polyurethane (Figure 1B.3.1). The idea is to reduce weight and cost, the polyurethane being designed for superior scratch resistance.

Transparent polyurethanes are finding many uses and presently permeation studies are being carried out for possible use against chemical warfare agents, such as mustard gas.

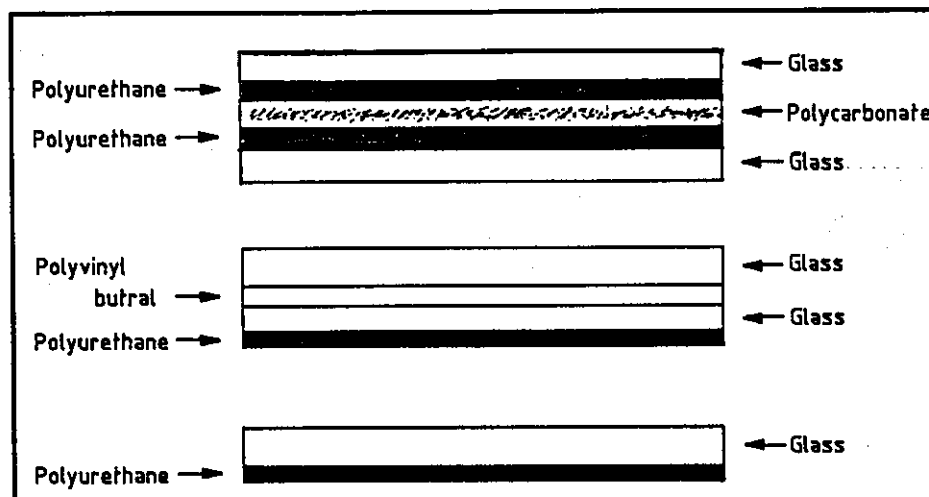


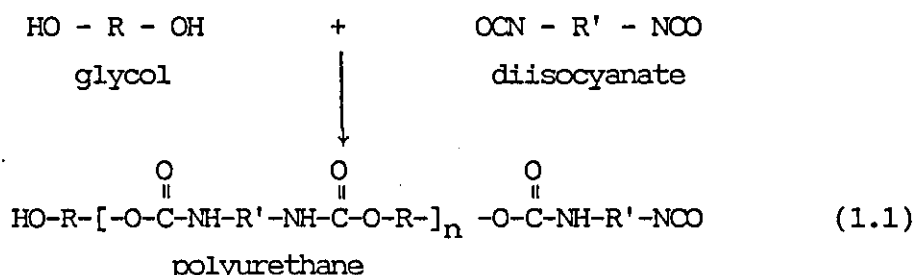
FIGURE 1B3.1: TYPICAL NEW SECURITY GLASS CONSTRUCTION

Typical of new security glass is construction (a) based on glass polycarbonate laminate with an optically clear adhesive film of modified aliphatic polyurethane. Windshield safety glass construction (b) retains^a PVB interlayer and adds^{an} inner layer of polyurethane. Another version (c) has single glass ply and inner layer of scratch-resistant polyurethane for safety functions.

1B.4 CHEMISTRY OF POLYURETHANES

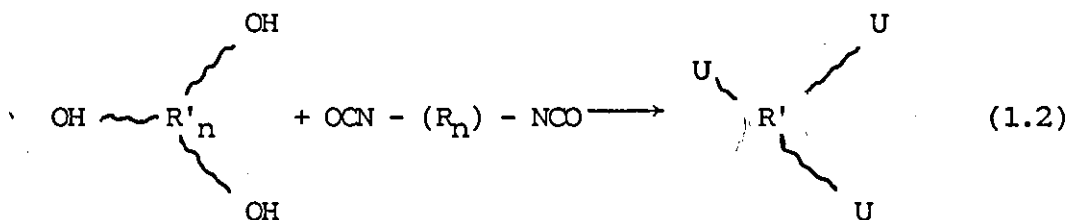
A variety of reactions can be used to produce polyurethanes, such as the reaction of chloroformic esters with diamines and carbamic esters with diols [20]. By far the most widely used method to polyurethane synthesis is the reaction of^s isocyanates with active hydrogen containing groups, this reactivity forms the basis of polyurethane chemistry [21].

Polyurethanes are most commonly made by the reaction of equivalent amounts of a glycol and a diisocyanate according to the equation:



Although these are shown to have reactive end groups the molecular weights of the polymers are high enough to make the end group concentration quite low. The actual processes would depend on the nature and arrangement of chemical groups between the urethane links. Thus materials which are rubbery, fibre forming or conventionally thermoplastic could all be formed.

If either the glycol or diisocyanate contains more than two functional groups then a more complicated situation occurs



Crosslinked polyurethane

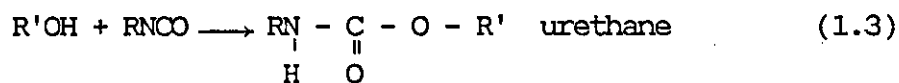
R = alkyl or Aryl group

U = urethane link

Crosslinks will form to produce hard, soft or rubbery materials. The properties will be affected by many factors such as intensity of crosslinking, functionality of reactants, molecular weight

distribution between reactants, prepolymer molecular weight etc. The most important primary reactions of isocyanates are shown below:

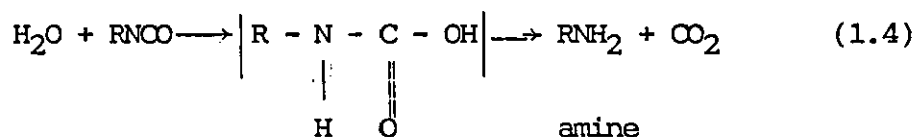
i) Reaction with Alcohols



Primary alcohols are more reactive than secondary, which in turn are more reactive than tertiary alcohols.

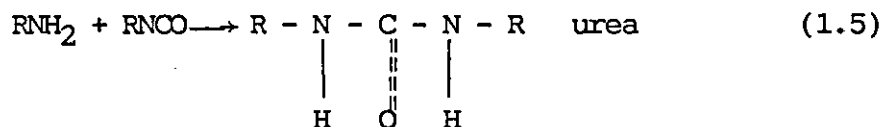
ii) Reaction with water

Isocyanate reacts with water to give an unstable intermediate product of carbamic acid followed by amines and carbon dioxide.

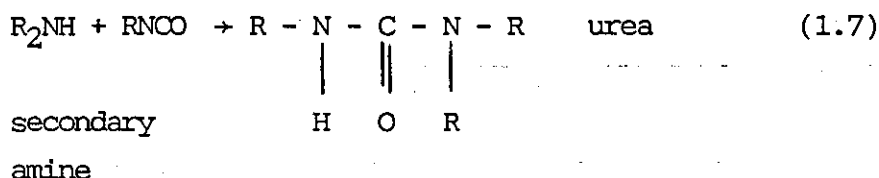
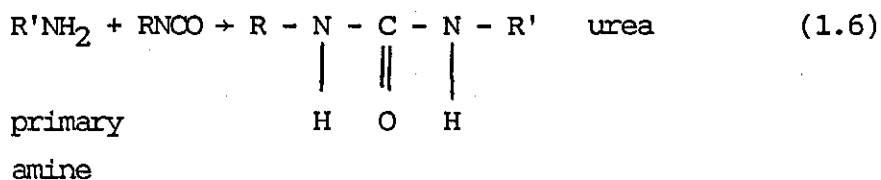


unstable carbamic acid

The primary amine produced reacts with more isocyanate to form a substituted urea



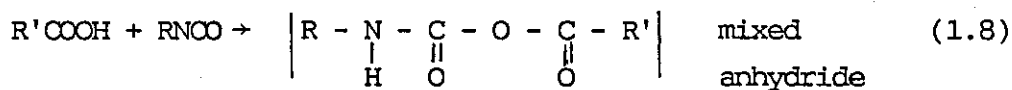
The above reaction shows the importance of handling urethane raw materials in perfectly dry conditions during the formation of solid elastomers, in order to avoid undesirable bubble formation due to the carbon dioxide formed [40].

iii) Reaction with amines

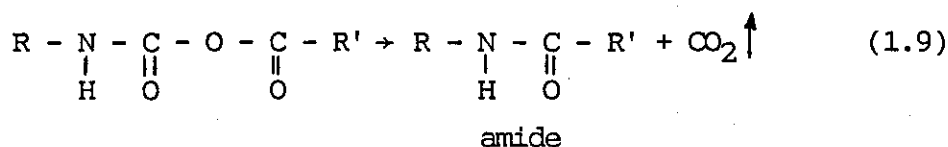
This reaction is particularly valuable in chain extensions of isocyanate terminated prepolymers, forming urethane-urea elastomers.

iv) Reaction with carboxylic acids

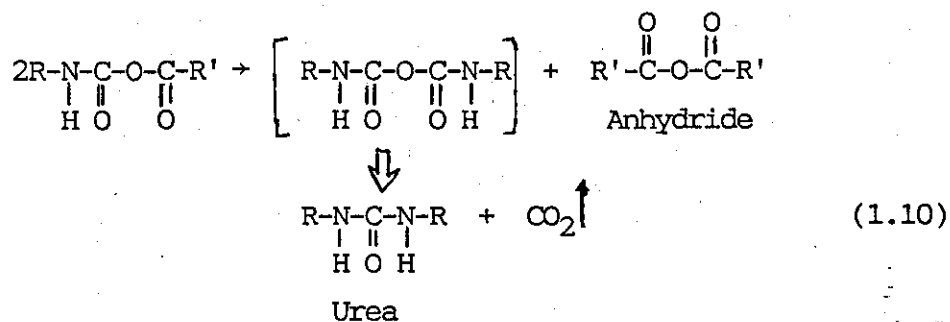
Isocyanates react readily with carboxylic acids, and the reaction proceeds via an unstable intermediate (mixed anhydride) whose decomposition products depend on the type of isocyanate and carboxylic acid strength [41]



a) in the case of strong acids

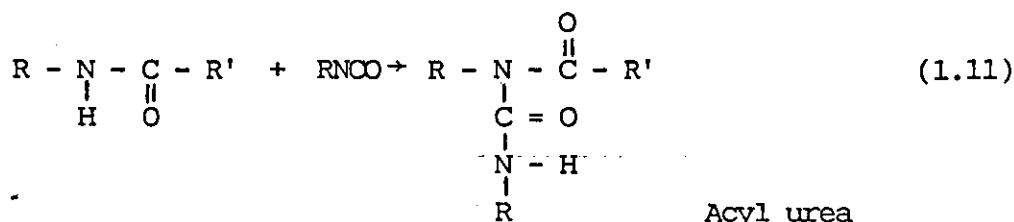


b) in the case of weak acids

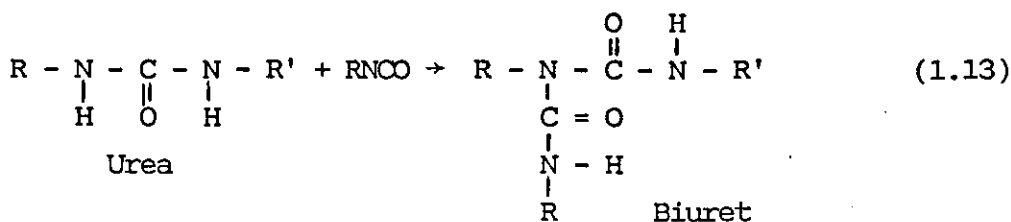
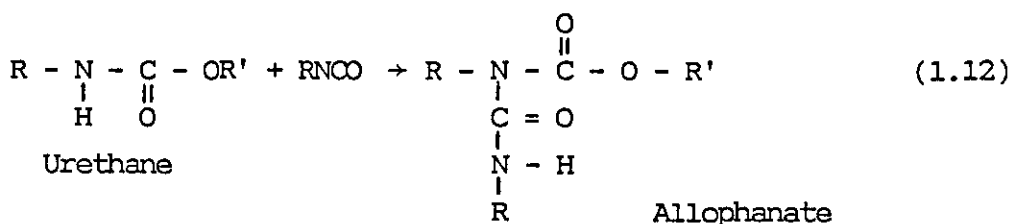


v) Reaction with Amides

Amides, and substituted amides, can react under certain conditions [21] with isocyanates to give acyl ureas

vi) Reaction with Ureas and Urethanes

Primary isocyanate reaction products which still contain active hydrogen atoms, can react further with isocyanates at elevated temperatures (above 100°C) or at lower temperatures in the presence of certain catalysts to form biuret and allophanate linkages.



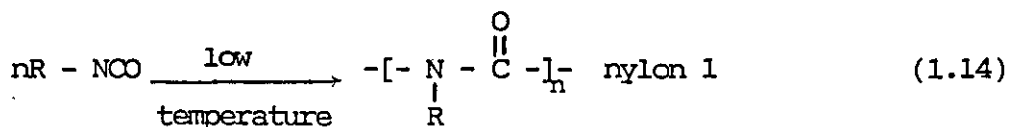
Both reactions are potential crosslinking reactions, but the biuret linkage is of greater practical importance because urethanes are less reactive to isocyanates than are ureas.

Self-Addition Reactions

In addition to the above mentioned reactions, isocyanates can react with themselves under certain catalytic conditions. The four most important reactions of this type are as follows:

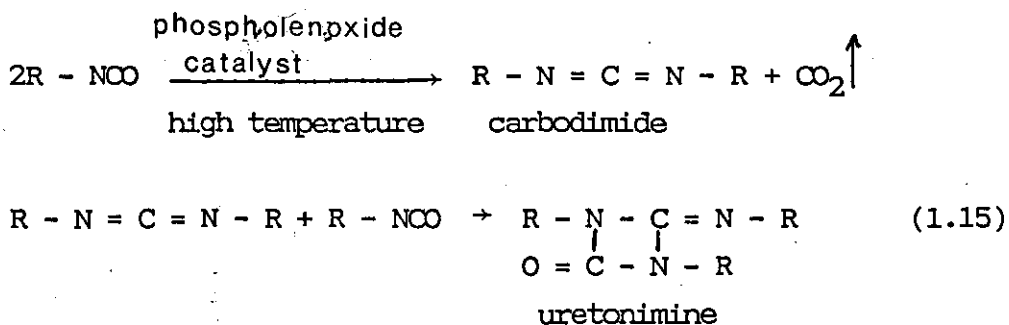
i) Linear polymerisation

The linear polymerisation of isocyanate is obtained in a manner similar to vinyl polymerisation with anionic catalysts (such as sodium cyanide in N,N-dimethyl formamide at temperatures of -20°C to -100°C). However, this reaction is usually not observed in normal urethane polymerisation reactions [42].



ii) Carbodiimide formation

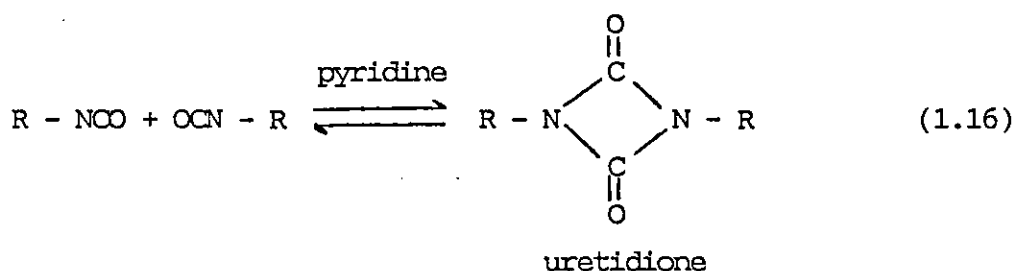
Isocyanates condense easily to form carbodimides with evolution of carbon dioxide [42]. The reaction occurs easily on heating but the products react with further isocyanate, during and after cooling, to yield a substituted uretonimine. Traces of uretonimine are thus present in many modified isocyanates.



Carbodiimides are used as anti-hydrolysis additives in polyester based urethanes [20].

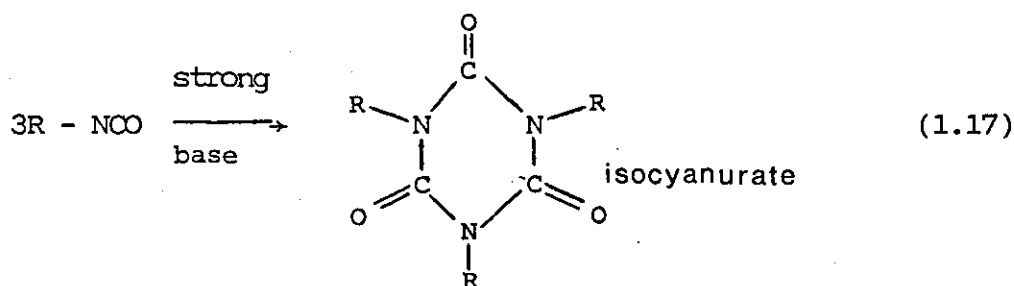
iii) Dimerisation

Dimerisation of isocyanates takes place in the presence of pyridine giving rise to uretidione rings. This reaction is an equilibrium reaction and can be reversed by heat



iv) Trimerisation

Trimerisation of isocyanates takes place in the presence of a basic catalyst such as sodium methoxide or a strong organic base giving rise to isocyanurate rings [43].



Both uretidione and isocyanurate formation are important in isocyanate chemistry, but isocyanurate formation is significant in a wider range of polyurethane applications [44]. Isocyanurate structures are extremely stable to both thermal and hydrolytic attack, and decomposition does not begin until well above 300°C.

1B.5 RAW MATERIALS

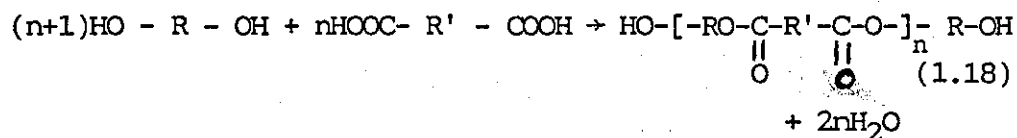
Most commercial polyurethane elastomer systems employ the use of di- or poly-isocyanates, polyols and chain extension diols or amines.

a) Polyols

The polyols are generally hydroxyl terminated polyesters or polyethers, the choice strongly influences the final properties of the urethanes. Polyesters generally provide better mechanical properties than polyethers which yield more hydrolytically stable polyurethanes. Hydroxy-polyethers, which are obtained by alkoxylation, are used in far greater quantities than hydroxy-polyesters obtained by esterification [45].

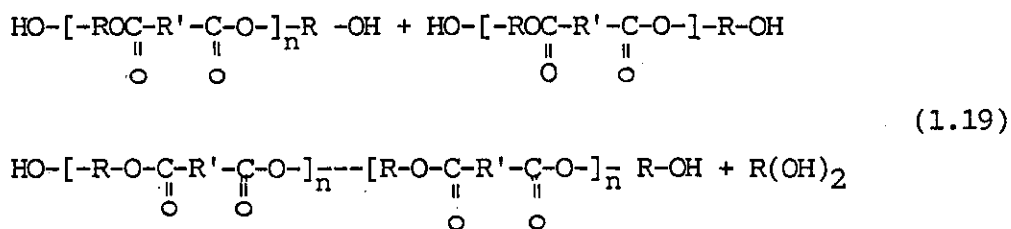
- i) Polyesters: The polyesters are usually prepared by reaction of dibasic acids with excess diols. The most common new materials used in polyesters for the urethane polymers are adipic acid, sebacic or phthalic acid with ethylene glycol, 1,2-propylene glycol, and diethylene glycol, where linear polymer segments are required, and glycerol, trimethylolpropane, pentaerythritol, and sorbitol, if chain branching or ultimate crosslinking is sought.

In the preparation of polyesters, conventional methods of polyesterification are used. As the polyesters are required to be hydroxyl terminated, it is usual to react an excess of the stoichiometric amount of the glycol with the acid.

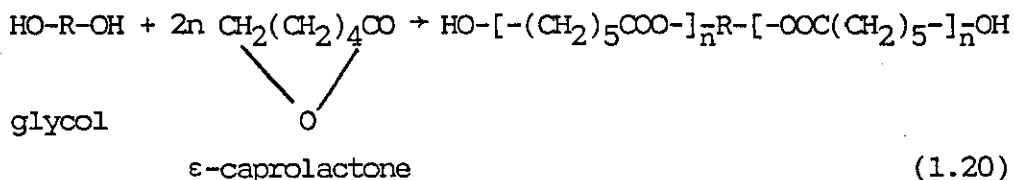


This esterification reaction results in a mixture of low molecular weight polymers. Continued reaction at high temperatures and, in some cases, reduced pressures leads to

the elimination of some glycol with the formation of higher molecular weight polyesters.

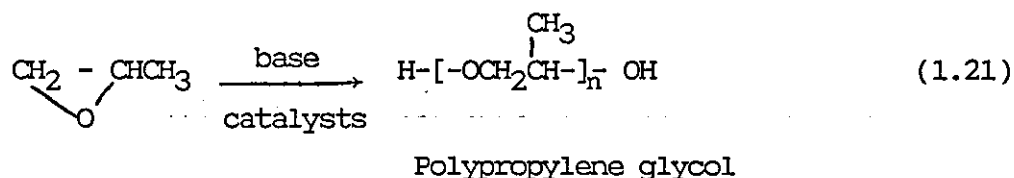


Another type of polyester of interest is polycaprolactone, which was used in this research, first described by Young and co-workers [46] is obtained by the addition polymerisation of ϵ -caprolactone in the presence of an initiator. This type of polyester exhibits improved hydrolytic stability and low temperature properties as compared to adipate-polyester based urethane elastomers. ϵ -caprolactone, the internal ester of hydroxy caproic acid is produced from cyclohexanone by a novel route based on peroxygen technology developed by Interlox Chemicals Ltd. Polymerisation is carried out by a ring opening mechanism which allows control of molecular weight and functionality.

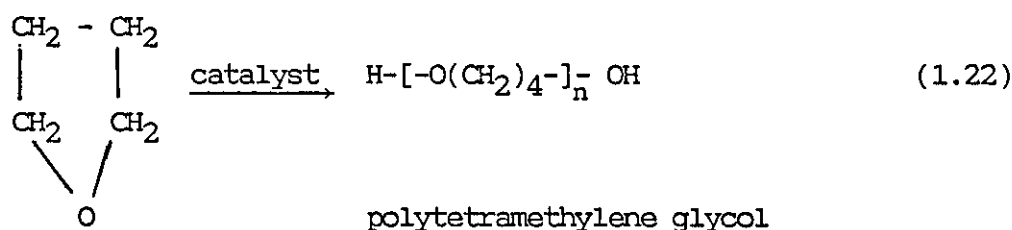


Polycaprolactones are saturated aliphatic polyesters, containing a single repeat unit and as no water is produced during the polymerisation the polyol produced is exceptionally pure. These polyols are found to blend with a wide range of chemicals yielding mixed and compatible systems. The high polarity in these polyols increases the intermolecular attraction in urethanes and hence improves mechanical properties.

ii) Polyethers: The polyethers are commercially the most important of the polyhydroxy compounds used to prepare polyurethanes. They are generally prepared by catalytic polymerisation of the epoxide group in the alkylene oxide with suitable initiators



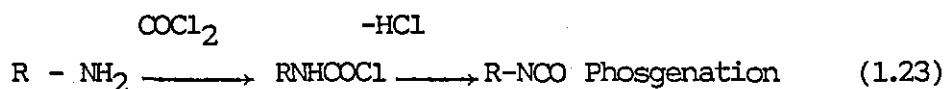
The first polyether designed specifically for preparing polyurethanes was a polytetramethylene glycol derived from tetrahydrofuran



In general polyether glycols are light coloured viscous liquids, non-volatile and soluble in common organic solvents.

b) Diisocyanates

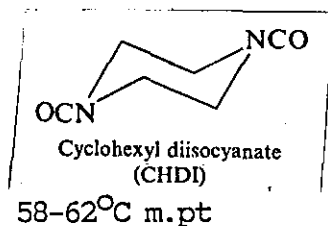
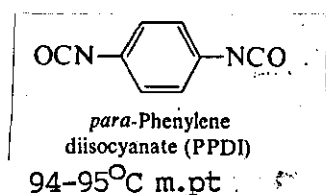
There are several diisocyanates established in polyurethane elastomer systems. The most common are 4,4'-diphenylmethane diisocyanate (MDI); 2,4- and 2,6-toluene diisocyanate (TDI); 1,5-naphthalene diisocyanate (NDI) and 1,6-hexamethylene diisocyanate (HDI) (see Appendix I). The commercially important method of preparing isocyanates is the reaction between phosgene and amines in an inert solvent like ortho dichlorobenzene at temperatures of 25-100°C, via a number of intermediate steps



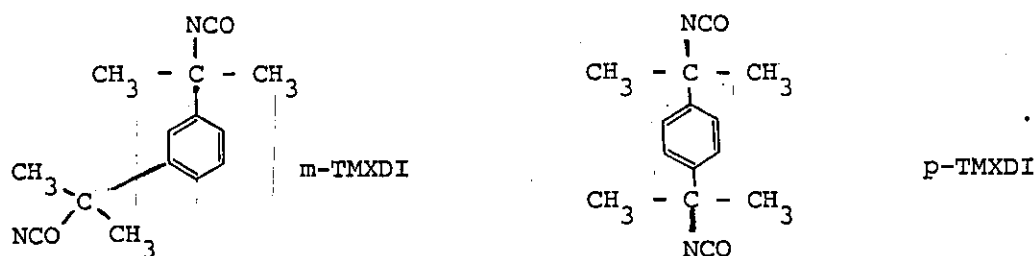
The aromatic diisocyanates give polyurethanes which discolour in the presence of ultra-violet (UV) light. The addition of UV absorbers, antioxidants and certain pigments improves the light stability but is limited to the life of the additives used. Polyurethanes based on aliphatic isocyanates can, however, give similar physical properties with good light stability.

Commercial amounts of a diisocyanate became available about 1965 which produced light stable urethanes [47]. This came about through the efforts of Dr Bailey of the Allied Chemical Corporation who designated their product as Nacconate H-12. This is a low volatility, cycloaliphatic diisocyanate (H_{12}MDI). Bayer now supplies this product as Desmodur 'W', which they took over from Du Pont who used to sell it as Hylene 'W'. H_{12}MDI is a clear liquid at 25°C and consists of a mixture of stereo-isomers produced by the reduction of the intermediate 4,4'-methylene bis (aniline), followed by phosgenation. Aliphatic isocyanates are less subject to thermal degradation and discolouration as compared to aromatic polyisocyanates [48-50]. There are several other diisocyanates which are now known to yield colour stable urethanes [47] such as IPDI, TMDI, HDI etc (see Appendix I).

There have been some recent new additions in the isocyanate family. Two of these are claimed to produce elastomers of better physical properties which are retained at much higher temperatures than MDI and NDI. These are paraphenylene (PPDI) diisocyanate and 1,4-cyclohexane diisocyanate (CHDI) [51]



Both diisocyanates are white flaked solids with the stated toxicity of TDI. The reactivity of PPDI is greater than MDI, while CHDI reactivity is greater than IPDI but lower than MDI. Recently developed pseudo-aliphatic diisocyanates are the meta- and para-tetramethylxylene diisocyanate (m- and p-TMXDI) [52]. They have characteristics typical of aliphatic diisocyanates such as light stability, even though they contain aromatic rings. The m-TMXDI is a colourless liquid at 25°C, while the para compound is a white solid (m.pt 72°C). The p-TMXDI is similar in reactivity to IPDI, while the m-TMXDI is lower, comparable to H₁₂MDI



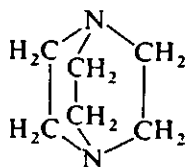
c) Chain Extenders

There are many glycols and diamines which are used as chain extenders, in the manufacture of solid polyurethanes. The most widely used chain extension agents are 1,4-butanediol and MOCA [53] (3,3'-dichloro-4,4'-diaminodiphenylmethane) (see Appendix II for manufacture of these chain extenders).

d) Catalysts

These are used in polyurethane technology to control and balance the polymer forming reactions. They are generally either of two types: metal salts or tertiary amines.

- 1) Tertiary amines: Their catalytic effect increases with base strength, but structural effects can be important and the triethylene diamine (DABCO) which has little or no steric hindrance is of relatively high catalytic activity [20]



Triethylene diamine,
1,4-Diazo-(2,2,2)-bicyclo-octane (DABCO)

ii) Organometallic compounds: While a number of metal complexes have catalytic effects on reactions of the isocyanate group, those based on tin are extremely effective [54]. They promote isocyanate-hydroxyl reactions in preference to reaction with water, catalysts of this type include stannous octoate, stannous oleate and dibutyltin dilaurate.

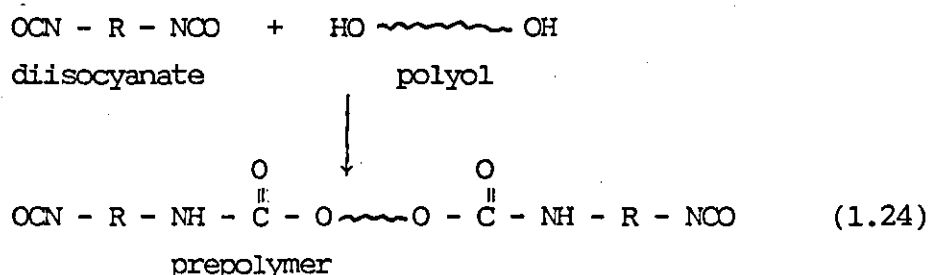
In general the catalytic activity of tin complexes are much higher in isocyanate-hydroxyl reactions than the tertiary amines, but are less effective than the amines in catalysing isocyanate-water reactions.

1B.6 SYNTHESIS

In the synthesis of polyurethane elastomers a common term NCO/OH ratio is used to relate the stoichiometric proportions of materials used with the properties of the polymer. As with other chemical reactions, temperature, time, rate of mixing etc, are important variables controlling the end product properties. The techniques generally used in the synthesis of polyurethanes are the 'prepolymer', 'quasi-prepolymer' and 'one-shot' methods.

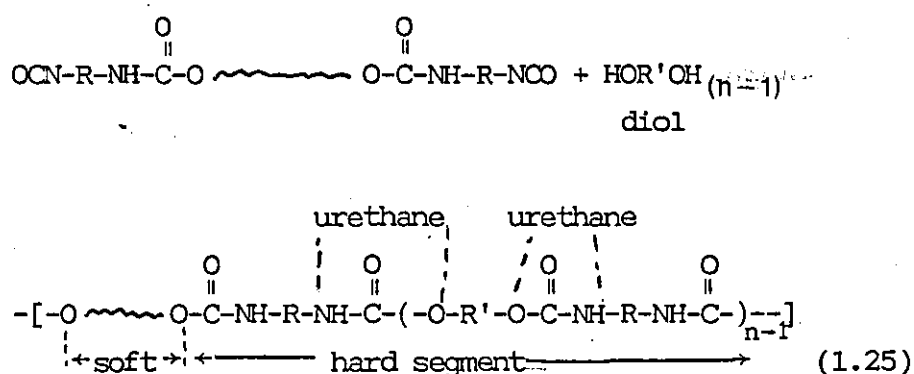
i) Prepolymer Method

Most polyurethane elastomer systems are based on this technique and are by far the most widely used providing better handling, controlled processing and consequently better properties. The prepolymer is obtained by reacting a long chain polyol (polyether or polyester) with an excess of diisocyanate to give an isocyanate terminated polymer of moderate molecular weight, which in the second stage can be chain extended with low molecular weight diol or diamine to yield the final product. A typical prepolymer reaction is shown:

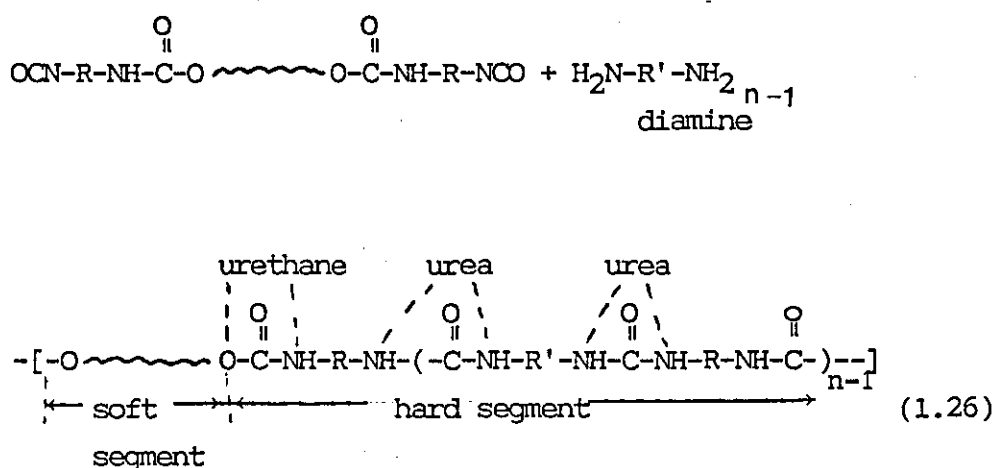


The prepolymer can be prepared either by melt polymerisation or solution polymerisation. In melt polymerisation the predried diisocyanate and polyol at NCO/OH greater than one, are mixed in molten form under dry nitrogen. The prepolymers are relatively stable high viscosity liquids or low melting solids at room temperature, which should be stored in the dark under nitrogen to prevent photodegradation, dimerisation or moisture contact with NCO groups.

Further reaction of the prepolymer with chain extender gives a higher molecular weight polymer. Diol chain extenders are comparatively less reactive than diamines and sometimes necessitates the use of catalysts which should be added to the prepolymer before mixing. As the pot life of melt polymerised urethanes is short the reacting mix is quickly cast into a mould. This is then cured in an oven at 50-120°C for several hours. Typical chain extension with diol and diamine are shown:



Reaction of prepolymer with diol



Reaction of prepolymer with diamine

Solution polymerisation is similar to melt polymerisation, except that the process is carried out in a common non-reactive solvent. Although the properties of polymers are not good as melt polymerisation, this technique has the following advantages:

- i) Possibility of using high melting points and highly reactive diisocyanates and chain extension agents
- ii) Rapid and efficient dispersion of reactants
- iii) Overcome disadvantages of short pot lives
- iv) Easier casting to form thin film by solvent evaporation.

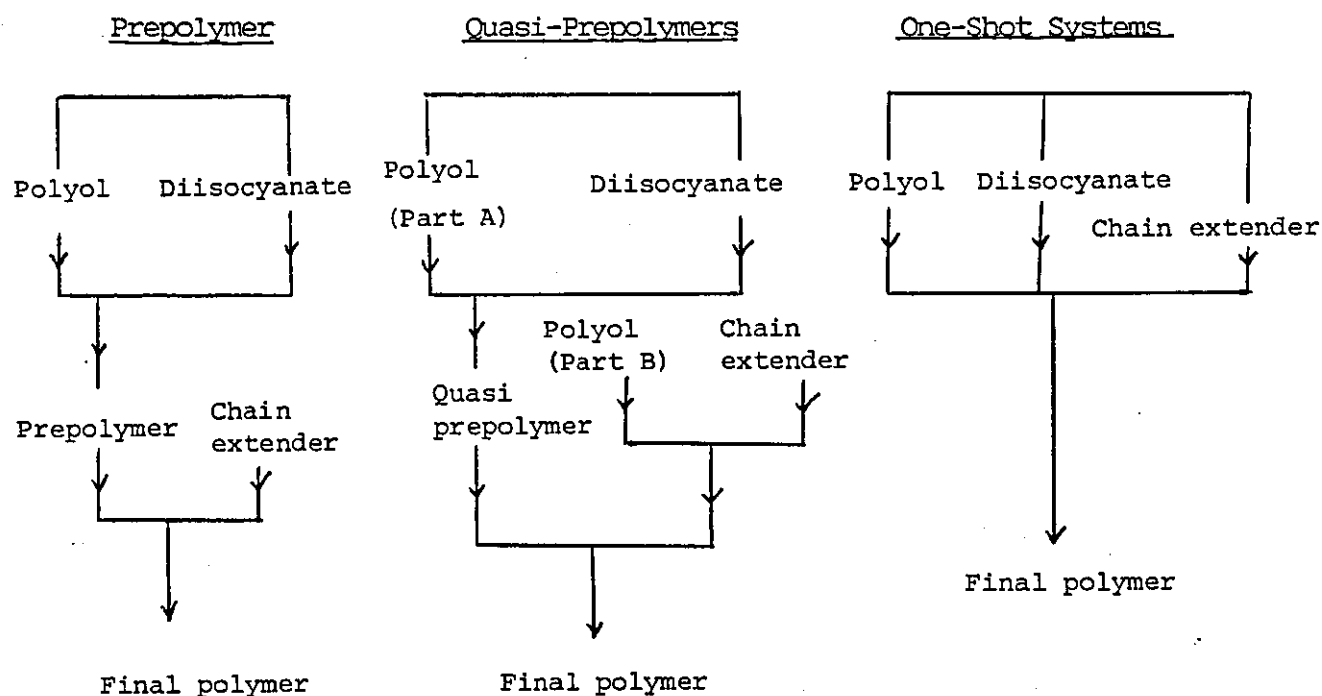
ii) Quasi-prepolymer method

In this method only part of the polyol is reacted with all of the diisocyanate to form the semi- or partial (quasi) prepolymer. This prepolymer is then reacted with the remainder of the polyol (which is previously mixed with the chain extender) to give the final polymer.

iii) One-shot method

This involves the simultaneous mixing together of stoichiometric amounts of polyol diisocyanate and chain extender. In practice the polyol and chain extender are first mixed, dried and then added to the diisocyanate. There is no control over the reaction priority, hence random polyurethane structures are produced. Sometimes for solid elastomers, one-shot systems are used for economical reasons, where the components are mixed and extruded in a continuous process, but generally this technique is used more in foam production.

FIGURE 1B.6.1: SYNTHESIS TECHNIQUES COMMON FOR POLYURETHANE ELASTOMERS SHOWN SCHEMATICALLY



1B.7 HEALTH AND SAFETY

The hazards associated with polyurethanes have been primarily associated with the isocyanates. All known isocyanates are harmful and therefore limits have been set from results based on animal and clinical analysis to give a threshold limit value (TLV expressed in ppm). The TLV in the USA has been set at 0.01 ppm for H₁₂MDI and 0.02 ppm for isocyanates such as MDI, TDI, IPDI and HDI.

The characteristic and important physiological effects of isocyanates can be shown by the effects of exposure to H₁₂MDI. This causes bronchial irritation, coughing, insomnia, irritation of the eyes and upper respiratory tract. It is a strong irritant and can cause sensitization dermatitis, reflected in rash and redness with swelling of the skin, and may cause permanent damage to eyes. Different isocyanates vary in their effects.

Other hazardous materials include diamines, particularly MOCA (suspected carcinogen); catalysts (such as tertiary amines), fire retardants (organic phosphates, containing halogens), blowing agents and others. Technical information on isocyanates and decontaminants [55-57] is readily available.

CHAPTER 2

GENERAL STRUCTURE AND PROPERTY RELATIONSHIPS

2.1 INTRODUCTION

The characteristics of thermoplastic polyurethane elastomers have led to an extensive study of their synthesis, morphology and properties [20,58-67]. In general these materials are formed by joining blocks of two chemically dissimilar segments along the polymer backbone. These segments are rubbery (soft segment) and glassy or semi-crystalline (hard segment) in nature. The properties of these copolymers are related to their two phase microstructure, with the hard segments acting as a reinforcing filler. This segmented polymer structure can vary its properties over a wide range of strength and stiffness by modification of its three basic building blocks: the polyol, diisocyanate and chain extender. The hardness range covered is that of very soft elastomers to hard, rigid plastics (Figure 2.1.1 [67]).

A number of additional structural features also influence the final properties, these are intermediate forces, stiffness of chain units, ease of rotation of chain segments and crystallisation. The interaction between the polar entities like urethane, urea, ester and other groups are important in determining the properties of polyurethanes, where local concentration of polar groups occur together, leading to a supramolecular organisation with aggregated structures, which may be in the form of glassy domains or crystallites.

2.2 CHEMICAL STRUCTURE, MORPHOLOGY AND PROPERTY RELATIONS

There have been several reviews on the effect of chemical structure on final properties [e.g. 68-72]. The importance of phase separation in thermoplastic polyurethane elastomers in determining

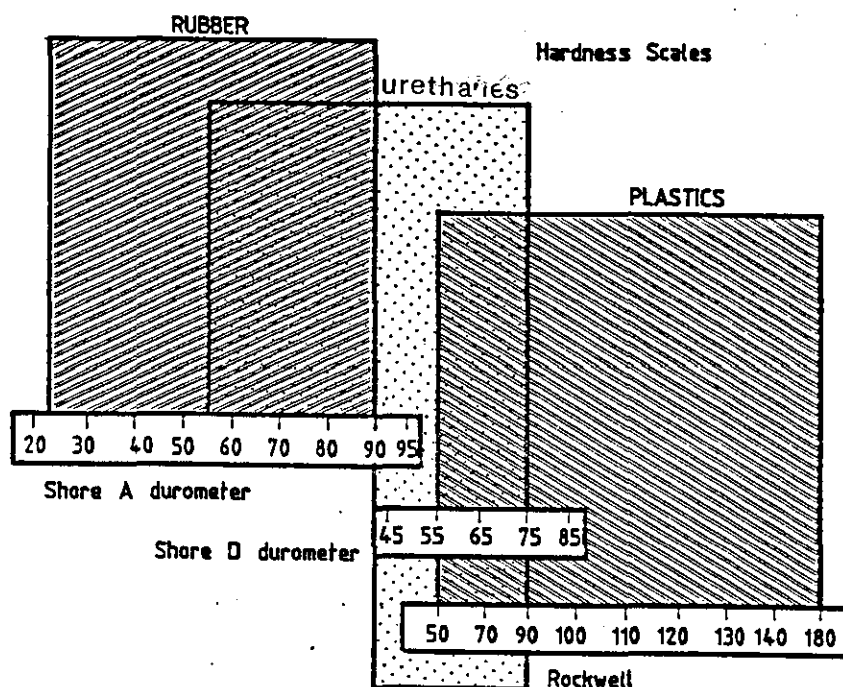


FIGURE 2.1.1: Shows the Hardness Range Covered by Polyurethanes

structure-property relationships was first pointed out by Cooper and Tobolsky [73]. Much work has been carried out since to elucidate the extent of microphase separation and the structure of the resulting components [62,63,74-76]. Many studies of the morphology of these hard-soft segmented systems have demonstrated that the two kinds of chain segments can preferentially cluster into separate microphases [66,76-83]. On the basis of these morphological studies it has become clear that the strength and modulus of these elastomers arise from physical crosslinking or reinforcement caused by the hard segment domains dispersed in a soft segment matrix [84-87].

The linear segment polyurethanes have the general structure $(-A-B-)_n$, where B (soft segment) is usually formed from a polyether or polyester macroglycol [73]. The hard segment is formed by extending a diisocyanate with a low molecular weight diol or diamine. In the segmented polyurethanes, phase separation of the

hard segments into microdomains has been observed even when the segment length is relatively short. The primary driving force for domain formation is the strong intermolecular interactions between the urethane units which are capable of forming inter-urethane hydrogen (H) bonds. Factors that control the degree of microphase separation include copolymer composition, block lengths [88], crystallisability of either segment, size of chain extender and the method of sample synthesis. In general interconnected or isolated hard segment domains are present along with a rubbery phase of soft segment material, though this soft segment may contain some hard segments due to incomplete phase separation [89,90].

Bonart [74] and Clough et al [77] investigated the scale of the microdomain structure which results from phase segregation of the hard and soft segment units. The microheterogeneous nature of polyurethanes has been the subject of numerous investigations [85,91-96] and many models of phase aggregated polyurethane systems have been proposed [74,76,80,97,98].

Bonart [74] proposed a model for the structure of segmented polyurethane elastomers under varying degrees of extension from X-ray diffraction studies. Polyether and mixed-polyester urethane urea copolymers were studied. The hard segments were found to form discrete highly ordered regions (about 25 Å in width) separated by soft domains (about 100-200 Å wide). Polyether soft segments were found to stress crystallise at about 150% elongation, whereas polyester soft segments showed only paracrystalline behaviour, maybe due to the more irregular chemical structure present. At all elongations the soft segments tended to orient into the direction of stretch. Hard segment behaviour was more complex and the orientation was followed as a function of strain. The hard segments became oriented perpendicular to the stretch direction at elongations below 200%. Further stretching indicated that the hard segments were then orienting into the stretch direction (Figure 2.2.1). Further elongation causes hard segments to slip past one another, breaking up the original structure. As elongation

continues, hard segments become progressively more oriented into the stretch direction (Figure 2.2.2). This model provides a possible explanation of the stress softening phenomena and high hysteresis observed in polyurethane elastomers.

Estes [91] proposed the domain structure in an unstrained segmented polyurethane (Figure 2.2.3) in which the shaded areas are the hard domains. Both phases are represented as being continuous and interpenetrating, showing a polymer molecule which traverses several domains. The model also presumes that phase separation is not completed and some urethane blocks are also dispersed in the rubbery matrix.

In an unstrained state, the soft segments are randomly arranged so the rubbery domains are isotropic. Urethane segments are aligned approximately perpendicular to the long direction of the hard domains, thereby making the hard domains locally anisotropic. Overall the hard domains are randomly arranged so that the bulk sample appears mechanically and optically isotropic.

Direct evidence of such an interpenetrating two-phase morphology in segmented polyurethanes was first provided by Koutsky et al [97]. They used prepared samples of polyester and polyether based elastomers by staining samples with iodine and observing the darkened areas by transmission electron microscopy. Electron microscopy [97-100] can provide direct information on the domain structure under favourable conditions, such as when the domains are crystalline. While some electron microscopy has been carried out using surface replication [101,102], the most extensive work has been with transmission electron microscopy through thin films.

The development of a heterogeneous structure during the polymerisation of a polyurethane system was monitored by Castro et al [103] following the amount of light transmitted by the sample and the increase in viscosity of the reacting mixture. The amount of light transmitted by the reacting sample was observed to decrease

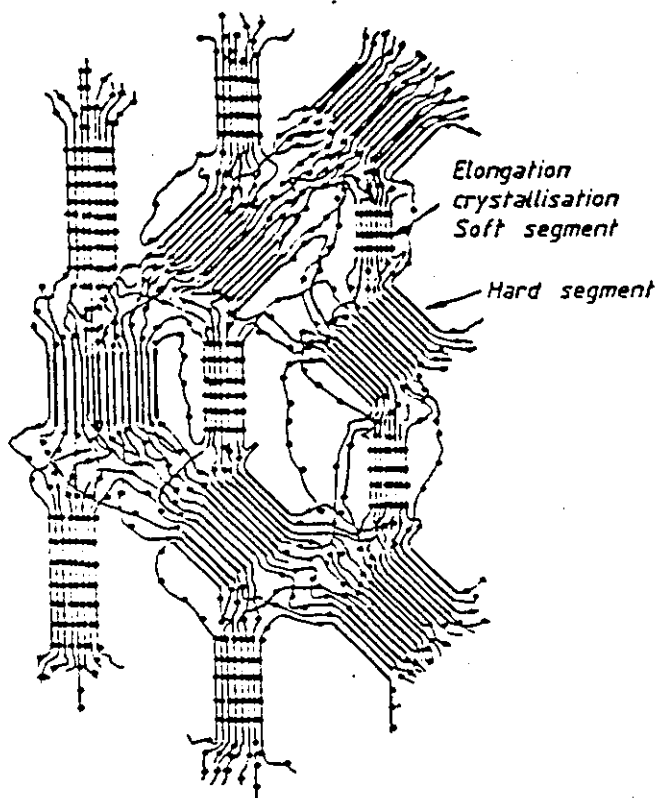


FIGURE 2.2.1: SCHEMATIC DIAGRAM OF THE STRUCTURE OF A POLYETHER POLYURETHANE ELASTOMER STRETCHED TO APPROXIMATELY 200% [76]. THE THICK STROKES REPRESENT HARD SEGMENTS AND THE THIN STROKES SOFT SEGMENTS. INDIVIDUAL PARTICULARLY STRONG STRETCHED SOFT SEGMENTS ARE CONSIDERED TO ACT AS NUCLEI AROUND WHICH CRYSTALLISATION CAN OCCUR DURING ELONGATION

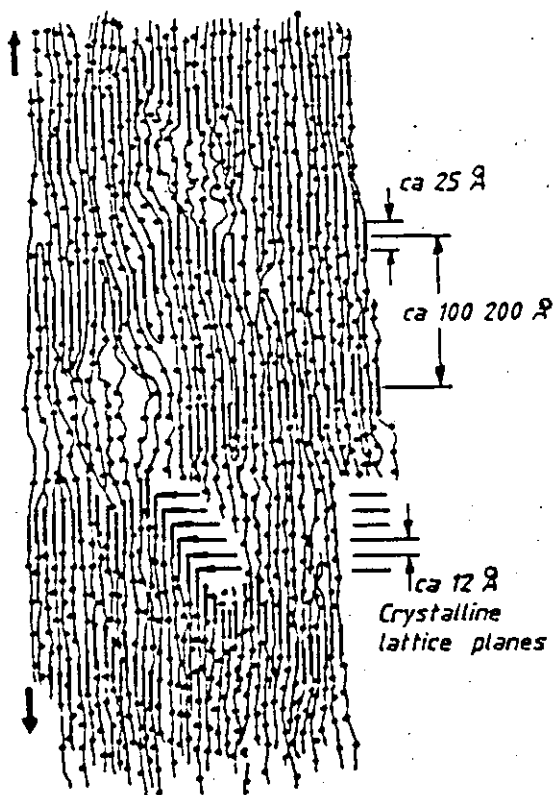


FIGURE 2.2.2: THE POLYETHER POLYURETHANE ELASTOMER AT 500% EXTENSION AND PLACED IN WARM WATER AT 80°C [58]. THE HARD SEGMENTS HAVE TURNED INTO THE DIRECTION OF ELONGATION AND FORM PARACRYSTALLINE LAYER LATTICES. THE ELONGATION CRYSTALLISATION OF THE SOFT SEGMENT HAS BEEN REDUCED OR HAS DISAPPEARED. ON RELAXATION THE ORIENTATION OF THE HARD SEGMENTS IS LARGELY MAINTAINED.

sharply at a given point in the reaction. Castro et al suggested that at the onset of phase separation the number average hard segment sequence length was about 1.3. Chen [104] et al used optical microscopy to follow the copolymerisation of a model polyurethane system (HTPBD/2,4 or 2,6-TDI/1,4-BD) and found that initial reactant incompatibility was the key factor in determining the final morphology of the bulk sample. Based on these and previous [105] findings, models are proposed to describe the morphology during polymerisation of this particular polyurethane system for several hard segment compositions where both macro-phase separation and micro-phase separation of reactants can occur during polymerisation.

During phase separation in a segmented polyurethane, the T_g of the soft segment phases has been shown to decrease logarithmically with time [106]. The kinetics of phase separation for the soft segment T_g has been described by first order kinetics [107]. The studies suggest that the phase-segregation mechanisms involve two elementary steps which can be characterised by two discrete relaxation times. It also shows quantitatively that a polyether-based polyurethane recovers its original domain structure faster than a polyester soft segment material.

The role of hydrogen bonding in promoting the degree of crystallinity and domain formation in segmented polyurethane elastomers has received much attention. The use of IR spectroscopy has been very helpful in detecting variations of H-bonding with composition, temperature, and/or deformation history [85,91]. It is generally recognised that extensive H-bonding is present in most segmented polyurethanes, being of higher extent in the polyester based than the polyether based ones. H-bonding interactions between urethane or urea groups contribute to hard segment domain formations.

H-bonding interactions between hard segment NH groups and soft segment O atoms have been suggested [108]. This is explained as a

result of incomplete domain separation of hard segments dispersed in a soft segment matrix. It is also postulated that part of these interactions may occur at the domain-matrix interface. The polymer chain mobility and ability to organise extensively into crystalline lattices is restricted due to H-bonding, resulting in sub-ordered regions. Bonart [64] described these as 'paracrystalline' regions, Van-der-Waals forces also take place at all parts of the polymer chain.

Crystallisation of either segment in the polyurethane elastomer can lead to the development of a macroscale superstructure beyond the domain level. The morphology depends on several factors such as the nature and concentration of the crystallisable component, solvent and thermal history. Wilkes [78,109,110] reported this in materials incapable of H-bonding as well as H-bonded elastomers. It appears that the superstructure entities (spherulites) contain preferentially oriented domains (Figure 2.2.4). Spherulitic structure of the soft segment is readily apparent at high soft segment content, whereas at lower soft segment content spherulites are formed by aggregation of hard segment domains. Spherulites have also been observed in the polyurethane-urea [111], segmented polycaprolactone-urethane [99] and segmented polyether-ester thermoplastic elastomers [112-115]. The effect of different spherulitic structures on the mechanical properties of segmented polyether-esters has also been reported [115].

The phenomena of stress softening on repeated extension has been attributed to disruption of the domain structure leading to a decrease in the number of effective crosslinking sites [116-118]. T L Smith [84,119-121] reported that, in general, the behaviour of a strained system depends on the size and concentration of hard-segment domains, the strength of hard segment aggregation, the ability of the segments to orient in the direction of stretch and the ability of the soft segments to crystallise under strain.

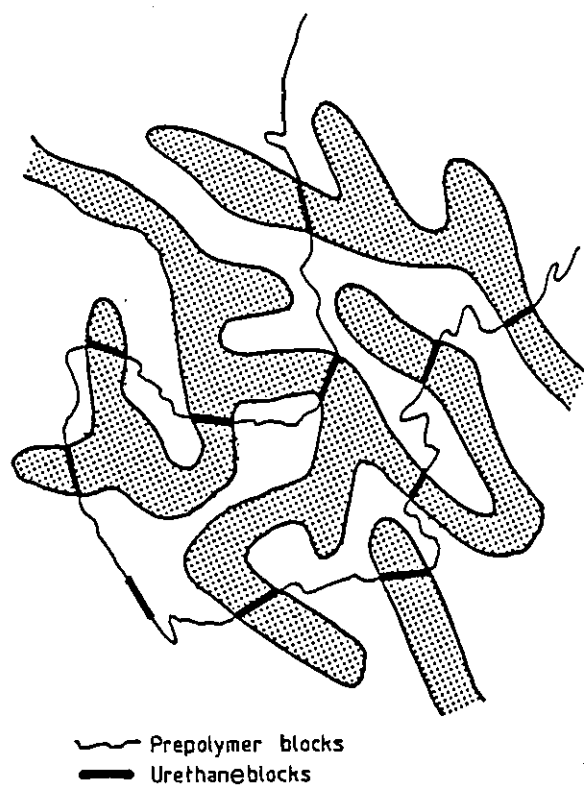


FIGURE 2.2.3: SCHEMATIC REPRESENTATION OF DOMAIN STRUCTURE IN A POLYURETHANE

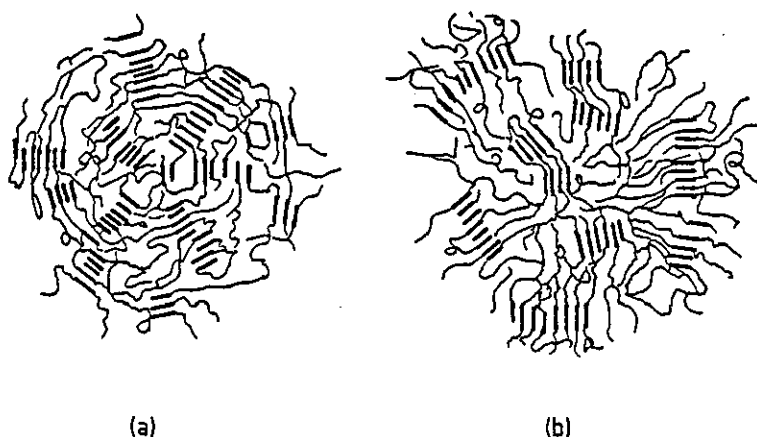


FIGURE 2.2.4: POSSIBLE MODELS OF SPHERULITIC STRUCTURES [66]

Stress hysteresis is prominent in segmented copolymers because of the disruption of hard segments with strain [122]. Stress softening is a function of domain restructuring, ductility and the nature of the mixed hard- and soft-segment interfacial regions [64]. In segmented polyurethanes, hard segment crystallisation has been found to increase stress hysteresis, permanent set and tensile strength. Heat build-up in polyurethanes which is attributed to their high hysteresis losses has limited their suitability in some applications.

The fracture process, as regards ultimate properties, can be represented in three stages: initiation of microcracks, slow crack propagation and catastrophic failure [84,119-121]. Dispersed phases tend to interfere with the crack propagation step, redistributing energy that would otherwise cause the cracks to reach catastrophic size. Thus a two phase morphology is essential to the achievement of high strength in elastomers. The presence of hard segment domains increases energy dissipation by hysteresis and other viscoelastic mechanisms. The high modulus hard phase can also

relieve stress concentration by undergoing deformation or internal structural reorganisation. In segmented polyurethanes, strength is enhanced by long, rigid hard segments with high cohesive energy. Although H-bonding can contribute to domain cohesiveness, H-bonding itself is not directly responsible for high strength.

2.3 EFFECTS OF SOFT SEGMENT

The soft segment is derived from the polyol and predominantly influences the elastic nature of the material and its low temperature properties. There are two major classes of polyols of commercial importance, these are aliphatic polyesters and aliphatic polyethers. They are low melting solids or liquids having Tg's below room temperature and are generally amorphous. Selection of polyol along with the other components, depends upon the properties required. Polyethers generally give elastomers having a lower level of physical properties than the polyester based materials [40], due to the weaker interchain attractive forces present. Table 2.3.1 [106] gives the energies of interaction between groups commonly present in polymeric materials.

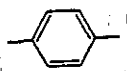
Group		Energy of Cohesion kJ/mole
Hydrocarbon	$-\text{CH}_2-$	2.85
Ether	$-\text{O}-$	4.18
Carbonyl	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$	11.10
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}- \end{array}$	12.10
Aromatic		16.30
Amide	$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad \\ -\text{C}-\text{N}- \end{array}$	35.30
Urethane	$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad \\ -\text{O}-\text{C}-\text{N}- \end{array}$	36.60

TABLE 2.3.1: Cohesive energy of functional groups common in polyurethane elastomers

The ester groups have almost three times the energy of cohesion of ether groups, due to the presence of the additional carbonyl group giving increased polar interactions. Table 2.3.1 shows that the presence of a polar group will increase the energy of cohesion and thus increase physical properties of the material.

Crystallisation of the elastomer is dependent on the structure and molecular weight of polyol, nature of isocyanate and chain extender and the formulation used. The structural regularity of many polyesters and polyethers enable them to crystallise on stretching which contributes to their high tensile strength. Low molecular weight polyols tend to increase hard segment concentration giving greater physical bonding and higher mechanical properties. Any pendant groups present which reduce the interaction packing will give materials of lower physical strength.

Polyethers have better hydrolytic stability than polyesters and this is explained by the greater resistance to hydrolytic attack by the ether groups, as shown in Table 2.3.2 [40]. The poly (ϵ - caprolactone) diols used are of polyester type which exhibit improved hydrolytic stability and low temperature properties as compared to the adipate polyester based urethanes.

Increasing the soft segment molecular weight at fixed, hard segment length generally gives lower tensile properties, higher elongations, increased tendency to crystallise especially at low hard segment content and increased tendency for the hard segment domains to be isolated in the soft segment matrix.

Polyol		Type	% Tensile strength* retained on hydrolysis
Polyethylene adipate glycol	PEA	Polyester	40
Polyhexamethylene adipate glycol	PMA	Polyester	30
Polyoxytetramethylene glycol	POTM	Polyether	88
Polyoxypropylene glycol	POP	Polyether	88

* 21 days in water at 70°C

TABLE 2.3.2: Effect of polyol on hydrolysis properties of polyurethane [121]

2.4 EFFECT OF HARD SEGMENT

The reaction of diisocyanate with chain extender form the hard segments, the properties of which determine the interactions in the elastomers and therefore the network structure of the materials. Interchain attractive forces between the hard segments are far greater than those present in the soft segments, due to the high concentration of polar groups and the possibility of extensive H-bonding. Hard segments predominantly affect modulus, hardness, tear strength and its high temperature properties. The effect of the diisocyanate structure on the physical properties of the polyurethane elastomers has been investigated by several workers [e.g. 123-125]. Symmetrical, bulky aromatic structures have been shown to give elastomers of high modulus and hardness.

General effects of increasing hard segment content at constant soft segment molecular weight are: increased hard segment crystallisation; increased hard segment melting point due to the thicker lamellae possible with larger hard segments; increased tendency of the materials to form a morphology with a hard segment matrix and isolated soft segment domains; and increased interfacial area. Seefried [126] et al studied urethanes prepared from polycaprolactone diols/MDI and 1,4-BD at varying hard segment content. A series of polymers were synthesised for each of two polycaprolactone diols (PCL) of Mn 830 and Mn 2100. They found that increasing hard segment content yielded an increase in hardness and tear value. Urethanes based on 830 Mn PCL exhibited a progressive increase in Tg at increased levels of hard segments, while the 2100 Mn PCL maintained a relatively constant Tg. These differences were attributed to the relative degree of phase separation between the constituent blocks of the copolymer. At the 830 Mn PCL increasing the hard segment leads to a larger amount of phase mixed materials whereas for the higher soft segment molecular weight there is not as noticeable an effect on phase mixing, because the ratio of phase mixed or interfacial material to purer soft segment material is much less.

A series of segmented polyurethanes based on poly (tetramethylene oxide) ether of 2000 Mn with MDI and 1,4-BD have been investigated [127]. Hard segment crystallisation has been shown to occur at high hard segment content (45%) from X-ray studies. Other morphological changes take place as the hard segment increases from a low level (15%) where the existence of domains are small to high levels (35% and 45%) when the polymer has a more interlocking domain morphology. The study showed that where low hysteresis and high extension are preferred, a 25% hard segment is recommended at which level isolated hard segment domains would exist. Thermal treatment of the sample would result in domain disruption and the mixing of hard-soft segments. This disruption and the recovery of structures on ageing is composition dependent. In general the crystalline domains when present are disrupted the least while the fastest recovery is displayed by samples with the non-crystalline domains.

As the proportion of hard segment content increases from 0% the T_g (attributable to the soft segment) initially rises rapidly and then more or less levels off [128]. This increase in T_g at lower hard segment content is due partly to decreased mobility of the soft segment because of their attachment to stiffer groups. The T_g remaining almost constant on increasing hard segment indicates a limited solubility of the hard segments in the soft segment phase, or hard segments remaining together to form ordered domains due to their high concentration. This finding is reported for elastomers in which 2,6-TDI replaces MDI [128]. In this case there is a greater tendency for the hard segment to penetrate the soft segment phase which raises the T_g to a higher value before levelling off. In the same study using 2,4-TDI no levelling off value was reached within the hard segment content concentrations studied.

The factors that influence MDI based hard segments to exist as a separate phase are (a) the tendency to crystallise, (b) low steric hindrance, for access of urethane groups in the H-bonding process and (c) the insolubility of the soft segment phase. These factors would also contribute to 2,6-TDI based materials, but to a lesser

extent. In the case of 2,4-TDI (a) would be absent, (b) would be reduced and the insolubility would be similar to the 2,6-TDI based materials. This suggests that elastomers based on unsymmetrical diisocyanates would give little or no phase separation whereas symmetrical diisocyanates would result in substantial phase separation.

2.5 EFFECT OF CHAIN EXTENDER

The most commonly used chain extenders are diols and diamines. The diamines generally give higher physical properties probably due to the urea linkages found having stronger hydrogen bonded interactions as compared to diols having urethane linkages. Aromatic, cycloaliphatic and heterocyclic diols would give elastomers with greater heat resistance and better retention of properties at higher temperatures than aliphatic diols. Chain extenders of differing chain lengths have shown an oscillating effect, on general physical properties.

The effect of chain extender (aliphatic glycols) length on poly (tetramethylene adipate)/MDI has been investigated [129]. It was found that for butanediol and longer diol chain extenders (up to octane diol) the structure of the hard segment depends on whether the diol has an even or odd number of CH_2 groups. The even diol elastomers adopt the lowest energy fully extended conformation that allows for H-bonding in both directions perpendicular to the chain axis. Such an H-bonding network would not be possible for the odd diol elastomers in the extended conformation, and these adopt contracted higher energy conformations. Both the odd and even diol elastomers, adopt staggered chain structures (with trichinic unit cells) but the even diols have a higher crystalline order. This is found with butanediol and longer chain diols, the lower ethylene glycol and propanediol chain extenders are exceptions and adopt contracted unstaggered structures. These lower diols are possibly too short to permit packing of the MDI units in the same way as for the longer diol chain extenders. This result suggests that better

overall properties are obtained by using butanediol and higher even diols, the hard segments of these can crystallise more easily in the lowest energy extended conformation.

The choice of chain extender has a considerable effect on the elastomer properties. A symmetrical, rigid and bulky chain extender is desirable for good physical properties while disorder, molecular flexibility and assymetry would lead to lowering of physical properties due to the weakening of the interchain forces between the hard segments.

2.6 EFFECT OF SEGMENT SIZE

The effect of varying segment size generally indicates that increase in physical and mechanical properties is associated with increase in urethane concentration in the elastomer. The effect of hard segment size and molecular weight distribution were investigated [130,131] using poly(tetramethylene oxide glycol) as the soft segment and a piperazine/1,4-BD hard segment. These systems provided no possible sites for H-bonded interactions. Polymers having a narrow hard segment molecular weight distribution were found to have a higher modulus than polymers with a wide molecular weight distribution. Tensile strength and elongation at break were found to be highest for polymers having a narrow soft segment molecular weight distribution. Permanent set was found to increase as the molecular weight distributions of hard and soft segments were narrowed. By preparing blends of polymers with different sized hard segments it was found that compatibility depended on the relative sizes of the hard segments combined. Explanation of the increase in modulus found for materials of higher hard segment content and narrower hard segment molecular weight distribution was given in terms of phase separation and domain formation.

2.7 EFFECT OF CROSSLINKING

The crosslinking of polymer chains is of primary importance in controlling many polymer properties. Large increases in the degree of crosslinking make amorphous polymers more rigid and cause them to have higher softening points and higher modulus, reduce elongation and swelling by solvents, and raise the glass transition temperature. Chemical crosslinking in segmented polyurethane elastomers can be produced by the following ways:

- i) The use of an excess of the diisocyanate which can react with chain backbone urethane or urea linkages to give allophanate, biuret and isocyanurate groups
- ii) The use of a branched polyether or polyester having hydroxyl functionality greater than two
- iii) The incorporation of a low molecular weight triol in the reactions such as trimethylolpropane.

The use of a trifunctional chain extender would produce the strong chemical linkages, especially at higher temperatures. The effect of chemical crosslinking is influenced largely by the presence of intermolecular attractive forces such as H-bonding in the linear polymer. Polyurethane elastomers having strong secondary interactions tend to suffer a general decrease in physical properties as the extent of crosslinking increases, as in polyester based materials. Elastomers having relatively weak secondary interactions show a general increase in physical properties with increasing crosslink density, such as polyether extended diols. This is due largely to the influence of non-covalent intermolecular attractive forces such as hydrogen bonding, which lose their effectiveness as increased chemical crosslinking causes increased chain separation in the linear polymer. Havlik and Smith [132] demonstrated the importance of these non-covalent interactions in a soluble polyurethane elastomer based on polyoxypropylene diol/2,4-

TDI extended with 2,4-toluene diamine. This material showed a high modulus compared with a chemically crosslinked elastomer based on the same system. This effect has been explained by the disruption of non-covalent intermolecular forces by the introduction of chemical crosslinks which cause spatial separation of polymer chains.

The existence of domain structure for crosslinked systems was suggested by Nishi [133] on interpretation of results on creep experiments. It is reasonable to expect that the presence of crosslinks in a segmented system could restrain the chains from achieving those configurations necessary for phase separation. This hypothesis is supported by Cooper and Tobolsky [134] who modified linear thermoplastic elastomers by adding various crosslinking agents. On the basis of the observed changes in the thermomechanical spectra, they suggested that the domain structure initially present in the linear system could be either maintained or destroyed when crosslinking was introduced depending on the numbers and location of the crosslinks in the segmented copolymer chains.

Phase separation has also been found by Lagasse [135] in crosslinked polyurethanes. He found microphase separation into amorphous hard segment domains in a 31 weight percent of hard segment polyurethane based on hydroxy terminated polybutadiene (functionality 2.3), 2,4-TDI with a mixture of 2-ethyl-1,3-hexanediol and N,N-bis (2-hydroxypropyl) aniline as chain extender. No crystalline structure could be detected in this material by wide angle X-ray diffraction. A domain structure due to microphase separation was, however, detected by SAXS (small angle X-ray study) and transmission electron microscopy. Lagasse concluded that the presence of crosslinks in a segmented elastomer does not necessarily prevent microphase separation between the hard and soft segments. Transmission electron microscopy is useful in detecting the phase morphology at and before the micron scale [98,100,136-139].

A study of a series of polyurethanes [140] based on polycaprolactone diols (of 530 Mn and 830 Mn) and triols (of 540 Mn and 900 Mn) reacted with MDI and 1,4-BD to give varying weight % of hard segment content (0%, 23% and 43%). With these model polyurethanes it is possible to see phase separation in both linear and crosslinked polyurethanes. Particular attention was paid to the synthesis conditions and to the compatibility of reactant, as the degree of phase separation is also related to the speed and temperature of reaction [136]. These materials exhibit a range of mechanical behaviour from soft elastomers to tough semicrystalline materials. The 0% hard segment samples are single phase amorphous materials. All the 23% and 45% hard segment content materials are semicrystalline and show phase separation on the scale of microns and below. In macrodiol samples hard segment rich spherulites are present, while in macrotriol samples only hard segment rich globules are observed. Indications of two phase behaviour in the 23% and 43% hard segment content materials were also deduced from thermal analysis and dynamic mechanical behaviour.

CHAPTER 3

EXPERIMENTAL SECTION

3.1 INTRODUCTION

Polyurethanes are usually prepared by bulk polymerisation techniques, where the prepolymer and chain extender are mixed in the molten state at elevated temperatures. The product is then normally cured in a mould at temperatures of 50-130°C for several hours. Some disadvantages in this preparation are noted:

- i) Choice of diisocyanate is restricted to those having a relatively low melting point
- ii) Chain extenders must also be liquids or low melting solids
- iii) Chain extender reactivity with diisocyanate must be low enough to allow efficient mixing of the chain extender with the prepolymer prior to casting
- iv) Efficient dispersion of reactants is important and can be hindered by the relatively high viscosity of the molten mixture
- v) Efficient mixing can be hindered by use of reactive chain extenders which lead to a short pot life.

These disadvantages can be limited by using solution polymerisation techniques. However, this too has its difficulties as shown below:

- i) The solvent must contain no active hydrogen atoms
- ii) The solvent must be dry to prevent water-isocyanate reactions from occurring
- iii) The solvent must be a pure and non-reactive medium, in which all reactants are readily soluble.

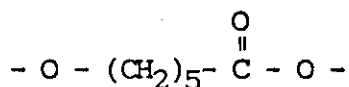
In this research the bulk polymerisation technique was followed due to the low reactivity of the constituents involved. The raw

materials used are given in Appendices I and II with their relevant technical information.

3.2 SELECTION OF RAW MATERIALS

3.2.1 Polyol

Polycaprolactone polyols of varying molecular weights have been used throughout this study. These are saturated aliphatic polyesters similar in type to adipates. The polarity in the polyols due to the polar C=O groups in their chemical structure backbone increases the intermolecular attractions in urethane elastomers and hence improves their physical and mechanical properties. One disadvantage is their tendency to crystallise on ageing, if the hard segment content is not sufficient to restrict the mobility or regularity of the soft segment, due to the polyol having a single repeat unit



3.2.2 Diisocyanates

It is well known that aliphatic diisocyanates impart superior colour stability to polyurethanes. A few of these were primarily examined but the study was mostly based on 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI). This diisocyanate has three isomeric forms (see Appendix I), one of these (trans-trans) isomers crystallises out if stored below 10°C. It is important to keep the isomeric ratios within certain limits to obtain optimum transparency and strength. Being aliphatic the H_{12} MDI is low in reactivity and would allow good mixing of the reactants in the synthesis of the polyurethane. The synthesis temperature used was 130°C due to this low reactivity and the requirement that no catalyst be used and so eliminating this as a source of degradation on ageing.

Some work was also carried out using isophorone diisocyanate (IPDI). This is a cycloaliphatic diisocyanate chemically derived from isophorone with no tendency to crystallise at low storage temperatures. Due to its relatively high molecular weight its vapour pressure is very low which simplifies handling this isocyanate. Isophorone diisocyanate has two differently combined isocyanate groups (see Appendix I). The aliphatic isocyanate group is claimed to be ten time more reactive as the cycloaliphatic group (see data sheet in Appendix I). This difference in reactivity enables prepolymers to be produced which have a low diisocyanate monomer content and hence give controlled structure urethanes.

Trimethylhexamethylene diisocyanate (TMDI), another aliphatic diisocyanate was looked at, but due to its structure gave soft and flexible materials. Two recent new isocyanate systems developed were also investigated, these are 1,4 cyclohexane diisocyanate (CHDI) and paraphenylene diisocyanate (PPDI). The disadvantage of these are their high reactivity (especially PPDI), high vapour pressure (hazardous) and produce translucent-opaque polymers.

3.2.3 Chain Extenders

Several low molecular weight aliphatic and cycloaliphatic diols were used as chain extension agents. When using H_{12} MDI, the selection of the chain extender should be based on the stereo isomer content in the diisocyanate. As for optically clear elastomers, it is considered necessary that the monomeric diol be symmetrical when the diisocyanate is low in trans, trans isomer content, e.g. less than 30% [141]. Symmetrical and unsymmetrical diols were used, the cyclohexanedimethanol was used as a blend with 1,4-butanediol, on its own it is difficult to mix and tends to condense on the walls of the reaction flask.

The crosslinking systems used were trimethylolpropane (TMP) and polycaprolactone 305, both these are trifunctional. They were used as a blend with other chain extenders. Crosslinking was also

introduced via the polyol system by using tetrafunctional polycaprolactones.

3.3 SYNTHESIS

Critchfield [142] found that polyurethane elastomers with the best clarity were obtained at the highest possible initial reaction temperature with the cure temperature being of secondary importance. The prepolymer method of synthesis was used in this research and the precise conditions were optimised for each particular system.

3.3.1 Reactivity of Raw Materials

This was carried out to optimize the conditions for synthesis. A synthesis method was recommended [143] which essentially is to make a prepolymer for 60-90 minutes at 130°C and then chain extend below 100°C. The reactivity rates used an infrared technique which monitored the decreasing isocyanate (-NCO) content with reaction time. The -NCO absorbance at 2270 cm^{-1} was compared with the internal standard -CH absorbance at 2935 cm^{-1} , this overcame the problem of sample thickness.

The chain extension agents were reacted with the diisocyanates (H_{12} MDI and IPDI) at 95°C as this would be the approximate recommended temperature of reaction. These were reacted at a 1:1 equivalent ratio under dry nitrogen with continuous stirring. At timed intervals a small drop was taken from the reaction flask and placed between two clean sodium chloride discs and an infrared spectra recorded. The calculation showing the amount of unreacted isocyanate with time is given in Appendix III.

The rates of reaction of chain extender with diisocyanates were very fast giving solid products at the end of each reaction. Practically only a few infrared spectras could be taken as once the chain extender had mixed fully with the diisocyanate the viscosity

increased very quickly. This made it difficult to obtain samples thin enough for infrared analysis. It was found that the time taken for the reactants to gel and solidify was sufficient to cast the material (see Table 3.3.1). It can be assumed that the prepolymer/chain extender reaction would give longer gelation/solidification times due to the dilution of the isocyanate groups in the prepolymer. This would keep the viscosity sufficiently low to cast the molten polymer with ease.

Diisocyanate	Chain Extender			
	1,4-BD	1,3-BD	1,6-HD	1,4-BD + 1,4-CHDM(1:1)
H ₁₂ MDI	30	30-35	40	35-40
IPDI	15		15-20	

TABLE 3.3.1: Approximate times (minutes) of gelation/solidification of isocyanate/chain extender reactions at 95°C on a 1:1 equivalent ratio

A similar technique was applied to the prepolymer stage, i.e. isocyanate reacted with polyol at a 1:1 equivalent ratio at 130°C. This reaction was followed in the same manner and a range of polycaprolactone polyols with differing molecular weights were used (see Graph 3.3.1). It is observed that the viscosity increases such that below 25-20% unreacted NCO content, the infrared analysis becomes difficult. An extension of this was taken to include reactions of one polyol (Capa 210) with H₁₂MDI in the ratios of 1:2, 1:3 and 1:4 to monitor the reactivity and observe the viscosity changes with higher isocyanate content (see Graph 3.3.2).

The observations made indicate that after 60-80 minutes the reactivity slows down and is becoming constant. So to cover all the polyol systems a prepolymer formation time of 90 minutes at 130°C was used for all thermoplastic H₁₂MDI based polymers. The polyols of varying molecular weights used in the study are given in Appendix II.

3.3.2 Synthesis Method Used

The melt polymerisation technique was used and all the polyurethanes reported here were synthesised in the laboratory. The following procedure was used:

1. The polyol to be used was melted and dried under vacuum at 90-95°C for one hour before use. The chain extender was similarly dried for 30 minutes and the H₁₂ MDI was warmed (30-40°C) before use
2. The required amounts of polyol and diisocyanate were placed in a round bottomed 250 ml reaction flask over nitrogen
3. The flask was fitted to a five necked flange lid and equipped with a nitrogen inlet and an anchor stirrer fitted to a variable speed constant torque stirrer motor (see Figure 3.3.1). White spot nitrogen (BOC) was used throughout and further dried by passing through silica gel guard tubes
4. The reaction flask was placed in a temperature controlled hot oil bath set at 130°C, which was also monitored by using a mercury thermometer immersed in the oil by the side polymerisation flask. The contents of the flask was then continuously stirred for 90 minutes under dry nitrogen
5. The oil bath was then removed and the contents allowed to cool for a few minutes. The required amount of chain extender is added to the reaction flask and stirred until the contents clarified. Stirring was then continued for a further 1-2 minutes to ensure that complete mixing had taken place.
6. This polymer mix was then degassed under vacuum and cast onto a highly polished preheated aluminium tray coated with release

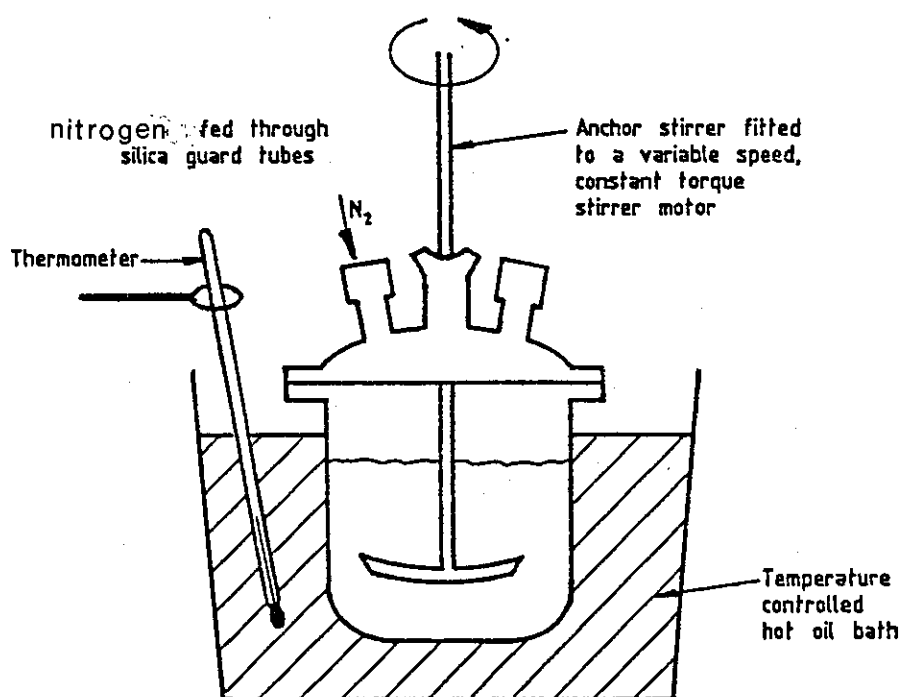


FIGURE 3.3.1: TYPICAL LABORATORY APPARATUS USED FOR THE SYNTHESIS OF POLYURETHANE ELASTOMERS

agent*. The tray was placed in a hot air circulated oven kept at 120°C for about 18 hours, followed by a post cure of one week at ambient temperatures before testing.

The whole process was carried out in a fume cupboard with the use of safety goggles, laboratory coats, latex gloves and general good housekeeping.

3.4 QUANTITIES AND RATIOS OF REACTANTS USED

The stoichiometric proportions of reagents used in the synthesis of polyurethanes has generally been given in terms of 'block ratio'. This means that a polyurethane based on a block ratio of 1:3:2 denotes the equivalent weight ratios of polyol:diisocyanate:chain extender that are reacted to form the polyurethane. Shown below are some worked examples for producing linear and crosslinked polyurethanes.

Example 1: A linear thermoplastic system based on Capa 210:H₁₂MDI:1,4-BD

Reactants	Functionality	Equivalent Weight	Block Ratio	Stoichiometric amounts needed	Amounts used (g)
Capa 210	2	500	1	500	100
H ₁₂ MDI	2	131	3	393	78.6
1,4-BD	2	45	2	90	18

* Ambersil's polyurethane release agent was used

Example 2: A crosslinked system using a triol as part of the chain extender system

Reactants	Functionality	Equivalent Weight	Block Ratio	Stoichiometric amounts needed	Amounts used (g)
Capa 210	2	500	1	500	100
H ₁₂ MDI	2	131	3	393	78.6
1,4-BD	2	45	1	45	9
TMP	3	44.7	1	44.7	8.94

The stoichiometric amounts of the chain extender are first mixed in larger quantities and then used as required i.e. $9 + 8.94 = 17.94\text{g}$.

Example 3: A crosslinked system with the polyol as the crosslinking additive

Reactants	Functionality	Equivalent Weight	Block Ratio	Stoichiometric amounts needed	Amounts used (g)
Capa 800/ 031	4	250	1	250	100
H ₁₂ MDI	2	131	3	393	157.2
1,4-BD	2	45	2	90	36

The calculations show that the polyol (Capa 210) has a molecular weight (equivalent weight times functionality) of 1000. This is strictly not true and the actual equivalent weight can be calculated from the hydroxyl value supplied by the manufacturers for each batch of polyol. The hydroxyl number is defined as the number of

milliweights (or milligrams) of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 gram of the compound or polyol

$$\text{Hydroxyl number} = \frac{56100}{\text{Equivalent Weight}}$$

The hydroxyl value of Capa 210 is 113.4

$$\text{Equivalent weight} = \frac{56100}{113.4} = 494.7$$

So Example 1 would be:

Reactants	Equivalent Weight	Block Ratio	Stoichiometric Amounts Needed	Amounts Used
Capa 210	494.7	1	494.7	100
H ₁₂ MDI	131	3	393	79.44
1,4-BD	45	2	90	18.19

The stoichiometric amounts were calculated from hydroxyl values for all the polyurethanes synthesised.

3.5 PROBLEMS ASSOCIATED WITH THE PREPARATION OF POLYURETHANES

These were mainly connected with transparency and bubbles in the final polymer. The factors influencing the turbidity and opacity in the cast polyurethane elastomer could include:

1. Strong polar interactions between polymer chains associated with the formation and crystallisation of polyurethane segments rather than the formation of primary crosslinks

2. Separation of phases which may either be crystalline or amorphous due to a wide variation in polymer species arising from block size distribution
3. Inhomogeneity due to poor mixing, limited compatibility or differences in rates of reaction of chain extenders or crosslinking agents.

Other problems are noted and the ways they are overcome are discussed.

4. Once the prepolymer and chain extender have been fully mixed, these should be degassed sufficiently to remove any air bubbles from the mixing stages. Prolonged evacuation can lead to higher viscosities, volatile unreacted materials (e.g. chain extender) being taken off leading to stoichiometric problems. The high viscosity also gives casting problems and could leave pour marks on the cast sheet. Once the prepolymer/chain extender mixture is sufficiently degassed it should be slowly poured into the aluminium tray from one edge, while the tray is tilted slightly to eliminate any entrapment of air while pouring
5. The release agent Cilase 1818 was used, but the release of the elastomer from the tray became more difficult after 3 or 4 castings. This was later rectified by using a mild abrasive metal polish (i.e. Brasso) after each polymerisation, before applying the release agent. This also degraded the surface quality of the tray and hence the surface finish of the elastomer. On using other release agents it was found that 'Polyurethane Release Agent' by Ambersil was very effective and was hence used. This gave no problems of release from the moulds on repeated use

6. In some polymerisations the elastomer has wavy patterns and wrinkles formed on the surface, however the mechanism of this is not clearly understood. It may be due to the initial high viscosity of the polymer melt which starts to gel and when placed in the oven, the high speed fan in the oven gives the surface effect on curing. Another reason could be insufficient mixing of the chain extender, because of its lower viscosity which would be near the surface, and hence difference in reactivity of the surface and bottom layers giving the surface appearance.
7. The final polymer tends to yellow if the curing temperature is above 130°C as degradation/oxidation can occur. At temperatures below 100°C the cured polymer tends to become hazy, and in some cases the cured elastomer although initially clear becomes translucent on ageing.
8. The mould surfaces were found to have a profound effect on the optical clarity of polyurethanes. The highly polished aluminium trays were found to give transparent materials with good release properties with the release agent used. The other advantages of aluminium trays is their low cost, light weight and good optical finish; they are however easily scratched and difficult to polish. Steel moulds with highly polished surfaces (mirror finish or chrome plated) which are less susceptible to scratches and can be repolished, produce clearer materials. A slight roughening on the mould surface can produce translucent polymers. To ensure that the translucency is only a surface effect, transparency measurements can be made with the polymer first coated with a liquid of the same refractive index.* This eliminates the surface blemishes due to mould surface or release agent and give samples with transparency readings as if they were cast onto a perfect polished surface.

* Cedarwood oil.

It was required to prepare sheets of differing thicknesses:

- a) 2 mm thick sheets for general tensile measurements
- b) 3 mm thick sheets for impact testing
- c) 3 mm, 4mm, 6 mm, 8 mm and 10 mm thick sheets for ballistic testing.

Suitable samples from the prepared sheets were used for other analysis work e.g. DMTA. The main problem of synthesising the thicker sheets were the formation of bubbles in the final polymer. A polymer of uniform thickness was initially cast by pouring into a vertical mould clamped together using spacers (Figure 3.5.1). There were difficulties in pouring especially at high viscosities, and there were also problems with bubbles in the final polymer. The casting into a horizontally levelled tray was then used for making all the various thicknesses of sheets. It was observed that using fresh materials (e.g. polyol) longer drying times and casting at low viscosities of the polymer melts helps in the formation of bubble free polyurethanes.

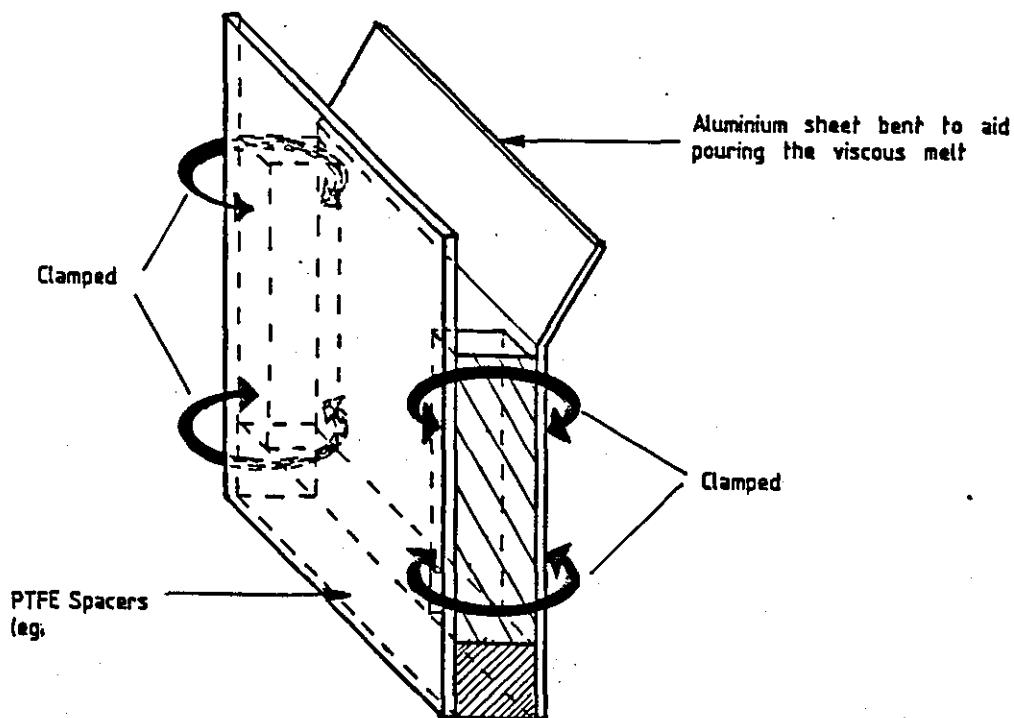


FIGURE 3.3.2: A VERTICAL MOULD MADE OF HIGHLY POLISHED ALUMINIUM SHEETING FOR PREPARING ELASTOMERS OF UNIFORM THICKNESS

3.6 OTHER SYNTHESIS METHODS USED

3.6.1 Isophorone Diisocyanate (IPDI)

This diisocyanate is liquid and the synthesis method is similar to that earlier described for H₁₂MDI. As IPDI is more reactive the temperature and time for prepolymer formation is lower, this being 100°C for 30 minutes. The chain extension reaction is then followed in the same manner, after which 0.1% DABCO (of total weight) is added and mixed before deaeration and casting. Transparent polyurethanes of high hardness and rigidity have been prepared.

3.6.2 Cyclohexane Diisocyanate (CHDI) and Paraphenylene Diisocyanate (PPDI)

These diisocyanates tend to produce hard rigid polymers due to their chemical structure and give translucent-opaque elastomers. They are difficult to handle in a safe manner and are very reactive, especially PPDI. They are synthesised under the same conditions as the IPDI method but at lower temperatures i.e. at 85-90°C. Transparency may be introduced by using bulky structured chain extenders such as Dianol 22, Dianol 33 or mixtures thereof (see Appendix II), but these also produce translucent polymers. It was found that both CHDI and PPDI dimerize and we were also informed by the suppliers that they may also contain some traces of organic chlorides which may interfere with the transparency. One way to overcome this problem is to distill the diisocyanates and then use immediately, as on shelf ageing the same problems may arise. The distillation of these diisocyanates has its practical difficulties concerning its high vapour pressure and health problems, therefore this operation was not carried out. The CHDI is supplied in the trans, isomeric form; in its pure state colour stable polyurethanes can be made using appropriate chain extenders and polyols. Another way of introducing transparency is if the cis isomeric form of CHDI could be made and then mixed with the trans isomer, such that the mixed isomer CHDI be made, it is predicted to lead to transparent polyurethanes.

3.6.3 Crosslinked Polyurethane Systems

Crosslinking was introduced as part of the chain extender system, these are lightly crosslinked and are synthesised in the same manner as the H_{12} MDI elastomers. Higher crosslinking was introduced via the polyol system and the synthesis method in this case was similar to that used for IPDI (except that no catalyst addition was made in these syntheses) with the prepolymer temperature of 95°C.

The polyurethanes prepared in this study are shown in Tables 3.6.1 to 3.6.5.*

* The key to these tables is:

Trans: Transparent

F: Flexible

R: Rigid

B: Brittle

TABLE 3.3.2: Thermoplastic Polyurethanes Prepared

H ₁₂ MDI/1,4-BD based elastomer	Block Ratio	Hardness (Shore D)	Observations
Capa 240	1:3:2	52	Opaque, F
Capa 231	1:3:2	54	Opaque, F
Capa 220	1:3:2	27	Trans, F
	1:4:3	32	Trans, F
	1:5:4	38	Trans, F
	1:6:5	44	Trans, F
	1:7:6	53	Trans, F
	1:8:7	56	Trans, F
	1:9:8	60	Slight hazy, F
Capa 215	1:3:2	34	Trans, F
	1:4:3	47	V.slightly hazy, F/R
	1:5:4	58	Slightly hazy, F/R
	1:6:5	64	Slightly hazy, R/F
	1:7:6	69	Hazy, R
Capa 210	1:2:1	<20	Trans, F
	1:3:2	45	Trans, F
	1:4:3	58	Trans, F/R
	1:5:4	72	Trans, R/F
	1:6:5	74	Trans, R
	1:7:6	77	Trans, R/(B)
	1:8:7	79	Slightly hazy, R/B
Capa 205	1:3:2	54	Trans, F
	1:4:3	65	Trans, R/F
	1:5:4	74	Slightly hazy, R/B
Capa 200	1:2:1	41	Trans, F
	1:3:2	77	Trans, R
	1:4:3	80	Trans, B/R
H ₁₂ MDI/1,4-BD + 1,4-CHDM			
Capa 220	1:7:3+3	60	Trans, R/F
	1:9:4+4	68	Trans, R
Capa 215	1:4:1.5+1.5	48	Trans, F
	1:5:2+2	60	Trans, R/F
	1:6:2.5+2.5	70	Trans, R
	1:7:3+3	73	Trans, R/B
Capa 210	1:3:1+1	46	Trans, F
	1:4:1.5+1.5	66	Trans, R
	1:5:2+2	76	Trans, R
Capa 205	1:2:0.5+0.5	21	Trans, very F
	1:3:1+1	45	Trans, F/(R)
	1:4:1.5+1.5	74	Trans, R/B
Capa 200	1:2:0.5+0.5	53	Trans, R/F
	1:3:1+1	79	Trans, R/B

Table 3.3.2 (continued)

H ₁₂ MDI/1,6-BD based elastomer	Block Ratio	Hardness (Shore D)	Observations
Capa 215	1:5:4	47	Trans, F
	1:6:5	53	Trans F/R
	1:7:6	61	Trans, R/F
	1:8:7	70	Slightly hazy, R/F
Capa 210	1:5:4	64	Trans, R/F
	1:6:5	71	Trans, R
	1:7:6	74	Trans, R
Capa 205	1:4:3	55	Trans, F/R
	1:5:4	73	Trans, R/F
Capa 200	1:2.9:1.9	68	Trans, R
	1:3.3:2.3	75	Trans, R
	1:4:3	78	Trans, R
H ₁₂ MDI/1,3-BD based elastomer			
Capa 220	1:4:3	<20	Trans, F
	1:5:4	20	Trans, F
	1:6:5	33	Trans, F
	1:7:6	43	Trans, F
	1:8:7	55	Trans, F/R
	1:9:8	67	Trans, F/R
	1:10:9	66	Trans R/F
	1:11:10	73	Trans R/B
Capa 210	1:3:2	26	Trans, F
	1:4:3	46	Trans, R/F
	1:5:4	75	Trans, R/(B)

TABLE 3.3.3: Thermoplastic Polyurethanes Based on Other Isocyanates

PPDI Based elastomer	Block Ratio	Hardness (Shore D)	Observations
Capa 220/1,4-BD	1:2:1	31	Opaque R/F
	1:3:2	41	Opaque R/F
Capa 220/1,3-BD	1:2:1	<20	Translucent, F
	1:3:2	20	Translucent, F
	1:4:3	32	Translucent, F
	1:5:4	36	Translucent/opaque, F
Capa 210/D33	1:3:2	54	Translucent, R
CHDI Based elastomer	Block Ratio	Hardness (ShoreD)	Observations
Capa 220/1,4-BD	1:2:1	27	Opaque F
	1:3:2	42	Opaque R/F
	1:5:4	57	Opaque B/R
	1:9:8	67	Opaque B
Capa 210/1,4-BD	1:3:2	54	Opaque R/F
	1:5:4	75	Opaque B/R
	1:9:8	83	Opaque B
Capa 220/CHDI/D22	1:3:2	41	Translucent, R
Capa 210/TMDI/	1:5:4	<20	Trans, very F
1,4-BD	1:9:8	<20	Trans, very F
IPDI/1,4-BD based elastomers	Block Ratio	Hardness (Shore D)	Observations
Capa 220	1:3:2	35	Translucent, F
	1:5:4	39	Trans, F
	1:7:6	44	Trans, F/(R)
	1:9:8	60	Trans, R/F
Capa 215	1:6:5	55	Trans, F/R
Capa 210	1:3:2	26	Trans, F
	1:5:4	66	Trans, R/F
	1:7:6	81	Trans, R
	1:9:8	85	Trans, R/B
Capa 205	1:4:3	63	Trans, F/R
Capa 200	1:3:2	78	Trans, R

TABLE 3.3.4: Polyurethanes lightly crosslinked with various chain extenders based on Capa 205/H₁₂MDI at 1:4:3 block ratio

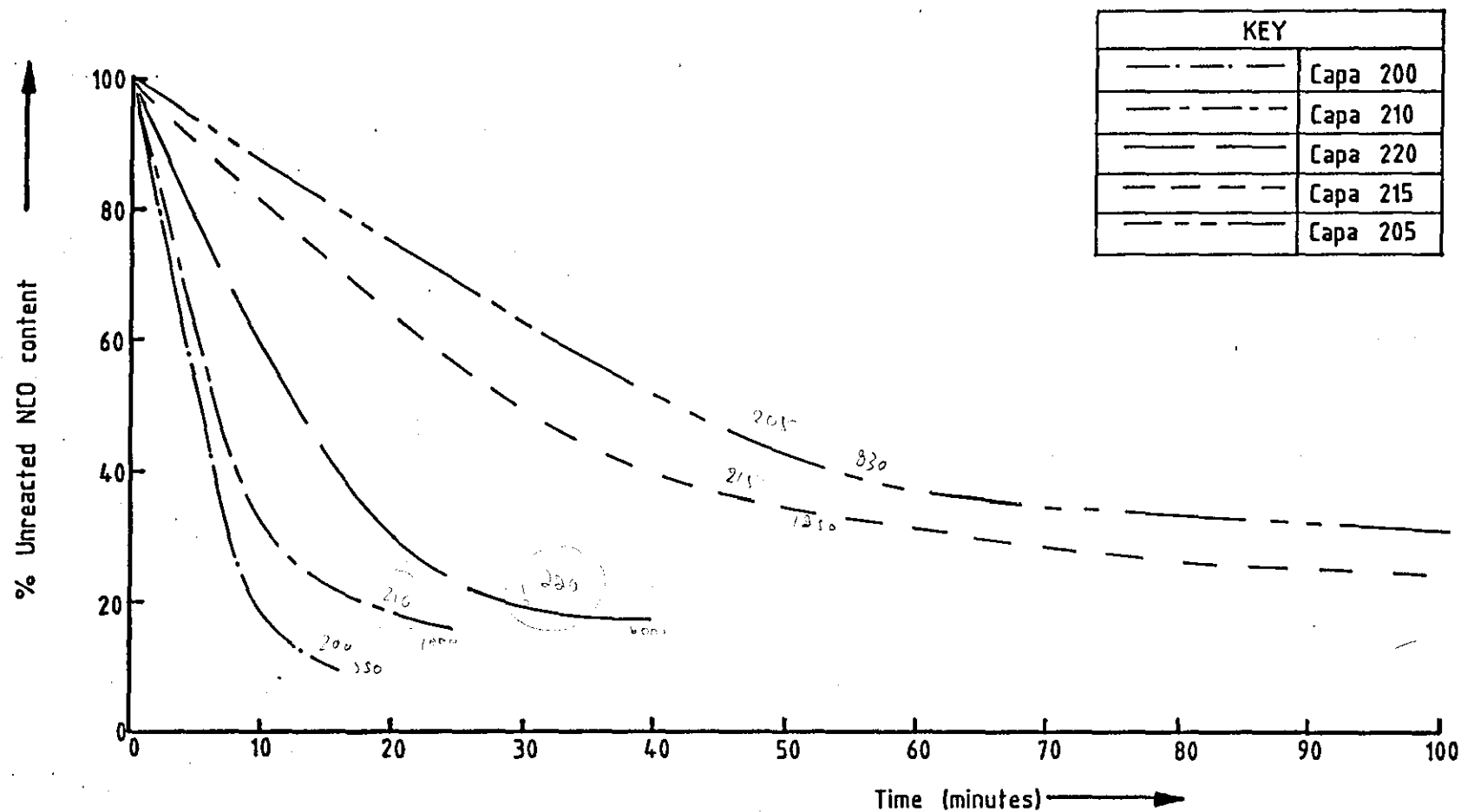
Chain Extender System	Block Ratio	Hardness (Shore D)	Observations
1,4-BD + TMP	1:1	68	Trans, R
	1:0.5	65	Trans, R
1,4-BD + Capa 305	1:1	28	Trans, F
	1:0.5	50	Trans, F/R
D22 + TMP	1:1	81	Trans, R
	1:0.5	82	Trans, R/B
D22 + Capa 305	1:1	59	Trans, R/F
	1:0.5	78	Trans, R
D33 + TMP	1:1	81	Trans, R
	1:0.5	80	Trans, R
D33 + Capa 305	1:1	63	Trans, R/F
	1:0.5	77	Trans, R

TABLE 3.3.5: H₁₂MDI based polyurethanes lightly crosslinked via the chain extender

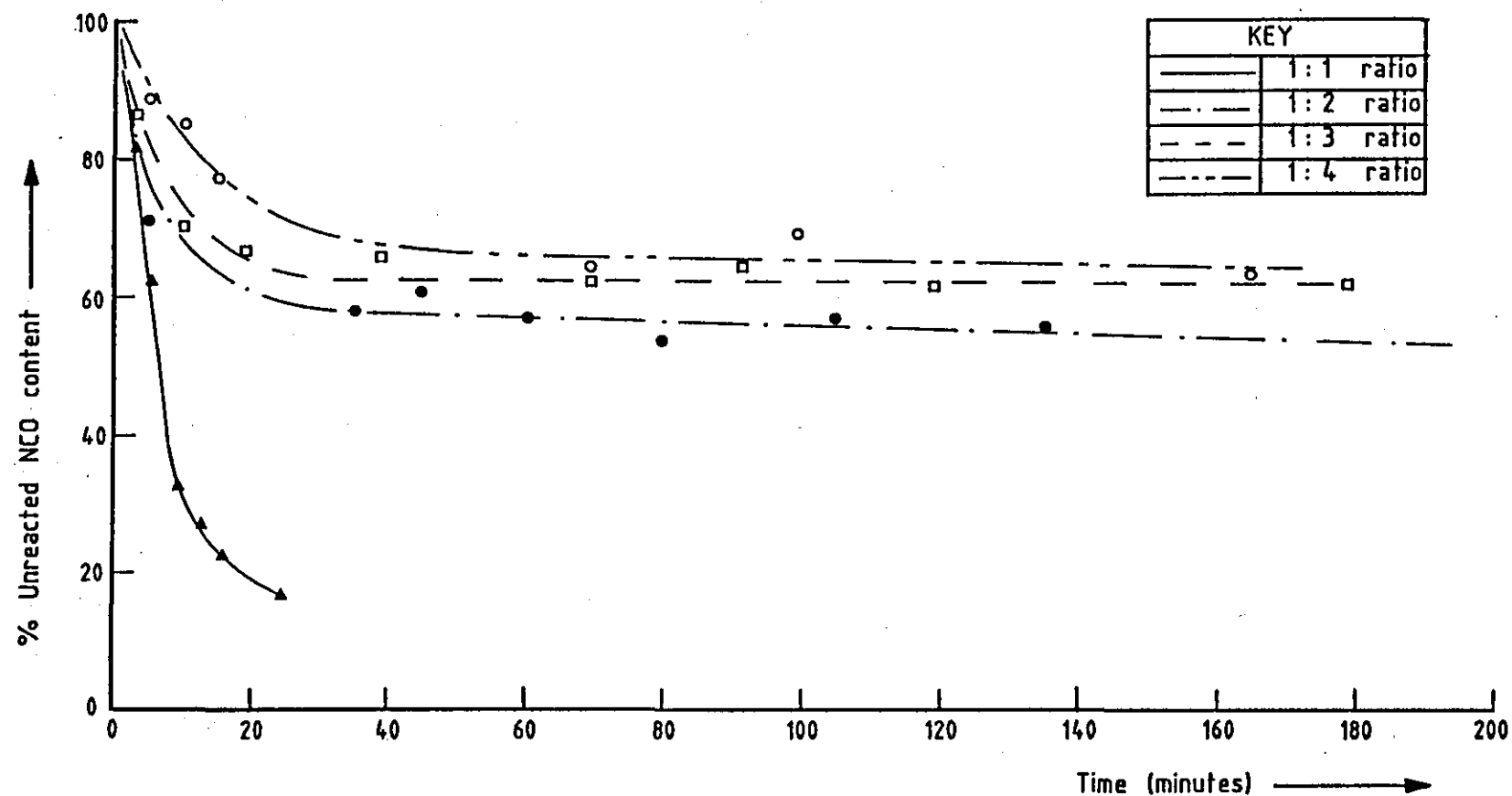
1,4-BD + TMP 1 : 1 Chain extended	Block Ratio	Hardness (Shore D)	Observations
Capa 215	1:6:5	59	Trans, R/F
Capa 210	1:5:4	73	Trans, R
Capa 205	1:4:3	68	Trans, R
Capa 200	1:3:2	79	Trans, R
1,4-BD + Capa 305 1 : 1 Chain extended	Block Ratio	Hardness (Shore D)	Observations
Capa 215	1:6:5	37	Trans, F
Capa 210	1:5:4	36	Trans, F
Capa 205	1:4:3	28	Trans, F
Capa 200	1:3:2	54	Trans, R/F
D33 + Capa 305 1 : 1 Chain extended	Block Ratio	Hardness (Shore D)	Observations
Capa 215	1:6:5	54	Trans, R/F
Capa 210	1:5:4	71	Trans, R
Capa 205	1:4:3	63	Trans, F/R
Capa 200	1:3:2	78	Trans, R
D22 + Capa 305 1 : 1 Chain extended	Block Ratio	Hardness (Shore D)	Observations
Capa 215	1:6:5	54	Trans, R/F
Capa 210	1:5:4	65	Trans, R/F
Capa 205	1:4:3	59	Trans, F/R
Capa 200	1:3:2	76	Trans, R

TABLE 3.3.6: Highly crosslinked polyurethanes via the polyol system

H ₁₂ MDI/1,4-BD based elastomer	Block Ratio	Hardness (Shore D)	Observations
Capa 305	1:2:1	81	Trans, R
	1:3:2	82	Trans, R/B
	1:4:3	83	Trans, R/B
Tetra-ol 600	1:2:1	84	Trans, R/B
	1:3:2	84	Trans, R/B
	1:4:3	85	Trans, R/B
Tetra-ol 1000	1:2:1	79	Trans, R
	1:3:2	81	Trans, R/B
	1:4:3	82	Trans, R/B
	1:5:4	84	Trans, R/B
IPDI/1,4-BD based elastomer	Block Ratio	Hardness (Shore D)	Observations
Capa 305	1:2:1	84	Trans, R
	1:3:2	85	Trans, R/B
	1:4:3	87	Trans, R/B
Tetra-ol 600	1:2:1	86	Trans, R/B
	1:3:2	87	Trans, R/B
	1:4:3	88	Trans, B/R
Tetra-ol 1000	1:2:1	81	Trans, R
	1:3:2	84	Trans, R/B
	1:4:3	86	Trans, R/B



Graph: 3.3.1: Shows the change in unreacted NCO content with the time for the polyols shown on reaction with H_{12} MDI at 130°C and at 1:1 molar ratio.



Graph: 3.3.2. Shows the change in unreacted NCO content with time for reaction between capa 210 and M₁₂MD1 at the ratios 1:1, 1:2, 1:3 and 1:4 respectively at a temperature of 130°C.

CHAPTER 4

CHARACTERISATION OF PREPARED POLYURETHANE ELASTOMERS

4A.1 DIFFERENTIAL SCANNING CALORIMETRY

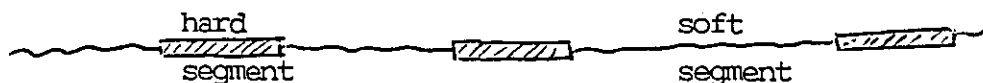
Thermoanalytical techniques have been used in the study of the morphology and intermolecular bonding in polyurethane elastomers. These techniques include: differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermomechanical analysis (TMA) and thermogravimetry (TG) [144]. DSC is known to be a useful technique in determining the morphological state of polyurethanes as it can provide information on the two phase structure and extent of phase segregation which contributes to the performance of the polymer.

A DSC instrument basically heats or cools a small sample (10-15 mg) under carefully controlled and reproducible conditions. The technique measures the heat flow into or out of the sample (enclosed in a small aluminium pan) relative to an inert reference material (empty enclosed aluminium pan). Any temperature difference between the sample cell and the reference cell is measured using thermocouples connected to the cells. When the temperature of the sample equals that of the reference the two thermocouples produce identical voltages, and the net voltage output is zero. At this point there is no change in the heat capacity of the sample. When the two temperatures differ there is then a net voltage produced proportional to the temperature difference. This net voltage is amplified and recorded on the y-axis of an x-y recorder. The temperature of the sample and reference is varied at a constant rate and monitored on the x-axis.

The sample heat capacity changes whenever the temperature reaches a point where a change in the organisation of the chains occurs in the sample. Such detectable changes are called thermal responses or

transitions. Chain regularity and block length as well as thermal history during and after polymerisation all play important roles in determining the degree of phase separation as well as the degree of order of the soft- and hard-segment domains. Better phase separation is favoured for less polar polyol (soft segment) systems and with longer sequence lengths of the respective hard and soft segments. Seymour et al [91] in their work involving various polyols revealed that polyester based samples have a greater tendency for the hard segment units to be trapped in the soft matrix when compared to polyethers. This was believed to be due to greater polarity of the polyester segment which is considered desirable for transparency.

The polyurethane elastomers are usually made from a diisocyanate, a high molecular weight polyol and a low molecular weight chain extender. The relative amounts used and the order in which they chemically react under the synthesis conditions is important as this determines the organisation of the chemical structure of the elastomer. A linear polyurethane system may be represented by the following concept:



The soft segments tend to be low melting and the hard segments tend to be high melting entities. Such hard segment domains form a structural feature of the polyurethane elastomer since they tie the polymer primary chains together. The nature of the hard segment has been extensively studied [64,70,73,79,88,145-8], and whilst it is expected to be crystalline, its crystallinity cannot be detected by conventional tests such as with wide angle X-ray studies (WAXS). It appears that the strong mutual attraction of the hard segments (e.g. urethane-urethane hydrogen bonding) restricts their mobility and thus their ability to organise themselves into a crystalline

lattice. As a result the hard segments in the polymer primary chains form aggregates (domains) in the mobile soft segment matrix and a two phase system results.

The hard segment domains cannot be shown to be crystalline by the WAXS technique possibly because of their small size. However, with small angle X-ray studies the existence of these domains is detectable giving some idea of their order, size and separation in the soft segment matrix. The subcrystalline state of the elastomers hard segment domains has been referred to as the para-crystalline state [64].

4A.2 PHASE SEGREGATION OF HARD AND SOFT SEGMENTS

Studies [148] have shown that melting the elastomer, such as occurs during processing, results in the re-mixing of its soft and hard segments. This is followed by their tendency to de-mix or segregate in the cooled solid elastomer. It can be appreciated that an elastomer whose hard segments have not aggregated has not developed its ultimate property potential. Often the segregation of hard and soft segments increases with time. In some elastomer compositions the intermolecular forces favouring the mixed or the demixed states seem to largely balance each other, and de-mixing is largely retarded. In any case, phase segregation in the elastomer is a time dependent phenomenon which is important in the study and use of these polymers.

4A.3 THERMAL TRANSITIONS

Several transitions are seen and an important low temperature transition is the glass transition temperature (T_g). This is observed by heating the elastomer slowly from low temperature (typically -100°C) and monitoring its heat absorption (Figure 4A3.1). At point A the heat absorption changes and reverts back to its original rate at point B. The AB region is the temperature range in which the elastomer soft segment changes from a rigid

'glassy' state to a flexible 'rubbery' state. This is the glass transition region of the soft segments and the change occurs when the applied thermal energy is adequate to overcome a set of relatively weak, interchain attractive forces which immobilise the chain segments allowing them to move. By convention, the midpoint C of AB is taken as the glass transition temperature (T_g).

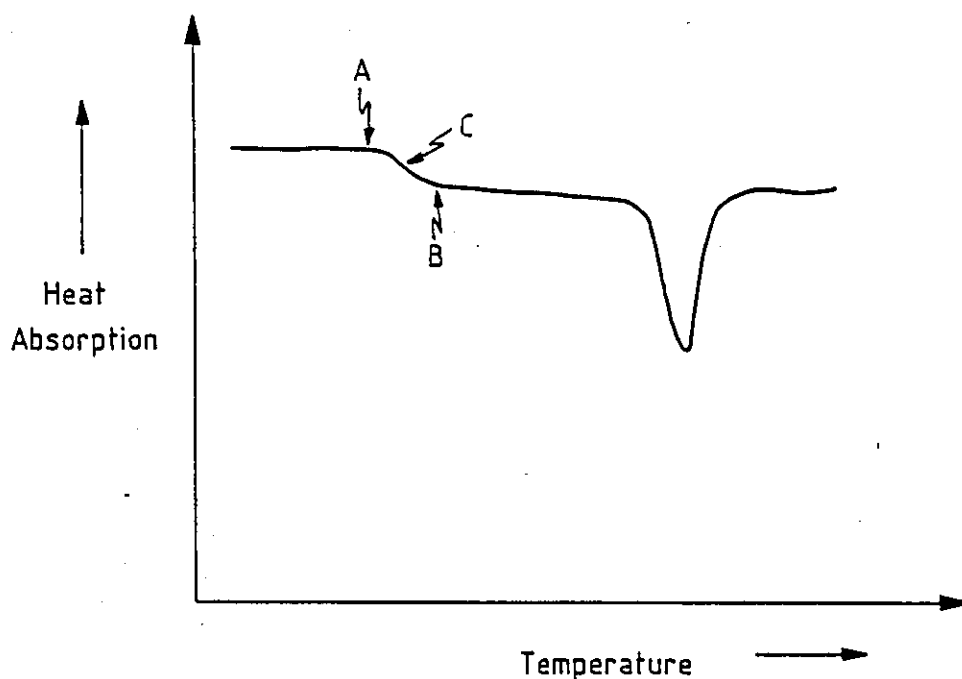


FIGURE 4A3.1: TYPICAL THERMOGRAM OF A POLYURETHANE ELASTOMER BY DSC

The T_g has a practical significance as it indicates the temperature at which the polymer loses appreciable flexibility as it cools. Low temperature flexibility can be significantly regulated by the choice of polyol molecular weight and thus soft segment length. The variation in T_g of the soft segment as a function of composition or segmental chemical structure may be used to indicate the degree of microphase separation in the polymer.

Three endothermic transitions are normally seen and these were attributed to the break up of intersegmental hydrogen bonds.

Specifically in a polyurethane the endotherm in the region of 80°C is ascribed to the dissociations of urethane soft segment hydrogen bonds while the endotherms at 150-170°C are related to the break up of inter-urethane hydrogen bonds [145]. A small transition at about 190°C which is more prominent in materials having longer urethane segments, result from melting of microcrystalline hard segment regions. Recent DSC studies [85,130,131] of urethane block copolymers confirm that the DSC endotherms do not result from disruption of secondary bond interactions. It appears that these transitions are morphological in origin.

The endotherms may be termed as T_1 , T_2 and T_3 in progressively increasing temperature order. These multiple endotherms are believed to reflect the segmental melting or disruption of hard segment domains with different degrees of organisation developed during prior polymer thermal and processing history. The transition at 70-80°C (T_1) is attributed to the melting temperature of the shortest average hard segment. Sometimes this reflects the melting of soft segment crystallites. Likewise the transition at 140-170°C (T_2) represents hard segment melting but of a relatively long range order. The highest melting endotherm (T_3) may be assigned to relatively well ordered microcrystalline aromatic polyurethane segments, the number and perfection of which are determined by segment length and thermal history. It is noticeable that the T_3 peak due to microcrystalline regions cannot be seen in elastomers with short hard segment length. Seymour et al [85] confirmed that the appearance of the DSC endotherm is a function of hard segment length. Polyurethanes having shortest average hard segments, exhibited only the T_1 peak, moderate hard segments showed T_1 and T_2 whereas the highest hard segment content gives all three endotherms.

Thus in segmented polyurethanes strength is enhanced by long rigid hard segments with high cohesive energy. Although hydrogen bonding can contribute to domain cohesiveness, H-bonding itself is not directly responsible for high strength. The presence of hydrogen bonds serves to increase the overall cohesion of the material as

these bonds are stronger and more directional than other intermolecular forces.

4A.4 PRESENT WORK

The DSC thermograms of prepared polyurethanes were measured on a Du Pont 990 Thermal Analyser in conjunction with a standard Du Pont heating cell. Thermograms were recorded using polyurethane samples of 10-15 mg encapsulated in small aluminium pans. An empty aluminium pan was used as the reference. The cell was cooled to about -125°C by pouring liquid nitrogen into a steel jacket surround and on reaching this temperature the jacket is replaced by a steel cover and glass surround. Precautions were taken to avoid liquid nitrogen entering the cell as the resulting ice formation would lead to undesired transitions due to water. The cell is then heated at a constant rate of 20° per minute with a steady purge of dry nitrogen passing through. All the thermograms were recorded between -100°C to $+280^{\circ}\text{C}$ on a two pen recorder, each pen being set at different sensitivities of 5 and 10 mV/cm.

The analysis of the thermograms of prepared polyurethanes and their constituents provide useful information on overall polymer morphology, explaining the manner in which the various chemical constituents of urethane elastomers control transparency and mechanical properties. It is useful to study the thermal behaviour of the individual hard and soft segments as this information helps in determining the phase mixing of these segments in the copolymer and hence their mutual effect on transparency.

The thermograms of the polycaprolactone polyols used in the synthesis are shown in Figures 4A4.1(a) and 4(b), the transitions observed are given in Table 4A4.1. The polycaprolactone diols range from 550 to 4000 molecular weight (see Appendix II). Trifunctional polycaprolactone polyol was used having a 540 m.wt and two tetrafunctional systems used were of 600 m.wt and 1000 m.wt. The polycaprolactone diol of lowest molecular weight (Capa 200) shows an

endothermic as well as an exothermic peak (see Figure 4A4.1(a)) whereas only endothermic peaks are observed with all the other polyols. The 830 m.wt (Capa 205), 1000 m.wt (Capa 210) and 1250 m.wt (Capa 215) polycaprolactone diols all show two endothermic peaks at about 14°C and 39°C. The 830 m.wt diol shows these endotherms similar in magnitude with the peak at about 39°C, which is slightly greater in height. It is observed (Figure 4A4.1(a)) that the lower temperature endotherm (about 14°C) decreases in magnitude with increasing molecular weight of the polyol (i.e. Capa 210 and Capa 215) in comparison to the higher temperature peak. This indicates that Capa 205, Capa 210 and Capa 215 may be a blend of two polyol systems, the ratio of the blend being suited to obtain a specific molecular weight and the required performance in the end product. The 2000 m.wt polyol (Capa 220) also shows two endothermic peaks, the lower temperature peak being very small in comparison to the higher temperature endotherm. The 3000 m.wt (Capa 231) and 4000 m.wt (Capa 240) polycaprolactone diols show a single endothermic peak indicating a pure polyol system. The tri- and tetra-functional polyols did not give any endothermic peaks (Figure 4A4.1(b)) but a change of slope is observed over a wide temperature range.

The polycaprolactone diols were reacted with the H₁₂MDI diisocyanate at a 1:1 ratio to produce the soft segment section of the polyurethane elastomer (Table 4A4.2). It was found that Capa 200, Capa 210 and Capa 220 required low reaction times to produce viscous mixtures, the low m.wt polyol (Capa 200) being the fastest. The Capa 205 and Capa 215 were observed to require much higher reaction times and in this case the lower m.wt polyol (Capa 205) being the slower of the two. This would have an effect on the final polymer properties and would need to be taken into account for comparative purposes with the other polyols. This low reactivity in two polyols and not in others may be due to the catalyst already in the polyol. An analysis for the presence of tin (as commercially available catalysts normally used are tin based) was made with the following results:

Polyol	Capa 200	Capa 205	Capa 210	Capa 215	Capa 220
M.wt	550	830	1000	1250	2000
Tin content (%)	0.03	0.03	0.03	0.03	0.06

The reactivity of the polyols does not compare with these tin contents, it may be that different tin based catalysts (of varying activity) are incorporated in the polyols. The Capa 200, Capa 210, and Capa 220 may have one type of catalyst whereas the Capa 205 and Capa 215 may have a lower catalyst activity for use in specific applications. The reactivity of Capa 200 is further enhanced by its low m.wt as it would have the highest concentration of reactive hydroxyl groups per unit chain in comparison.

The soft segments produced from the polycaprolactone diols of 550 m.wt, 830 m.wt and 1000 m.wt were transparent; the higher m.wt polyols produced opaque soft segments. Soft segment crystallisation is shown to occur with polyols of m.wt of greater than 1000 (Table 4A4.2). The DSC thermograms (Figure 4A4.2) show the transparent soft segments to have no endothermic peaks, the opaque soft segments do produce endothermic peaks as associated with soft segment melting. Melting of the Capa 215 soft segment and Capa 220 soft segment occurs at about the same temperature as that of the pure polyols themselves.

The low temperature transition of the soft segments have all moved to higher temperatures compared to the pure polyols. On reacting two polyols (Capa 210 and Capa 220) separately with another aliphatic diisocyanate, namely isophorone diisocyanate (IPDI), both soft segments were opaque and showed endothermic peaks. The IPDI produces a soft segment with Capa 210 which gives an endothermic peak, which is not present with H_{12} MDI and Capa 210 soft segment. A possible explanation could be that the IPDI being a smaller molecule would allow crystallisation of the polyol chains, although unlikely,

or phase separation has occurred accounting for the peak which appears at the same temperature as the pure polyol.

The hard segments have been prepared by reacting the diisocyanate with several different chain extender systems. These produce brittle solids and range from being transparent to hazy crystalline materials. The chain extension systems used were 1,4-butanediol (1,4-BD), 1,3-butanediol (1,3-BD), 1,6-hexanediol (1,6-HD) and a 1:1 mixture of 1,4-BD with 1,4-CHDM (1,4-cyclohexanedimethanol) all of which gave melting peaks below 100°C (Table 4A4.3).

The hard segment prepared from 1,4-BD gave a broad transition with two noticeable peaks on either side of the major peak (Figure 4A4.3). This may be due to the 1,4-BD reacting individually with the three different isomers of H_{12} MDI (cis-cis, trans-trans, and cis-trans) producing differing hard segments of varying melting points. The similarities in these melting points would produce a broad transition as is observed. The hard segment from the unsymmetrical chain extender 1,3-BD also gave three peaks, one major and two smaller peaks both at higher temperature than the main peak. This could be due to a combination of the non-symmetry of the chain extender and the differing isomers of the diisocyanate. The symmetrical 1,6-HD hard segment gives a similar thermogram to the 1,3-BD hard segment, but gives a broad transition where two peaks are visible in the 1,3-BD hard segment thermogram. The longer 1,6-HD chain extender appears to give a broad transition obscuring any hidden peaks there. The hard segment made with the mixed chain extender system (1,4-BD + 1,4-CHDM at 1:1) gives one major peak and a slight broadening at the temperature range where peaks have appeared with 1,3-BD and 1,6-HD. It is noticeable that the mixed chain extender system and the unsymmetrical 1,3-BD produce a clear glassy brittle material due to randomness introduced via the chain extender. The symmetrical 1,4-BD and 1,6-HD give a slightly hazy, brittle material, which would be more crystalline due to an increased order in the system. The higher the symmetry and order in the system, the more crystalline the material. The hard segment made

from IPDI and 1,4-BD is a clear slightly yellow brittle material. The IPDI has no isomers and only a broad transition is observed.

4A.5 LINEAR POLYURETHANES

These were prepared by reacting the difunctional polyol with an excess of the diisocyanate to make the prepolymer. This is then reacted with an equivalent amount of chain extender to make NCO/OH ratio equal to 1. This produces a linear polyurethane elastomer, the diisocyanate and chain extender amounts are increased in proportion with the same polyol system and their thermograms compared, as shown below:

	Polyol	:	Diisocyanate	:	Chain Extender
e.g.	Capa 210	:	HI2MDI	:	1,4-BD
	1	:	3	:	2*
	1	:	4	:	3
	1	:	5	:	4 etc

* These are molar equivalent ratios used, with examples of increases in diisocyanate and chain extender in equivalent amounts to produce linear elastomers.

The polyurethanes prepared with butanediol as the chain extender are shown in Table 4A5.1, with the data obtained from their DSC analysis. The polyurethanes prepared from Capa 210 and Capa 220 are shown in Figures 4A5.1 and 2 which show the variations observed in increasing the block ratio from 1:3:2 onwards. As the block ratio increases the Tg's become more difficult to distinguish due to the increase in hard segment content. The Capa 210 based polyurethane shows a peak in the 60-70°C region, whereas the Capa 220 polyurethanes due to the higher polyol molecular weight show an endothermic peak at around 70-80°C. These peaks appear to be constant and are associated to the melting of the soft segment of the elastomer, which has later been found to be a time dependent relaxation. A higher melting transition is also observed and is

associated with melting of the hard segment. The higher temperature transition is generally not observed at low block ratio, but becomes more prominent on increasing the block ratio and hence the hard segment content.

The effect of molecular weight of polyol at a constant block ratio has been observed and is shown in Figures 4A5.3 and 4. The traces of the 1:3:2 and 1:4:3 block ratios are given and these show that the T_g of the elastomer is much more easily identified in elastomer of increasing polyol molecular weight. The transition at about 70°C is generally found to move towards higher temperatures with increasing polyol molecular weight. This is expected due to the transition being associated with the soft segment melting. It is, however, observed that there are some anomalies to these general trends, such as with Capa 231 and Capa 240. These 3000 and 4000 (Capa 231 and Capa 240 respectively) molecular weight polyol based polyurethanes do follow the trends in themselves, but give lower melting peaks than the lower molecular weight polyol elastomers at the 1:3:2 block ratio. This may be due to the Capa 231 and Capa 240 being pure polyol systems, whereas most of the lower molecular weight polyols are shown to be a blend of two components. Another possibility is that as these have later shown to be time dependent relaxations, the higher molecular weight polyols may require a greater time period in which to attain the optimum which would thereafter follow the general trend. This is unlikely and the actual reason may be more associated with the Capa 231 and Capa 240 being pure polyol systems, as observing the Figure 4A5.3 more carefully it is seen that the melting transition generally increases up to the polyol Capa 215, then drops at Capa 220; the Capa 215 is a blend of two components, whereas Capa 220 is almost a pure polyol system.

On changing the chain extender from the symmetrical 1,4-BD to the unsymmetrical 1,3-BD for the Capa 220 polyol system (Tables 4A5.2 and Figure 4A5.5) the trends observed are similar in comparison. The T_g 's become more difficult to observe as the block ratio is increased and the soft segment melting occurs at a slightly lower

temperature in comparison with the 1,4-BD extended elastomers. The peaks are small at lower block ratios in comparison to the 1,4-BD based elastomers for the soft segment melting transition, probably due to disorder introduced by the 1,3-BD; at high block ratios the peaks are of comparable size. This may be due to these elastomers requiring more time to reach an optimum as the disorder is created with the unsymmetrical chain extender. The lower melting transitions observed in elastomers extended with 1,3-BD compared to 1,4-BD would again be due to the unsymmetrical 1,3-BD not allowing complete orientation of the soft segments, as with 1,4-BD so that the melting occurs at lower temperatures. The 1,3-BD elastomers do not show any higher melting transitions associated with the hard segment even at high block ratios again probably due to the disorder introduced by the chain extender. The mixed chain extender system used (1,4-BD + 1,4-CHDM at 1:1 ratio) gave elastomers which show similar trends as observed with the 1,3-BD extended elastomers. In comparison to 1,4-⁸D elastomers (Table 4A5.3 and Figure 4A5.6) it is noticed that no melting transition associated with the hard segment is observed for the mixed chain extender system due to the disorder introduced. The T_gs are once again more difficult to observe with increasing block ratios, and the soft segment melting transitions appear weaker in comparison to the 1,4-BD elastomers.

The 1,6-hexanediol (1,6-HD) was also used as a chain extender (Table 4A5.4). This is similar to 1,4-BD, except longer by two units of CH₂ and gives more flexible elastomers as expected. Similar trends are shown with respect to block ratio and polyol molecular weight as seen with the 1,4-BD extended elastomer. It is observed that the 1,6-HD chain extended elastomers show transitions at lower temperatures in comparison to 1,4-BD elastomers. These similarities are shown with the hard segment made from these chain extenders (Table 4A4.3) and is caused by the more disruptions introduced by the lower 1,6-HD chain extender preventing, to a greater extent, the order within the system in comparison with 1,4-BD.

On changing the diisocyanate from H_{12} MDI to IPDI for the polyols Capa 200, Capa 210 and Capa 220 chain extended with 1,4-BD (see Table 4A5.5) shows distinct differences. The Tgs are difficult to detect with the IPDI polyurethanes, due to the unsymmetrical structure of IPDI and thereby increasing disorder in the system. More noticeable is the hard segment melting transition which is observed even at low block ratios. Although these are small transitions they do increase in size with increasing block ratio, but occur at higher melting temperatures possibly due to the aromatic nature of the IPDI structure. The soft segment melting transition of the IPDI elastomers occurs at lower temperatures than the corresponding H_{12} MDI elastomers which would be due to disorder introduced by the IPDI molecule not allowing complete orientation or build up of soft segment chains.

4A.6 CROSSLINKED POLYURETHANES

The thermal transitions of polyurethanes were prepared by using mixtures of chain extenders consisting of a diol and a triol to induce crosslinking (see Table 4A6.1). Several mixed chain extenders were used, the diols being 1,4-BD, Dianol 22 (D22) and Dianol 33 (D33), and the triols were trimethylolpropane (TMP) and Capa 305 (trifunctional 540 m.wt polycaprolactone polyol). The diols and triols were first mixed in several combinations of 1:1 and 2:1 ratios, and used as the chain extender system with the prepolymer made from Capa 205 and H_{12} MDI at a block ratio of 1:4:3 for comparative performance and clarity assessments. The thermograms of these elastomers show transitions at about 60°C relating to the soft segment melting, but the Tg's were difficult to distinguish due to the crosslinking and disorder effect from the mixed chain extender system. It is noticed that the soft segment melting transition is about the same for those elastomers having TMP as part chain extender and differs with Capa 305 as part chain extender. This is due to the higher molecular weight of Capa 305 and its compatibility with the diols compared to TMP.

Highly crosslinked elastomers were also prepared by using tri- and tetra-functional polycaprolactone polyols with diisocyanate and 1,4-BD chain extended. The trifunctional polyol used was Capa 305 and the tetrafunctional polyols were tetra-ol 600 (600 m.wt) and tetra-ol 1000 (1000 m.wt). These crosslinked elastomers show the soft melting transitions to increase very slightly with block ratio (Figures 4A6.1 and 4A6.2, Table 4A6.2). This is observed for both the H₁₂MDI and IPDI elastomers and it is noticed that at higher block ratios the increase in temperature of this transition is minimal. The Tg's of these elastomers are difficult to see due to the high crosslinking in the elastomer matrix. On comparing the tri- and tetra-functional polyol based elastomers of similar molecular weight with the difunctional polyol based elastomers, the soft segment melting is lower for the difunctional polyol elastomer system. This would be expected due to the crosslinking effect of the trifunctional polyol based elastomer giving higher melting transitions and the tetrafunctional polyol based elastomer giving even higher melting transitions. This melting at higher temperatures could be due to the higher stabilising effect of the crosslinking polyol to the structure of the elastomer. On changing the diisocyanate from H₁₂MDI to IPDI, there is little change in the melting transition of the elastomer, due to this transition being related to the polyol and its overall crosslinking effect. There are no higher melting transitions observed probably due to the crosslinking effect prohibiting hard segment build up.

4A.7 DISCUSSION

The transition at the soft segment melting stage is prominent in all the elastomers. The effect of moisture content was thought to have an effect on this melting transition. An elastomer was synthesised and a sample of the cured material was placed under full vacuum at ambient temperature in a dessicator with silica gel for one week. The resulting thermogram of this dried sample and the original cured material gave the melting transition at the same temperature. It thus appears that water is not a parameter affecting

the position of the peak temperature, more interesting is the effect of annealing on the elastomer.

Several elastomers were selected from the range of polyurethanes synthesised and their thermograms observed before and after annealing. A sample of polyurethane prepared with Capa 220 (2000 m.wt), H₁₂MDI and 1,4-BD at a high block ratio of 1:9:8 (Figure 4A7.1) was left in the oven at about 110°C for 30 minutes. The thermogram of this annealed sample was quite different to the original which showed a broad endotherm at about 65°C and a small peak at 148°C. The annealed sample showed no low temperature transition, but did show a much larger peak at 151°C. The same annealed sample 9 days later showed a peak to appear around 65°C. This would indicate that on annealing the soft segment chains melt and have appeared to strengthen the high temperature peak. However, with time this rearranged structure reverts back to its original regularity, showing that the broad 65°C transition is dependent on time and thermal history. A sample of the same polyurethane system (Capa 220:H₁₂MDI:1,4-BD) but of a lower block ratio, 1:3:2, was similarly treated (Figure 4A7.1). The lower temperature peak again disappeared on annealing, and the small peak at 123°C became a larger peak at 128°C, the low temperature reappears after 5 days for the annealed sample. A polyurethane elastomer made from a similar system but having a lower polyol m.wt (Capa 210:H₁₂MDI:1,4-BD) at a low block ratio of 1:3:2 was similarly analysed. The low temperature peak disappeared on annealing and the small peak at about 130°C was shifted to a more prominent peak at 141°C and after 9 days the low temperature peak was observed at 61°C on the annealed sample.

The crosslinked samples treated in a similar manner gave different observations. Two polyurethane samples were taken, one based on the trifunctional polyol (Capa 305:H₁₂MDI:1,4-BD) and the other based on the tetrafunctional polyol (tetra-ol 1000:H₁₂MDI:1,4-BD) both at the same block ratio of 1:2:1 (Figure 4A7.2). The tetra-ol 1000 sample on annealing showed the low temperature peak at 58°C to disappear;

no high temperature peak was observed in the original or annealed samples. The annealed sample, 9 days later, showed a peak at 57°C. The trifunctional sample originally had a peak at 68°C which disappeared on annealing and after 9 days showed a slight broadening around the peak temperature, suggesting a longer time is required for the chains of the trifunctional polyol to revert back to its original state than does the tetrafunctional polyol. It is to be remembered that the tetra functional polyol has a 1000 m.wt chain, almost twice that of the Capa 305, and therefore would require shorter time to rearrange back. The crosslinking effect of the polyols prevents the high temperature peak in the original sample and for the same reason on annealing no high temperature peak appears, due to the crosslinking network.

The transitions that appear in the 60°C region shown for most elastomers tested, regardless of them being crosslinked or not, are shown to be time dependent on annealing. This is probably the reason why elastomers do not attain their full physical properties until some period after cure.

TABLE 4A4.1: THERMAL TRANSITIONS OBSERVED BY DSC FOR THE POLYOL SYSTEMS USED

Polyol	Low Temperature Transitions	High Temperature Transitions	Comments
Capa 200 (550 m.wt)	-72°C; -37°C	+9°C	The -37°C is an exothermic peak
Capa 205 (830 m.wt)	-70°C; -30°C	+14°C; +38°C	Baseline shifts at -70°C and -30°C. Hazy liquid
Capa 210 (1000 m.wt)	-60°C	+14°C; +39°C	Second baseline shift not detectable, solid/liquid
Capa 215 (1250 m.wt)	-61°C; -30°C and -4°C	+19°C; +43°C	Three shifts detected, solid (white)
Capa 220 (2000 m.wt)	-60°C	+19°C; +54°C (small)	Solid-white
Capa 231 (3000 m.wt)	-50°C	+63°C	Baseline just observable, solid-white
Capa 240 (4000 m.wt)	-50°C	+65°C	Baseline difficult to detect - white solid
Capa 305 (540 m.wt) Triol	-70°C		Broad baseline shift clear liquid
Tetra-ol 600 (600 m.wt)	-70°C to -30°C		Very broad baseline shift, clear liquid
Tetra-ol 1000 (1000 m.wt)	-50°C		Very broad baseline shift, clear liquid

TABLE 4A4.2: TRANSITIONS OBSERVED BY DSC FOR SOFT SEGMENTS PREPARED

Soft Segment	Low Temperature Transitions	High Temperature Transitions	Comments
Capa 200:H ₁₂ MDI 1:1	-10°C		Baseline shift Transparent (tacky)
Capa 205:H ₁₂ MDI 1:1	-32°C		Baseline shift Transparent (tacky)
Capa 210:H ₁₂ MDI 1:1	-30°C		Baseline shift Transparent
Capa 215:H ₁₂ MDI 1:1	-33°C	43°C	Hazy - opaque
Capa 220:H ₁₂ MDI 1:1	-32°C	53°C	Opaque
Capa 210:IPDI 1:1	-30°C	39°C	Opaque
Capa 220:IPDI 1:1	-31°C	49°C	Opaque

TABLE 4A4.3: THERMAL TRANSITIONS OBSERVED BY DSC FOR HARD SEGMENTS PREPARED

Hard Segment	Thermal Transitions	Comments
H ₁₂ ^{MDI:1,4-BD} 1:1	80°C, 96°C, 120°C	The 96°C is the main peak. Brittle - clear/hazy
H ₁₂ ^{MDI:1,3-BD} 1:1	71°C, 98°C, 108°C	The 71°C is the main peak. Brittle - clear
H ₁₂ ^{MDI:1,6-HD} 1:1	70°C, 107°C	The 70°C is the main peak, brittle - clear/hazy (crystalline)
H ₁₂ ^{MDI:1,4-BD+} 1,4-CHDM 1:0.5+0.5	73°C	Transparent - brittle
IPDI:1,4-BD 1:1	82°C	Slight peak. Yellowish transparent - brittle

TABLE 4A5.1: DSC DATA OBTAINED FOR THERMOPLASTIC POLYURETHANES CHAIN EXTENDED WITH 1,4-BUTANEDIOL (H₁₂MDI BASED)

BLOCK RATIO									
Polyol:H ₁₂ MDI 1,4-BD	1:2:1	1:3:2	1:4:3	1:5:4	1:6:5	1:7:6	1:8:7	1:9:8	Comments
Capa 200, Tg	-43	-42	-42						Tg's difficult to assess at 1:3:2 and 1:4:3 A small transition
Other transitions	-22 65	54	59						
			Small 107						
Capa 205, Tg		-43	-43						Tg's just detectable Transition becoming broader
Other transitions		79	73 Small 140	70-79 165					
Capa 210, Tg		-43	-43	-43	-44	-44	-43		Tg's become detectable with increasing block ratio
Other transi-		77 Small 126	77 V.small 135	63	62	61	61		
Capa 215, Tg		-43	-43	-43	-44	-43			Less detectable with high block ratios. Becoming smaller. Becoming larger
Other transi-		86	70	80 Small 163	76 Small 139 164	76 166			
Capa 220, Tg		-43	-41	-46	-46	-44	-44	-43	Less detectable with block ratio increase. Becoming larger
Other transi-		79 Small 123	82	81 Small 141	79	76	77 Small 137	79 148	
Capa 231		24 46 76		Tg very difficult to detect The 46°C is the main peak					
Capa 240, Tg		- 54		Tg very difficult to detect					

TABLE 4A5.2: COMPARISON OF SYMMETRICAL AND UNSYMMETRICAL BUTANEDIOL CHAIN EXTENDED POLYURETHANES BY DSC

BLOCK RATIO										
Capa 220: H ₁₂ ^{MDI} chain extender	1:3:2	1:4:3	1:5:4	1:6:5	1:7:6	1:8:7	1:9:8	1:10:9	1:11:10	Comments
Tg 1,4-BD	-43	-41	-46	-46	-44	-44	-43			
Other transi- tions	79 Small 123	82	81 Small 141	79	76	78 Small 137	79 148			
Tg 1,3-BD		-44	-44	-45	-45	-43	-44	-44	-44	Becoming less detec- table with block ratio
Other transi- tions		49 80		Small 64	Small 64 Small 79	66	67	66	66	Peaks becoming larger

TABLE 4A5.3: THERMAL TRANSITIONS OF 1,4-BD+1,4-CHDM (1:1) MIXED CHAIN EXTENDER BASED POLYURETHANES

	BLOCK RATIO						
Polyol System	1:3:2	1:4:3	1:5:4	1:6:5	1:7:6	1:8:7	1:9:8
Capa 200 Tg H ₁₂ MDI	-44						
Other transitions	56						
Capa 205 Tg H ₁₂ MDI	-43						
Other transitions	56						
Capa 210 Tg H ₁₂ MDI	-44	-44	-44				
Other transitions	Not noticeable	57	56				
Capa 215 Tg H ₁₂ MDI		-44	-45	-44	-43		
Other transitions		79	81	60	61		
Capa 220 Tg H ₁₂ MDI							-44
Other transitions							66

TABLE 4A5.4: THERMAL TRANSITIONS OF 1,6-HEXANEDIOL BASED POLYURETHANES BY DSC

Elastomer System	BLOCK RATIO						Comments
	0.7:2:1.3	0.6:2:1.4	1:4:3	1:5:4	1:6:5	1:7:6	
Capa 200 Tg H ₁₂ MDI 1,6-MD	-43	-42	-43				Tg's just detectable
Other transitions	46	51	57				
Capa 205 Tg H ₁₂ MDI 1,6-HD				-43			The 46,75 temperature peak is small and broad
Other transitions				46,75	50		
Capa 210 Tg H ₁₂ MDI 1,6-HD				-43	-44		
				53	52		
Capa 215 Tg H ₁₂ MDI 1,6-HD				-42	-42	-43	
				76	73 Small 104	75 Small 115	

TABLE 4A5.5: DSC TRANSITIONS OBSERVED FOR IPDI BASED POLYURETHANES

Polyol IPDI 1,4-BD Elastomer	BLOCK RATIO				Comments
	1:3:2	1:5:4	1:7:6	1:9:8	
Capa 200 Tg	-				Tg's not detected
Other	49				
transitions	Small 232				
Capa 210 Tg	-	-	-	-	Tg's not detected
Other	-	-	61	65	
transitions	234	Small & broad 234	239	256	
Capa 220 Tg	-	-	-	-	Tg's not derived
Other	44	51	-	64	
transitions	Small 235	Small 234	Small 240	245	

TABLE 4A6.1: THERMAL TRANSITIONS OBTAINED BY DSC WITH DIFFERING CHAIN EXTENDERS

Chain exten- der	1,4-BD:2	D22:1	D22:2	D33:2	D22:2	1,4-BD:2	D33:1
Poly- urethane system	+ TMP:1	+ TMP:1	+ TMP:1	+ Capa 305:1	+ Capa 305:1	+ Capa 305 :1	+ Capa 305:1
Capa 205 H ₁₂ MDI 1:4:3	61	61	60	54	51	Broad 90	57
Capa 210 H ₁₂ MDI 1:5:4	64				49		

TABLE 4A6.2: THERMAL TRANSITIONS OF CROSSLINKED POLYURETHANES

Crosslinked Urethane System	BLOCK RATIO			
	1:2:1	1:3:2	1:4:3	1:5:4
Capa 305:H ₁₂ MDI:1,4-BD	69	72	74	
Tetra-ol:H ₁₂ MDI:1,4-BD 600	75	76	78	
Tetra-ol:H ₁₂ MDI:1,4-BD 1000	58	66	70	70
Capa 305:IPDI:1,4-BD	68	74	78	
Tetra-ol:IPDI:1,4-BD 600	78	80	82	
Tetra-ol:IPDI:1,4-BD 1000	58	67	72	

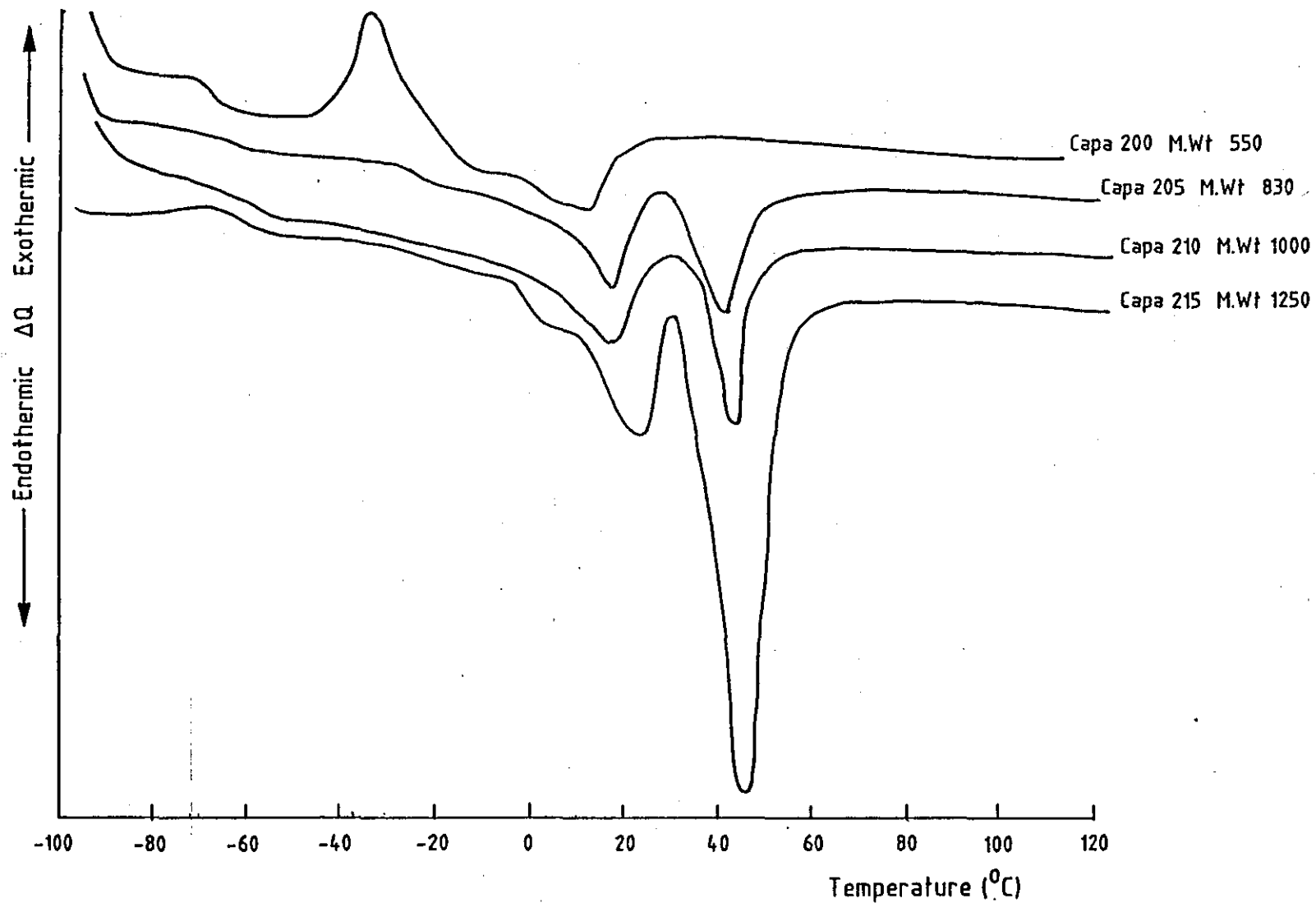


Fig. 4A4 . 1(a) DSC thermograms of the Polyol systems used in the elastomer synthesis.
(550-1250 MW)

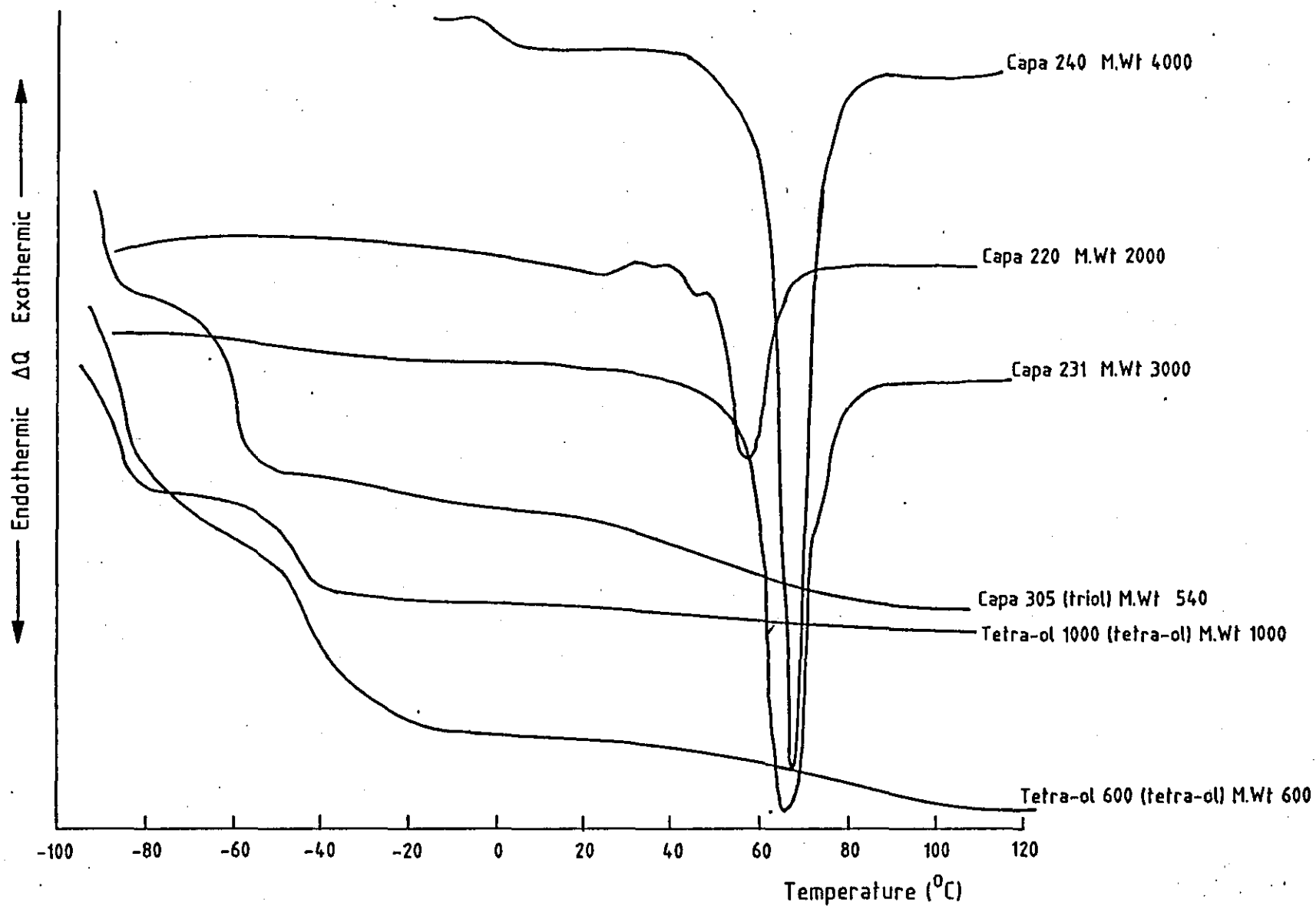


Fig. 4A4 . 1(b). DSC thermograms of the Polyol systems used in the elastomer preparation.

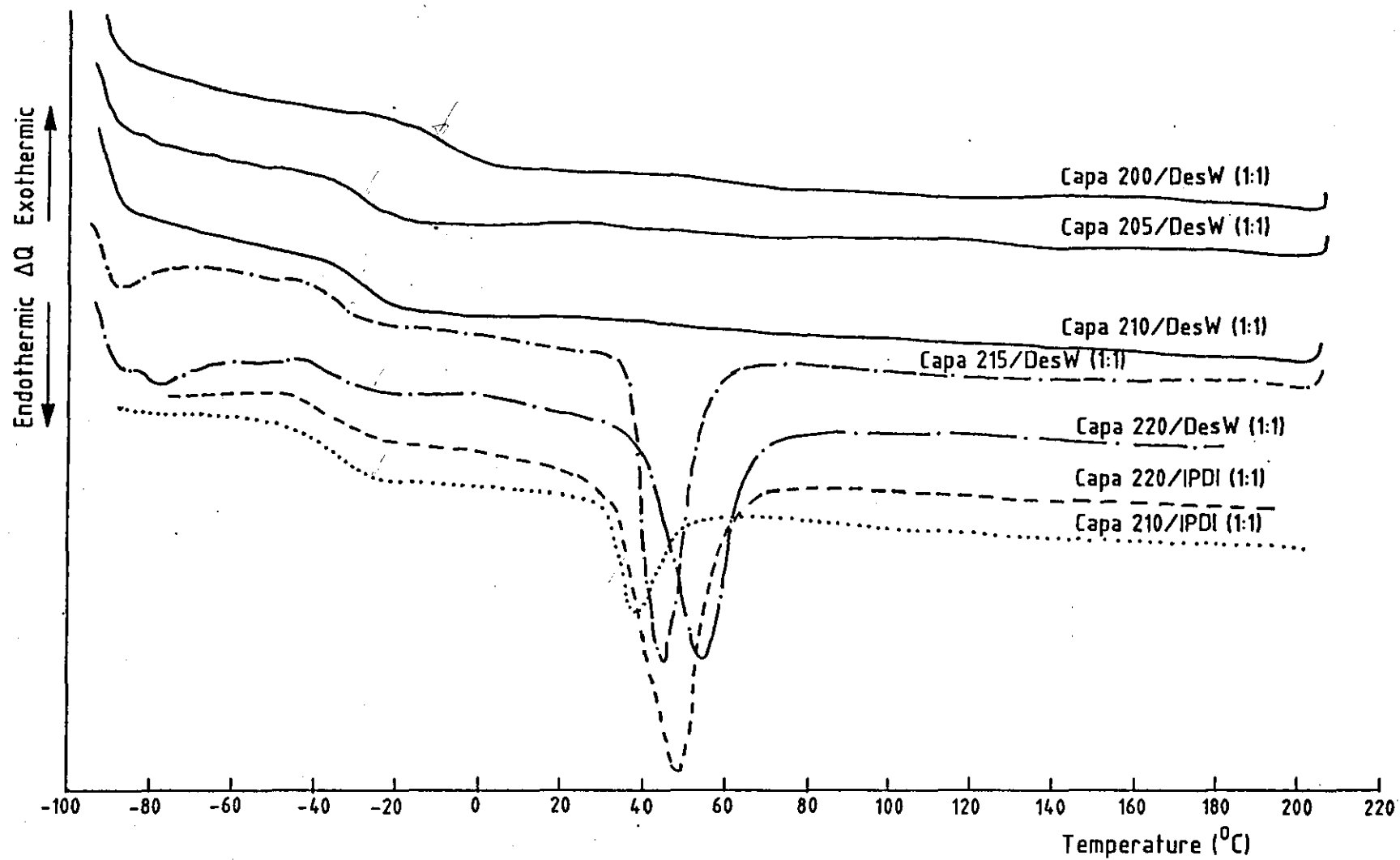


FIG. 4A4 . 2. DSC traces of soft segments synthesised with Polyol and Diisocyanate at 1 : 1 ratio

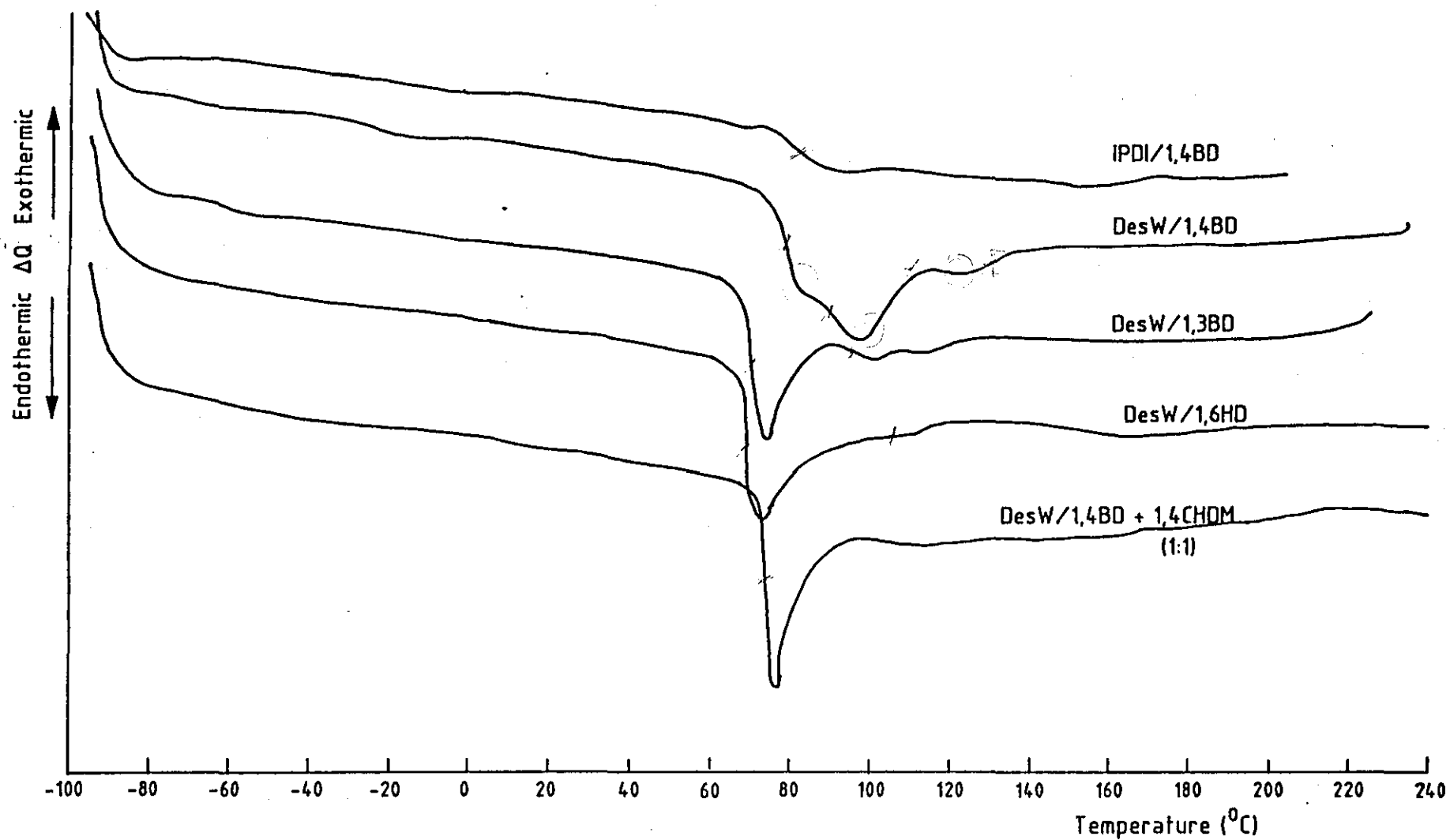


FIG. 4A4 . 3. DSC traces obtained from hard segments prepared by reacting Diisocyanate with a chain extender at 1 : 1 ratio.

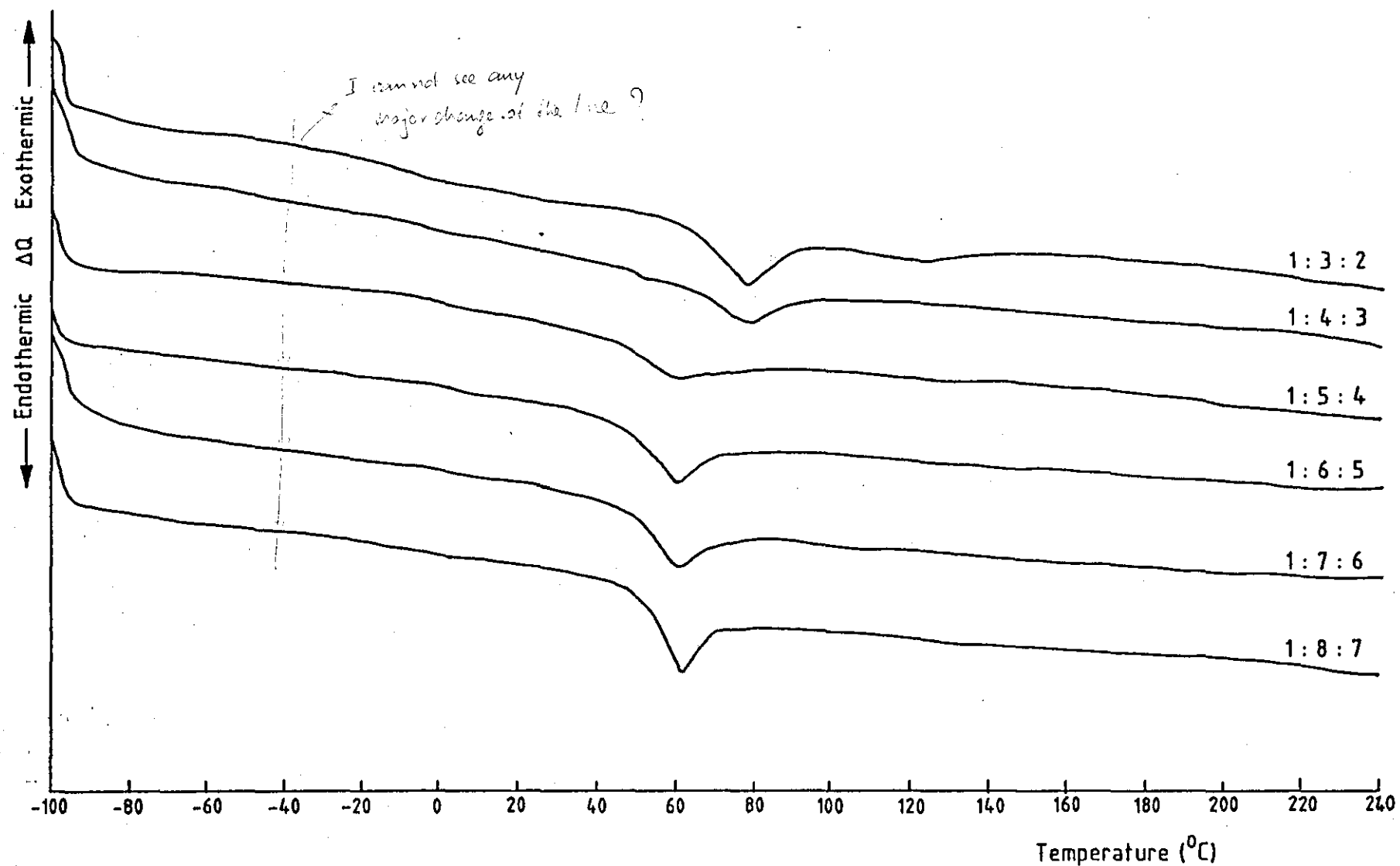


FIG. 4A5 . 1. DSC traces of elastomers based on Capa 210/H₁₂MD1/1,4BD at varying block ratios

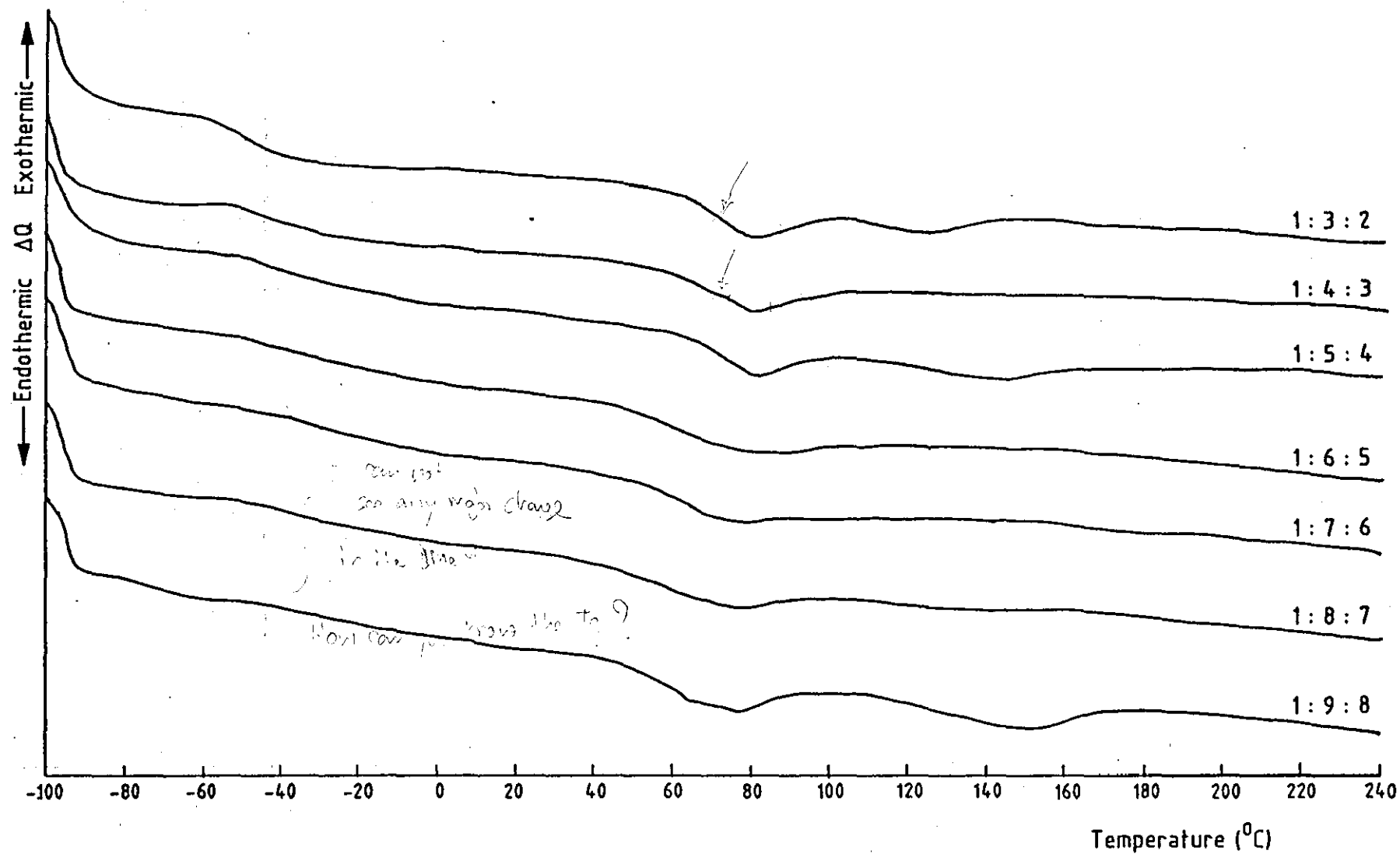


FIG. 4A5 . 2. DSC traces of elastomers based on Capa 220/H₁₂MD1/1,4BD at varying block ratios

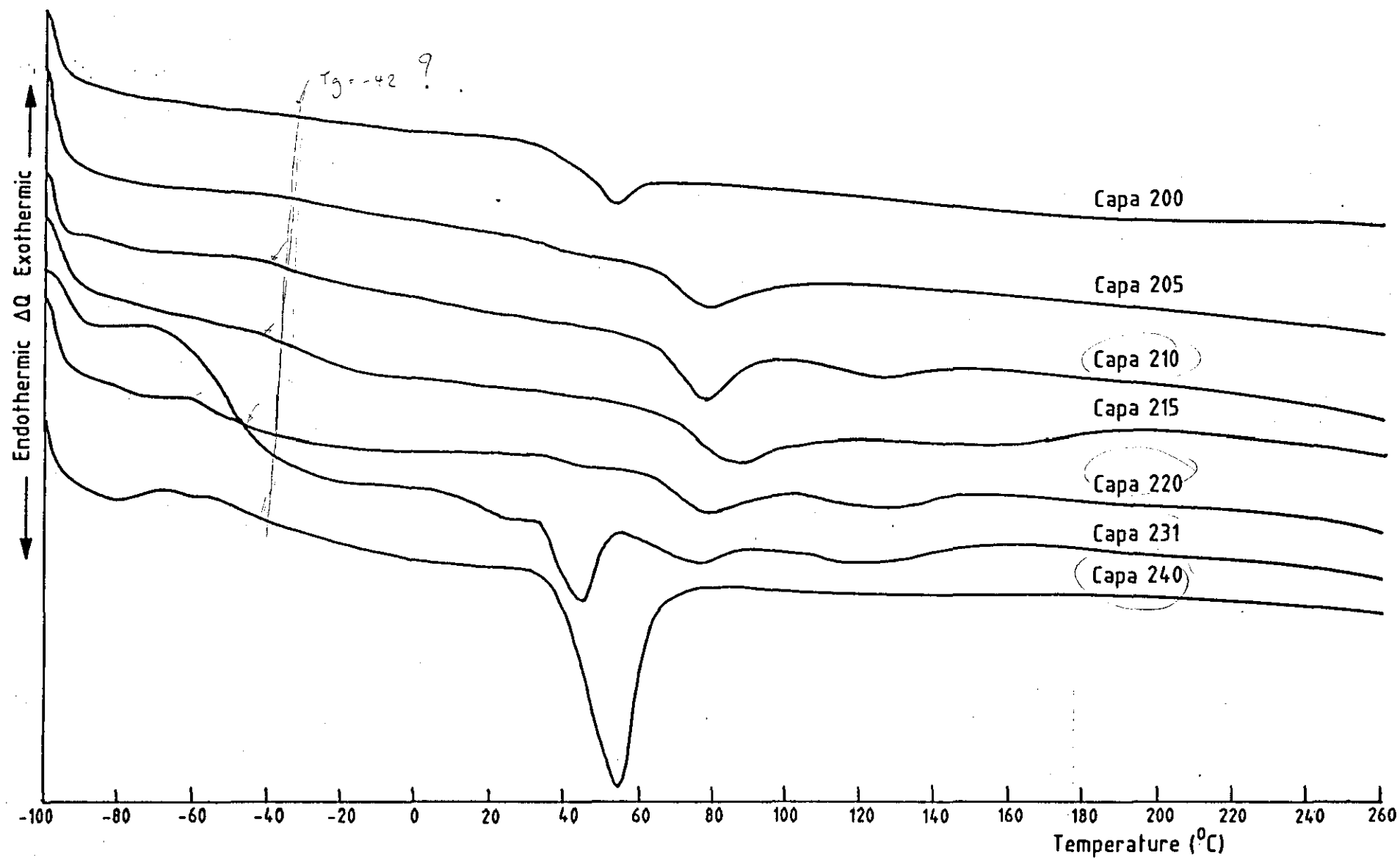


FIG. 4A5 . 3. DSC traces of elastomers based on Poly-ol/ H_{12} MDI/1,4BD at 1 : 3 : 2 block ratio varying the Poly-ol system

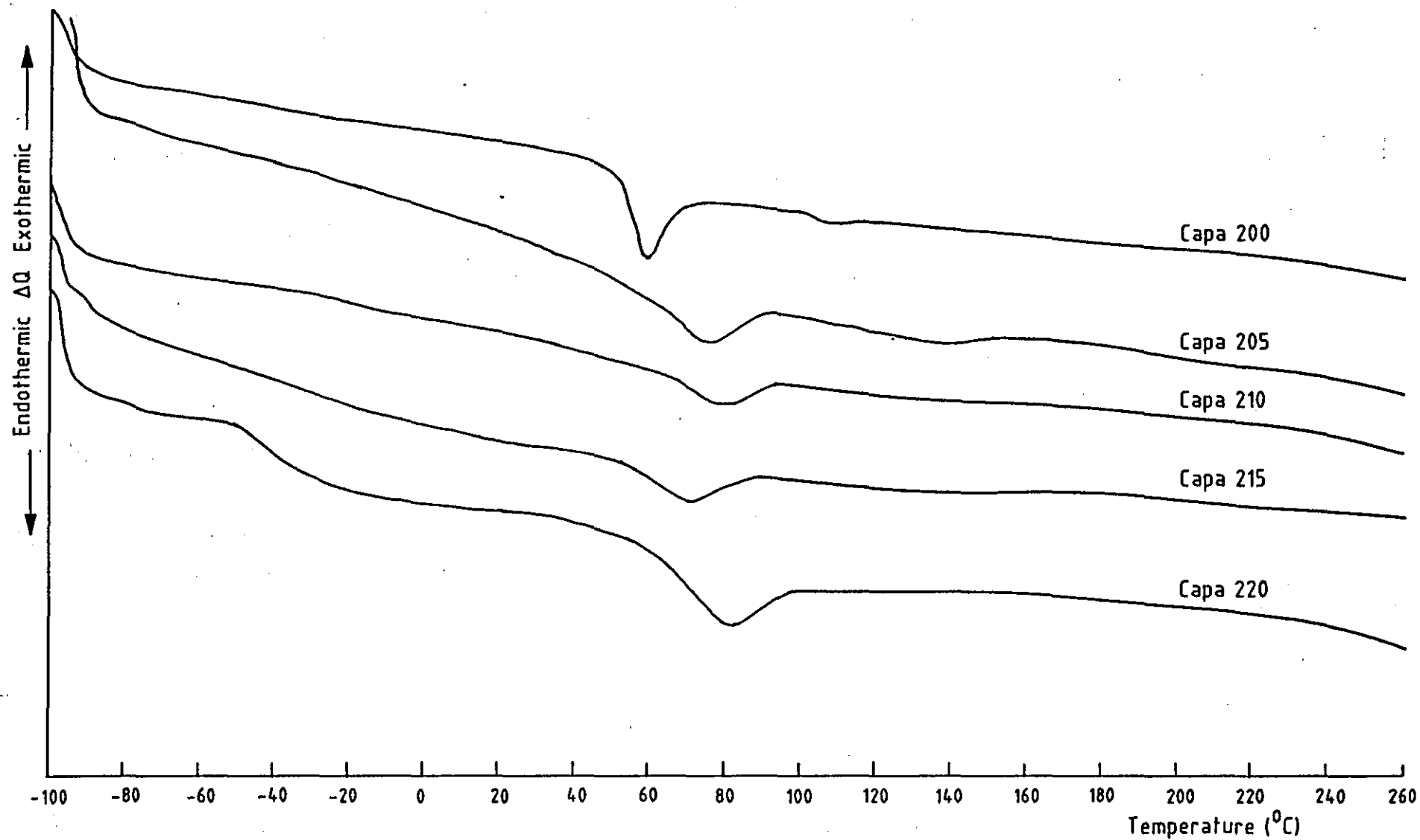


FIG. 4A5 . 4. DSC traces of elastomers based on Poly-ol/H₁₂MDI/1,4BD at 1 : 4 : 3 block ratio varying the Poly-ol system

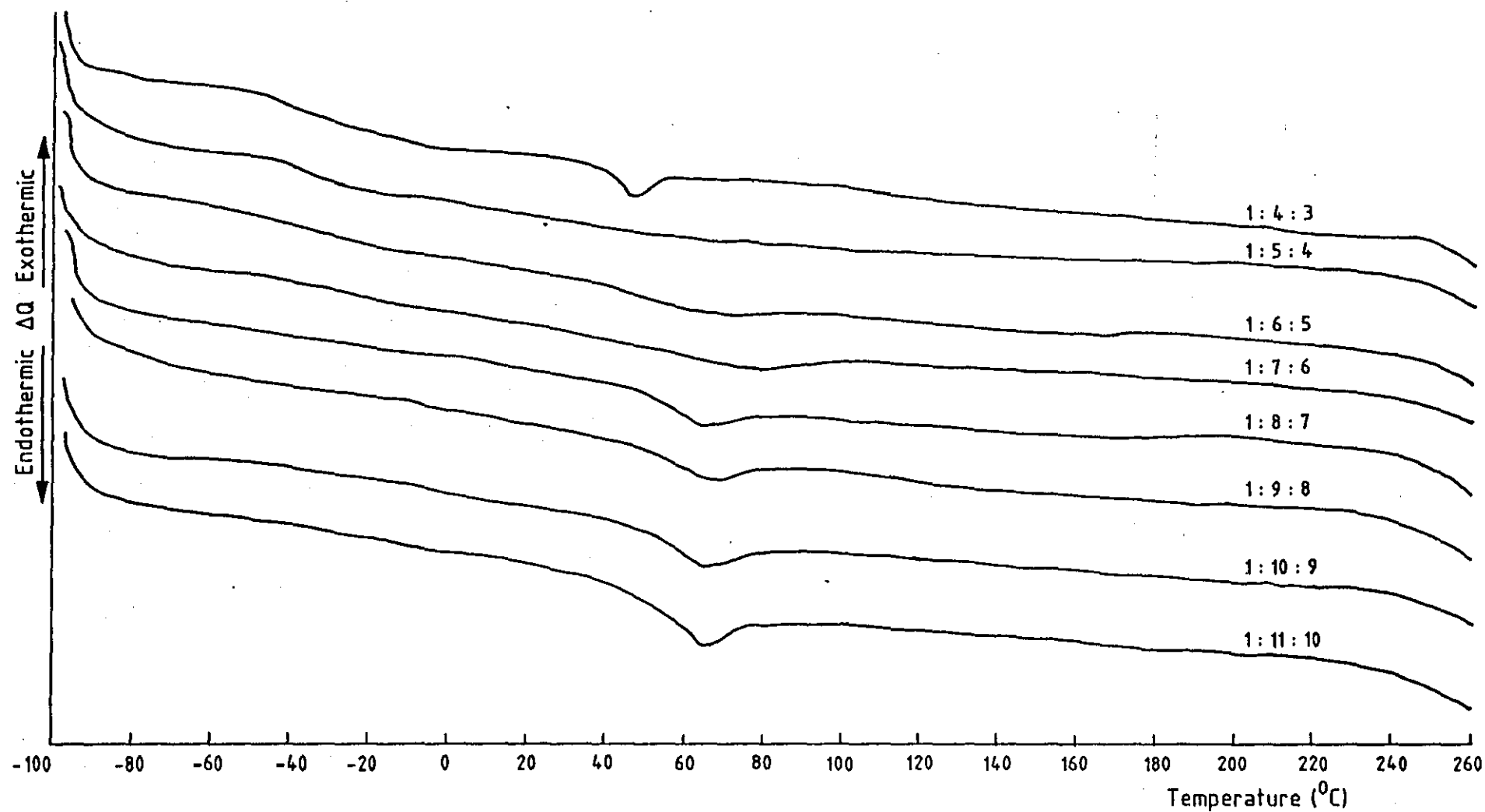


FIG. 4A5 . 5 DSC traces of elastomers based on Capa 220/H₁₂MDI/1,4BD at various block ratios.

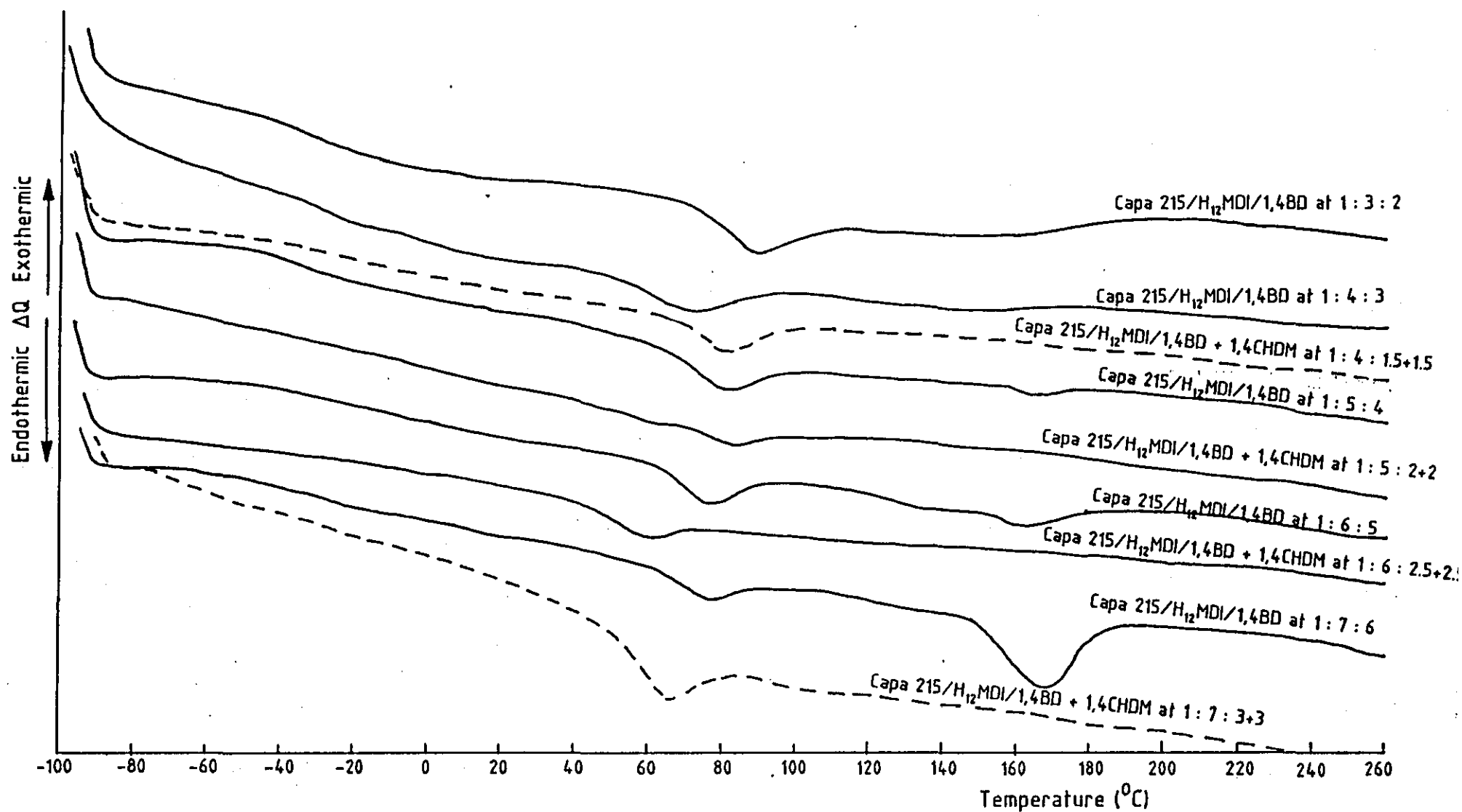


FIG. 4A5 . 6 DSC traces of elastomers based on Capa 215/ H_{12} MDI/1,4BD and Capa 215/ H_{12} MDI/1,4BD + 1,4CHDM (1:1) at various block ratios.

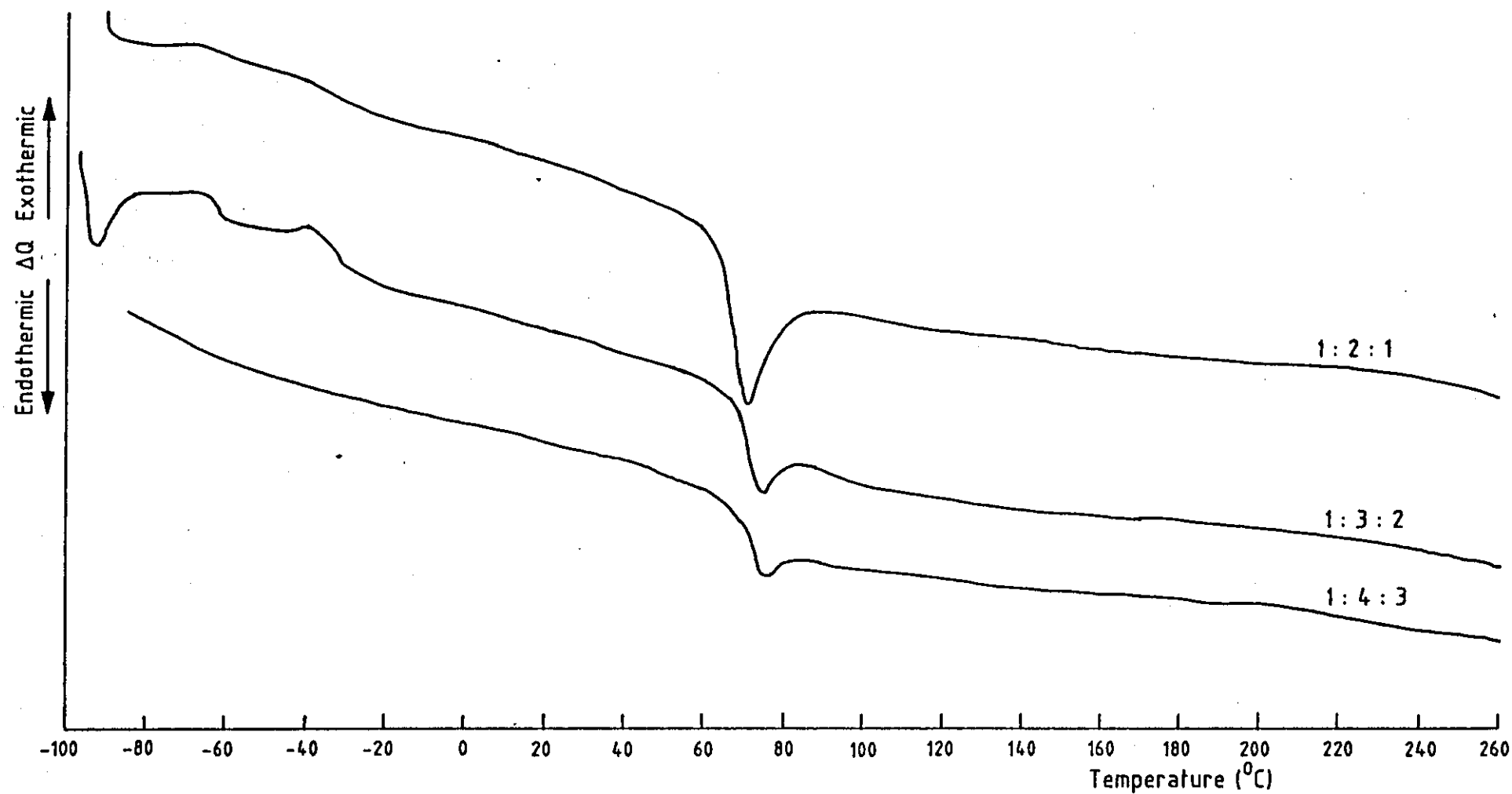


FIG. 4A6 . 1(a) DSC traces of elastomers based on Capa 305/H₁₂MDI/1,4BD at various block ratios.

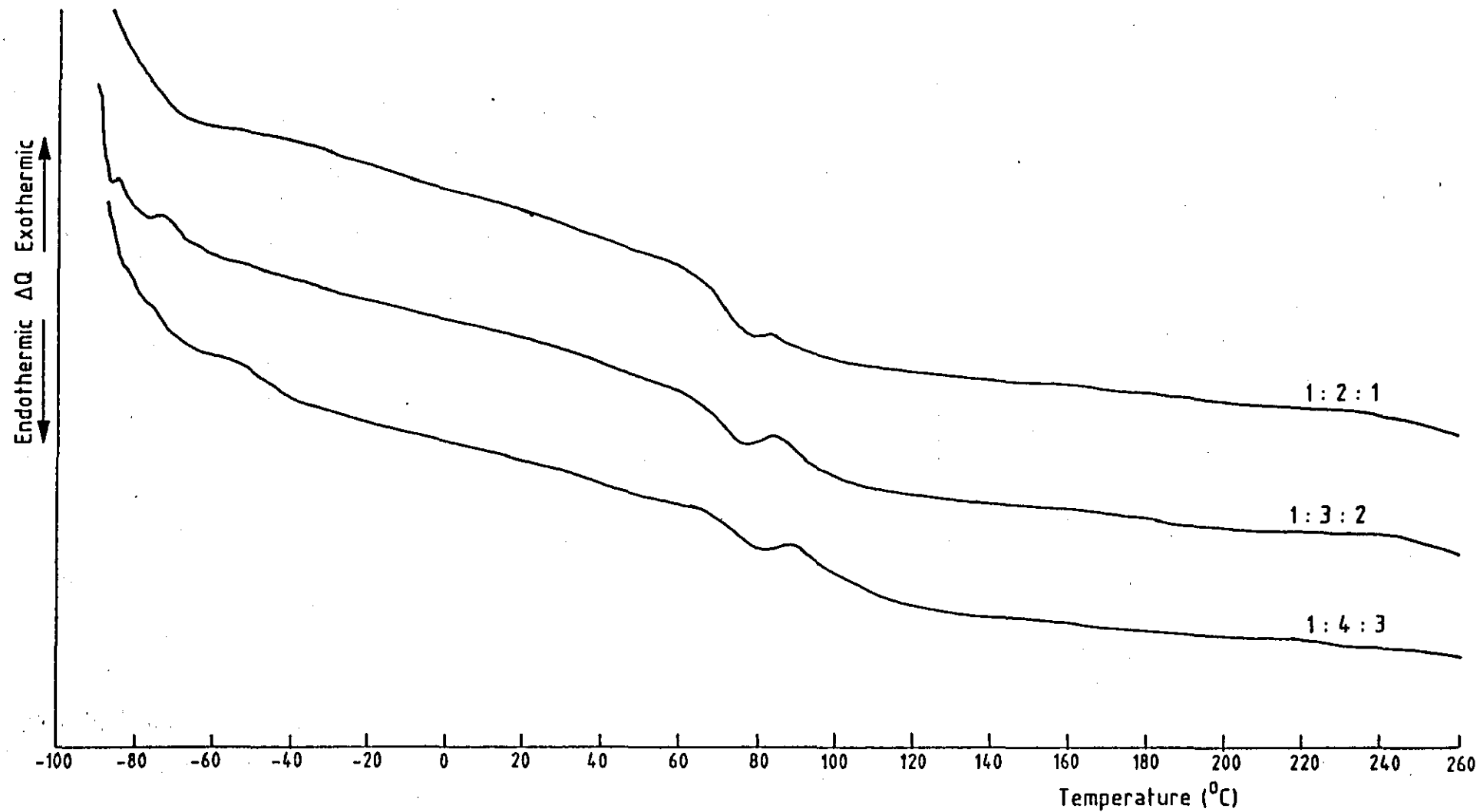


FIG. 4A6 . 1(b) DSC traces of elastomers based on Tetra-ol600/H₁₂MDI/1,4BD at various block ratios

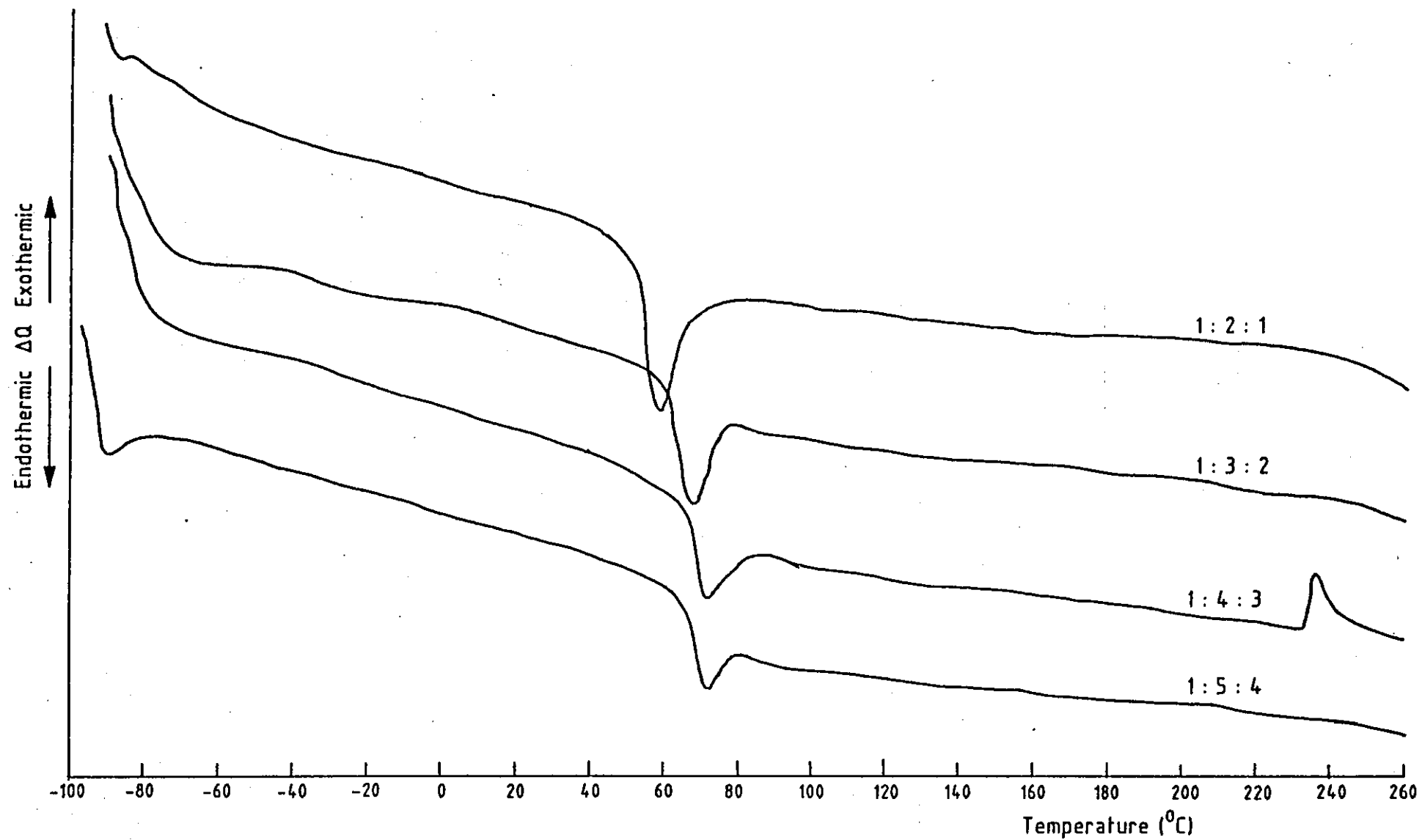


FIG. 4A6 . 1(c) DSC traces of elastomers based on Tetra-ol 1000/H₁₂MDI/1,4BD at various block ratios.

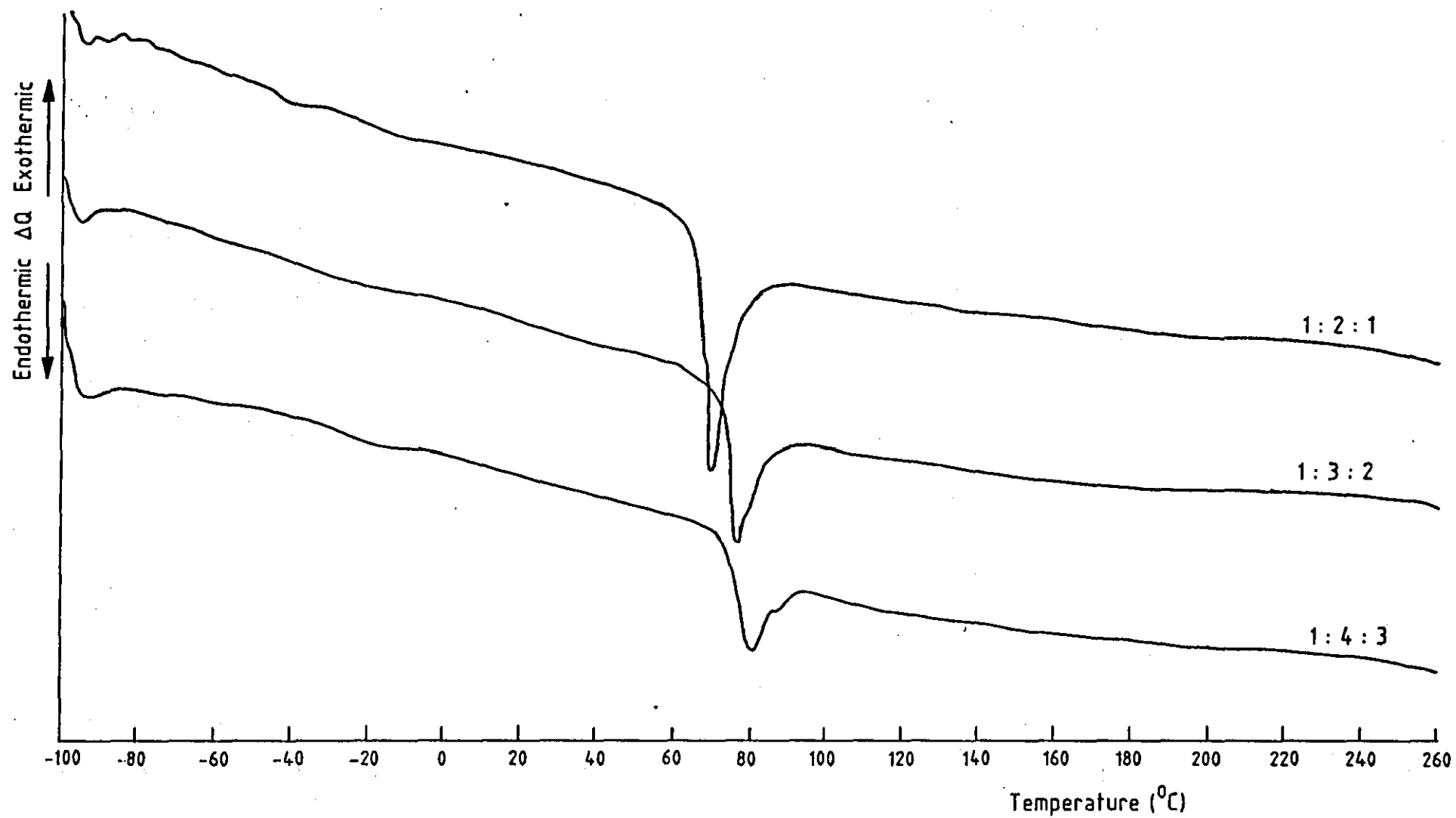


FIG. 4A6 . 2(a) DSC traces of elastomers based on Capa 305/IPDI/1,4BD at various block ratios.

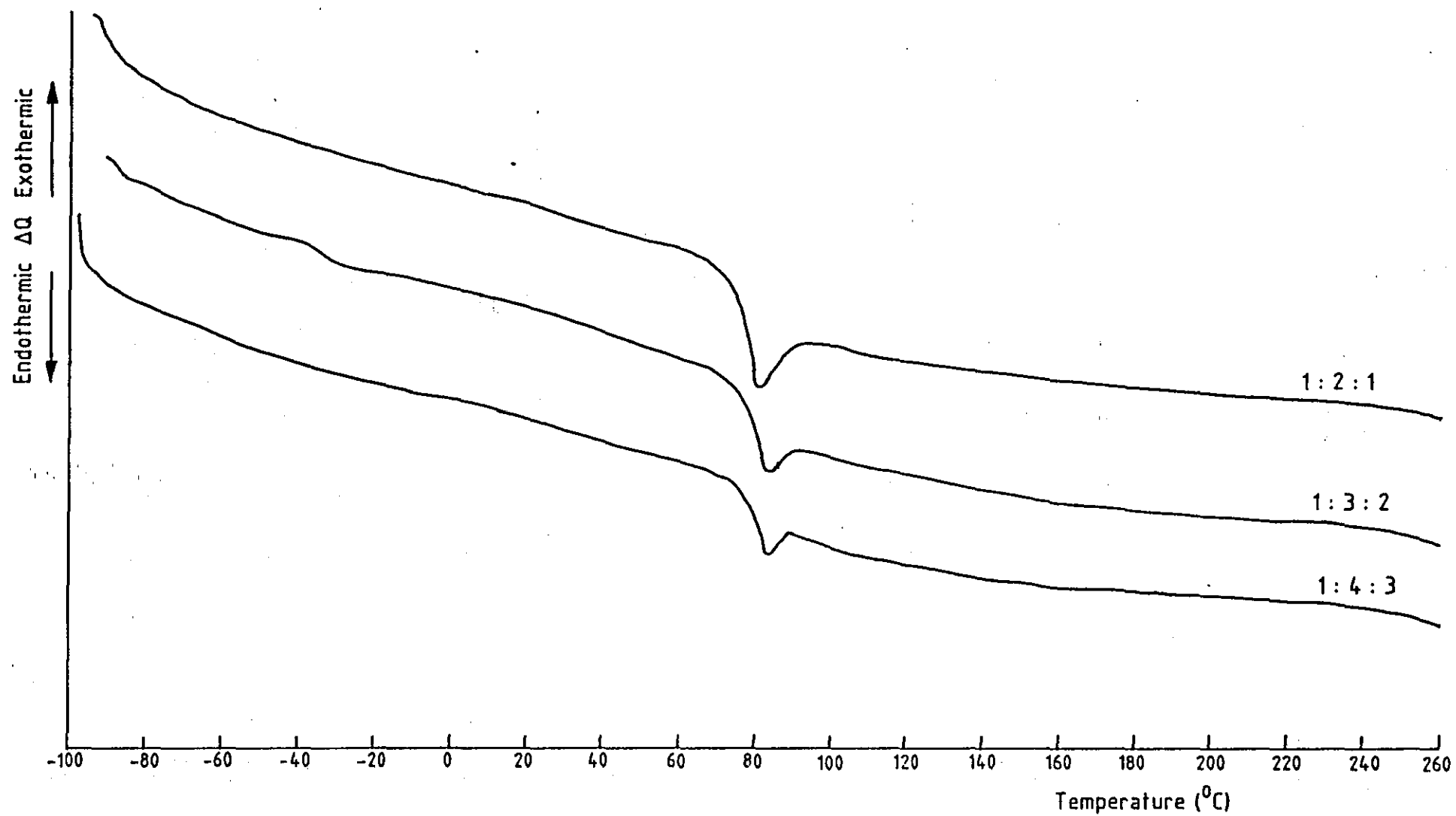


FIG. 4A6 . 2(b) DSC traces of elastomers based on Tetra-ol 600/IPDI/1,4BD at various block ratios.

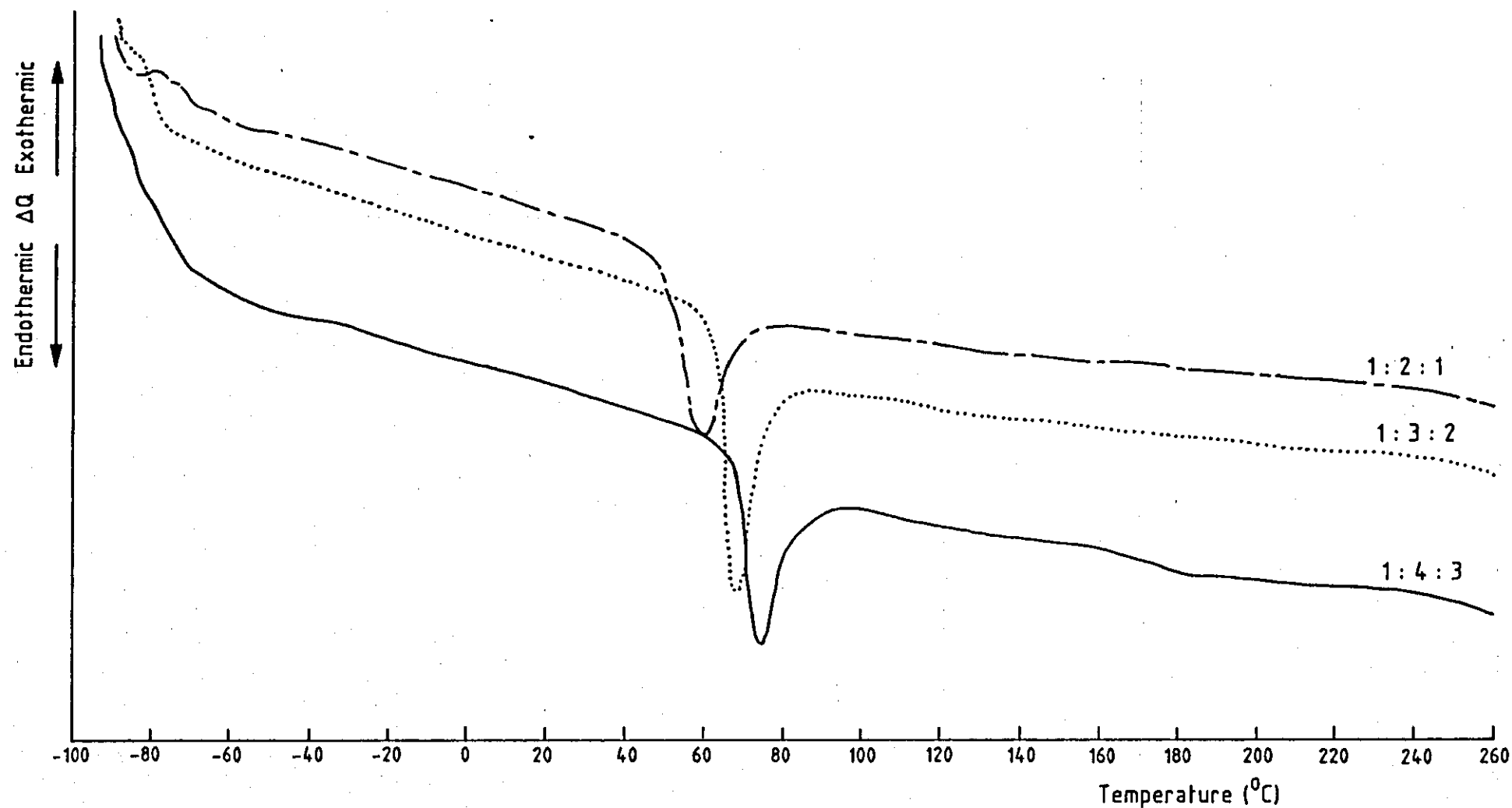


FIG. 4A6 . 2(c) DSC traces of elastomers based on Tetra-ol 1000/IPDI/1,4BD at various block ratios

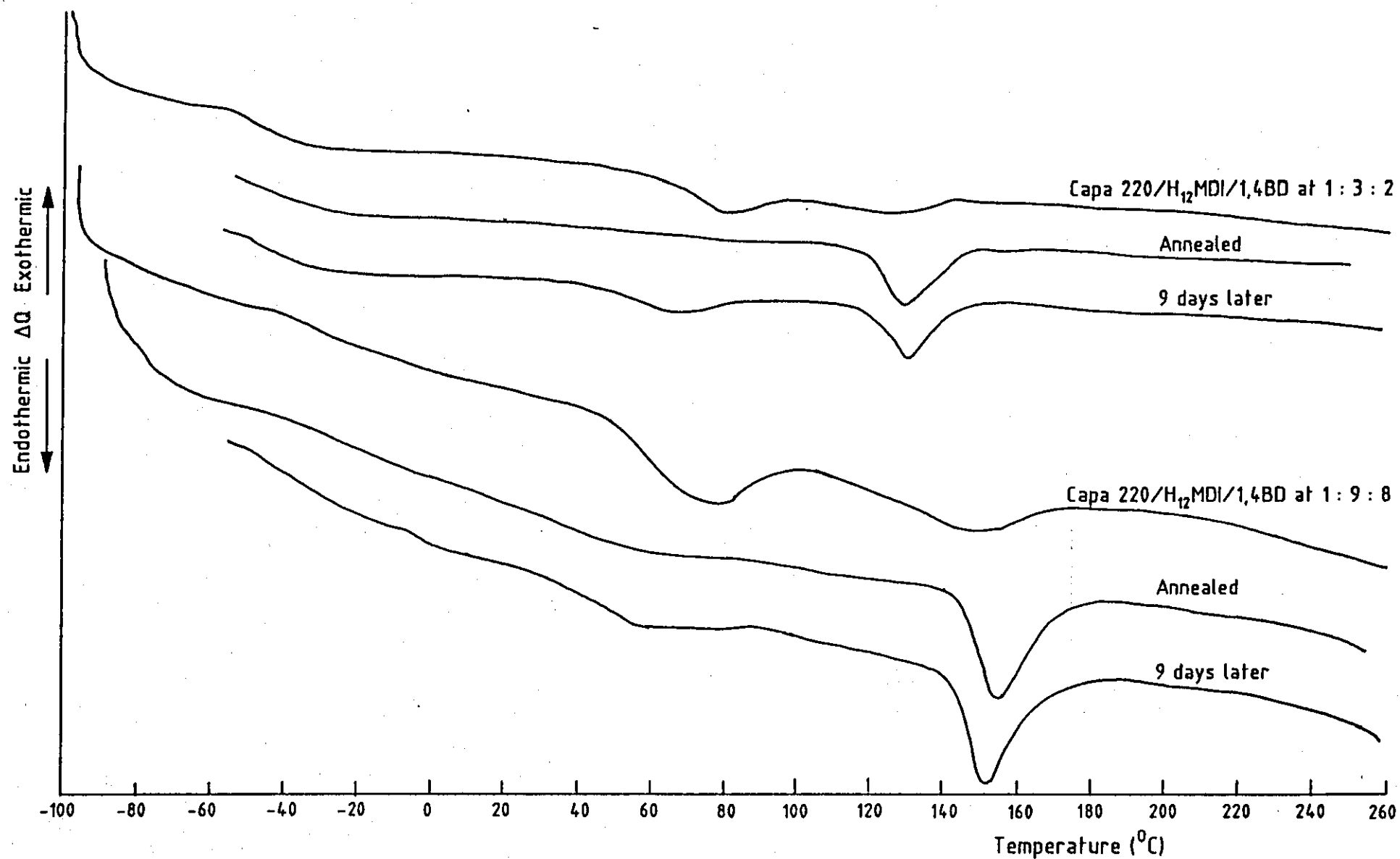


FIG. 4A7 . 1. DSC traces of Capa 220/H₁₂MDI/1,4BD at 1:3:2 and 1:9:8 before and after annealing.

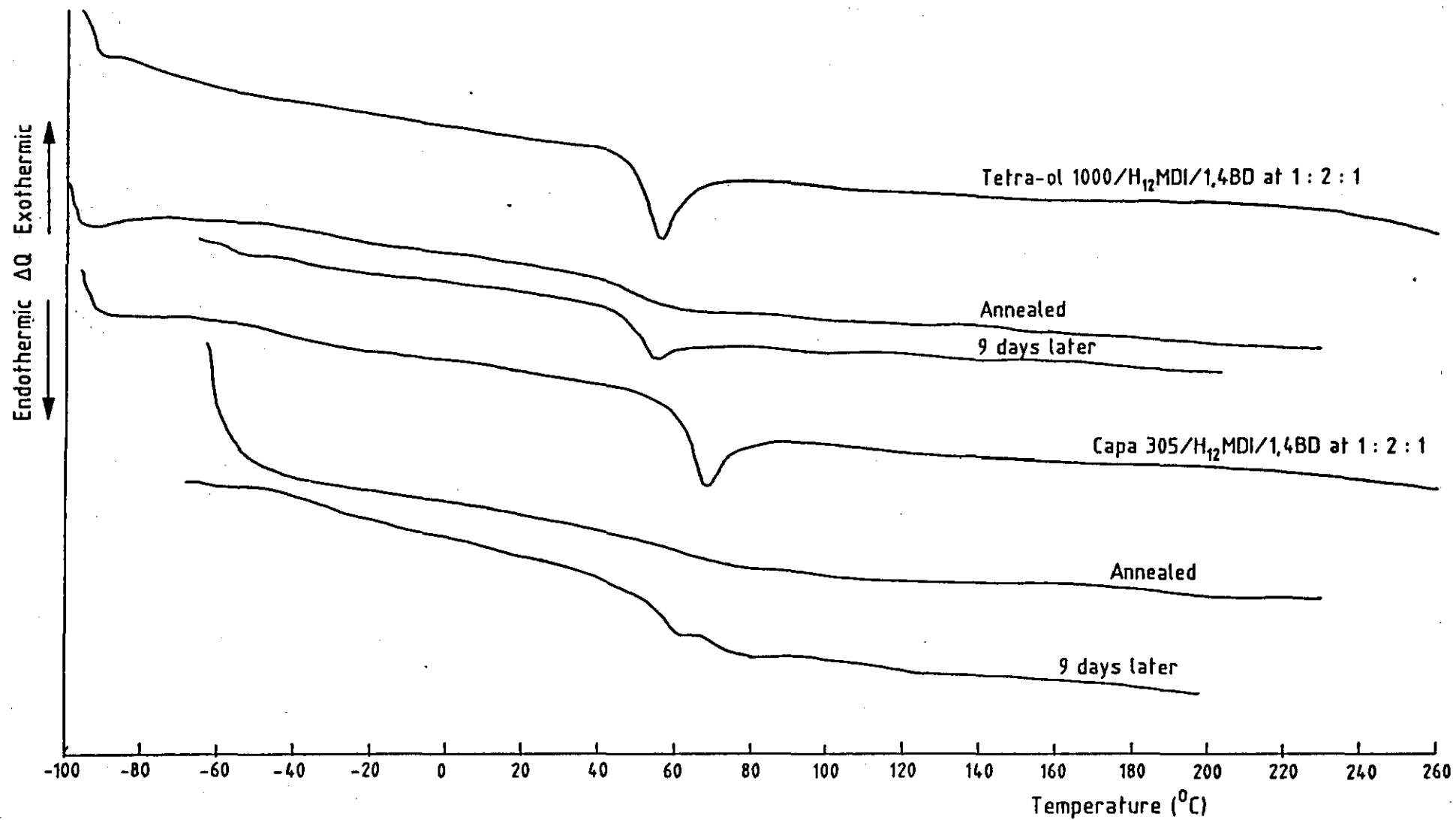


FIG. 4A7 . 2. DSC traces of crosslinked elastomers before and after annealing

4B.1 DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA)

This analysis technique is useful in providing information on first and second order transitions (such as T_m and T_g), phase separation and mechanical behaviour of polymers. Studies based on this type of analysis are becoming increasingly important and have been made by several authors [65,69,71,126,140,149-150]. The technique assesses the damping factor ($\tan \delta$) and dynamic storage modulus (E' or G') which essentially detects all motional and structural transitions in polymeric materials as they occur during a wide temperature sweep.

The Dynamic Mechanical Thermal Analyser used was obtained from Polymer Laboratories Ltd. A sample (typical size 2 mm x 10 mm x 40 mm) is clamped rigidly at both ends and its central point vibrated sinusoidally by the drive clamp (Figures 4B1.1 and 4B1.2). The stress experienced by the sample is proportional to the current supplied to the vibrator. The strain in the sample is proportional to the sample displacement. The stress and strain are monitored over a selected temperature range. The general form of the effect of temperature on storage modulus and $\tan \delta$ is shown in Figure 4B1.3, the change in storage modulus with morphology is shown in Figure 4B1.4.

Polymers have high modulus values at temperatures below the glass transition (T_g - taken as the temperature at the α -peak position) where the glassy state prevails. On increasing the temperature through the T_g and above the modulus of the polymer rapidly decreases. A linear amorphous polymer (which has not been crosslinked - curve A, Figure 4B1.4) after the T_g , shows a short (rubbery) plateau region followed by a continued rapid drop of the modulus. The effect of crosslinking causes the modulus to stabilise to higher temperatures (curve B, Figure 4B1.4) after its initial drop through the T_g . In block copolymer (curves D and E, Figure 4B1.4) above the T_g , an enhanced rubbery plateau region appears where the modulus changes little with increasing temperature, before a drop in modulus occurs associated with the hard segment

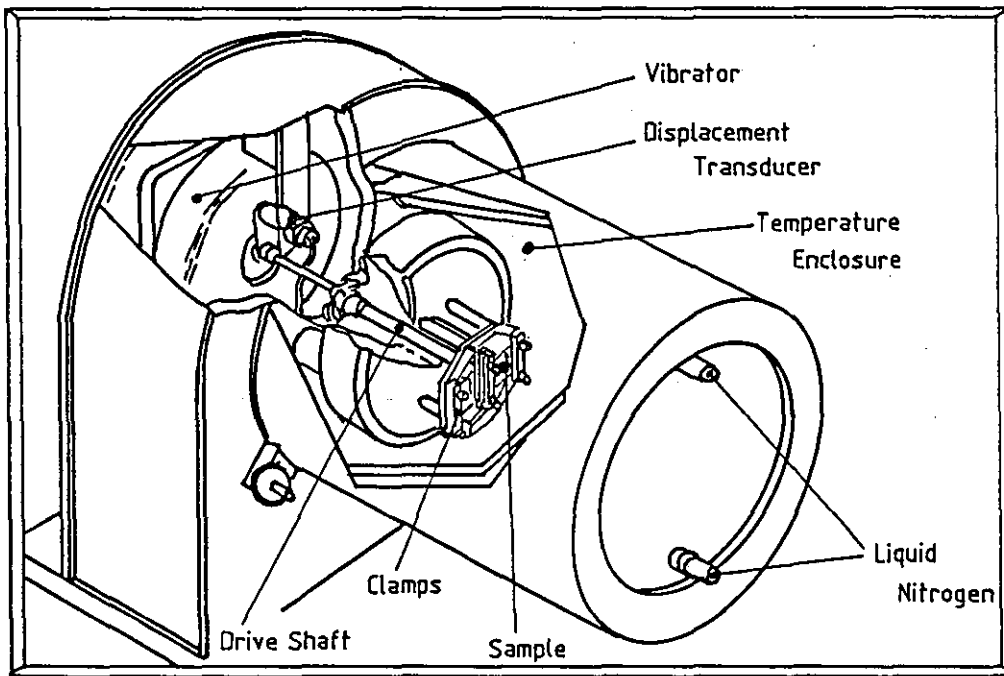


Fig. 4B1 . 1 A Schematic View of the Mechanical Head -
- cut away view.

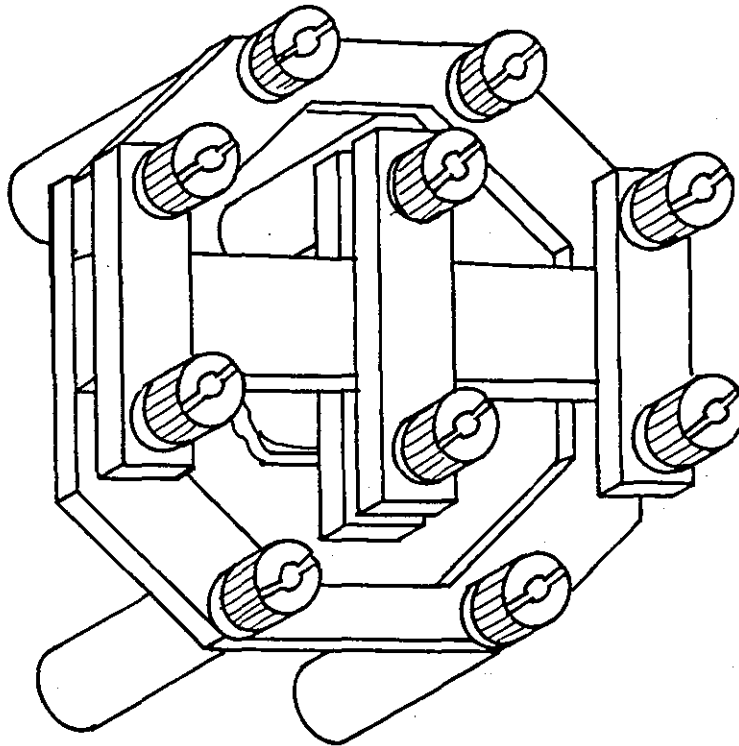


Fig. 4B1 . 2 Urethane sample clamped in the PL - DMTA
prior to measurement.

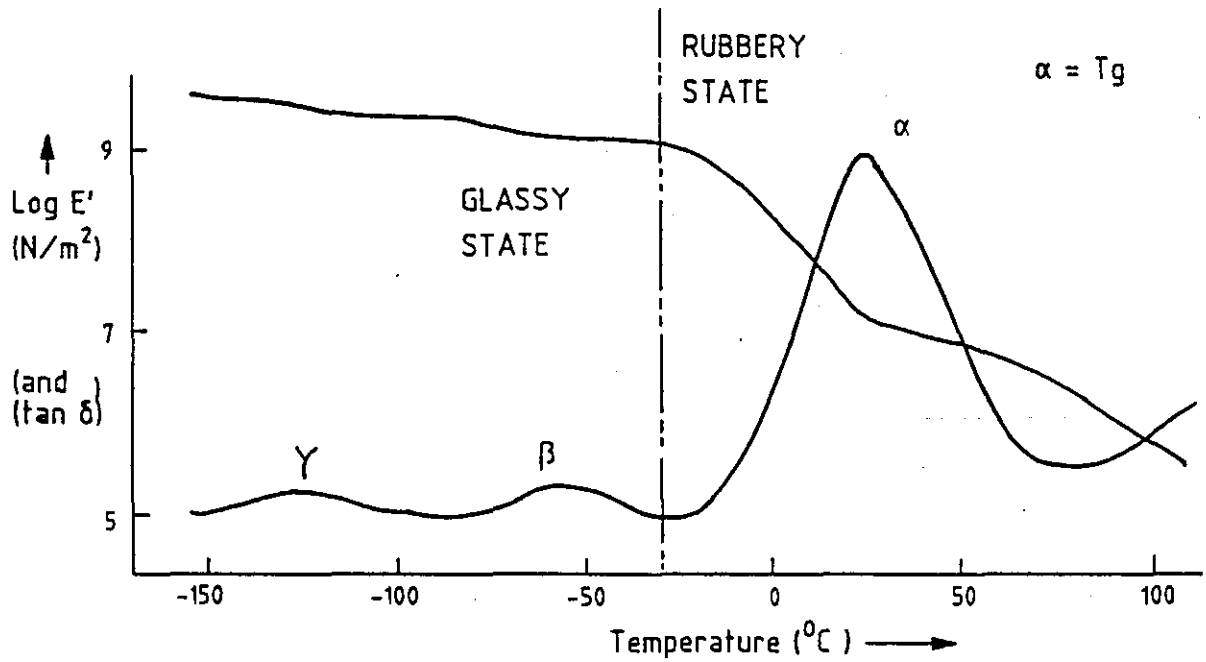


Fig. 4B1.3. Typical dynamic mechanical properties of amorphous polymers (e.g. amorphous polyurethane)

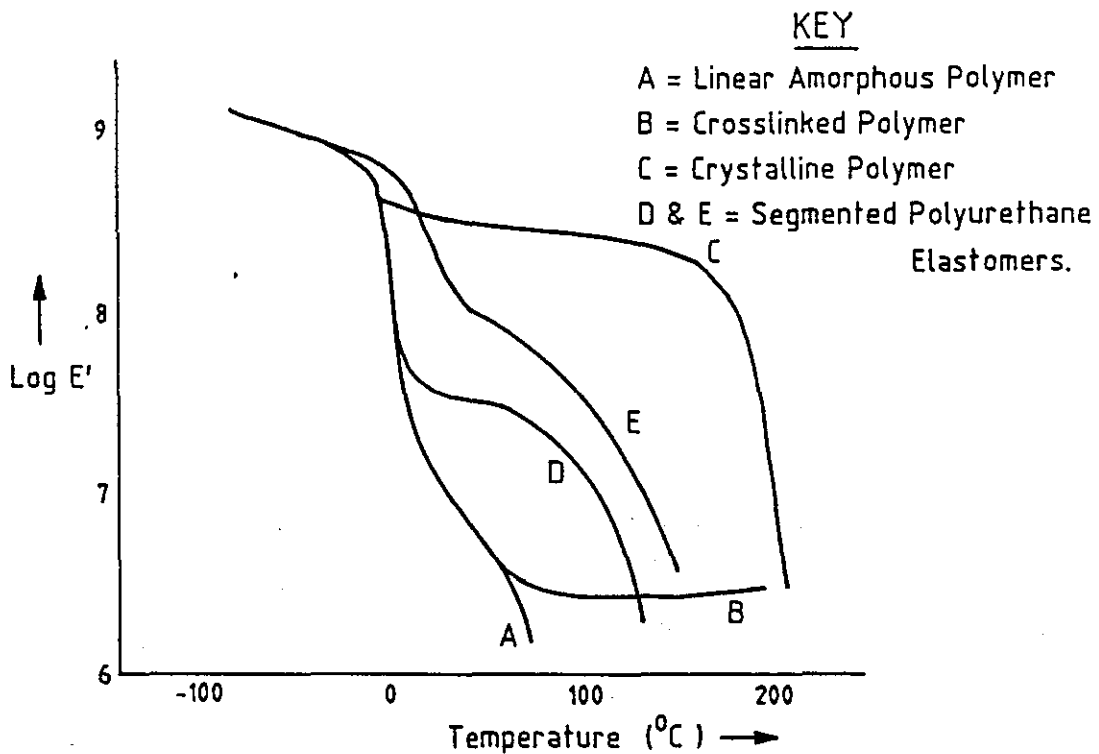


Fig. 4B1.4. Typical relationships of storage modulus and morphology of the polymer (e.g. polyurethanes)

transition. A semi-crystalline material (curve C, Figure 4B1.4) maintains a high modulus through the glass transition region and above up to the crystalline melting point, beyond which the structural identity of the crystallites is destroyed followed by a rapid drop in modulus.

In segmented polyurethanes the T_g is related to the transition of the soft segment rich phase. When this phase is relatively pure in soft segments (little phase mixing) the correlation of the storage modulus and T_g of the segmented polymer to the soft segment homopolymer is very good. A second and higher temperature transition is usually seen in segmented polyurethanes and can be related to the temperature at which the hard segment domains disrupt. Higher purity in these domains moves the transition to higher temperatures approaching the softening temperature of the hard segment homopolymer. Sample composition, segmental length, inherent intersegment solubility and sample preparation can all influence the degree of phase separation and thereby the shape and temperature location of the transition points.

The largest damping peak, termed as the α -peak is associated with the glass transition (T_g) of the polymer. This transition occurs in the amorphous regions of the polymer with the initiation of the micro Brownian motion of the molecular chains. The magnitude of the α -peak in the amorphous polymer is much higher than in the semi-crystalline polymer, because the chain segments of the amorphous polymer are more free from the restraints which are imposed by the crystalline polymers in the glass transition region.

A second relaxation often appears at low temperatures (Figure 4B1.3); this is termed as the β -peak. The magnitude of the β -peak is small in comparison with the α -peak and is associated with motion about the chain backbone of a relatively small number of monomer units or with motion of side groups. In the case of amorphous polymers the β -peak is very broad and may appear as a shoulder to the α -peak. It has been shown in some polyurethanes [149] that the

presence of water can affect the magnitude of the β -peak along with a shift to lower temperatures of the α -peak.

At very low temperatures a third or γ transition can sometimes be observed. At these low temperatures, the chain segments are frozen in, while side group motion is made possible by defects in packing or configuration in the glassy or crystalline state. This γ peak can generally be related to side group motion in the amorphous and crystalline phases, end group rotation, backbone chain motions of short segments or groups and phase separation of impurities and diluents. In polyurethanes the γ transition results from the local mode action of the methylene sequences in the polyol soft segment. The determination of these low temperature transitions is important as nearly all tough ductile glassy polymers and those with high impact strength have these prominent transitions [151].

4B.2 EXPERIMENTAL TECHNIQUES USED

The samples were mainly tested from -100°C to $+200^{\circ}\text{C}$ at a frequency of 1 Hz with a heating rate of $1^{\circ}\text{C}/\text{min}$. A few samples were tested at the lower starting temperature of -150°C to determine the presence of the γ -transition. This relaxation was usually evident in the temperature range of -115°C to -125°C for both the linear and crosslinked samples tested.

In the technique used to test the effect of water present in the polymer, on the β -transition, two samples (one linear and one crosslinked) were placed under full vacuum for one week at 25°C before testing. These dried samples showed little change in the α -transition (T_g) in comparison with tests of the original (undried) sample. The magnitude of the β -transition also showed little change after drying. This suggests that no effective change occurred as a result of this drying period. It is considered that any presence of water in the polyurethanes is quite low in the original samples. This is because the samples are prepared with the exclusion of water (moisture) and use of high synthesis temperature. It can therefore

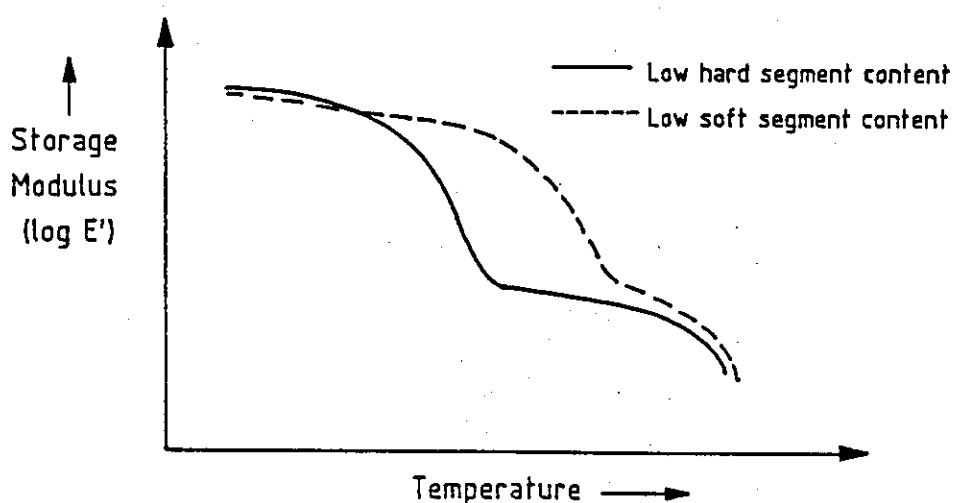
be said that the β -transitions observed, which are higher in magnitude than the γ -transitions have been little affected by any presence of water in the polymer.

4B.3 EFFECT OF HARD SEGMENT CONCENTRATION AND ITS INFLUENCE ON DMTA ANALYSIS

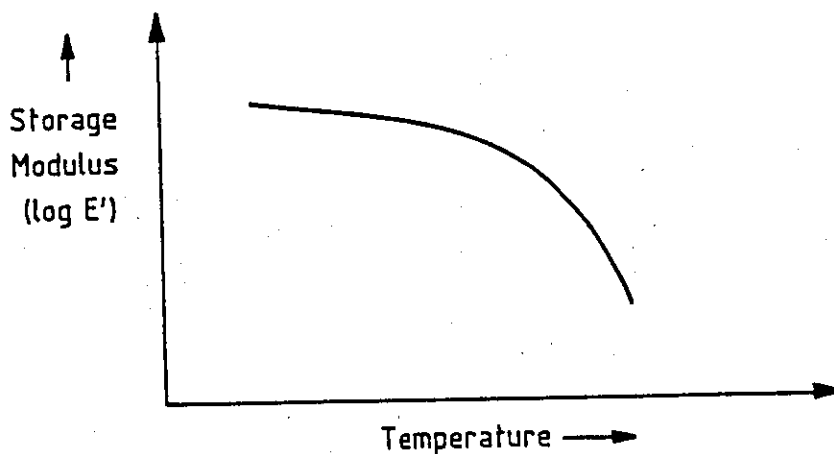
The polyurethanes are synthesised by reacting the polyol, diisocyanate and chain extender and these may be reacted in the ratio of 1:3:2 respectively. The hard segment of this polyurethane system may be increased by increasing the ratio (termed block ratio) to 1:4:3 or higher. A linear thermoplastic system of Capa 220, H_{12} MDI and 1,4-BD (chain extender) is synthesised from a block ratio of 1:3:2 up to 1:9:2⁸ and its effect is observed on the storage modulus and $\tan \delta$ loss curves (Figure 4B3.1(a) and (b)). These show that at low block ratios a broad α -transition is observed which then becomes smaller and narrower as the block ratio increases. This is due to the decreasing amount of soft segment involved in the transition as the block ratio increases. This increase of hard segment increases the interphase contact area, where the mobility of the soft segments can be locally affected resulting in less flexible polymer. The T_g (Table 4B3.1) recorded as the α -peak temperature, moves to higher temperatures with increasing block ratio indicating a certain degree of mixing between the two phases. At the 1:7:6 block ratio and above the T_g does not change significantly indicating that there is no further appreciable change of the soft segment phase and can be ascribed to hard segment phase separation. This change may be further reinforced by the shift in the smaller β -transition (Table 4B3.1) from -75°C at lower block ratios to -50°C above the 1:7:6 block ratio.

Phase separation may be indicated from the temperature dependence of the storage modulus curve. There are two regions in which the storage modulus decreases, the first due to soft segment T_g and the second due to melting of the hard segment domains. Above the T_g a plateau region occurs followed by a rapid drop at the hard segment

softening as shown below:



In the same system a plateau is found with increasing block ratio which has a higher concentration of hard segments acting as physical crosslinks for the flexible soft segment phase. Sometimes a sample, as was found with the 1:6:5 block ratio (Figure 4B3.1(a) and (b)) for the system described, the behaviour is of a pseudo-one-phase material exhibiting no double drop of the modulus as shown below. A behaviour such as this, likely results from an increased T_g due to hard segment influence, whose temperature is similar to the melting of the hard segment domains and so gives a simple relaxation.



In the same linear thermoplastic system of polyol:H₁₂MDI:1,4-BD lowering the molecular weight from 2000 of the polyol (Capa 220) to 1250 (Capa 215) shows similar behaviour (Figure 4B3.2(a) and (b)). This similarity is shown by the storage modulus having a higher plateau and the α -transitions becoming smaller and narrower with increasing block ratio. This occurs due to the morphology changing from a mixed phase to a separate phase system. This change is shown (Table 4B3.1) as the T_g increases sharply from a ratio of 1:4:3 to 1:5:4; this change is also observed in the transition which changes from -75°C to -48°C at these block ratios.

Similar trends are observed for the 1000 m.wt polyol (Capa 210) in the same system of diisocyanate and chain extender as with Capa 215 and Capa 220 (Figure 4B3.3(a) and (b), Table 4B3.1). The storage modulus and T_g values increase with increasing block ratio similar to Capa 215 and Capa 220 based elastomer, earlier described. The Capa 210 based polyurethane shows the highest difference in T_g from the block ratios of 1:3:2 to 1:4:3 suggesting a change in phase morphology above this block ratio. The magnitude of the α -transition at the block ratio of 1:3:2 is broad which becomes narrow and remaining about constant at the block ratio 1:5:4 and above. This indicates that a constant amount of soft segment is involved in the α -transition at 1:6:5 and 1:7:6 block ratios (Figure 4B3.3(a) and (b)), with the T_g shifting slightly to the higher temperature with influence of hard segment content.

The variation of T_g with block ratio for the three different molecular weight polyols is shown in Graph 4B3.1. This shows that for the highest molecular weight polyol (Capa 220 - 2000 m.wt) the change in slope of the T_g's is clearly observed, whereas for the lower molecular weight polyols (Capa 215 and Capa 210) this change is more gradual. It is also observed that the lower m.wt polyol based elastomers show a change in slope of T_g at lower block ratios. However, on comparison of hard segment content the lower m.wt polyol (Capa 210) at 1:3:2 is similar in value to the higher m.wt polyol (Capa 220) at the higher block ratio of 1:6:5. The block ratio does

not give the amount of hard segment present and a weight percent hard segment is calculated as shown below and recorded in Table 4B3.A.

Example:

A calculation of the weight percent hard segment content based on Capa 220 at 1:3:2 block ratio is shown below:

Capa 220	:	H ₁₂ MDI	:	1,4-BD	
1	:	3	:	2	Block ratio
2000 x 1	:	262 x 3	:	90 x 2	m.wt x ratio
2000	:	786	:	180	

$$\begin{aligned} \text{soft segment} \quad \quad \quad \text{hard segment} &= 786 + 180 \\ &= 966 \end{aligned}$$

$$\begin{aligned} \text{Total m.wt} &= 2000 + 966 \\ &= 2966 \quad = 100\% \end{aligned}$$

$$\text{Theoretical wt\% hard segment} = \frac{100}{2966} \times 966$$

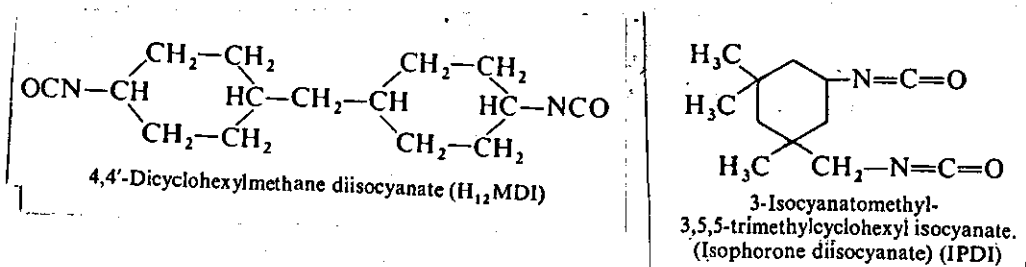
$$= \underline{32.6\%}$$

Graph 4B3.1 shows the change of T_g with respect to weight percent hard segment content (wt% HS) giving similar trends as seen in Graph 4B3.1) but observations are made more clearer. The Capa 220 polyol shows a change in T_g to occur at 45-50 wt% HS which would correspond to the change in phase morphology. This change is less clear for the lower m.wt polyol systems but can be estimated at 45-55 wt% HS for the 1250 m.wt based elastomer and 50-60 wt% HS for the 1000 m.wt based elastomer. This indicates that a change in morphology occurs at higher wt% HS value for lower m.wt polyol based elastomers. It

is also observed, as before, that the lower m.wt polyol systems show a gradual change as opposed to a more clear abrupt change in slope for the higher polyol m.wt systems.

4B.4 EFFECT OF ISOPHORONE DIISOCYANATE BASED ELASTOMERS ON DMTA ANALYSIS

The molecular structure of IPDI differs from H_{12} MDI and is also more reactive:



The IPDI based elastomers synthesised with Capa 220 and 1,4-BD shows by DMTA analysis (Figure 4B4.1(a) and (b)) an increase in T_g and increase in magnitude of the α -transition on raising the block ratio. The behaviour could be associated with more soft segment involvement in the α -transition, producing more rigid polymers due to the molecular structure of IPDI compared to H_{12} MDI polyurethanes. Any change in phase morphology is not indicated for the samples prepared of varying block ratios in IPDI polymers. This may be due to the unsymmetric structure and higher reactivity of IPDI which enhances a mixed phase morphology and any change to phase separation is gradual with increase in block ratio. The change in the slope of T_g values (Graphs 4B3.1 and 4B4.1) is much sharper for the corresponding H_{12} MDI polymers.

The IPDI polymers prepared from Capa 210 show lower Tg values but follow similar trends to Capa 220 based polymers. Similar trends are observed for the Capa 210 polymers and increase in block ratio as with the corresponding H₁₂MDI polymers. Again a more phase mixed system is indicated for the IPDI polymers in comparison with H₁₂MDI elastomers. Graph 4B3.1 of Tg against block ratio for the IPDI polymers shows a very gradual change. Graph 4B4.1 shows a less gradual change and indicates that a change in morphology occurs at a higher wt% HS for the lower (Capa 210) m.wt polyol based elastomer.

4B.5 INFLUENCE OF POLYOL MOLECULAR WEIGHT ON DMTA ANALYSIS

The molecular weight of the polyol was varied from 550 to 4000 (Table 4B5.1) for the H₁₂MDI and 1,4-BD systems at a constant block ratio of 1:3:2. Transparent elastomers were produced from polyols with up to 2000 m.wt, above which crystalline and opaque polymers were obtained. The crystalline elastomers become transparent above a temperature of about 60°C, which is above the melting temperature of the polyol. The DMTA analysis (Figure 4B5.1(a) and (b)) shows the storage modulus to decrease progressively to lower temperatures with increase in polyol molecular weight. The Tg decreases with increase in polyol molecular weight for the transparent polyurethanes (Table 4B5.1), where this is not the case (above 2000 polyol m.wt) the samples should be heated until transparent and quenched before analysis. This would give a result of the amorphous polyurethane (based on high polyol m.wt) and these have been shown to give lower Tg's [126] as expected with increase in polyol m.wt.

The magnitude of the α -transition increases with increasing polyol m.wt as more soft segment is involved in the transition, for the H₁₂MDI/1,4-BD system at constant (1:3:2) block ratio. As the polyol m.wt rises in the elastomer the restrictive influences of the hard segment structures become less important and accordingly the Tg occurs at lower temperatures at constant block ratios. There is an obvious change in the opaque high molecular weight polyol based elastomers due to the soft segment crystallisation.

Similar trends have been found at constant block ratios of 1:4:3 and 1:5:4 with polyol m.wt (Table 4B5.1, Graph 4B5.1). At the block ratios of 1:3:2 and 1:4:3 the β -transition shows a shift from -48°C to -74°C from the 1000 to 1250 polyol m.wt respectively. At the higher block ratio of 1:5:4 the same β -transition shift occurs at the 1250 to 2000 polyol m.wt. This suggests that at (constant) high block ratios any change in phase morphology would take place at higher polyol m.wt.

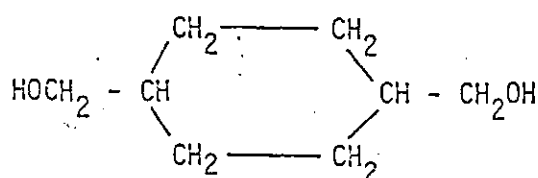
The T_g values obtained may give a better comparison for the polyurethanes having similar wt% HS for each polyol m.wt system used. This has been calculated as shown earlier and tabulated (see Tables 4B3(B) and (C)). The thermal data from the DMTA analysis for polyurethanes of similar wt% HS are shown in Table 4B3.D. The T_g values are found to increase slightly with increase in the polyol molecular weight (Graph 4B5.2) with the exception of Capa 215. This may be due to the lower reactivity of this polyol in comparison with the other polyol systems. The T_g values increase with wt% HS as expected. The β -relaxation shows a shift in temperature (from -48 to -75) at the lower wt% HS (Table 4B3.D) between Capa 210 and Capa 215, however there is no shift observed in the higher wt% HS. A possible shift in the β -transition for the higher wt% HS may occur at higher polyol molecular weights.

4B.6 INFLUENCE OF DIFFERING CHAIN EXTENDER SYSTEMS ON DMTA ANALYSIS

The trends observed for polyurethanes based on the symmetrical 1,4-BD and unsymmetrical 1,3-BD are similar (Table 4B3.1, Figure 4B6.1(a) and (b)). The unsymmetrical chain extender shows higher magnitude of α -transitions for the corresponding symmetrical chain extender. This indicates that more soft segment (polyol) is involved in the α -transition and this is supported by the 1,3-BD polymers being more flexible and soft.

The polyurethanes based on Capa 215/ H_{12} MDI show similar trends on chain extension with 1,4-BD and the mixed 1,4-BD + 1,4-CHDM (at 1:1)

on DMTA analysis (Table 4B3.1, Figure 4B6.2(a) and (b)). The magnitude of both the α - and β -relaxations are much greater for the mixed chain extender system. In the earlier comparison of the unsymmetrical diol (1,3-BD) only the α -transitions were greater in magnitude compared to the symmetrical diol (1,4-D); with the mixed chain extender system both α - and β -transitions are greater suggesting a more harder, tougher impact resistant polymer than the corresponding 1,4-BD based elastomer. The mixed chain extender system does give a more rigid harder polymer, due to the more rigid structure of 1,4-CHDM compared to 1,4-BD.



1,4-cyclohexanedimethanol
(1,4-CHDM)

A polyurethane based on the 1,6-hexanediol chain extender gives a much lower T_g than the 1,4-BD chain extended polyurethanes, due to chain length of 1,6-HD producing more flexible polymers.

4B.7 THE INFLUENCE OF DIFFERENT TYPES OF CROSSLINKING SYSTEMS

i) Crosslinking introduced via the chain extender system

The crosslinking agent was incorporated as part of the chain extender system on a 1:1 basis with diols. The crosslinkers were triols, namely trimethylolpropane (TMP) and Capa 305 (trifunctional polycaprolactone polyol of 540 m.wt) which were mixed in many combinations (Table 4B7.1) with the diols, which were 1,4-BD, Dianol 22 (D22) and Dianol 33 (D33). Polymers made with the mixed chain extender 1,4-BD + Capa 305 (1:1), D33 + Capa 305 (1:1) and D22 + Capa 305 (1:1) have high wt% HS compared to the single 1,4-BD chain extender, but give lower T_g values. This is due to the high molecular weight of Capa 305, D33 and D22 which gives more flexible polymers.

The mixed chain extender TMP + 1,4-BD (1:1) shows the modulus to stabilise to higher temperatures (Figure 4B7.1(a) and (b)) due to the crosslinking effect. The chain extender Capa 305 + D33 (1:1) does not show the modulus to stabilise to higher temperature, due to Capa 305 having a higher molecular weight and therefore weaker crosslinking effect and also its combination to a high m.wt diol.

ii) Crosslinking via the polyol system

The polyol used was Capa 305 with both H_{12} MDI and IPDI diisocyanates and chain extended with 1,4-BD. The DMTA analysis (Table 4B7.2, Figure 4B7.2(a) and (b)), generally shows that for the same block ratio, the drop in storage modulus occurs at slightly higher temperatures for the IPDI polymers compared to H_{12} MDI polymers. This is due to the more rigid molecular structure of IPDI and is reflected in the T_g values being slightly higher (Table 4B7.2). It is also noticed that on comparing these triol based (H_{12} MDI and IPDI) systems with the difunctional polyol (Capa 200, 550 m.wt) systems, the T_g 's are found to be much higher for the triol based elastomers as expected due to their crosslinking effect and increased rigidity. The T_g 's are found to increase with block ratio for both diisocyanate systems.

The β -relaxations for the triol based polyurethanes are much larger in magnitude than the corresponding diol polymer. The H_{12} MDI/triol based polyurethanes show larger β -transitions than the IPDI/triol polymers. The temperature at which the β -transition occurs for the polymer (at -47°C) corresponds well with the β -transition of H_{12} MDI/diol polymer. The IPDI/triol based polyurethane shows the β -transition at -66°C , compared to -73°C for the corresponding IPDI/diol elastomer.

These triol based polyurethanes also show another transition (Figure 4B7.2(a) and (b)), which appears as a shoulder on the low temperature side of the α -transition. This shoulder is not detected for the IPDI polymer at 1:2:1 block ratio but becomes more prominent

with increasing block ratio. This shoulder is detectable at a 1:2:1 block ratio for the H_{12} MDI elastomer and increases in magnitude with block ratio to a distinct peak. The magnitude of these low temperature transitions are associated with toughness and impact strength [151]. The higher magnitude of these transitions for the H_{12} MDI polymers would indicate higher impact strength than the IPDI polymers.

iii) Crosslinking with tetrafunctional polyols

In general the trends observed follow a similar pattern to the triol based polyurethanes discussed. Two tetrafunctional polyols of 600 and 1000 m.wt were used with H_{12} MDI and IPDI diisocyanates, chain extended with 1,4-BD (Table 4B7.2, Figure 4B7.3(a) and (b), Figure 4B7.4(a) and (b)). The 600 m.wt tetrafunctional polyol (tetra-ol 600) can be compared to the triol polyol based polymers as the polyols are similar in molecular weight. The Tg's are found to occur at higher temperatures for the tetra-ol based polyurethanes due to the increased crosslinking effect compared to the triol based polymer. The Tg values are found to increase with block ratio.

The IPDI based tetra-ol 600 polyurethanes have slightly lower Tg values compared to H_{12} MDI based tetra-ol 600 polymers. In the case of the triol polyol based polyurethanes, IPDI gave slightly higher Tg values when compared with H_{12} MDI, this may be due to the lower crosslinking effect and lower m.wt of the triol compared to the tetra-ol 600. The β -transition for H_{12} MDI/tetra-ol 600 based polyurethanes occurs at -47°C (similar to the triol and diol based polymers). For IPDI this β -transition occurs at -68°C (similar to triol, but not diol based systems). The transition at the shoulder of the α -peak is again larger for H_{12} MDI than IPDI based elastomers and these are in turn larger (in magnitude) than the corresponding triol polymers. This indicates that the H_{12} MDI/tetra-ol 600 based elastomers will have higher impact strength than the corresponding IPDI polymers which will in turn be of higher strength than the triol based polymers.

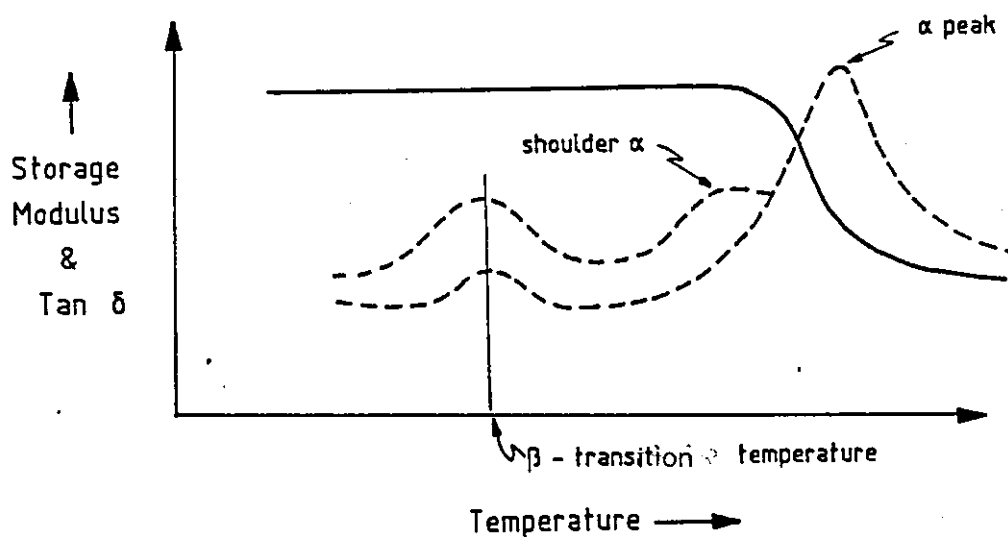
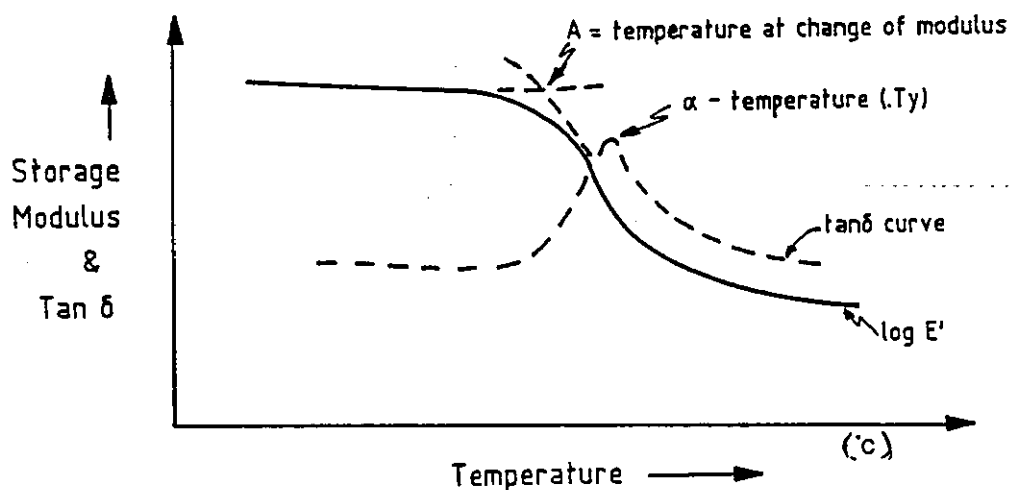
The tetrafunctional 1000 m.wt (tetra-ol 1000) based polymers have lower Tg's in comparison with the tetra-ol 600 based polymers, this is expected to be due to increase in polyol m.wt. The IPDI tetra-ol 1000 polymers show lower Tg values compared with H₁₂MDI, as was found earlier with the tetra-ol 600 systems. The difference in Tg values between H₁₂MDI and IPDI for tetra-ol 1000 polymers is greater than in polymers based on tetra-ol 600 due to the higher polyol m.wt. The β -transitions of H₁₂MDI/tetra-ol 1000 polyurethane systems are again larger in magnitude than IPDI/tetra-ol 1000 systems, and appear at the same temperature as with the tetra-ol 600 polymers. The transition at the shoulder of the α -peak is much smaller in comparison with both the tetra-ol 600 and triol based polymers. This shoulder transition is just detected for IPDI/tetra-ol 1000 at the 1:4:3 block ratio and at 1:3:2 for H₁₂MDI/tetra-ol 1000 polymers. This suggests that higher strength would be observed for H₁₂MDI compared to IPDI for the tetra-ol 1000 polymers, but these in turn would have lower strength compared to the triol and diol based polymers.

The presence of chemical crosslinks produces a change in the dynamic mechanical properties at temperatures above the melting of the hard phase, shown by the storage modulus remaining stable to higher temperatures. It has been observed that with increasing block ratio this stabilising effect on storage modulus shifts to higher temperatures. On comparison of polyols with similar m.wt the tetra-ol polymer shows higher temperature stability than the triol polyurethane. This occurs due to the greater amount of crosslinking present. With increase in m.wt of polyol for the tetra-ol systems the stabilisation effect of the storage modulus decreases, due to the lower concentration of crosslinks per unit length.

The chemical crosslinks are likely to prevent phase separation, and evidence of this phase separation has been found in crosslinked polyurethanes by Lagasse [135]. The almost constant Tg for H₁₂MDI/tetra-ol 1000 polymers at 1:4:3 and 1:5:4 block ratios may then suggest a phase separated morphology in comparison with the

lower 1:2:1 and 1:3:2 block ratios. The classification of polymers as compatible or incompatible is not a strict one. These terms are used to designate the extremes of possible segmented elastomer morphologies. A real material exhibits aspects of both types of behaviour. The hard and soft segment domains in a two phase system can behave somewhat independently, each displaying characteristic thermal and mechanical behaviour analogous to an incompatible system. The transition zone between the two types of domain consists of a continuum of mixed hard segment-soft segment regions with hard-segment content decreasing as one proceeds from a predominantly hard-segment domain to a predominantly soft segment domain. This transition zone will have the characteristics of a compatible system.

Key to the following tables:



The size of the β and 'shoulder α ' peaks have been given subscripts a, b, c, d and e, i.e.

a = very small peak or shoulder

e = large peak or shoulder

and ab would be $a < ab < b$

TABLE 4B3.A: WEIGHT PERCENTAGE HARD SEGMENT CONTENT (wt% HS)

Polymer Systems	1:3:2	1:4:3	1:5:4	1:6:5	1:7:6	1:8:7	1:9:8	1:10:9	1:11:10
Capa 220: DesW 1,4-BD or 1,3-BD	32.6	39.7	45.5	50.3	54.3	57.7	60.6	63.2	65.4
Capa 215: DesW 1,4-BD	43.6	51.3	57.2	61.8	65.5				
Capa 215: DesW 1,4-BD + 1,4-CHDM	50.1	58.3	64.2	68.7	72.2				
Capa 210: DesW 1,4-BD	49.1	56.9	62.6	66.9	70.4	73.2			
Capa 220: IPDI 1,4-BD	29.7		42.4		51.2		57.6		
Capa 210: IPDI 1,4-BD	45.9		59.5		67.7		73.1		

TABLE 4B3.B: WEIGHT % OF HARD SEGMENT VALUES FOR POLYURETHANES BASED ON DIFFERING POLYOLS AT SEVERAL BLOCK RATIOS

H ₁₂ MDI/1,4-BD with	Weight Percent Hard Segment (wt% HS)	Block Ratio
Capa 200 (<50)	52.8, 63.7, 70.6	1:2:1 to 1:4:3
Capa 205 (830)	53.8, 61.4, 66.8	1:3:2 to 1:5:4
Capa 210 (1000)	49.1, 56.9, 62.6, 66.9, 70.4	1:3:2 to 1:7:6
Capa 215 (1250)	43.6, 51.3, 57.2, 61.8, 65.5	1:3:2 to 1:7:6
Capa 220 (2000)	32.6, 39.7, 45.5, 50.3, 54.3, 57.7, 60.6	1:3:2 to 1:9:8

TABLE 4B3.C: SHOWS TWO SYSTEMS OF SIMILAR WT% HS AND THEIR CORRESPONDING BLOCK RATIOS

H ₁₂ MDI/1,4-BD with	Wt% HS	Block Ratio	Wt% HS	Block Ratio
	(1)		(2)	
Capa 200	52.8	1:2:1	63.7	1:3:2
Capa 205	53.8	1:2:2	61.4	1:4:3
Capa 210	49.1	1:3:2	62.6	1:5:4
Capa 215	51.3	1:4:3	61.8	1:6:5
Capa 220	54.3	1:7:6	60.8	1:9:8

TABLE 4B3.D: DMTA DATA OF POLYURETHANES BASED ON DIFFERING POLYOLS AT SIMILAR WT% HS VALUES

Polyol mwt	550	830	1000	1250	2000
Wt% HS	52.8	53.8	49.1	51.3	54.3
Tg	36	40	32	26	52
β-transition	-49 ^c	-48 ^{bc}	-48 ^b	-75 ^{ab}	-75 ^{ab}
Tg adjusted to 52.8 wt% HS	36	38	40	33	50
Polyol mwt	550	830	1000	1250	2000
Wt% HS	63.7	61.4	62.6	61.8	60.8
Tg	50	52	55	59	57
β-transition	-48 ^c	-48 ^c	-48 ^c	-49 ^b	-50 ^a
Tg adjusted to 63.7 wt% HS	50	54	56	61	58

TABLE 4B3.1: DMTA RESULTS ON VARYING BLOCK RATIOS FOR THE TPU's

		1:3:2	1:4:3	1:5:4	1:6:5	1:7:6	1:8:7	1:9:8
Capa 220	A	-37	-35	-33	-30	-30	-24	-23
H ₁₂ MDI (Tg)	α	-12	+12	+42	-	+52	+56	+57
1,4-BD	β	-75 ^a	-75 ^a	-74 ^a	-	-75 ^a	-50 ^a	-50 ^a
Capa 220	A	-36		-30		-31		-24
IPDI	α	-2		+21		+39		+48
1,4-BD	β	-75 ^{ab}		-76 ^b		-75 ^b		-75 ^b
Capa 215	A	-33	-30	-29	-21			
H ₁₂ MDI	α	+20	+26	+54	+59			
1,4-Bd	β	-74 ^a	-75 ^{ab}	-47 ^b	-49 ^b			
Capa 210	A	-20	-11	+2	+9	+15		
H ₁₂ MDI	α	+32	+48	+55	+59	+63		
1,4-BD	β	-48 ^b	-48 ^{bc}	-48 ^c	-48 ^c	-50 ^c		
Capa 210	A	-15		-3		+18		+25
IPDI	α	+24		+41		+59		+63
1,4-BD	β	-73 ^c		-71 ^c		-68 ^c		-74 ^c
Capa 215	A		-20	-11	-8	-5		
H ₁₂ MDI	α		+37	+51	+56	+65		
1,4-BD	β		-52 ^b	-43 ^c	-48 ^c	-49 ^c		
1,4-CHDM								
		1:5:4	1:6:5	1:7:6	1:8:7	1:9:8	1:10:9	1:11:10
Capa 220	A	-28	-26	-24	-26	-25	-30	-20
H ₁₂ MDI	α	+31	+44	+52	+58	+60	-	+66
1,3-BD	β	-51 ^a	-45 ^a	-50 ^a	-48 ^a	-45 ^{ab}	-47 ^{ab}	-45 ^{cb}

TABLE 4B5.1: DMTA RESULTS ON VARYING POLYOL MOLECULAR WEIGHT FOR THE TPU's

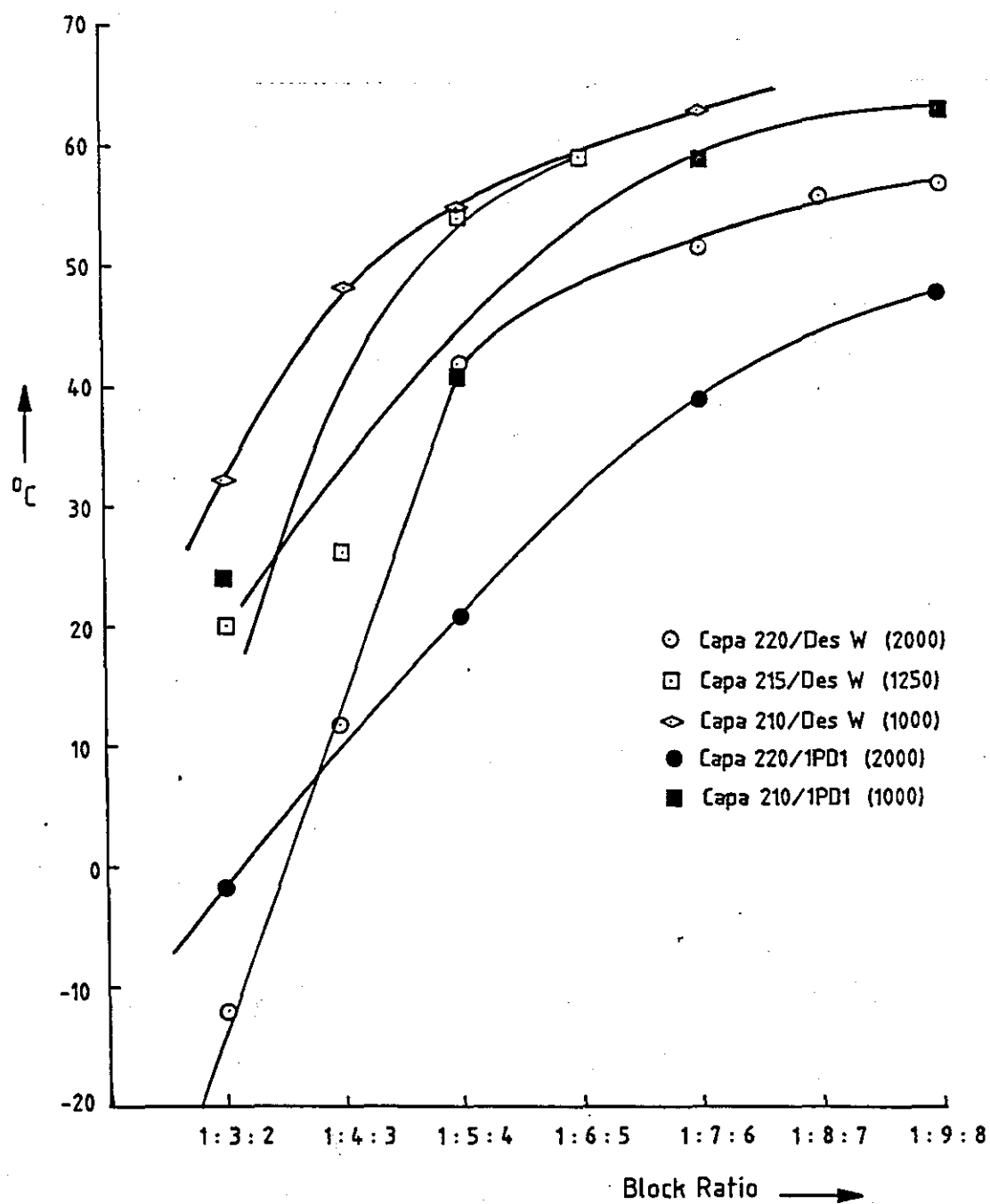
H ₁₂ MDI 1,4-BD	Polyol mw	550	830	1000	1250	2000	3000	4000
1:3:2	A	+4	-9	-20	-33	-37	-41	-43
	α	+50	+40	+32	+20	-12	-34	-26
	β	-48 ^c	-48 ^{bc}	-48 ^b	-74 ^a	-74 ^a	-75 ^a	
1:4:3	A	+30	-2	-11	-30	-35		
	α	+55	+52	+48	+26	+12		
	β	-48 ^c	-48 ^c	-48 ^{bc}	-75 ^b	-75 ^b		
1:5:4	A		+9	+2	-29	-33		
	α		+57	+55	+54	+42		
	β		-47 ^c	-48 ^c	-46 ^b	-72 ^a		
IPDI 1,4-BD								
1:3:2	A	+10		-15		-37		
	α	+39		+24		-2		
	β	-73 ^{cd}		-73 ^c		-75 ^b		

TABLE 4B7.1: DMTA RESULTS FOR THERMOPLASTIC AND CROSSLINKED POLYURETHANES

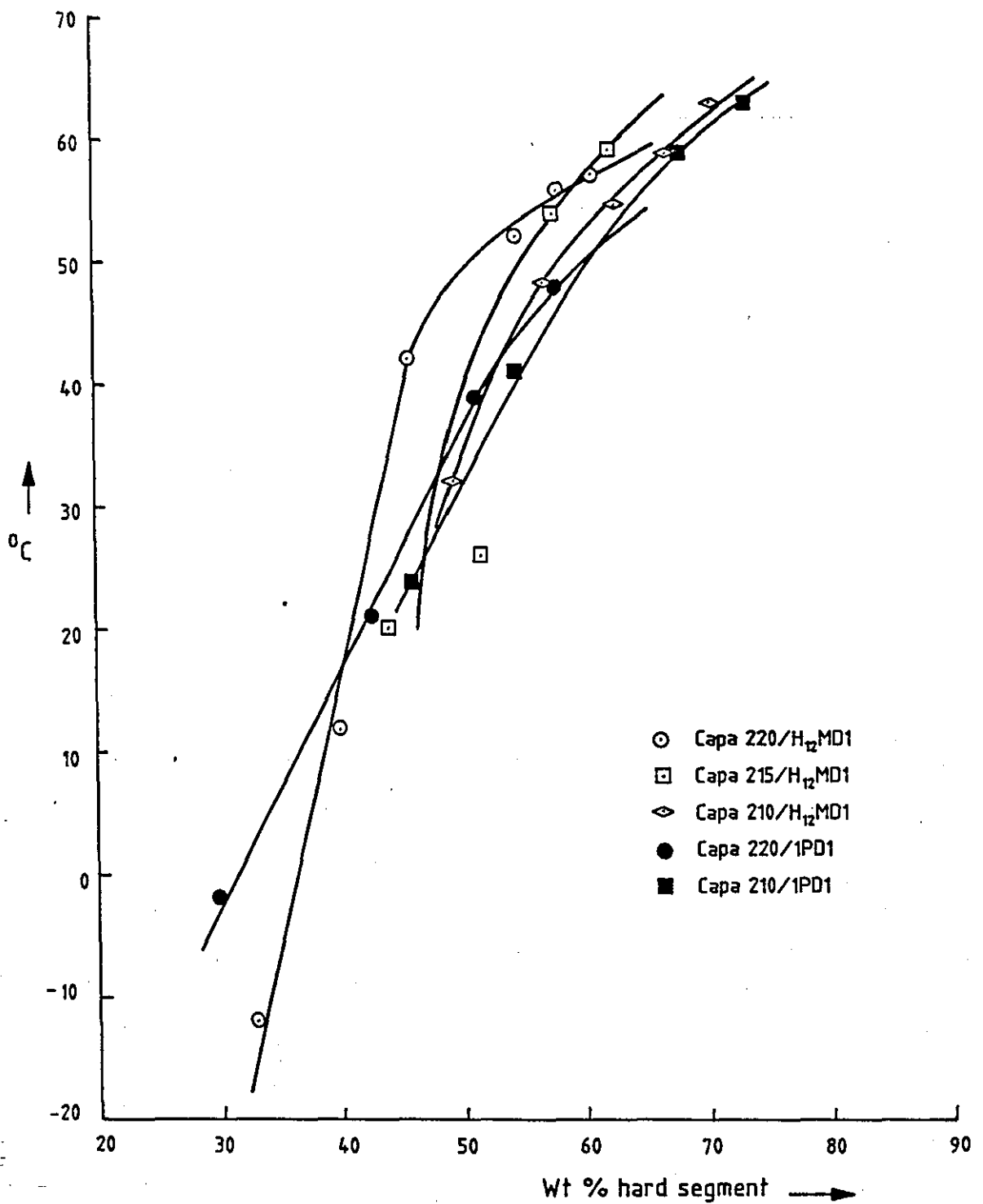
Capa 205 H ₁₂ MDI	Chain Extender	1,6-HD	1,4-BD	1,4-BD + 1,4-CHDM	1,4-BD + TMP	1,4-BD + Capa 305	Capa 305+ D33	Capa 305+ D22
1:4:3	A	+2	-2	+7	+8	-2	+10	+8
	α	+41	+52	+52	+52	+33	+43	+42
	β	-48 ^c	-48 ^c	-48 ^{cd}	-47 ^c	-46 ^c	-46 ^c	-47 ^c
wt% HS		62.8	61.4	62.8	62.5	70.6	74.1	73.8
Capa 210 H ₁₂ MDI								
1:5:4	A	+8	+2	+12	+9	-1	+14	+11
	α	+46	+55	+57	+5	+34	+48	+44
	β	-48 ^c	-48 ^c	-47 ^{cd}	-46 ^{cd}	-46 ^{cd}	-46 ^c	-47 ^c
wt% HS		64.1	62.6	64.0	63.8	72.0	75.5	75.1

TABLE 4B7.2: DMTA RESULTS FOR CROSSLINKED POLYURETHANES

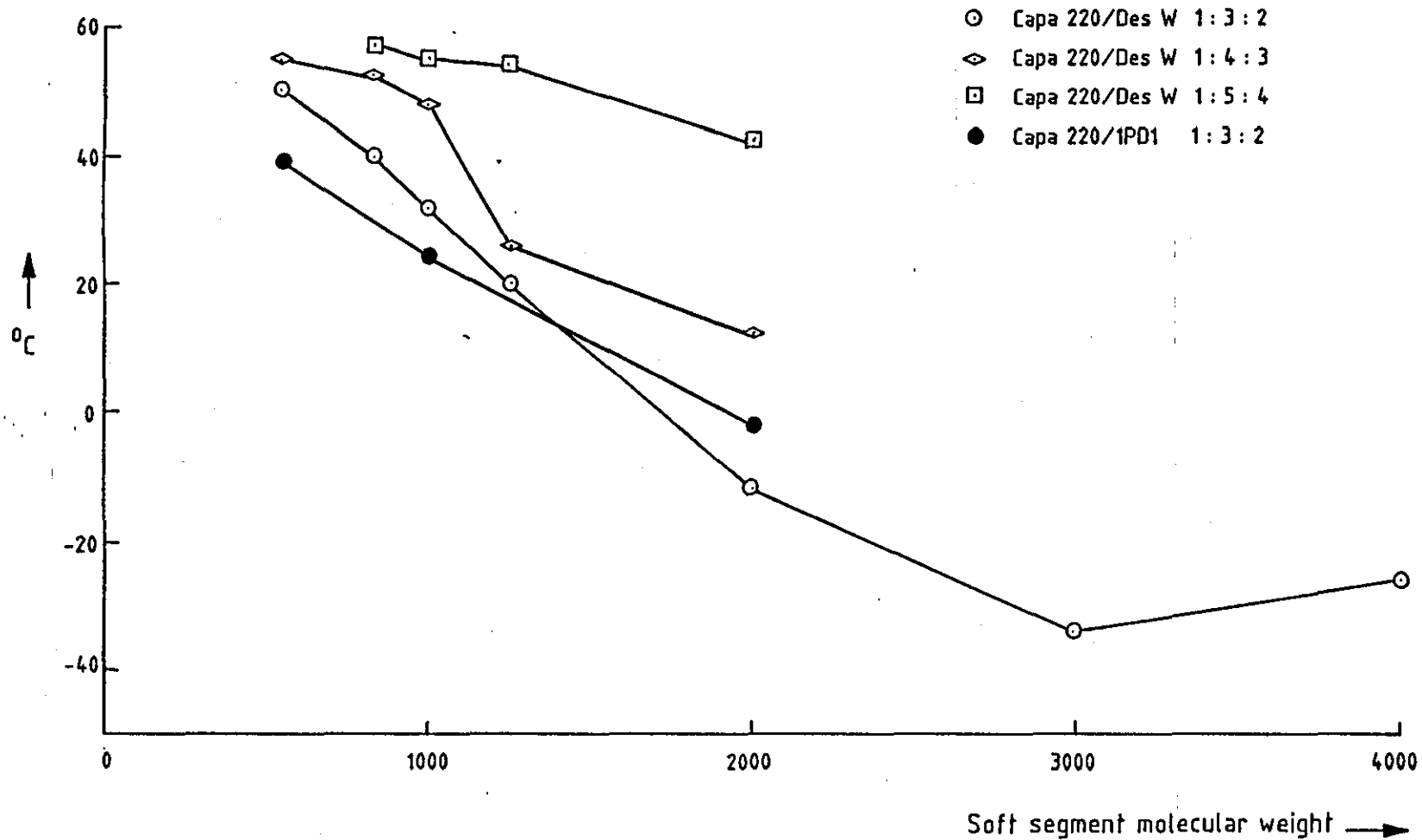
H ₁₂ MDI:1,4-BD		1:2:1	1:3:2	1:4:3	1:5:4
Capa 305	A	+40	+50	+56	
(triol	α	+63	+70	+78	
540 mwt)	β	-46 ^d	-47 ^d	-46 ^d	
Shoulder	α	+ shoulder	+24 ^d	+23 ^d	
wt% HS		53.2	64.1	70.9	
Tetra-ol	A	+64	+69	+70	
600 mwt	α	+84	+87	+91	
	β	-44 ^d	-47 ^d	-44 ^d	
Shoulder	α	+24 ^d	+24 ^{de}	+25 ^e	
wt% HS		50.6	61.9	68.7	
Tetra-ol	A	+30	+45	+50	+51
1000 mwt	α	+54	+64	+73	+74
	β	-46 ^d	-46 ^d	-46 ^d	-47 ^d
Shoulder	α	No shoulder	+ shoulder	+26 ^d	+26 ^{de}
wt% HS		38	49.1	56.9	62.6
IPDI:1,4-BD					
Capa 305	A	+48	+53	+60	
	α	+65	+74	+82	
	β	-67 ^c	-66 ^c	-65 ^c	
Shoulder	α	No shoulder	Slight shoulder	+35 ^d	
wt% HS		49.8	61.1	68.2	
Tetra-ol	A	+57	+64	+68	
600	α	+80	+86	+89	
	β	-69 ^c	-68 ^c	-70 ^c	
Shoulder	α	+34 ^d	+35 ^d	+35 ^d	
wt% HS		47.1	58.5	65.9	
Tetra-ol	A	+27	+43	+51	
1000	α	+47	+59	+68	
	β	-70 ^c	-68 ^c	-68 ^c	
Shoulder	α	No shoulder	No shoulder	Slight shoulder	
wt% HS		34.8	45.9	53.9	



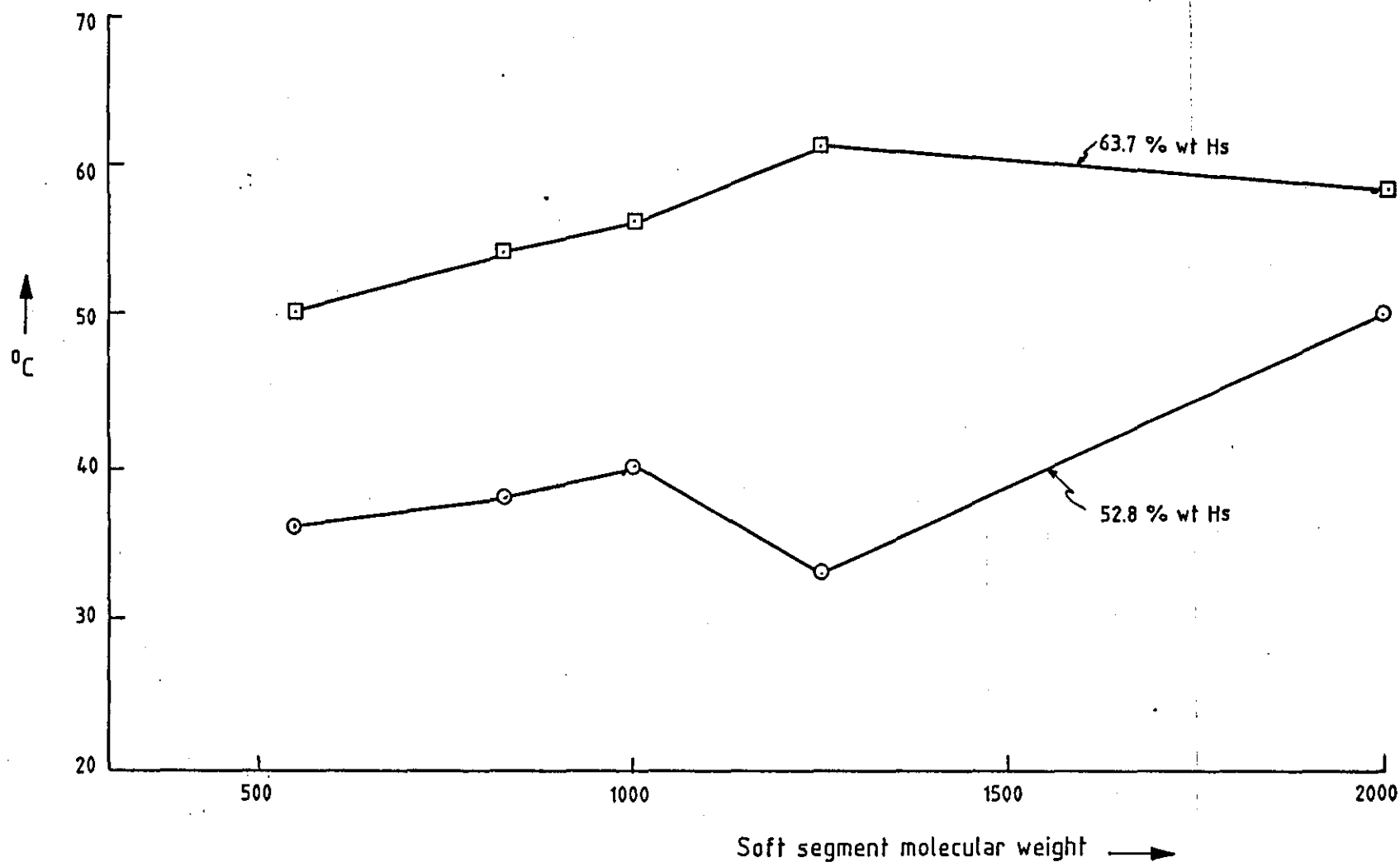
Graph 4B3 . 1 . T_g vs Block Ratio for some H_{12} MD1 and 1PD1 Polyurethanes



Graph 4B4.1. T_g vs wt % hard segment content for $\text{H}_{12}\text{MD1}$ and 1PD1 Polyurethanes.



Graph 4B5.1. T_g vs soft segment molecular weight.



Graph 4B5.2. T_g vs polyol molecular weight at constant wt % Hs content.

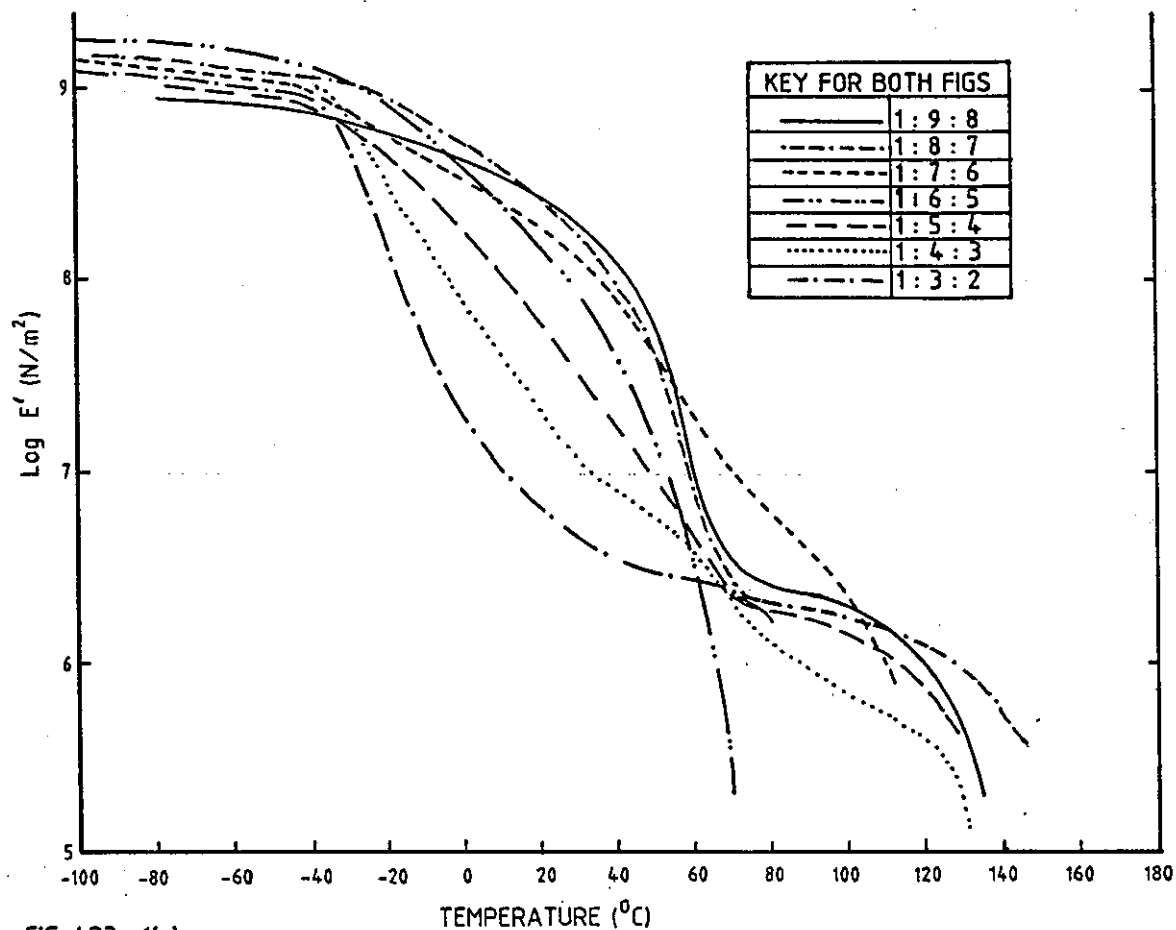


FIG. 4B3. 1(a)

DMTA Log MODULUS CURVES FOR Capa 220 : Des W : 1,4BD.

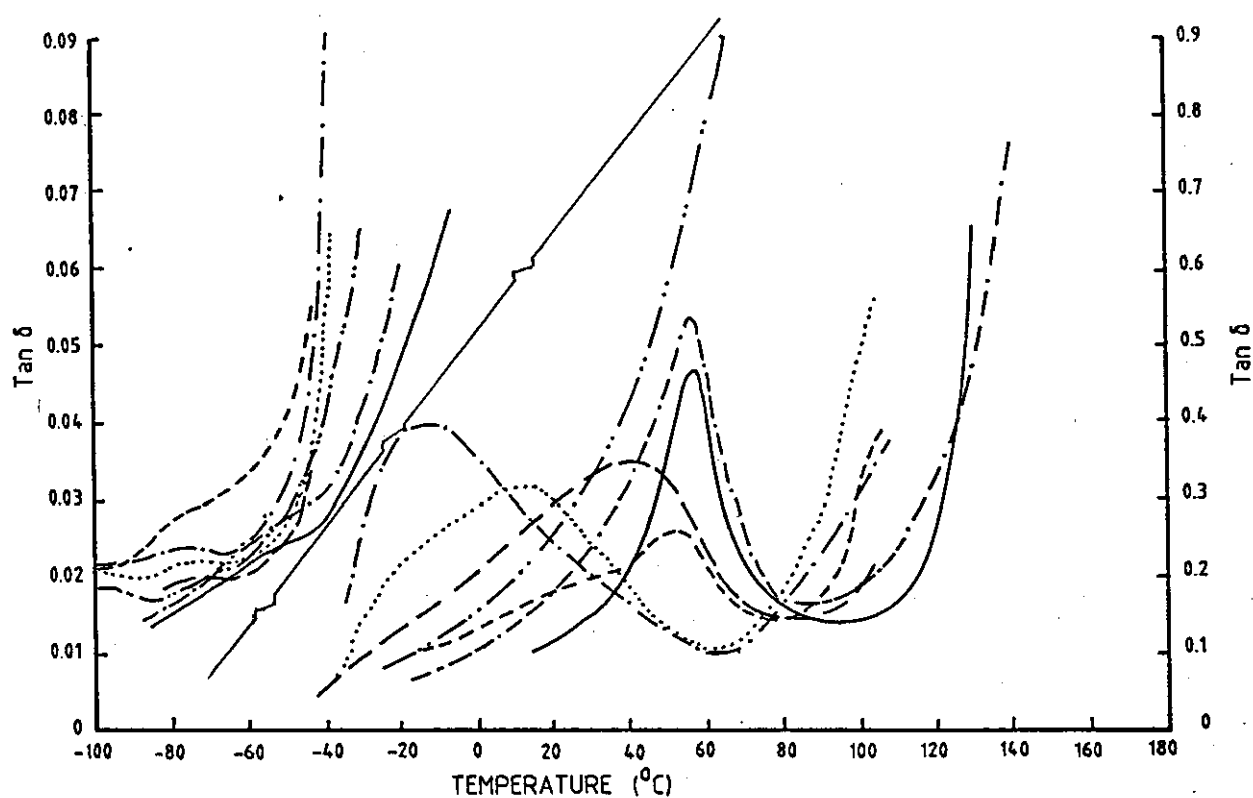


FIG. 4B3. 1(b)

DMTA Tan δ CURVES FOR Capa 220 : Des W : 1,4BD.

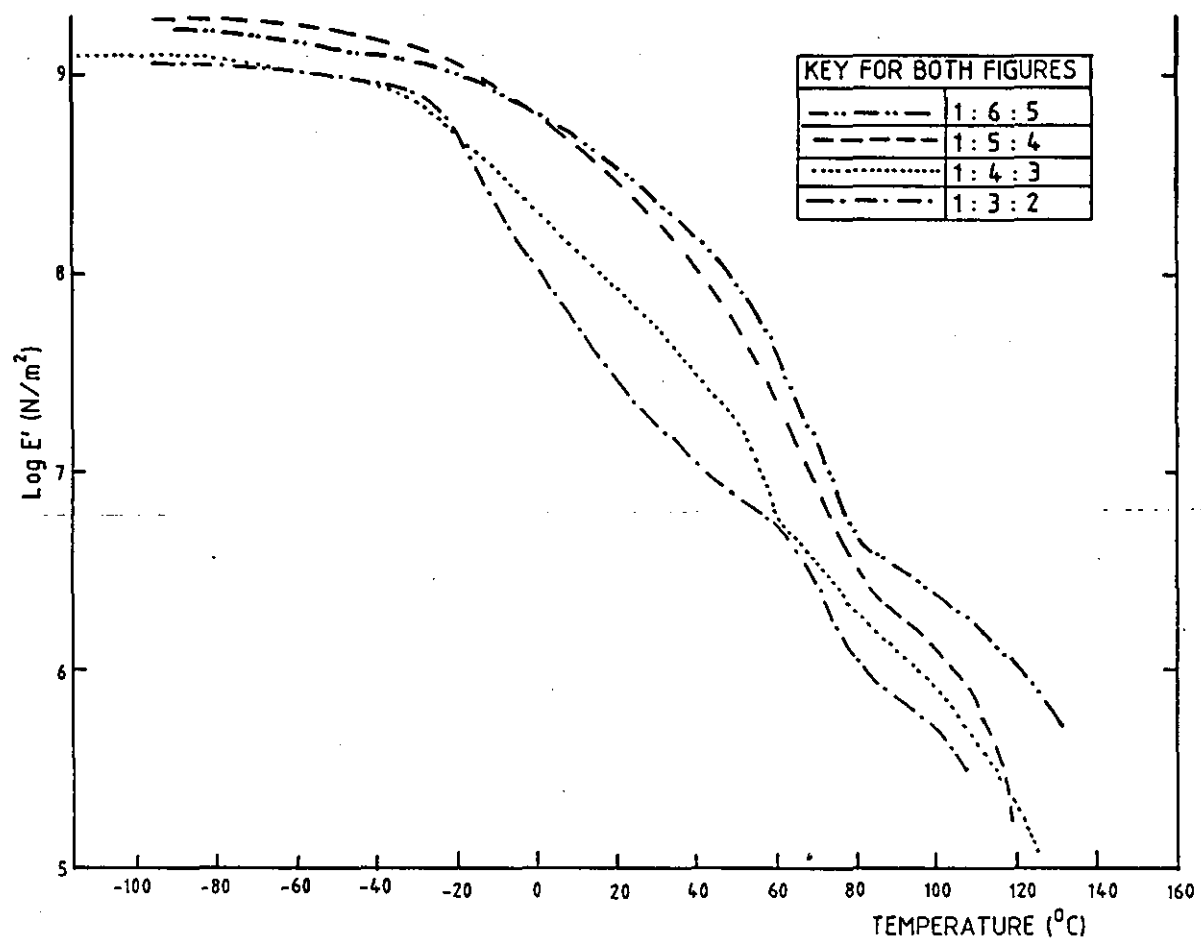


FIG. 4B3 . 2(a) DMTA - Log MODULUS CURVES FOR Capa 215 : H₁₂MDI : 1,4BD AT VARYING BLOCK RATIOS.

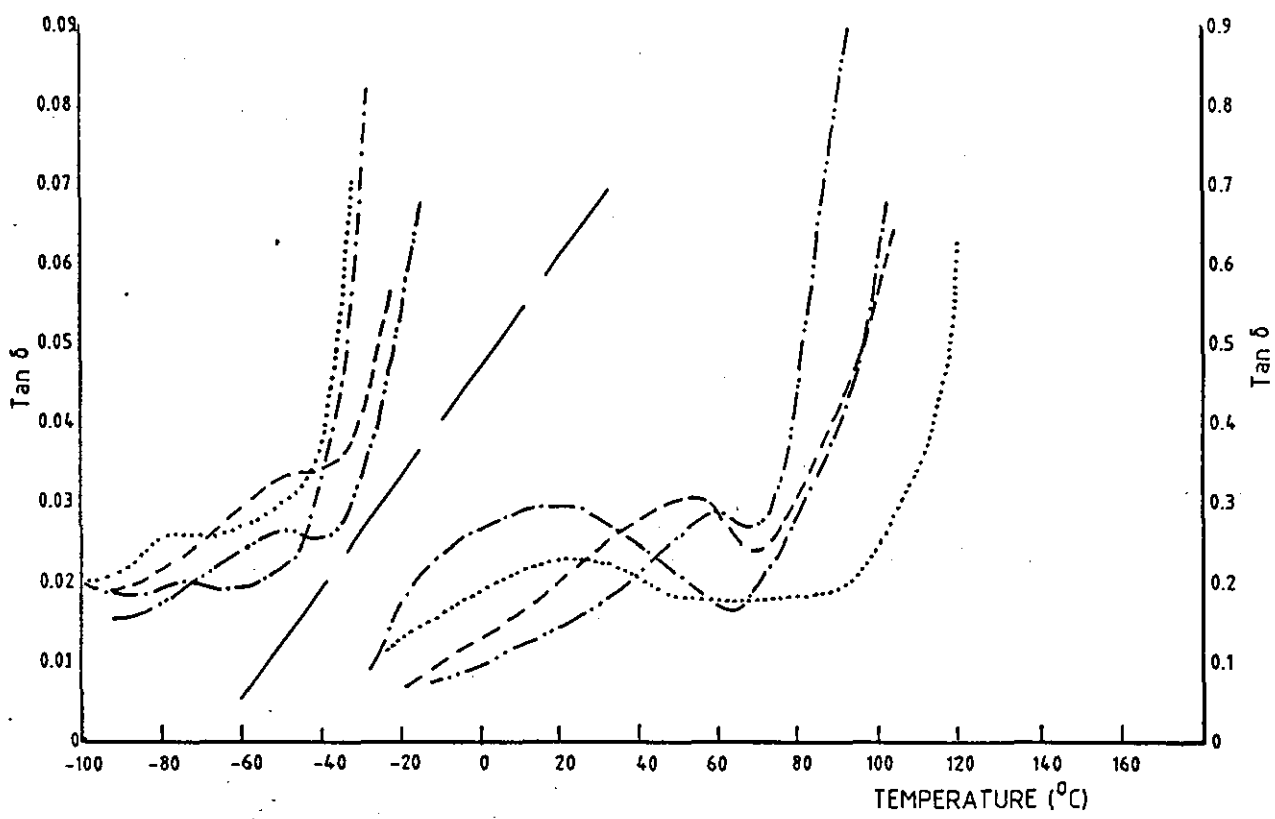


FIG. 4B3 . 2(b) DMTA - Tan δ CURVES FOR Capa 215 : H₁₂MDI : 1,4BD AT VARYING BLOCK RATIOS

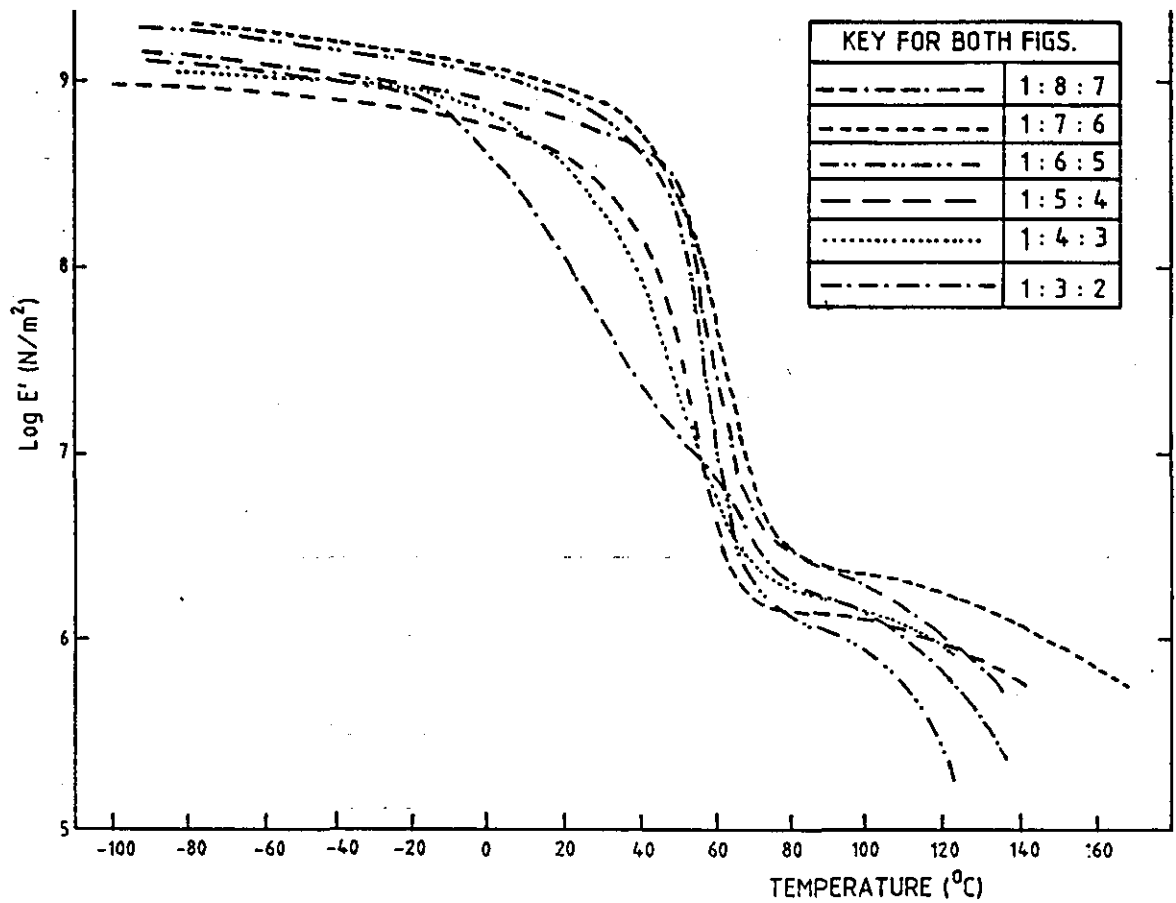


FIG. 4B3.3(a). DMTA - Log MODULUS CURVES FOR Capa 210 : Des W : 1,4BD AT VARYING BLOCK RATIOS.

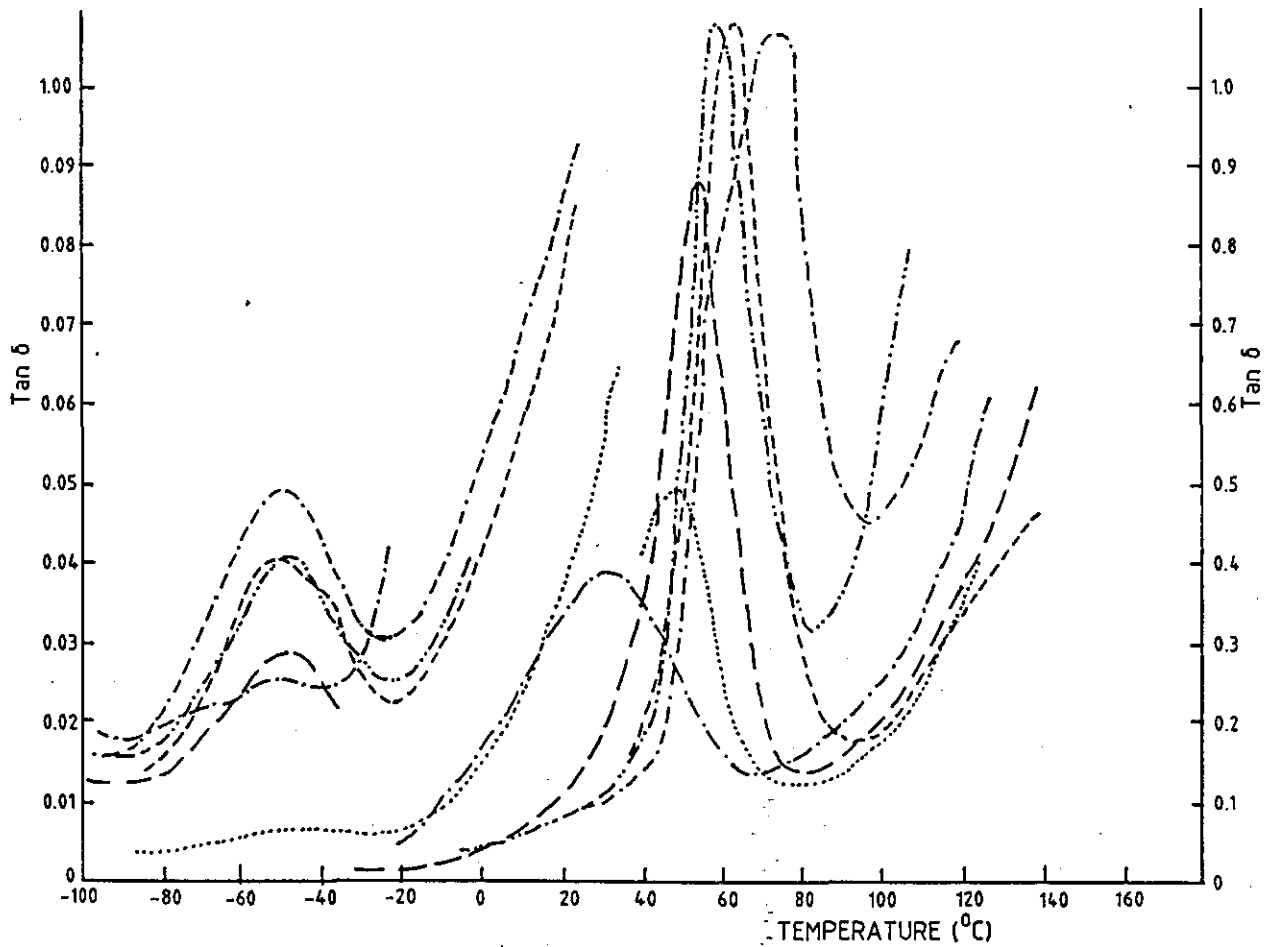


FIG. 4B3.3(b). DMTA - Tan δ CURVES FOR Capa 210 : H₁₂MDI : 1,4BD AT VARYING BLOCK RATIOS.

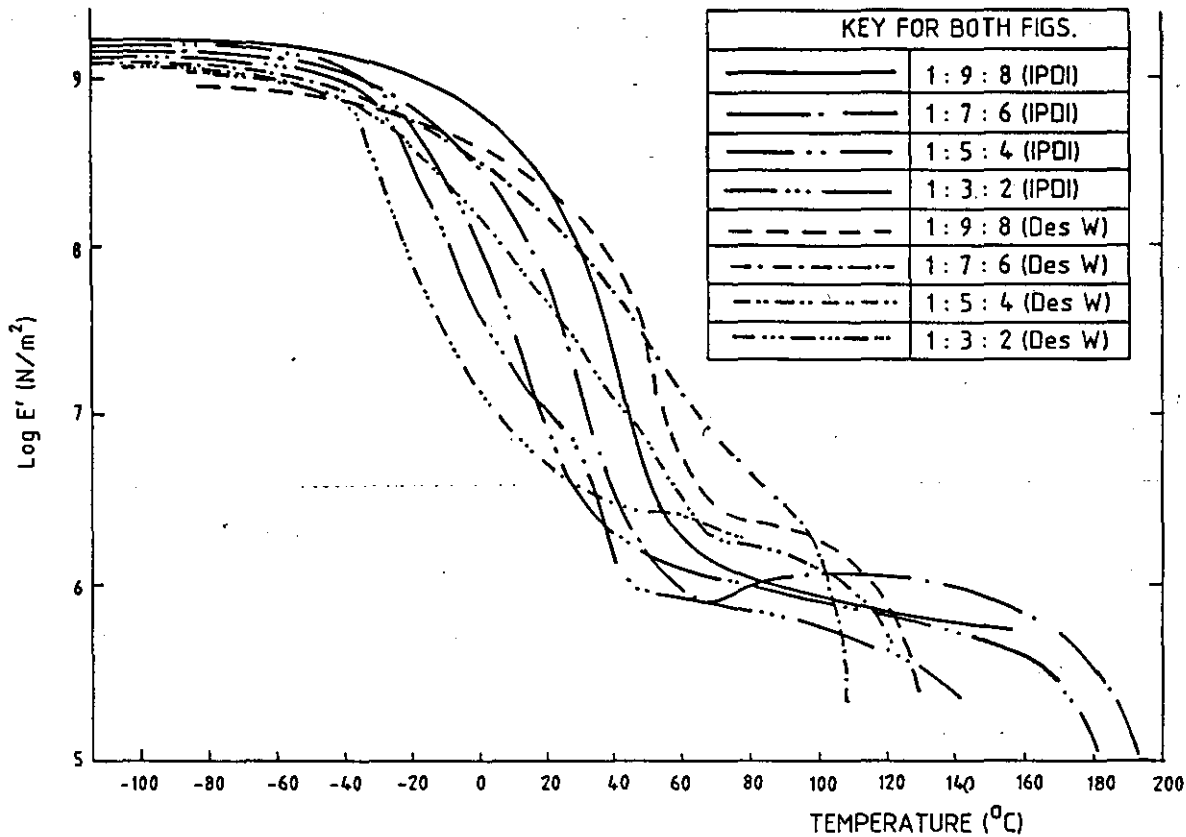


FIG. 4B4 . 1(a). DMTA - Log MODULUS CURVES FOR Capa 220 : IPDI : 1,4BD AND Capa 220 : H₁₂MDI : 1,4BD AT VARYING BLOCK RATIOS

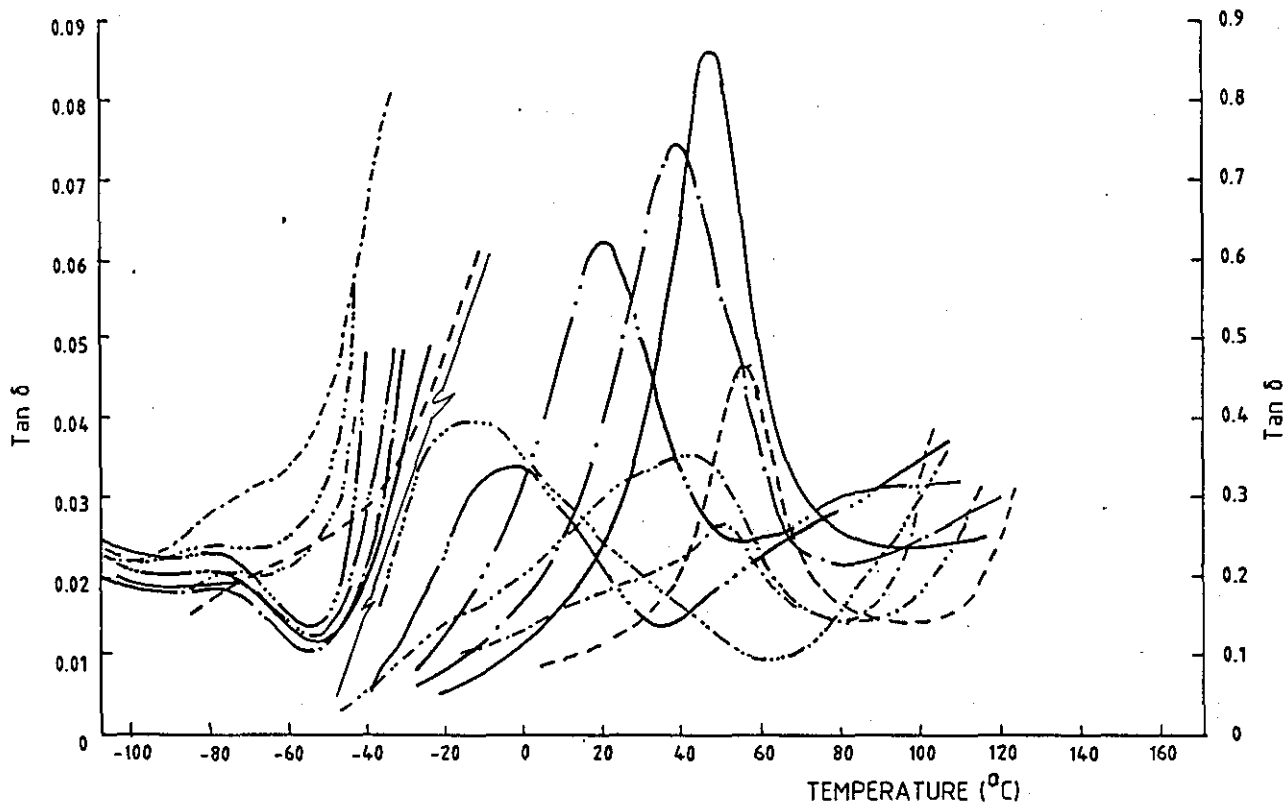


FIG. 4B4 . 1(b) DMTA - Tan δ CURVES FOR Capa 220 : IPDI : 1,4BD AND Capa 220 : H₁₂MDI : 1,4BD AT VARYING BLOCK RATIOS.

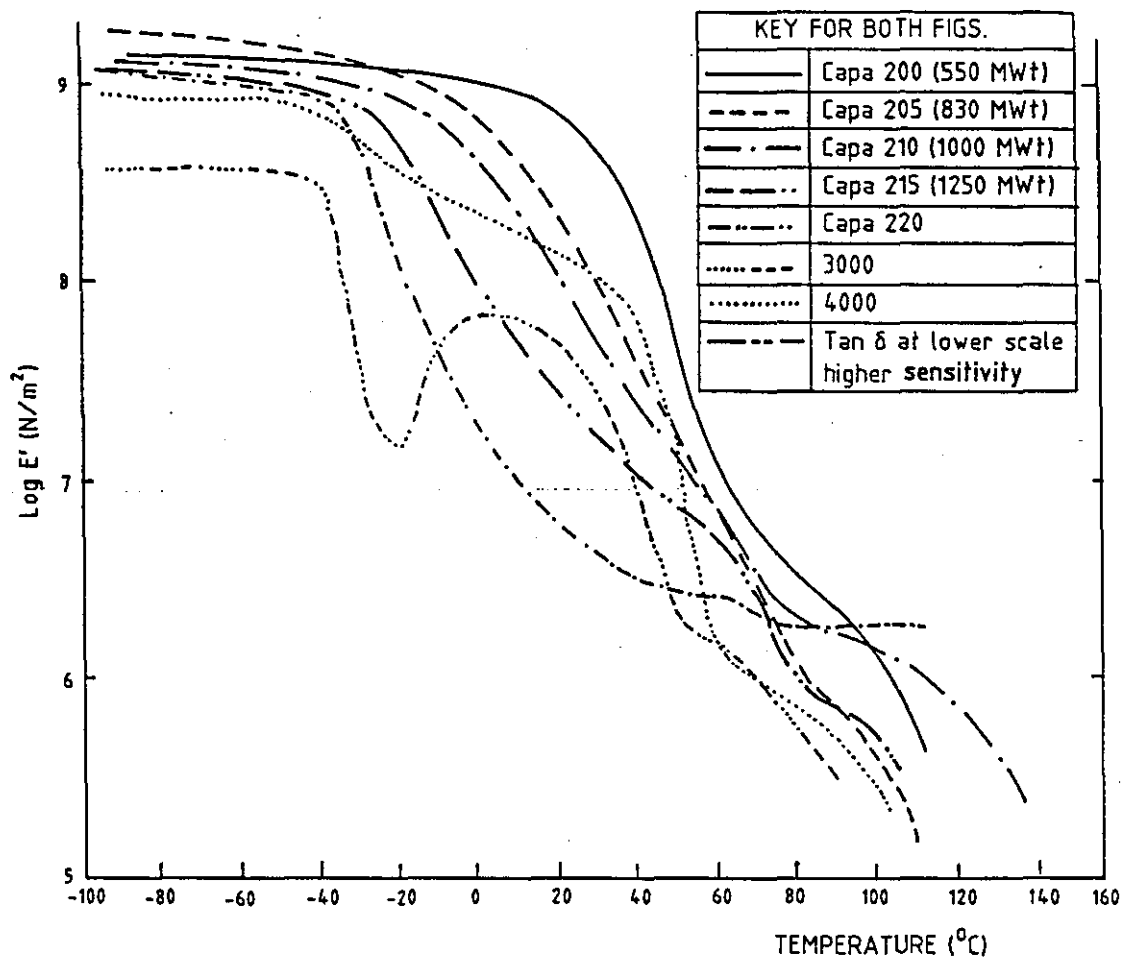


FIG. 4B5. 1(a) DMTA - Log MODULUS CURVES FOR BLOCK RATIO
1 : 3 : 2 (Capa : Des W : 1,4BD)

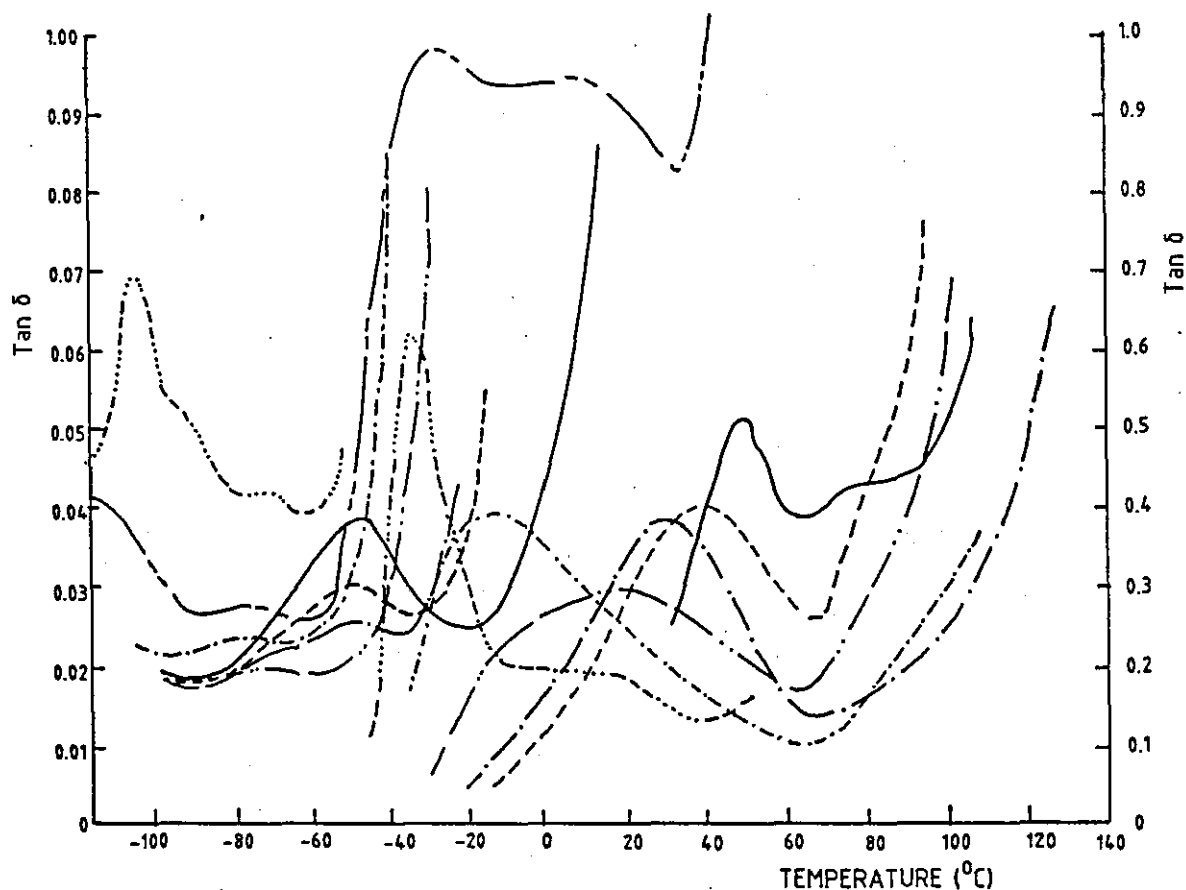


FIG. 4B5. 1(b) DMTA - Tan δ CURVES FOR BLOCK RATIO 1 : 3 : 2
(Capa : H₁₂MDI : 1,4BD)

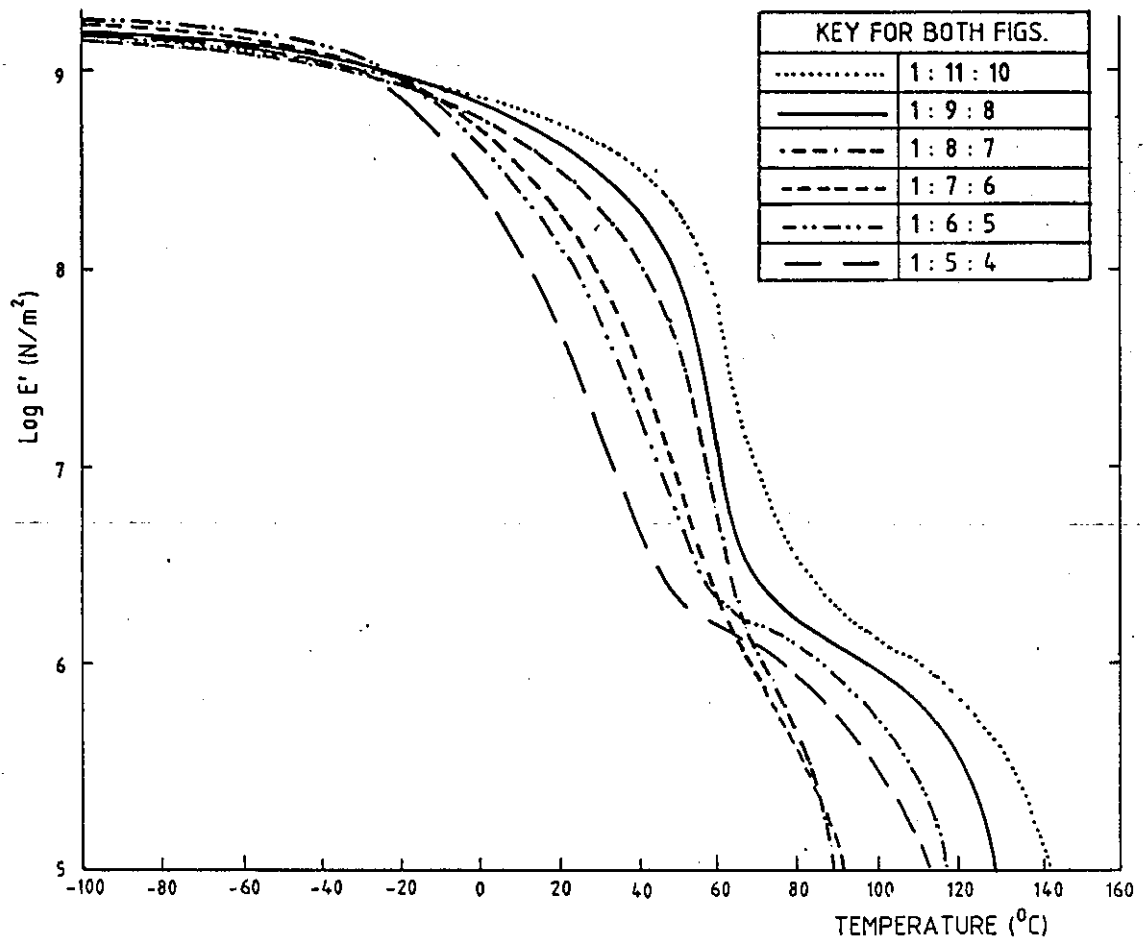


FIG. 4B6 . 1(a). DMTA - Log MODULUS CURVES FOR Capa 220 : Des W : 1,3BD

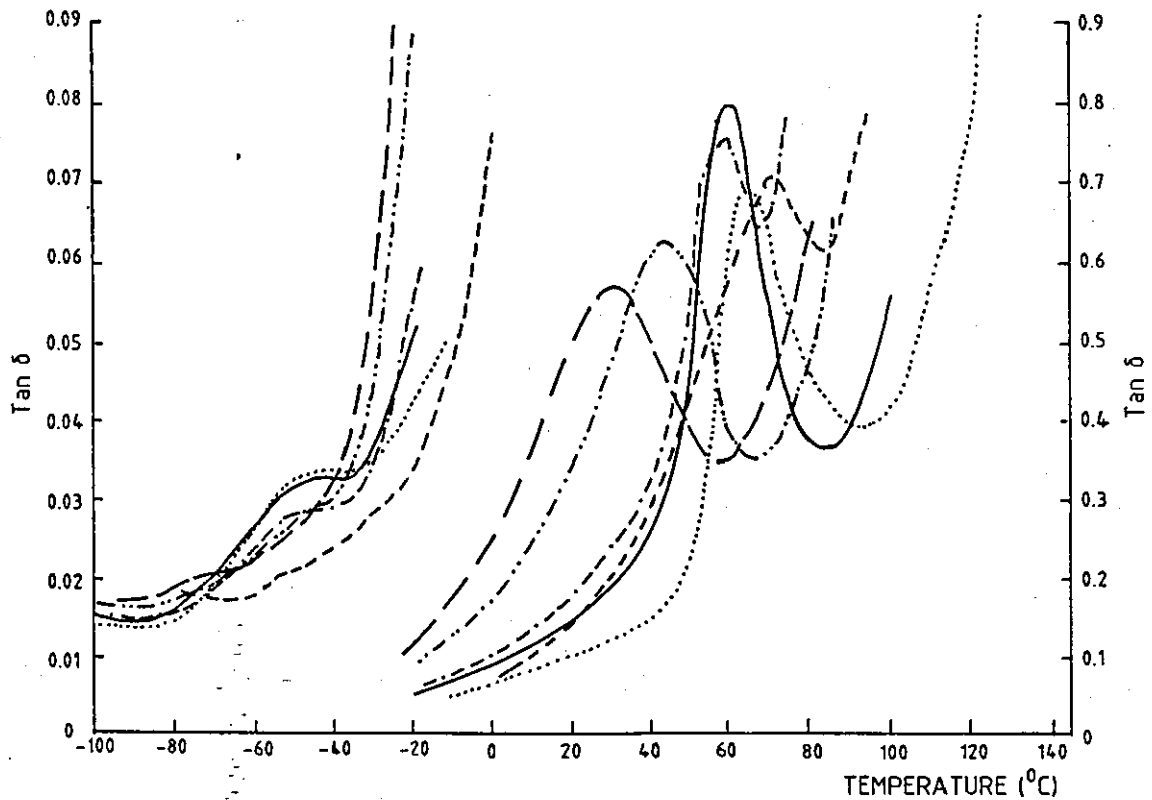


FIG. 4B6 . 1(b). DMTA - Tan δ CURVES FOR Capa 220 H₁₂MDI : 1,3BD

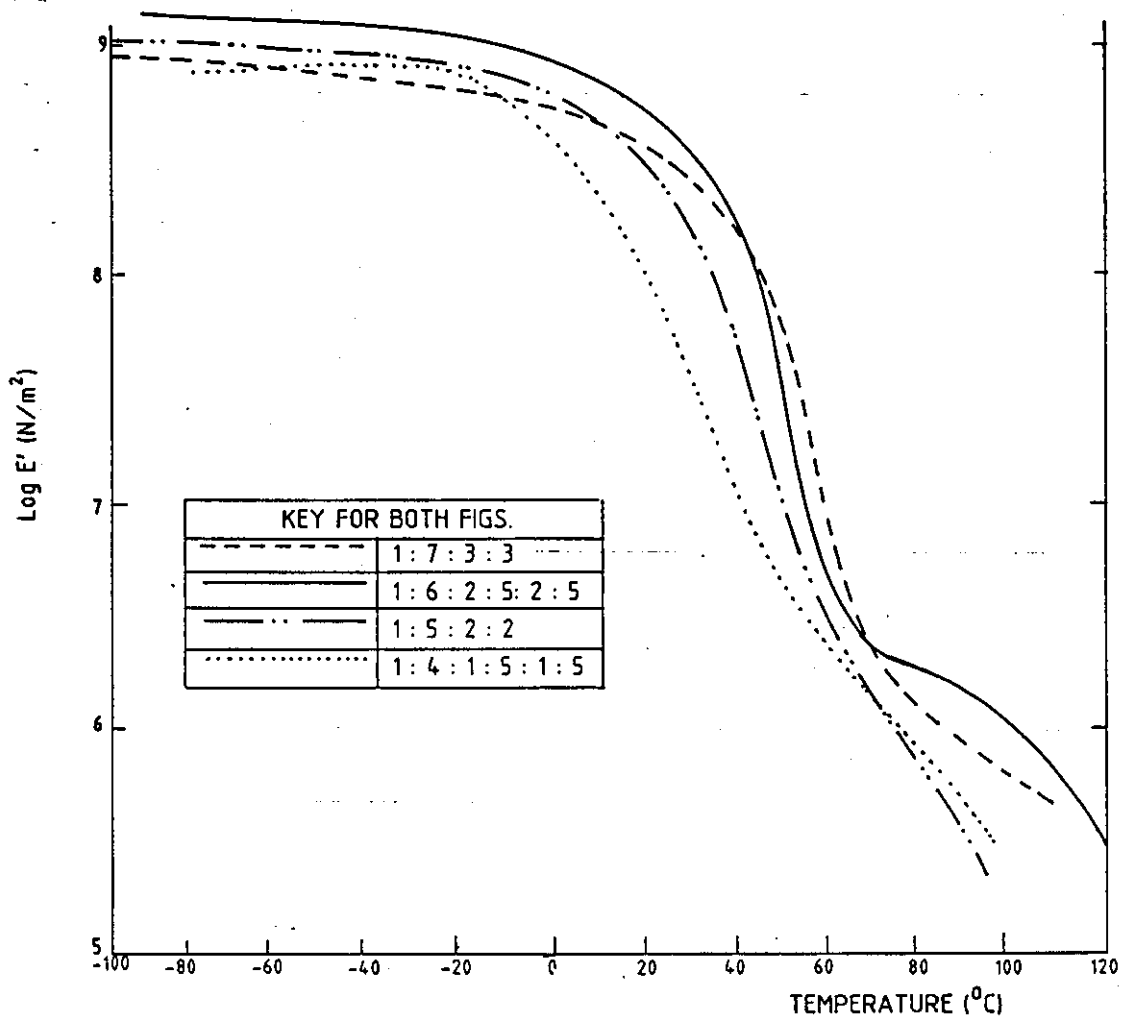


FIG. 4B6 . 2(a) DMTA - Log MODULUS CURVES FOR Capa 215 : Des W : 1,4BD + 1,4CHDM.

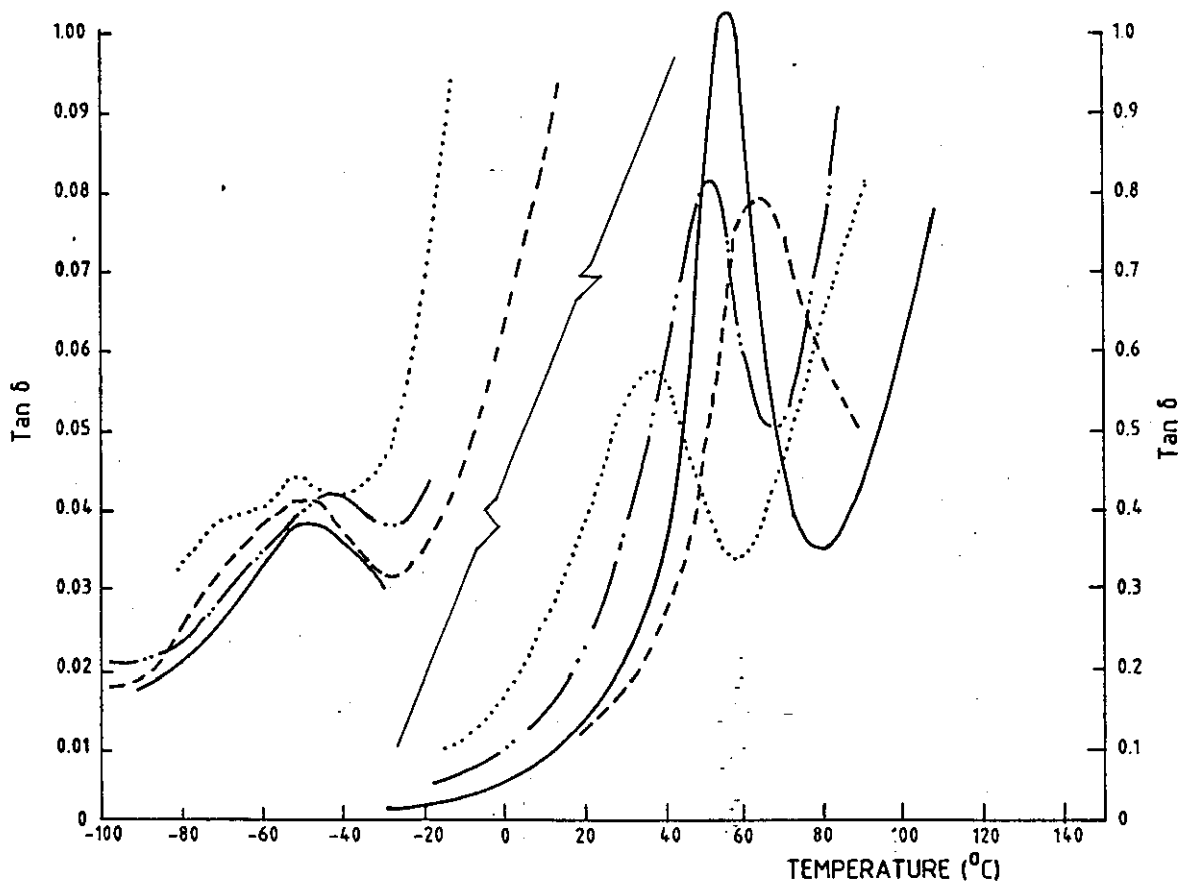


FIG. 4B6 . 2(b). DMTA - Tan δ CURVES FOR Capa 215 H₁₂MDI : 1,4BD + 1,4CHDM AT VARYING BLOCK RATIOS.

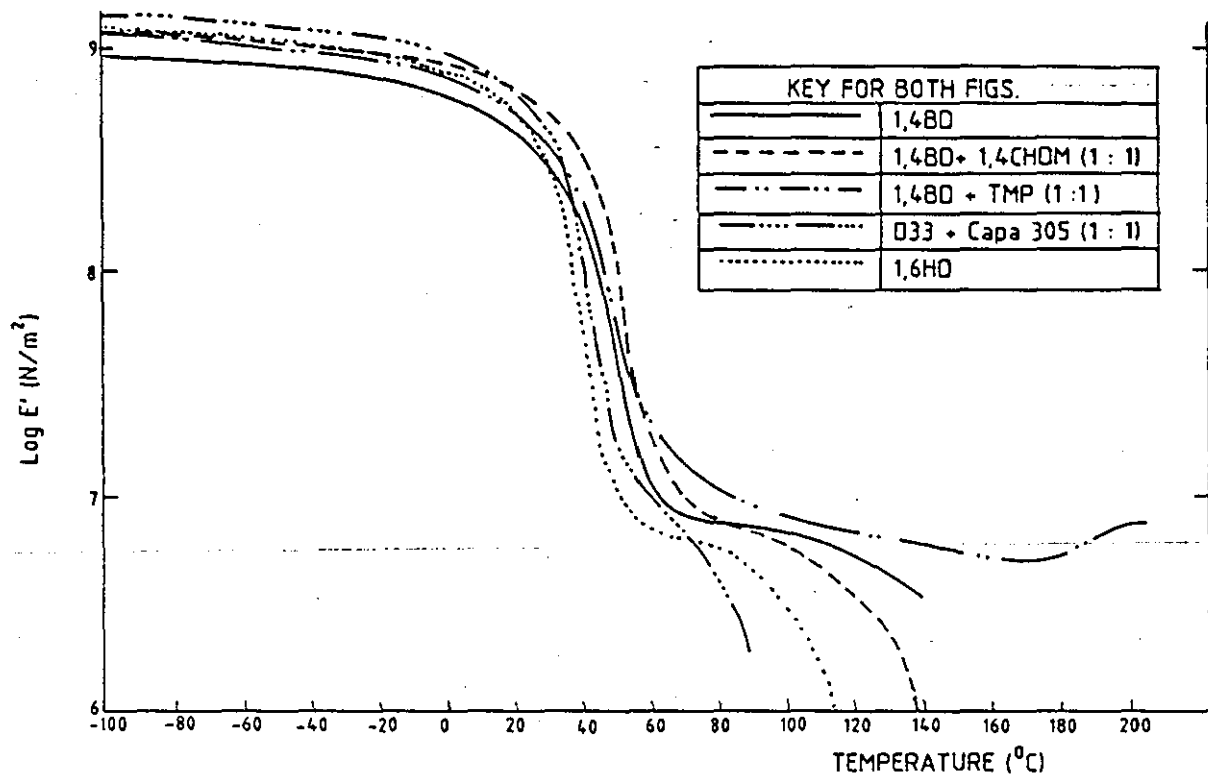


FIG. 4B7. 1(a) DMTA - Log MODULUS CURVES FOR Capa 210 : H₁₂MDI : VARIOUS CHAIN EXTENDERS AT A CONSTANT 1 : 5 : 4 BLOCK RATIO.

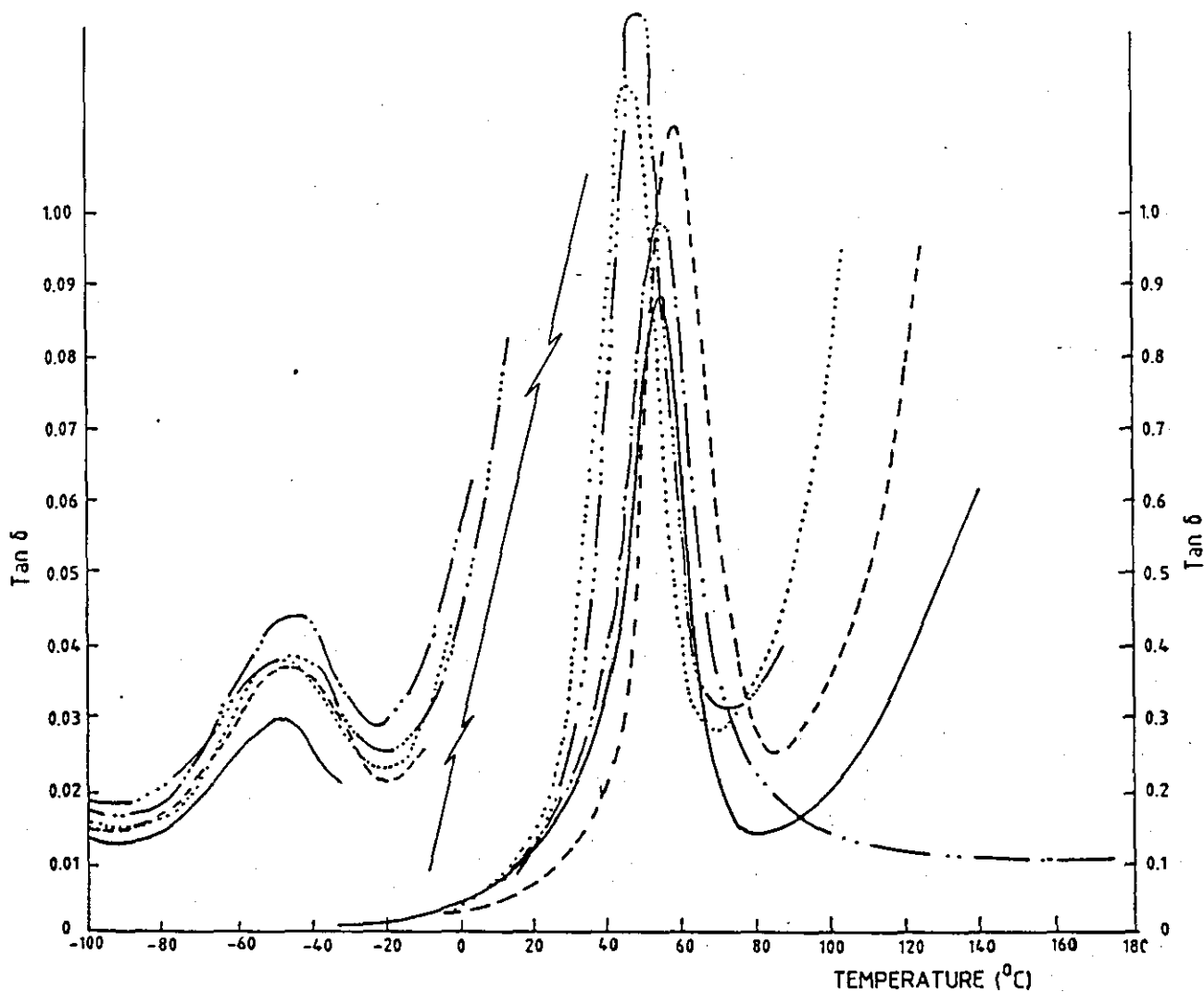


FIG. 4B7. 1(b) DMTA - Tan δ CURVES FOR Capa 210 : H₁₂MDI : VARIOUS CHAIN EXTENDERS AT A CONSTANT 1 : 5 : 4 BLOCK RATIO.

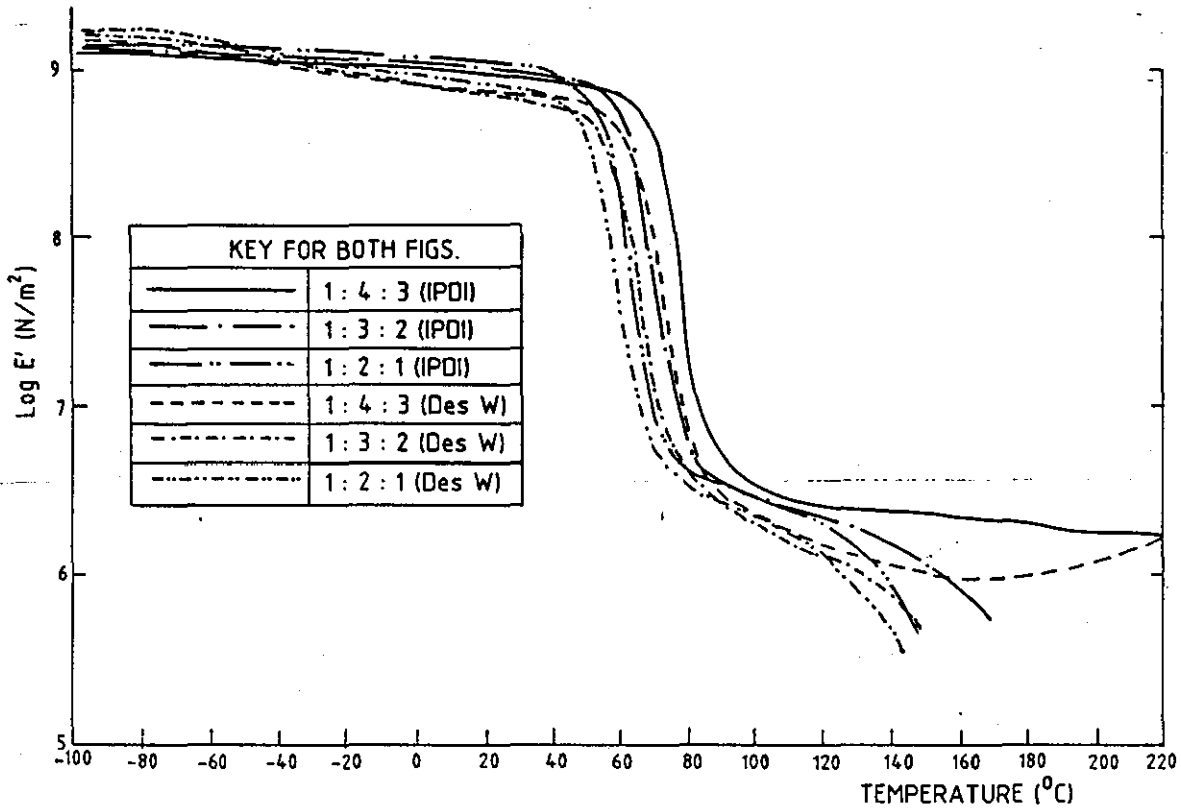


FIG. 4B7 . 2(a) DMTA - Log MODULUS CURVES FOR Capa 305 : H₁₂MDI OR IPDI : 1,4BD AT VARYING BLOCK RATIOS.

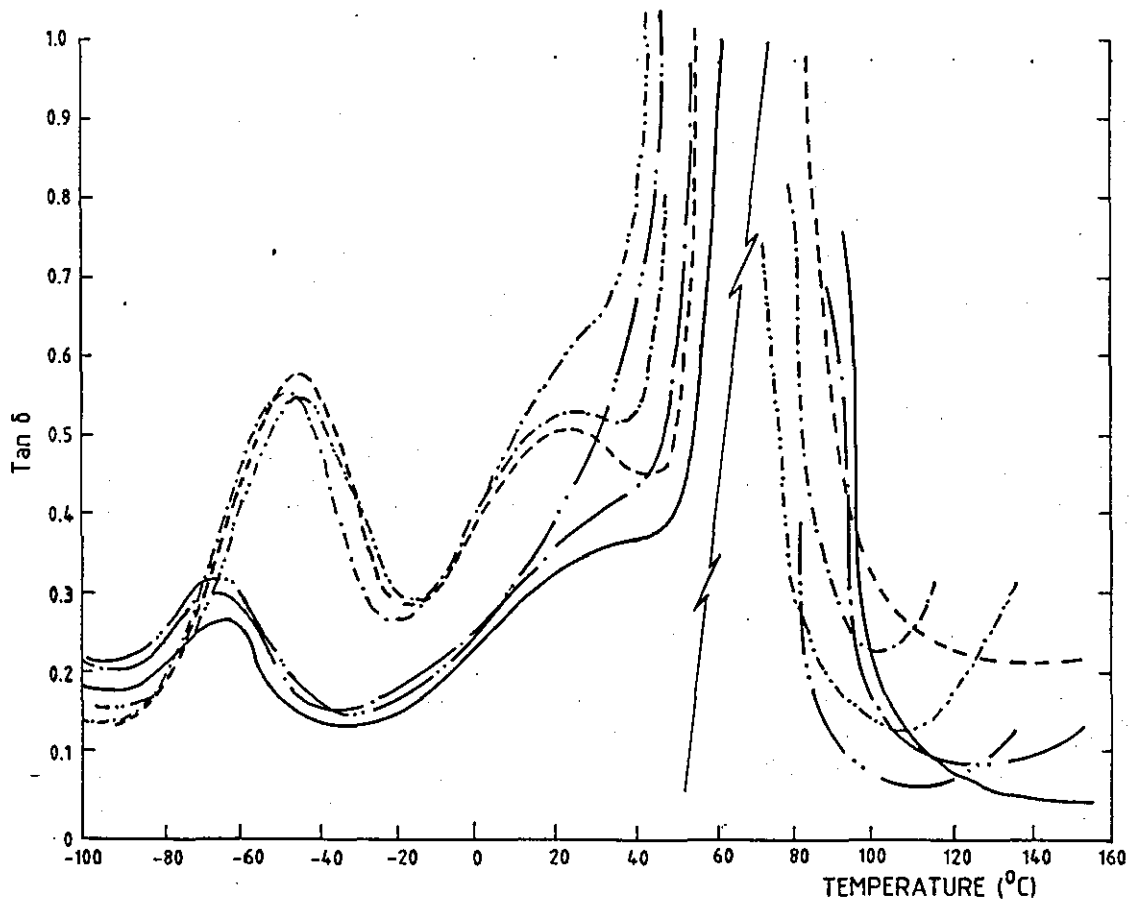


FIG. 4B7 . 2(b) DMTA - Tan δ CURVES FOR Capa 305 H₁₂MDI OR IPDI : 1,4BD AT VARYING BLOCK RATIOS.

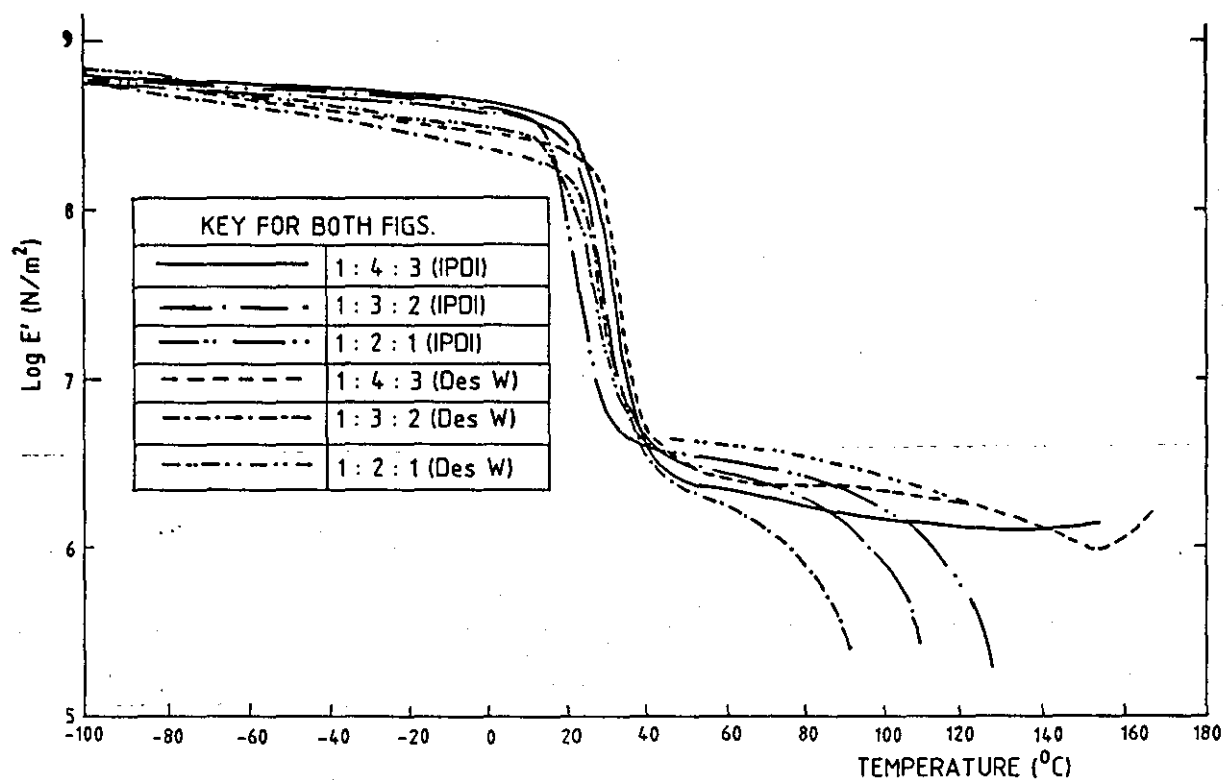


FIG. 4B7.3(a) DMTA - Log MODULUS CURVES FOR Tetra-ol 600 : H₁₂MDI OR IPDI : 1,4BD AT VARYING BLOCK RATIOS.

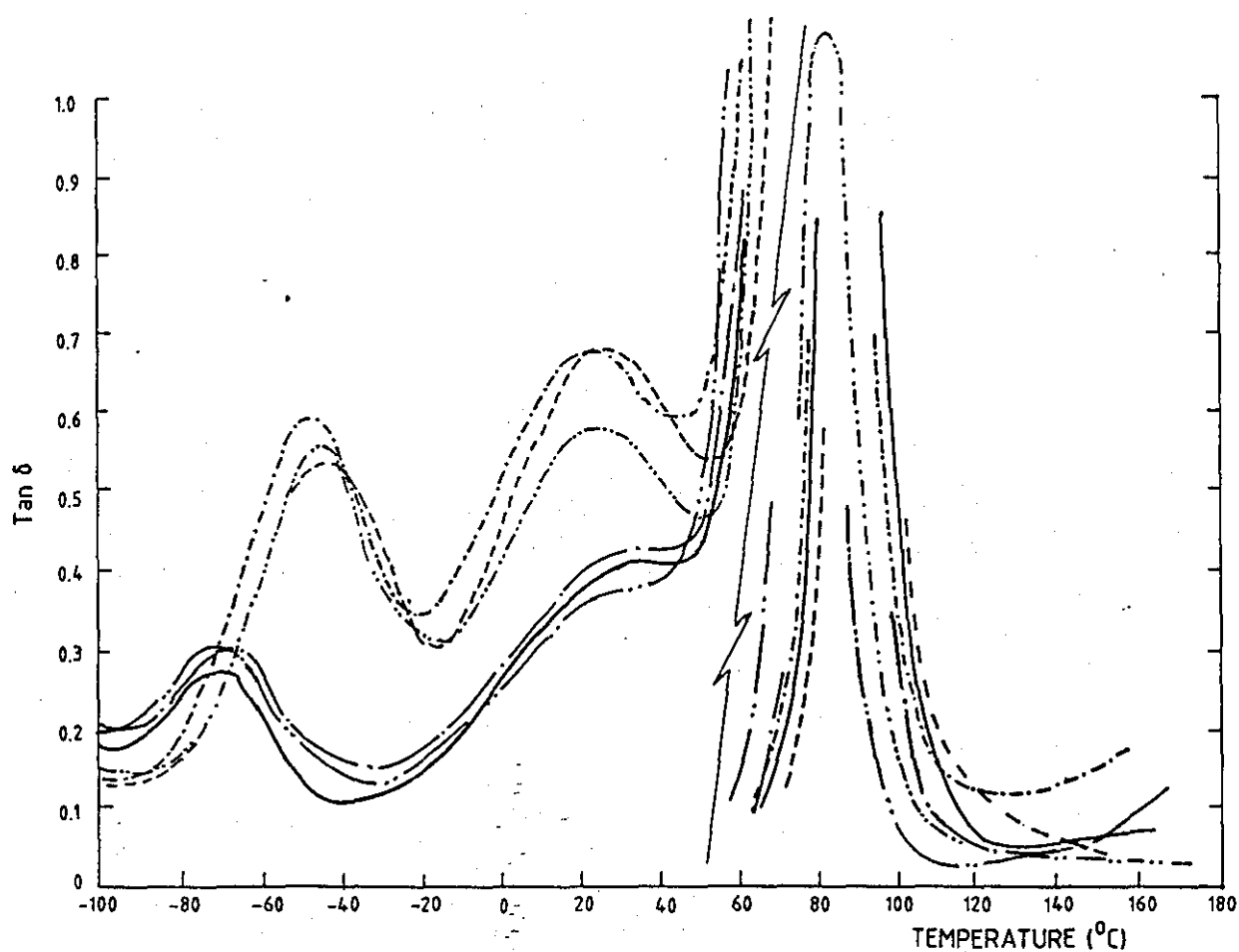


FIG. 4B7.3(b) DMTA - Tan δ CURVES FOR Tetra-ol 600 : H₁₂MDI OR IPDI : 1,4BD AT VARYING BLOCK RATIOS.

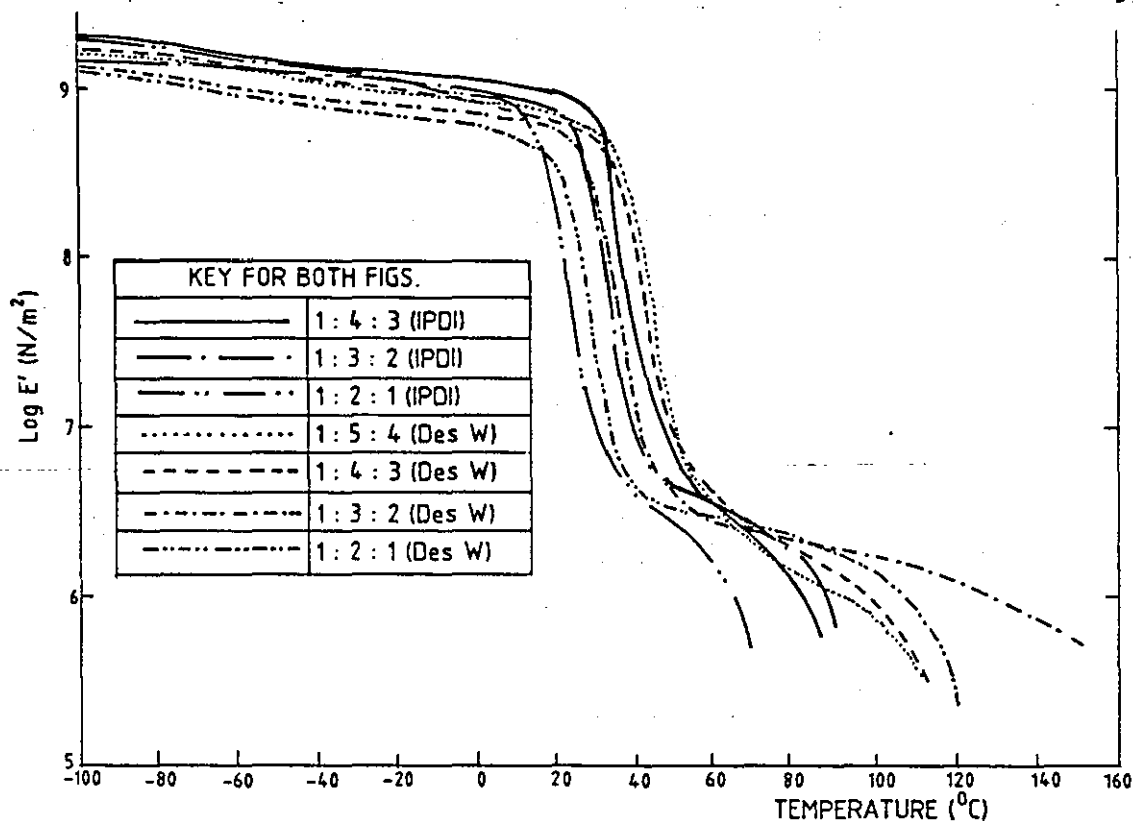


FIG. 4B7 . 4(a) DMTA - Log MODULUS CURVES FOR Tetra-ol 1000 : H₁₂MDI OR IPDI : 1,4BD AT VARYING BLOCK RATIOS.

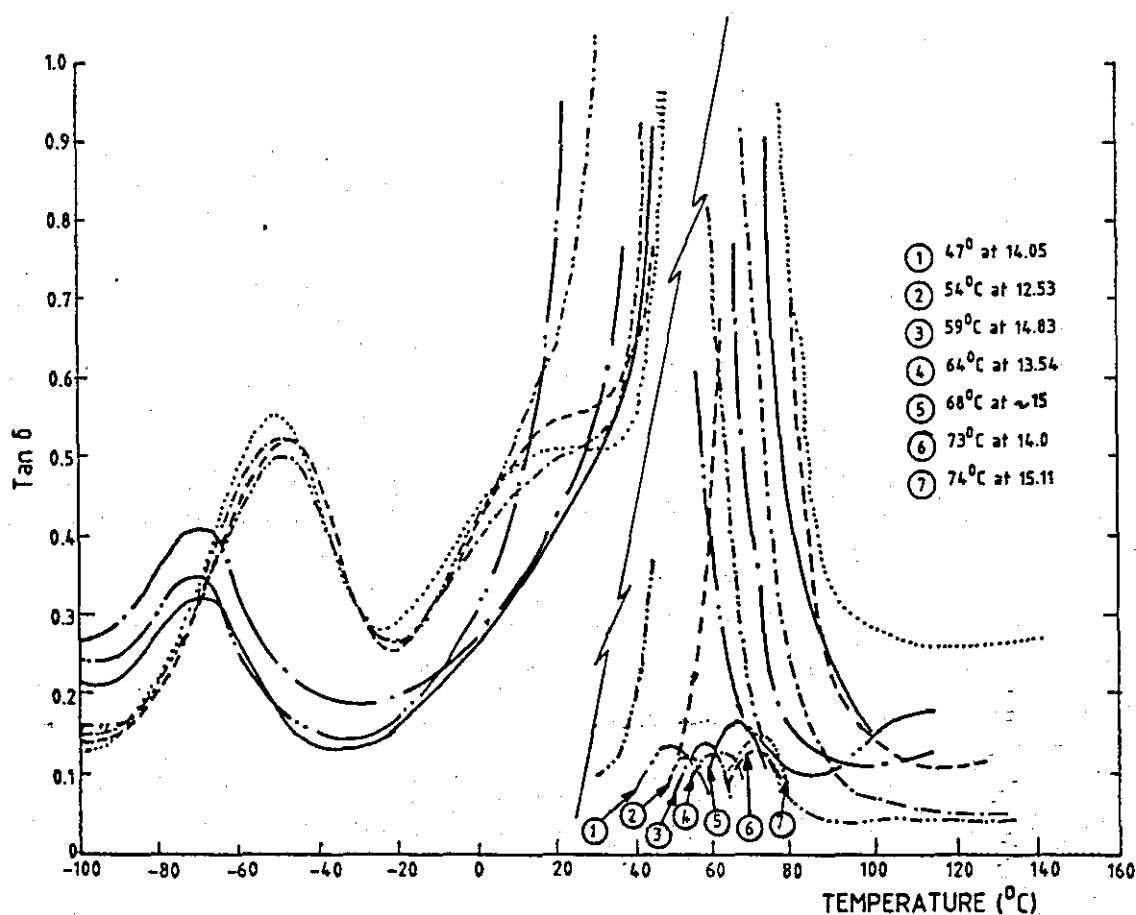


FIG. 4B7 . 4(b) DMTA - Tan δ CURVES FOR Tetra-ol 1000 : H₁₂MDI OR IPDI : 1,4BD AT VARYING BLOCK RATIOS.

4C.1 MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

A molecular weight distribution (MWD) exists in any polymer sample because of the statistical nature of polymerisation. The width of the MWD is determined by the kinetics and mechanisms of polymerisation and is often characterised by the ratio of the weight average molecular weight to the number average molecular weight. The position of MWD on the molecular weight axis and the shape (unimodal, bimodal etc) of the MWD are both important in influencing the physical and mechanical properties of a polymer.

The determination of MWD requires the separation of the polymer into fractions in order to find the weight fraction of polymers as a function of molecular weight. Gel permeation chromatography (GPC) in which this separation is achieved, is a widely used technique in the determination of molecular size and distribution of polymer molecules. The GPC analysis consists of two steps: firstly the fractionation and secondly the isolation of fractions. The separation takes place in a chromatographic column (an example of which is shown in Figure 4C1.1) filled with beads of a rigid porous gel. Highly crosslinked polystyrene gel particles are available having pore sizes comparable to the dimensions of polymer molecules.

The gel is completely immersed in the solvent with the exclusion of any gases. As a sample of a dilute polymer solution is introduced the solvent surrounding the gel and filling the column is replaced by the polymer solution. The polymer molecules are free to move into and out of the internal pore structure of the gel to an extent depending on their size and the pore size distribution of the gel. Very large molecules are unable to enter the gel pores and are confined to the solvent between particles in the column. Smaller molecules can permeate into the gel; the extent of diffusion into the gel increases as molecular size decreases. Thus large molecules are eluted first and very small molecules are eluted last. The concentration of the species eluting from the column as a function of elution volume is measured using a differential refractometer. A

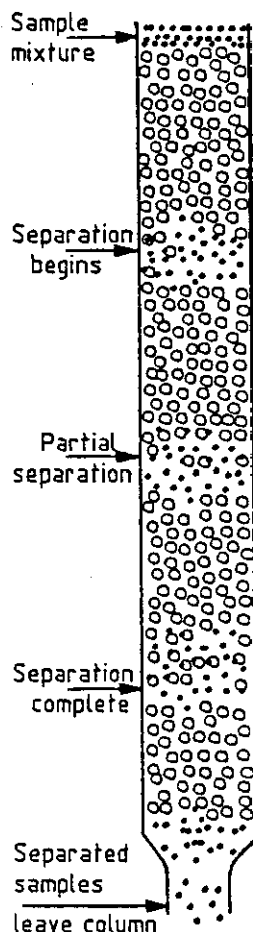


FIGURE 4C1.1: PRINCIPLE OF THE SEPARATION OF MOLECULES ACCORDING TO SIZE BY GEL PERMEATION CHROMATOGRAPHY

schematic diagram of a typical commercially available GPC is shown in Figure 4C1.2.

The flow system consists of solvent reservoir, pump and associated devices. The stream is split, one half going through a dummy column to provide pressure drop and into the reference side of the detector, the other through the column for separation and to the sample side of the detector. The sample is injected into the sample stream, at the head of the column preferably through a loop and valve system, whereby equivalent volumes of sample are injected each time. A differential refractometer is normally used as the detector, but ultra-violet, infra-red or flame ionisation detectors have also been used. GPC columns typically have a diameter of 10 mm and 30-110 cm long, made of steel. Three or four may be used in

series packed with gels having different pore sizes to ensure good separation capability over a wide range of molecular weights.

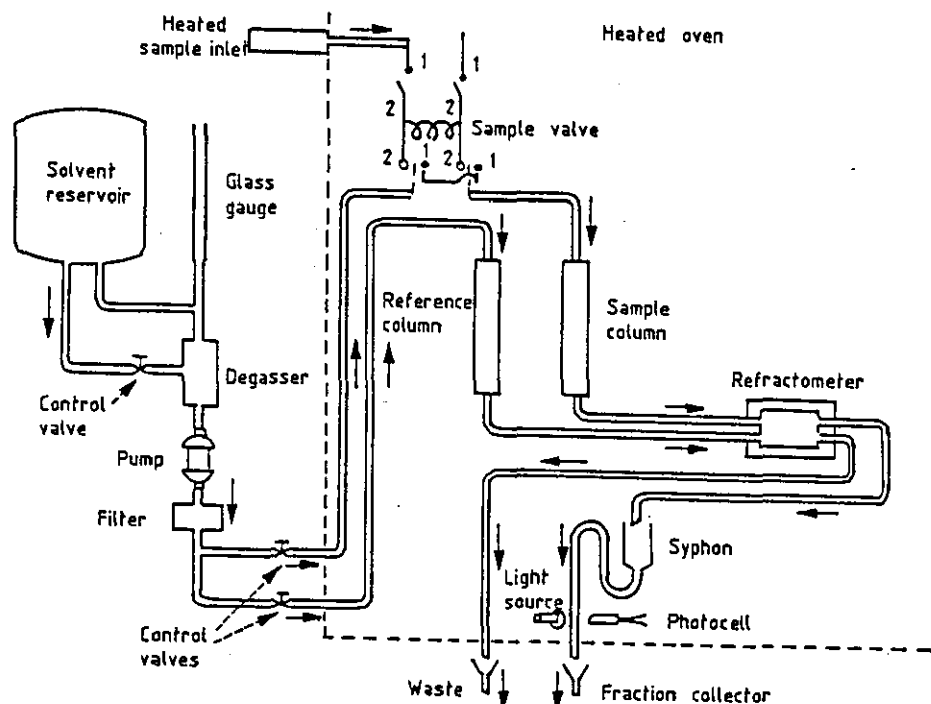


FIGURE 4C1.2: FLOW SYSTEM OF A GEL PERMEATION CHROMATOGRAPH

The final product from the GPC analysis is the chromatogram. This trace shows the difference in refractive index of the eluent from the sample columns to that from the reference columns. The reading is a function of the concentration and refractive index of the dissolved species eluting. The 'elution volume' is the quantity of solvent that has passed through the sample columns from the point of sample injection. A sample must be completely dissolved and filtered before injection. The species eluting first in the column would be the highest molecular weight material in the sample. Subsequent eluent carries material of progressively lower molecular weight. With suitable calibration the elution volume scale is transposed to a molecular weight scale. Before a chromatogram is interpreted a suitable baseline must be constructed.

As a complete theory predicting retention times or volumes has not appeared for GPC, it is necessary to determine a calibration relation between molecular weight distribution and elution volume for the column used. Commercially available narrow distributed polystyrenes are often used for this calibration which gives a linear plot of log molecular weight versus retention. As the separation is based on hydrodynamic volume and not molecular weight, a calibration made with samples of narrow distributed linear polystyrenes, in tetrahydrofuran at 25°C, will not apply to a polymer of another composition or a branched polystyrene, or to measurements made in another solvent or at another temperature. Since narrow distributed molecular weight polymers other than polystyrenes are not generally available, this becomes a serious problem. An approximate correction factor (Q) which takes account of differences in molecular weight per unit chain length but ignores the effect of solvent power is often applied. This requires that the calibration be made directly in terms of hydrodynamic volume, which is plotted as $\log [\eta]M$ versus V_r (where M is the molecular weight, η is the intrinsic viscosity and V_r the retention volume). This gives a fairly linear plot and results for a wide variety of linear and branched polymers fall on it.

The use of this technique does present problems for copolymers in that (a) V_r is determined at least in part by chemical composition which influences molecular size because of polymer-solvent interactions, and (b) refractive index, and thus detector response per unit concentration, also depend upon chemical composition. Similarly, if the refractive index of a homopolymer depends upon molecular weight, as it inevitably must at sufficiently low molecular weight, detector response is no longer constant over the entire chromatogram and a separate calibration must be made.

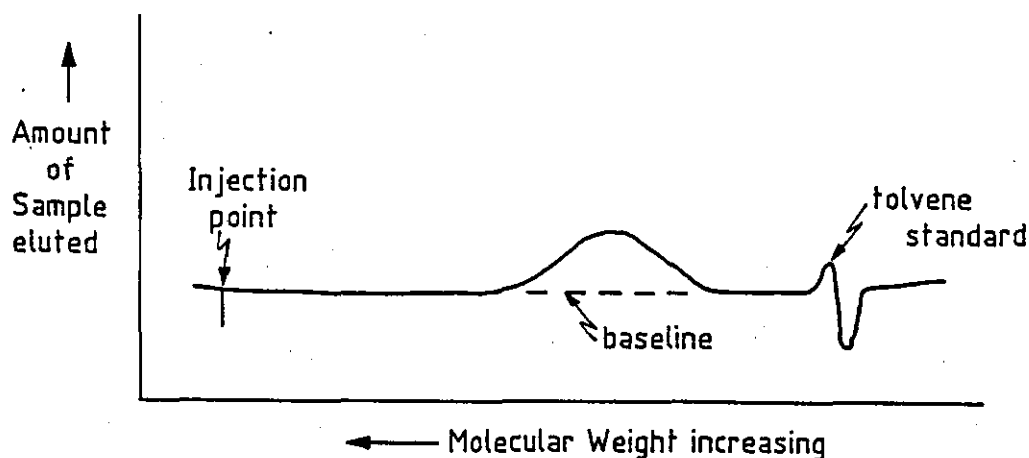
4C.2 EXPERIMENTAL PROCEDURE

A Waters Liquid Chromatograph Model ALC-202 having a 60 cm column packed with a Polymer Laboratories 10 μ mixed gel was used to carry

out the GPC work. All experiments were carried out at laboratory temperature. Samples for GPC analysis were dissolved in tetrahydrofuran (THF) and left overnight to ensure good mixing and enable the polymer to dissolve. The recommended concentration for narrow molecular weight distributed polymers is 0.025%, which is 0.5 mg in 2 ml solvent (THF) and a 0.025 to 0.075% concentration for broad molecular weight distributed polymers. Samples for analysis were made to approximately 0.05% solution as these are not narrow distributed polymers. To each solution prepared is added $0.25 \mu\text{l}$ of toluene as an internal standard. All solutions prior to injection into the GPC are filtered using glass filter papers. A run is complete after the internal standard is eluted, which takes 20 to 25 minutes.

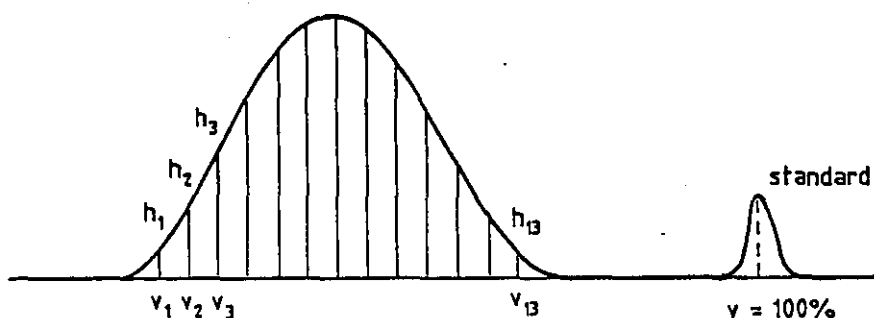
The column was calibrated using several narrow molecular weight distributed polystyrene standards obtained from Polymer Laboratories. These standards were dissolved in the same solvent (THF) and used the same internal reference. Six polystyrene standards of varying molecular weights (1850 to 470,000) were used and a calibration plot of log molecular weight against percent elution volume (percent volume retention) is drawn (Graph 4C2.1).

A typical GPC chromatogram obtained is shown below:



Calculation of the molecular weights is carried out by splitting the peak into segments and expressing these as retention volumes which

are then changed into molecular weight by the calibration plot. the method of calculation is shown below:



Retention Volume (%)	Height (arbitrary units)	Mn (from calibration plot)
V_1	h_1	m_1
V_2	h_2	m_2
.	.	.
.	.	.
V_{11}	h_{11}	m_{11}

The molecular weight data was obtained by placing the data of the height (h_i) and molecular weight (m_i) into a PET computer (see Appendix for programme), which then prints out the Mn, Mw, Mp and MWD. The molecular weight data and distribution is obtained by using the following formulae:

$$\overline{Mn} = \frac{\sum N_i M_i}{\sum N_i}$$

$$\overline{Mw} = \frac{\sum N_i M_i^2}{\sum N_i}$$

$$MWD = \frac{\overline{Mw}}{\overline{Mn}}$$

$$\overline{Mp} = (\overline{Mn} \cdot \overline{Mw})^{1/2}$$

N_i = number of molecules of the i^{th} kind of molecular weight m_i .

4C.3 GPC ANALYSIS OF THE POLYOLS USED

The chromatograms obtained from the 60 cm column for the polycaprolactone polyols used are shown in Figure 4C3.1. Values of molecular weight data obtained for these polyols from the computer print out are shown in Table 4C3.1. It is seen that the polyols give Gaussian type distribution curves and all gave much higher M_n values than expected. The lower molecular weight polyols do show higher M_n values, but as they appear towards the bottom end of the chromatogram there is interference with the toluene ((standard) peak. This has produced the slightly higher values being out of sequence with the other polyols. As M_n is sensitive to changes in weight fractions of low molecular weight species, higher than expected values have been obtained. The values of M_w and M_p are also greater, and the molecular weights obtained are based upon polystyrene standards (not polycaprolactone) and are therefore of use on a comparative basis. In this respect the polyol molecular weight does increase as expected and the molecular weight distribution is found to be 1.25 to 1.38, this value is lower for Capa 200 and Capa 205 as there is interference with the standard in these cases. This indicates that polyurethanes synthesised from these polycaprolactones will also show a broad molecular weight distribution.

It is interesting that the chromatograms of the polyols do not show the presence of blends in some polyols as was indicated by the DSC work. However, the 60 cm column contains packing designed for higher molecular weight fractions and therefore does not provide the resolution that is required. Also the high molecular weight distribution of these polyols helps in obscuring peaks which may be resolved. In order to resolve these polyols further they were run through a lower molecular weight 500 A column. These chromatograms (Figure 4C3.2) show the polyols to be composed of differing molecular weight species, especially the lower molecular weight polyols. In the case of Capa 200 several distinct varying molecular weight peaks are seen and as such will affect the soft segment

molecular weight and distribution. The Capa 205 and 210 both show similar peaks with less pronounced smaller peaks on the lower molecular weight side of the main peak. The Capa 215 and Capa 220 shows, less noticeably, the presence of blends but does show similar molecular weight species, whereas the Capa 231 and Capa 240 show even less these low molecular weight peaks. At even higher resolution these less noticeable lower molecular weight peaks may show up better, but again the high molecular weight distribution of these polyols can hide similar molecular weight species.

A similar but more pronounced picture is seen on changing to an even lower molecular weight 50 A column (Figure 4C3.3). This has the effect of narrowing the peak, but shows a better resolution at lower molecular weight. It is now certain that the polyols consist of more than one molecular weight species and so will affect the final morphology and properties of the polyurethanes synthesised. The polycaprolactone triols and tetra-ols used in the synthesis are run through the 500 A and 50 A columns (Figure 4C3.4). These chromatograms show that Capa 305 and Tetra-ol 600 are composed of several molecular weight species, which appear similar in many cases due to their similar molecular weights as supplied from the manufacturer. Capa 305 and tetra-ol 600 has 540 and 600 molecular weights respectively. The tetra-ol 1000 does show other molecular weight species but to a much lesser extent.

It is thus seen that polyols, as sent by the manufacturer, do consist of varying molecular weights. This may be done with prior knowledge and polyols may be made up of several blends to give the required final specification properties. As polyols are usually sent with specific hydroxyl values, the addition of other molecular weight species may be made such that the hydroxyl value falls within a specified range. The hydroxyl values are required for stoichiometric calculations to be made. These molecular weight additions made to the polyol would be expected to affect the morphology and properties of the polymer dependent on the amounts used.

4C.4 GPC ANALYSIS OF THE HARD AND SOFT SEGMENTS

In the earlier synthesis work, some hard and soft segments were prepared. The GPC analyses on these were carried out using the 500 A column, their chromatograms are shown in Figures 4C4.1 and 4C4.2.

In considering the soft segment, the polyol and diisocyanate were reacted on a 1:1 molar basis to give a solid product. On a qualitative basis the chromatogram (Figure 4C4.1) shows the soft segments to have several peaks indicating the presence of many varied molecular weight species. This can be explained by the fact that the respective polyols themselves are composed of several molecular weight species. The molecular weights of the soft segments are shown to be higher than their respective polyols as expected due to the polyol/diisocyanate reaction (compare Figure 4C3.2 and Figure 4C4.1).

It is noticed from the chromatogram (Figure 4C4.1) that as the polyol molecular weight increases for the soft segment based on H_{12} MDI a broadening of the whole peak is observed with higher resolution of the varying molecular weight peaks. This splitting of the whole peak could be associated with the diisocyanate reacting with the various molecular weight components present in the polyol. The presence of three isomers in the H_{12} MDI may, to a lesser extent, also affect the split in the main peak. These isomers of H_{12} MDI, although of the same molecular weight, would therefore not show any difference in the chromatography, but due to their differing molecular conformations would have varying reactivities. This preferential reactivity would enhance some molecular weight peaks and not others.

On changing the diisocyanate from H_{12} MDI to IPDI (Figure 4C4.1) the chromatogram shows little change for the Capa 210 soft segment. The Capa 220 soft segment for IPDI shows a much narrower peak compared to H_{12} MDI and this is maybe associated with IPDI having no isomers.

It is noticed that the Capa 220 soft segments for both H_{12} MDI and IPDI are opaque due to the crystalline nature of the polyol. However in the case of Capa 210 the IPDI soft segment is opaque whereas the H_{12} MDI gives a clear product - possibly due to the randomness introduced by the H_{12} MDI isomers. The structure of IPDI itself should produce a clear material, however this is not found and so the Capa 210 polyol can overcome the irregular structure introduced by IPDI and still form a crystalline material. This is indicated by the DSC work which shows a melting peak for Capa 220 soft segments of H_{12} MDI and IPDI and also Capa 210/IPDI, but not for Capa 210/ H_{12} MDI soft segment. It is to be noted that the reactivity of IPDI is greater than H_{12} MDI, and the synthesis method is different for these soft segments which may well affect the rate of molecular build up.

The chromatograms of the hard segments, prepared by reacting diisocyanate with chain extender on a 1:1 molar ratio are shown in Figure 4C4.2. The H_{12} MDI/1,4-BD hard segment prepared was found not to dissolve in the THF for a GPC run to be made. The hard segments show much broader peaks (similar to their DSC thermograms) with smaller peaks appearing at the lower molecular weight end of the broad peak. These peaks, as expected, appear at lower molecular weights than the soft segments (compare Figure 4C4.1 and 4C4.2). It can be seen that on combination of soft and hard segments to form the polyurethane, a broad molecular weight peak would result at higher molecular weight values. A broad peak is observed in the polyurethanes synthesised, but it is to be noted that the soft segment in the polyurethane synthesis has been prepared with excess diisocyanate present (by the prepolymer route) and so its molecular weight would probably be lower than if reacted on a 1:1 molar basis. However, the chain-extension stage of the prepolymer in the polyurethane synthesis would increase the molecular weight producing a broad peak in the GPC chromatogram.

4C.5 GPC ANALYSIS OF THE POLYURETHANE ELASTOMERS

The molecular weight data was obtained by the GPC method for many of the polyurethanes synthesised. GPC analyses were not carried out for crosslinked polyurethanes, as these did not readily dissolve in the solvent (THF). All the GPC chromatograms of polyurethanes analysed were treated in the way earlier described and the information obtained put through the computer to give values of M_n , M_w , M_p and MWD. (Tables 4C5.1 to 4C5.4). Graphs are drawn of M_n values obtained from the tables showing the variation of polyol molecular weight based polyurethanes at constant block ratio (Graph 4C5.1) and the variation of block ratio for polyurethanes based on constant polyol molecular weight (Graph 4C5.2). In general at constant block ratio and increase in polyol molecular weight of the polyurethane showed an increase in the M_n values for transparent polyurethanes. On increasing block ratio, the M_n values have generally been found to decrease. The molecular weight distribution (MWD) for the polyurethanes analysed varies from 1.71 to 2.39, the average MWD value being 2.1.

There is noticed (see Figure 4C5.1) the presence of low molecular weight species of high molecular weight distribution being eluted after the main peak and just before the toluene standard peak. This low molecular weight peak is not observed with the mixed chain extender system (1,4-BD + 1,4-CHDM) and 1,3-BD based polyurethanes, however it is noticed in the 1,6-HD extended polyurethanes. No explanation at present is offered except that due to the linear structure of 1,4-BD and 1,6-HD it may be easier to form low molecular weight species, when possible, as even with these linear chain extenders this low molecular weight peak is not always present. Low molecular weight impurities may be the cause of this peak, although unlikely as all samples were filtered before running.

Most of the GPC analysis was carried out on polyurethanes based at low block ratios, primarily as most of the high block ratio polymers did not dissolve in the solvent. At low block ratios there is

considered to be a greater tendency for phase mixing which results in higher molecular weight polymers. Therefore with increasing block ratio type polyurethanes, due to incomplete phase mixing, the overall molecular weight should fall and this in general, was found to be the case. For example, a polyurethane based on Capa 200 was found to have a higher hard segment content than the Capa 220 of the same block ratio. This is considered to indicate that more phase mixing will occur in Capa 220 polymers than with Capa 200 based polyurethanes thus producing a higher molecular weight for the Capa 220 based polymer. Such a deduction has been verified by GPC (Table 4C5.1, Graph 4C5.1) in which it is seen that as the molecular weight of the polyol rises for the polyurethane (H_{12} MDI/1,4-BD based on a block ratio of 1:3:2) the molecular weight of the polymer produced is also found to increase.

However, there are exceptions shown (Graph 4C5.1) in which the molecular weight is found to be lower, for example with Capa 205, Capa 215 and also for Capa 231 and Capa 240 based polymer. Also it is now known from the manufacturers that catalysts are incorporated in these polyols. From these results the type and concentration of catalysts employed for Capa 205 and Capa 215 are indicated to be different to those of Capa 200, Capa 210 and Capa 220. The decrease in molecular weight of polyurethanes based on Capa 231 and Capa 240 compared with Capa 220 (Graph 4C5.1) could again be due to the former possessing only lower catalyst activity coupled with phase separation. This may be explained by the fact that the hard segment content of Capa 231 and Capa 240 based polymers is much lower in comparison to the other polyol based polyurethanes of the same block ratio, such that phase separation occurs. The polyurethanes based on Capa 231 and Capa 240 were observed to be opaque, whereas the others are transparent and such opaqueness indicates phase separation.

Polyurethanes based on chain extenders other than 1,4-BD (Table 4C5.2 to 4C5.4, Graph 4C5.2) do not show a definite trend in properties at differing block ratios. On changing the chain

extender from 1,4-BD to the mixed 1,4-BD + 1,4-CHDM system the polymer formed would be expected to favour more phase mixing and hence a higher molecular weight. The results, however, show higher M_n values in some cases and not in others. The large structure of 1,4-CHDM and its reactivity must be taken into account as this would be expected to affect the rate of molecular build up in the mixed chain extender based polymer. The 1,3-BD and 1,6-HD based elastomers did not show any apparent difference when compared with 1,4-BD based polymers. It is to be noted that the 1,4-BD based polymers did not dissolve in the solvent (THF) at the high block ratios, whereas this was possible with the other chain extender systems used.

On changing the diisocyanate from H_{12} MDI to IPDI a more phase mixed morphology would be expected to occur resulting in higher molecular weight of the polymer. The observation of the experimental results of the IPDI polyurethanes analysed show that such polymers do possess higher molecular weights when compared with their H_{12} MDI analogues (Table 4C5.3).

TABLE 4C5.1: MOLECULAR WEIGHT DATA FOR DesW BASED POLYURETHANES CHAIN EXTENDED WITH 1,4-BD

Polyurethane (DesW Based)	Block Ratio	M_n	M_w	M_p	MWD
Capa 200/1,4-BD	1:2:1	46,473	94,504	66,272	2.03
	1:3:2	51,816	111,183	75,902	2.15
Capa 205/1,4-BD	1:3:2	38,180	74,600	53,369	1.95
	1:4:3	32,929	70,024	48,019	2.13
Capa 210/1,4-BD	1:2:1	58,783	119,517	83,819	2.03
	1:3:2	59,799	123,500	85,937	2.07
	1:4:3	50,389	101,667	71,575	2.02
Capa 215/1,4-BD	1:3:2	41,050	77,225	56,304	1.88
Capa 220/1,4-BD	1:3:2	77,287	169,186	114,350	2.19
	1:4:3	68,313	139,219	97,522	2.04
	1:5:4	41,761	87,240	60,359	2.09
Capa 231/1,4-BD	1:3:2	62,351	125,374	88,279	1.99
Capa 240/1,4-BD	1:3:2	39,960	76,945	54,538	2.03

TABLE 4C5.2: MOLECULAR WEIGHT DATA FOR DesW BASED POLYURETHANES CHAIN EXTENDED WITH 1,6-HD

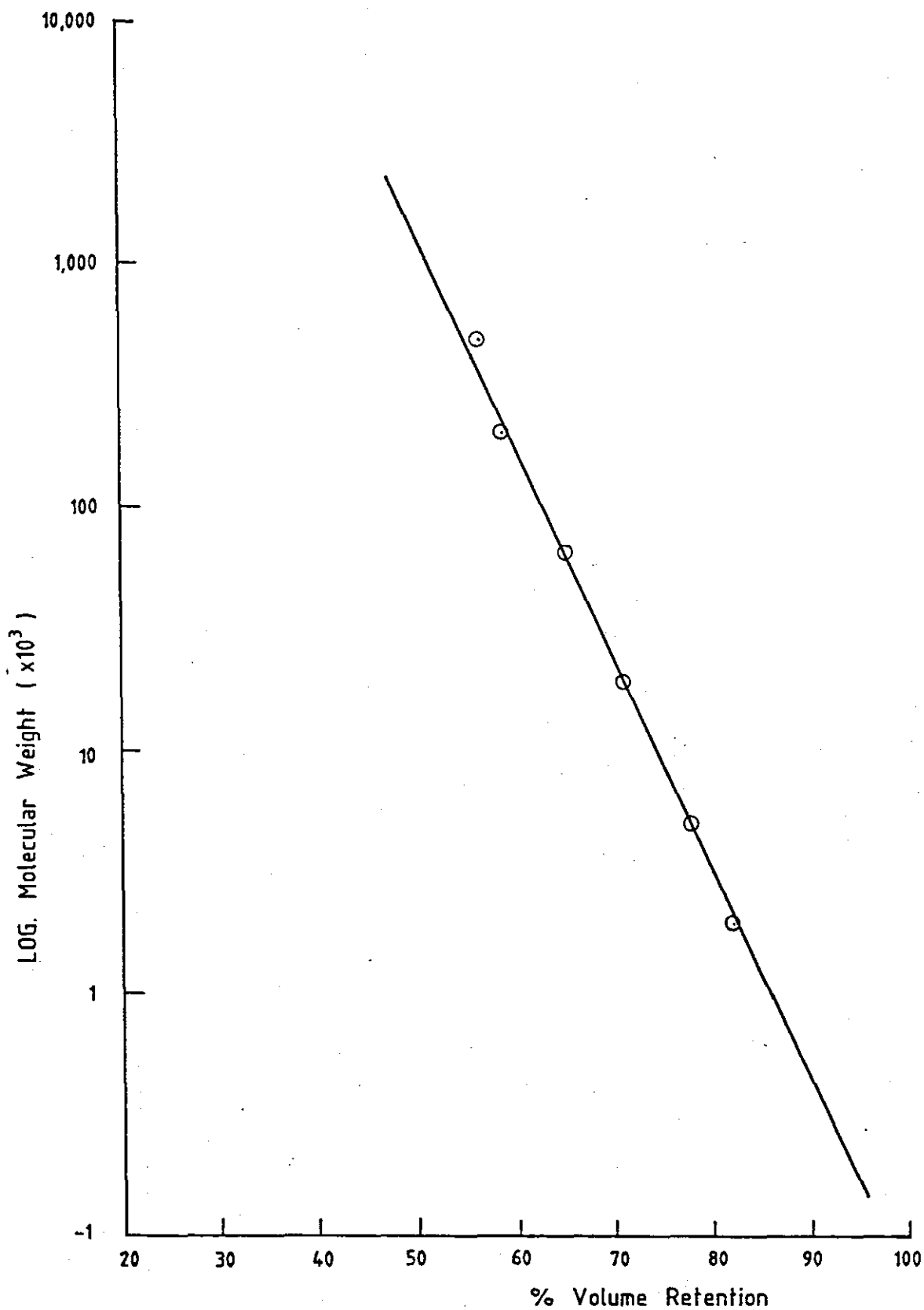
Polyurethane (DesW Based)	Block Ratio	M_n	M_w	M_p	MWD
Capa 200/1,6-HD	0.7:2:1.3	43,876	79,182	58,942	1.80
	0.6:2:1.4	47,590	97,615	68,158	2.05
	1:4:3	43,452	96,773	64,846	2.23
Capa 205/1,6-Hd	1:4:3	41,961	76,919	56,812	1.83
	1:5:4	32,185	61,178	44,374	1.90
Capa 210/1,6-HD	1:5:4	59,038	128,171	86,988	2.17
	1:6:5	50,533	97,176	70,076	1.92
	1:7:6	54,713	111,173	77,991	2.03
Capa 215/1,6-HD	1:5:4	55,499	114,505	79,718	2.06

TABLE 4C5.3: MOLECULAR WEIGHT DATA FOR IPDI BASED POLYURETHANES CHAIN EXTENDED WITH 1,4-BD

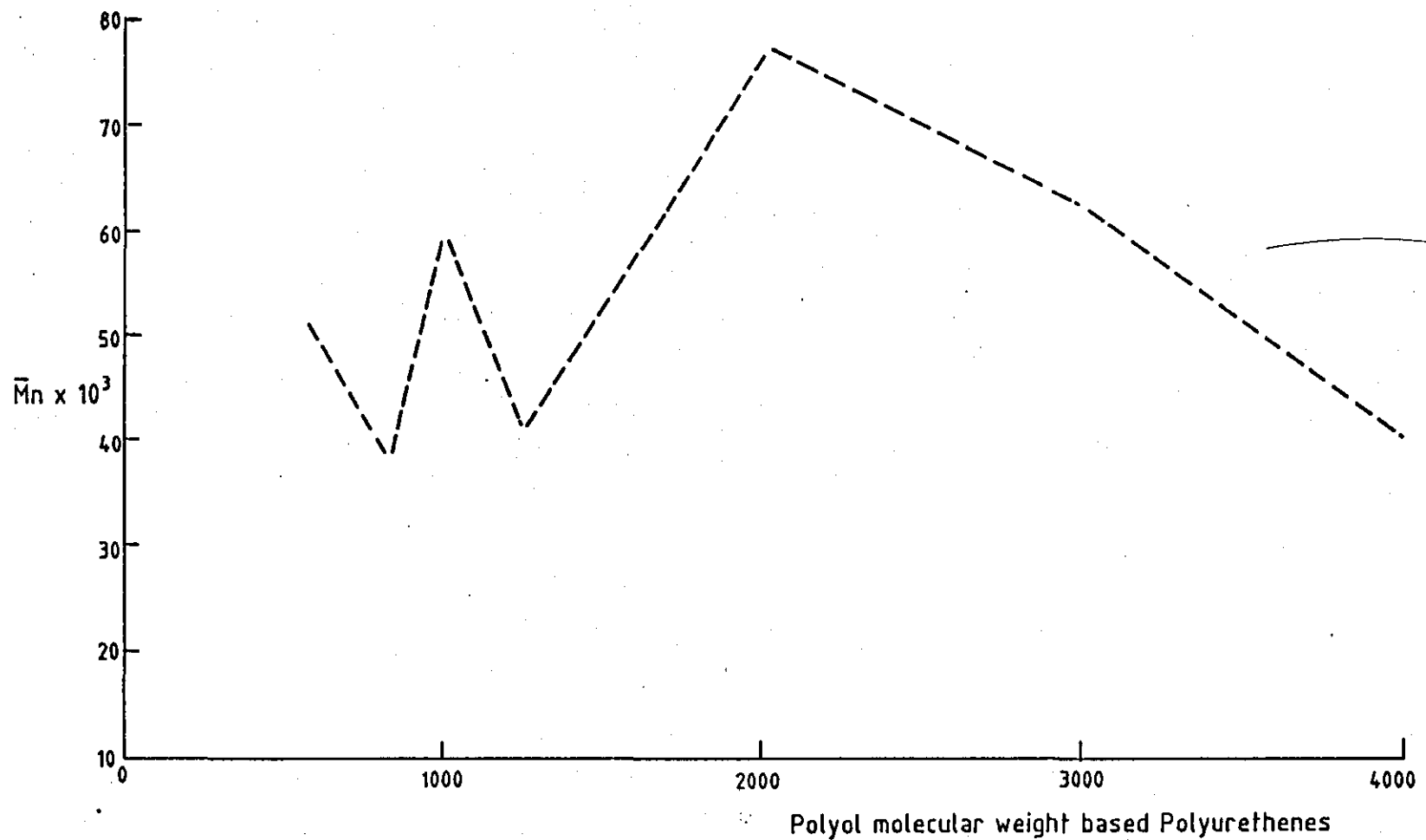
Polyurethane (DesW Based)	Block Ratio	M_n	M_w	M_p	MWD
Capa 200/1,4-BD	1:3:2	65,886	157,738	101,945	2.39
Capa 205/1,4-BD	1:4:3	49,185	96,014	68,720	1.95

TABLE 4C5.4: MOLECULAR WEIGHT DATA FOR DesW BASED POLYURETHANES CHAIN EXTENDED WITH 1,4-BD + 1,4-CHDM AND 1,3-BD

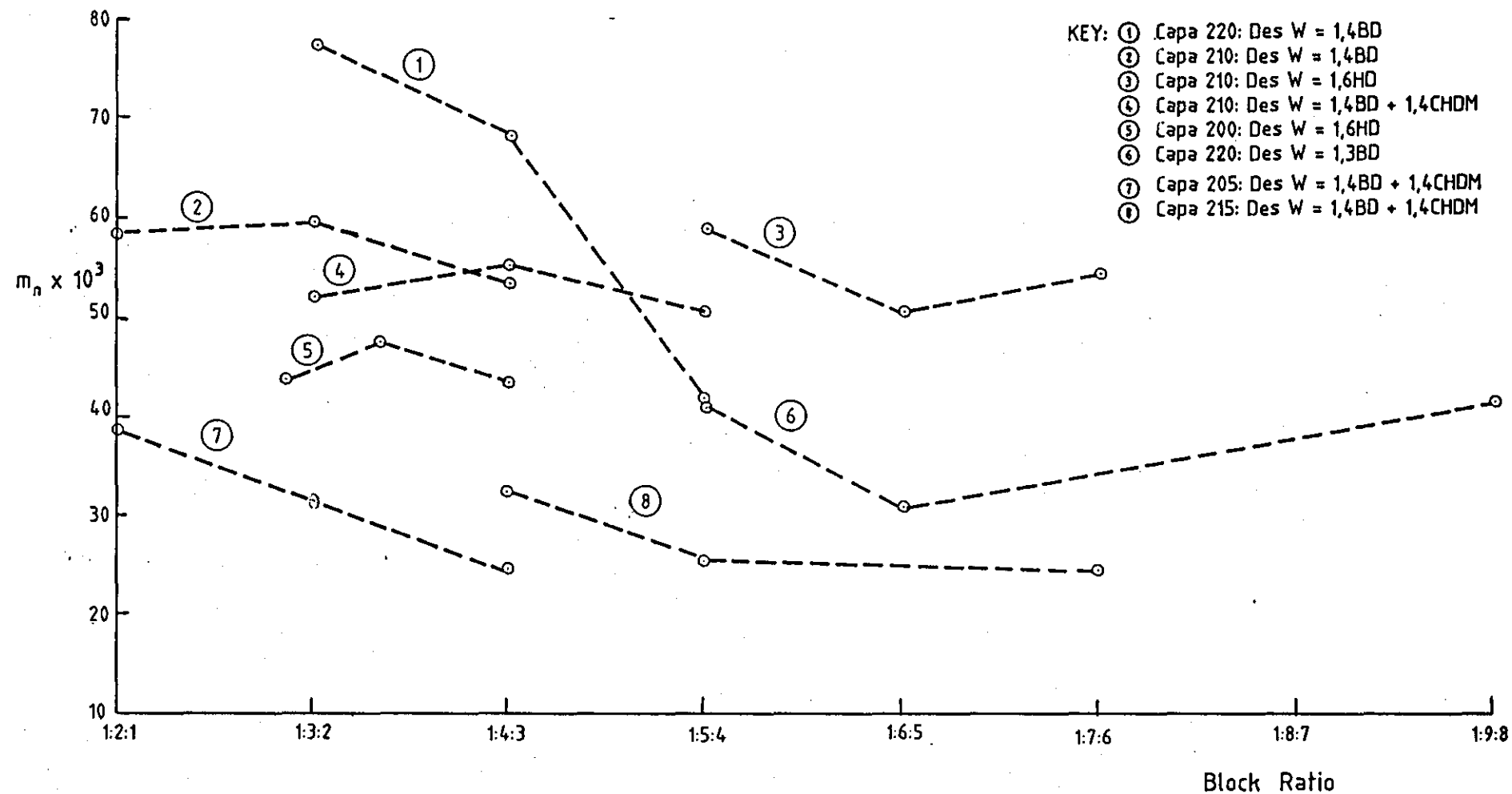
Polyurethane (DesW Based)	Block Ratio	M_n	M_w	M_p	MWD
Capa 200/1,4-BD + 1,4-CHDM	1:2:0.5+0.5	60,947	131,908	89,662	2.16
	1:3:1+1	34,876	68,918	1.97	
Capa 205/1,4-BD + 1,4-CHDM	1:2:0.5+0.5	38,467	66,862	50,715	1.74
	1:3:1+1	31,312	67,792	46,073	2.17
	1:4:1.5+1.5	24,821	47,052	34,174	1.90
Capa 210/1,4-BD + 1,4-CHDM	1:3:1+1	52,085	106,618	74,520	2.05
	1:4:1.5+1.5	55,472	110,450	78,274	1.99
	1:5:2+2	50,697	105,138	73,008	2.07
Capa 215/1,4-BD + 1,4-CHDM	1:4:1.5+1.5	32,435	55,446	42,408	1.71
	1.5:2+2	25,648	43,280	33,318	1.69
	1:7:3+3	24,679	45,074	33,352	1.83
Capa 220/1,4-BD + 1,4-CHDM	1:9:4+4	70,220	143,925	100,530	2.05
Capa 220/1,3-BD	1:5:4	41,302	78,003	56,760	1.89
	1:6:5	30,070	50,520	38,976	1.68
	1:9:8	41,351	71,965	54,551	1.74



Graph 4C2 . 1 . Calibration Plot of Polystyrene Standards of known molecular weight against their percent elution volume (percent volume retention) .



Graph 4C5 . 1. Plot of \bar{M}_n against Polyurethanes based on Des W/1,4BD at various polyol molecular weights, at 1 : 3 : 2 block ratio.



Graph 4C5 . 2 Differing Des W Based Polyurethane systems of constant polyol molecular weight with varying block ratio.

	Polyol	Mp	Mw	Mn	MWD
Capa 200	550	1111	1036	966	1.15
Capa 205	830	1565	1449	1342	1.17
Capa 210	1000	2007	1786	1589	1.26
Capa 215	1250	2305	2062	1845	1.25
Capa 220	2000	4214	3586	3052	1.38
Capa 231	3000	5590	4892	4298	1.31
Capa 241	4000	8376	7461	6703	1.26

Table 4C3 . 1 . Molecular Weight data obtained for Polycaprolactone polyols.

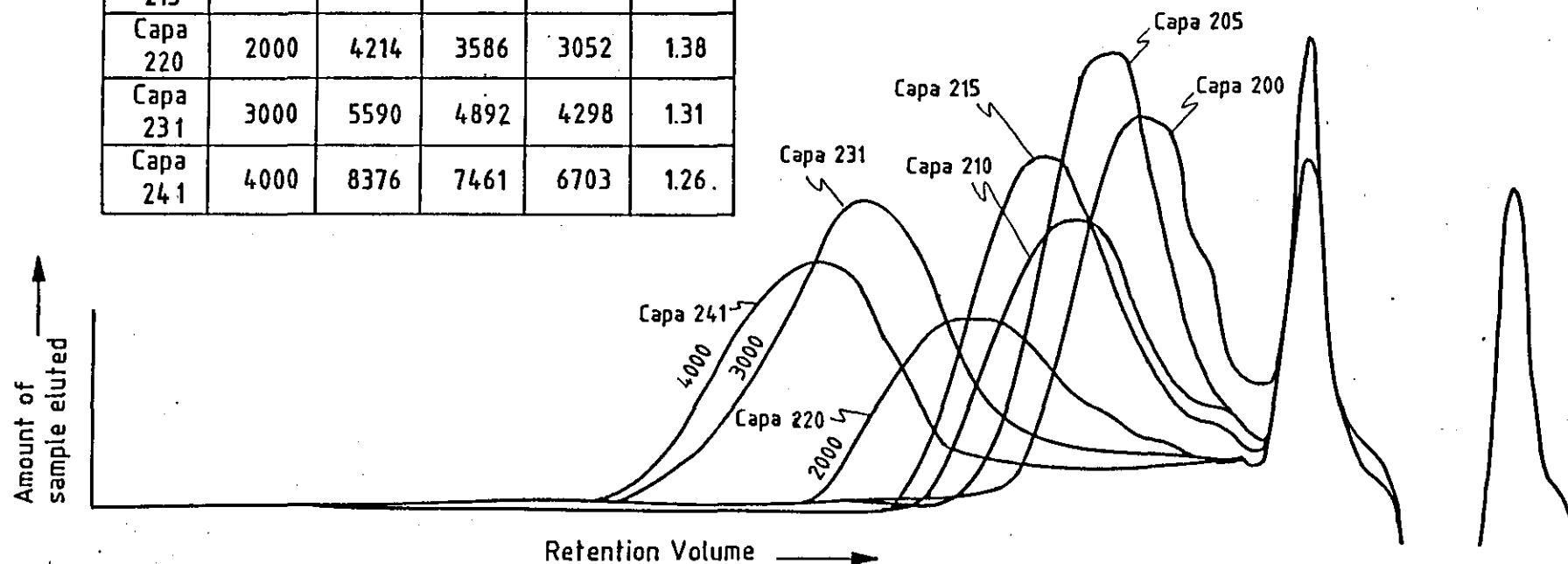


Fig. 4C3 . 1 . G P C plots of molecular weight distribution of Polycaprolactone polyols.

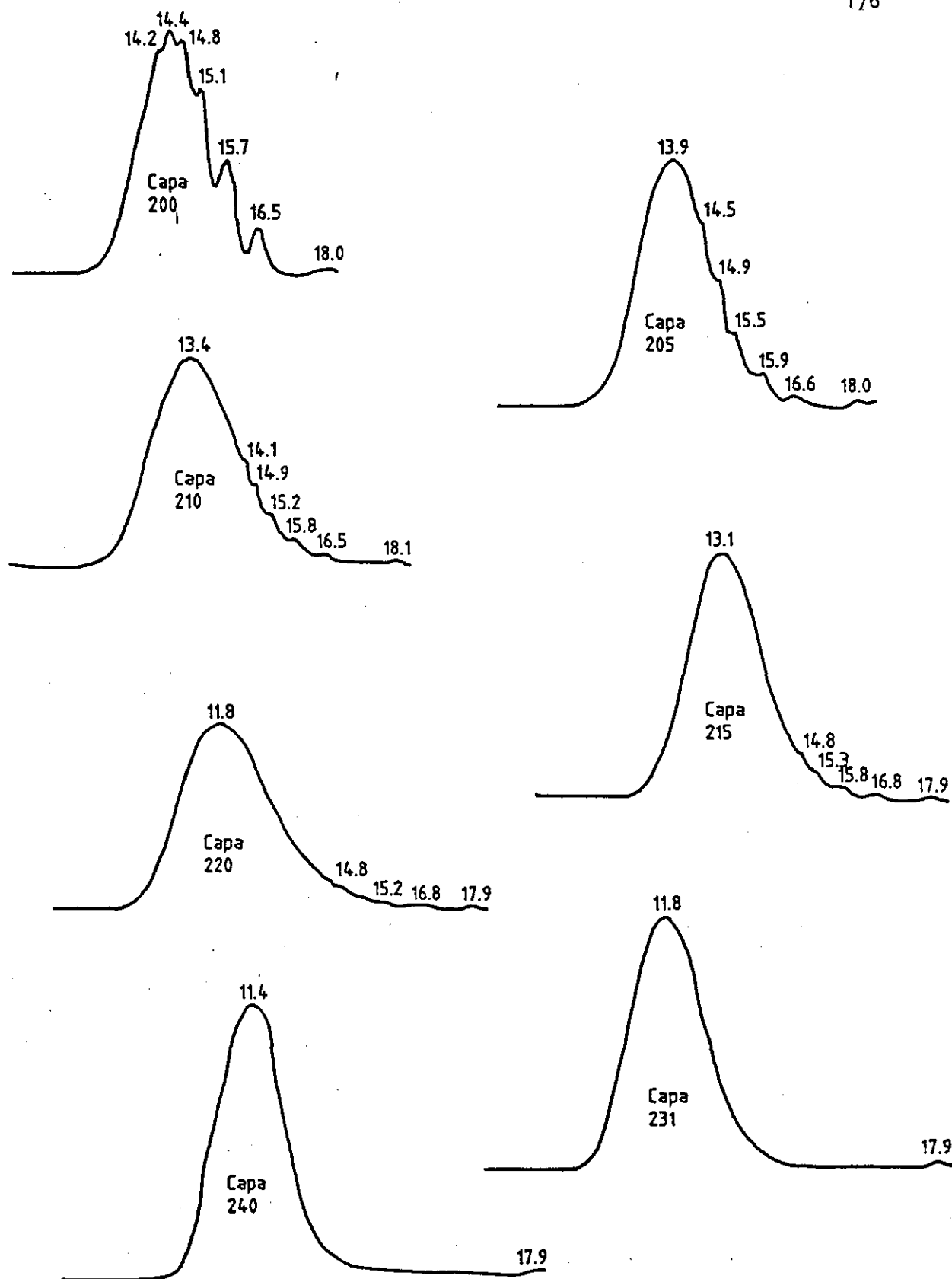


FIG. 4C3 . 2. GPC chromatogram of each polycaprolactone polyols using a 500Å column is shown separately. The figures indicate the Retention Volume from the point of injection.

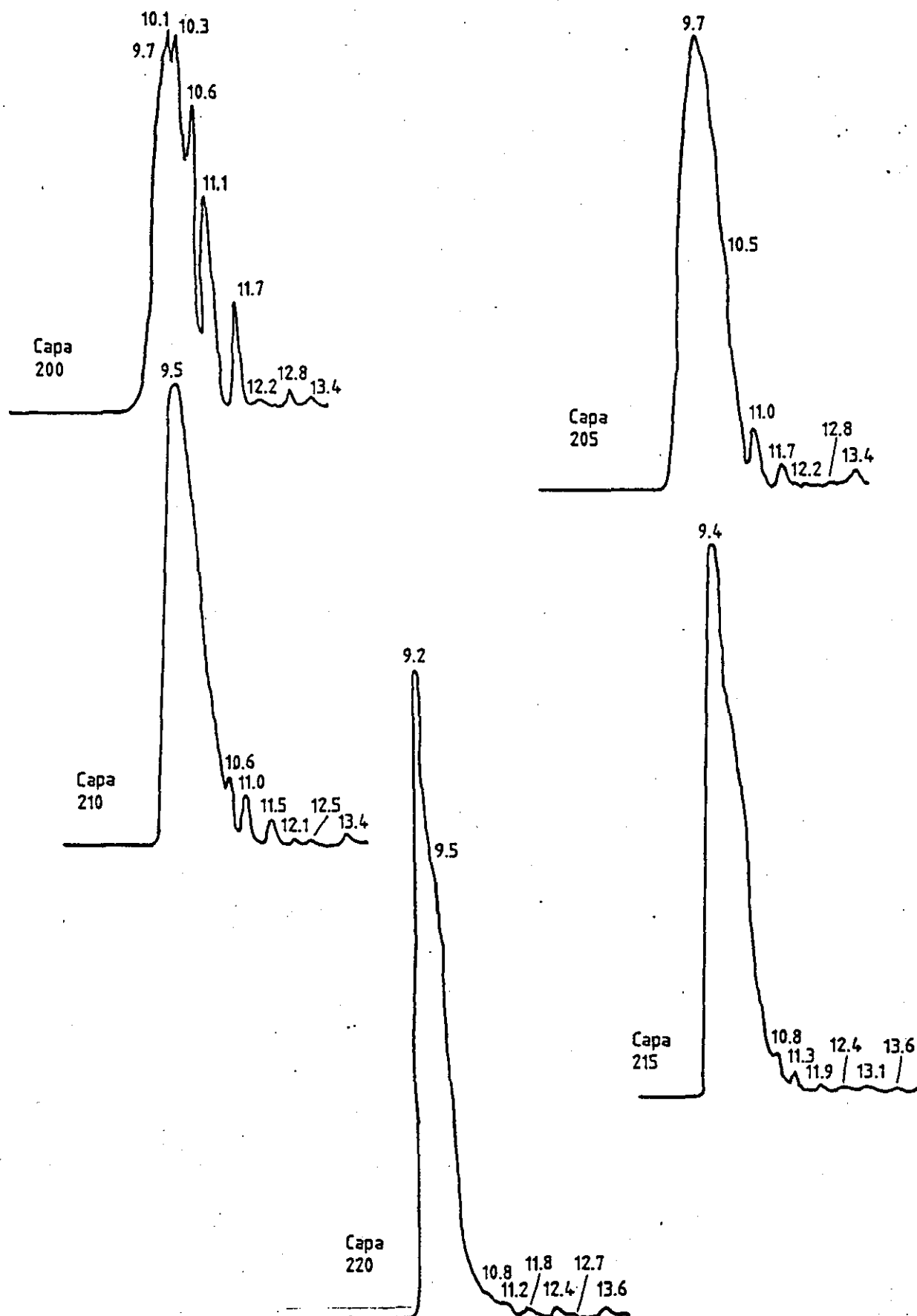


FIG. 4C3 : 3. GPC chromatograms of polycaprolactone polyols
using a 50A column shown separately.
The figures indicate the Retention Volume from
point of injection.

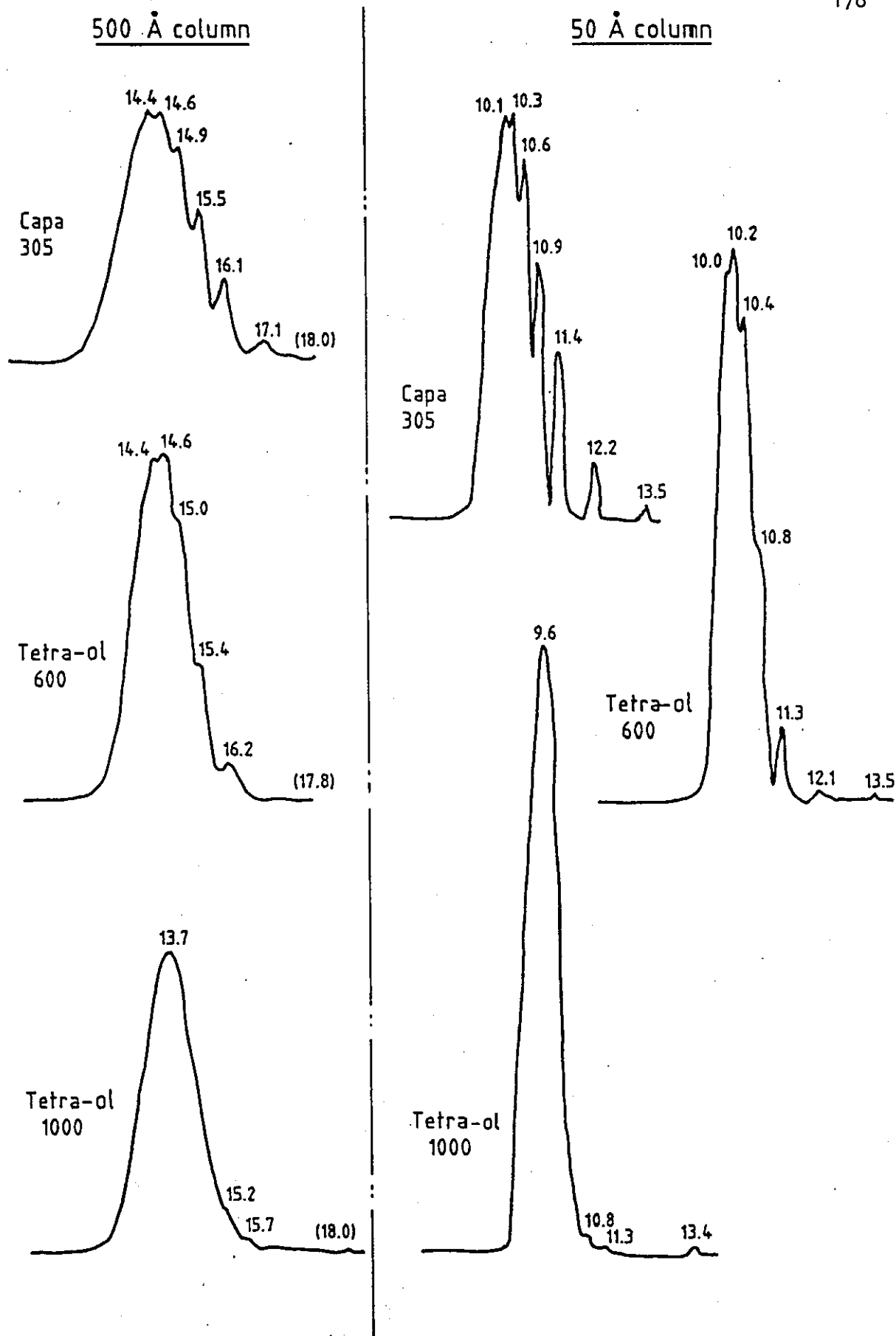


FIG. 4C3 . 4. GPC chromatograms of polycaprolactone triol and tetra-ol using 500Å and 50Å columns shown separately.

The figures indicate the Retention Volume from point of injection.

Injection Point

Amount of Sample Eluted

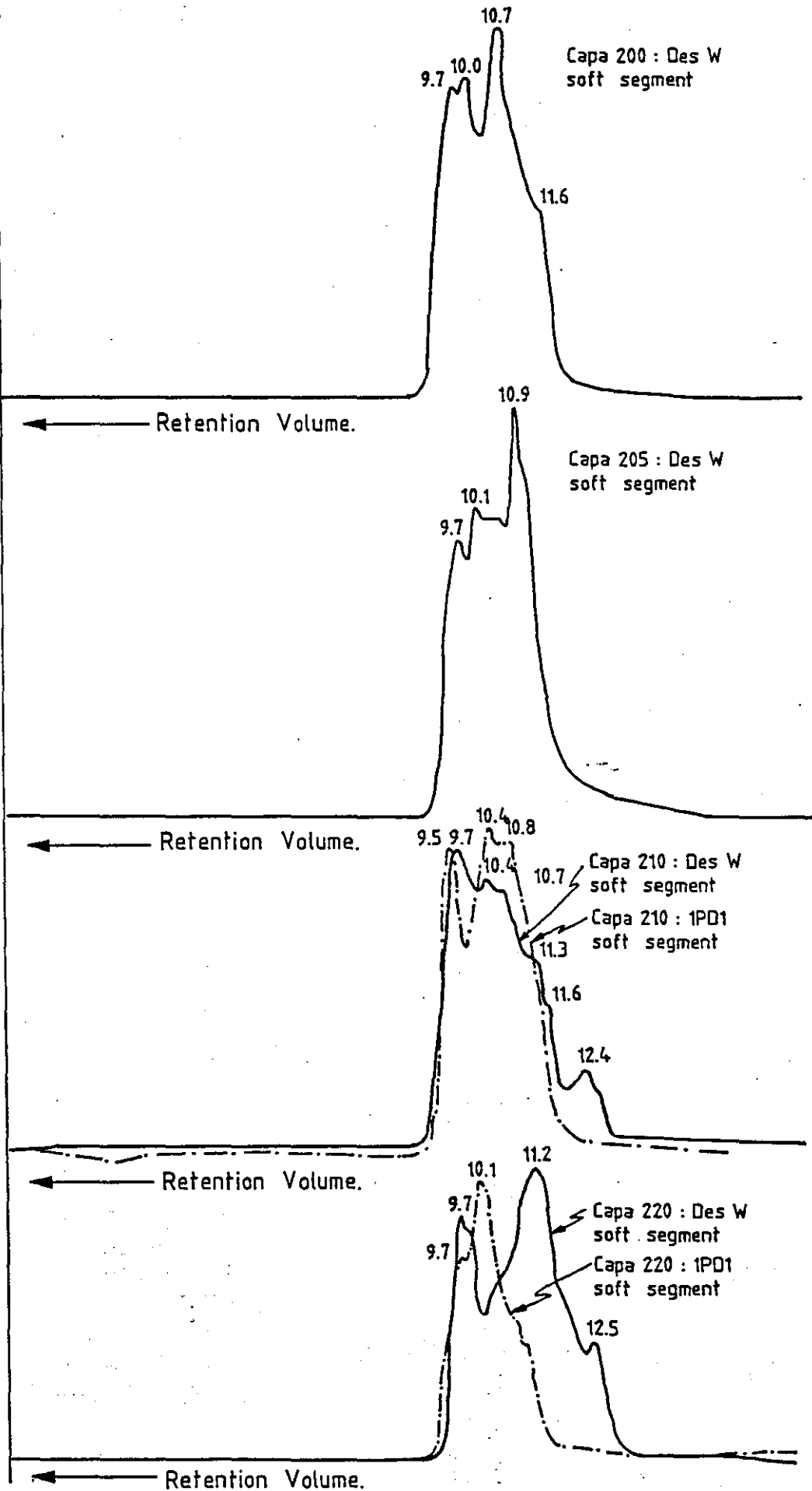


FIG. 4C4 . 1 GPC chromatograms of some soft segments separated using the 500A column

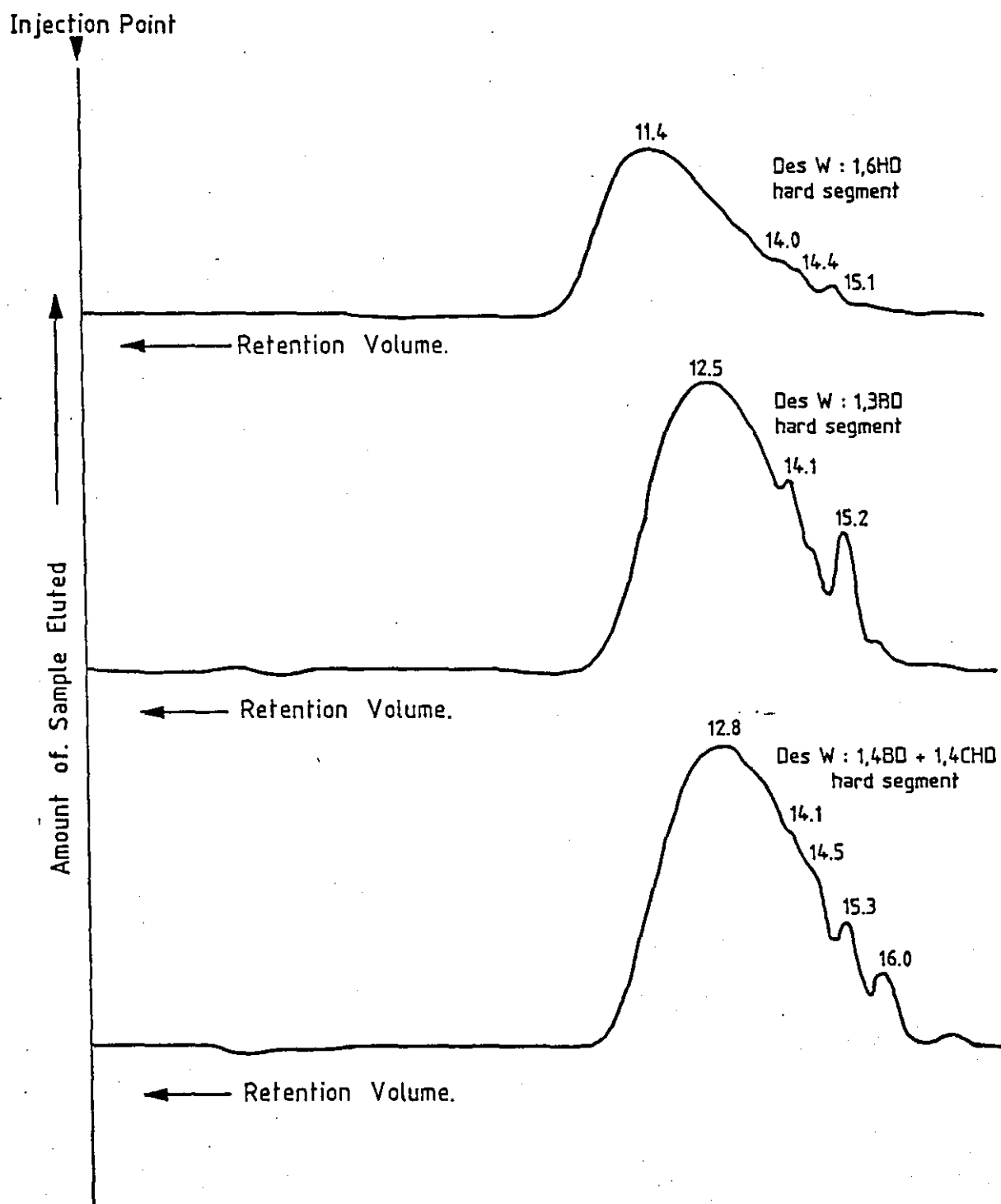


FIG. 4C4 . 2. GPC chromatograms of some hard segments separated using the 500Å column.

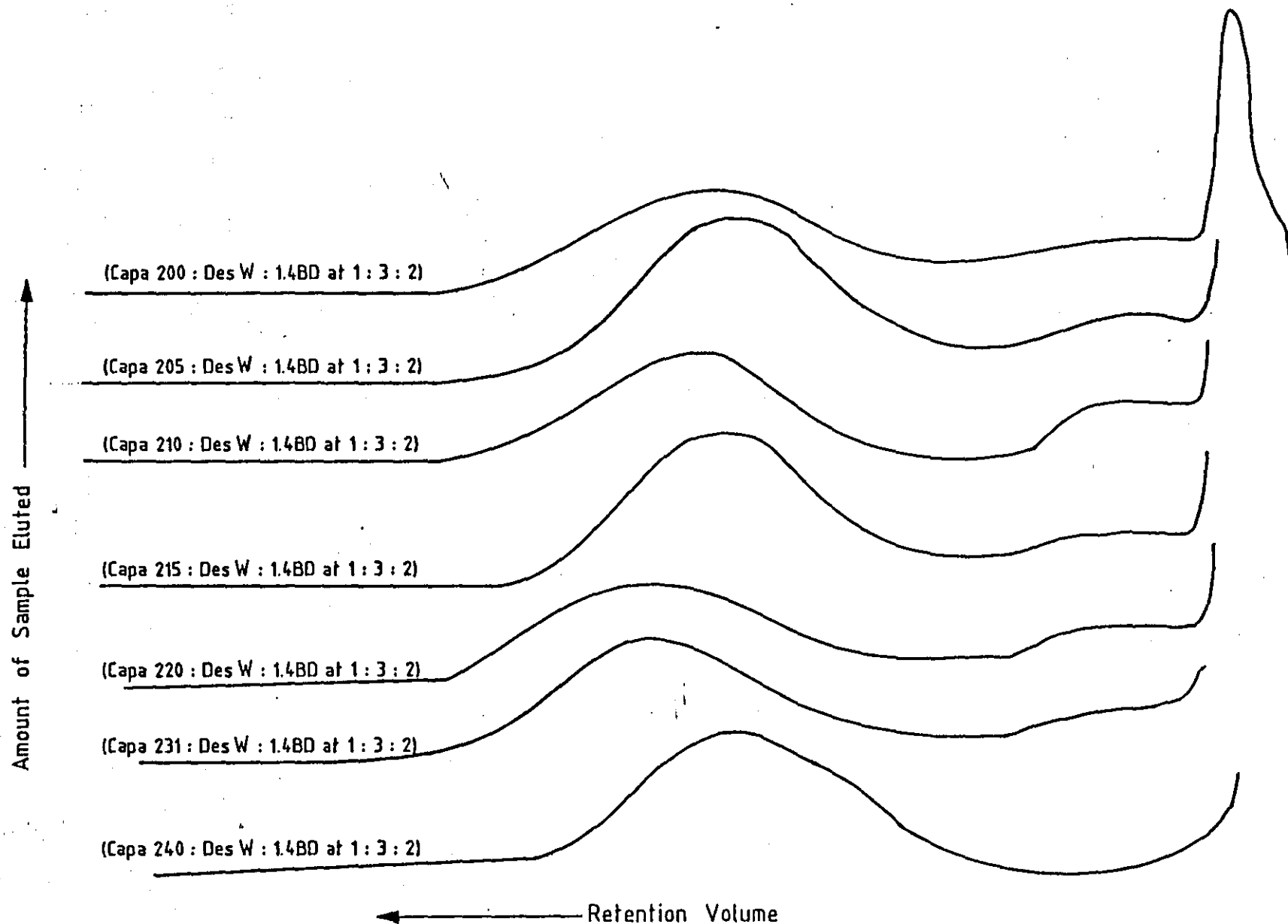


FIG. 4C5 . 1. GPC chromatograms of Des W based Polyurethanes at 1:3:2 block ratio , chain extended with 1,4BD.

4D.1 INFRARED SPECTROSCOPY - INTRODUCTION

Several notable investigations into the nature and extent of hydrogen bonding in segmented polyurethane elastomer systems have been reported [152-155]. Hydrogen bonding in polyurethane often dominates the crystalline structure, influences physical properties of the amorphous state through relatively strong interchain interactions or through the formation of paracrystalline structures. Infrared spectroscopic techniques have been used to determine the groups involved in H-bonding in these materials. While the majority of hydrogen bonding occurs between hard segments, it appears that a significant proportion also occurs between NH groups of the polyurea or polyurethane hard segments and the oxygen atom of the soft segment polyester carbonyl. Similarly in polyether based urethanes, hydrogen bonding occurs between the NH groups and the ether oxygen.

The polyesters and polyethers from which urethane elastomers can be obtained vary in structure and consequently they can contain different proton acceptor groups. This is also the case for other intermediates like chain extenders. Hence, the extent and possible forms of hydrogen bonding are dependent on many factors including the electron donating ability and relative proportion and spatial arrangements of the proton acceptor groups in the polymer chain. Functional groups of a molecule possess vibrational frequencies and by observing these absorption frequencies, information on the overall molecular structure can be obtained. Typically in hydrogen bonded polyurethanes the NH group of the hard segment serve as proton donors, while the proton acceptors can be the carbonyl group of the hard segment unit/polyester chain or ether group of the polyether chain.

Paik Sung and Schneider [156] investigated hydrogen bonding in two series of toluene diisocyanate polyurethanes based on the individual 2,4- and 2,6-TDI isomers, a polyether soft segment and butane diol. Three major absorption regions were investigated:

1. NH stretching band in the region of $3460\text{--}3300\text{ cm}^{-1}$
2. Carbonyl (C=O) stretching band in the region of $1740\text{--}1700\text{ cm}^{-1}$
3. Ether (C-O-C) stretching band in the region of $1300\text{--}1000\text{ cm}^{-1}$.

The major NH bond at near 3300 cm^{-1} is attributed to the hydrogen bonded NH groups, while a shoulder on the high frequency side (near 3460 cm^{-1}) is assigned to the non-bonded NH group. Their results indicated that 95% of all NH groups are hydrogen bonded in the solid state at room temperature.

The regions that are mentioned above, together with the CH_2 stretch absorption region ($3000\text{--}2700\text{ cm}^{-1}$) are important in polyurethane analysis. Participation in hydrogen bonding decreases the frequency of the NH and C=O vibrations and increases their intensity, making these absorptions very useful in the study of hydrogen bonding effects. Changes in hydrogen bonding can thus be followed, in principle, by frequency or intensity measurements.

The dependence of the segment size on hydrogen bonding was considered by Tanaka et al [157]. They showed that in polyether based polyurethane materials, the increase in hydrogen bonding between NH and ether groups is accompanied by the increase in soft segment size. Further evidence of this effect is provided by the result of Nakayama et al [155] on polyether/MDI/ethylene diamine based materials.

The measure of hydrogen bonding between NH protons and possible proton acceptors can indicate the extent of phase segregation. Estimation of hydrogen bonding is based on the resolution of urethane NH and carbonyl bond into the bonded and non-bonded components. In a polyether urethane the determination of phase separation through hydrogen bonding is simple, as the only proton acceptors are the C=O group of the urethane hard segment and the ether oxygen of the polyether soft segment, which give absorbances at different wavelengths. Polyester urethanes on the other hand, contain two different carbonyl groups each belonging to hard and

soft segment units, thus four possibilities of absorption peaks exist. This gives rise to a much broader carbonyl absorption region in polyester urethanes which result in making the hydrogen bonding estimation difficult.

4D.2 INFRARED TECHNIQUE

When electromagnetic radiation falls on a material energy is absorbed due to molecular transitions between quantum states, corresponding to different internal energies. This occurs in infrared analysis which is normally observed using a double beam infrared spectrophotometer. This consists basically of a source of infrared radiation and a dispersion system to give a spectrum of varied wavelength radiation. Prisms of inorganic salts and diffraction gratings are commonly used as dispersion agents. The beam of monochromatic radiation is split into two beams of equal intensity by means of a system of mirrors. One beam is arranged to pass through the sample and the other through a suitable reference medium.

If the frequency of a vibration of the sample molecule falls within the range of the instrument, the molecule will absorb energy at this frequency, resulting in a difference in intensities of the sample and reference beams which is detected by a photocell system. The final spectrum is recorded on a chart recorder which is coupled to the dispersion and detection systems. Spectra show peaks corresponding to absorption plotted against wavelength (or frequency). In this system, absorption of infrared radiation by the sample can be brought about using two techniques:

1. Transmission of radiation through the sample
2. Reflection of radiation from the sample.

Transmission techniques are most commonly used, in which infrared radiation is passed directly through the sample. Solutions, vapours, liquid films and mulls provide suitable samples for this

technique. Solid samples, particularly polymeric films and sheets, can be readily investigated using infrared reflection methods. In this research, the infrared reflection method was used for the polyurethanes investigated.

4D.3 INFRARED REFLECTION SPECTROSCOPY

A spectrum obtained by reflection of the radiation from the surface of a material is usually very poor. A technique known as Attenuated Total Reflectance (ATR) was conceived by Fahrenfort [158] in 1961. This enables reflection spectra of satisfactory quality to be produced. The infrared ATR unit consists essentially of a flat crystal (usually thallium iodide) arranged in the sample beam of the spectrophotometer so that infrared radiation can pass through it by total internal reflection. Samples are clamped firmly on either surface of the crystal. When radiation is totally internally reflected at the surface of the crystal, a small proportion actually passes through the surface of the sample and may be absorbed. On repeated internal reflection along the crystal, the sum intensity of absorption increases. Therefore the emerging radiation has a lower intensity than the reference beam and a spectrum is obtained in the usual way. Figure 4D3.1 shows the optical path in a simple ATR unit and also shows the totally internally reflected infrared radiation.

4D.4 EXPERIMENTAL PROCEDURE

Spectra of several prepared polyurethanes were recorded using a Beckman TR-9 ATR unit (giving 9 internal reflections) installed in a Pye Unicam SP3-200 Grating Infrared Spectrophotometer. Samples approximately 2mm thick were cut to cover both sides of the crystal. The samples were vacuum dried prior to analysis to remove any surface moisture which would give rise to characteristic OH absorption bands. The samples were clamped firmly against the crystal surface and spectra recorded between 4000 cm^{-1} and 600 cm^{-1} (2.5 μm to 16.5 μm) using a normal scanning mode.

In the present investigation the spectra were studied for their intermolecular interactions and the extent of hydrogen bonding. Figure 4D4.1 shows the three main types of hydrogen bonds observed in polyurethanes. Since the prepared polyurethanes are based on polycaprolactone (polyester) polyols only the first two types of H-bonding shown are expected and considered:

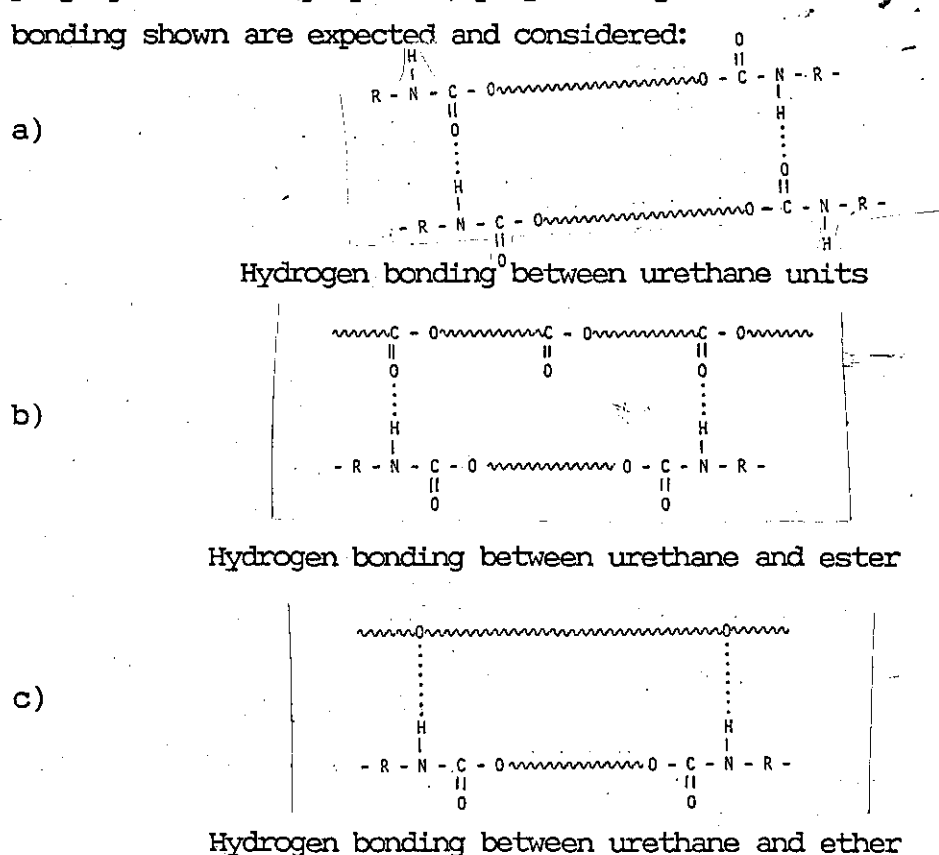


FIGURE 4D4.1 SCHEMATIC DIAGRAM OF THE THREE MAIN TYPES OF HYDROGEN BONDING FOUND IN POLYURETHANE ELASTOMERS

Spectra of all polyurethane elastomers studied were found to be similar to that shown in Figure 4D4.2. Assignments of the most pronounced absorption bands are shown in Table 4D4.1. The spectra below 1500 cm^{-1} , the 'Fingerprint' region is characteristic of the individual molecular structure it represents. Assignment of absorption bands in this region to particular functional group

vibration can be misleading, especially as combination and overtone bands may be present.

4D.5 EXTENT OF HYDROGEN BONDING IN POLYURETHANE ELASTOMERS

The characteristic NH absorption band at around 3300 cm^{-1} assigned to hydrogen bonded NH groups is seen to have a shoulder near 3460 cm^{-1} associated to free NH groups. A simple estimation of the extent of hydrogen bonded interactions was made by using the 'baseline density' method [159]. The absorbances of the absorption maxima were calculated according to Beer-Lambert's law of absorption which states:

$$A = \log_{10} \left(\frac{I_0}{I} \right) = E.C.L.$$

where A = absorbance

I_0 = intensity of incident radiation

I = intensity of transmitted radiation

E = extinction coefficient

C = concentration of the NH groups

L = radiation path length (cm)

The absorbance A_b of the hydrogen bonded absorption maxima is given by:

$$A_b = E_b C_b L_b$$

Similarly for the free NH absorption maxima

$$A_f = E_f C_f L_f$$

As an approximation, assuming $E_b = E_f$ then

$$A_b = K.C_b$$

$K = \text{constant}$

and

$$A_f = K.C_f$$

Values of A_b and A_f were calculated from the infrared spectra using the 'baseline density' method as shown in Figure 4D5.1, this shows

$$A_b = \frac{AC}{BC}$$

and

$$A_f = \frac{DF}{EF}$$

The proportion of bonded NH groups is then given by:

$$\% \text{ hydrogen bonded NH} = \frac{A_b}{(A_b + A_f)} \times 100$$

Using this approximation, the values of hydrogen bonding percentage were calculated from the spectra and given in Table 4D5.1.

4D.6 RESULTS AND DISCUSSION

The spectra obtained of the analysed polyurethanes by ATR are similar to the one shown in Figure 4D4.2. It is noticed that all polyurethanes analysed showed the absence of an isocyanate ($-NCO$) absorption band at 2270 cm^{-1} indicating the complete reaction of H_{12} MDI. It is also noticed that as these polyurethanes are diol chain extended and give urethane groups, a distinct band at 1635 cm^{-1} indicating the urea ($C=O$) stretching mode is absent.

The increase in polyol molecular weight at a constant block ratio of 1:3:2 gave the following principal changes in the infrared spectra:

- i) The bands at 1440 cm^{-1} (CH_2 bend) and 1370 cm^{-1} (CH_2 wag) increase in intensity
- ii) The NH absorption band at 3300 cm^{-1} decreases in intensity and becomes broader. The percentage hydrogen bonding in this absorption band gave similar values (Table 4D5.1), although a slight decrease is seen with polyol molecular weight
- iii) The carbonyl absorption at $1680\text{--}1720\text{ cm}^{-1}$ is broad and at low polyol molecular weight the split in this band attributed to the free and bonded C=O groups is difficult to resolve. With increasing polyol molecular weight the band becomes sharper and easier to resolve. A typical value for percent hydrogen bonding associated to the carbonyl group was obtained by the baseline density method and found to be 38% for the Capa 215 based polyurethane
- iv) The transparent and opaque (Capa 231 and 240 based) materials studied show similar levels of hydrogen bonding indicating that transparency is not directly influenced by hydrogen bonding.

As the block ratio in the polyurethane increases for Capa 220, the following principal changes in the infrared spectra were observed:

- i) The absorptions at 1440 cm^{-1} and 1370 cm^{-1} decrease in intensity
- ii) At 1:3:2 block ratio the NH stretch at 3300 cm^{-1} is short and broad, but becomes slightly longer and sharper in intensity with increasing block ratio. The free hydrogen bonded NH absorption (shoulder at 3440 cm^{-1}) remains relatively constant as is indicated by the values calculated (Table 4D5.1)

- iii) The carbonyl absorption ($1680-1720\text{ cm}^{-1}$) shows the splitting of the band to be less resolved at lower block ratios. At a block ratio of 1:5:4 and above the absorption band is better resolved.

The polyurethanes analysed show the H-bonding in the NH absorption to be between 51 to 59%. Since the polyurethanes studied are all based on cycloaliphatic diisocyanate (H_{12}MDI) their polarity or proton donating capability is expected to be the same throughout the samples and which actually give H-bonding values in the same region. This indicates that the extent of hydrogen bonding is largely dependent on the proton donating ability of NH groups which in turn depends on the diisocyanate structure and substituents attached to the NCO group. Similarly the carbonyl group present in the sample having proton accepting affinity comes from the polyol employed. In the present study only polycaprolactone polyols of varying molecular weights were used and these would provide similar affinity towards the protons in the sample. The splitting of the carbonyl band $1680-1720\text{ cm}^{-1}$ is difficult to resolve making the estimation of extent of carbonyl H-bonded interactions difficult to assess.

TABLE 4D4.1: MAJOR ABSORPTION ASSIGNMENTS IN INFRARED SPECTRA FOR PREPARED POLYURETHANE ELASTOMERS

Wavenumber (cm^{-1})	Relative Intensity	Assignment
3440	W, Sh	Free NH stretch
3300	M	H-bonded NH stretch
2915	S	Asymmetric CH_2 stretch
2845	M	Symmetric CH_2 stretch
1720	Vs	Free (C=O) carbonyl stretch
1680	Vs	H-bonded (C=O) carbonyl stretch
1500-1550	S	N-H bending and C-N stretching
1440	M	CH_2 bending
1150	S	C-O-C stretch

What it stand for?

TABLE 4D5.1: EXTENT OF HYDROGEN BONDING ON THE POLYURETHANE ELASTOMERS ANALYSED

Capa 220 Based Varying Block Ratio	Percent Hydrogen Bonding	Varying Polyol m.wt. % 1:3:2	Percent Hydrogen Bonding
1:3:2	52	Capa 200	54
1:4:3	53	Capa 205	56
1:5:4	54	Capa 210	59
1:6:5	55	Capa 215	53
1:8:7	54	Capa 220	52
1:9:8	52	Capa 231	51
		Capa 240	51

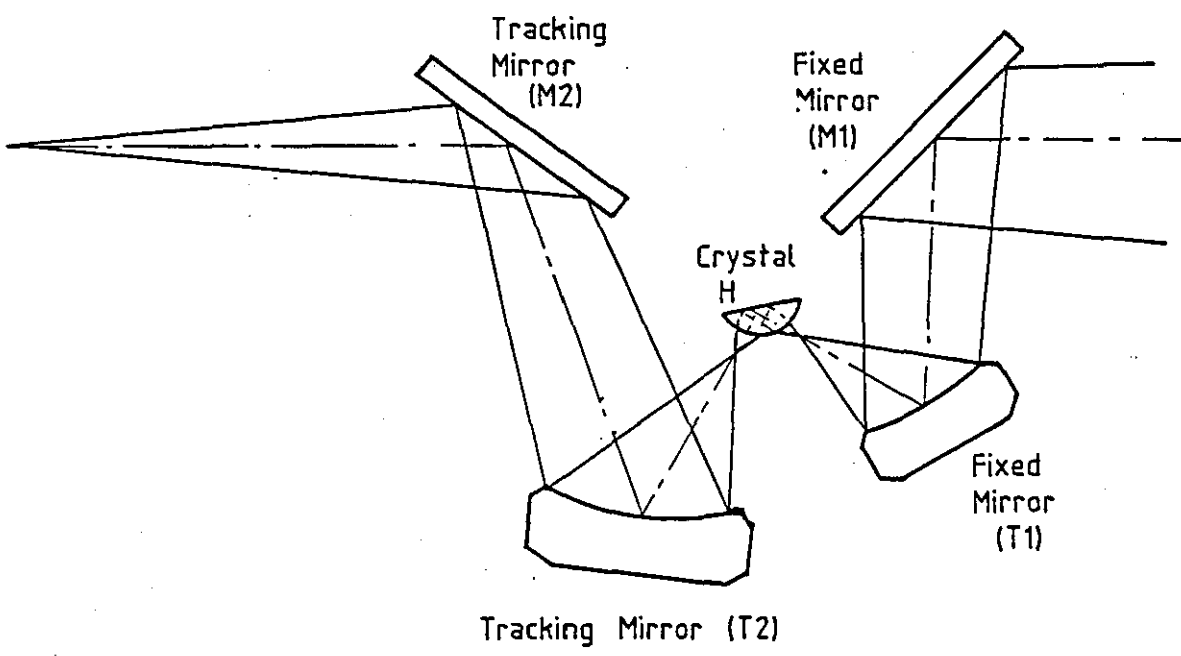


Fig. 4D3 . 1(a) The optical path in a simple ATR unit.

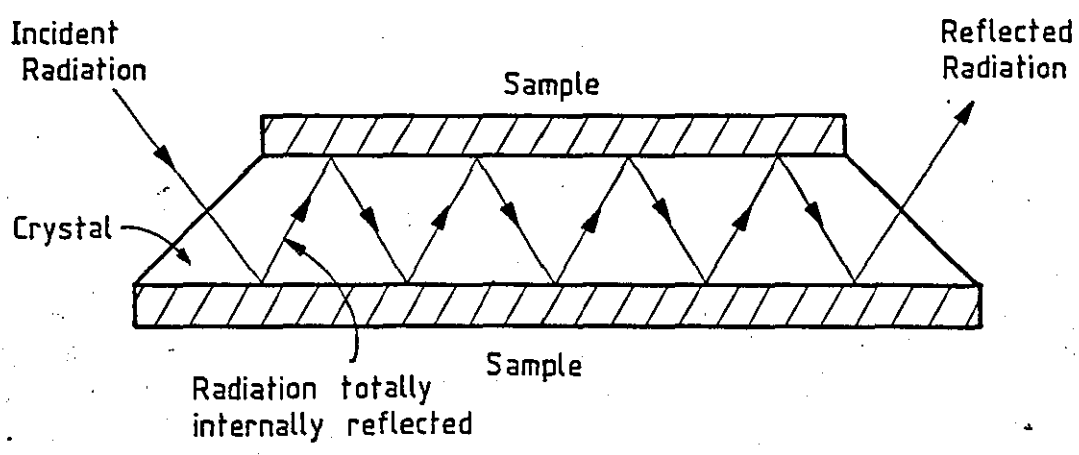


Fig. 4D3 . 1(b) Totally internally reflected IR radiation.

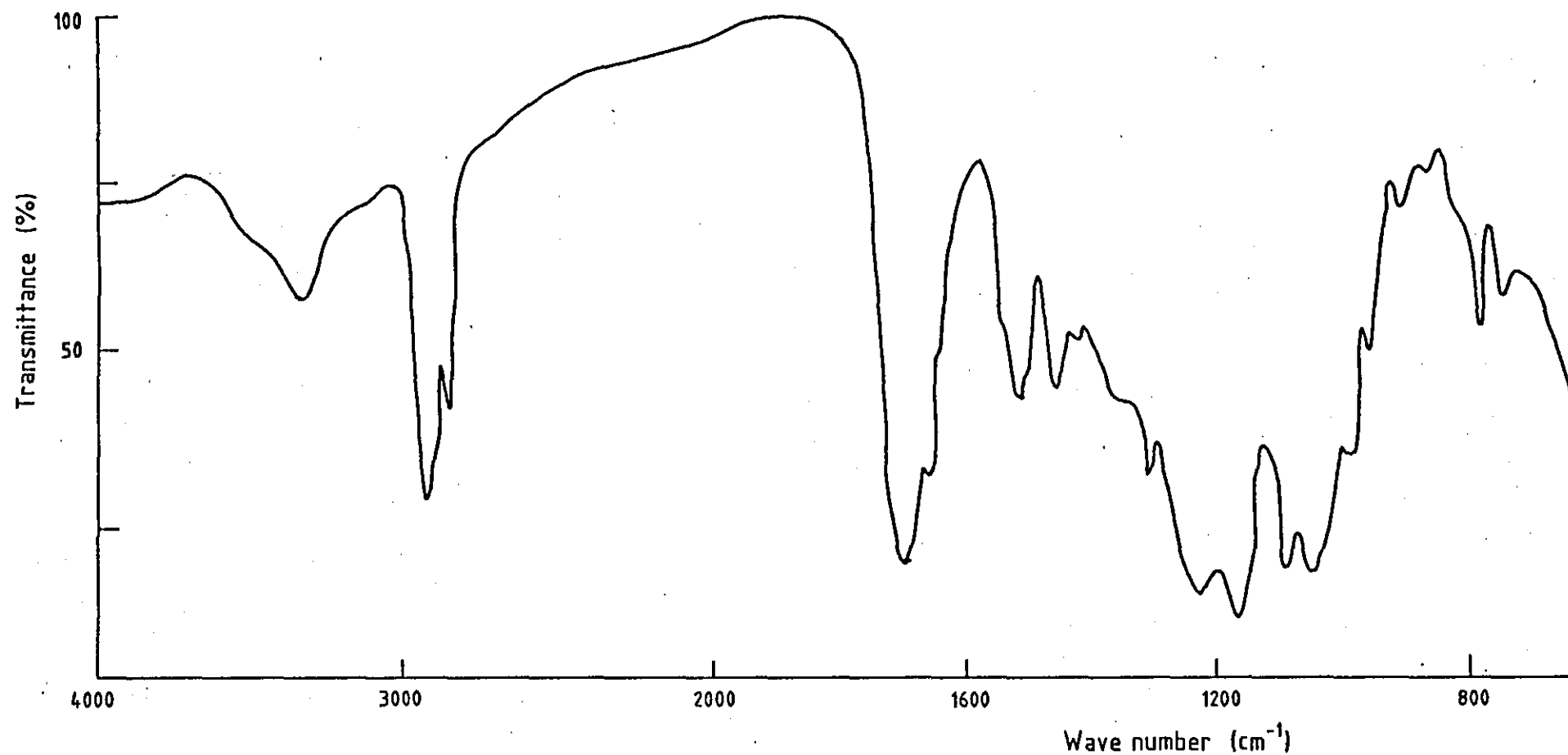


Fig. 4D4 . 2 . ATR spectra of a prepared polyurethane elastomers.

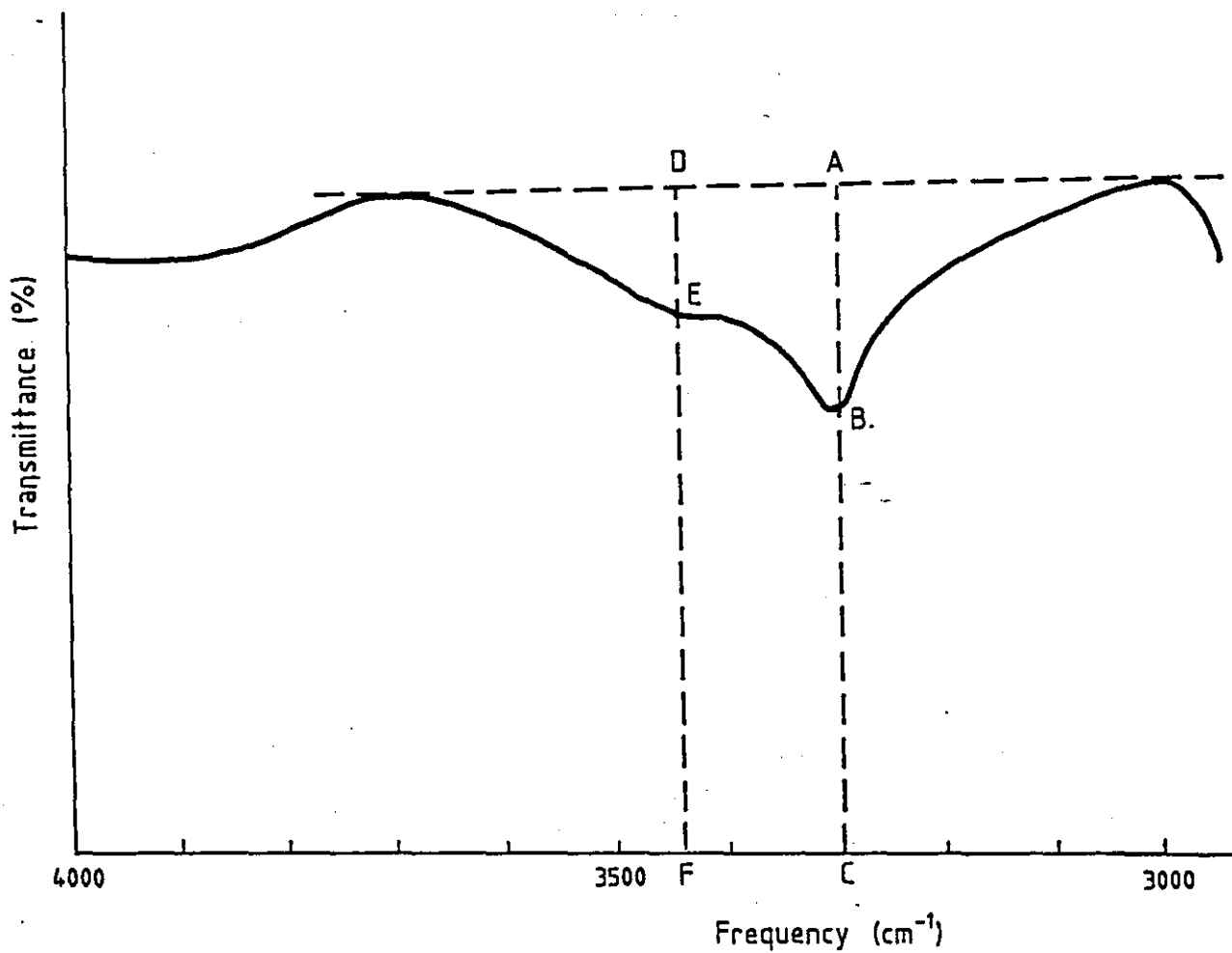


Fig. 4D5 . 1 . Showing Baseline Density Method in a Typical NH Absorption Band of PU Elastomer.

4E.1 X-RAY DIFFRACTION

This study provides a useful method of investigating the presence of ordered arrangements of atoms and molecules within a solid substance. X-rays are produced when high speed electrons strike a metal (copper) target causing ionization of surface atoms and subsequent jumping of electrons into vacant orbitals. Radiation is produced by this process consisting of several distinct wavelength maxima and by use of a suitable filter (nickel) radiation of a well defined specific wavelength ($\lambda = 1.542 \text{ \AA}$) is obtained. The beam is collimated with suitable pinholes, passes through and is diffracted by the sample which is placed in the path of the X-ray beam. A flat plate camera is used for the record of the entire diffraction pattern. The distance between sample and plate is kept constant throughout. The general features of the unit are shown in Figure 4E1.1.

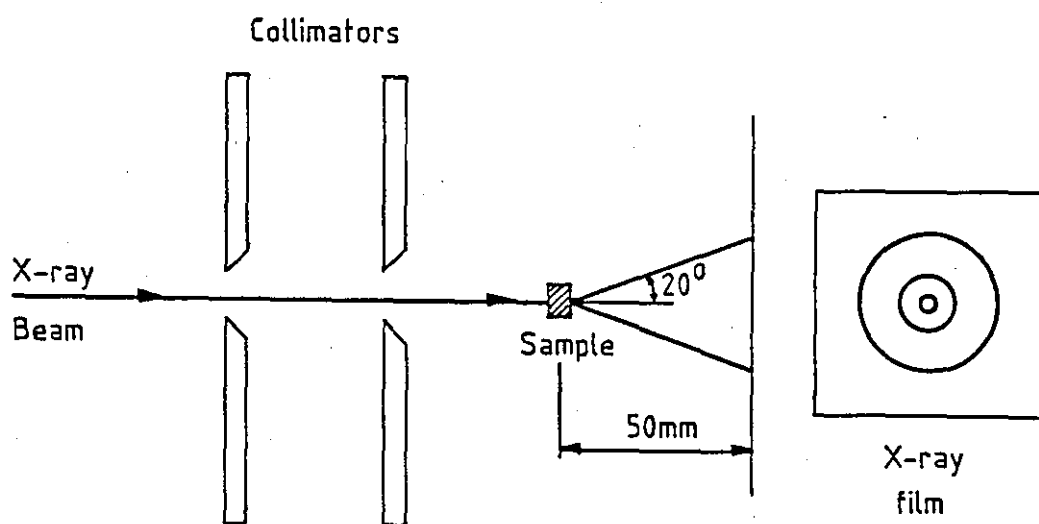


FIGURE 4E1.1: ESSENTIAL FEATURES OF THE X-RAY DIFFRACTION INSTRUMENT (WAXS)

As the wavelength of X-rays are comparable to interatomic distances, diffraction effects will occur when X-rays are focussed on a solid substance containing regularly arrayed atoms. By using X-rays of known wavelength it is possible to determine the geometry of the regularly repeating unit cells and polymer segments in block copolymers. For constructive interference of X-rays reflected from parallel atomic layers, Bragg's law must be obeyed:

$$2d \sin \theta = n \lambda \quad (1)$$

where d = distance between the atomic layers

θ = angle of incidence and reflection of X-rays at the atomic layers

n = a constant i.e. 0, 1, 2, 3, etc

λ = wavelength of X-rays

In a typical X-ray scattering experiment, the solid sample is placed in the path of the X-ray beam and a photographic plate is arranged to receive scattered radiation. Knowing the distance between the sample and the camera plate, angle θ can be determined. Using (1) and inserting the value of λ for the radiation used and also the appropriate value of n , the d spacing can be obtained.

The reinforced waves reflected by all the small crystallites produce diffraction rings, or haloes, which are sharply defined for highly crystalline materials and become increasingly diffuse when the amorphous content is high. WAXS gives information describing the spatial arrangements of atoms in a solid material, where 2θ is greater than 3° . SAXS is useful in detecting larger periodicities such as morphological features at a high dimensional level.

The structural morphology change detected by X-ray diffraction techniques is widely used [e.g. 64, 76, 80, 160]. The technique can also detect the amorphous and crystalline nature of the material.

Depending upon segment length, block polymers (polyurethanes) may exhibit crystallinity in both the soft and hard segments. The d-spacings observed in the copolymer can generally be related to spacings found in the constituent homopolymers. However, the primary use of X-ray techniques with polyurethanes has not been in crystal structure analysis but rather in orientation studies.

Bonart [64] carried out the early X-ray diffraction studies of structure-property relationships on polyether and mixed polyester urethane-urea copolymers. He found the urethane-urea polyether segments to form discrete highly ordered regions about 25 Å in width separated by 'soft' polyether or polyester domains of about 100-200 Å in width. Polyether soft segments tended to stress crystallise, whereas polyester soft segments showed only paracrystalline behaviour. On following hard segment orientation as a function of strain Bonart found these hard segments to orient perpendicular to the stretch direction at elongations below 200%. On further stretching the hard segments were then orienting into the stretch direction. This restructuring of the hard segments was suggested by Bonart as being due to stress hysteresis, a phenomena characteristic of these polymers.

In another series of investigations [76, 80, 160], Bonart with co-workers studied a polyurethane elastomer based on hydrazine. They observed a broad amorphous halo at 0.450 nm in the relaxed samples and a weak interference ring at 1.2 nm in the WAXS photographs, indicating the absence of crystallinity. However at 500% elongation these samples showed clear fibre-type diagrams having highly oriented crystal reflexes. This was considered due to crystallisation of the soft segment polyol on extension. When elongated samples were treated with warm water the crystallinity disappeared. However, the 1.2 nm interference was found to persist which was attributed to interplanar spacings associated with hydrogen bonded hard segments.

Clough and Schneider [77, 145] et al studied domain structure in both polyether and polyester based polyurethanes. Light scattering and small angle X-ray scattering (SAXS) indicated separation into domains in both cases, but to a higher degree in polyether based polymers than in equivalent polyester based polymers. This may possibly be due to restrictions in polyester systems imposed by the interaction of the ester and urethane groups. Wide angle and small angle X-ray diffraction studies were carried out by Wilkes and Yusek [79] investigating diol extended polyether and polyester derived polyurethanes of varying urethane content. They found that the domains are generally lamellar in shape with average centre-to-centre separation of 100-250 Å. These domains were suggested to serve as crosslinks which prevent rapid relaxation of the chains, allowing stress crystallisation on high extension leading to high tensile strength in the polymer. Annealing the extended polymers caused the domains to break up and reform, relieving stress but retaining considerable orientation.

Chang and Wilkes [66] reported X-ray studies on a series of segmented polyether urethanes with polyethylene oxide, polypropylene oxide of both soft segments. Hard segments were composed of H_{12} MDI and diamines of varying structures. A series of polyether/ H_{12} MDI/diamine materials of varying soft segment/hard segment relative sizes were investigated. Only samples with high molecular weight soft segments gave crystalline reflexes. All other samples showed no evidence of crystallinity.

4E.2 EXPERIMENTAL PROCEDURE

Wide angle X-ray diffraction studies of the several polyurethanes synthesised were carried out. The polyurethanes were selected to show the effect of increasing block ratio at a constant polyol molecular weight, and the effect of polyol molecular weight at constant block ratio. The X-ray generator used in this research was a Jeol DX-GE-25 model, operating at 40 kilovolts and 30 milliamperes. Nickel filtered copper k radiation ($\lambda = 1.542 \text{ Å}$) was

used throughout, photographs being obtained using a flat plate camera. Samples in the form of a small rectangular strip (15 x 10 x 2 mm) were mounted in the path of the X-ray beam with the face of the largest surface area perpendicular to the beam. The photographs were taken using a sample to camera distance of 5.8 cm. These were developed in the normal way after exposure to the sample for 90 minutes, and the photographs were obtained by contact printing, so scattered X-rays show up as light regions on a dark background.

Diffraction traces were also taken of the same but larger samples (25 x 25 x 3 mm) under the following operating conditions. The X-ray photographs were obtained under the same power and amperage:

Power:	40 kV	Ampere:	30
Range:	8×10^3	Time constant:	2
Scan Speed:	$1^\circ/\text{min}$	Chart speed:	10 mm/min
Angle of scan from 5° to 50°			

4E.3 RESULTS AND DISCUSSION

The X-ray photographs of polyurethanes based on Capa 220:H₁₂MDI:1,4-BD were taken at each block ratio increasing from 1:3:2 to 1:9:8. These polyurethanes are transparent and their X-ray photographs produce a circular halo. There is no indication of any distinct or sharp circular patterns to suggest the presence of crystallinity in these polyurethanes. The X-ray photographs of the following polyurethanes are shown in Figures 4E3.1(a) to (d).

- Capa 220:H₁₂MDI:1,4-BD at 1:3:2 block ratio
- Capa 220:H₁₂MDI:1,4-BD at 1:5:4 block ratio
- Capa 220:H₁₂MDI:1,4-BD at 1:7:6 block ratio
- Capa 220:H₁₂MDI:1,4-BD at 1:9:8 block ratio

A circular halo is observed to be present in all these X-ray photographs.

In order to observe the effect of polyol molecular weight change, X-ray photographs of a series of polyurethanes of varying molecular weight were taken. A constant block ratio of 1:3:2 was chosen with polyol molecular weight changing from 550 to 4000. It is observed that elastomers synthesised with polyols of molecular weights up to 2000 are transparent, such polyurethanes are shown below and gave a circular halo in the X-ray photograph (some shown in Figures 4E3.2(a) and (b)) indicating no crystallinity to be present:

	Polyol m.wt	
i) Capa 200:H ₁₂ MDI:1,4-BD	550	
ii) Capa 205:H ₁₂ MDI:1,4-BD	830	all at the
iii) Capa 210:H ₁₂ MDI:1,4-BD	1000	1:3:2
iv) Capa 215:H ₁₂ MDI:1,4-BD	1250	block ratio
v) Capa 220:H ₁₂ MDI:1,4-BD	2000	

On increasing the polyol molecular weight to 3000 the X-ray photograph (Figure 4E3.3(a)) of this elastomer shows distinct circular lines in association with the halo indicating soft segment crystallisation. Increasing the polyol molecular weight further to 4000 produces even more distinct circular lines and less of the halo (Figure 4E3.3(b)) seen in the X-ray photograph and this observation is reflected in the elastomer being opaque considered to be due to soft segment crystallisation.

Diffraction traces were also carried out for the polyurethanes of Capa 220:H₁₂MDI:1,4-BD at various block ratios (Graph 4E3.1). No evidence is found of either soft or hard segment crystallinity, only a diffuse peak resulting from an amorphous arrangement of chain segments is seen. The position of the maximum in the peak shifts slightly to lower angles as the hard segment content increases. Thus as the sample changes from a predominantly amorphous H₁₂MDI/1,4-BD homopolymer, the maximum shifts from 19.2 to 18.4 degrees. The diffuse peaks observed correspond to the haloes seen in the X-ray photograph.

Diffraction traces for the varying polyol molecular weight against a constant block ratio are shown in Graph 4E3.2. A diffuse single peak is observed for the polyurethanes based on polyols of molecular weights up to 2000, indicating no soft segment crystallisation. On increasing the polyol molecular weight to 3000, two large peaks are seen at 21.0° and 23.3° on top of the diffuse peak; there is a smaller, just noticeable peak at 19.4° . These peaks correspond to the X-ray photographs showing circular lines and the crystallinity in the polymer. On further increasing the polyol molecular weight to 4000 a similar trace is observed and the peaks appear at the same angle; the 19.4° peak is more noticeable in this elastomer. The X-ray photograph shows this as distinct circular lines indicating crystallinity in the polymer.

The d spacings can be calculated from the positions of the 3 diffraction peaks using Bragg's equation

$$2d \sin\theta = n\lambda$$

$$d = \frac{n\lambda}{2 \sin\theta}$$

$$\text{at } 2\theta = 23.3,$$

$$\theta = 11.65$$

$$d = \frac{n \cdot 1.542}{2 \times 0.2019} = n \cdot 3.819$$

$$\text{at } n = 1 \quad d = 3.82$$

$$\text{at } 2\theta = 21.0$$

$$\theta = 10.5$$

$$d = \frac{n \cdot 1.542}{2 \times 0.1822} = n \cdot 4.232$$

$$\text{at } n = 1 \quad d = 4.23$$

$$\text{at } 2\theta = 19.4$$

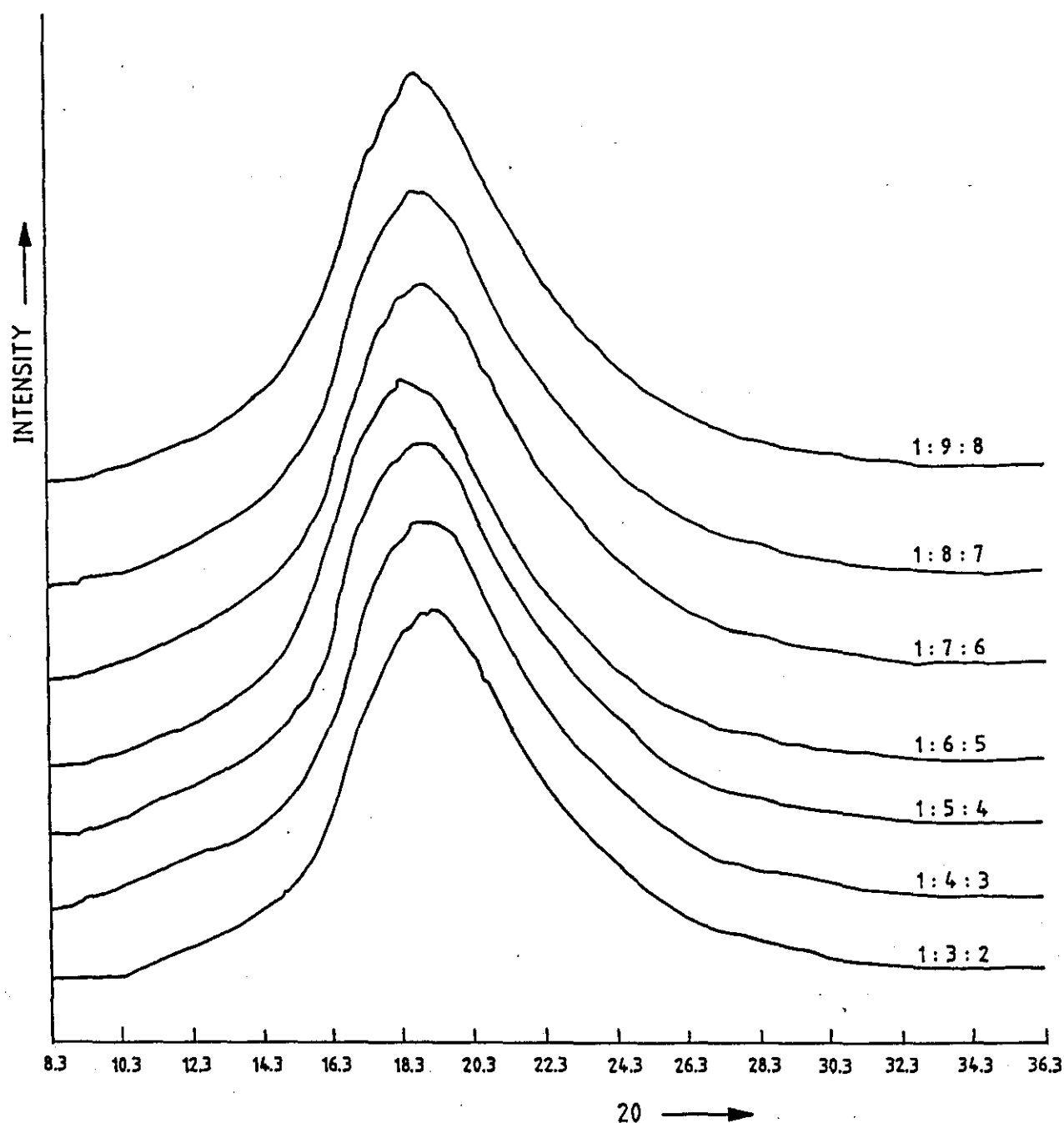
$$\theta = 9.7$$

$$d = \frac{n \cdot 1.542}{2 \times 0.1685} = n \cdot 4.675$$

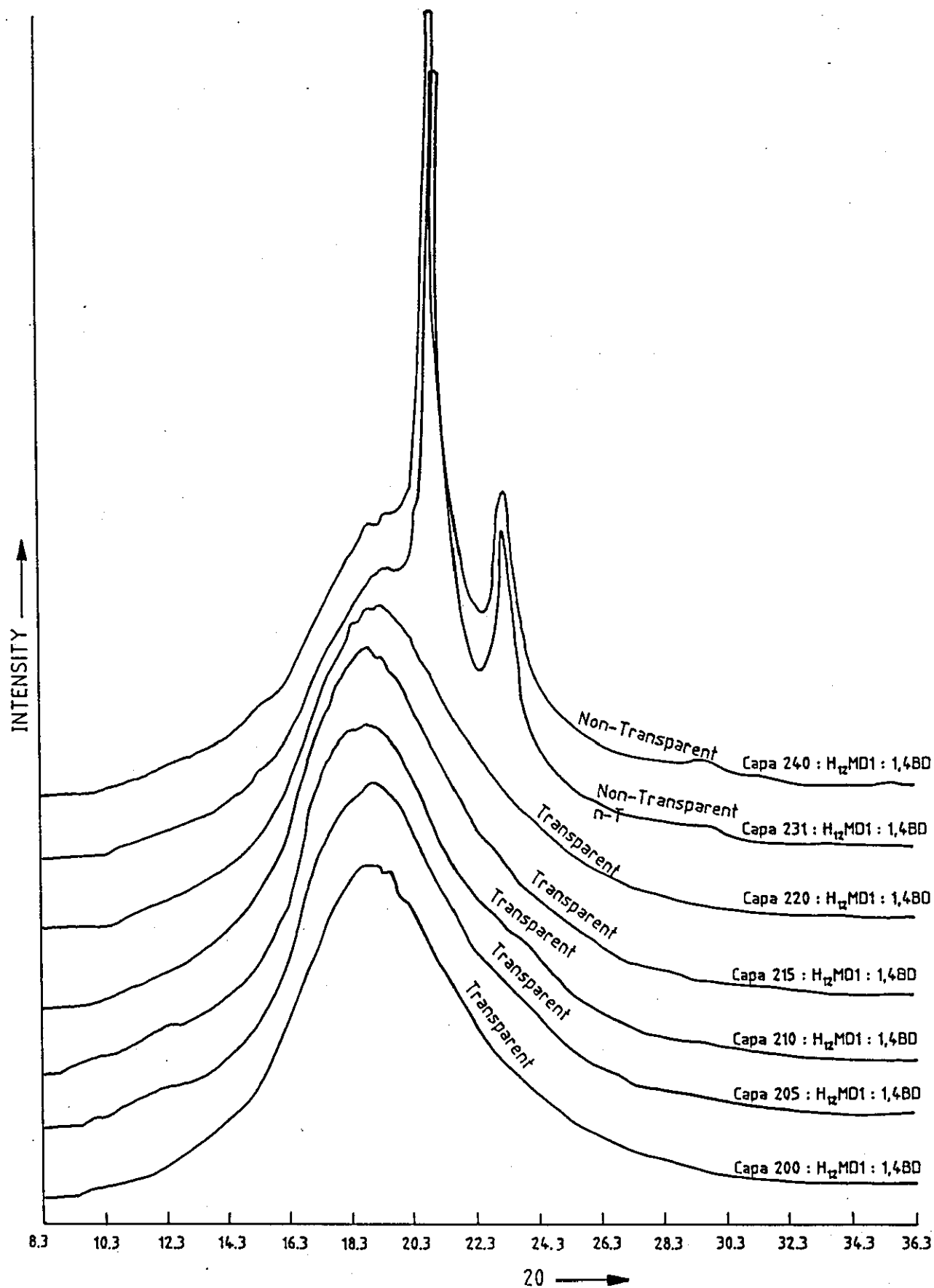
at $n = 1$ $d = 4.58$

Bragg's equation gives the d values at 3.82, 4.23 and 4.58 Å, these are in good agreement to the crystal structure proposed for polycaprolactone homopolymer [10-11] of 3.75, 4.14 and 4.57 Å, the slight variation may be due to the crystalline entity in a mixed soft-hard block morphology producing the scatter. The values for the unit cell determined for the polycaprolactone homopolymer [11] are $a = 7.47$ Å, $b = 4.98$ Å and $c = 17.05$ Å. It may be that the unit cell values for the polyurethanes would be similar as the d spacings are found to be about the same. The peak in the diffractometer trace found at 19.4° is more distinguishable in the 4000 m.wt based elastomer probably due to the higher crystalline order, producing a more opaque material and giving more intense circular lines in the photographs compared to the 3000 m.wt based polymer.

The observations made show that even at high block ratios (1:9:8) crystallinity is not induced in the Capa 220 (2000 m.wt) based polyurethane. This is due to the disruptive nature of the H_{12} MDI/1,4-BD hard segment, as the diisocyanate is a bulky molecule consisting of three isomeric forms. At the low 1:3:2 block ratio, crystallinity can however be induced by having the polyol molecular weight greater than 2000. The polyol molecular weight at which the elastomer becomes opaque depends on the nature of the diisocyanate, chain extender and on how these induce or hinder crystallinity in the final polymer.



GRAPH. 4E3 . 1. Diffractometer traces for polyurethanes based on Capa 220 : H₁₂MD1 : 1,4BD at various block ratios.



Graph 4E3 . 2 Diffractometer traces for polyurethanes at a constant 1 : 3 : 2 block ratio with varying polyol molecular weight.



FIGURE 4E3. 1(a). X-ray photograph of polyurethane based on Capa 220 : H₁₂MDI : 1,4 BD at 1:3:2 block ratio



FIGURE 4E3. 1(b). X-ray photograph of polyurethane based on Capa 220 : H₁₂MDI : 1,4 BD at 1:5:4 block ratio

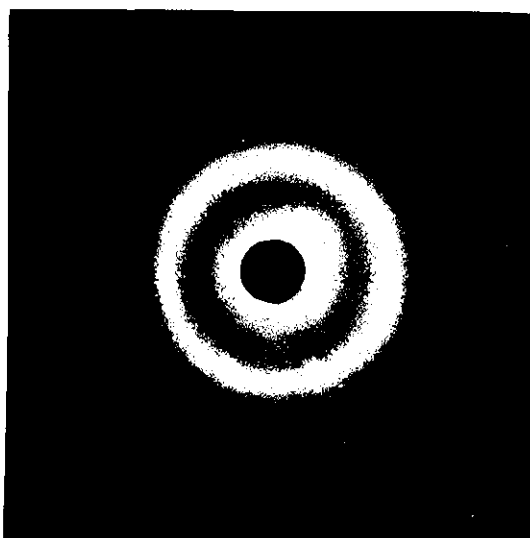


FIGURE 4E3. 1(c) X-ray photograph of polyurethane based on
Capa 220 : H₁₂MDI : 1,4 BD at 1:7:6 block ratio

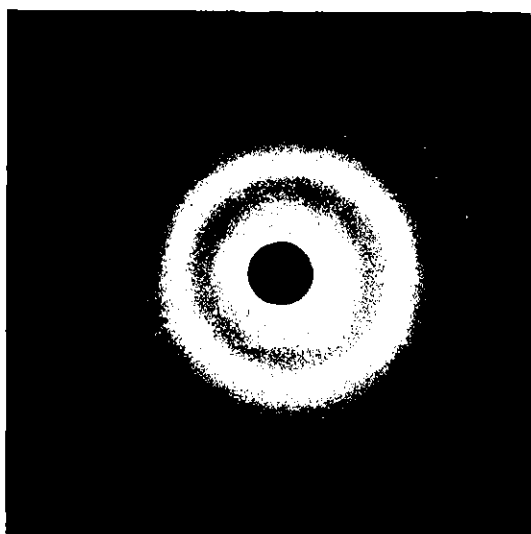


FIGURE 4E3. 1(d). X-ray photograph of polyurethane based on
Capa 220 : H₁₂MDI : 1,4 BD at 1:9:8 block ratio

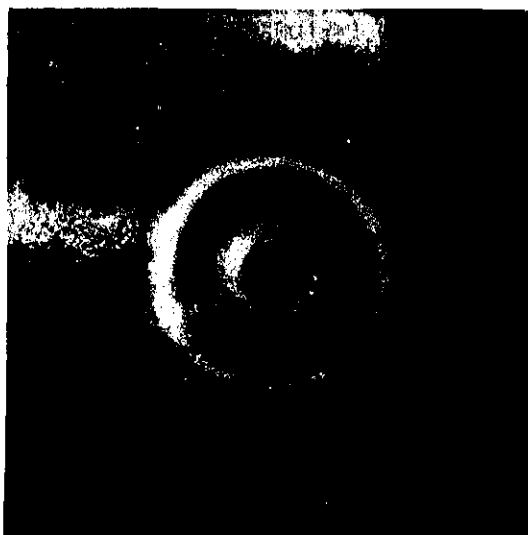


FIGURE 4E2. 1(a) X-ray photograph of polyurethane based on
Capa 200 : H₁₂MDI : 1,4 BD at 1:3:2 block ratio

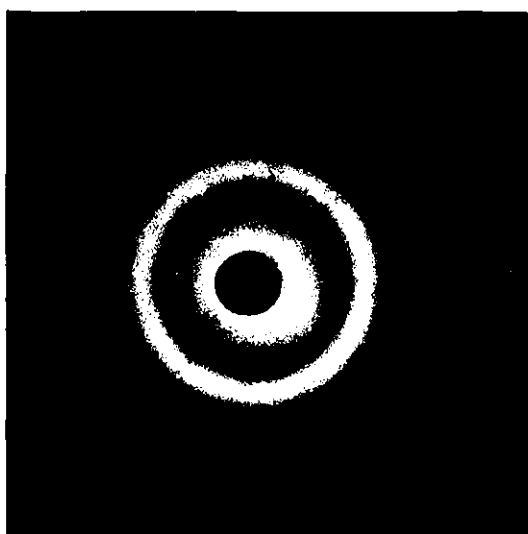


FIGURE 4E2. 1(b). X-ray photograph of polyurethane based on
Capa 210 : H₁₂MDI : 1,4 BD at 1:3:2 block ratio

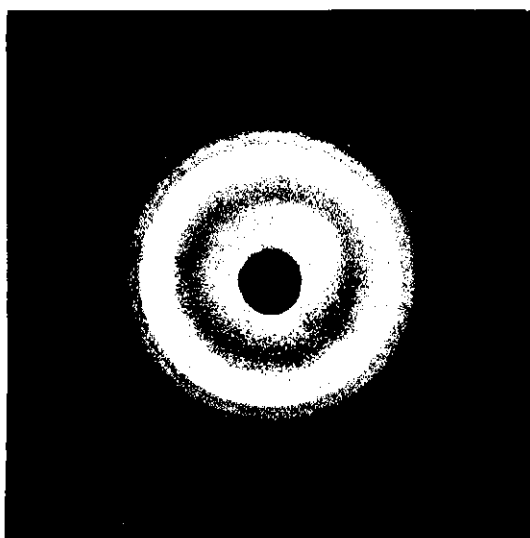


FIGURE 4E3. 3(a) X-ray photograph of polyurethane based on Capa 231 : H₁₂MDI : 1,4 BD at 1:3:2 block ratio

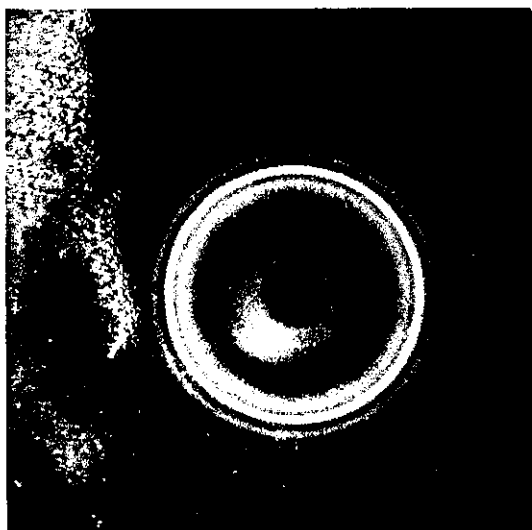


FIGURE 4E3. 3(b). X-ray photograph of polyurethane based on Capa 241 : H₁₂MDI : 1,4 BD at 1:3:2 block ratio

CHAPTER 5

GENERAL PHYSICAL AND MECHANICAL PROPERTIES

The present chapter deals with the effect of structural variation on the general mechanical properties of the polyurethane elastomers. These include tensile strength, elongation, hardness, impact and some ballistic measurements. Transparency assessment on some elastomers was carried out and Tables 5.1 to 5.5 show the elastomers prepared and observations made.

5.1 TRANSPARENCY MEASUREMENTS

A measurement of transparency was made by the use of a hazemeter (see Figure 5.1.1) to obtain a percentage haze in the material. Other methods of transparency assessments known are 'light transmittance' and 'see through clarity'. Light transmittance is the amount of light that will pass through the material without deviation and see-through clarity is regarded as a measure of distortion of the image seen through the material.

The Integrating Sphere Hazemeter consists of a light source and lens which gives a collimated beam that passes either directly or through the specimen into an integrating sphere. The inside of the sphere is coated with a highly reflective white powder. The sphere can be

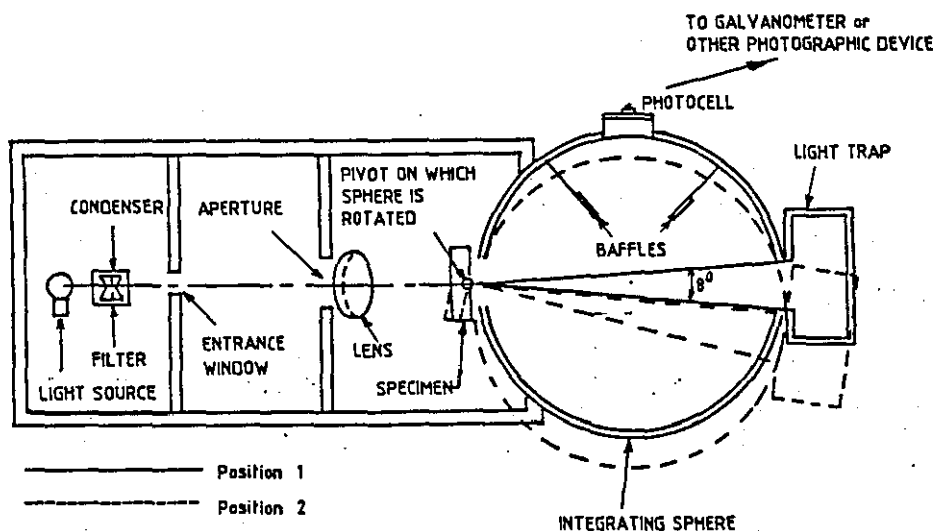


FIG. 5.1.1. DIAGRAM OF APPARATUS FOR THE INTEGRATING SPHERE HAZEMETER.

moved so that all the light entering it either passes into a light trap, or falls on the wall of the sphere where it is repeatedly reflected until it reaches a photocell. Output from the photocell is displayed on a galvanometer.

The instrument is first set to read zero on the galvanometer without the sample in position (i.e. all the light passes into the trap) and 100 when the sphere is tilted and all the available light reaches the photocell. On placing the sample in position causes the galvanometer reading to fall to a value of less than 100. The galvanometer reading is increased from its value to read 100 exactly by using the sensitivity setting. The sphere is then moved so that all the light, except that scattered by haze, passes into the light trap. The scattered light or haze then registers on the photocell which outputs the value directly on the galvanometer. When the percentage of haze is greater than 30 the material is considered to be translucent rather than transparent.

5.2 TENSILE STRENGTH PROPERTIES

The tensile strength properties of the material were carried out in accordance with BS903 Part A:1971 The JJ tensile testing machine* model T5002 was used in conjunction with an X-Y plotter (PL100 of JJ). The crosshead speed was maintained at 100 mm/min and a load cell giving a load of 500 and 5000 Newtons was used throughout. Test specimens were BS dumbbell type 2 cut from 2-3 mm thick cast sheets using a die punch cutter. Four to five specimens were used for each determination and all the samples were conditioned for at least two weeks at room temperature (25°C) and 60% relative humidity prior to testing. The following tensile parameters were calculated and the results cited in appropriate tables.

* J J Lloyd Instruments Ltd, Warsash, Southampton, England

5.2.1 Ultimate Tensile Strength

Ultimate tensile strength (UTS) is calculated from the recorded load at break using the following formula:

$$\text{UTS} = \frac{\text{Force at break}}{\text{Initial cross-sectional area}} \text{ MPa}$$

5.2.2 Modulus at 100% and 300% Strain

Modulus at a given strain (elongation) is the tensile stress at the given strain and is obtained as follows:

$$\text{Modulus (at 100\% or 300\%)} = \frac{\text{Force at a given strain}}{\text{Initial cross sectional area}} \text{ MPa}$$

5.2.3 Elongation at Break

This is calculated by subtracting the initial distance between the marked reference lines on the dumbbell test piece from the distance between the lines at breaking point. This result is expressed as a percentage of the initial distance, which was 20 mm.

5.3 RESULTS AND DISCUSSION

5.3.1 Haze Measurements

These measurements were carried out on most of the polyurethanes prepared (see Tables 5.1 and 5.5). The observations made show that almost all the elastomers prepared are transparent, except those based on paraphenylene diisocyanate (PPDI) and trans-1,4-cyclohexane diisocyanate (CHDI).

Haze is the amount of light scattered in a forward direction due to the inhomogeneity within the material. This scatter of light is

also affected by surface irregularities. This can be eliminated by first coating the sample on both sides with a liquid of the same refractive index. All the specimens were treated in this way with cedarwood oil (found to be of the same refractive index) before taking measurements.

The percentage haze for all the polyurethanes measured was well below 30% and therefore considered to be transparent. On a visual observation some elastomers appear to be slightly hazy but in fact are transparent. This is due to the elastomer surface most probably being marred from the mould imperfections. As the block ratio of hard segment content increases, there does appear to be a general increase in the percentage haze value. This would be due to increase in scattering as the amount of hard segment blocks increase in the polymer. Other trends are not so easy to observe as indicated by the values obtained.

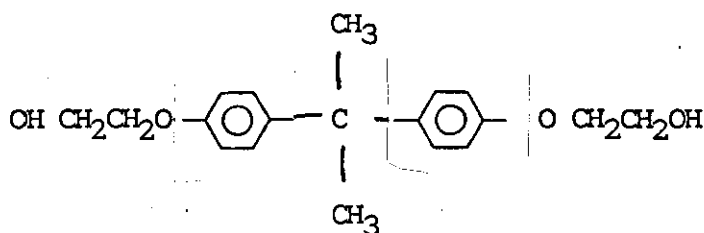
5.3.2 Tensile Strength Properties

The values obtained for the mechanical properties of the prepared thermoplastic and crosslinked polyurethanes are shown in Tables 5.3.1-5.3.4 and graphically in Graphs 5.3.1-5.3.14. In the synthesis of polyurethanes a variety of chain extenders and diisocyanates were looked at. Two diisocyanates used, namely CHDI and PPDI, produced opaque elastomers (Table 5.2). This is due to the small linear molecular structure of these diisocyanates which enhances crystallinity when chain extended with 1,4-butanediol (1,4-BD), unlike H_{12} MDI which has a bulky flexible molecular structure resulting in transparent elastomers.

On changing the chain extender to 1,3-BD, translucency was introduced. In order to disrupt further the order in the system bulky structured chain extenders, such as Dianol 22 and Dianol 33, were tried, later used in conjunction with crosslinking chain extenders.

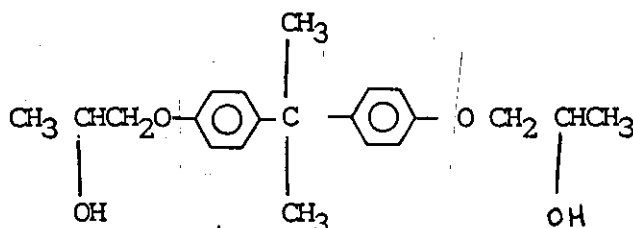
Dianol 22, 1,1'-isopropylidene-bis-(p-phenylene-oxy)-di- β -ethanol

MWT 316



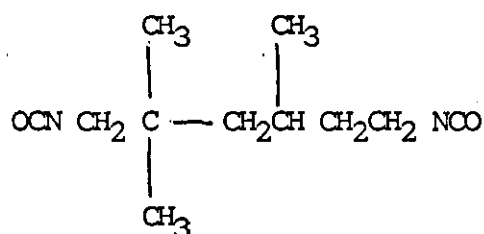
Dianol 33, 1,1'-isopropylidene-bis-(p-phenylene-oxy)-di- ω -propanol-2

MWT 344

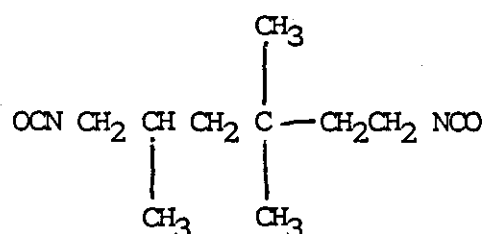


These again produced translucent polyurethanes. Two reasons became known as to the cause of this hazy effect. One was that CHDI and PPDI dimerize with time and so to produce transparent polymers distillation of the diisocyanate has to be carried out immediately prior to the synthesis. The other reason is the presence of organochlorides which may significantly affect the transparency of the final polymer. In either situation, distillation is necessary and this was considered too hazardous to carry out. There may, however, be a more suitable grade of these diisocyanates available in the near future which may give transparent polyurethanes without the need to distill.

Transparent polyurethanes were also synthesised with TMDI.

TMDI

2,2,4-trimethyl hexamethylene
diisocyanate (TMDI)



2,4,4-trimethyl hexamethylene
diisocyanate (TMDI)

The elastomers produced were soft and remained flexible at high block ratios (Table 5.3.2). This is due to the long linear structure of the diisocyanate, the transparency occurs due to its bulky irregular structure and presence of two isomeric forms.

Isophorone diisocyanate (IPDI) generally gave transparent rigid elastomers but tended to give brittle failures on impact (see later) and so the bulk of the work concentrated on 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI) based elastomers.

5.3.3 Thermoplastic Polyurethane Elastomers

The polyurethanes based on caprolactone polyols, H_{12}MDI and 1,4-BD (Table 5.3.1) show the following trends on increase in block ratio:

- i) On increasing the block ratio for any molecular weight polyol shown results in an increase in the hardness of the elastomer (Graph 5.3.4). The observations made show this change by the increase in rigidity with block ratio. This is to be expected so when the soft segment content remains constant while hard segment increases then stiffness and hardness also increase

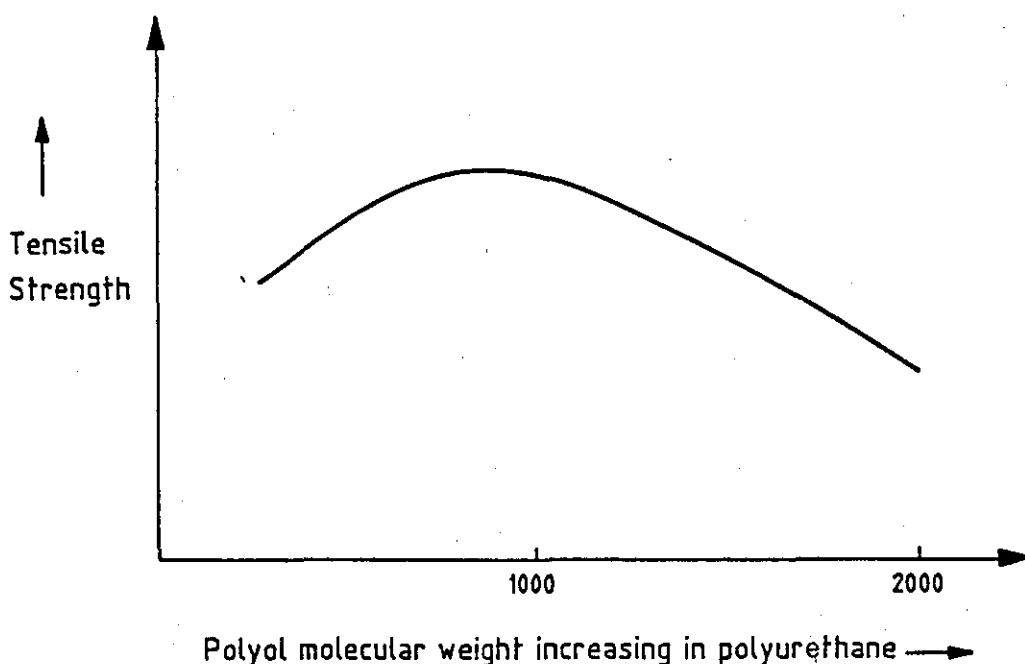
- ii) The increase in hardness and rigidity is more pronounced in the lower molecular weight polyol based elastomers. As with high polyol molecular weight the extent of rigidity and hardness is lower, due to the lower hard segment content in comparison (Table 5.1, Graph 5.3.7)
- iii) The modulus at 100% elongation increases with block ratio (Table 5.3.1, Graph 5.3.2) whereas the tensile strength increases to a certain block ratio then falls again. This is observed in the range of polyols used (Table 5.3.1, Graph 5.3.1). The tensile strength when plotted against hard segment content (Tables 5.1 and 5.3.1, Graph 5.3.5) for these elastomers, shows that the tensile strength increases up to a hard segment content of 56-62% (depending on polyol used), then decreases. This is to be expected as hard segment content increases the tensile property increases up to the stage when rigidity and brittleness take over reducing this strength.
- iv) The elongation of the elastomer decreases with increase in block ratio (Table 5.3.1, Graph 5.3.3) as explained earlier.

The trends observed by varying the molecular weight of the polyol at a particular block ratio are shown to be:

- a) The hardness values are higher for the higher block ratios (Table 5.3.1, Graph 5.3.10) as expected. On increasing the polyol molecular weight the hardness decreases, due to increase in soft segment content. However, the hardness is seen to increase above the polyol molecular weight of 2000 (Table 5.3.1, Graph 5.3.10). It is noted that elastomers based on polyols greater than 2000 molecular weight are opaque (Table 5.1) due to soft segment crystallisation, which in turn increases the hardness value of the elastomer.

- b) The elongation values (Table 5.3.1, Graph 5.3.9), increase with increasing polyol weight as expected
- c) The tensile strength does not increase as expected with polyol molecular weight but shows low values at 830 (Capa 205) and 1250 (Capa 215) molecular weights (Table 5.3.1, Graph 5.3.8). This is observed for all the block ratios shown with highest tensile values for the 1000 (Capa 210) molecular weight polyol.

It can be expected that for lower block ratios (as shown) a pronounced trend can be observed such that the elastomer based on 1000 molecular weight polyol has the highest tensile strength. The hard segment content for polyol molecular weights lower than 1000 at a constant block ratio will be greater and would show lower tensiles due to the rigid, brittle nature of the elastomer. The hard segment content for polyols of higher molecular weight than 1000 would be lower and reduce tensile property as the elastomer is too flexible.



This shows that the 1000 molecular weight polyol based elastomer shows optimum properties when chain extended with 1,4-BD and in this respect the general trend is followed. However for Capa 205 and Capa 215 the tensiles are much lower than the trends would predict. The main reason for this, as explained in an earlier chapter, is the manufacture of the polyols. It was found that catalysts were already incorporated in these polyols, for their special end use applications. The type and concentration of catalyst varied for each polyol. It is shown that Capa 205 and Capa 225 have a lower catalyst content or activity as employed in comparison to the other polyol. It is also to be noted that catalyst may not be required at low polyol molecular weights. As the concentration of hydroxyl groups per unit length is high enough a reasonable reactivity can be achieved without the need for an initiator system such as a catalyst.

On changing the chain extender from the 1,4-BD does have a significant variation on the properties of the final polymer as shown below:

- 1) On changing the chain extender from 1,4-BD to 1,3-BD a similar trend is observed. The hardness increases with block ratio along with a decrease in elongation. The tensile strength increases with block ratio then falls at very high block ratios, due to the high hard segment content. Table 5.3.3.1 below shows a comparison of the properties obtained for 1,4-BD and 1,3-BD chain extended elastomers

Physical property	Chain extender used	BLOCK RATIO							
		1:6:5		1:7:6		1:8:7		1:9:8	
		1,4-BD	1,3-BD	1,4-BD	1,3-BD	1,4-BD	1,3-BD	1,4-BD	1,3-BD
Hardness Shore D		44	33	53	43	56	55	60	62
Elongation (%)		360	390	340	370	330	360	320	330
Tensile strength (MPa)		48.2	41.1	54.4	44.6	60.5	49.2	49.9	56.1

TABLE 5.3.3.1: PROPERTIES OF CAPA 220/H₁₂MDI BASED ELASTOMERS CHAIN EXTENDED WITH 1,4-BD AND 1,3-BD AT VARIOUS BLOCK RATIOS

The 1,3-BD chain extended elastomer shows lower hardness and tensile except at very high block ratios. The tensile strength is lower for 1,3-BD as it disrupts the alignment of soft segment and hard segment chains, due to its molecular structure. The 1,4-BD being linear reinforces this alignment process on stretching thus giving higher tensile properties. The 1,4-BD extended elastomer shows higher hardness values achieved through the whole molecular structure being more closely packed in comparison to 1,3-BD elastomers.

At high elongations the elastomer goes through the stress induced crystallisation process which is more favoured by the 1,4-BD based elastomer. The 1,3-BD based elastomer also goes through this process but requires greater elongation in achieving this, and this is borne out in the higher elongation values being obtained. It is seen that at high block ratios, the 1,3-BD based elastomer shows the greater tensile strength. On observing the trend for tensile properties against block ratio (Table 5.3.1, Graph 5.3.1) for 1,4-BD elastomers, it is seen that the tensile strength rises to a maximum then falls again at high block ratios. In the case of 1,3-BD based elastomer the optimum strength is achieved at a comparatively higher block ratio (Table 5.3.1) due to its difference in molecular structure.

- ii) The other chain extenders used were 1,6-hexanediol (1,6-HD) and a 1:1 equivalent mixture of 1,4-BD and 1,4-CHDM (1,4-cyclohexanedimethanol). Tables 5.3.3.2 and 5.3.1 with Graphs 5.3.11 and 5.3.12 compare their properties

Property	Chain Extenders		
	1,4-BD	1,4-BD+1,4-CHDM	1,6-HD
Hardness (Shore D)	65	74	55
Elongation (%)	320	220	470
Tensile (MPa)	40.3	31.8	48.6

TABLE 5.3.3.2: PROPERTIES OF ELASTOMERS BASED ON CAPA 205/H₁₂MDI CHAIN EXTENDED WITH THOSE SHOWN AT A BLOCK RATIO OF 1:4:3

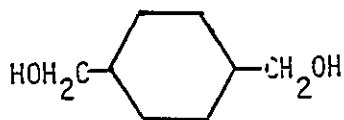
The 1,6-HD is a longer chain extender than 1,4-BD and consequently gives higher elongation and lower hardness. It is for this reason that 1,6-HD was used with low molecular weight polyols which would normally be too rigid and brittle with 1,4-BD. The tensile strengths of 1,6-HD extended elastomers are generally higher, due to the increased alignment of chains introduced. At low polyol molecular weight (Capa 200) the tensile strengths of 1,6-HD and 1,4-BD extended elastomers are very similar, the 1,6-HD being slightly lower. It is expected that the 1,6-HD would have the higher tensile value, but it is noted that not a proper comparison of block ratios is made i.e:

1,4-BD	1,6-HD
1:3:2	1:2.9:1.9

The next ratio for 1,6-HD used is 1:3.3:2.3 which also shows lower tensile strength values. The maximum tensile strength (as observed with 1,4-BD based elastomers) of these elastomers may fall in between the ratio 1:2.9:1.9 and 1:3.3:2.3 or slightly lower block ratio. It is also of interest that the Capa 210 and Capa 200 give the higher tensile values in comparison to Capa 215 and Capa 205 based elastomers, as observed earlier.

On using the mixed chain extender system of 1,4-BD and 1,4-CHDM at 1:1 equivalent mixture, generally gave lower tensile values and

elongation (Tables 5.3.3.2 and 5.3.1) in comparison to 1,4-BD extended elastomers. This is consistent with the effect of changing the chain extender from the more flexible 1,4-BD to greater rigidity introduced by 1,4-BD+1,4-CHDM mixed system. This rigidity is introduced due to the molecular structure of 1,4-CHDM



1,4-cyclohexanedimethanol

On increasing the polyol molecular weight to 2000 (Table 5.3.1) the tensile strength of the mixed chain extender system based elastomer is slightly higher in comparison to the 1,4-BD elastomer. At this high molecular weight the flexible nature of the polyol becomes important and may override the rigidity introduced by the mixed chain extender. This would then give reinforcement by the alignment of chains and in so doing increase the tensile strength. Once again it is seen (Table 5.3.1) that the Capa 210 and Capa 200 have better tensile properties in comparison to the Capa 215 and Capa 205 based elastomers.

On changing the aliphatic isocyanate from H₁₂MDI to other isocyanates the following observations were made:

- a) TMDI, as explained earlier, gave very soft and flexible transparent elastomers, whereas PPDI gave hard more rigid but opaque elastomers. CHDI also produced rigid, but opaque polymers which generally gave highest hardness values in comparison to the H₁₂MDI and IPDI based elastomers
- b) The polyurethanes based on Isophorone diisocyanate (IPDI) were transparent, except the one at low block ratio (1:3:2) based on the 2000 molecular weight polyol (Capa 220). On increasing the block ratio for this polyol system produced a transparent elastomer. The translucency is observed at the low block ratio as the amount of hard segment content is low and the molecular

structure of IPDI is not great enough to disrupt the crystallinity under the synthesis method used.

In comparison to H_{12} MDI the tensile strength of IPDI is lower for Capa 220 and Capa 210 (not for Capa 215 and Capa 205), although with increasing block ratios the tensile values become closer together (Tables 5.3.1 and 5.3.2, Graph 5.3.13). The hardness values of IPDI are generally lower than for H_{12} MDI at low block ratio (especially Capa 210) which become closer at higher block ratios (Tables 5.3.1 and 5.3.2, Graph 5.3.14). The elongation at break values are generally greater for IPDI based elastomers.

As the IPDI structural configuration would tend to disrupt the alignment of chains, a lower hardness value at low block ratios is obtained. At high block ratios the contribution of the excessive hard segment present and the rigidity of the IPDI structure give higher hardness values in comparison. The tensile values of IPDI are lower for similar reasons, the disorder introduced reduces the stress induced crystallisation process to occur.

The elastomers based on Capa 215 and Capa 205 show similar trends for tensile strength, which is actually greater for the IPDI based elastomers. In the synthesis of IPDI based elastomers, an external catalyst (DABCO at 0.1 pbw) was used. The influence of this catalyst on the polyols may have produced the difference in tensile trends for Capa 220, Capa 210 and Capa 215, Capa 205. The Capa 200 based elastomer shows little variation in property in comparison with IPDI and H_{12} MDI, probably due to the rigidity introduced by its own low molecular weight.

5.3.4 CrossLinked Polyurethane Elastomers

The thermoplastic polymers produced a trend for the flexible nature of the elastomer. This shows that for each molecular weight based polyol a certain block ratio produces an elastomer which was neither brittle nor too flexible, as shown below:

Polyol m.wt (HI2MDI/1,4-BD based)	1:3:2	1:4:3	1:5:4	1:6:5
550	✓			
830		✓		
1000			✓	
1250				✓

TABLE 5.3.4.1: SHOWS THE BLOCK RATIO AND POLYOL m.wt NEEDED TO
PRODUCE \uparrow a BRITTLE NOR TOO FLEXIBLE AN ELASTOMER
neither

These block ratios and corresponding polyol molecular weights were used in some of the crosslinking systems prepared. Two basic types of crosslinking systems were introduced from the basic build of the elastomer i.e.

Polyol : Diisocyanate : Chain Extender NCO/OH = 1

The first type of crosslinking was introduced via the chain extender, by using a diol and triol mixed system e.g. 1,4-BD+TMP. This produces lightly crosslinked polyurethanes, as the amount of crosslinking present in the whole system is small. The second type of crosslinking was by replacing the difunctional polyol to a tri- and tetrafunctional polyol. This gives highly crosslinked polymers as the crosslinking present is considerably higher.

i) Lightly crosslinked systems

These were prepared by using diols namely 1,4-BD, Dianol 22 and Dianol 33, with the trimethylolpropane (TMP) and Capa 305 triols. Six systems are possible with these diol and triol combinations at an equivalent ratio of 1:1 with a further six at a 1:0.5 ratio, respectively. The Table 5.3.4.2 below shows the combinations used:

Combination of Diol and Triol	Ratio of Combination	
	1:1	1:0.5
1,4-BD + TMP	✓	✓
1,4-BD + Capa 305	✓	✓
D22 + TMP	✓	✓
D22 + Capa 305	✓	✓
D33 + TMP	✓	✓
D33 + Capa 305	✓	✓

TABLE 5.3.4.2: CHAIN EXTENDER SYSTEMS FOR LIGHTLY CROSSLINKED POLYURETHANES

A formulation was selected from Table 5.3.4.1, this being Capa 205 (830 m.wt) at 1:4:3 block ratio, which was then used with the above crosslinking systems. The properties measured for these elastomers are summarised in Table 5.3.4.3.

Properties and Ratio	CHAIN EXTENDERS					
	1,4-BD+ TMP	1,4-BD+ Capa 305	D22+ TMP	D22+ Capa 305	D33+ TMP	D33+ Capa 305
UTS						
1:1	34.4	42.9	B	49.8	B	43.3
1:0.5	26.5	40.7	31.0	43.8	B	24.0
% Elongation						
1:1	280	430	B	370	B	340
1:0.5	310	510	110	340	B	290
Hardness (Shore D)						
1:1	68	28	81	59	81	63
1:0.5	65	50	82	78	80	77

B = Brittle

TABLE 5.3.4.3: PROPERTIES OF CAPA 205/H₁₂MDI WITH VARIOUS CHAIN EXTENDERS AT A BLOCK RATIO OF 1:4:3

It is generally observed that the chain extender with Capa 305 gives higher tensile strength values than the TMP based and the thermoplastic 1,4-BD based. This is due to the crosslinking introduced and the more flexible nature of Capa 305 in comparison. Reducing the Capa 305 content in the chain extender (Table 5.3.4.3) increases the hardness and reduces the elongation due to the lower flexibility present in the system. The tensile strength also decreases as this crosslinking is reduced. The Dianol 22 and Dianol 33 are fairly bulky, rigid structures, especially when crosslinked. The Dianol 22 is more flexible as its hydroxyl groups appear at the end of the chains, which give higher elongation values as observed (Table 5.3.4.3). On crosslinking with TMP a rigid, brittle elastomer is produced, with Capa 305 the elastomer is not brittle.

The 1,4-BD+TMP extended elastomers show on comparison with 1,4-BD (Tables 5.3.1 and 5.3.4.3) elastomers, a lower tensile and similar hardness. Tensile strength is expected to be lower as TMP being small and trifunctional introduces the brittleness characteristics, however along with this the hardness should be greater than those found. Some trends that do not follow may be associated with the synthesis and appearance of the final polymer. On several occasions the elastomers produced, developed a crinkled surface on curing, frost glass type appearance also occurred. This may suggest that the surface reactivity is greater than at the base of the mould. Presence of moisture may react faster with the triol than the diol, another likely explanation is the possibility of the diol and triol not being fully homogeneous. This problem was overcome by ensuring the chemicals are dry and by increasing the mixing times at the chain extension (crosslinking) stage. Other trends not observed may also be due to the varying high hard segment content, with the elastomers not reacted at the optimum ratios for best physical properties.

A number of chain extenders were selected from Table 5.3.4.3 all at 1:1 ratio for better comparison. All the chain extenders with Capa 305 were selected due to the higher strength values obtained; 1,4-

BD+TMP was also chosen for comparison (Table 5.3.3). These selected chain extender systems were then used with the differing polyol molecular weights at the block ratios shown in Table 5.3.4.1. The physical properties of those obtained are given in Table 5.3.3. This shows that the Capa 305 chain extender systems in comparison with the TMP systems generally show higher tensile, greater elongation and lower hardness properties. This is due to the greater flexibility introduced by Capa 305 on comparison with TMP.

On comparing only the Capa 305 based extender (Table 5.3.3) the Capa 305/1,4-BD generally gives higher tensile values than Capa 305/D33 extender, as the flexibility is decreased with D33. The Capa 305/D22 extender generally gives higher tensile on comparison with Capa 305/D33 and Capa 305/1,4-BD (also 1,4-BD+TMP). The D22 is more linear than D33 giving better properties. The combination with Capa 305 (Capa 305/D22) is probably more reinforcing and thus gives better properties than Capa 305/1,4-BD. The trends are not so apparent at low polyol molecular weights (Capa 200), as other factors become involved, such as the similarity of polyol and Capa 305 molecular weight.

The 1,4-BD/TMP chain extender generally gave the highest hardness, followed by D33/Capa 305 than D22/Capa 305 and lowest for 1,4-BD/Capa 305. This is expected from the individual molecular structures of the chain extenders, hard segment content and varying optimum block ratio.

ii) Highly crosslinked polyurethanes

These elastomers gave much better tensile properties (Table 5.3.4) with very low elongations as expected, due to the high level of crosslinking present. The crosslinking, as explained earlier, was introduced via the polyol by substituting the diol by the tri- and tetra-functional polyols. The IPDI based elastomers gave higher tensile and hardness in comparison to H₁₂MDI, due to its more rigid structure with lower elongation. On increasing the block ratio, the

strength properties increase as the hard segment content increases while the amount of crosslinking polyol remains constant. Above a certain block ratio, the tensile property falls (e.g. tetra-ol 1000/IPDI/1,4-BD at 1:4:3, Table 5.3.4) as seen with other systems already described. The elongation decrease and hardness increase as expected with rise in block ratio.

The increase in tensile strength on comparison of thermoplastic and crosslinked elastomers is due to the high crosslinking introduced. The H_{12} MDI based elastomers tend to give higher elongation than IPDI due to its more flexible linear structure. As the synthesis method is the same for both, a similar crosslinking should be effected. The IPDI, however, is more reactive than H_{12} MDI and consequently would be more crosslinked and thus give higher tensile properties.

5.4 DENSITY

Density is defined as mass per unit volume. The density of a polymer may in some cases be critical to the ultimate end use potential as lower density will occupy more volume or cover more surface per mass than a polymer of higher density.

The displacement method was used to measure density of the sample at room temperature (23°C) according to method 509A of BS 2872:1970. Fine wire is used for the suspension of the specimen and care is taken to avoid air bubbles on the specimen causing variations in weight measurements. Values of density are calculated according to the following formula:

$$\text{Density} = \frac{\omega_1}{\omega_1 - \omega_2} \times \rho$$

where ω_1 = weight of specimen in air

ω_2 = weight of specimen in water

ρ = density of water usually taken as 1 g/cm³

5.4.1 Results and Discussion

Table 5.4.1 shows the density measurements taken. The expected trends are observed with increase in density with block ratio. At constant block ratio and decreasing polyol (soft segment) molecular weight there is a general increase in density as the hard segment content increases. This trend however, is not observed with the Capa 215 and Capa 205 based polyurethanes and is also noticed with the physical properties tested. The main reason found for this is in the manufacture of all the polyols used, where Capa 215 and Capa 205 are known to contain a differing catalytic activity than the other polyols.

TABLE 5.4.1: DENSITY MEASUREMENTS ON POLYURETHANES BASED ON CAPA POLYOLS: H_{12} MDI:1,4-BD AT VARYING BLOCK RATIOS

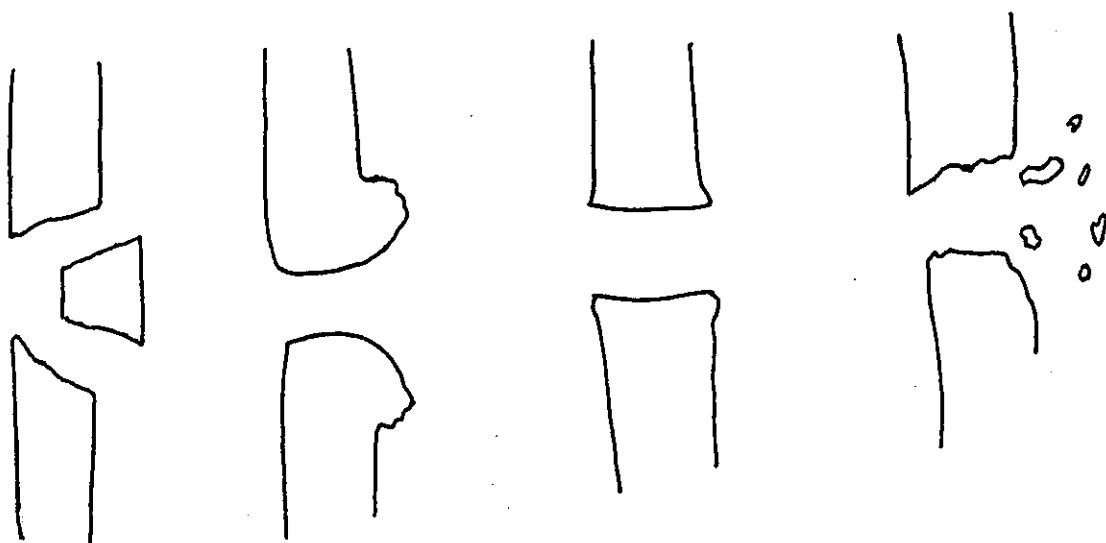
Block Ratio Capa:Dew: 1,4-BD	1:3:2	1:4:3	1:5:4	1:6:5	1:7:6	1:8:7	1:9:8
Capa 220	1.1191	1.1207	1.1221	1.1234		1.1266	1.1292
Capa 215	1.1201	1.1361					
Capa 210	1.1265	1.1307	1.1313	1.1324	1.1319	1.1282	
Capa 205	1.1348	1.1401					
Capa 200	1.1319	1.1326					

5.5 IMPACT AND BALLISTIC PROPERTIES

In efforts to analyse material for impact and ballistic resistance, a number of practical and theoretical considerations need to be addressed dependent on the end use. In the construction of face visors polycarbonate (manufactured by Bayer and GE under the tradenames Lexan and Makrolon) at present is mainly used as it has sufficient impact and ballistic resistance. The optical clarity of polycarbonate is however readily degraded by surface abrasion and

its impact resistance is very sensitive to surface scratches, which can also be aided when in contact with a stress cracking solvent.

Penetration of the material may be defined as the entrance of a missile (striker) into the target without completing its passage through the body; this action involves either the embedment or rebound of the striker and the formation of a crater. Physically failure appears to occur by a combination of the various patterns shown (Figure 5.5a), with one of the mechanisms predominating.



Plug formation Petal formation Ductile hole Fragmentation

FIGURE 5.5a: A VARIETY OF THE FAILURE PATTERNS OBSERVED ON PROJECTILES IMPACTING INTO A POLYCARBONATE SHIELD

Ballistic performance and hardness of materials are both affected by changes in copolymer formulation. The relationship of ballistic strength (V_{50}) against hardness (Figure 5.5b) has been noted for TDI-based (A.F. Wilde et al [31]) polymers which undergo ductile failure. The ballistic strength (V_{50}) is an estimate of the mean velocity at which an average 50 per cent of the projectiles striking the target will defeat it. A defeat is considered to have occurred when there is a through hole in the target which allows the projectile to pass through.

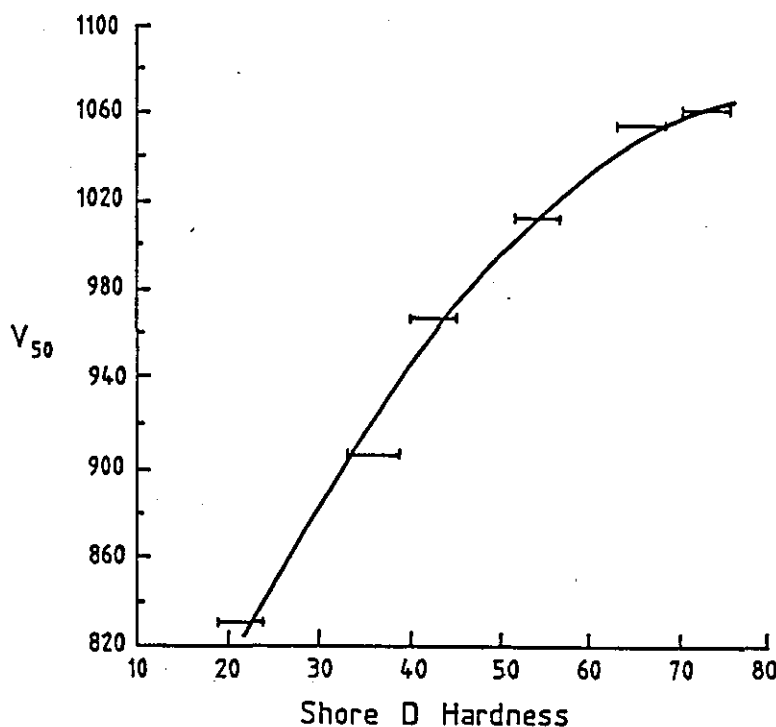


FIGURE 5.5b: BALLISTIC PERFORMANCE AS A FUNCTION OF SPECIMEN HARDNESS FOR 2,4-TDI/PTMO/BD BLOCK COPOLYMERS DISPLAYING DUCTILE FAILURE CHARACTERISTICS

An example of this general relationship for polymers which undergo ductile failure to ballistic impact was observed when polycarbonate was block copolymerised with various amounts of polydimethylsiloxane, a silicone rubber [6]. An explanation was made as follows: as long as the predominant response is ductile, the failure occurs by a plastic deformation process. The impact resistance of such a material may well depend upon its yield

strength because this is the energy absorbed during plastic deformation. Addition of further rubber (or soft segment material) would simply lower the yield strength without changing the deformation mechanism and this would only decrease the ballistic performance.

In the transparent armour application, further investigations with the TDI/PTMO/1,4-BD formulation were carried out [34]. The ratio of soft segment to hard segment has been shown to be quite sensitive to ballistic performance in a ductile response situation. In this case the lower the soft segment the greater the ballistic value. To locate the optimum composition, specimens composed of the standard TDI/PTMO and butanediol were synthesised with further reductions in the soft segment content to bring it down to 24.3 weight percent (Figure 5.5c).

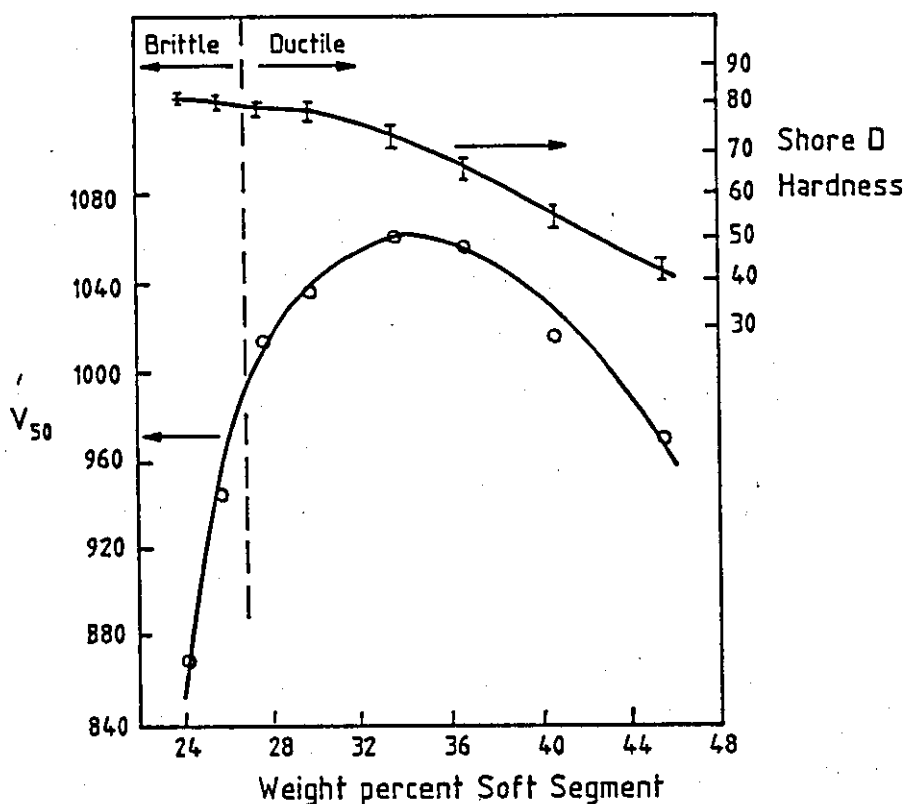
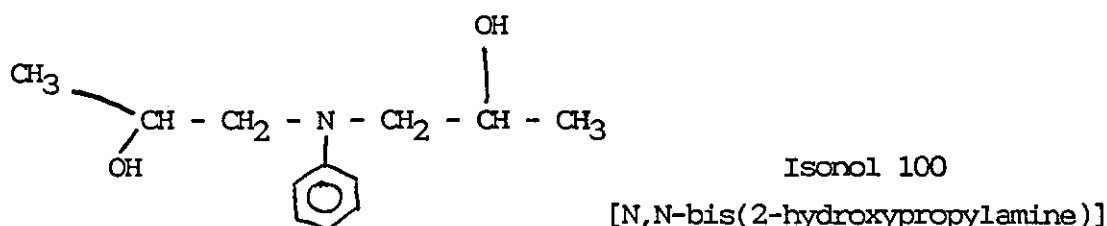


FIGURE 5.5c: V_{50} AND HARDNESS AS FUNCTIONS OF SOFT SEGMENT CONTENT FOR THE BUTANEDIOL SERIES

It was observed that the highest V_{50} value occurs at a soft segment content of about 34 weight percent. Further reductions in the soft segment content cause both a sharp decrease in V_{50} and an eventual change in failure mode from ductile to brittle. Concurrently the hardness continues to increase slightly. In the brittle response region, therefore, it is found that an increase in hardness is accompanied by a decrease in ballistic performance.

A similar series of experiments were carried out using Isonol 100 instead of 1,4-butanediol and similar general trends were observed



An ideal ballistic material should have a high degree of hardness to form a rigid structure, yet respond in a ductile fashion. The butanediol series approaches this ideal more closely. A simple comparison of the molecular structures of these two diols shows that butanediol (molecular weight 90) is more compact than Isonol 100 (molecular weight 209).

In another series of experiments the molecular weight of the PTMO was changed from the nominal 1000 to 670 and 2000 to observe the effects. The specimens were formulated with TDI and butanediol to give soft segments of weight percentages similar to the standard specimens already investigated. The PTMO 670 specimens were similar in appearance and properties to those observed for materials based on PTMO 1000, being clear and transparent, whereas the PTMO 2000 specimens were white, opaque, soft and flexible. The hardness decreases with increasing PTMO molecular weight, the V_{50} is found to be greatest for PTMO 1000, the ballistic responses are ductile however there is some evidence of a transition to brittleness beginning to appear in the PTMO 670 specimen. The opacity, softness

and poor ballistic performance of the PTMO 2000 molecular weight specimens are considered due to the longer segment lengths of the PTMO 2000 polyol which also allows the polymer to crystallise to a degree sufficient to cause loss of transparency. Also these longer or more fully developed polyether domains impart a higher degree of softness or flexibility to the specimen. Small amounts of TMP (0.2, 0.4, 0.6 and 0.8 moles) were added to the formulation, with the overall total number of moles of chain extender remaining constant (1,4-butanediol + TMP). The hardness was found to increase with TMP content, but no obvious trend relating TMP content to impact strength was noticed with the ballistic tests, which all gave ductile failures. It appears that there is insufficient TMP present in the whole system to produce a change to brittle failure.

5.5.1 Impact Strength, Results and Discussion

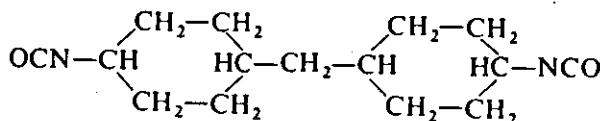
There are basically three types of impact tests which are published as British Standards for the specimen thicknesses used in the present work. These are the Izod test, the Charpy test and the Falling Weight Impact Strength test (FWIS). The FWIS is probably, in this instance, the most useful type of impact strength determination as the test is usually performed on actual finished products or on samples cut from them. The end use service performance is therefore more likely to be simulated in terms of the impact strength mode for the present work. The FWIS test is widely used for the testing of film, sheet and pipe where the sample is struck by a weight attached to a striker which falls from a constant height. By testing a number of specimens the energy which on average causes 50 percent of the samples to fail is determined. There are several factors which affect the measurement of impact strength and need to be standardised, such as the test temperature. It may be that some plastics undergo a ductile/brittle transition at the test temperature and this will affect the impact strength. Tests carried out below this transition temperature would produce a marked drop in impact strength.

The tests carried out on our specimens were to the BS 2782 method 306B at the SCRDE (MOD) Colchester, using a modified 1/4 inch diameter hemispherical impact head and consists of a vertically falling dart impacting on a square piece of material in sheet form. This type of head is more severe on impact in comparison with the 1/2 inch diameter hemisphere type of head used in the BS 2782. In a riot situation, a stone thrown at a visor or shield may either have a sharp or a blunt surface in contact at the point of impact. The drop height of this FWIS test method used is 2 metres, the maximum impact velocity generated from this height is 6.26 metres/second, whereas the maximum velocity of a thrown stone is believed to be 20 metres/second. Using increasing weights in the test raises the energy on impact, for example a weight of 2.216 kg at the 2 metre drop height has an impact energy of 19.6 joules. The impact resistance for a polycarbonate sample of 3 mm thickness just fails at an impact energy of 21-22 joules. The FWIS results will be used in conjunction with ballistic results for their assessment. In the ballistic test, velocities of several hundred metres per second are typical. The apparatus used for these samples at Colchester was made by Davenport, before testing samples are conditioned for a minimum of 3 hours at 23°C and 65 percent relative humidity. In a standard test a minimum of twelve samples was used although twenty samples are preferred and results averaged.

IPDI Series: Using polyurethanes synthesised in this research, the initial impact tests were carried out on two IPDI formulations (Table 5.5.1e). These were based on Capa 220:IPDI:1,4-BD at the block ratios 1:9:8 and 1:5:4 along with Capa 210:IPDI:1,4-BD at the block ratios 1:9:8 and 1:7:6. These were selected as they gave comparable hardness values to polycarbonate. It was observed that the Capa 220 based elastomers showed some ductile failure modes, whereas the Capa 210 polyols always failed in a brittle manner. The Capa 220 based elastomer has twice the average molecular weight (2000) of the Capa 210 and therefore has sufficient soft segment content to change the failure mode from brittle to ductile even at

the high OH/NCO block ratios used. In formulating with Capa 220 a high block ratio is needed to increase the hardness value. The Capa 210 based elastomer of similar block ratios to their Capa 220 analogues gave much higher hardness values, as expected, due to their lower molecular weight. At the high block ratios used (i.e. 1:9:8 and 1:7:6) the Capa 210 based elastomer was observed to fail in a brittle manner; this mode of failure can be changed from brittle to ductile if a low enough block ratio is used, however the hardness becomes much lower. The impact strength of the Capa 210 based elastomer is much lower than that of the Capa 220 elastomer, and both these elastomers have lower impact strength than that of polycarbonate. In Table 5.5.1e formulations based on the other polyols (Capa 215, Capa 205 and Capa 200) all showed a ductile failure mode with the block ratios used (Table 5.5.1e). This shows that with all the polyol systems used a ductile failure can be achieved when the hardness of the elastomer is reduced. The impact strength values overall show no significant change or trend with respect to the formulations shown in the Table.

H₁₂MDI Series: The average impact strength of the IPDI based elastomers is seen to be lower than that of polycarbonate. IPDI could be considered to have a rigid molecular structure, which as such would be expected to aid ductile failure in a polyurethane but would help to increase the surface hardness of the elastomer. In order for ductile failure to be achieved from the works of other researchers [6], a low block ratio PU with a high molecular weight polyol could be expected to be required to compensate for the brittleness introduced into the molecule by IPDI. One way of accomplishing this is to change the diisocyanate from IPDI to H₁₂MDI by which a more flexible molecule is introduced into the PU which would be expected to be beneficial to the failure mode as a means of introducing ductility.



Isophorone diisocyanate (IPDI)

4,4'-Dicyclohexylmethane
diisocyanate (H_{12}MDI)

Table 5.5.1a shows the impact test results of the H_{12}MDI based elastomers synthesised and so a direct comparison with the IPDI elastomers in Table 5.5.1e can be made. As can be seen in general with Capa 220, Capa 210 and Capa 200, the H_{12}MDI elastomers mostly show ductile failure, however lower surface hardness values are also obtained. This trend is not followed with the Capa 215 and Capa 205 based elastomers which seem to give some brittle failures for the H_{12}MDI elastomers and ductile failures in the case of the IPDI elastomers. The overall impact strengths are in general slightly higher for the H_{12}MDI elastomer series and, as before, the Capa 215 and Capa 205 based elastomers give the lower impact strength values of the series.

A dramatic change in the impact strength and failure mode is therefore not seen to occur with changing the diisocyanate from IPDI to H_{12}MDI . Surprisingly the Capa 215 and Capa 205 give higher impact strength values in the IPDI formulations than in their H_{12}MDI analogues. This may be due to the different reactivities of Capa 215 and Capa 205 by comparison with other polyols, as found previously, when these are used in combination with a diisocyanate of higher reactivity such as IPDI. The impact strength test results for the H_{12}MDI elastomers (Table 5.5.1a) have their highest values at their lower block ratios and lower polyol molecular weights. For constant block ratio and increasing polyol molecular weight the impact strength is found to increase. However the use of a polyol of high molecular weight in combination with a low block ratio gives low hardness values and flexible elastomers.

1,3-Butane Diol Series: In changing the chain extender system from the linear 1,4-butanediol to the unsymmetrical 1,3-butanediol (Table 5.5.1b) a slight drop in impact strength is observed to occur as can be seen by comparing the Capa 220 series of Tables 5.5.1a and 5.5.1b.

Mixed Chain Extender, 1,4-BD + 1,4-CHDM: In the mixed chain extender system (1,4-BD + 1,4-CHDM at 1:1 ratio, Table 5.5.1c), the impact strength is seen to be slightly higher with the Capa 220 based polyols, but lower with the other polyols in comparison with the 1,4-butanediol chain extended elastomers (Table 5.5.1a). This shows that the combination of high polyol molecular weight and block ratio with the mixed chain extender system and with the relatively rigid 1,4-CHDM chain extender incorporated does enhance the impact strength. At lower polyol molecular weights the reverse is seen, due to the lower amount of soft segment present and the rigid 1,4-CHDM part of the chain extender playing a more major role. It is also observed that with the mixed chain extender system, a greater degree of brittle failure in general occurs. On replacing the linear 1,4-butanediol chain extender system with 50 percent of a bulky rigid structure like 1,4-CHDM, this brittle failure characteristic is to be expected. However the surface hardness of the material with this mixed chain extender system is increased compared with its 1,4-butanediol analogue.

1,6-Hexane Diol Series: Impact strength tests were also carried out on elastomers chain extended with 1,6-hexanediol (Table 5.5.1d) and these in general showed an increase in impact strength by comparison with the 1,4-butanediol extended elastomers. The failure mode was ductile and this might be considered predictable due to the presence of the longer more flexible 1,6-hexanediol molecule compared with the shorter rigid 1,4-butanediol. The impact strength is greater and this may be due to the fact that as the chain extender forms part of the hard segment, a more flexible hard segment is produced with 1,6-hexanediol. This more 'flexible' hard segment would be expected to

have better impact absorbing properties and hence higher impact strength. The softening effect of the longer chain extender system also affects the hardness of the material and this is reflected by the lower values obtained by comparison with the 1,4-butanediol series.

Light Crosslinking: A selection of lightly crosslinked elastomers via the chain extender system were tested for impact strength (Table 5.5.1f). The impact strength values in general were higher in comparison with the 1,4-butanediol elastomers (Table 5.5.1a). This is considered due to the slight crosslinking effect introduced into the whole system by the chain extender system. It is however seen that the crosslinking effect does not change the mode of failure from ductile to brittle. The hardness in general when crosslinked systems are compared with their analogues tend to be comparable in some cases and lower in others illustrating the secondary nature of the crosslinking effect. The hardness values are observed to be lower in most cases with the mixed diol and triol chain extender systems used. The crosslinking chain extenders used were TMP and Capa 305 in combination with the 1,4-butanediol, D22 and D33 diols. The observations of crosslinking to impact strength do not show any general trends; however the hardness values are greater with the TMP extender system by comparison with Capa 305 extended elastomers.

Heavy Crosslinking: There is a more dramatic change in impact strength and mode of failure in the highly crosslinked elastomers (Table 5.5.1g). The elastomers are crosslinked via the polyol by using tri- and tetra-functional polyols. This higher crosslinking is reflected in the much higher hardness values obtained by comparison with the linear extended elastomers (Table 5.5.1a) and also their brittle failure mode. The H_{12} MDI highly crosslinked elastomers generally gave better impact strength by comparison with the IPDI based elastomers. This is due to the fact that the H_{12} MDI/1,4-BD hard segment has greater flexibility than the IPDI/1,4-BD hard segment which is attributed to their molecular design. On increasing the block ratio in the case of tetra-ol 1000/ H_{12} MDI the

impact strength increases. This could be due to the increase in hard segment content, as the hard segment itself contains some flexible links which increases with block ratio. This hard segment flexibility in combination with the higher tetra-functional polyol molecular weight may be the reason for the impact strength increase with block ratio. In the case of tetra-ol 600 the reverse is apparent. The molecular weight is much lower (almost half) for the tetra-ol 600 polyol which increases the brittle nature of the elastomer to such an extent that any natural flexibility present in the hard segment portion due to the presence of diisocyanate is more than compensated.

The Capa 305 based crosslinked elastomers based on both the H_{12} MDI and IPDI diisocyanates gave relatively low impact strength values. In comparison with the tetra-ol 600 elastomers, as the molecular weights of the final polymers are similar, a small increase in the impact strength of the tetra-ol 600 elastomers is observed. This may be due to their higher functionality and to the slightly higher molecular weight of the tetra-ol 600 polyols. In general the highly crosslinked systems give brittle failures and lower impact strength values than the linear systems. In the linear based systems, the 1,4-butanediol and 1,6-hexanediol chain extended elastomers give the higher impact strength values with a ductile failure mode.

5.5.2 Ballistic Strength, Results and Discussion

The ballistic tests on the samples were all carried out by the Ministry of Defence (MOD) at Colchester. The normal sample thickness of the elastomer was 3 mm and initially a few were selected for ballistic evaluation in order to compare them with polycarbonate. These PUs were all linear and based on H_{12} MDI, chain extended with 1,4-butanediol and the 1,4-BD + 1,4-CHDM (1:1) mixed chain extender systems (see Table 5.5.2a). The indication from these results showed that the Capa 220: H_{12} MDI:1,4-BD + 1,4-CHDM formulation at 1:9:4+4 block ratios, although equivalent to polycarbonate on ballistic assessment showed a tendency towards brittle failure. This

mixed chain extender system had a tendency towards brittle failure especially at the high block ratios used. On changing the chain extender to 1,4-butanediol and at lower block ratios the failure mode became ductile. The ballistic assessment given is equivalent to polycarbonate for all these elastomers. Although the ballistic evaluation is equivalent and the failure mode is ductile, other factors such as hardness (e.g. Capa 210:H₁₂MDI:1,4-BD at 1:3:2, Table 5.5.2a) are much lower.

These first elastomers gave promising ballistic results and therefore a few more elastomers were selected for further ballistic study and these had higher or improved hardness values. Samples were chosen with a variety of base polyol molecular weights and for each sample a range of thicknesses of the elastomer were prepared (Table 5.5.2b). When the mixed chain extender system was used in conjunction with the Capa 215 and Capa 210 polyols a brittle failure was recorded for all the various thicknesses prepared. As in the case of the previous ballistic results with this chain extender system (Table 5.5.2a) a much lower block ratio was required to induce the ductile failure mode. In using the linear 1,4-butanediol and 1,6-hexanediol chain extenders a ductile failure was recorded. On varying the thickness of the elastomer for the 2000 polyol molecular weight (Capa 220) the ballistic evaluation does not change significantly and remains similar to polycarbonate. By lowering the polyol molecular weight to 1000 (i.e. Capa 210) and using it at its optimum block ratio, quite a dramatic increase in ballistic resistance is observed making this material superior, by comparison, to polycarbonate. This increase makes the PU 22 percent better for the sample thickness of 4 mm and an average of 17 percent better for the increasing thicknesses in the range 6 mm to 10 mm, in comparison with polycarbonate. This formulation shows promising results especially with its combination of other physical properties. On lowering the polyol molecular weight further to 500 (Capa 200) and using the longer 1,6-hexanediol chain extender, quite good ballistic results are also obtained. These elastomers on average gave an increase of 15 percent on ballistic performance over the range of 4

mm samples to the 10 mm thickness samples. This formulation also shows a very good overall result in ballistic and physical performance.

By comparing with the impact test results, the mixed chain extender system gave some brittle failures and some ductile failures on impact. These same formulations all gave brittle failures on ballistic assessment, due to the much greater velocities introduced in this type of testing. This observation suggests that any material which has slightly brittle characteristics which may not be observed by means of the low velocity impact test should be quite clearly characterised by means of the ballistic assessment test. The samples that showed ductile failure on ballistic testing (Table 5.5.2b) also all possessed good overall physical properties. On one of the ductile failure samples it is interesting to see how the material is pushed aside by the impacting projectile to form a petal-like formation and ductile hole shown in Figure 5.5a; a closed hole has also been observed. Magnified photographs were taken of a sample which had the projectile caught and embedded in the sample. Photograph 5.5.2a shows the elastomer viewed from the direction at which the projectile is fired, the projectile being visibly embedded. On the left hand corner of this picture another hole is seen through which a projectile has passed straight through. A couple of air bubbles can also be seen at the bottom of this photograph - air bubble entrapment was one of the problems in synthesising these elastomers. Photograph 5.5.2b shows the reverse side of this elastomer and the material pushed aside by the projectile can be seen. Photographs 5.5.2c and 5.5.2d are the same as photographs 5.5.2a and 5.5.2b, but with much higher magnification of the projectile and failure modes.

TABLE 5.1: THERMOPLASTIC POLYURETHANES

H ₁₂ MDI/1,4-BD Based Elastomer	Block Ratio	Hard Segment Content (%)	Hardness (Shore D)	Observations	Haze Measurement (%)
Capa 240	1:3:2	19.5	52	Opaque, F	-
Capa 231	1:3:2	24.4	54	Opaque, F	-
Capa 220	1:3:2	32.6	27	Trans, F	1.5
	1:4:3	39.7	32	Trans, F	1.4
	1:5:4	45.5	38	Trans, F	2.7
	1:6:5	50.3	44	Trans, F	3.2
	1:7:6	54.3	53	Trans, F	8.8
	1:8:7	57.7	56	Trans, F	13.1
	1:9:8	60.6	60	Slightly hazy, F	21.4
Capa 215	1:3:2	43.6	34	Trans, F	3.9
	1:4:3	51.3	47	V.slightly hazy, F/R	6.2
	1:5:4	57.2	58	Slightly hazy, F/R	6.8
	1:6:5	61.8	64	Slightly hazy, R/F	9.2
	1:7:6	65.5	69	Hazy, R	11.9
Capa 210	1:2:1	38.0	<20	Trans, F	3.7
	1:3:2	49.1	45	Trans, F	4.3
	1:4:3	56.9	58	Trans, F/R	5.9
	1:5:4	62.6	72	Trans, R/F	0.6
	1:6:5	66.9	74	Trans, R	9.4
	1:7:6	70.4	77	Trans, R/(B)	4.1
	1:8:7	73.2	79	Slightly hazy, R/B	14.9
Capa 205	1:3:2	53.8	54	Trans, F	4.9
	1:4:3	61.4	65	Trans, R/F	6.2
	1:5:4	66.8	74	Slightly hazy, R/B	14.0
Capa 200	1:2:1	52.8	41	Trans, F	2.0
	1:3:2	63.7	77	Trans, R	2.0
	1:4:3	70.6	80	Trans, B/R	8.5

F = Flexible, R = Rigid, B = Brittle

TABLE 5.1 (continued)

H ₁₂ MDI/1,4-BD + 1,4-CHDM	Block Ratio	Hard Segment Content (%)	Hardness (Shore D)	Observations	Haze Measure- (%)
Capa 220	1:7:3+3	55.9	60	Trans R/F	3.6
	1:9:4+4	62.2	68	Trans R	1.0
Capa 215	1:4:1.5+1.5	52.8	48	Trans F	
	1:5:2+2	58.7	60	Trans R/F	2.6
	1:6:2.5+2.5	63.3	70	Trans R	0.8
	1:7:3+3	70.0	73	Trans R/B	
Capa 210	1:3:1+1	50.5	46	Trans F	0.3
	1:4:1.5+1.5	58.3	66	Trans R	1.9
	1:5:2+2	64.0	76	Trans R	
Capa 205	1:2:0.5+0.5	43.6	21	Trans, V.F.	7.7
	1:3:1+1	55.1	45	Trans F/(R)	11.2
	1:4:1.5+1.5	62.8	74	Trans R/B	3.0
Capa 200	1:2:0.5+0.5	53.8	53	Trans R/F	
	1:3:1+1	65.0	79	Trans R/B	
H ₁₂ MDI/1,6-BD Based	Block Ratio	Hard Segment Content (%)	Hardness (Shore D)	Observations	Haze Measure- (%)
Capa 215	1:5:4	58.8	47	Trans F	14.2
	1:6:5	63.4	53	Trans F/R	0.7
	1:7:6	67.0	61	Trans R/F	4.4
	1:8:7	70.0	70	Slightly hazy, R/F	
Capa 210	1:5:4	64.1	64	Trans R/F	2.2
	1:6:5	68.4	71	Trans R	
	1:7:6	71.8	74	Trans R	2.8
Capa 205	1:4:3	62.8	55	Trans F/R	11.4
	1:5:4	68.2	73	Trans R/F	4.6
Capa 200	1:2.9:1.9	63.8	68	Trans R	2.1
	1:3.3:2.3	67.6	75	Trans R	1.1
	1:4:3	71.8	78	Trans R	1.7

TABLE 5.1 (continued)

H ₁₂ MDI/1,3,BD Based	Block Ratio	Hard Segment Content (%)	Hardness (Shore D)	Observations	Haze Measure- (%)
Capa 220	1:4:3	39.7	<20	Trans F	
	1:5:4	45.5	20	Trans F	9.3
	1:6:5	50.3	33	Trans F	8.6
	1:7:6	54.3	43	Trans F	
	1:8:7	57.7	55	Trans F/R	3.9
	1:9:8	60.6	67	Trans F/R	3.8
	1:10:9	63.2	66	Trans R/F	14.1
	1:11:10	65.4	73	Trans R/B	15.0
Capa 210	1:3:2	49.1	26	Trans F	
	1:4:3	56.9	46	Trans R/F	
	1:5:4	62.6	75	Trans R/(B)	

TABLE 5.2: THERMOPLASTIC POLYURETHANES BASED ON OTHER DIISOCYANATES

PPDI Based	Block Ratio	Hard Segment Content	Hardness (Shore D)	Observations
Capa 220/1,4-BD	1:2:1	17.0	31	Opaque R/F
	1:3:2	24.8	41	Opaque R/F
Capa 220/1,3-BD	1:2:1	17.0	<20	Translucent F
	1:3:2	24.8	20	Translucent F
	1:4:3	31.3	32	Translucent F
	1:5:4	36.7	36	Translucent/ Opaque F
CHDI Based	Block Ratio	Hard Segment Content	Hardness (Shore D)	Observations
Capa 220/1,4-BD	1:2:1	17.4	27	Opaque F
	1:3:2	25.3	42	Opaque R/F
	1:5:4	37.3	57	Opaque B/R
	1:9:8	52.5	67	Opaque B
Capa 210/1,4-BD	1:3:2	40.4	54	Opaque R/F
	1:5:4	54.3	75	Opaque B/R
	1:9:8	68.9	83	Opaque B
Isocyanate System	Block Ratio	Hard Segment Content	Hardness (Shore D)	Observations
Capa 210/PPDI/D33	1:3:2	53.9	54	Translucent, R
Capa 220/CHDI/D22	1:3:2	36.1	41	Translucent, R
Capa 210/TMDI/1,4-BD	1:5:4	58.5	<20	Trans, very R
	1:9:8	72.3	<20	Trans, very F
IPDI/1,4-BD Based	Block Ratio	Hard Segment Content	Hardness (Shore D)	Observations
Capa 220	1:3:2	29.8	35	Translucent F
	1:5:4	42.4	39	Trans F
	1:7:6	51.2	44	Trans F/(R)
	1:9:8	57.6	60	Trans R/F
Capa 215	1:6:5	58.8	55	Trans F/R
Capa 210	1:3:2	45.9	26	Trans F
	1:5:4	59.5	66	Trans R/F
	1:7:6	67.7	81	Trans R
	1:9:8	73.1	85	Trans R/B
Capa 205	1:4:3	58.3	63	Trans F/R
Capa 200	1:3:2	60.6	78	Trans R

TABLE 5.3: POLYURETHANES LIGHTLY CROSSLINKED WITH VARIOUS CHAIN EXTENDERS
BASED ON CAPA 205/H₁₂MDI

Chain Extender System	Chain Extender Ratio	Hard Segment Content	Hardness (Shore D)	Observations
1,4-BD+TMP	1:1	61.3	68	Trans R
	1:0.5	61.4	65	Trans R
1,4-BD+Capa 305	1:1	67.5	28	Trans F
	1:0.5	65.7	50	Trans F/R
D22+TMP	1:1	66.6	81	Trans R
	1:0.5	68.1	82	Trans R/B
D22+Capa 305	1:1	71.3	59	Trans R/F
	1:1	71.3	59	Trans R/F
	1:0.5	71.1	78	Trans R
D33+TMP	1:1	67.2	81	Trans R
	1:0.5	68.7	80	Trans R
D33+Capa 305	1:1	71.7	63	Trans R/F
	1:0.5	71.6	77	Trans R

TABLE 5.3.1: PHYSICAL PROPERTIES OF THERMOPLASTIC POLYURETHANES

H ₁₂ MDI/ 1,4-BD	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 240	1:3:2	40.9	590	4.3	15.3	52
Capa 231	1:3:2	37.7	570	4.0	12.4	54
Capa 220	1:3:2	31.0	480	5.4	15.8	27
	1:4:3	40.6	420	7.2	25.0	32
	1:5:4	43.2	410	9.8	26.9	38
	1:6:5	48.2	360	11.9	36.3	44
	1:7:6	54.4	340	14.3	44.8	53
	1:8:7	60.5	330	17.5	49.8	56
	1:9:8	49.9	320	18.2	46.0	60
Capa 215	1:3:2	16.4	460	7.9	12.7	34
	1:4:3	30.2	415	9.2	20.7	47
	1:5:4	38.5	400	15.7	31.1	58
	1:6:5	31.9	290	20.5	-	64
	1:7:6	28.8	280	18.6	-	69
Capa 210	1:3:2	47.8	400	13.0	47.7	45
	1:4:3	59.6	340	19.2	50.0	58
	1:5:4	55.8	320	23.4	49.6	72
	1:6:5	54.5	275	25.3	-	74
	1:7:6	51.5	260	28.8	-	77
Capa 205	1:3:2	29.9	420	11.9	23.2	54
	1:4:3	40.3	320	17.4	38.3	65
	1:5:4	31.0	215	20.2	-	74
	1:2:1	52.1	600	-	-	41
Capa 200	1:3:2	45.6	290	21.7	-	77

TABLE 5.3.1 (continued)

H ₁₂ MDI/ 1,4-BD+ 1,4-CHDM 1:1	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 220	1:9:4+4	50.9	310	19.7	49.7	68
Capa 215	1:4:1.5 +1.5	27.4	440	6.8	17.4	48
	1:5:2+2	29.9	290	13.9	-	60
	1:6:2.5 +2.5	36.4	270	21.9	-	70
	1:7:3+3	18.4	60	-	-	73
Capa 210	1:3:1+1	42.9	430	6.7	19.2	46
	1:4:1.5 +1.5	46.8	310	20.6	45.9	66
	1:5:1+2	47.6	250	29.9	-	76
Capa 205	1:2:0.5 +0.5	26.2	710	4.1	9.4	21
	1:3:1+1	27.9	440	7.2	14.7	45
	1:4:1.5 +1.5	31.8	220	18.7	-	74
Capa 200	1:2:0.5 +0.5	53.3	500	8.1	20.5	53
	1:3:1+1	36.6	40	-	-	79
H ₁₂ MDI/ 1,6-HD	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 215	1:5:4	41.8	550	7.8	19.6	47
	1:6:5	34.8	370	14.2	29.4	53
	1:7:6	29.7	350	11.2	26.9	61
Capa 210	1:5:4	58.9	375	20.1	52.5	64
	1:6:5	54.6	295	25.4	-	71
	1:7:6	50.9	230	28.0	-	74
Capa 205	1:4:3	48.6	470	13.2	31.2	55
	1:5:4	35.1	350	17.4	28.3	73
Capa 200	1:2.9: 1.9	41.6	325	16.3	38.5	68
	1:3.3: 2.3	38.2	220	22.6	-	75
	1:4:3	36.2	210	24.1	-	78

TABLE 5.3.1 (continued)

H ₁₂ MDI/ 1,3-BD	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 220	1:6:5	41.1	390	8.1	27.5	33
	1:7:6	44.6	370	12.1	32.4	43
	1:8:7	49.2	360	15.8	39.7	55
	1:9:8	56.1	330	18.7	51.2	67
	1:10:9	48.1	300	19.1	46.3	66
	1:11:10	42.5	270	21.4	-	73

TABLE 5.3.2: PHYSICAL PROPERTIES OF THERMOPLASTIC POLYURETHANES BASED ON ISOCYANATES OTHER THAN H₁₂MDI

IDPI/ 1,4-BD	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 220	1:3:2	21.9	1200	-	-	35
	1:5:4	32.3	700	<2	5.8	39
	1:7:6	44.8	650	3.4	8.6	44
	1:9:8	48.1	500	8.0	19.5	60
Capa 215	1:6:5	57.8	680	8.2	16.9	55
Capa 210	1:3:2	32.8	620	<2	3.9	36
	1:5:4	47.7	590	10.3	20.9	66
	1:7:6	42.6	280	19.3	81	
	1:9:8	45.1	175	30.2	-	85
Capa 205	1:4:3	51.5	690	8.8	17.2	48
Capa 200	1:3:2	45.6	380	11.8	34.0	-
TMDI/ 1,4-BD	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 210	1:5:4	<5	>1000	-	-	<20
	1:9:8	5.4	1000	-	<2	<20

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TABLE 5.3.3: PHYSICAL PROPERTIES OF LIGHTLY CROSSLINKED POLYURETHANES

1,4-BD+ TMP 1:1	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 215	1:6:5	32.1	290	14.9	-	59
Capa 210	1:5:4	38.6	245	26.9	-	73
Capa 205	1:4:3	34.4	280	20.6	-	68
Capa 200	1:3:2	45.4	100	45.4	-	79
1,4-BD+ Capa 305 1:1	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 215	1:6:5	36.3	490	3.3	10.5	37
Capa 210	1:5:4	40.1	330	9.6	25.8	36
Capa 205	1:4:3	42.9	420	7.1	20.8	28
Capa 200	1:3:2	36.7	295	15.9	-	54
D33 + Capa 305 1:1	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 215	1:6:5	34.5	320	14.7	29.9	54
Capa 210	1:5:4	36.8	220	25.4	-	71
Capa 205	1:4:3	43.3	340	19.6	40.5	63
Capa 200	1:3:2	46.8	50	-	-	78
D22 + Capa 305 1:1	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness Shore D
Capa 215	1:6:5	38.9	320	15.2	33.2	54
Capa210	1:5:4	39.2	230	24.9	-	65
Capa 205	1:4:3	49.8	370	19.6	39.2	59
Capa 200	1:3:2	38.1	60	-	-	76

TABLE 5.3.4: PHYSICAL PROPERTIES OF HIGHLY CROSSLINKED POLYURETHANES

H ₁₂ MDI/1,4-BD	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Hardness (Shore D)
Capa 305	1:2:1	61.4	30	81
	1:3:2	50.6	30	82
	1:4:3	Too brittle		83
Tetra-ol 600	1:2:1	56.6	35	84
	1:3:2	59.7	30	84
	1:4:3	69.0	30	85
Tetra-ol 1000	1:2:1	51.7	30	79
	1:3:2	57.7	30	81
	1:4:3	60.4	30	82
	1:5:4	64.3	25	84
IPDI/1,4-BD	Block Ratio	Tensile Strength (MPa)	Elongation (%)	Hardness (Shore D)
Capa 305	1:2:1	64.7	20	84
	1:3:2	65.5	25	85
	1:4:3	68.0	20	87
Tetra-ol 600	1:2:1	73.6	25	86
	1:3:2	76.3	20	87
	1:4:3	77.6	20	88
Tetra-ol 1000	1:2:1	61.9	30	81
	1:3:2	64.1	20	84
	1:4:3	60.9	20	86

TABLE 5.4: H₁₂MDI BASED POLYURETHANES LIGHTLY CROSSLINKED VIA THE CHAIN EXTENDER

1,4-BD+TMP 1 : 1 Chain Extended	Block Ratio	Hard Segment Content	Hardness (Shore D)	Observations
Capa 215	1:6:5	63.0	59	Trans R/F
Capa 210	1:5:4	53.8	73	Trans R
Capa 205	1:4:3	62.5	68	Trans R
Capa 200	1:3:2	64.8	79	Trans R
1,4-BD+Capa 305 1 : 1 Chain Extended	Block Ratio	Hard Segment Content	Hardness (Shore D)	Observations
Capa 215	1:6:5	71.6	37	Trans F
Capa 210	1:5:4	72.0	36	Trans F
Capa 205	1:4:3	70.6	28	Trans F
Capa 200	1:3:2	72.0	54	Trans R/F
D33 + Capa 305 1 : 1 Chain Extended	Block Ratio	Hard Segment Content	Hardness (Shore D)	Observations
Capa 215	1:6:5	75.2	54	Trans R/F
Capa 210	1:5:4	75.5	71	Trans R
Capa 205	1:4:3	74.1	63	Trans F/R
Capa 200	1:3:2	75.2	78	Trans R
D22 + Capa 305 1 : 1 Chain Extended	Block Ratio	Hard Segment Content	Hardness (Shore D)	Observations
Capa 215	1:6:5	74.8	54	Trans R/F
Capa 210	1:5:4	75.1	65	Trans R/F
Capa 205	1:4:3	73.8	59	Trans F/R
Capa 200	1:3:2	74.9	76	Trans R

TABLE 5.5: POLYURETHANES HIGHLY CROSSLINKED VIA THE POLYOL SYSTEM

H ₁₂ MDI/1,4-BD Based	Block Ratio	Hard Segment Content (%)	Hardness (Shore D)	Observations	Haze Measurement (%)
Capa 305	1:2:1	53.2	81	Trans R	4.3
	1:3:2	64.1	82	Trans R/B	
	1:4:3	70.9	83	Trans R/B	6.9
Tetra-ol 600	1:2:1	50.6	84	Trans R/B	7.5
	1:3:2	61.7	84	Trans R/B	
	1:4:3	68.7	85	Trans R/B	3.1
Tetra-ol 1000	1:2:1	38.0	79	Trans R	6.8
	1:3:2	49.1	81	Trans R/B	
	1:4:3	56.9	82	Trans R/B	
	1:5:4	62.6	84	Trans R/B	4.6
IPDI/1,4-BD Based	Block Ratio	Hard Segment Content (%)	Hardness (Shore D)	Observations	Haze Measurement (%)
Capa 305	1:2:1	49.8	84	Trans R	2.4
	1:3:2	61.1	85	Trans R/B	
	1:4:3	68.2	87	Trans R/B	1.6
Tetra-ol 600	1:2:1	47.1	86	Trans R/B	3.3
	1:3:2	58.5	87	Trans R/B	
	1:4:3	65.9	88	Trans B/R	4.5
Tetra-ol 1000	1:2:1	34.8	81	Trans R	5.4
	1:3:2	45.9	84	Trans R/B	
	1:4:3	53.7	86	Trans R/B	3.5

TABLE 5.5.1a: IMPACT TEST RESULTS CARRIED OUT ON THE CAPA: H₁₂MDI: 1,4-BD BASED SYSTEMS AT DIFFERENT POLYOL MOLECULAR WEIGHTS AND VARYING BLOCK RATIOS

Formulation	FWIS (Joules)	Hardness (Shore D)	Failure Mode
Capa 220:H ₁₂ MDI:1,4-BD			
1 : 9 : 8	13	60	Ductile
1 : 8 : 7	13-14	56	Ductile
1 : 7 : 6	14-15	53	Ductile
Capa 215:H ₁₂ MDI:1,4-BD			
1 : 7 : 6	11	69	Brittle
1 : 6 : 5	11-12	64	Brittle
Capa 210:H ₁₂ MDI:1,4-BD			
1 : 7 : 6	12	77	Some brittle failures
1 : 6 : 5	14	74	Ductile
1 : 5 : 4	15-16	72	Ductile
1 : 4 : 3	15	58	Ductile
1 : 3 : 2	17	45	Ductile
Capa 205:H ₁₂ MDI:1,4-BD			
1 : 4 : 3	12-13	65	Some brittle failures
1 : 3 : 2	11	54	Ductile
Capa 200:H ₁₂ MDI:1,4-BD			
1 : 3 : 2	14	77	Ductile
1 : 2 : 1	13	41	Ductile

TABLE 5.5.1b: IMPACT TEST RESULTS CARRIED OUT ON THE CAPA 220:H₁₂MDI:1,3-BD BASED SYSTEMS

Formulation	FWIS (Joules)	Hardness (Shore D)	Failure Mode
Capa 220:H ₁₂ MDI:1,3-BD			
1 : 9 : 8	13	67	Ductile
1 : 8 : 7	12	55	Ductile

TABLE 5.5.1c: IMPACT TEST RESULTS CARRIED OUT AT VARYING BLOCK RATIOS AND POLYOL MOLECULAR WEIGHTS FOR THE CAPA:H₁₂MDI:1,4-BD + 1,4-CHDM BASED SYSTEMS

Formulation	FWIS (Joules)	Hardness (Shore D)	Failure Mode
Capa 220:H ₁₂ MDI:1,4-BD+1,4-CHDM			
1 : 9 : 4 + 4	16	68	Some brittle failures
1 : 7 : 3 + 3	15-16	60	Some brittle failures
Capa 215:H ₁₂ MDI:1,4-BD+1,4-CHDM			
1 : 6 : 2.5 + 2.5	11	70	Some brittle failures
Capa 210: H ₁₂ MDI:1,4-BD+1,4-CHDM			
1 : 5 : 2 + 2	13	76	Some brittle failures
Capa 205:H ₁₂ MDI:1,4-BD+1,4-CHDM			
1 : 4 : 1.5 + 1.5	12-13	74	Some brittle failures
Capa 200:H ₁₂ MDI:1,4-BD+1,4-CHDM			
1 : 3 : 1 + 1	13	79	Some brittle failures
1 : 2 : 0.5 + 0.5	11-12	53	Ductile

TABLE 5.5.1d: IMPACT TEST RESULTS CARRIED OUT ON THE CAPA:H₁₂MDI:1,6-HD BASED SYSTEMS AT DIFFERENT POLYOL MOLECULAR WEIGHTS AND VARYING BLOCK RATIOS

Formulation	FWIS (Joules)	Hardness (Shore D)	Failure Mode
Capa 215:H ₁₂ MDI:1,6-HD			
1 : 8 : 7	13	70	Ductile
1 : 7 : 6	12	61	Ductile
Capa 210:H ₁₂ MDI:1,6-HD			
1 : 7 : 6	15-16	74	Ductile
1 : 6 : 5	16	71	Ductile
1 : 5 : 4	17-18	64	Ductile
Capa 205:H ₁₂ MDI:1,6-HD			
1 : 5 : 4	12-13	73	Ductile
1 : 4 : 3	12	55	Ductile
Capa 200:H ₁₂ MDI:1,6-Hd			
0.5 : 2 : 1.5	15	78	Some brittle failures
0.6 : 2 : 1.4	18	75	Ductile
0.7 : 2 : 1.3	17	68	Ductile

TABLE 5.5.1e: IMPACT TEST RESULTS CARRIED OUT ON THE CAPA:IPDI:1,4-BD BASED SYSTEMS. DIFFERENT POLYOL MOLECULAR WEIGHTS AND VARYING BLOCK RATIOS WERE USED

Formulation	FWIS (Joules)	Hardness (Shore D)	Failure Mode
Capa 220:IPDI:1,4-BD			
1 : 9 : 8	19.6*	60	Ductile
1 : 9 : 8	9.8*	60	No failure
1 : 7 : 6	13-14	44	Ductile
1 : 5 : 4	12.5*	39	No failure
Capa 215:IPDI:1,4-BD			
1 : 6 : 5	14	55	Ductile
Capa 210:IPDI:1,4-BD			
1 : 9 : 8	9.8*	85	Brittle
1 : 7 : 6	9.8*	81	Brittle
Capa 205:IPDI:1,4-BD			
1 : 4 : 3	13	48	Ductile
Capa 200:IPDI:1,4-BD			
1 : 3 : 2	13	58	Ductile

* These were the first impact tests carried out. Weights were selected to give fixed FWIS values such that only a failure or no failure type result could be recorded

TABLE 5.5.1f: IMPACT TESTS CARRIED OUT ON SOME OF THE LIGHTLY
CROSSLINKED POLYURETHANES SYNTHESISED

Formulation	FWIS (Joules)	Hardness (Shore D)	Failure Mode
Capa 215:H ₁₂ MDI:1,4-BD+TMP 1 : 6 : 2.5 + 2.5	14	59	Ductile
Capa 210:H ₁₂ MDI:1,4-BD+TMP 1 : 5 : 2 + 2	16-17	73	Ductile
Capa 205:H ₁₂ MDI:1,4-BD+TMP 1 : 4 : 1.5 + 1.5	15	68	Ductile
Capa 200:H ₁₂ MDI:1,4-BD+TMP 1 : 3 : 1 + 1	15	79	Ductile
Capa 200:H ₁₂ MDI:1,4-BD+Capa 305 1 : 3 : 1 + 1	13	54	Ductile
Capa 215:H ₁₂ MDI:D33+Capa 305 1 : 6 : 2.5 + 2.5	13	54	Ductile
Capa 210:H ₁₂ MDI:D33+Capa 305 1 : 5 : 2 + 2	15	71	Ductile
Capa 205:H ₁₂ MDI:D33+Capa 305 1 : 4 : 1.5 + 1.5	15-16	63	Ductile
Capa 200:H ₁₂ MDI:D33+Capa 305 1 : 3 : 1 + 1	14-15	78	Ductile
Capa 215:H ₁₂ MDI:D22+Capa 305 1 : 6 : 2.5 + 2.5	15	54	Ductile
Capa 210:H ₁₂ MDI:D22+Capa 305 1 : 3 : 2 + 2	15	65	Ductile
Capa 205:H ₁₂ MDI:D22+Capa 305 1 : 4 : 1.5 + 1.5	13-14	59	Ductile
Capa 200:H ₁₂ MDI:D22+Capa 305 1 : 3 : 1 + 1	15-16	76	Ductile

TABLE 5.5.1g: IMPACT TEST RESULTS FOR THE HIGHLY CROSSLINKED ELASTOMERS
BASED ON IPDI AND H₁₂MDI DIISOCYANATES

Formulation	FWIS (Joules)	Hardness (Shore D)	Failure Mode
Tetra-ol 1000:H ₁₂ MDI:1,4-BD			
1 : 5 : 4	17	84	Some brittle failures
1 : 4 : 3	15-16	82	Some brittle failures
1 : 3 : 2	14	81	Some brittle failures
1 : 2 : 1	10	79	Some brittle failures
Tetra-ol 600:H ₁₂ MDI:1,4-BD			
1 : 3 : 2	<8	84	Brittle
1 : 2 : 1	8	84	Brittle
Capa 305:H ₁₂ MDI:1,4-BD			
1 : 2 : 1	<8	81	Brittle
Tetra-ol 1000:IPDI:1,4-BD			
1 : 4 : 3	9	86	Brittle
1 : 3 : 2	9	84	Brittle
1 : 2 : 1	12	81	Some brittle failures
Tetra-ol 600:IPDI:1,4-BD			
1 : 4 : 3	12-13	88	Brittle
1 : 2 : 1	8	86	Brittle
Capa 305:IPDI:1,4-BD			
1 : 2 : 1	<8	84	Brittle

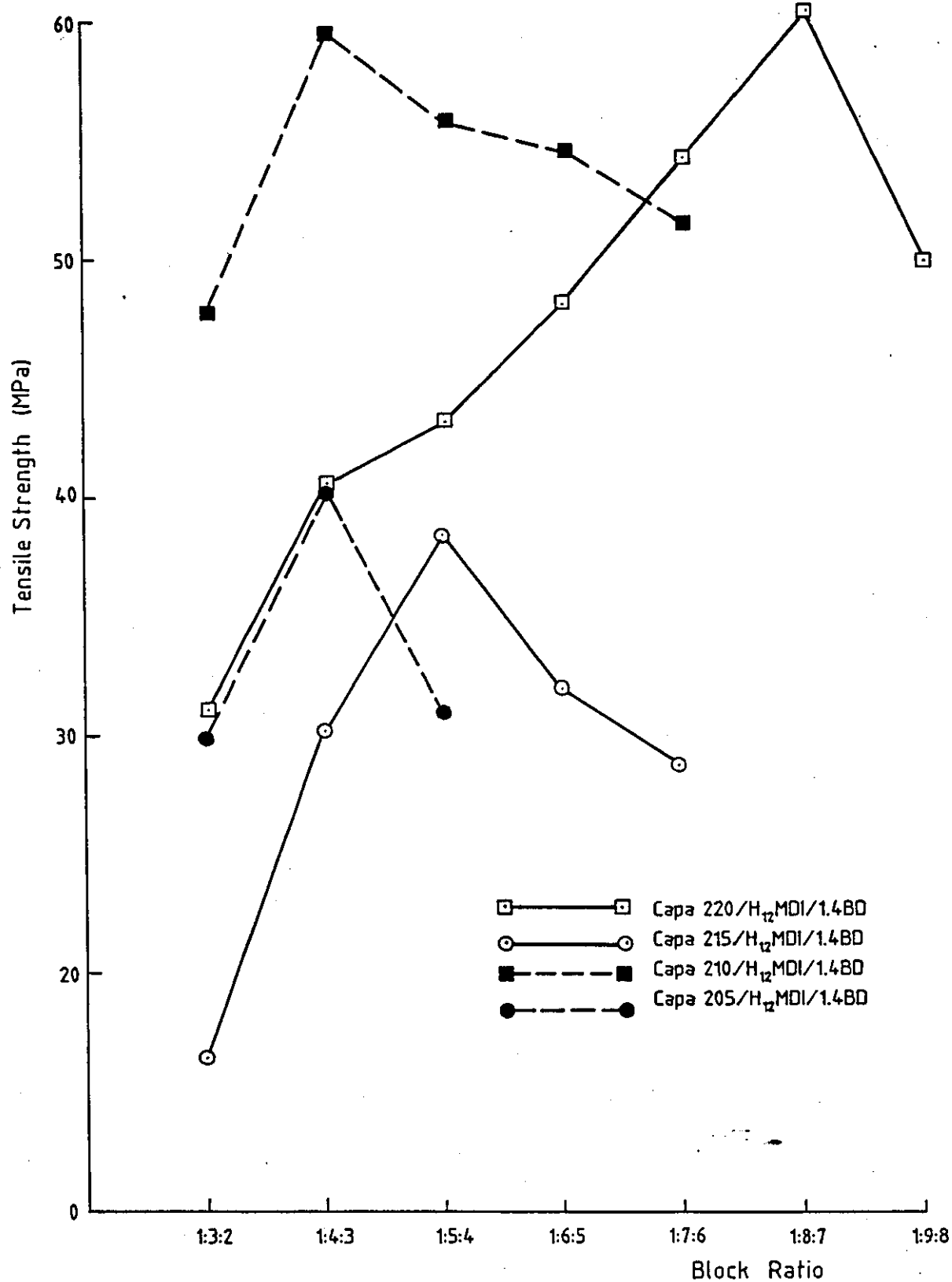
TABLE 5.5.2a: BALLISTIC TEST RESULTS OBTAINED FROM THE MOD ON THE FEW FORMULATIONS SHOWN

Formulation	Ballistic Assessment	Hardness (Shore D)	Failure Mode
Capa 220:H ₁₂ MDI:1,4-BD+1,4-CHDM 1 : 9 : 4 + 4	Equivalent to Poly-carbonate	68	Some brittle failures
Capa 220:H ₁₂ MDI:1,4-BD 1 : 7 : 6	Equivalent to Poly-carbonate	53	Ductile
Capa 210:H ₁₂ MDI:1,4-BD 1 : 5 : 4	Equivalent to Poly-carbonate	72	Ductile
Capa 210:H ₁₂ MDI:1,4-BD 1 : 3 : 2	Equivalent to Poly-carbonate	45	Ductile
Polycarbonate	-	82	Ductile

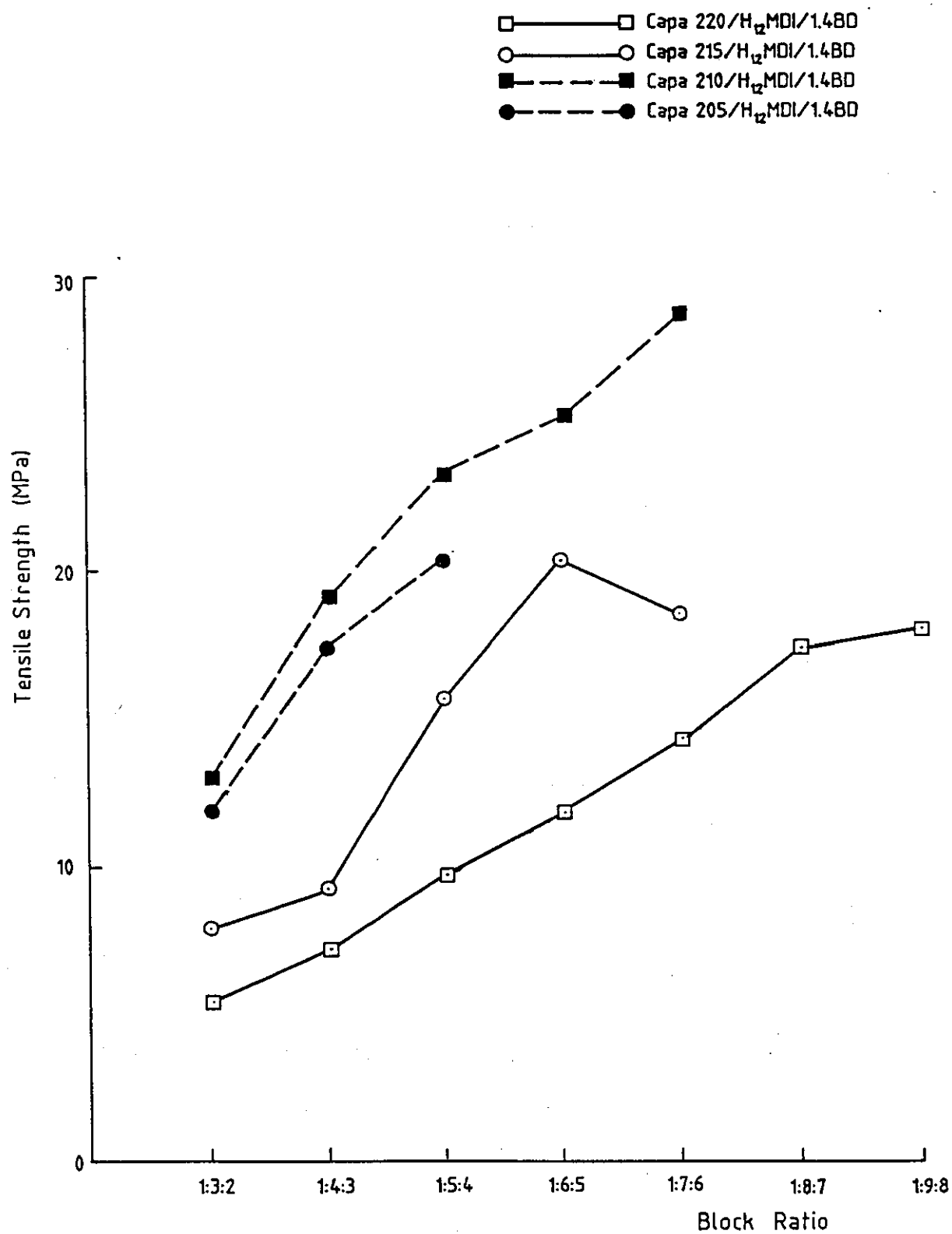
TABLE 5.5.2b: BALLISTIC TEST RESULTS OBTAINED FROM THE MOD ON THE FORMULATIONS SHOWN AT VARYING THICKNESSES

Formulation	Nominal Thickness	Hardness (Shore D)	Ballistic Merit Factor*
Capa 220:H ₁₂ MDI:1,4-BD			
1 : 7 : 6	a) 4 mm	53	1.05
	b) 8 mm	53	1.03
	c) 10 mm	53	1.06
Capa 210:H ₁₂ MDI:1,4-BD+1,4-CHDM			
1 : 5 : 2 + 2	a) 4 mm	76	Brittle failure
	b) 6 mm	76	Brittle failure
	c) 8 mm	76	Not tested
	d) 10 mm	76	Brittle failure
Capa 215:H ₁₂ MDI:1,4-BD+1,4-CHDM			
1 : 6 : 2.5 + 2.5	a) 6 mm	70	Brittle failure
	b) 8 mm	70	Brittle failure
Capa 210:H ₁₂ MDI:1,4-BD			
1 : 5 : 4	a) 4 mm	72	1.22
	b) 6 mm	72	1.14
	c) 8 mm	72	1.18
	d) 10 mm	72	1.17
Capa 200:H ₁₂ MDI:1,6-HD			
0.7 : 2 : 1.3	a) 4 mm	68	1.13
	b) 6 mm	68	1.14
	c) 8 mm	68	1.16
	d) 10 mm	68	1.16

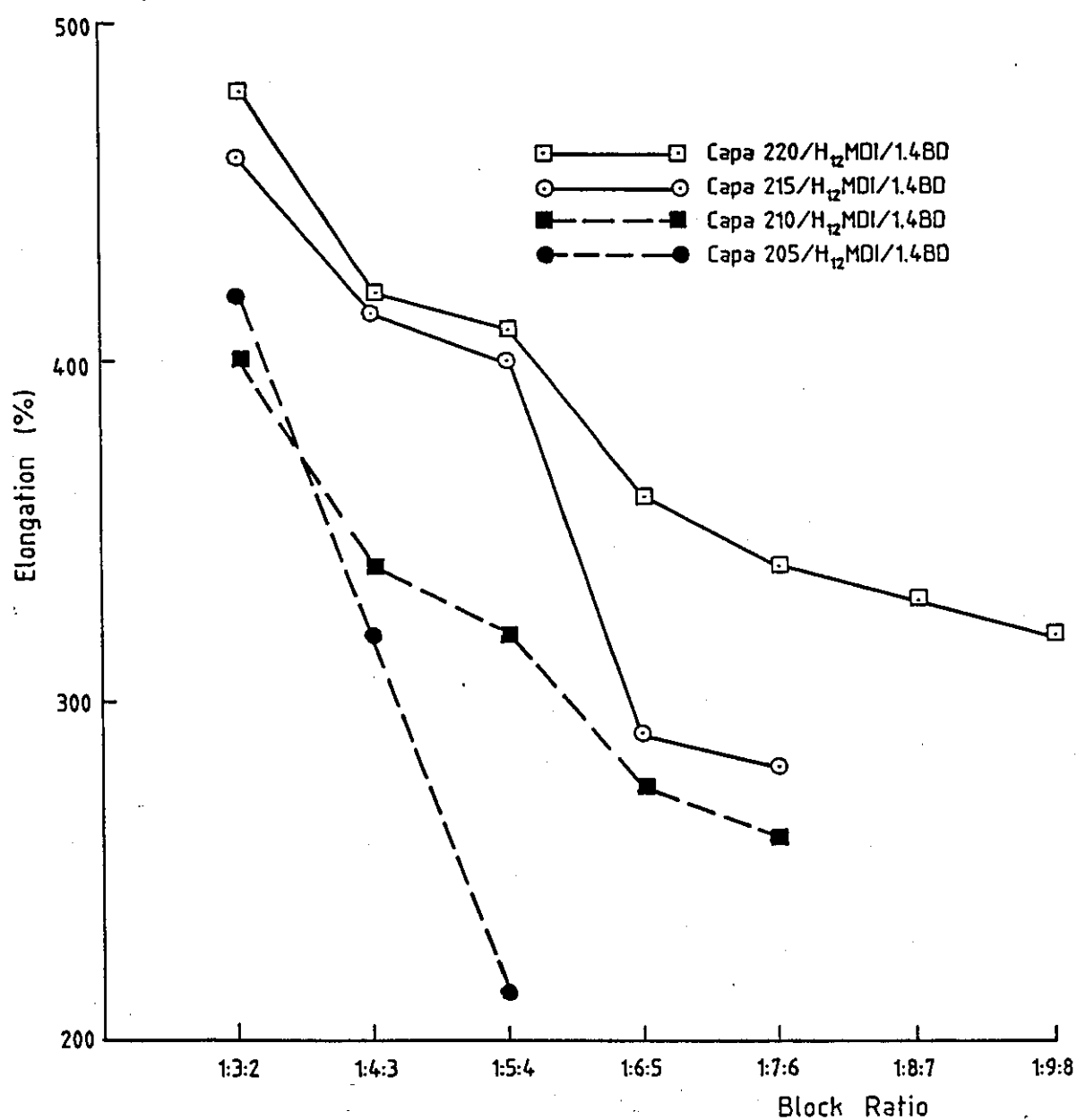
* This merit factor is based on a comparison with polycarbonate, which is taken at 1.00.



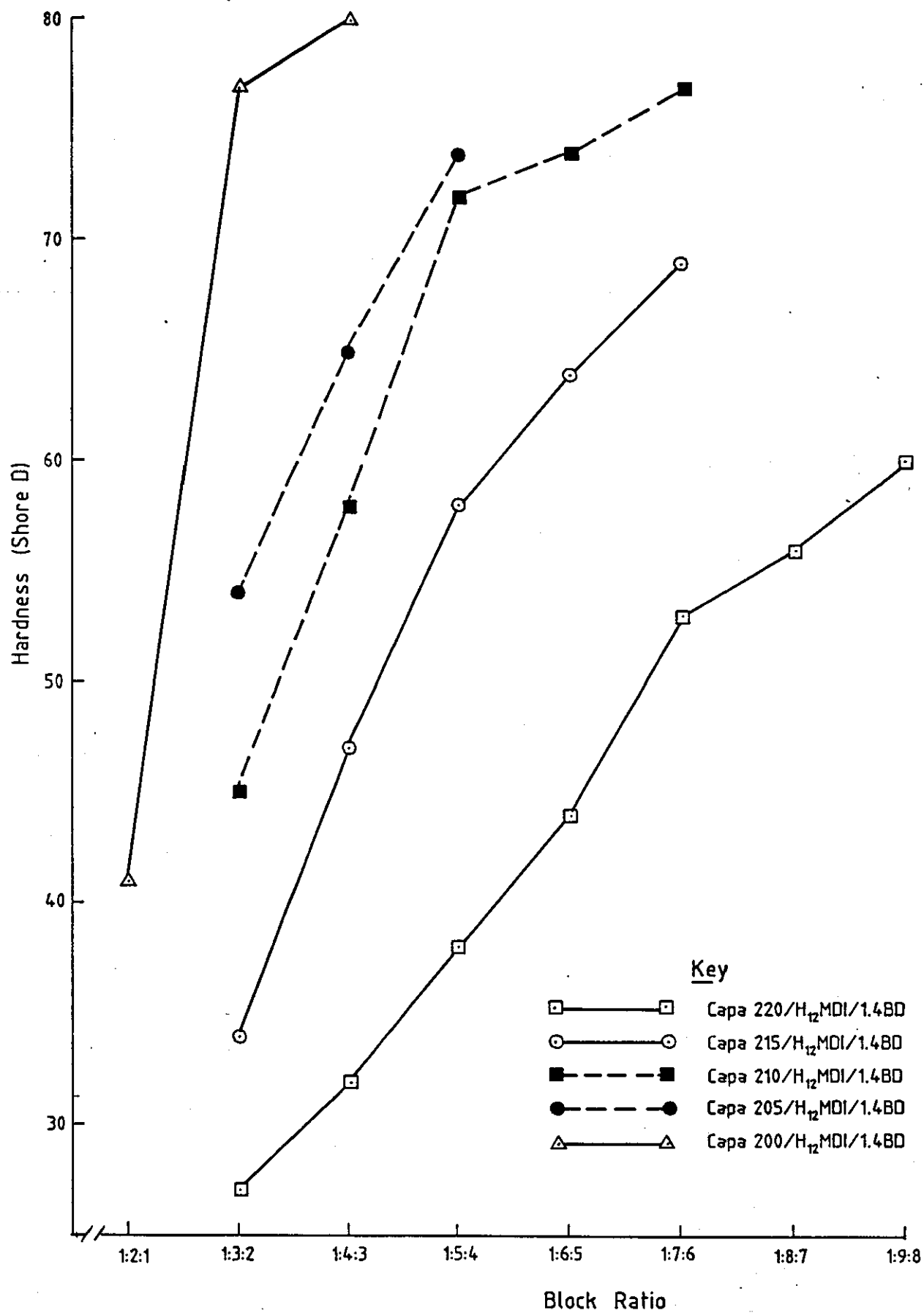
Graph 5 . 3 . 1 . Tensile Strength vs Block Ratio for H_{12} MDI/ 1,4BD based elastomers. (See Table 11).



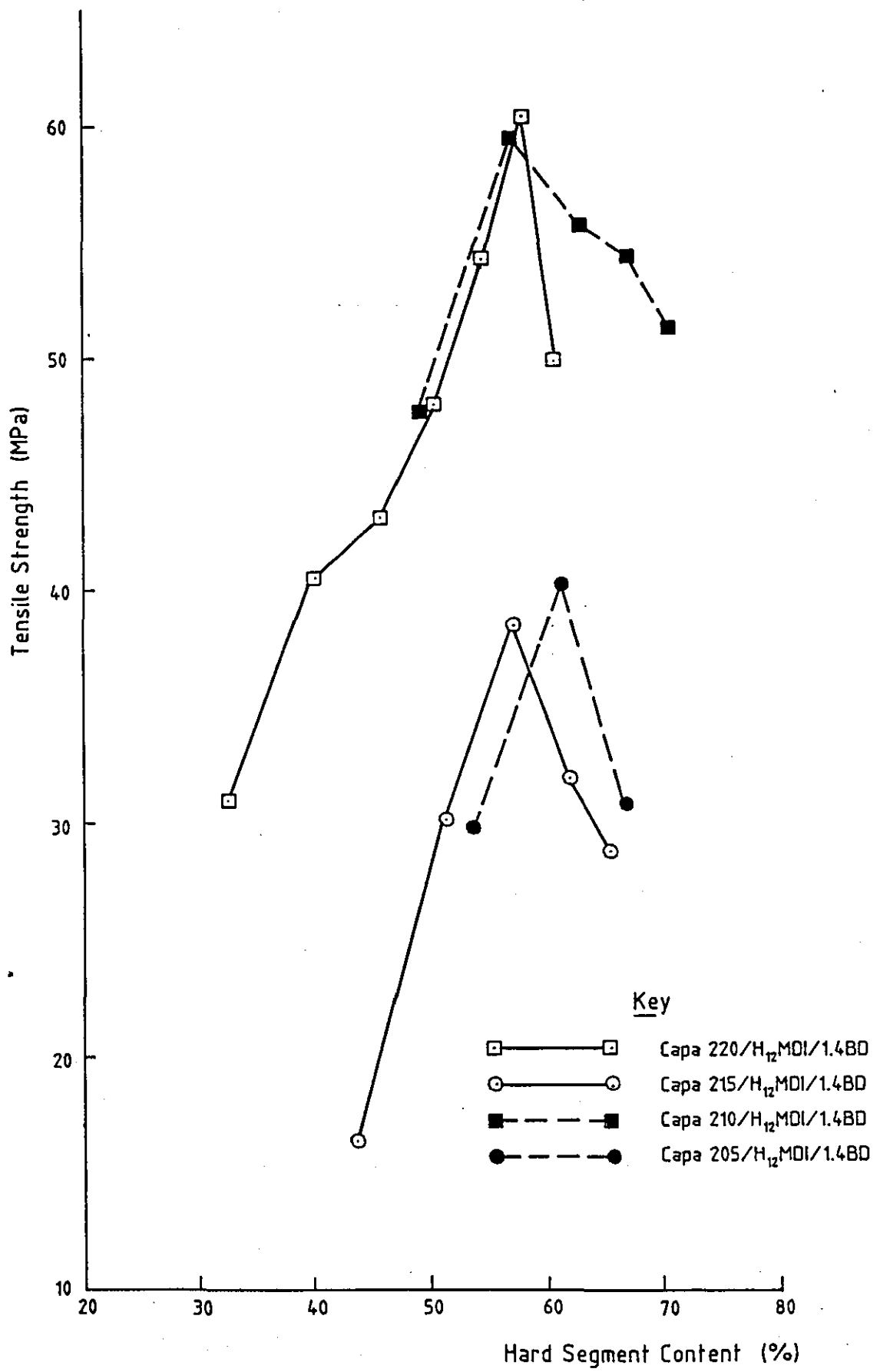
Graph 5 . 3 . 2 . Modulus at 100% vs Block Ratio for H_{12} MDI/1,4BD based elastomers. (See Table 11).



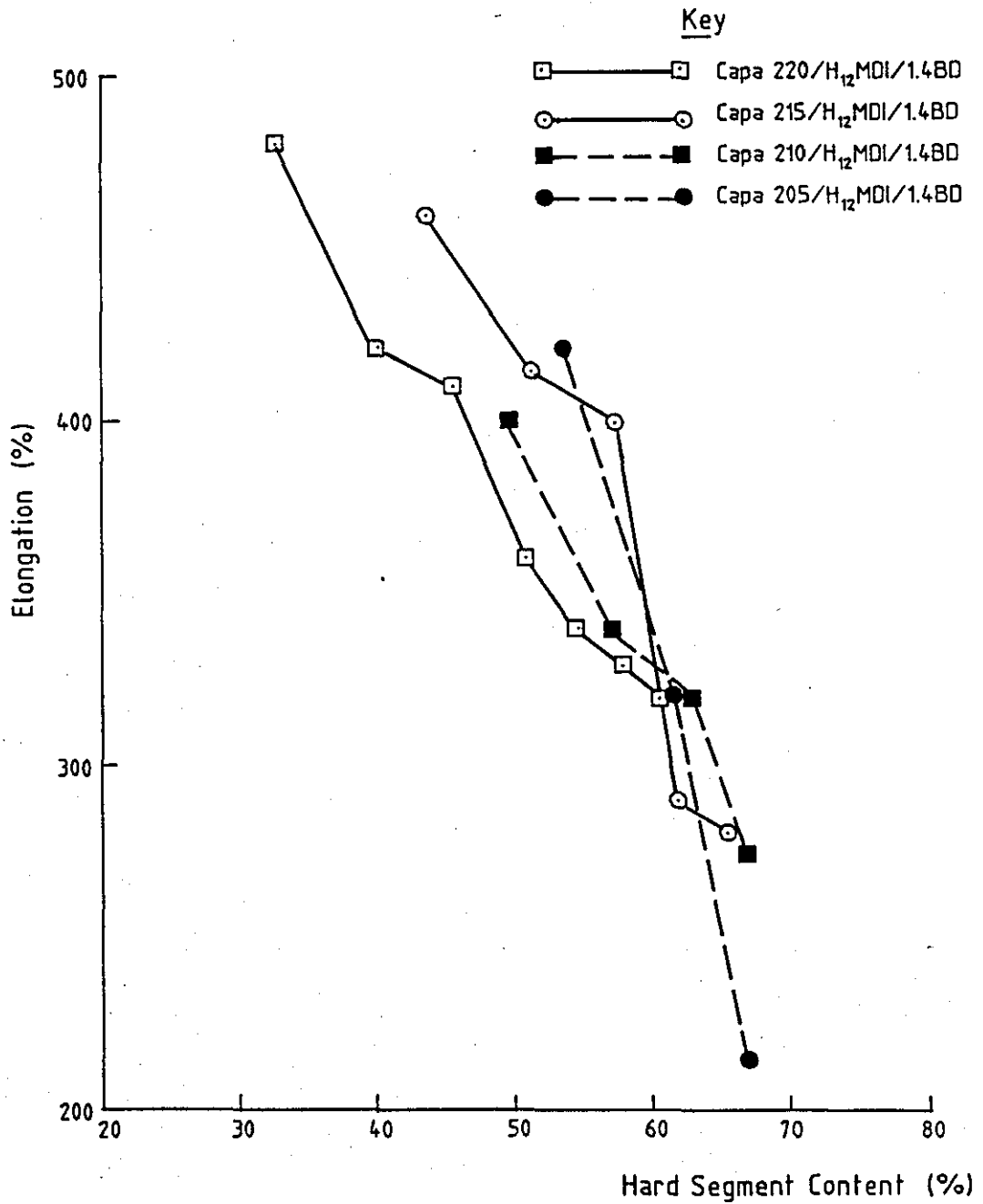
Graph 5 . 3 . 3 . Elongation (%) vs Block Ratio for H_{12} MDI/1,4BD based elastomers. (See Table 11).



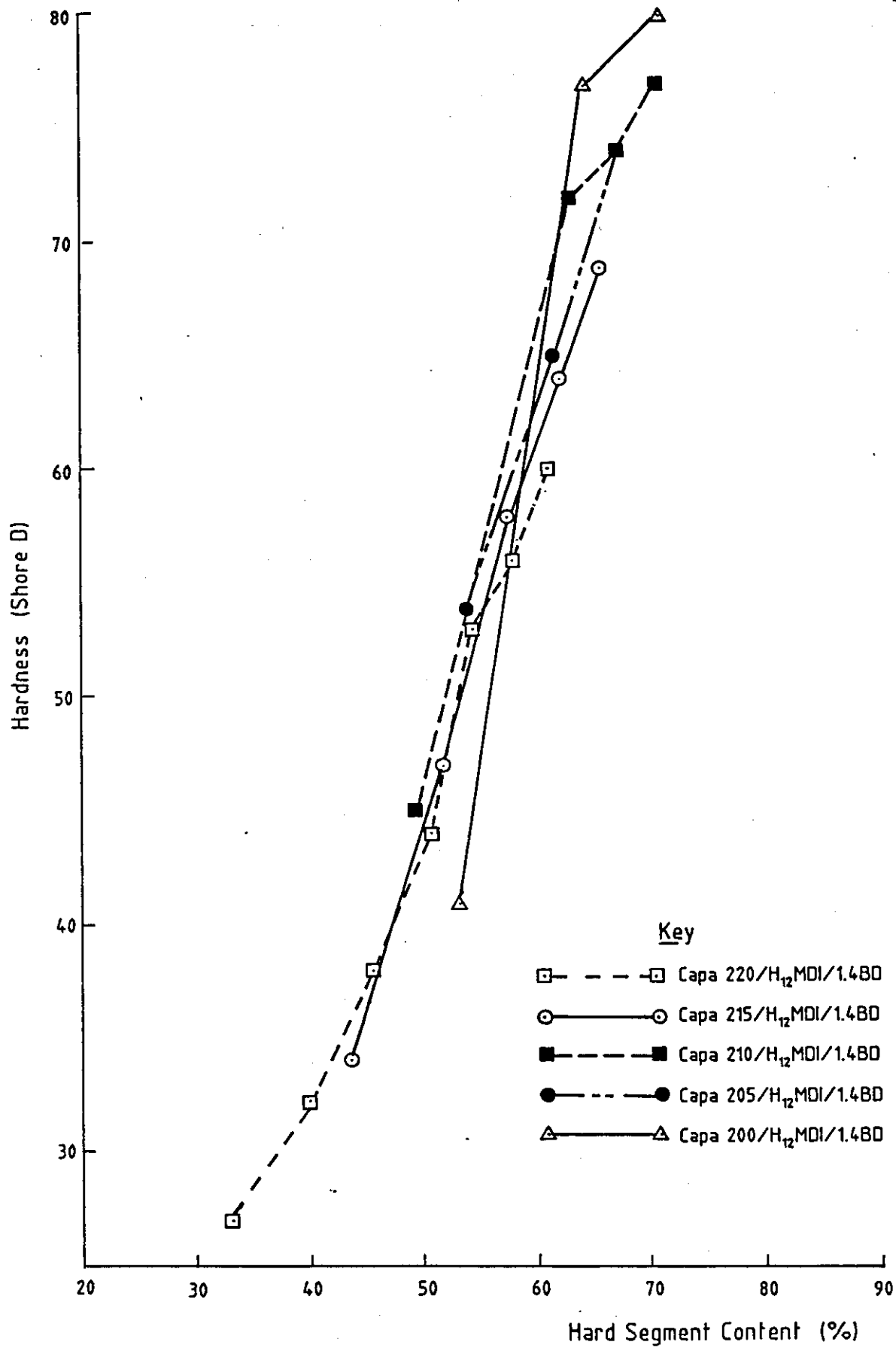
Graph 5 . 3 . 4 . Hardness vs block ratio for H₁₂MDI/1,4BD based elastomers.



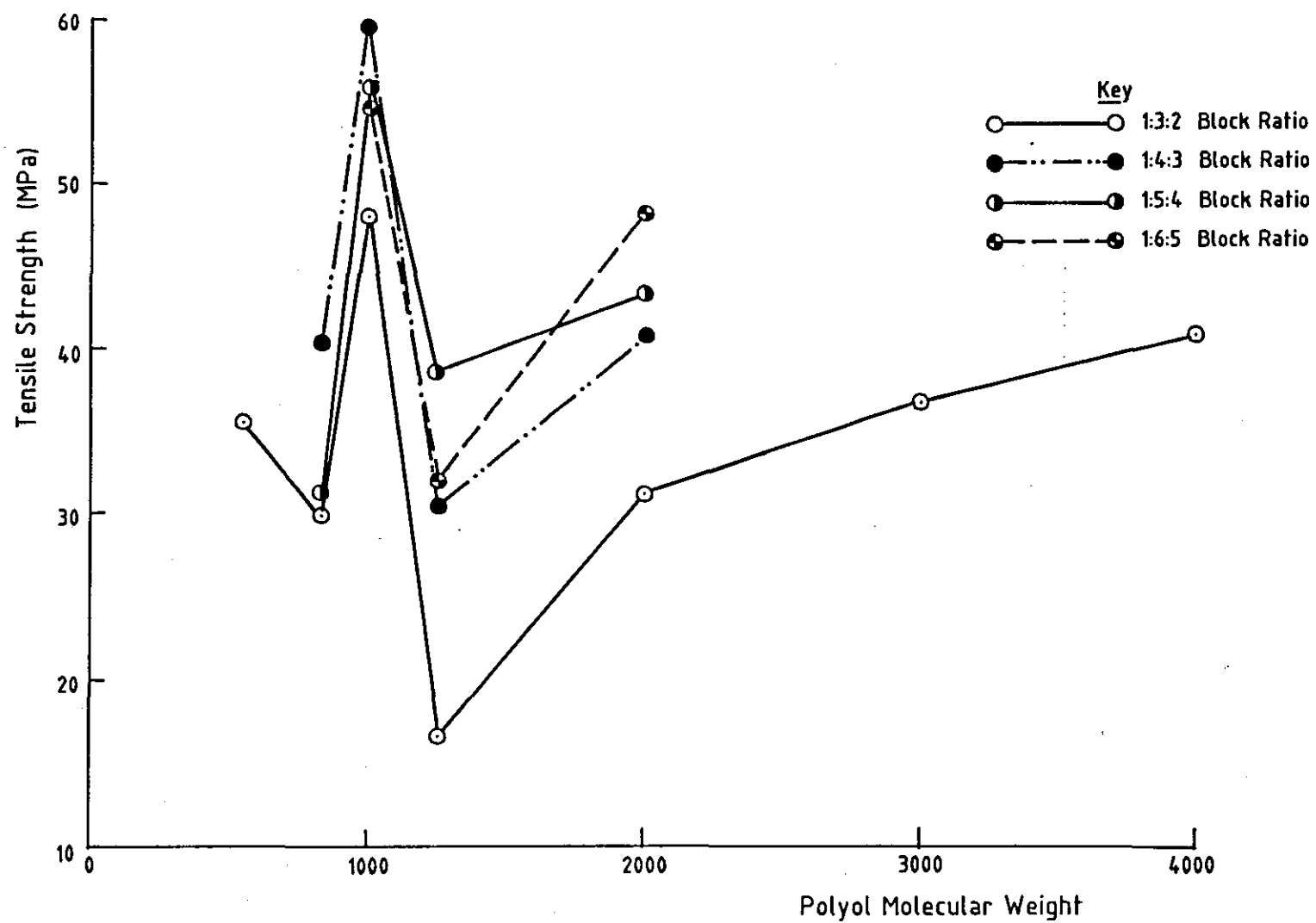
Graph 5 . 3 . 5 . Tensile strength vs hard segment content
for H_{12} MDI/1,4BD based elastomers



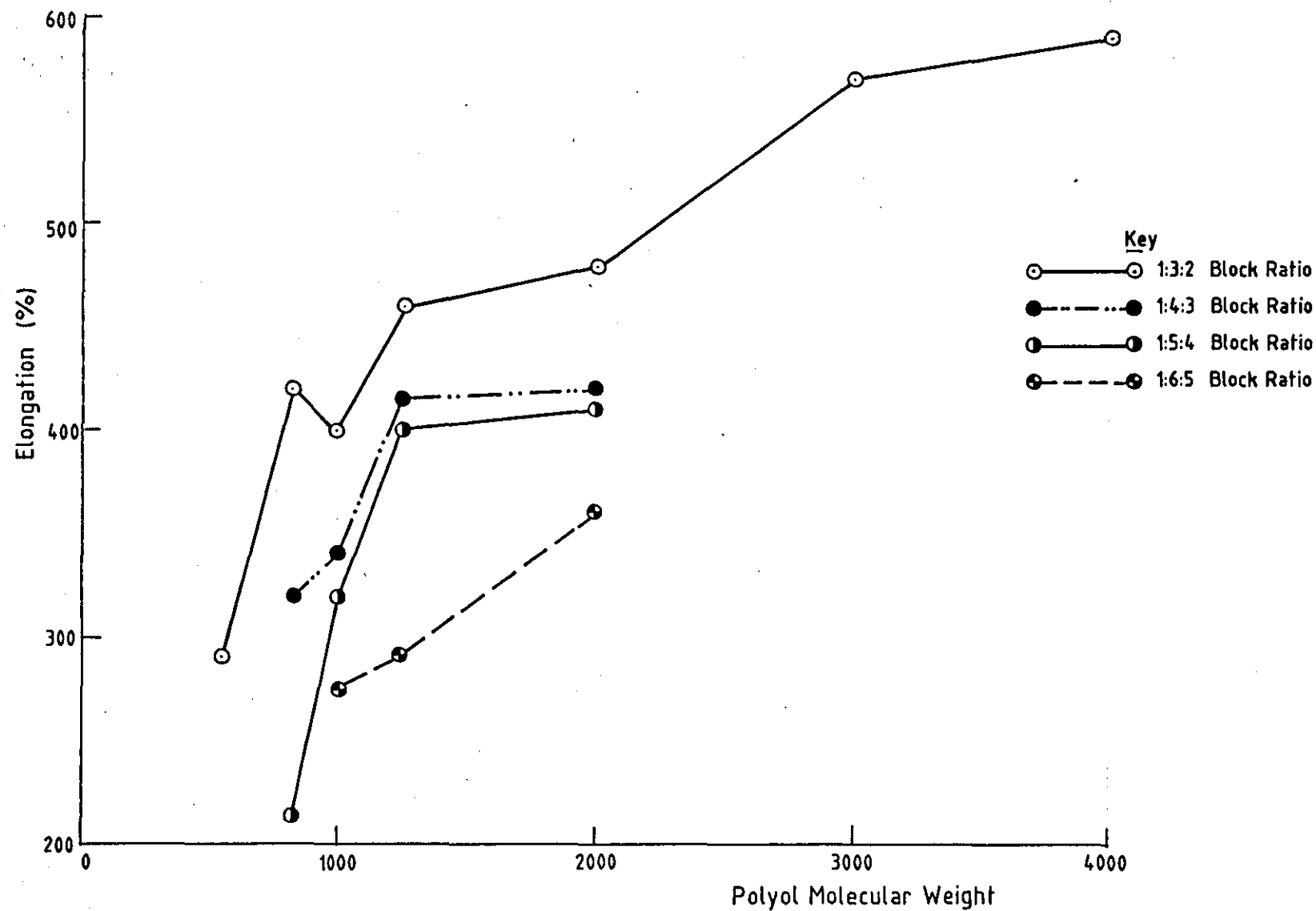
Graph 5 . 3 . 6 . Elongation at break vs hard segment content
for H_{12} MDI/1,4BD based elastomers



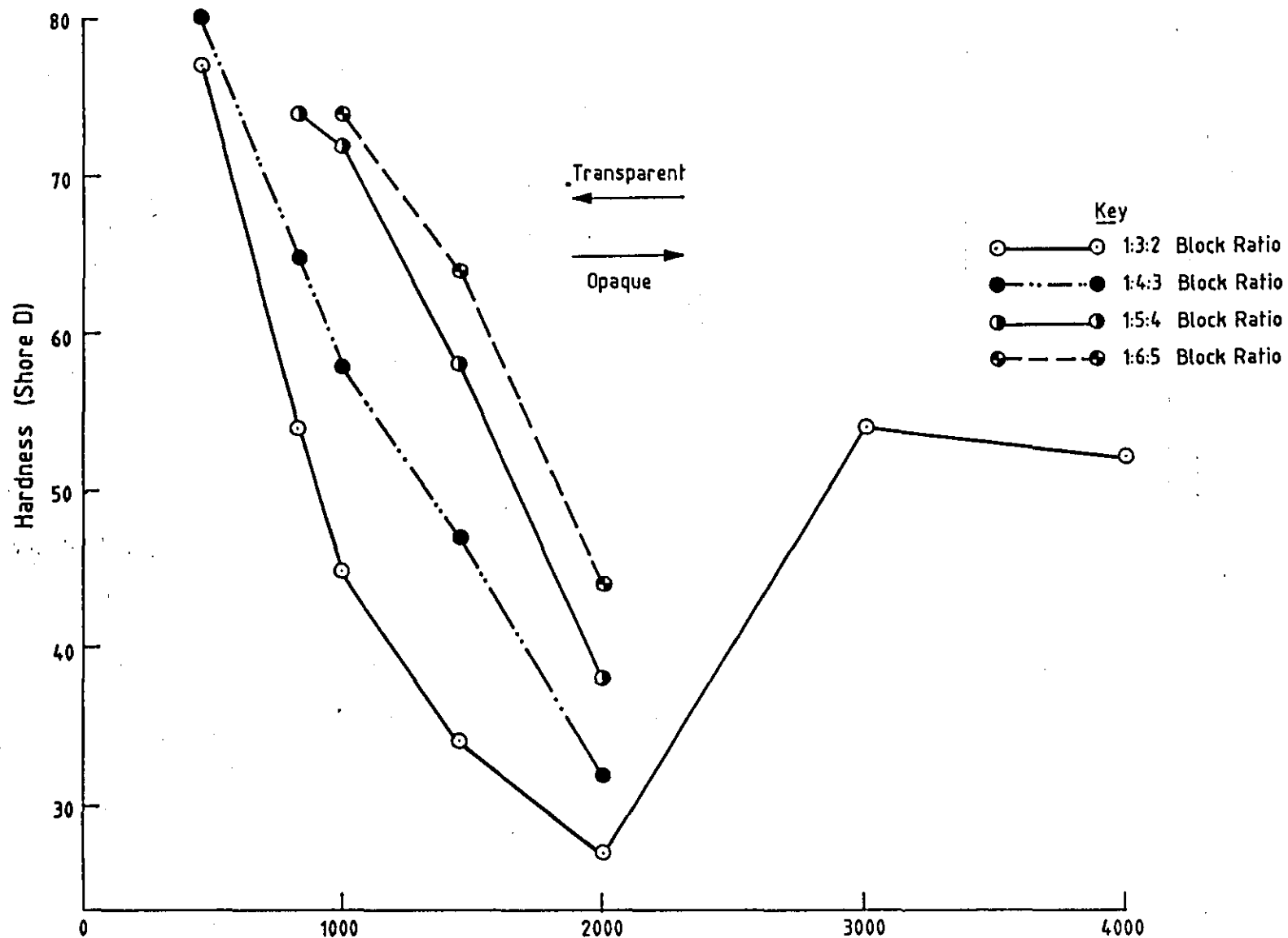
Graph 5 . 3 . 7 . Hardness vs hard segment content for H₁₂MDI/1,4BD based elastomers.



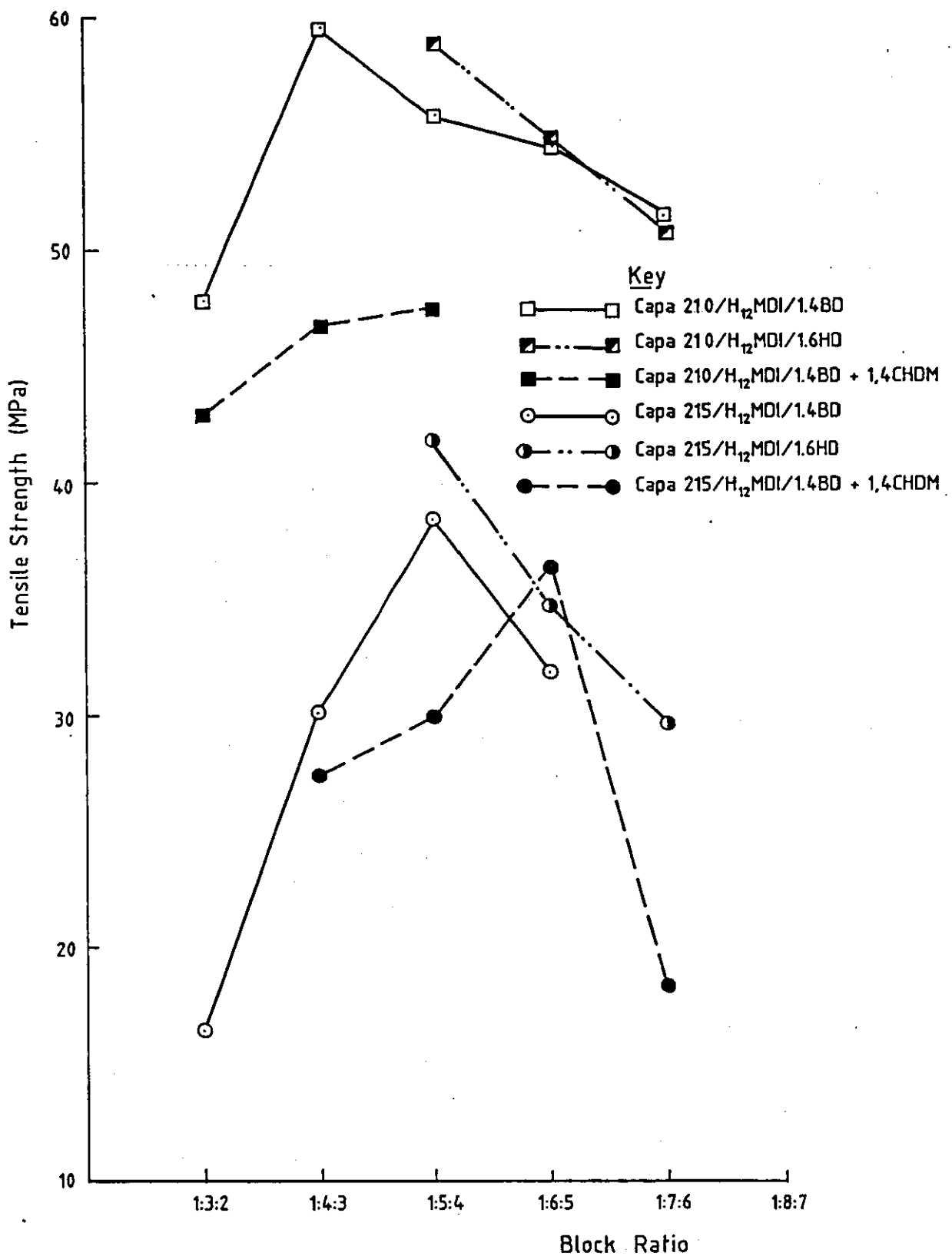
Graph 5 . 3 . 8 . Tensile strength vs elastomers of varying molecular weight based on H₁₂MDI/1,4BD



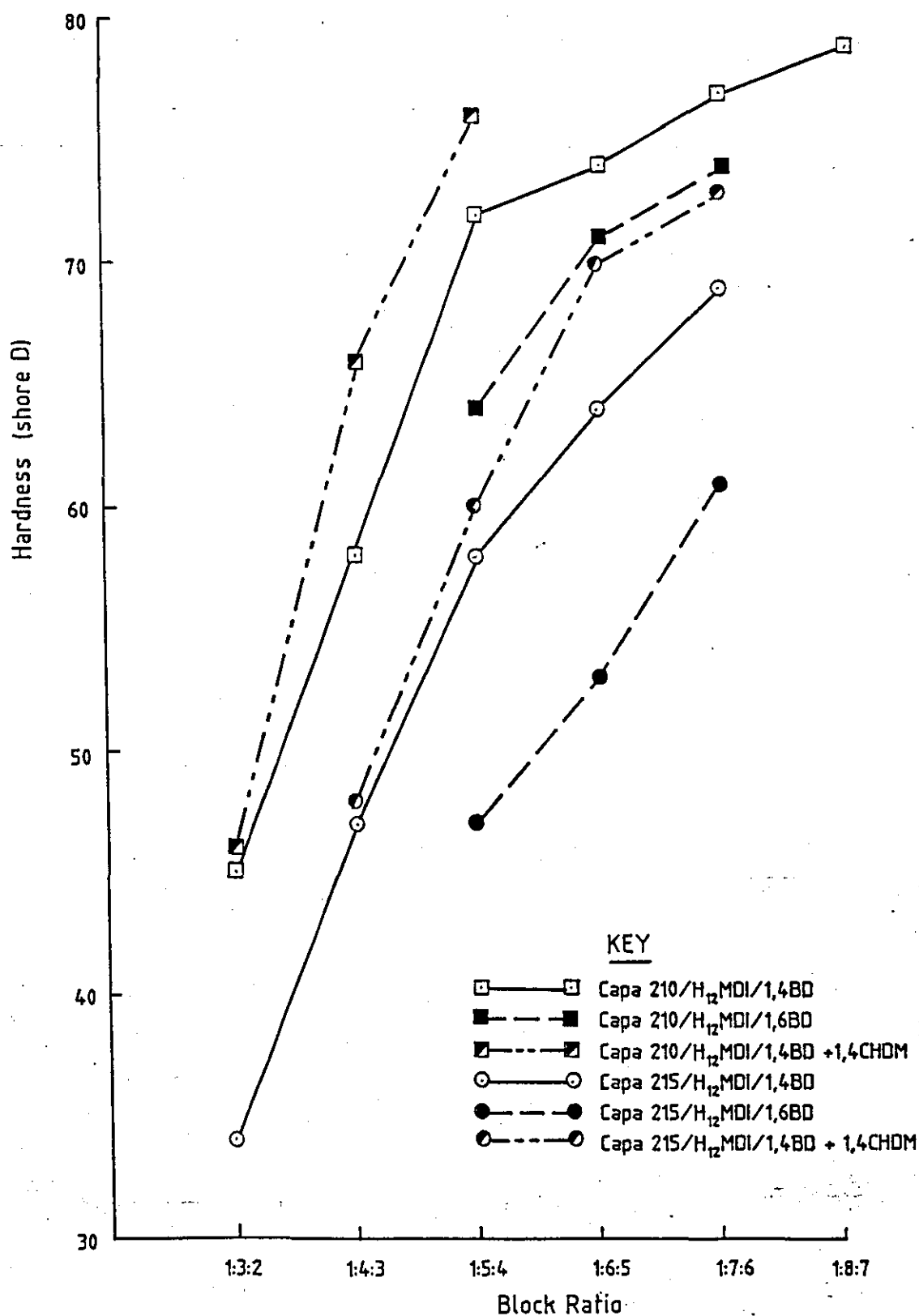
Graph 5 . 3 . 9 . Elongation at break vs elastomers of varying polyol molecular weight based on H_{12} MDI/1,4BD at differing block ratios.



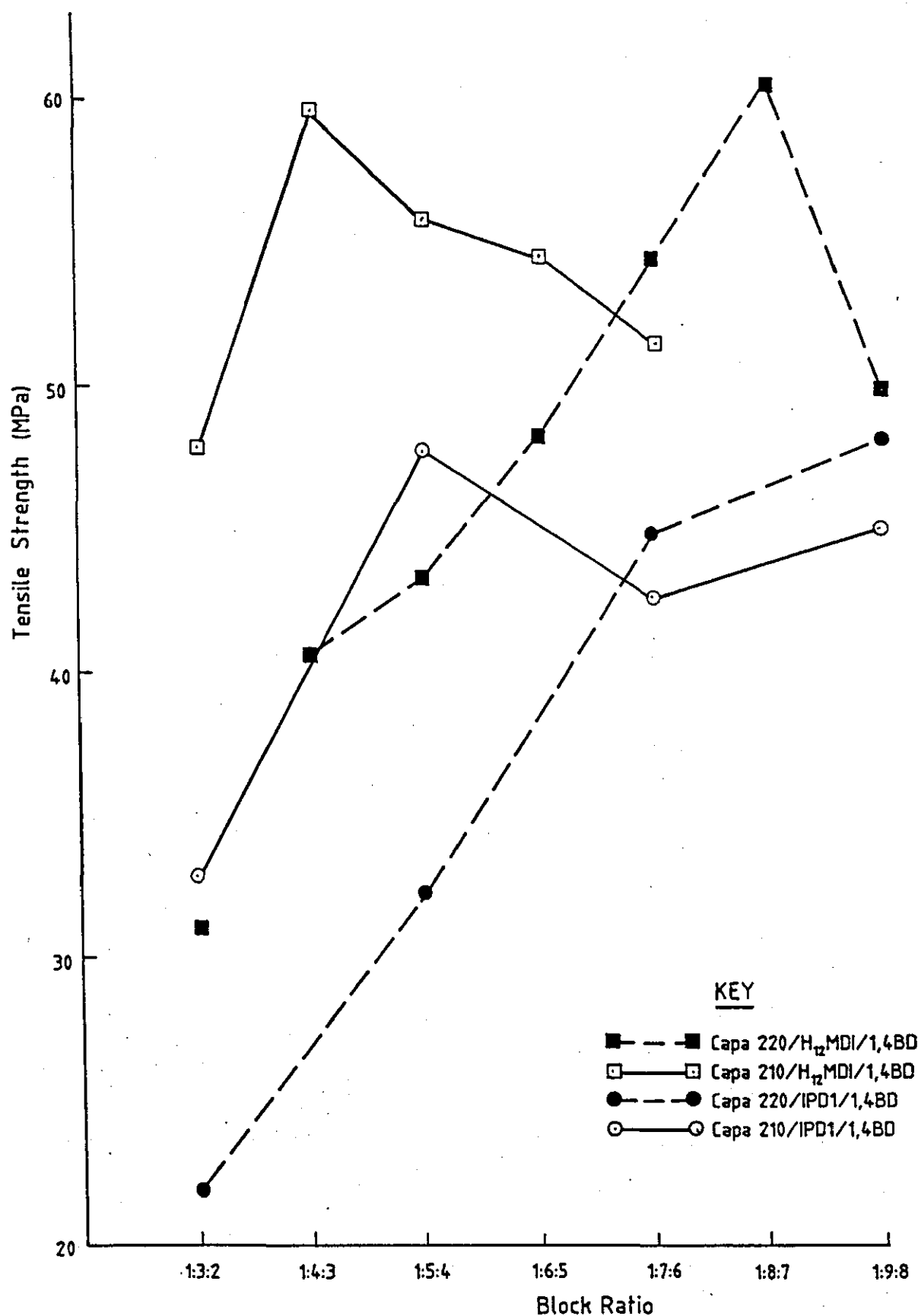
Graph 5 . 3 . 10 . Hardness vs elastomers of varying polyol molecular weight based on H_{12} MDI/1,4BD at differing block ratios



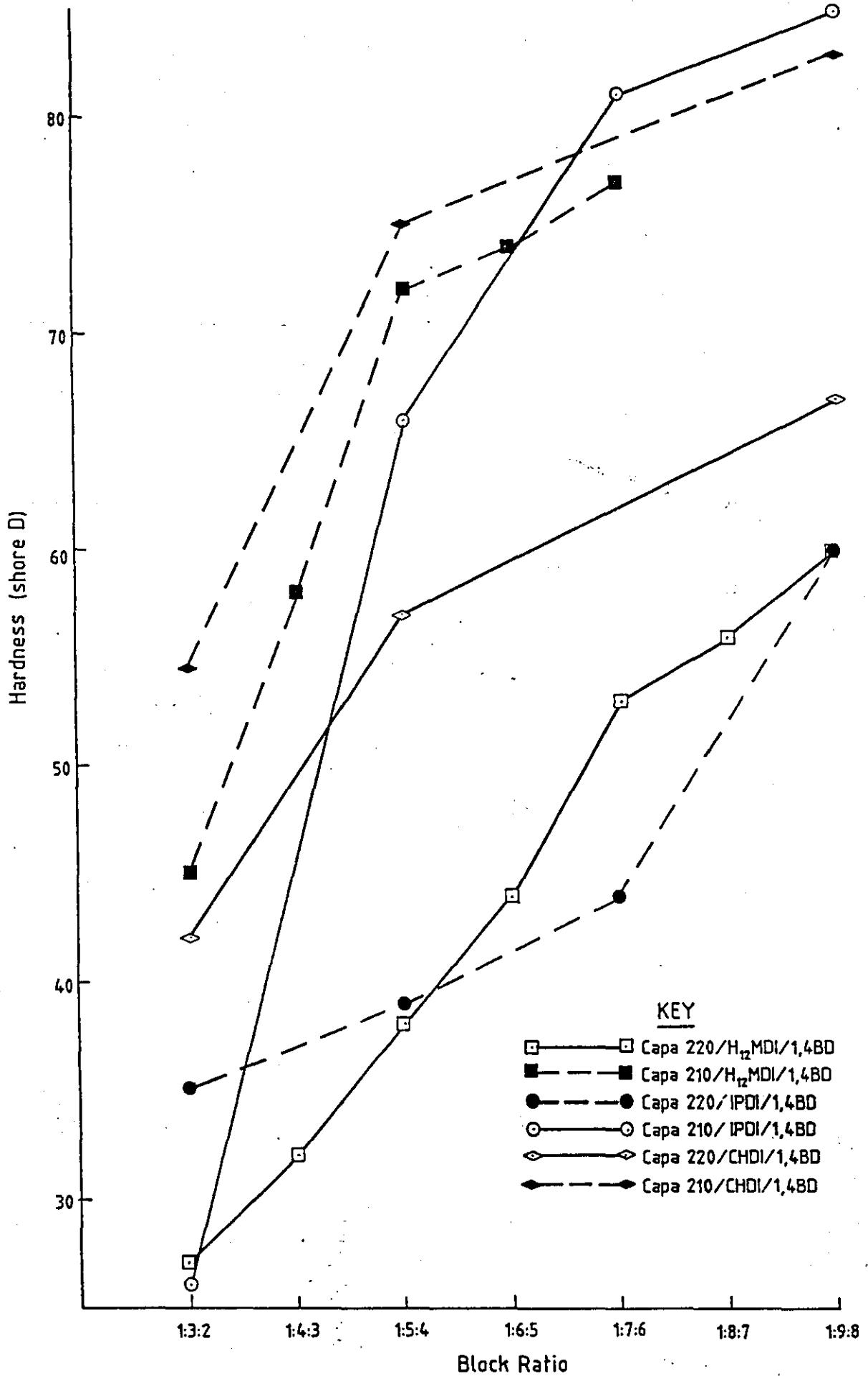
Graph 5 . 3 . 11 . Tensile strength vs block ratio for elastomers based on Capa 215/ H_{12} MDI and Capa 210/ H_{12} MDI extended with various chain extenders.



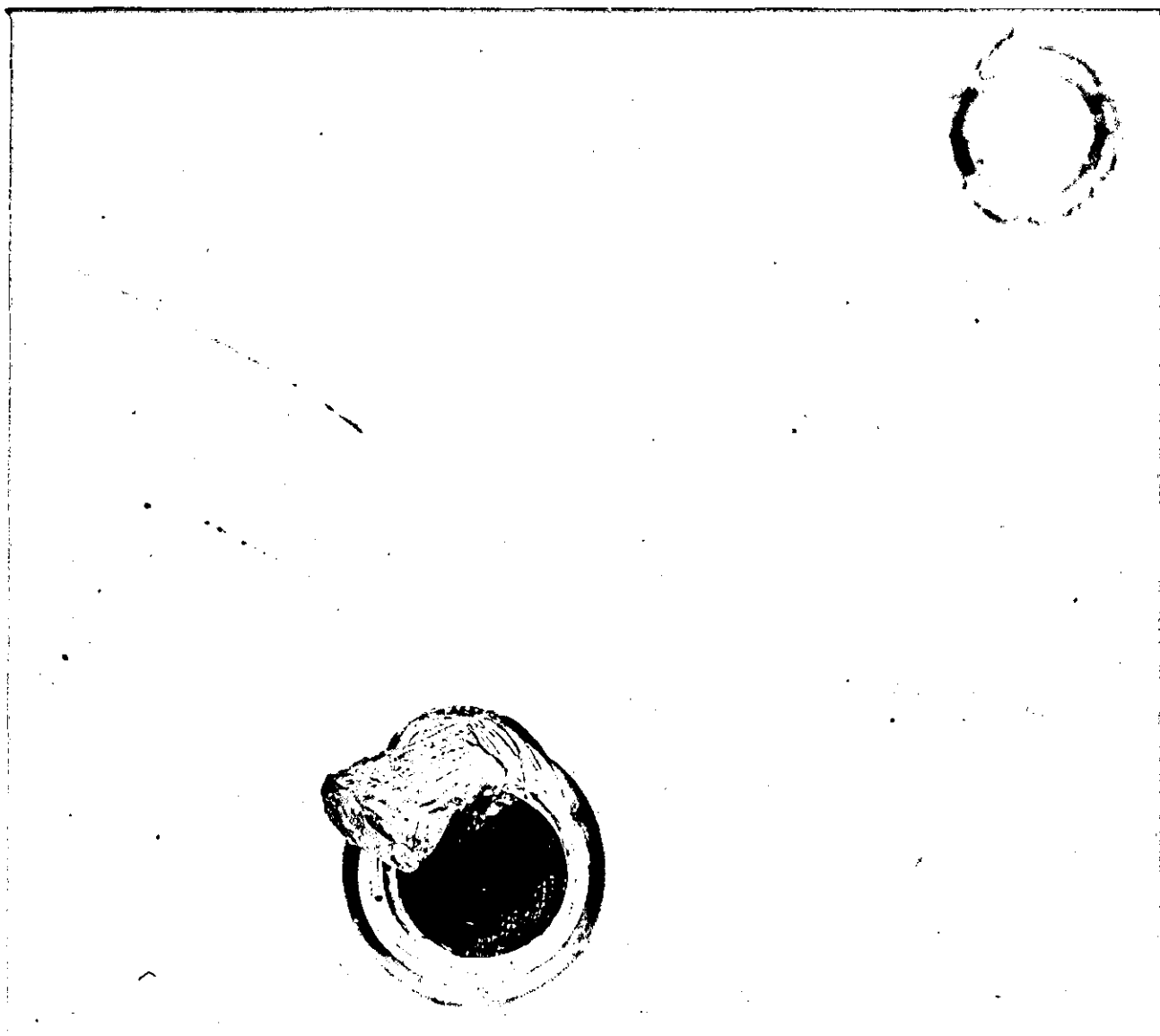
Graph 5.3.12 Hardness vs Block Ratio for Capa 215/ H_{12} MDI and Capa 210/ H_{12} MDI elastomers extended with various chain extenders.



Graph 5 . 3 . 13 Tensile Strength vs Block Ratio for IPDI/ 1,4BD and H_{12} MDI/1,4BD based thermoplastic elastomers.



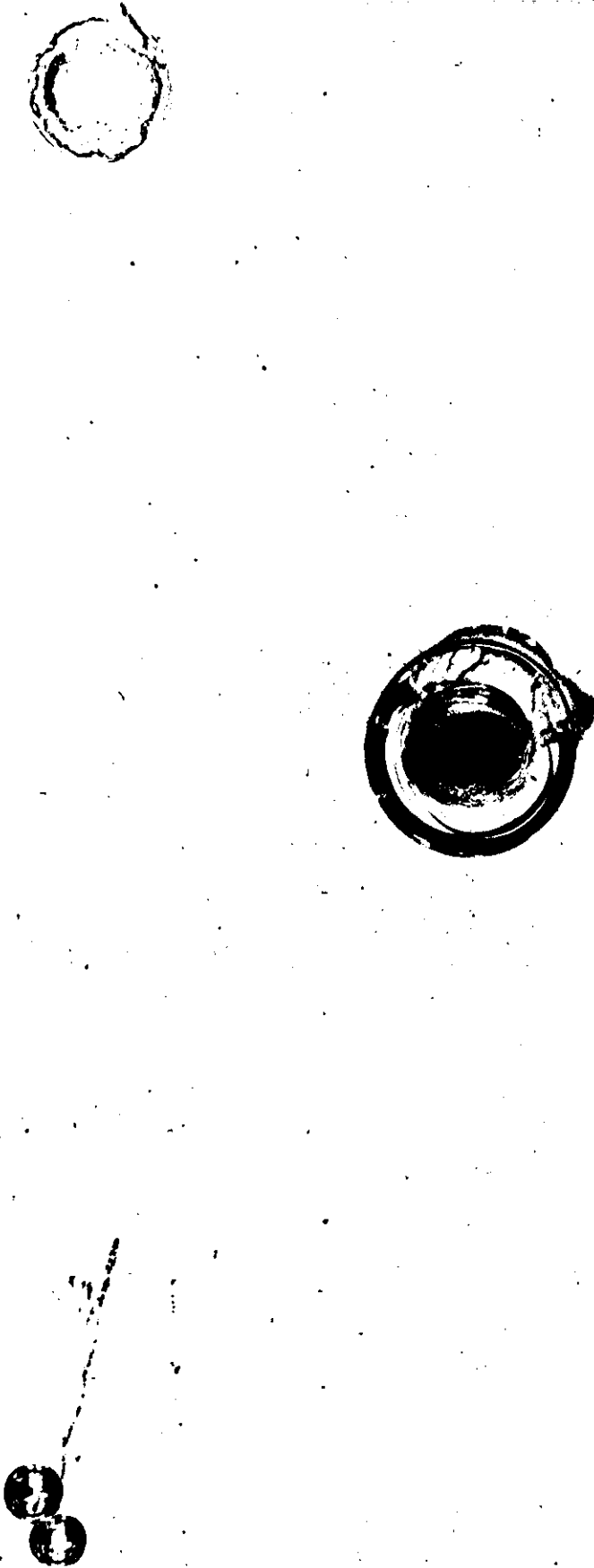
Graph 5 . 3 . 14. Hardness vs Block Ratio for thermoplastic elastomers based on several different diisocyanates



PHOTOGRAPH 5. 5. 2^b: reverse of photograph 5.5.2a

Formulation: Capa 210 : H₁₂MDI : 1,4-BD

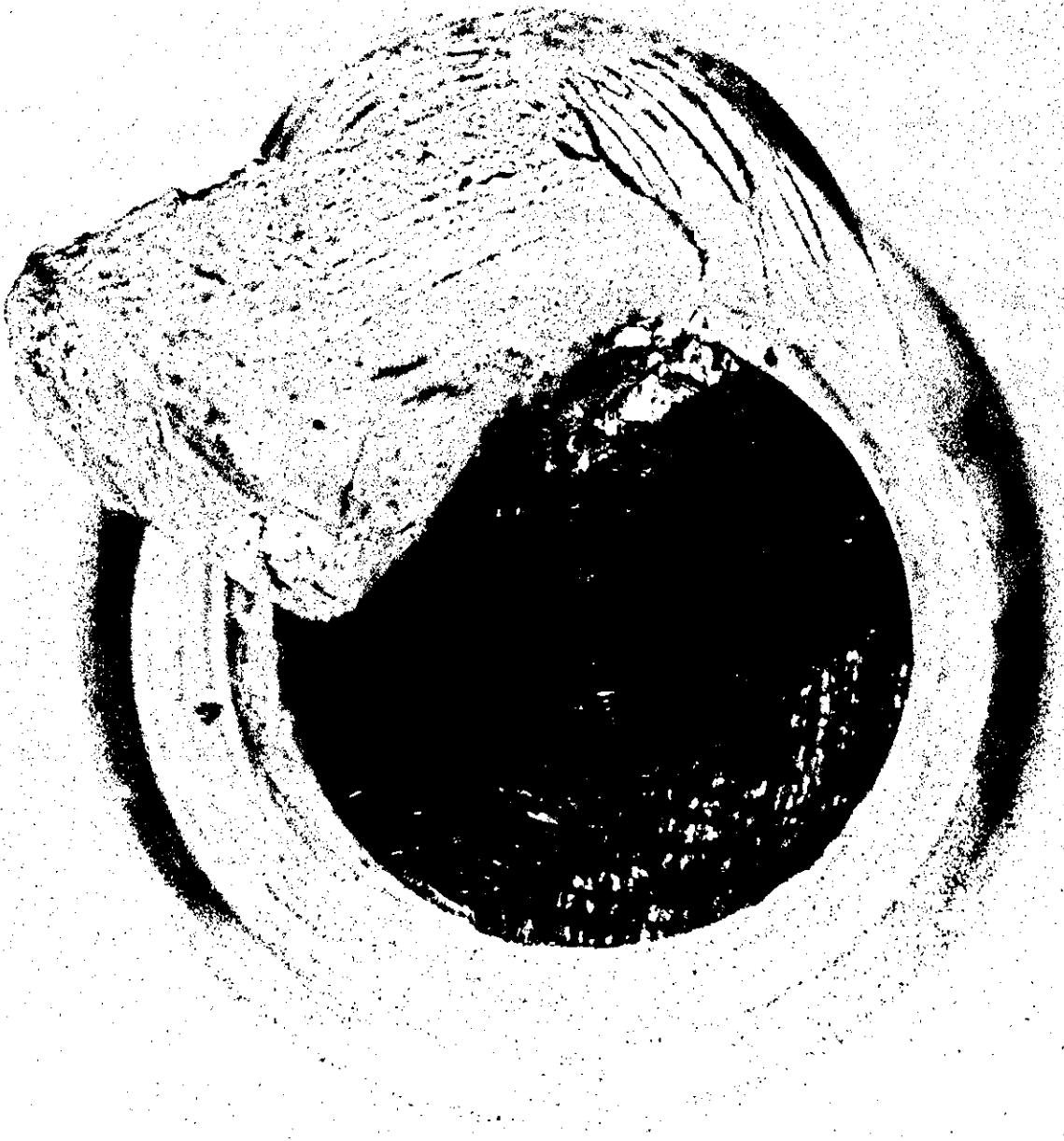
1 : 5 : 4



PHOTOGRAPH 5. 5. 2a: in direction of projectile fire

Formulation: Capa 210 : H₁₂MDI : 1,4-BD

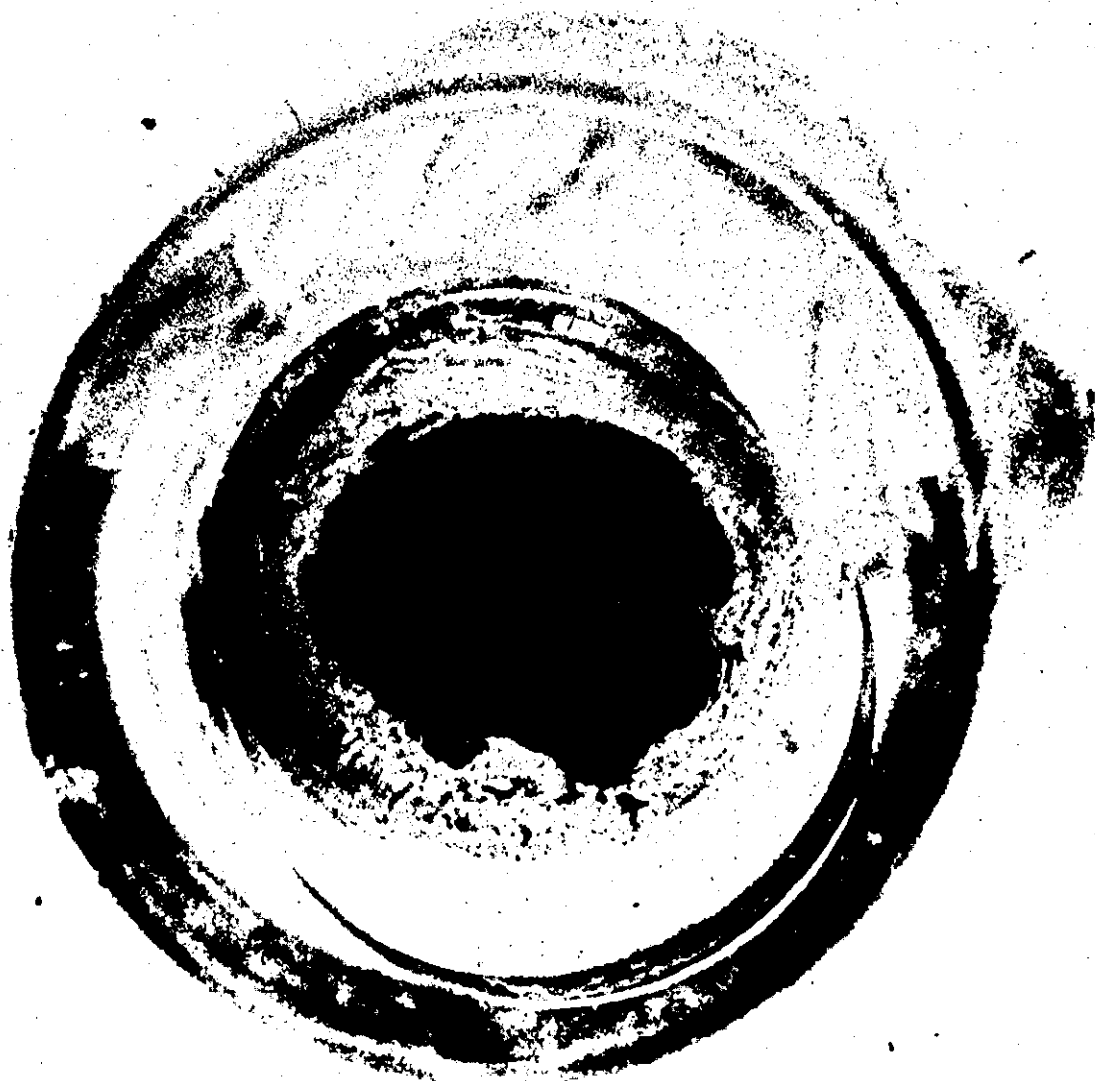
1 : 5 : 4



PHOTOGRAPH 5. 5. 2d

Formulation: Capa 210 : H₁₂MDI : 1,4-BD

1 : 5 : 4



PHOTOGRAPH 5. 5. 2c

Formulation: Capa 210 : H₁₂MDI : 1,4-BD

1 : 5 : 4

CHAPTER 6

GENERAL DISCUSSION AND CONCLUSIONS

The aim of this research was to synthesise transparent polyurethanes which could be compared to the physical properties of polycarbonate, presently used as a face visor and riot shield material. Polycarbonate has the advantages of high hardness, impact strength and ballistic property but is readily degraded by abrasion. Polyurethanes were synthesised from a range of low hardness flexible elastomers through to rigid, high hardness and brittle materials in order to observe and follow trends by varying the following in the synthesis of the elastomers.

- i) The type of diisocyanate used
- ii) The molecular weight of polyol used
- iii) The chain extender system incorporated
- iv) The block ratio
- v) The introduction of crosslinking via the chain-extender system
- vi) The introduction of crosslinking via the polyol system.

A range of polyurethane elastomers was synthesised and characterised by using IR, X-ray, thermal techniques, GPC, physical and mechanical properties. The reactivity of raw materials was carried out (generally for the H₁₂MDI based elastomers) to optimise the synthesis conditions. An infrared technique was used to observe the change in isocyanate content with reaction time. The temperature and time of reaction was adjusted when other diisocyanates were used and crosslinking introduced. There were problems in casting void free elastomers, especially in preparation of test pieces for ballistic studies at the various thicknesses required. The drying of raw materials is an essential requirement in the synthesis of these elastomers.

In these reactivity assessments it was observed that soft segments prepared using Capa 205 and Capa 215 gave lower viscosity mixtures in comparison with Capa 200, Capa 210 and Capa 220 at standard times. It was later found that Laporte use catalysts in the manufacture of the Capa polyols and this suggests that Capa 205 and Capa 215 are of lower reactivity due to catalyst concentration or use of lower activity catalyst.

GPC studies were carried out on all the polycaprolactone polyols used in this study and with higher resolution columns these polyols were found to have more than one molecular weight peak. The GPC studies of the soft segments (polyol: diisocyanate at 1:1 ratio) also show several molecular weight peaks, this would indicate that the polyol is composed of several different molecular weight species. It is noticed that the H_{12} MDI soft segment gives a broader molecular weight peak in comparison with the IPDI soft segment, and this may be due to the presence of isomers of H_{12} MDI. The H_{12} MDI is supplied as a mixture of three isomers and although these are all of the same molecular weight they would vary in reactivity and therefore would contribute in broadening the molecular weight peak. GPC studies of hard segments could not be carried out as these did not dissolve in the solvent used.

DSC studies carried out on all the polyols showed that Capa 205, Capa 210 and Capa 215 have two endothermic peaks. The high melting endotherm corresponded well with the published melting point of the polyol, whereas the lower melting endotherm was similar to the melting transition of the low molecular weight polyol (Capa 200). This, together with the GPC analysis suggests, that the polyols may be composed of a blend, the ratio of which being suited to obtain the required hydroxyl value. The ratio of the polyol blend is uncertain, as the two techniques used did not give any quantitative data. The Capa 220 also shows two peaks in the DSC, the lower temperature peaks being much smaller in magnitude; only one peak is observed for Capa 231 and Capa 240 indicating these to have no mixtures of differing melting transitions. The DSC thermograms of

the soft segments showed no endothermic peaks for those based on Capa 200, Capa 205 and Capa 210 as these are not crystalline but transparent. The opaque soft segments were based on Capa 215 and Capa 220 and these gave endothermic transitions at the same temperature as the pure polyols. There is little molecular weight build up of the chains at this soft segment stage which is sufficient to increase the melting point of this transition. After chain extension the melting transition increases by 30 to 40°C. DSC thermograms of the hard segments (H_{12} MDI/1,4-BD) gave one main peak with two smaller peaks on either side of this large peak. The possibility exists of three types of hard segment arising from the three isomeric forms of H_{12} MDI. Similar thermograms are observed with the H_{12} MDI/1,3-BD hard segments, in the case of H_{12} MDI/1,6-HD hard segment a much broader transition is observed which may obscure the presence of other peaks.

The resultant elastomers of the above segments were generally transparent when based on H_{12} MDI, except when the higher molecular weight polyols (i.e. Capa 231 and Capa 240) were used producing opaque materials. It is to be noticed that soft segments of the Capa 200, Capa 205 and Capa 210 are transparent and so after chain extension a transparent polyurethane should result. However, the soft segments of Capa 215 and Capa 20 are opaque, yet the resultant elastomer is transparent and this is due to the disruption introduced by the chain extension process and curing. In the case of Capa 231 and Capa 240 this disruption is not sufficient to hinder the crystallisation of these soft segments. Some of the lower polyol molecular weight based elastomers did appear to be translucent, but on immersing in a liquid of the same refractive index, they were found to be transparent. The translucency is due to the surface imperfections of the elastomer picked up from the mould surface. The GPC studies show a gradual increase in molecular weight of the elastomer with increase in the molecular weight of the base polyol. The molecular weight of the elastomer decreases, when the base polyol molecular weight is above 2000, i.e. when Capa 231 and Capa 240 (3000 and 4000 m.wt. respectively) are used.

The Capa 231 and Capa 240 based elastomers are opaque, this loss of transparency is due to phase separation of the soft segment and is indicated by the GPC by lowering of the overall elastomer molecular weight. In the X-ray studies (WAXD) the elastomers based on Capa 231 and Capa 240 show distinct circular lines in the photographs. The lines appear as peaks in the diffractometer traces taken which give good correlation with the crystal structure of the polycaprolactone homopolymer [10-11]. This further indicates the phase separation of soft segment in these elastomers. The elastomers prepared with base polyol molecular weight of 2000 and lower all gave diffuse halos in the photographs and a broad diffuse peak in the diffractometer traces.

Polyurethane elastomers were synthesised from various different diisocyanates, these being CHDI, PPDI, TMDI, IPDI and mainly H_{12} MDI (see Appendix I). The CHDI and PPDI based elastomers produced were generally translucent to opaque. The problem with these diisocyanates is that they dimerize quite readily. The manufacturers (Akzo Chemie) reported that transparent polyurethanes can be synthesised by using fresh diisocyanate. This in practice would mean the distilling of diisocyanate immediately prior to use. This procedure is far too hazardous and not attempted. TMDI synthesised elastomers were transparent but soft and flexible even at the high block ratios used. IPDI based elastomers were transparent and generally of higher hardness and rigidity at lower block ratios in comparison with the H_{12} MDI elastomers.

In the synthesis of the IPDI elastomers a catalyst was added (DABCO at 0.1 pbw) at the very end of the synthesis after the chain extension stage and mixed prior to casting. The catalyst was only added in the preparation of linear IPDI elastomers, and not the crosslinked polyurethanes. In comparison of the tensile strength results with the H_{12} MDI based elastomers, the IPDI materials gave lower values when based on the Capa 220 and Capa 210 polyols at lower block ratios. As the block ratio was increased these tensile results became closer together. The tensile test results for

elastomers based on Capa 215 and Capa 205 did not follow this general trend and gave higher values for the IPDI polyurethanes. This suggests some difference in polyol reactivity and correlates with the earlier findings of Capa 215 and Capa 205 being of low reactivity than the other polyols due to lower catalyst concentration or activity. The other indication is that the catalyst used in the preparation of Capa 225 and Capa 205 is different to that of Capa 220 and Capa 210, this is deduced as the synthesis method is the same for all the linear IPDI elastomers but in comparison with H_{12} MDI elastomers, the polyurethanes containing Capa 215 and Capa 205 gave a different result to the general trend. It can be said that the catalyst incorporated in the Capa 225 and Capa 205 polyols has a greater beneficial effect (as regards tensile property) than the Capa 220 and Capa 210 in the IPDI synthesis in which 0.1 pbw DABCO is added. In the case of the highly crosslinked elastomers, the IPDI based polyurethanes generally gave higher tensile and hardness values in comparison with the H_{12} MDI elastomers, but gave lower elongation at break values.

The tensile strength of the linear H_{12} MDI elastomers chain extended with 1,4-butane diol showed, as expected, an increase in hardness and rigidity with increase in block ratio. These properties are more pronounced with the elastomer based on lower molecular weight polyols. The tensile strength of the elastomer is found to increase with block ratio to an optimum (generally at approximately 60 weight per cent hard segment content) then decreases. The elongation at break generally decreases in value with increase in block ratio. The surface hardness is found to decrease with increase in the base polyol molecular weight for the transparent polyurethanes. Further increase in polyol molecular weight produces opaque elastomers which show an increase in the surface hardness. The elongation at break is found to increase with increase in the base polyol molecular weight. The tensile strength generally increases with polyol molecular weight and reaches an optimum at Capa 210 (1000 m.wt) above which the tensile property is reduced. The elastomer based on Capa 210 is the optimum, as a reduction in polyol molecular weight results in a

more rigid and tends towards the brittle nature of the material. In the other situation increasing the polyol molecular weight above 1000 produces a more flexible and softer elastomer. The polyurethanes based on Capa 225 and Capa 205 do fit in the general trend, but give lower than expected values for the tensile property. In the case where IPDI is used instead of H_{12} MDI, the Capa 215 and Capa 20 elastomers give higher than expected values, as an external catalyst was used. This again shows the difference in reactivity of these two polyols when compared generally with the other polyols used.

In the same system of H_{12} MDI linear polyurethanes but chain extended with the unsymmetrical 1,3-butanediol similar general trends are observed as with the symmetrical 1,4-butanediol as the chain extender. In general lower tensile and hardness values are obtained with the 1,3 butanediol extended elastomers. With increase in block ratio the optimum tensile property is reached at a higher block ratio in comparison to the 1,4-butanediol extended polymers. In using a symmetrical but longer chain length extender as in the case of 1,6-hexanediol, higher elongation and lower hardness values are generally obtained in comparison with the 1,4-butanediol elastomers. The tensile strength property is generally higher for the 1,6-hexanediol extended elastomers, although once again the Capa 215 and Capa 205 based elastomer gave lower than expected values. On changing to a mixed chain extender system (1,4-BD + 1,4-CHDM at 1:1 ratio) more rigid elastomers are produced with lower elongation and tensile values. With the Capa 220 polyol and the mixed chain extender system the tensile strength values were found to be slightly higher in comparison with the butanediol extended polymers. This indicates that the higher molecular weight of the polyol reduces the brittle nature introduced by the mixed chain extender sufficiently to give the higher tensile property. The Capa 225 and Capa 205 polyol based elastomers extended with the mixed chain extender system gave lower tensile values than expected.

The tensile strength results of the crosslinked elastomers show little significant change in trends when crosslinking is introduced via the chain extender system. The crosslinked elastomers obtained by using higher functionality polyols showed an improvement in tensile and hardness property. The elongation at break is reduced and decreases further with block ratio as hardness increases. Comparing the H₁₂MDI and IPDI highly crosslinked elastomers, higher elongation but lower tensile property is obtained for the former diisocyanate. As the same synthesis method is used for both diisocyanate systems, a greater crosslinking would be induced by the IPDI as it is more reactive giving the lower elongation, but higher tensile strength property.

Molecular weight studies of the elastomers prepared were carried out using the gel permeation chromatography (GPC) technique. In general, at constant block ratio and increase in the base polyol molecular weight showed an increase in the M_n values for the transparent linear polyurethanes. On increasing the block ratio it was found that the elastomers became more difficult to dissolve in the solvent and therefore the GPC analysis was limited to the polyurethanes synthesised at the lower block ratio. The elastomers that did dissolve showed the molecular weight to decrease with increase in block ratio. At low block ratios there is considered to be a greater tendency for phase mixing resulting in higher molecular weight polymers. As the block ratio increases phase separation is more pronounced which reduces the molecular weight. This reduction in molecular weight with block ratio would increase the hardness and the tensile strength property (up to an optimum ratio) and reduce the elasticity or elongation, and generally this was found to be the case. The exceptions found were those based on Capa 215 and Capa 205 polyols and the opaque elastomers. Changing the diisocyanate from H₁₂MDI to IPDI a more phase mixed morphology would be expected with an increase in molecular weight. The IPDI elastomers in comparison with the H₁₂DI elastomers show an increase in molecular weight.

Thermal characterisation of the elastomers was carried out by the Differential Scanning Calorimetry (DSC) method and the Dynamic Mechanical Thermal Analysis (DMTA). In the DSC technique the glass transition temperature is taken at the midpoint when there is a shift in the baseline, and the Tg's of the elastomer become easier to detect with increase in the base polyol molecular weight. In the case of the crosslinked elastomers the Tg's are difficult to observe. As the hard segment content increased (with block ratio) for the linear elastomers the Tg becomes more difficult to detect. This was found in two linear elastomers based on Capa 220 and Capa 210 chain extended with 1,4-butanediol. The elastomers based on Capa 210 showed an endotherm in the region of 60-70°C, with the Capa 220 this endotherm is observed in the 70-80°C region. These endotherms are associated with the melting of the soft segment. A higher melting transition was also noticed and is associated with the melting of the hard segment. This hard segment transition however is not seen at low block ratios as a more phase mixed morphology would exist.

The DMTA results show that as the block ratio is increased (e.g. for Capa 220/H₁₂MDI/1,4-BD system) the α -transition which is associated with the soft segment becomes narrower and smaller. This again suggests that at low block ratios there is a greater mixing of these two phases such that this transition is much larger. It is also observed that the Tg increases up to a certain block ratio then does not change appreciably indicating phase separation shown in the DSC as two melting transitions. It is found that the block ratio at which the Tg remains constant is dependent on the polyol molecular weight. The higher the molecular weight of the polyol, the higher the block ratio after which the Tg becomes constant. The average hard segment content (based on this block ratio) was found to be about 45-55 weight percent for the systems looked at in the linear H₁₂MDI based elastomers. On increasing the polyol molecular weight at a constant block ratio the Tg decreases for the transparent polyurethanes and the magnitude of the α -transition increases. The linear IPDI elastomers show in comparison to H₁₂MDI, higher Tg

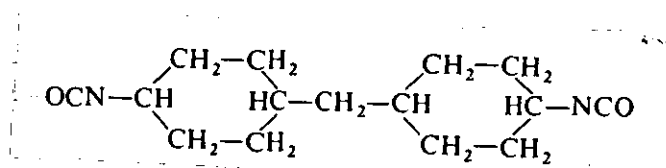
values and no change in phase morphology is seen at the block ratios investigated. This could be due to the higher reactivity and unsymmetrical nature of the IPDI. The crosslinked elastomer based on trifunctional polyols show a greater T_g value than the linear systems. The β -transitions of these crosslinked elastomers are also much greater in area in comparison to the linear elastomers. The lower temperature transitions of the H_{12} MDI crosslinked elastomers are generally greater in magnitude when compared to the IPDI crosslinked elastomers.

A real test of these materials is their impact and ballistic resistance, along with the mode of failure when compared with polycarbonate. Rigid elastomers of high surface hardness values were first prepared from the IPDI. These however had low impact strength and failed in a brittle manner; those elastomers that did fail in a ductile mode had much lower hardness values. In comparison linear H_{12} MDI based elastomers generally failed in a ductile manner due to their more flexible molecular structure. The linear H_{12} MDI/1,4-butanediol elastomers showed higher impact strength at the lower block ratios and lower polyol molecular weight. An increase in impact strength is observed as the base polyol molecular weight is increased, block ratio remaining constant. This is due to the greater impact absorbing property of the higher polyol molecular weight chain, the surface hardness is consequently reduced. In the linear systems, a higher hardness is achieved by changing the chain extender from 1,4-butanediol to the mixed 1,4-butanediol + 1,4-cyclohexanedimethanol (1:1 ratio) but these tend to give lower impact strength. When the Capa 220 polyol is used it is of sufficient high molecular weight to compensate for the rigidity/brittleness introduced by the mixed chain extender system. With the 1,6-hexanediol chain extender the elastomers gave a ductile failure mode and better impact strength values in comparison with the 1,4-butanediol elastomers. The reason for this is that comparisons were mostly made with the lower block ratio and lower base polyol molecular weight, in which case the more flexible hard segment (i.e. 1,6-hexanediol/ H_{12} MDI) would give the higher impact

strength values. The hardness values for the 1,4-hexanediol elastomers are lower for the same reason. The highly crosslinked elastomers prepared generally showed brittle failures with lower impact strength. The H₁₂MDI highly crosslinked elastomers generally gave better impact results than the corresponding IPDI elastomers.

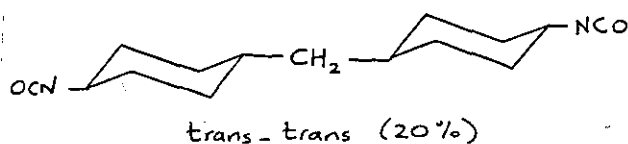
The ballistic testing was carried out by the Ministry of Defence, Colchester, and results were given as a comparison with the polycarbonate used as riot gear material. In this type of testing the difference between brittle and ductile failure shows up even more as the velocity of the projectile is much greater than the impact test carried out. Brittle failure was recorded for an elastomer based on the mixed chain extender system, which shows not total but few brittle failures by the impact test. Ductile failures were recorded for the linear polyurethanes extended with 1,4-butanediol and 1,6-hexanediol. In comparison with polycarbonate an increase of up to 22 percent was obtained for the 1,4-butanediol systems and up to 16 percent was obtained on the 1,6-hexanediol systems on ballistic assessment. The most promising formulation was based on Capa 210, H₁₂MDI and 1,4-butanediol at a 1:5:4 block ratio and this showed a ductile failure mode, a reasonable impact strength value with hardness and a better ballistic evaluation. There is a need to test out these tests at differing temperatures in order to observe the changes in the ballistic/impact value with temperature and comparisons made with polycarbonate. Although catalysts have been avoided in the synthesis (except in the last stage of the IPDI elastomers) as they may have an adverse effect on the transparency of the material on ageing, they should be used and observations made. In the case of the IPDI elastomers an external catalyst had beneficial effects on the physical properties. Such effects may be observed in the H₁₂MDI polymers, but this would require screening of the type of catalyst used. A stainless steel riot shield mould has been made and pilot plant equipment for scale up has been organised. The next criteria is the processing of these polyurethane elastomers and any changes in the final properties due to the processing needs to be investigated.

APPENDIX I

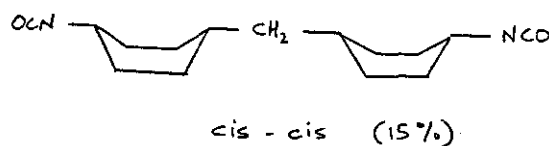
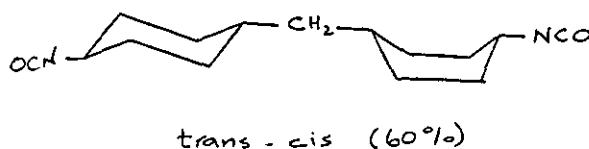
1. 4,4'-Dicyclohexylmethane diisocyanate (H_{12} MDI)

clear liquid of 262 m.wt.

supplied from Bayer, trade name Desmodur W, formerly from Du Pont, trade name Hylene W, comes in the following isomeric forms:

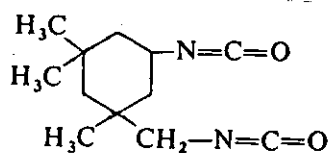


(solidifies at low temperatures)



plus 5% ortho isomer.

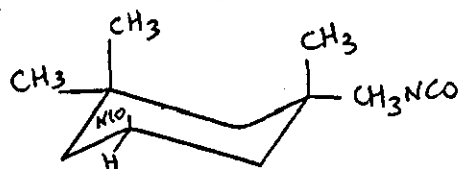
2. Isophorone diisocyanate (IPDI)



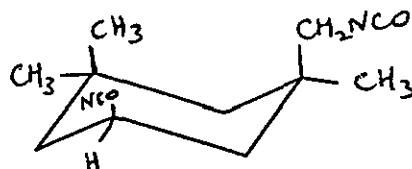
3-Isocyanatomethyl-3,5,5-trimethyl
cyclohexylisocyanate
(m.wt. 222)

A colourless liquid supplied by Veba
Chemie and Huls

comes in two isomeric forms



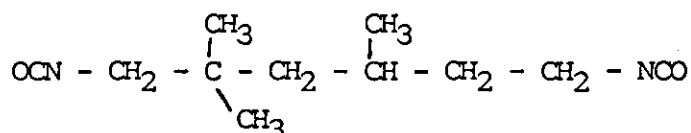
trans 28%



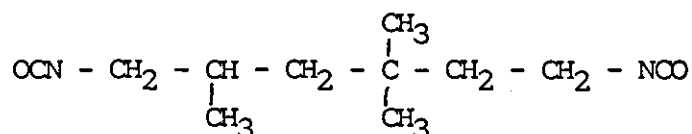
cis 72%

3. Trimethylhexamethylene diisocyanate (TMDI)

This is a low viscosity, colourless to slightly yellowish liquid with a weak, but specific odour, having a m.wt. of 210. It is supplied by Veba Chemie and Huls and comes in two isomeric forms (approximately 1:1 ratio).

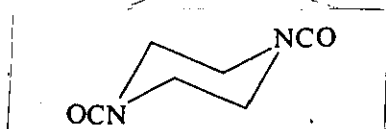


2,2,4-Trimethylhexamethylene
diisocyanate



2,4,4-Trimethylhexamethylene
diisocyanate

4. 1,4-Cyclohexane diisocyanate (CHDI)

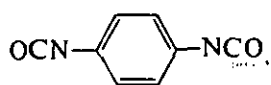


This is a white flaked solid supplied by Akzo Chemie as Elate 166. This comes in the trans isomeric form, m.wt. 166.

In theory the cis isomer could be made



5. Paraphenylene diisocyanate (PPDI)



This is a white flaked solid supplied by Akzo Chemie as Elate 160 (m.wt. 160).

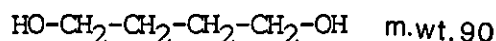
APPENDIX II
POLYCAPROLACTONES

These were the polyols used in the synthesis of the elastomers and are supplied by Interlox Chemicals Ltd as Capa polyols. These are linear polyester diols derived from caprolactone, terminated by primary hydroxyl groups.

Product	Molecular Weight	OH Value	Functionality	Physical Form	Melting Point (°C)
Capa 200	550	204.4	Diol	Liquid	20
Capa 205	830	135.8	Diol	Liquid/ paste	25
Capa 210	1000	113.4	Diol	Paste	38
Capa 215	1250	89.4	Diol	Wax-like solid	40
Capa 220	2000	56.5	Diol	Wax-like solid	47
Capa 231	3000	36.0	Diol	Wax-like solid	55
Capa 240	4000	28.0	Diol	Wax-like solid	58
Capa 305	540	312.8	Triol	Liquid	
Capa 793/ 059	600	372.3	Tetra- functional	Yellowish liquid	
Capa 800/ 031	1000	220.8	Tetra- functional	Yellowish liquid	

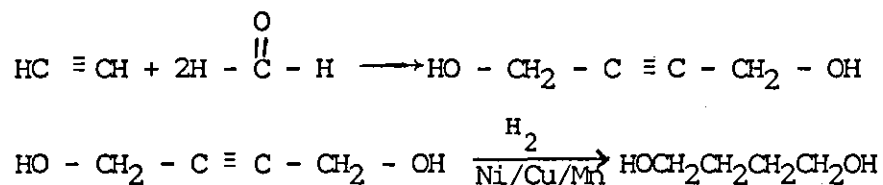
CHAIN EXTENDERS

1. 1,4-butane diol (1,4-BD)

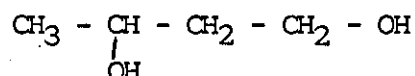


This is a water white hygroscopic liquid and supplied by Gaf and Huls.

The manufacture of 1,4-butanediol involves the high pressure hydrogenation of 1,4-butyndiol using a nickel-copper-manganese catalyst. The 1,4-butyndiol is obtained by the reaction between acetylene and formaldehyde.



2. 1,3-butanediol (1,3-BD)



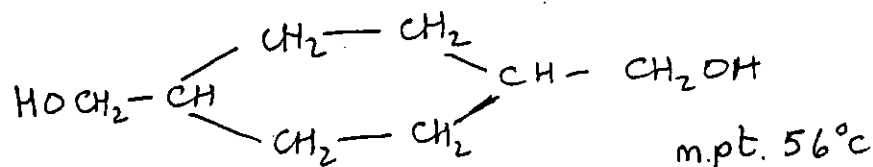
This is a clear hygroscopic liquid of 90 m.wt. Supplier: Koch Light Laboratories Ltd.

3. 1,6-hexanediol (1,6-HD)



This is a clear liquid (on heating) having a m.pt. of 40-42°C and 118 m.wt. supplied by Koch Light Laboratories Ltd.

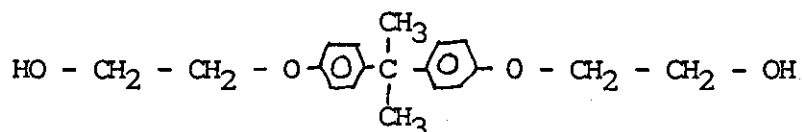
4. 1,4-cyclohexanedimethanol (1,4-CHDM)



1,4-bis-(hydroxymethyl) cyclohexane m.wt. 144

This is a solid and comes in a mixture of the cis and trans isomers. Supplied by Aldrich Chemical Co. Ltd.

5. Dianol 22



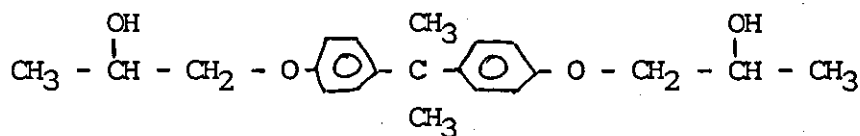
m.wt. 316

m.pt. >175°C

1,1'-Isopropylidene-bis-(p-phenylene-oxy)-di- -ethanol.

This is a white solid and is supplied by Akzo Chemie.

6. Dianol 33



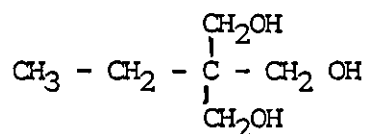
m.wt. 344

m.pt. 70-80°C

1,1'-Isopropylidene-bis-(p-phenylene-oxy)di-w-propanol-2

This is a white solid, supplied by Akzo Chemie.

7. Trimethylol propane (TMP)



m.wt. 134

m.pt. 56-58°C

2-ethyl-2-hydroxymethyl propanediol

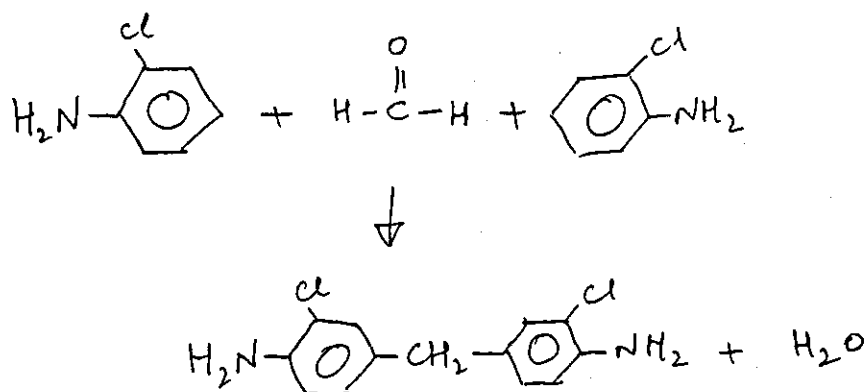
This is a white solid and is supplied by BDH Chemicals Ltd.

8. Release Agents

Ambersil Polyurethane release agent used, supplied by Ambersil Ltd.

9. Addendum

MOCA is manufactured by the condensation of ortho-chloroaniline with formaldehyde in acid medium. The condensation is started at low temperature, which is gradually increased to about 80°C. After reaction the mixture is made alkaline, washed with water, filtered and dried.



APPENDIX III

CALCULATION ON THE EXTENT OF ISOCYANATE AND POLYOL REACTION

The components were reacted in a vessel and a sample taken at timed intervals for I.R. analysis using an SP3 200 Pye Unicam Infra Red Spectrophotometer. Using air in the reference beam, spectra were recorded at normal scanning speed, a typical spectra is shown later.

The reaction was followed by observing the disappearance of the -NCO absorption (2270 cm^{-1}) with time. Using an internal reference as the -CH absorption (2035 cm^{-1}) the calculations were carried out as follows:

Using Beer Lambert's Law of Absorption:

$$A = \log_{10} \frac{I_0}{I} = ECL \quad (1)$$

A = Absorbance

E = Extinction coefficient

L = Path length (cm)

I = Intensity of transmitted radiation

I_0 = Intensity of incident radiation

C = concentration

A standard is required as the concentration of isocyanate at the beginning or start of reaction. For each analysis, the starting point was taken as the concentration of isocyanate after mixing the reactants (e.g. isocyanate and polyol) together for one minute at room temperature and then a further one minute at the temperature of reaction (e.g. 130°C). After this, the spectras were recorded at timed intervals and the value of percent unreacted NCO content at that time was calculated via:

Using (1) and the standard representing 100% unreacted NCO, the relative $\left[\frac{A_{\text{NCO}}}{A_{\text{CH}}}\right]_{\text{CH}_2}$ absorbance is

$$\left[\frac{A_{\text{NCO}}}{A_{\text{CH}}}\right]_{\text{standard}} = \frac{E_{\text{NCO}} (C_{\text{NCO}})_s L_s}{E_{\text{CH}} (C_{\text{CH}})_s L_s} = \frac{E_{\text{NCO}} (C_{\text{NCO}})_s}{E_{\text{CH}} (C_{\text{CH}})_s} \quad (2)$$

Similarly for a sample recorded after a certain time of reaction

$$\left[\frac{A_{\text{NCO}}}{A_{\text{CH}}}\right]_{\text{reaction}} = \frac{E_{\text{NCO}} (C_{\text{NCO}})_r L_r}{E_{\text{CH}} (C_{\text{CH}})_r L_r} = \frac{E_{\text{NCO}} (C_{\text{NCO}})_r}{E_{\text{CH}} (C_{\text{CH}})_r} \quad (3)$$

Combining (2) and (3) and assuming concentration of CH remains constant i.e.

$$(C_{\text{CH}})_s = (C_{\text{CH}})_r$$

then the percent unreacted NCO in the sample would be

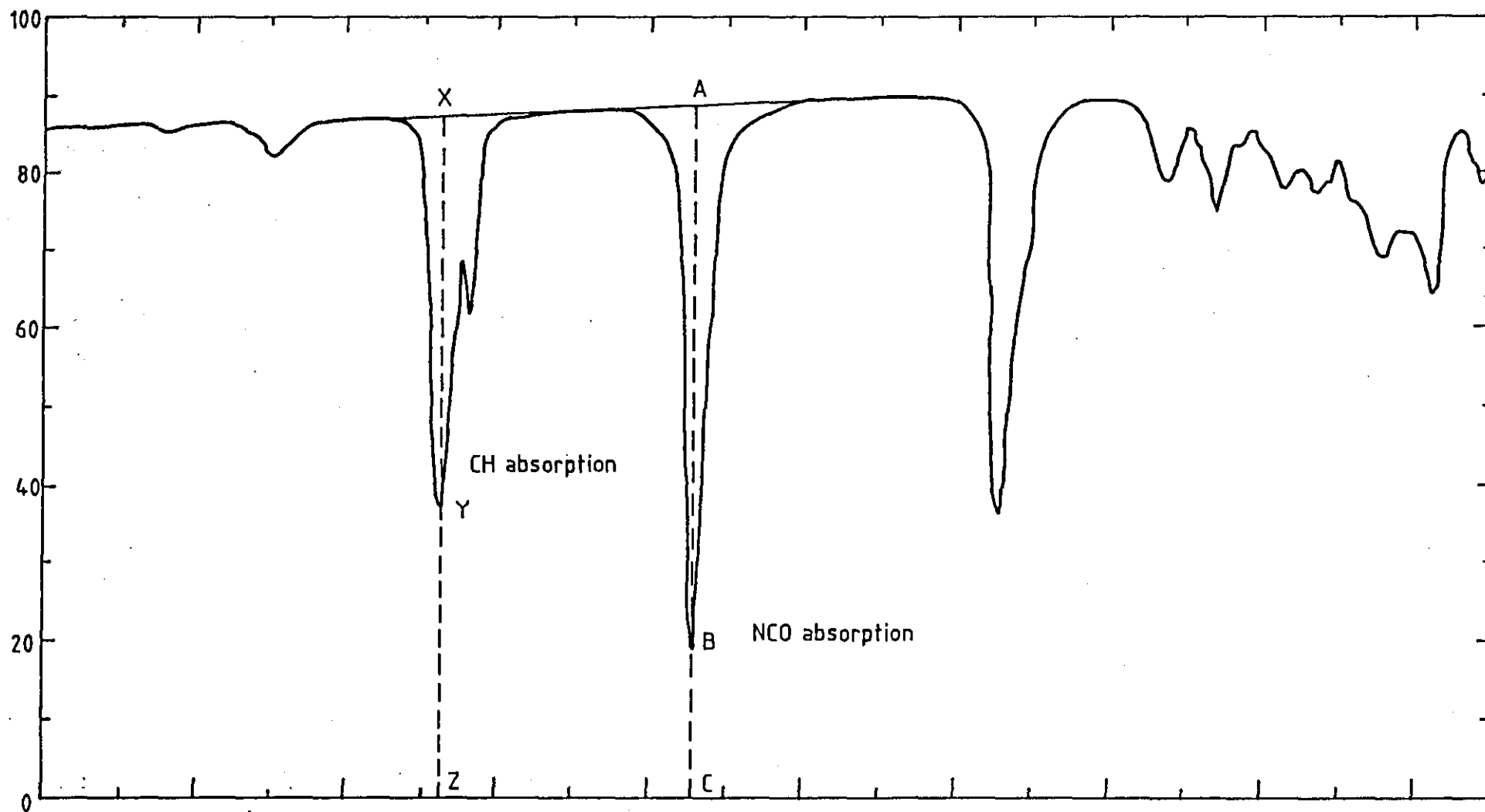
$$\begin{aligned} \frac{(C_{\text{NCO}})_r}{(C_{\text{NCO}})_s} \times 100 &= \frac{\left[\frac{A_{\text{NCO}}}{A_{\text{CH}}}\right]_r \times \left(\frac{E_{\text{CH}} (C_{\text{CH}})_r}{E_{\text{NCO}}}\right)}{\left[\frac{A_{\text{NCO}}}{A_{\text{CH}}}\right]_s \times \left(\frac{E_{\text{CH}} (C_{\text{CH}})_s}{E_{\text{NCO}}}\right)} \times 100 \\ &= \frac{\left[\frac{A_{\text{NCO}}}{A_{\text{CH}}}\right]_r}{\left[\frac{A_{\text{NCO}}}{A_{\text{CH}}}\right]_s} \times 100 \end{aligned} \quad (4)$$

The values of (A_{NCO}) and (A_{CH}) can be calculated from the infrared spectra using the baseline density method (see spectra, also Figure 4D5.1).

$$A_{\text{NCO}} = \log_{10} \left[\frac{I_0}{I} \right]_{\text{NCO}} = \log_{10} \left[\frac{AC}{BC} \right] \quad (5)$$

$$A_{\text{CH}} = \log_{10} \left[\frac{I_0}{I} \right]_{\text{CH}} = \log_{10} \left[\frac{XY}{YZ} \right] \quad (6)$$

So $(A_{\text{NCO}}/A_{\text{CH}})$ for both the standard and reacted samples can be calculated and by using (4) the percent unreacted NCO determined.



Typical spectra of sample taken from Isocyanate and Polyol reaction vessel, showing true -CH and -NCO absorption required for calculating the present unreacted NCO

APPENDIX IV

COMPUTER PROGRAM FOR OBTAINING MOLECULAR WEIGHT DATA

READY

```

50 PRINT"  "
100 PRINT"MOL.WTS.FROM GPC"
200 PRINT"===== "
300 DIM P(50),H(50),TS(20)
400 RESTORE
500 READ MI,N,B,SH,SM,SP,MO,N2,MC,HC
600 DATA 0,0,0,0,0,0,0,0,0,0
620 PRINT"WHAT IS THE TITLE OF YOUR DATA"
630 INPUT TS$
700 PRINT"INOUT DATA AS MARK(%),HEIGHT (MM).END      WITH 0,0"
800 PRINT"NUMBER.MARK(%).HEIGHT"
900 FOR I=1 TO 50:PRINTI,:INPUT P(I),H(I)
1000 IFH(I)=0 THEN 1100
1010 N=N+1
1020 NEXTI
1100 PRINT"IS THE DATA CORRECT":GOSUB5000
1200 IFA$="Y" THEN 2100
1300 PRINT"TYPE NUMBER OF POINTS TO BE CHANGED":INPUT N2
1400 PRINT"TYPE IN NEW POINT AS MARK,HEIGHT":INPUT MC,HC
1500 P(N2)=MC:H(N2)=HC
1600 PRINT"ANY MORE CHANGES":GOSUB5000
1700 IF A$="N" THEN 1900
1800 GOTO 1300
1900 PRINT"HERE IS A LIST OF YOUR DATA":PRINT"MARK,HEIGHT":PRINT"===== "
2000 FORI=1TON:PRINTP(I),H(I):NEXTI
2100 PRINT"DATA IS NOT SKEW CORRECTED, THIS IS FOUND UNNECESSARY, BUT IS
CORRECTED"
2200 PRINT"FOR SYMMETRICAL BAND BROADENING":B=.997
2300 FOR I=1TON
2400 MI=10 (10.7230-(P(I)*89.00 E-3))
2450 GOTO 2600
2501 END
2600 SH=SH+H(I):SM=SM+(H(I)/MI):SP=SP+H(I)*MI
2700 NEXT I
2730 PRINT TS$
2740 PRINT
2800 PRINT"          UNCOR. COR."
2900 PRINT"MN=",INT(SH/SM),INT(SH*B/SM)
3000 PRINT"MW=",INT(SP/SH),INT(SP/(SH*B))
2050 PRINT"MP=",INT((SP/SM) .5)
3100 PRINT"MMD=",SP*SM/(SH 2),SP*SM/((SH*B) 2)
3200 FOR I=1 TO 3:PRINT:NEXTI
3210 PRINT"DO YOU WANT A PRINTOUT OF YOUR RESULTS":GOSUB 5000
3230 IF A$="N" THEN 3300
3240 GOSUB 6000
3300 PRINT"DO YOU WANT ANOTHER GO":GOSUB5000
3400 IFA$="N" THEN 4000
3500 PRINT" ":GOTO 400
4000 END
5000 PRINT"TYPE Y OR N AND PRESS RETURN":INOUT A$

```

```
5100 IF A$="Y" THEN 5500
5200 IF S$="N" THEN 5300
5300 PRINT"ANSWER";A$;"NOT UNDERSTOOD"
5400 GOTO 5000
5500 RETURN
6000 OPEN 5,4
6100 CMD 5
6200 PRINT T$
6300 PRINT
6400 PRINT"          UNCOR. COR."
6500 PRINT"MN=",INT(SH/SM),INT(SH*B/SM)
6600 PRINT"MW=",INT(SP/SH),INT(SP/(SH*B))
6700 PRINT"MP=",INT((SP/SM) .5)
6800 PRINT"MWD=",SP*SM/(SH 2),SP*SM/((SH*B) 2)
6900 PRINT 5:CLOSE5
7000 RETURN
READY
```

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