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CHEMICAL MODIFICATIONS OF SOME  
SYNTHETIC ELASTOMERS

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ORIGINALITY.

All the work presented in this thesis has been carried out by the author, except where otherwise acknowledged and has not been presented for a degree at this University or any other institution.

## SUMMARY.

The aim of this investigation was to prepare a thermoplastic elastomer via the chemical modification of an existing commercially produced polymer. Two separate polymer modification studies were carried out. In the first, solution polymerised polybutadiene and styrene-butadiene copolymers were hydrogenated and in the second, ethylene-propylene-diene terpolymers were anionically metalated and subsequently carboxylated or graft polymerised with styrene.

Fundamental differences in the two techniques employed, hydrogenation and metalation, resulted in the emphasis of the two studies being somewhat different. Thus, the hydrogenation process was quite simple, enabling a systematic investigation of products to be carried out whereas the metalation process required considerable development resulting in only limited investigation of the products.

The first study commenced with the hydrogenation of non-polymeric olefins. This enabled each of two catalysts to be optimised and compared with regard to their reductive ability. It also furnished information on the relative reactivities of double bonds in different configurations. It was found that a catalyst formed from triisobutylaluminium and nickel diisopropylsalicylate (NiDIPS) was more active than one formed from n.butyllithium, and NiDIPS. The rate at which double bonds were reduced was in the order vinyl > cis > trans and aromatic unsaturation was not reduced.

The two catalysts were compared in polymer hydrogenation and although the aluminium alkyl based catalyst again proved more active, the one based on n.butyllithium was selected for general use since it combined greater ease of handling with adequate activity.

A number of polymers were obtained with systematic variations in composition and these were hydrogenated so that the effect on properties of the following variables could be determined.

1. Degree of saturation.
2. Vinyl content.
3. Molecular weight.
4. Styrene content.

The properties of greatest interest initially were ultimate tensile strength and elongation set and values for these were determined for each of the hydrogenated polymer samples. The degree of crystallinity was also determined, this was influenced by both the degree of hydrogenation and the vinyl content and was shown to be the major factor affecting product properties. Reference to the literature revealed that partially crystalline polymers such as these contain isolated crystallites. These clearly functioned as physical crosslinks in a manner similar to the thermoplastic domains in commercial thermoplastic elastomers.

An improvement in tensile strength with increase in molecular weight was ascribed to an effective increase in the number of crystallite crosslinks per chain and a decrease in the number of free chain-ends.

The effect of styrene content was found to be rather more complex, the best combination of ultimate tensile strength and elongation set

being obtained with hydrogenated polymers containing approximately 5 mole % styrene. Polymers such as these were found to have crystallinities similar to those of hydrogenated polybutadienes, when compared at equivalent degrees of saturation. It was postulated that as the styrene units had not decreased the overall crystalline content then they might have influenced the crystallisation process by their bulk, so that a larger number of smaller crystallites were formed. If this were true the improved properties of these polymers would be explained by the effective increase in the crosslink density.

Notwithstanding this effect, products with a fairly wide range of compositions were found to have properties which would qualify them as thermoplastic elastomers.

The study of ethylene, propylene, diene terpolymer (EPDM) modification through metalation was hampered, as expected, by the relatively low concentration of active sites. Because of this it was necessary to apply very stringent purification procedures and to find a very active metalating agent.

Reactions were carried out in hexane solution and techniques were evolved to achieve the substantial absence of any species capable of preventing reaction between metalating agent and polymer. The finalised procedure involved dearomatisation and drying of solvent, column purification of polymer solution and scavenging with n.butyllithium.

The metalating agent used by other workers in polymer reaction, n.butyllithium/tetramethylethylenediamine complex, proved unreactive towards EPDM. However n.butyllithium/potassium t.butoxide proved to be highly active, reacting with virtually 100% efficiency under certain conditions.



These metalation techniques were used to introduce carboxyl functionality and to graft polymerise styrene.

Polymers were carboxylated by reacting metalated polymer with solid carbon dioxide. The products were either isolated as formed in a neutralised state or acidified, isolated and neutralised wholly or partially with sodium methoxide. The ionically crosslinked products thus formed were evaluated as thermoplastic elastomers and found to have ultimate tensile strengths similar to reinforced, vulcanised rubbers but rather poor melt flow properties.

The differing views expressed by other workers concerning the nature of ionically crosslinked polymers were considered and an attempt made to rationalise them. It was decided that the properties of these polymers were best explained by the postulate that the ionic bonds were present in conglomerates, which acted in the dual role of crosslinks and filler particles.

Polystyrene grafted EPDM was prepared by reacting metalated polymer with styrene, very high graft efficiencies being obtained under optimised conditions. Analogies were drawn between these polymers and the ABA block copolymer thermoplastic elastomers commercially produced by Shell. Lessons that had been learnt by other workers in a study of Shell-type polymers were applied to the present system. The product composition with regard to polystyrene content and molecular weight, number of grafts per chain and graft efficiency had therefore to be kept within very strict limits. This proved to be rather difficult but some products were obtained which had compositions approaching those desired. Unfortunately, these materials could not be classified as true thermoplastic elastomers because although they exhibited a

thermoplastic nature and moderately high ultimate tensile strengths the elastic recovery was very poor.

The shortcomings of these materials were explained by analogy to the Shell-type block copolymers and methods by which they might be improved were discussed.

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7. "Thermoplastic Elastomer Compositions".  
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## GENERAL INTRODUCTION.

Recent events, notably the sharp increases in price of oil, coal and some other commodities, have served to underline the limited availability of many natural resources and the need to effect the maximum economy in their use. The notion of disposability has at last given way to "re-usability" where this is practicable. This change in attitude is illustrated by the case of degradable plastics. Here techniques were developed to overcome the problems arising from the casual disposal of plastics containers and yet within a very few years of their inception the situation changed so that now these materials are considered too costly to be merely thrown away. At the present time a considerable amount of effort is being devoted towards turning the potential recyclability of thermoplastics into a commercial reality. Elastomers, on the other hand, being essentially thermosets have not been recyclable as elastomers but the recent development of thermoplastic elastomers has made even this a possibility. The major reason behind the development of these materials was not however their re-cyclability but, as might be expected, a potential saving in cost through, in this case, improved methods of processing. Maybe the present situation will give added impetus towards their development and commercialisation in the future.

The original drive which started the development of thermoplastic elastomers was the desire to produce an elastomer without the elaborate and costly procedures of compounding and vulcanisation.

The two main methods for producing elastomers, sulphur vulcanisation and peroxide crosslinking, both require a similar four-stage procedure.

1. Curing agents have to be blended in to the rubber.
2. The compound has to be placed in a mould.
3. The mould has to be compressed.
4. The material has to be heated for several minutes to effect crosslinking.

This process results in an irreversibly crosslinked product, and rejects or "flash" cannot be re-cycled but have to be scrapped. On the other hand if a thermoplastic elastomer is produced with built-in, heat sensitive crosslinking system then the first stage can be eliminated, the second and third stages can be combined by injection moulding techniques and the fourth stage can be considerably shortened as the material has only to cool after moulding. Any rejects or "flash" can simply be granulated and fed back into the system.

A search for a suitable heat sensitive crosslinking system leads to the following possibilities, grouped into two main types.

I. Physical.

- (i) Glassy.
- (ii) Crystalline.
- (iii) Entanglements.

II. Chemical.

- (i) Ionic.
- (ii) Co-ordinate.
- (iii) Rearrangement reaction.

Physical crosslinks can be produced by arranging that the elastomeric chains are linked to thermoplastic chain segments, either glassy or crystalline. The overall thermoplastic content is controlled so that it is less than 50% of the total. this resulting in a two-phase system with thermoplastic domains dispersed in and linked to a rubbery matrix. If the rubbery chains are chemically linked only to thermoplastic chains and not to each other then when the material temperature is raised above the melting point or glass transition temperature of the thermoplastic phase the crosslinking system will break down and allow melt flow. As soon as the temperature is reduced sufficiently the crosslinking system will reform.

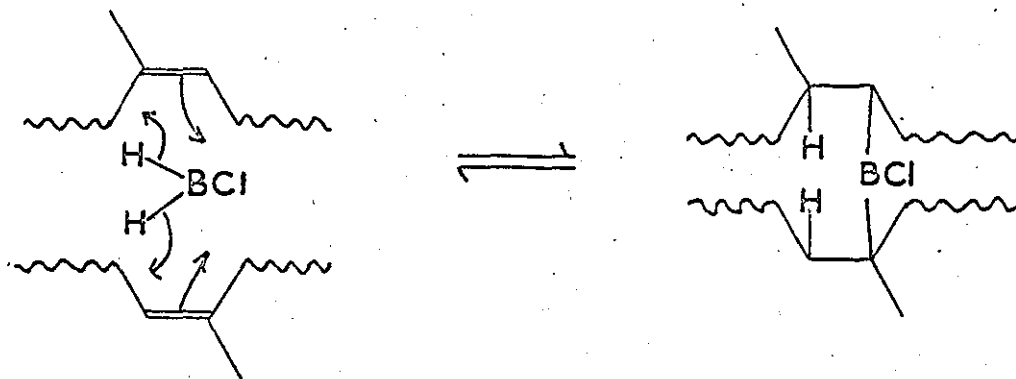
Entanglement crosslinks are present in all polymeric systems but are clearly only important if chain disengagement is prevented by a primary crosslinking system.

The chemical form of crosslink has to involve a heat sensitive chemical reaction. In the simplest form this involves a link between atoms in two polymer chains which will break when the material temperature is raised above a critical value and reform when the temperature is reduced. Normal covalent links are of too high an energy to allow this to occur. If sufficient energy was put into a system to break this form of bond then clearly catastrophic failure would occur in the system as a whole. Ionic or co-ordinate bonds are of a lower order of strength and if the links between polymer chains are of this type then the desired heat sensitive dissociation and association might be achieved. If covalent links are to be employed then they would have to occur through a system capable of rearrangement, bonds breaking and reforming by exchange between suitable atoms.

All of these systems have been investigated previously by other workers but so far only three of them, the glassy, crystalline and ionic have proved to be of any commercial utility. These will be discussed in turn after examples have been given of the other two.

Only a very limited amount of work in these fields has in fact been published. Some Russian workers<sup>(1)</sup> investigated the vulcanisation of nitrile and vinyl pyridine rubber with zinc chloride and found that under mild conditions weak co-ordinate crosslinks were formed. They suggested that these bonds would regroup easily but their study of thermoplasticity was hampered by the fact that a second type of linkage formed when temperatures were raised slightly. They deduced that these linkages were covalent

and formed due to the catalytic activity of the zinc chloride. A somewhat more satisfactory example can be given of the heat sensitive rearrangement reaction form of crosslink. This is referred to in a review article by Melville.<sup>(2)</sup> Polyisoprene was reacted with  $\text{BH}_2\text{Cl}$  and crosslinks were formed. On heating, rearrangement occurred and the bonds were broken,



It was stated that these polymers exhibit high creep but were however still in an early stage of development.

The three forms of crosslinking that have been developed commercially have received considerable attention in the literature and an excellent general review of these materials has been written by Wells.<sup>(3)</sup>

Except for the ionically crosslinked Dupont, Surlyn A ionomers (not mentioned in the review), the rest can be broadly classified as block copolymers. A brief description of the ionomers will be given before considering the block copolymers as a separate group.

The Dupont ionomers are described in two papers by Rees and Vaughan.<sup>(4,5)</sup> They are ethylene, acrylic or methacrylic acid copolymers which have been neutralised wholly or partly by reaction with metal salts. A typical product contains 3.5 mole % acid of which 70% is ionised with sodium ions. The materials are generally rather more flexible thermoplastics than thermoplastic elastomers as they appear to exhibit high "set" characteristics.

However it is stated that they are characterised by unusual elasticity and toughness and that many of them are very resilient, superficially resembling cured elastomers. They illustrate well the reinforcing but heat sensitive nature of ionic crosslinking.

Block copolymers have been the subject of many symposia<sup>(6,7)</sup> and reviews<sup>(8,9,10,11)</sup> so they need not be discussed here in too great a detail. The different types of block copolymer can be classified in a number of ways but probably the simplest is to use the method of polymerisation used in their production. These are:

- A. Sequential
- B. Graft
- C. Random
- D. Condensation
- E. Addition

Each of these methods will be discussed, relating each to the relevant commercial product.

#### A. Sequential Polymerisation.

The production of block copolymers by sequential polymerisation requires that the growing chain-ends should have a significantly long "life-time" thus enabling the polymerising monomer to be changed and a new monomer added which can continue polymerising on the old chains. The most suitable system in this respect is anionic polymerisation. This involves no termination step, the chain ends remaining "live" indefinitely. This method is used in the production of the Shell, Kraton block copolymers<sup>(12-16)</sup> these being introduced in 1965, probably causing the surge of interest in thermoplastic elastomers. Phillips<sup>(17,18)</sup> have also been marketing similar materials but until now this seems to be in little more than developmental quantities.

Polymerisation is typically carried out using n.butyllithium as initiator with styrene as first monomer. As soon as the required molecular weight is produced and all the styrene used, a diene, usually butadiene, is added and the second block is polymerised until all the monomer is used. More styrene is then added and polymerised so that an ABA type of block copolymer is produced. Other methods can be used such as coupling after the second block has polymerised but generally the best products seem to be produced by the straightforward sequential polymerisation.

Numerous papers have been published<sup>(19-25)</sup> on the morphology of these products and it is generally agreed that they are two phase systems with glassy, polystyrene domains dispersed within an amorphous rubbery matrix. The shape of these domains appears to depend on both the composition of the polymers and the way in which the sample is prepared. However, generally, for the more rubbery materials these domains can be considered as spheres. The end of each chain is therefore imbedded in a glassy domain, the domain acting as crosslink and filler particle. When the temperature of the material is raised above the polystyrene glass transition then the domains break down and allow thermoplastic flow. These materials are thus an excellent example of the way in which glassy, physical, crosslinks can be employed to produce thermoplastic elastomers. In fact, these are the only commercial products to use glassy crosslinks, the others all being semi-crystalline materials.

Other companies have shown interest in producing block copolymers via anionic polymerisation, albeit using rather more "exotic" materials. G.E. use bisphenol A carbonate for the thermoplastic, <sup>glassy</sup> crystalline segments and dimethylsiloxane for the rubbery segments, Dunlop use ethylene sulphide for the former and propylene sulphide for the latter.



Block copolymers have also been prepared via sequential polymerisation using Ziegler-Natta catalysts.<sup>(10,29)</sup> Typically, propylene is polymerised, then ethylene is added to give an ethylene propylene copolymer block, finally when the ethylene is exhausted the propylene polymerisation is continued. Ideally, this results in an ABA block copolymer with crystalline polypropylene end segments and rubbery ethylene propylene copolymer centre segments. Unfortunately, it appears rather difficult to obtain a pure product in this way due both to the limited chain end lifetime and the difficulty of finding a catalyst which will both polymerise propylene to high isotacticity and randomly copolymerise ethylene with propylene. This system has therefore not, as yet, been developed commercially.

#### B. Graft Polymerisation.

Thermoplastic chain segments can be grafted onto rubbery chains to produce "comb" shaped polymers. The essential requirements for a block copolymer thermoplastic elastomer can thus be fulfilled, viz, thermoplastic chain segments separated by rubbery segments. This system is demonstrated in the Allied Chemical Corporation's ET polymers.<sup>(30)</sup> Unfortunately, no definitive paper has yet been published on the method of preparation but it has been stated that butyl rubber is grafted with polyethylene using a suitable phenolic resin. The heat sensitive crosslinking system in this case would be via polyethylene crystallites.

A somewhat similar system has been developed by Uniroyal, the product being called TPR. The method of production has not yet been openly disclosed, it being stated simply that it is an olefin block copolymer.<sup>(3)</sup> However, a recent British patent<sup>(3)</sup> granted to Uniroyal claims a thermoplastic elastomer prepared by reacting a highly isotactic polypropylene with ethylene, propylene, diene terpolymer (EPDM) rubber using a "dynamic crosslinking system for example, peroxides. The procedure appears to depend on a very limited crosslinking of the rubber occurring together with grafting of the rubber onto the polypropylene. The heat sensitive crosslinking system in this

material would therefore presumably be via polypropylene crystallites. The published<sup>(32)</sup> elastomeric properties of these polymers are inferior to the Shell, Kraton block copolymers, however they do have the advantage that they are both more heat stable and have better ageing characteristics, the former being due to the polypropylene melting point being much higher than the glass transition temperature of polystyrene and the latter being due to the saturated nature of the polymer.

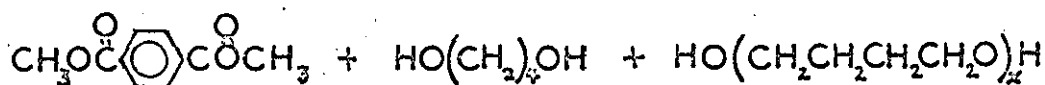
### C. Random polymerisation.

Random polymerisation would not normally be thought of as a method for the production of block copolymers. However, if one considers the case of two monomers being copolymerised where there is a much higher proportion of one monomer than the other then random copolymerisation must result in the production of polymer chains with some segments having a near equal proportion of the two monomers and others being blocks of the monomer present in the highest proportion. If the former segments are amorphous and rubbery and the latter are crystalline then an essentially ABABAB etc. block copolymer is produced. This sort of system can even be produced by homopolymerisation as long as the monomer employed is capable of polymerising in different ways in the same system, one producing crystalline segments and others producing amorphous segments. Precipitated natural balata rubber is an example <sup>of a partially crystalline homopolymer</sup> ~~of this~~ and a similar material, Trans-Pip<sup>(3)</sup> a synthetic trans-1,4 polyisoprene has been produced and marketed as a thermoplastic rubber by Polymer Corp.

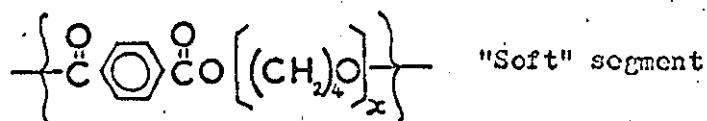
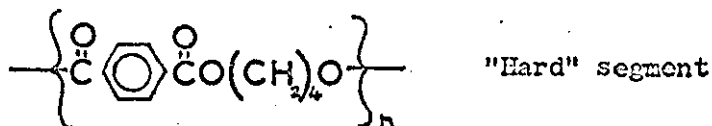
An example of the copolymer system can be found in the ethylene, vinyl acetate copolymers.<sup>(33)</sup> These two monomers can be copolymerised over a wide range of compositions, highly crystalline <sup>or glassy</sup> materials being produced when there is a preponderance of either one ~~or the other~~ <sup>or glassy</sup> monomer. However in the intermediate ranges of about 20-30% vinyl acetate, semi-crystalline rubbery materials are produced. In this case, chains are composed of segments of crystalline polyethylene and amorphous ethylene, vinyl acetate copolymer. The heat sensitive crosslinking system would therefore be via polyethylene crystallites.

#### D. Condensation Polymerisation.

This method has been used to produce the Du Pont Hytrel polymers. These are random block copolyesters, their method of preparation being described in a paper by Cella.<sup>(34)</sup> Melt transesterification is carried out of dimethylterephthalate (DMT), 1,4-butanediol (BD) and poly(tetramethylene ether) glycol (PTMEG). The material so produced can be considered to be a copolyester having been formed by randomly joining, head to tail, poly(tetramethylene ether) glycol terephthalate soft segments and tetramethyleneterephthalate hard segments.



—————→ copolyester elastomer.



The overall stoichiometry is chosen so that there is a preponderance of "hard" units in the mixture on a mole basis, resulting in a polymer containing relatively long sequences of crystallisable "hard" units. A system is thus obtained somewhat similar to that which is produced via random polymerisation vis. ABABA etc.

The crystalline melting point of the "hard" segments depends on the overall composition of the polymer but for commercial products it would be in the region of 200°C. This of course confers great heat stability on these materials but carries with it the disadvantage that high processing temperatures are required. The elastomeric properties have been published and compared with other thermoplastic elastomers.<sup>(35,36)</sup> In general, except for the heat stability they appear to be broadly similar to the Shell Kraton block copolymers.

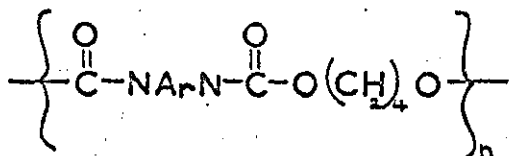
#### E. Addition Polymerisation.

The commercial products which fall within this classification are the polyurethanes. The general field of polyurethanes is rather complex there being a great variety of products. Here it is convenient to exclude the ionic urethanes<sup>(37,38)</sup> and concentrate on what might be termed the solid polyurethane elastomers. This exclusion still leaves a great number of materials, illustrated by the table given in the review by Wells<sup>(3)</sup> which lists twelve producers and 59 products.

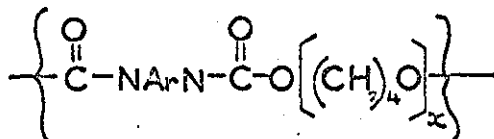
All these polymers may be classed into four categories. They may contain either ether linkages or ester linkages or be linear or branched and each of the first two types may be prepared so that they also fall within either of the latter two categories. Urethanes are formed typically

through the reaction product of a diisocyanate and a polyether or polyester glycol, hence the classification into polyether or polyester type. The linear polyurethanes are produced using stoichiometric quantities of isocyanate and alcohol. The branched polyurethanes are prepared using an excess of diisocyanate. This would normally result in a fully crosslinked product similar to the thermosetting cast polyurethanes, however in this case the crosslinking reaction is arrested during manufacture and it is only when processing is carried out at high temperatures that the crosslinking reaction continues. This partial crosslinking improves the compression set of the materials but results in imperfect thermoplasticity, hence they can only be reprocessed a limited number of times. A discussion of the branched polyurethanes can be found in a book by Wright and Cumming.<sup>(39)</sup>

The linear ether or ester type polyurethanes are of more interest in the present context as these are truly thermoplastic in nature. The first material of this type to be marketed was Estane, produced by D.F. Goodrich. One grade was prepared using polytetramethylene adipate, 4,4<sup>1</sup>-diphenylmethane diisocyanate and 1,4-butanediol, it is therefore a polyester type. The polyether types are the more expensive of the two, but they have much better hydrolytic stability and low temperature flexibility. These are typically prepared by reacting together an aromatic diisocyanate, 1,4-butanediol and polytetramethylene oxide, the resulting product being very similar to the Du Pont Hytrel polyesters.



"hard" segment.



"soft" segment.

Again, the overall stoichiometry is arranged so that there is a preponderance of "hard" units. The product thus consists of blocks containing a number of "hard" units separated by "soft" segments.

The properties of these materials, of course depends to a large extent on the starting materials. However, Wells<sup>(3)</sup> gives a list of the ranges within which each lie. Investigations have been carried out<sup>(40-43)</sup> into the effects of segment size and polydispersity, results being broadly similar to those found for the hydrocarbon ABA block copolymers. The properties of these materials have also been explained in an analogous way to the hydrocarbon block copolymers viz. high modulus domains, in this case crystalline, acting to reinforce the rubbery network.

This survey of existing commercial materials enables an idea to be gained of the requirements which may be thought necessary for an alternative product, those being:

- a) Good elastomeric properties.
- b) Easy processing.
- c) Good heat stability.
- d) Environmental resistance.
- e) Low cost.

None of the materials discussed excels on all counts, each having strong and weak points. Notably the better elastomers appear to require more stringent production control and this results in a higher cost, some of the cheaper polymers being rather more flexible, semi-rubbery, thermoplastics than elastomers. It is also evident that it is rather difficult to satisfy both b and c. If the heat sensitive crosslinking system is such that it is stable at relatively high temperatures then clearly even higher temperatures are required for processing. Environmental resistance must surely be one of the most important criteria to be satisfied, this being demonstrated by the fact that after the initial marketing of the Shell unsaturated Kraton block copolymers, a new saturated grade, Kraton G,

probably produced via hydrogenation, had to be introduced.<sup>(44)</sup> The above list of requirements may therefore be reorganised into a rough order of priorities.

- a) Low cost.
- b) Good elastomeric properties.
- c) Environmental resistance.
- d) Easy processing.
- e) Good heat stability.

The main reason that the majority of these materials have a comparatively high cost lies in the fact that they are still speciality polymers being produced in relatively small quantities. It was reasoned that if this is the case then a better approach might be to take an existing polymer already being produced in large quantities and to modify this in some way to give the desired end product. For good environmental resistance the product would ideally be mainly saturated. These two considerations led to three main possibilities.

- A. The hydrogenation of unsaturated polydienes.
- B. The graft polymerisation of ethylene, propylene, diene terpolymer (EPDM).
- C. The carboxylation and ionic crosslinking of EPDM.

The first was aimed at the sort of product which has been earlier described as being prepared via random polymerisation viz. Trans Pip and EVA copolymers. It was thought that if a polybutadiene or styrene butadiene copolymer was hydrogenated over an intermediate range then a product with a limited amount of crystallinity might be obtained and that this might function as a thermoplastic elastomer. If need be, not only could the degree of hydrogenation be varied but also, by minor variation in the polymerisation recipe, the composition and microstructure of the starting polymer could be varied. It was hoped that a systematic investigation into these variables might lead to an optimisation of properties.

The second possibility was aimed at the production of a graft polymer with a rather more specific composition than those described earlier as being prepared in this manner. It was thought that if sites on the EPDM could be activated in some way then a monomer such as styrene could be polymerised at these points. This should result in a product rather better defined and having better properties than those obtained simply by a random free radical reaction in a blend of two polymers.

The third possibility led from a consideration of the second; having activated the EPDM to enable graft polymerisation to occur, these same activated sites could also be used to introduce carboxyl groups into the chains. This would enable ionic crosslinking to be carried out via metal salt neutralisation of these groups. A rubbery, ionically crosslinked product should then result rather than the semi-rubbery, similarly crosslinked Surllyn A polymers described earlier.

In order to discuss the investigation into these three ideas the thesis has been split into two sections, the first dealing with the hydrogenation study and the second, as both materials stem from a similar beginning, dealing with the graft polymerisation and carboxylation of EPDM. Separate introductions to each of these two sections will be made so that relevant earlier work in these fields might be discussed.



PART I. HYDROGENATION OF POLYBUTADIENE AND BUTADIENE  
STYRENE COPOLYMERS.

## 1. INTRODUCTION.

The present state of art of polymer hydrogenation has arisen through a number of parallel developments in hydrogenation catalysis and polymerisation processes. It started in 1869 when Berthelot hydrogenated natural rubber to liquid products using hydriodic acid<sup>(45)</sup>. There followed a period in which the only rubber available was natural and the only catalysts available had to be used under such severe conditions that substantial polymer breakdown was inevitable.

The Second World War stimulated intensive research into practical means of producing synthetic rubbers and around the same time new supported catalysts<sup>(46)</sup> were developed which enabled hydrogenation to be carried out with preservation of high molecular weight. Work during this period has been reviewed by Wicklatz<sup>(47)</sup>, a typical example being that of Jones et al<sup>(48)</sup>, who found it necessary to purify emulsion polymers prior to use and then employ temperatures in the region of 300-400°F and a hydrogen pressure of 500 p.s.i. to effect hydrogenation. A later example of this period is the work of the Russian, Yakubchik, who used a palladium - or platinum - on calcium carbonate catalyst<sup>(49)</sup> at atmospheric pressure and temperatures in the region of 80°C to hydrogenate a variety of the earlier solution prepared polymers, sodium polymerised polybutadiene<sup>(50,51)</sup>, cis 1,4 polybutadiene<sup>(51)</sup> and cis 1,4 polyisoprene<sup>(52)</sup>.

During the early and middle sixties, two developments occurred. First the scope of solution polymerisation was considerably widened by the introduction of organolithium, anionic initiators and secondly the Ziegler-type homogeneous hydrogenation catalysts were developed. A highly active catalyst system was thus available to hydrogenate a range of new polymers and work until the present date has mainly concentrated on exploring the potentialities of this situation.

The variety of catalysts within the general Ziegler grouping, their great activity and the wide scope for reaction that they allow can best be illustrated by a consideration of the work carried out with non-polymers, polymeric reduction will then be returned to later.

Reviews of the literature on homogeneous catalysis have been carried out<sup>(53,54,55)</sup> but none covers the field of Ziegler catalysis very thoroughly. One of the earliest papers is by Sloan, Matlock and Breslow<sup>(56)</sup>. This is extensively referred to by other workers due to its containing a postulated mechanism for the action of these catalysts, it is interesting that no significant improvements have yet been made on this mechanism. Besides the mechanism they also covered a wide variety of two component systems including triisobutylaluminium with either triethyl vanadate or triisopropyltitanate. They stated that the most active catalysts appeared to be cobalt (III) > iron (III) > chromium (III) acetylacetonates, combined with triisobutylaluminium but also mentioned that they could be combined with n.butyllithium albeit with a resulting loss in activity.

Laporte and Schuett<sup>(57)</sup> found that a triethylaluminium, nickel (II) 2-ethyl hexanoate catalyst could reduce aromatics using temperatures in the region of 150-200°C and a pressure of 1000 p.s.i. They stated that this catalyst had a higher activity than Raney nickel or other supported nickel catalysts.

Tajima and Kunioka<sup>(58)</sup> used soluble cobalt complexes in conjunction with triethylaluminium to hydrogenate the conjugated diolefins, butadiene and isoprene.

Kroll<sup>(59)</sup> investigated various aspects of aluminium alkyl reduced, hydrocarbon soluble, non-noble metal catalysts and concluded that the cobalt system was the most active. He found also that the addition of a Lewis base such as <sup>para</sup>-dioxane reduced the poisoning effect of impurities.

Falk<sup>(60)</sup> found in 1970 that previous investigators had severely underestimated the reactivity of catalysts prepared from alkylolithiums and stated that the catalysts they had made from organolithium compounds and transition metal salts of 2-ethylhexanoic acid were fully as active as alkylaluminium based systems.

During the period in which these studies were being carried out, similar catalysts were being used to hydrogenate polymers. The Russians, Yakubchik and Tikhomirov<sup>(61-63)</sup> used cobalt or chromium acetylacetonate with aluminium triisobutyl to hydrogenate cis 1,4 polybutadiene, sodium polybutadiene, and styrene-butadiene copolymer. They found that using these catalysts 1,2 units were hydrogenated in preference to 1,4 and that in contrast to the heterogeneous catalysts the reduction was a chemically uniform process, all chains taking part equally in the reaction.

The less sterically hindered double bonds in poly-1, 4-butadiene were found by Falk<sup>(64)</sup> to be hydrogenated in preference to those in poly-1, 4-isoprene when organoaluminium or lithium compounds with nickel or cobalt salts of 2-ethylhexanoic acid were used as catalysts.

Amongst the multitude of patents published, two in particular are worthy of note. In one<sup>(65)</sup> the polymer to be hydrogenated was prepared using an organolithium initiator and the resulting "living" polymer was used as the organometallic component of the hydrogenation catalyst, necessitating only the transition metal complex addition before hydrogenation could be effected. On the face of it this procedure looks very interesting with regard to commercial operation, however, in practice commercially these polymerisations tend to be carried out under non-ideal conditions in order to maximise throughput and this results in a large degree of chain termination occurring. Clearly,

if most of the initiator is lost then more organolithium would have to be added before an effective catalyst was obtained.

The other patent<sup>(66)</sup> claims improved hydrogenation rates when a catalyst such as triethylaluminium, nickel naphthenate is mixed in the presence of the unsaturated polymer to be reduced.

The development of anionic polymerisation made possible the production of numerous block copolymers. This type of polymer is discussed in more detail in part II of the present study but the hydrogenation of materials such as these has been the subject of much work. Typically that of Falk and Schlott, who used Ziegler-type catalysts to hydrogenate<sup>(67)</sup> 1,4 butadiene-1,4 isoprene and 1,4 butadiene-1,4 isoprene-styrene block polymers to form ethylene-1,4 isoprene and ethylene-1,4 isoprene-styrene block copolymers. They have also used a modified polymerisation technique to produce<sup>(68)</sup> 1,4 butadiene-1,2 butadiene block copolymers and have hydrogenated them to form ethylene-butene-1 block copolymers.

A few miscellaneous examples of polymer hydrogenation are worth mentioning. Raney nickel continues to be used, Gregg<sup>(69)</sup> in 1968 employing this in very high concentrations to reduce poly-2-alkylbutadienes at a temperature of 240°C and pressure of 3,600 p.s.i. He stated that complete hydrogenation was effected and that only a moderate amount of polymer breakdown occurred. Ziegler type catalysts have been used to reduce the terminal unsaturation in polyolefins<sup>(70,71)</sup> as a means of improving stability. Similar catalysts have been used to hydrogenate polydienes grafted with vinyl aromatics<sup>(72)</sup> and polypentenamers having pendant ionic groups.<sup>(73)</sup>

Surprisingly little work has been published on the physico-mechanical properties of these materials, product evaluation in most cases consisting of no more than the determination of molecular weight, refractive index and glass transition temperature<sup>(47,49,50)</sup>. The review by Moberly<sup>(74)</sup> mentioned briefly that hydrogenated emulsion SBR<sup>(48)</sup> and alkyllithium polymerised butadiene tend to resemble polyethylene whereas hydrogenated branched or random copolymers are rubbery products but apart from that, most evaluation work has concentrated on vulcanised hydrogenated polymers<sup>(51,65)</sup>.

The only study of unvulcanised, hydrogenated polymer properties had been carried out by Falk<sup>(67, 68, 72)</sup> who concentrated virtually exclusively on block copolymers and found that he could only obtain strong, rubbery products by hydrogenating triblock polymers, the terminal blocks finishing as thermoplastic in nature and the centre segment being rubbery.

Despite the considerable amount of work carried out on polymer hydrogenation it therefore appeared that some of the basic studies of the effects of variables such as molecular weight, side group type and content, degree of hydrogenation had not been fully investigated by other workers. This was possibly due to the fact that when this work was commenced, the methods by which the polymers could be produced had not long been available.

A consideration of the other types of thermoplastic elastomer available (see general introduction) led to the conclusion that a good thermoplastic elastomer might be obtained in this way.

It was therefore decided to carry out a systematic investigation of the hydrogenation of polybutadiene and styrene butadiene random copolymer using the highly active and convenient Ziegler type of catalyst.

## 2. EXPERIMENTAL PROCEDURES.

### 2.1. CATALYST STUDIES.

Two different techniques, gas burette and pressure bottle were employed for the reasons given in section 3.1.1.

#### 2.1.2. Catalyst components.

##### 2.1.2.1. n-Butyllithium.

This was used as supplied by Metall G.S. as a 9.7% w/v solution in n-hexane. It was transferred from the bulk container in convenient sized quantities into a rubber sealed, two-hole crown capped  $\frac{1}{2}$  pt. beverage bottle. This was kept under a positive pressure of 10 p.s.i. with pure nitrogen and aliquots were removed by syringe as required.

##### 2.1.2.2. Triisobutylaluminium.

This was supplied as undiluted liquid by Cyclo Chemicals. Solutions of required concentration were made by syringing aliquots from the bulk container, under nitrogen, into a  $\frac{1}{2}$  pt., rubber sealed, two-hole crown capped beverage bottle containing a known amount of pure solvent, usually cyclohexane or toluene.

##### 2.1.2.3. Nickeldiisopropylsalicylate (NiDIPS).

This was supplied by Aspro-Nicholas Ltd. It was dried in a vacuum desiccator then dissolved in dry toluene to the desired strength. It was stored in a bottle in a similar way to the organometallic solutions.

### 2.1.3. Gas burette studies.

#### 2.1.3.1. Solvent and Olefin purification.

Cyclohexane and toluene were purified in two stages, first by refluxing for 1 hr. over sodium hydride, then, after transfer under  $N_2$  to a separate still, by distillation from butyllithium.

The olefins used, except styrene, were all obtained relatively pure and simply dried by storing them in crown capped,  $\frac{1}{2}$  pt. bottles containing approximately one inch depth of activated 5A molecular sieve. They were deaerated by purging the bottle and contents for about 2 hours with nitrogen introduced and vented through syringe needles.

The styrene contained a phenolic inhibitor which had to be removed. This was carried out by distillation under reduced pressure through a 6" column of 5A molecular sieve. The centre cut of the distillate was collected and purged with nitrogen for  $\frac{1}{2}$  hr. before being used.

#### 2.1.3.2. Procedure.

Reactions were carried out in a 250 ml, one necked (E24) round bottomed flask, in a water bath thermostatted at  $40 \pm 2^\circ C$ . Good mixing of the hydrogen with the solution was achieved by magnetic stirring.

As all reagents were liquid (or solutions) transfer to the flask was effected by syringe through a serum cap. The change in volume of hydrogen during reaction was measured at ambient pressure, with a simple gas burette of either 100 or 500 ml. capacity according to the accuracy required, and the anticipated speed and magnitude of the volume change. The displacement liquid was liquid paraffin.

A flexible connection between the reaction flask and the gas burettes was made by a coil of  $\frac{1}{8}$ " O.D. copper tubing. The dried



nitrogen and hydrogen were supplied through  $\frac{1}{4}$ " O.D. copper tubing. Each copper to glass connection was made using a sleeve of polyethylene tubing, which was sealed by heating above its softening point when in position then clamped with a Terry clip. The apparatus is illustrated in figure 2.1. and was used as follows:

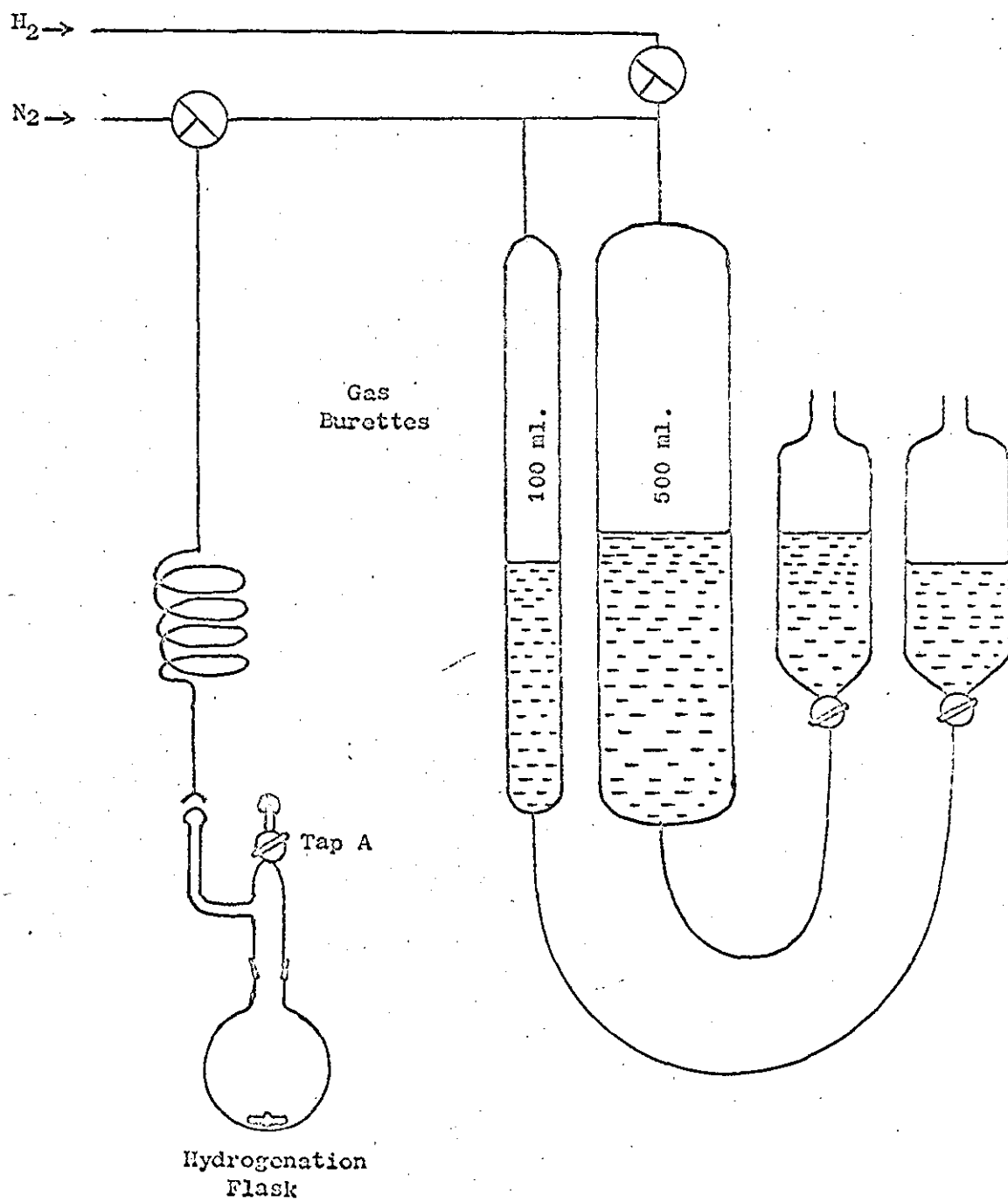
The flask and neck adapter were dried at  $130^{\circ}\text{C}$  for 4 hrs. then connected whilst still hot to the apparatus. The whole apparatus was then flushed with nitrogen, the gas passing out through tap A. When the flask was cold the required amount of solvent was added and the apparatus was flushed with hydrogen by repeatedly filling and emptying the burettes, venting again through tap A. When filled with hydrogen, the apparatus was allowed to equilibrate for a few minutes with stirring.

Solutions of catalyst components were then introduced followed by the olefin. The volume of hydrogen in the gas burette was noted and a stopclock started. The gas burette was kept constantly at atmospheric pressure by adjusting the height of the manostat and the change in volume in the burette was recorded at  $\frac{1}{2}$  minute intervals.

#### 2.1.3.3. Product analysis.

Usually product analysis was not required, the rate of reaction being measured by hydrogen absorption. However in the case of the hydrogenation of styrene, gas-liquid chromatography was carried out on the hydrogenated solution using a Perkin-Elmer F11 to determine the product composition.

FIGURE 2.1. Gas-burette hydrogenation apparatus.



#### 2.1.4. Pressure Bottle Studies.

##### 2.1.4.1. Cyclonpentadiene preparation.

Dicyclopentadiene (DCPD) was supplied by Velsicol Chemicals U.S.A. and contained less than 5 ppm of sulphur. This material was preferred to that of other supplies which had much higher sulphur contents. It was purified by passing through a column of sodium hydroxide pellets and alumina and then purged with nitrogen for several hours.

Cyclopentadiene (CPD) was obtained by thermal cracking of the dicyclopentadiene (DCPD). This was carried out by heating the DCPD in a stirred flask at 160°C under nitrogen. The vapour was fractionated through a warm water condenser (~40°C) so that uncracked DCPD was returned to the flask. The CPD vapour was condensed with a water cooled condenser and collected under nitrogen in an ice-cooled, rubber sealed, crown capped,  $\frac{1}{2}$  pt. bottle. This was stored in a refrigerator as necessary but whenever possible it was prepared just before use.

##### 2.1.4.2. Solvent purification.

Cyclohexane was employed as solvent and purified by distillation under nitrogen from n.butyllithium into a crown-capped bottle. This was then purged with nitrogen for a few hours and kept under a 10 p.s.i. pressure of nitrogen.

##### 2.1.4.3. Procedure.

Catalyst components were premixed in  $\frac{1}{2}$  pt. crown capped bottles by syringing in the required aliquots of solution. The bottles were then pressurised to about 20 psig with either hydrogen or nitrogen, and then generally allowed to stand overnight before use.

Hydrogenation was carried out in 1 pt. bottles. 50 ml. of cyclohexane were syringed into a 1 pt. crown-capped bottle then the required amount of cyclopentadiene was added. The catalyst solution was added by syringe then the bottle was placed in a cage and pressurised to 40 p.s.i.g. with hydrogen. The bottle was rotated in a water bath at the desired temperature and periodically samples were removed by syringe, the gas pressure in the bottle being measured at the same time by means of a gauge fitted with a syringe needle. The bottle was repressurised with hydrogen as necessary. At the end of the experiment the bottle was vented and the contents, together with the samples withdrawn were analysed.

After a few experiments had been carried out it was noticed that the hydrogen pressure fell at a faster rate when most of the CPD had been converted to cyclopentene. This allowed an estimate to be made of the "end-point" of hydrogenation without recourse to detailed product analysis. This is discussed more fully in section 3.1.3.1. and illustrated by an example.

#### 2.1.4.4. Product analysis.

The reaction products were analysed by gas liquid chromatography using a Perkin-Elmer F11 chromatograph. Tritolyl phosphate supported on Chromosorb P was employed as the stationary phase at 45°C. Detection was by flame ionisation.

## 2.2. POLYMER HYDROGENATION.

### 2.2.1. Polymer Preparation.

The polymers used were prepared at the request of the author in the Pilot Plant of The International Synthetic Rubber Co. Ltd.

#### 2.2.1.1. Polybutadiene, varying molecular weight.

Polymerisations were carried out in a 5 gallon reactor using hexane solvent and n.butyllithium initiator. Approximately 200 gm. samples of polymer were taken out at intervals during the polymerisations so that polymers of different molecular weights but similar vinyl contents were obtained.

Three polymerisations were carried out with slightly different levels of initiator so that samples with the required range of molecular weights were obtained.

#### 2.2.1.2. Polybutadiene, varying vinyl content.

Polymerisations were carried out similarly to those above but were modified by the addition of diglyme (dimethylether of diethylene glycol), according to the method of Duck and Locke<sup>(75)</sup>, to vary vinyl content of the polymer. A number of polymerisations had to be carried out in order to obtain products having similar molecular weights and vinyl contents in the region required.

#### 2.2.1.3. Styrene butadiene copolymers.

Commercial styrene butadiene random copolymers are generally produced by the incremental addition of butadiene, careful control of monomer feed resulting in a random product. On a smaller scale this procedure is not practicable so a randomising agent is used, both monomers being charged at the beginning of polymerisation.

If as randomising agent, a polar compound such as an ether is employed, this usually has a pronounced influence on the vinyl content of the polybutadiene portion of the polymer. However in 1969 Hsieh and Wofford published a paper<sup>(76)</sup> disclosing the use of potassium t.butoxid as a randomising agent and work at I.S.R. confirmed that, using this material, random copolymers could be obtained with virtually no increase in vinyl content.

The series of polymers with a range of styrene contents was therefore prepared in a similar manner to that previously described but with the addition of potassium t.butoxide.

#### 2.2.2. Polymer Analysis Before Hydrogenation.

##### 2.2.2.1. Molecular weight.

The number average molecular weight of the polymers was determined by osmometry according to the method discussed in the Part 2 experimental section number 2.3.2.1.

##### 2.2.2.2. Vinyl content.

The vinyl content was determined by infra-red analysis according to the method of Hampton<sup>(77)</sup> using a Grubb-Parsons G.S.4. spectrophotometer.

Samples were prepared by casting films from solution onto a potassium bromide disc. The spectra were then recorded between  $9_{\mu}$  and  $16.5_{\mu}$ . In order to achieve the desired level of accuracy the film thickness was regulated so that no absorption in the measured part of the spectrum exceeded 80%.

The peak positions for the different isomers were, trans 10.4 $\mu$ , vinyl 11.0 $\mu$ , cis 13.8 $\mu$ . Base lines were drawn, for trans from the troughs at 9.6 $\mu$  and 10.8 $\mu$ ; for vinyl from 10.8 $\mu$  to 11.4 $\mu$  and for cis from 12.5 $\mu$  to 16 $\mu$ . The absorbance for each peak was calculated from,

$$\text{Absorbance} = \log_{10} \frac{I_0}{I}$$

where  $I_0$  was the percentage transmission to base line and  $I$  was the percentage transmission to the top of the peak.

The absorbance figure for each peak was divided by the appropriate extinction coefficient viz:

Trans (10.4 $\mu$ ) 2.61, Vinyl (11.0 $\mu$ ) 3.285, cis (13.8 $\mu$ ) 0.608.

The values thus obtained were summed and each isomer was calculated as a percentage of the total.

#### 2.2.2.3. Bound styrene content.

This was determined using the Hilton method<sup>(78)</sup>. Samples weighing 0.15g were digested by refluxing with 70% nitric acid which converted styrene present to p-nitrobenzoic acid. The resulting solution was neutralised with sodium hydroxide, diluted to a standard concentration with distilled water, and the absorbances at 275nm, 287nm and 300nm measured using a Pye Unicam SP700 U.V. Spectrometer with distilled water as the blank.

The following formulae were used to determine the amount of styrene present in the sample, making allowance for excess nitric acid.

Styrene % = 92.86 Abs. 275 - 53.18 Abs. 235 - 2.04

Styrene % = 57.94 Abs. 275 - 21.09 Abs. 300 - 1.82

The values obtained from the two formulae needed to agree within 2% relative to be accepted.

This method gave the total styrene content of the polymer, the amount of random styrene present was found by subtracting the amount of block styrene determined as described in the next section.

#### 2.2.2.4. Block Styrene Content.

Although the polymerisation catalyst was expected to give completely random styrene distributions this was checked using the method of Kolthoff, Lee and Carr<sup>(79)</sup>.

A known weight of sample was decomposed by heating with t.butylhydroperoxide in the presence of osmium tetroxide. This treatment degraded the unsaturated regions of polymer but did not attack the saturated polystyrene segments.

As osmium tetroxide is poisonous and volatile and can cause irreversible damage to the eyes, this reagent and its solutions were used only in a fume cupboard.

After degradation the mixture was poured into industrial methylated spirit to which had been added a few drops of conc. sulphuric acid to destroy excess reagent. Any polystyrene present precipitated and was recovered by filtering through a weighed, sintered glass crucible (Porosity 3). The crucible was washed thoroughly with I.M.S. then dried at 110°C to constant weight. The block styrene content was calculated as being equal to the weight of precipitate, divided by the weight of sample, multiplied by 100.

Only those polymers which had an undetectable block styrene content were used for subsequent hydrogenation.



### 2.2.3. Hydrogenation Procedure.

#### 2.2.3.1. Solvent purification.

Toluene was refluxed over sodium hydride, under nitrogen then transferred to a second distillation flask under a positive pressure of nitrogen. It was then distilled from n.butyllithium under dry nitrogen into a "Christmas Tree" bottle receiver (figure 2.2.). This bottle permitted withdrawal of solvent using a small positive pressure of nitrogen via the dip-pipe through the L-tube directly into the nitrogen flushed hydrogenation reactor.

#### 2.2.3.2. Polymer.

The polymers required no further purification being obtained from the Pilot Plant as solid after having been isolated from solution by evaporating the hexane solvent in a steam heated vacuum oven.

#### 2.2.3.3. Procedure.

All glassware was dried in an oven at 180°C for 4 hr and assembled hot with a nitrogen purge. The nitrogen supply was obtained from a bulk supply of liquid nitrogen and had  $< 5$  ppm  $O_2$  content. It was used without purification. Hydrogen was obtained from an Air Products cylinder, fitted with an Engelhard Deoxo purifier. The gas was dried with 4A molecular sieve.

The apparatus was assembled as in figure 2.3.A. The condenser was removed from the flask, being flushed vigorously with nitrogen, and toluene was introduced from the "Christmas Tree" bottle, to a calibration mark. Small lumps of rubber were then added whilst stirring vigorously. The solution concentration was generally 3% w/v however with high molecular weight polymers ( $M_n > 150,000$ ) the higher solution viscosity necessitated the use of a 1% w/v solution.

FIGURE 2.2. "Christmas Tree" Bottles (2 lit.).

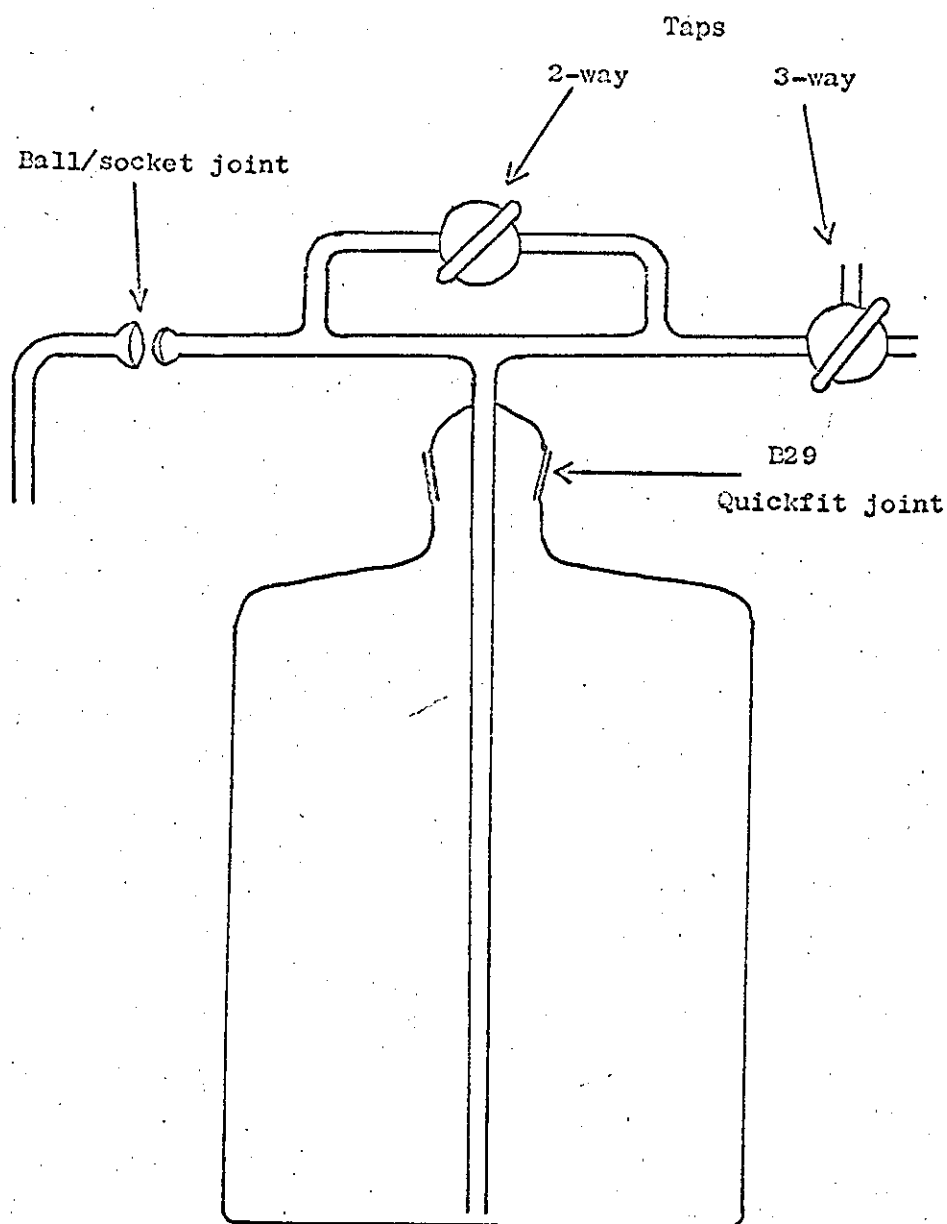


FIGURE 2.3.A. Polymer Hydrogenation Apparatus.

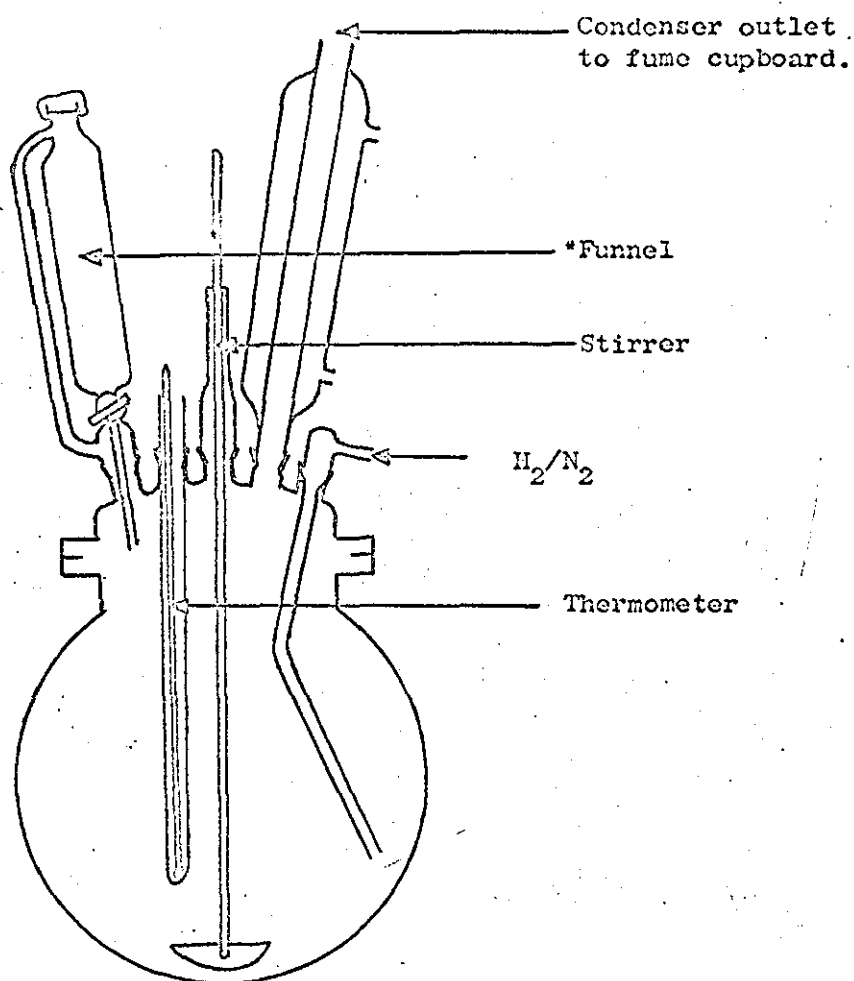
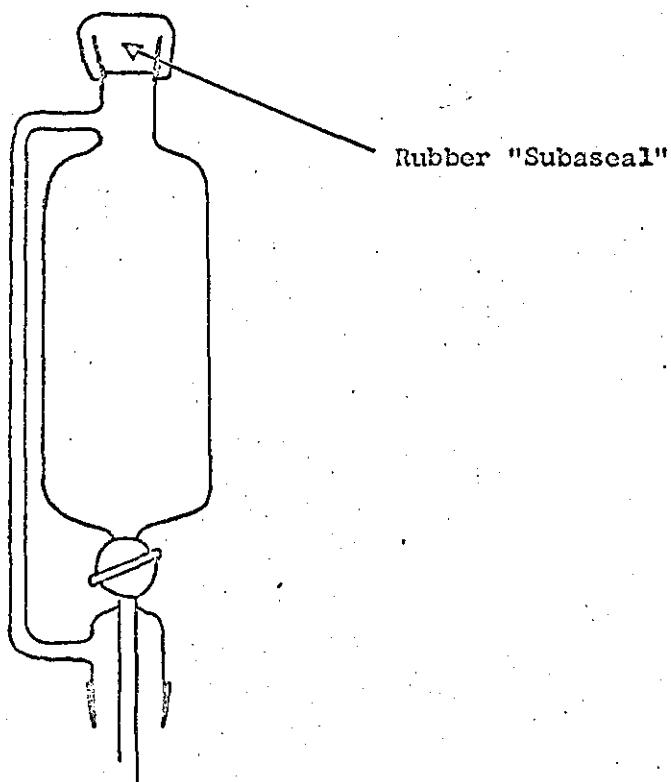


FIGURE 2.3.B. \*Pressure Compensating Funnel.



Nitrogen was bubbled through the stirred mixture and the temperature was slowly increased up to that required for the hydrogenation reaction. After the polymer had dissolved, the apparatus and solution were purged with hydrogen for 1 hr. The catalyst mixture was then made up in the pressure compensating funnel (figure 2.3.B), which was closed with a Suba seal. The nickel diisopropylsalicylate solution (section 2.1.2.3) was introduced by syringe, followed by the organometallic compound solution (sections 2.1.2.1. and 2.1.2.2). The catalyst mixture was a deep black-brown colour. In general n.butyllithium was used in a 5:1 molar ratio with the nickel complex, and the catalyst to polymer ratio was approximately 20g polymer : 1 mmole nickel.

The premixed catalyst was then added to the polymer solution and the reaction mixture was stirred at atmospheric pressure and a temperature of 70°C with hydrogen bubbling through for the required period.

The degree of hydrogenation was controlled simply by the length of time hydrogenation was continued, approximately 90% saturation being achieved in 4 hrs. At the end of the reaction period and after cooling the catalyst was destroyed and the polymer precipitated by pouring the solution into twice its volume of acetone. The solvent was then decanted and the polymer dried in a vacuum oven at 60°C.

#### 2.2.4. Product Analysis and Evaluation.

##### 2.2.4.1. Iodine number.

The degree of hydrogenation was calculated as mole percent saturation, as described in section 3.2.1.4, from the iodine number of the polymer before and after hydrogenation. This was determined by the method of Lee, Kolthoff and Mairs<sup>(80)</sup>, described in the part 2, experimental section no.

##### 2.2.4.1.

A check was made to determine if any cyclisation<sup>(75)</sup> had occurred during the preparation of the series of polybutadienes of varying vinyl content. After the iodine numbers of the polymers were determined they were compared with the theoretical value for a repeat  $C_4H_6$  unit (472). Fortunately all values were within experimental error so it was concluded that no cyclisation had occurred.

#### 2.2.4.2. Physical Testing.

Samples of polymer were compression moulded in a micro-tensile mould at  $160^{\circ}C$  and a pressure of 4000 p.s.i., the mould being cooled in cold water prior to removing the test sheet.

Physical properties were determined using the British Standard method<sup>(81)</sup>. Seven dumb-bells were obtained from the test sheet using a type E cutter. These were pulled on an Instron tester at a speed of 50cm/min. and a stress-strain curve obtained. Using this and the sample cross-sectional area the ultimate tensile strength, elongation at break and moduli were determined. Median figures were obtained by discarding the highest and lowest values for each determination and averaging the rest.

Elongation set was also determined. Two lines one inch apart were marked across the narrow parallel section of a dumb-bell which was then extended to 300% elongation for 10 mins., released and allowed to relax for one minute. The distance between the marks was re-measured, and the elongation set calculated:

$$\left( \frac{\text{Final separation}}{\text{Initial separation}} - 1 \right) 100$$

#### 2.2.4.3. Crystallinity.

This was determined using a Philips X-ray diffractometer. Samples were taken as moulded under standard conditions, cut to size and placed in the sample holder. A  $2\theta$  scan from  $4^\circ$  to  $60^\circ$  was then recorded using filtered copper  $K_\alpha$  radiation. A typical spectrum is reproduced in figure 2.4., which shows the broad peak associated with the amorphous regions of polymer with the two crystalline peaks superimposed. The positions of the crystalline peaks are equivalent to the polyethylene 1,1,0 and 2,0,0 crystal planes. The crystalline content of the polymer was calculated simply from a comparison of the peak areas due to the crystalline and amorphous regions viz.,

$$\text{crystallinity (\%)} = \frac{\text{crystalline peak area}}{\text{total peak area (crystalline + amorphous)}} \times 100$$

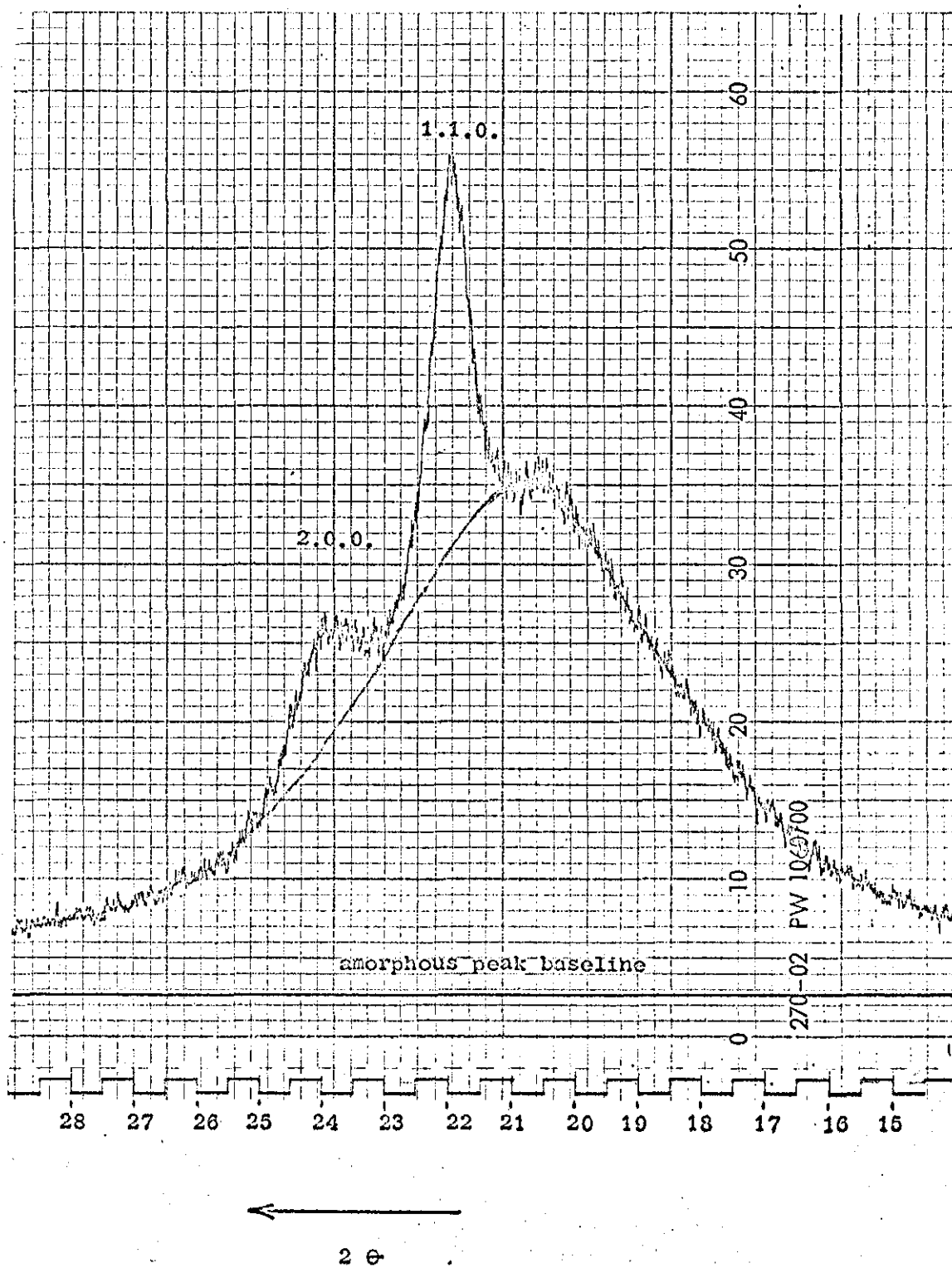
the amorphous peak being extrapolated through the base of the crystalline peaks and areas being measured by square counting.

Orientation effects in the moulded films were checked by scanning each sample both perpendicular and through the plane of the film. No differences were detected.

#### 2.2.4.4. Melt Flow Index.

This was determined using a Davenport melt flow indexer at a temperature of  $230^\circ\text{C}$  and a loading of 12.5 kg. according to the ASTM method (82). Samples were collected at 1 minute intervals for a period of 10 minutes. Results were quoted as the number of grams extruded in 10 mins.

FIGURE 2.4. X-ray Diffraction.



2.2.4.5. Glass Transition temperature.

This was determined using a Perkin-Elmer DSC-1B and the method described in the part 2 experimental section number 2.2.4.4.



### 3. RESULTS AND DISCUSSION.

#### 3.1. CATALYST STUDIES.

##### 3.1.1. General.

The two component (Ziegler) homogeneous catalysts described here were prepared with n.butyllithium or triisobutyl aluminium. In both, the transition metal component was nickel bis (diisopropylsalicylate) (NiDIPS) chosen for its high solubility in hydrocarbon solvents and known efficacy in Ziegler polymerisation systems.

In type, these catalysts were by no means novel and, as mentioned in the introduction, similar systems had been investigated by a number of workers and found to be extremely active. In the present work it was sufficient simply to conduct the minimum investigation required, to arrive at a catalyst showing suitable activity for polymer hydrogenation and then develop suitable techniques for its application.

The study of the n.butyllithium/NiDIPS catalyst was mainly carried out in a conventional manner using cycloocta 1,5 diene (COD) as a convenient hydrogen receptor and standard gas burette techniques. However, in general, the study of the triisobutylaluminium/NiDIPS catalyst was carried out using cyclopentadiene as substrate and a pressure bottle technique. These rather unusual conditions were employed because we were at the time also interested in a selective catalyst for the continuous low pressure hydrogenation of cyclopentadiene to cyclopentene. This project was carried through successfully, resulting in the process being patented,<sup>(83)</sup> and provided useful information on catalyst preparation, activity and selectivity.

The main results from these separate investigations were of course checked using polymer substrates.

### 3.1.2. n-Butyllithium/NiDIPS.

#### 3.1.2.1. Catalyst component ratios.

The most important variable was the ratio of the two catalyst components, the optimum depending to a large extent on the exact nature of the components. No references were found in the literature to the specific n-butyllithium, nickel diisopropylsalicylate catalyst used in the present work but n-butyllithium had been used in the ratio 3-6:1 with cobalt ethylhexanoate<sup>(60, 64)</sup> and 2.2:1 with cobalt octoate.<sup>(84)</sup> A substantial decrease in activity had been found when ratios deviated from the optimum. The ratio of n-butyllithium to NiDIPS was therefore investigated within the range 2-10:1.

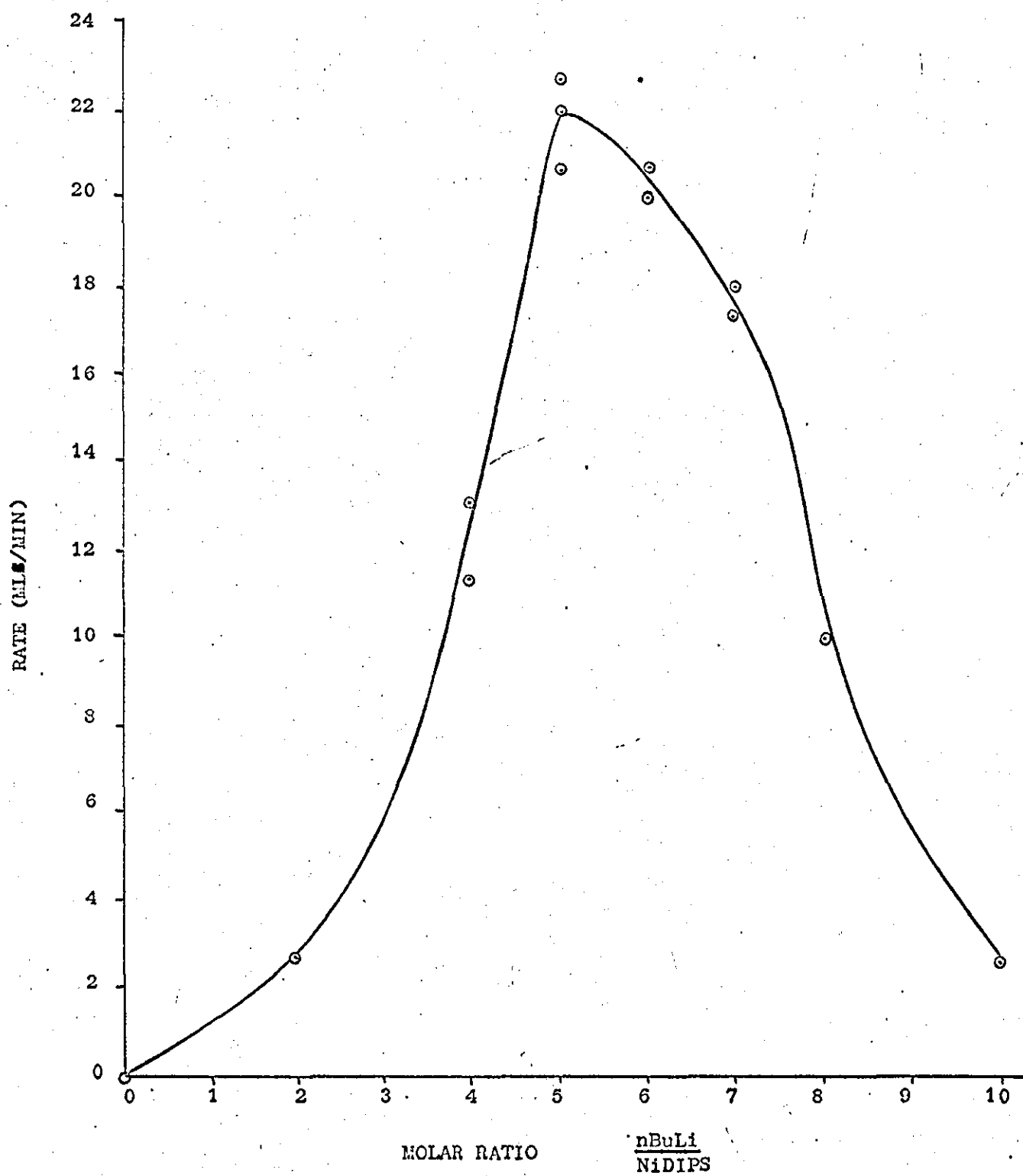
Hydrogenations were carried out at 40°C using 20 m.moles cycloocta 1,5 diene in 100 ml. cyclohexane, 0.5 m.moles NiDIPS and various amounts of n-butyllithium. The rate of hydrogen uptake was measured using a gas burette.

As shown in Figure 3.1.1. maximum activity was achieved at a mole ratio of 5 BuLi: 1 NiDIPS, activity declining steeply either side of this optimum. This optimum ratio probably varies a little due to the scavenging level of the system. However, in later studies a similar ratio was found to be ideal.

For ratios greater than 2:1 the catalysts were dark brown in colour and no precipitate formed on standing. This indicated the homogeneous nature of the catalyst but did not preclude the possibility of its being colloidal. The colour suggested the formation of a nickel (0) complex.

After the two components were mixed, and before the olefin was added, hydrogen was absorbed and GLC analysis of the solution showed the presence of n-butane. Quantitative investigations were not carried out but these observations are consistent with the generally accepted postulate of Sloan et al<sup>(66)</sup> that initial alkylation of the nickel complex occurs followed by the hydrogenolysis of the nickel-alkyl bond, this

FIGURE 3.1.1.     Hydrogenation of cycloocta-1,5-diene.



resulting in the formation of nickel hydride complex plus, in this case, n.butane.

If an active catalyst was deactivated by exposure to air the colour changed from dark brown to clear, yellow-orange, without observable precipitation. Addition of more n.butyllithium was found to regenerate some activity but as the quantities of dissolved air etc. were not known the optimum ratio could not be produced and hence it was not found whether the maximum previous activity could be regained. However, the fact that no precipitate was formed on deactivation and that some activity could be regenerated indicated that these catalysts were probably truly homogeneous and not colloidal.

### 3.1.2.2. Activity towards olefins.

An investigation was carried out, using the 5:1 catalyst, of the effect on rate of hydrogenation of extent of double bond substitution. Olefins containing double bonds which were, mono, di, tri and tetra-substituted were hydrogenated. The results are given in Table 3.1.1.

TABLE 3.1.1. RELATIVE RATES OF HYDROGENATION FOR VARIOUS EXTENTS OF DOUBLE BOND SUBSTITUTION.

DEGREE OF SUBSTITUTION	OLEFIN	FORMULA	RELATIVE RATE OF HYDROGENATION.
MONO	HEPT-1-ENE	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}_2$	100
DI	4 METHYL PENT-2-ENE	$\text{CH}_3\text{CH}=\text{CHCH}(\text{CH}_3)_2$	80
TRI	2 METHYL BUT-2-ENE	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	50
TETRA	2,3 DIMETHYL BUT-2-ENE	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	20

The rates of hydrogenation are quoted as percentages of the rate obtained for the mono-substituted olefin. As might have been expected, the rate of hydrogenation decreased with increasing substitution. These results were interesting when related to the hydrogenation of polymers as they indicated that vinyl double bonds would be saturated faster than internal double bonds and also that polyisoprene would be hydrogenated with much more difficulty than polybutadiene. This was in fact found (section 3.2.1.2).

The hydrogenation of styrene was carried out with the  $5nBuLi:1NiDIPS$  catalyst at temperatures up to  $80^{\circ}C$ . The sole product was ethylbenzene, no reduction of the ring occurring even at the highest temperature. This result was important as it showed that in the hydrogenation of styrene containing polymers reduction of the ring would not occur.

These olefin hydrogenation results agree very well with those obtained by Falk<sup>(60,64)</sup> using an n-butyllithium, cobalt-2-ethylhexanoate catalyst.

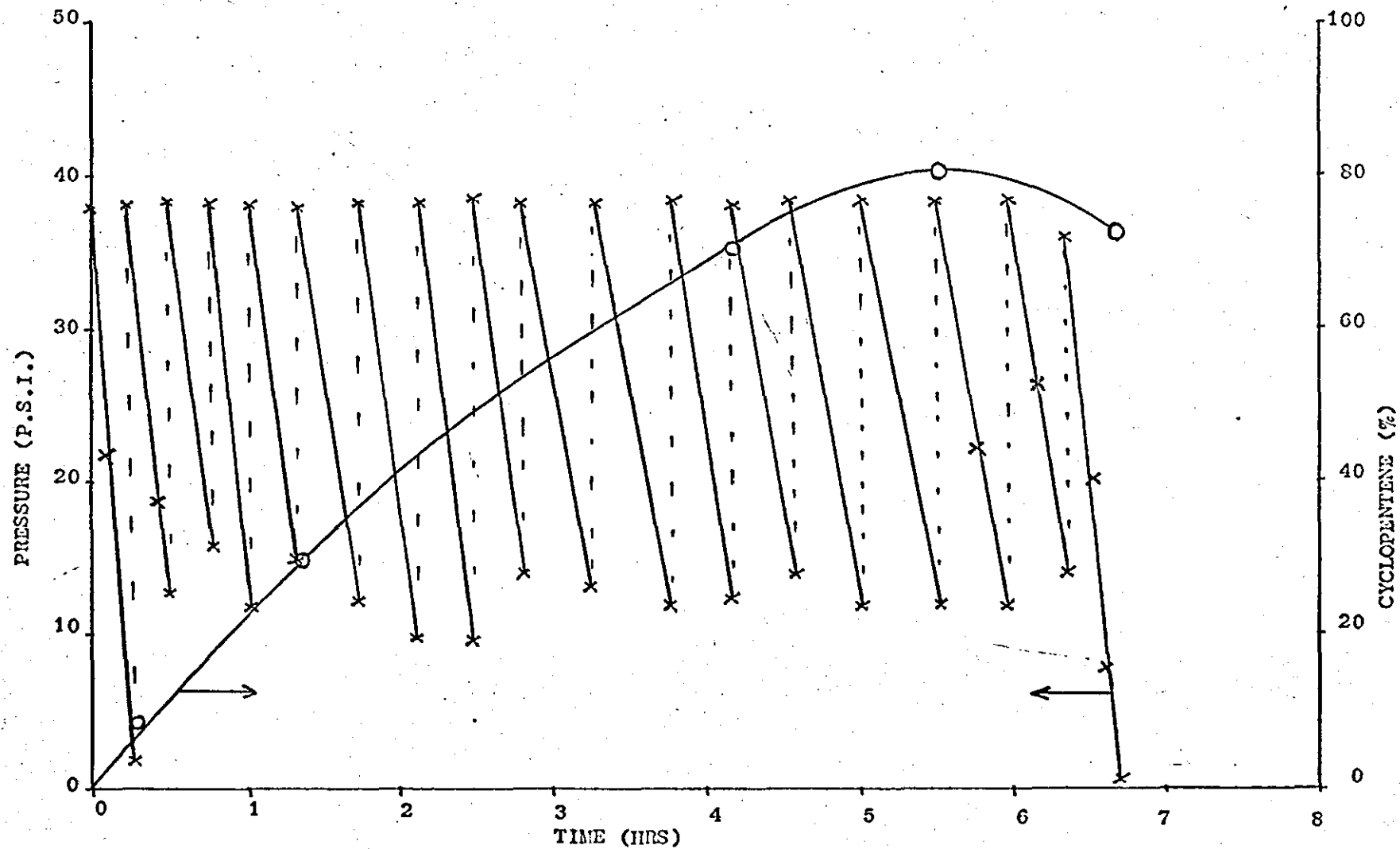
### 3.1.3. Triisobutylaluminium/NiDIPS catalyst.

#### 3.1.3.1. Procedures.

It was previously mentioned (3.1.1) that some of the catalyst studies were carried out using cyclopentadiene. For this purpose it was required that a large number of hydrogenations be carried out at elevated temperatures. The standard gas burette technique proved to be somewhat unsuitable since it was only possible to carry out one or two hydrogenations at a time, and monitoring hydrogen absorption was difficult under conditions of fluctuating temperature. A simple bottle technique was developed which met the needs quite adequately. Beverage bottles (1 pint) were crown capped using neoprene rubber seals then purged with hydrogen. Cyclopentadiene and cyclohexane were then added followed by the catalyst. The bottles were put into metal cages, as a precaution against explosion, pressurised with hydrogen then rotated in a water bath at the required temperature. The pressure in the bottles was periodically checked and more hydrogen was admitted as necessary.

Initially, samples were removed by syringe at suitable times and analysed by GLC to determine the extent of hydrogenation. It was observed that at the point of maximum conversion to cyclopentene, the rate of hydrogen uptake increased. This proved to be a simple method for the detection of "end-point" and is illustrated in figure 3.1.2. Here maximum conversion to cyclopentene occurred at approximately 6 hrs and shortly afterward the rate of hydrogen uptake increased sharply, as evidenced by the slope of the last solid line compared with the other, parallel lines. Conditions were selected to give adequate accuracy in determining the effect of variables by selecting the amount of cyclopentadiene (50 ml in 50 ml cyclohexane) to give long hydrogenation times.

FIGURE 3.1.2. "End-point" detection.



### 3.1.3.2. Catalyst component ratios.

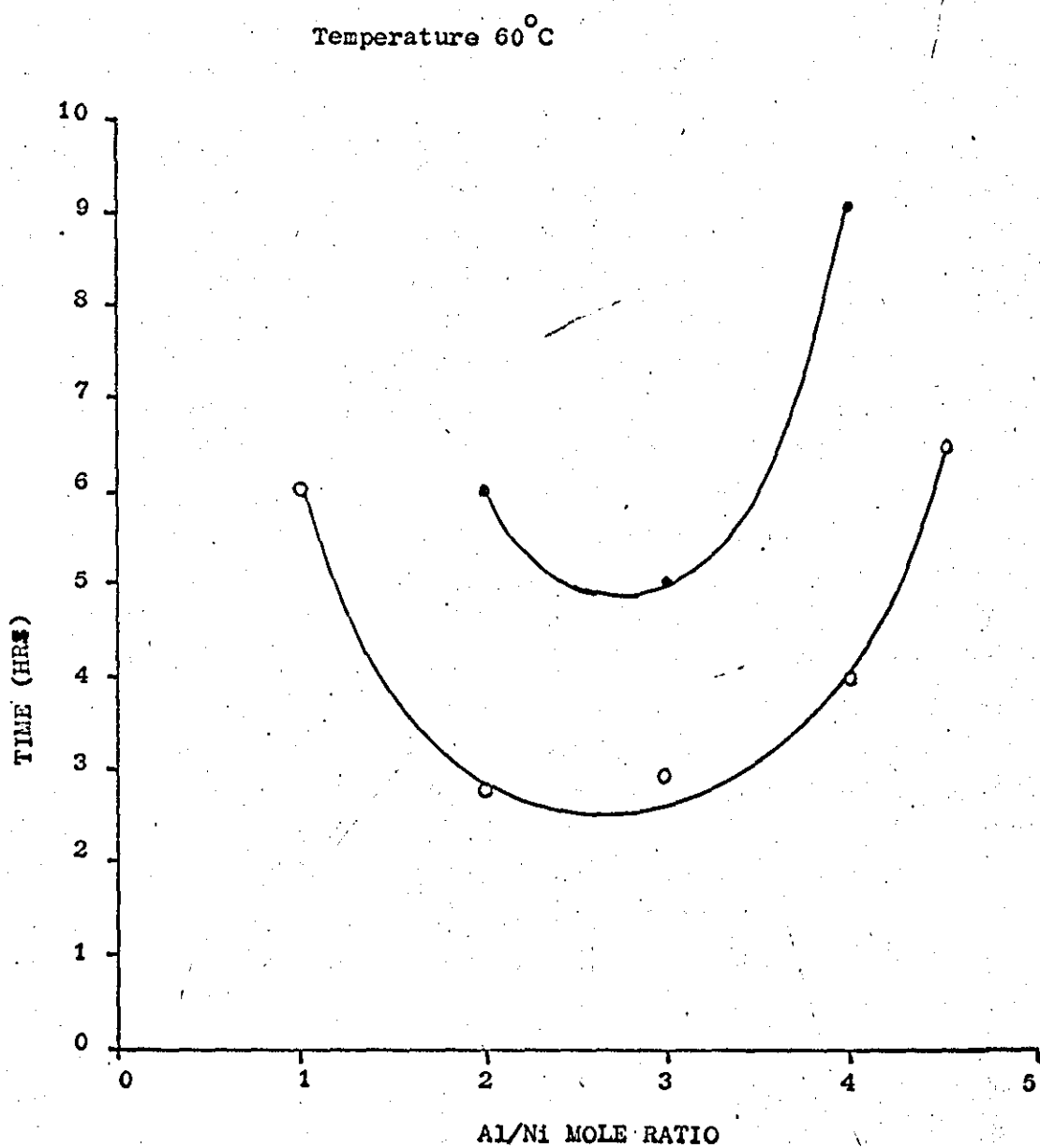
The triisobutylaluminium, nickel bis diisopropylsalicylate catalyst has been investigated by Sholl<sup>(74,85)</sup> and an active catalyst was obtained using a 4:1 aluminium to nickel ratio. Catalysts of triethylaluminium with cobalt 2-ethylhexanoate<sup>(60,64)</sup>, nickel naphthenate<sup>(86)</sup>, and nickel 2-ethylhexanoate<sup>(57)</sup> have also been investigated and maximum activities were all obtained with ratios of 3 to 4:1. Kroll<sup>(59)</sup> however, found that with triisobutylaluminium and either nickel or cobalt acetylacetonate the optimum ratio was 6 Al:1 Ni or Co, but also mentioned that with higher proportions of aluminium a poisoning effect occurred which could be partially eliminated by closely adjusting the ratio. He commented that this adjustment was very difficult due to the presence of impurities.

The ratio of triisobutylaluminium to NiDIPS was therefore investigated and Figure 3.1.3. shows the times taken for 50 ml cyclopentadiene to reach approximate maximum conversion to cyclopentene using varying catalyst ratios; in each case the two components were premixed in the presence of hydrogen before contact with olefin. Two catalyst levels were investigated, 1.25 m.mole and 2.5 m.mole nickel per 100g olefin. Hydrogenations were carried out at 60°C.

As can be seen for both catalyst levels the shortest hydrogenation times were obtained with similar ratios of about 3 Al : 1 Ni. This result agrees well with those of most other workers and whereas Kroll appeared to have difficulty in achieving satisfactory levels of purity this was apparently not the case in the present work.



FIG. 3.1.3. Effect on hydrogenation rate of catalyst ratio and concentration.



- 1.25 m.mole Ni/100g CPD
- 2.5 " " "

Attention needs to be drawn to the apparent importance of preparing the catalyst in the presence of hydrogen. In the present work it was found that pre-treatment of the catalyst with hydrogen before contact with olefin greatly improved activity. As far as the writer is aware other workers employed the reverse procedure, perhaps guided by the well established fact that Ziegler catalysts are often more active if the components are mixed in the presence of olefin. As an example of the advantage to be gained by pre-treatment with  $H_2$ , two similar hydrogenations were carried out at  $0^\circ C$ ; in one the  $3Al i Bu_3 / 1 Ni DIPs$  catalyst was mixed and aged under nitrogen for 20 hrs and in the other ageing was carried out under hydrogen. The former catalyst took 3 hrs to hydrogenate 10 ml of cyclopentadiene to maximum cyclopentene content, the latter 1 hr. It is perhaps surprising that no mention of this effect can be found in the literature as it is generally accepted that the transition metal complex hydride has to be formed before hydrogenation can occur. These results suggest that the hydrogenolysis reaction of the transition metal complex alkyl to form the hydride is comparatively slow. Catalysts which were stored under hydrogen lost none of their activity when kept for many weeks.

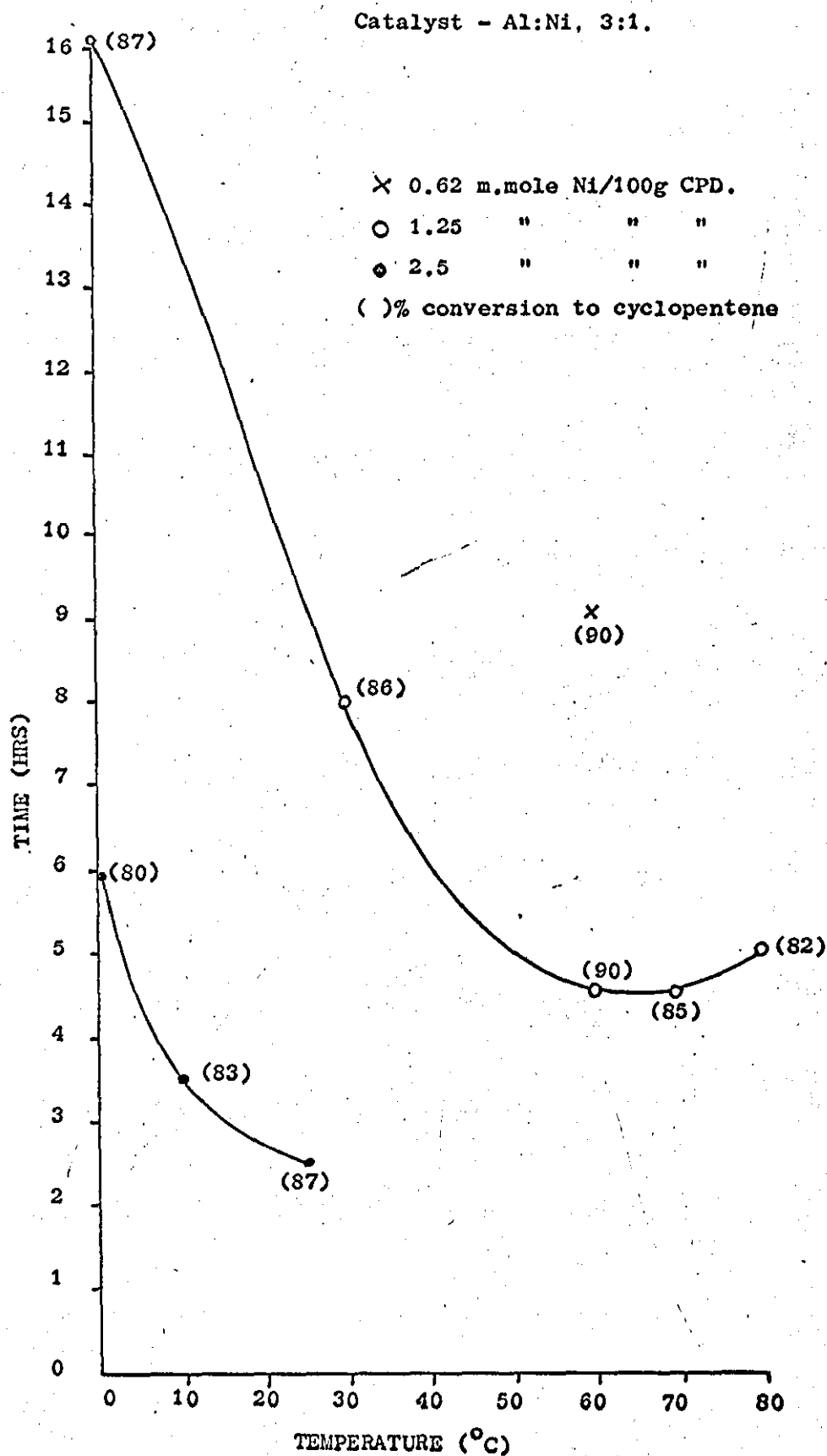
### 3.1.3.3. Other reaction parameters.

The other reaction parameters that were of interest were catalyst concentration, temperature and pressure. Figure 3.1.4. shows the effect of both catalyst concentration and temperature on the time taken to reach approximate maximum conversion to cyclopentene. In each case the catalyst  $3\text{AlEt}_3 : 1\text{NiDIPS}$  was premixed and then treated with hydrogen. Three different levels of catalyst were investigated viz. 0.62, 1.25 and 2.5 m.moles nickel per 100g cyclopentadiene. The figures in parenthesis refer to the actual conversion to cyclopentene, determined by G.L.C. analysis. As might be expected the rate of hydrogenation was increased by raising either the temperature (up to  $60^\circ\text{C}$ ) or the catalyst concentration. However, an interesting feature of these results is that the selectivity to cyclopentene did not decrease, with increase in temperature. This means that the hydrogenation was still highly selective even at  $60-80^\circ\text{C}$ .

The effect of pressure on rate of hydrogenation has not been fully investigated, however reference to figure 3.1.2. leads to the conclusion that the rate was independent of pressure. Admittedly only five absorptions have been followed by more than two readings but in each of these cases the results appear to fall on straight lines and cover a wide range of pressures. The reason for this is not clear as the literature<sup>(59,87)</sup> indicates a first order dependence on pressure. It might be thought that in the present work diffusion control may have existed but, if that were the case, no increase in hydrogenation rate would have occurred after the maximum conversion to cyclopentene.

FIGURE 3.1.4.

Effect on hydrogenation rate of catalyst  
amount and temperature.



#### 3.1.3.4. Comparison with n.butyllithium/NiDIPS.

Two similar hydrogenations were carried out, one with the  $3\text{Al}(\text{Bu})_3/1\text{NiDIPS}$  catalyst and the other with  $5\text{n.BuLi}/1\text{NiDIPS}$  catalyst. In both cases the nickel concentration was the same and catalyst ageing was carried out overnight under hydrogen. Hydrogenations were carried out at  $0^\circ\text{C}$ , and the time taken, to convert 10 ml cyclopentadiene in 10 ml cyclohexane to maximum cyclopentene content, was noted. The aluminium alkyl catalyst took 1 hr and gave 85% cyclopentene whereas the lithium alkyl took 3 hrs to give 90% cyclopentene. The former catalyst was therefore the more active of the two though the latter was still extremely good. Under the conditions used for polymer hydrogenation (section 3.2.1.1), the difference between these catalysts was much less marked.

These results are in general agreement with those of Falk<sup>(50)</sup> who stated that previous investigators severely underestimated the reactivity of reduction catalysts prepared from alkyllithiums. One of the previous investigators referred to was Sloan who stated that<sup>(56)</sup> the rates of hydrogenation with n-butyllithium catalysts were considerably slower than with the triisobutylaluminium containing counterparts.

### 3.1.4. Hydrogenation Mechanism.

The generally accepted<sup>(58,59,63)</sup> mechanism is that proposed by Sloan and Matlack<sup>(56)</sup> in 1963. This, however, was only a generalised scheme; a more definitive mechanism being unobtainable due to the unknown nature of the catalyst species. Since this time there has been no real improvement in the situation. Kroll in 1969 stated that in a subsequent publication, results would be discussed to allow suggestions to be made for the reduced and hydride form of the catalyst, however, to this date no such publication has been found. Obviously, there are profound difficulties in investigating species as unstable as these.

An investigation into the nature of the catalyst and the mechanism was outside the scope of the present study but a few comments can be made on the former and the Sloan mechanism can be modified to include the effects found during the selective hydrogenation of cyclopentadiene to cyclopentene.

One of the fundamental points of discussion with respect to these catalysts has been whether they are truly homogeneous or contain colloidal metal. The published evidence<sup>(56,57,59)</sup> now suggests that they are homogeneous and the results obtained here viz. no precipitate formed on standing for prolonged periods; no activity after reaction with air; no precipitate formed on reaction with air; loss of black colour on reaction with air, tend to support these conclusions.

The Sloan mechanism postulated the initial alkylation of the transition metal complex, followed by the hydrogenolysis of the metal-alkyl bond to form the metal hydride. Again, the present results tend to support this theory. On mixing the catalyst components, hydrogen

was absorbed and, when the reduction was carried out with n.butyllithium, n.butane was evolved. However, no results were obtained which would help in the discussion whether the active species was the metal hydride or a zero valent  $\pi$ -complex.

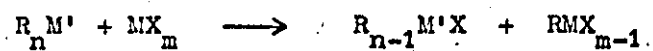
The results from the hydrogenation of cyclopentadiene indicated that the diene was hydrogenated in preference to the cyclopentene but at a slower rate. A modified Sloan mechanism (figure 3.1.5) shows how this may have occurred. For the sake of simplicity it has been assumed that the active catalyst species is the nickel hydride.<sup>(I)</sup> This could associate with either diene<sup>(II)</sup> or monoene,<sup>(III)</sup> the former producing a more stable complex due to the increased ease of  $\pi$ -bond formation. An equilibrium would exist between the hydride and both of the associated complexes but due to the greater stability of the diene complex its concentration would be much greater than that of the monoene complex. Hydrogenation of the diene would thus proceed in preference to the monoene.

The final stages of reaction would be: alkylation of the nickel and hydrogenolysis of the nickel-alkyl bond. This would yield the reduced hydrocarbon and regenerate metal hydride. As the diene complex is comparatively stable it would be expected to undergo the alkylation reaction more slowly than the monoene complex. The result would be an overall slower rate of reduction for the diene.

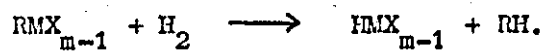
After the concentration of diene has been lowered to a sufficient level, substantial reduction of the monoene would then start to occur.

FIGURE 3.1.5. SELECTIVE HYDROGENATION.

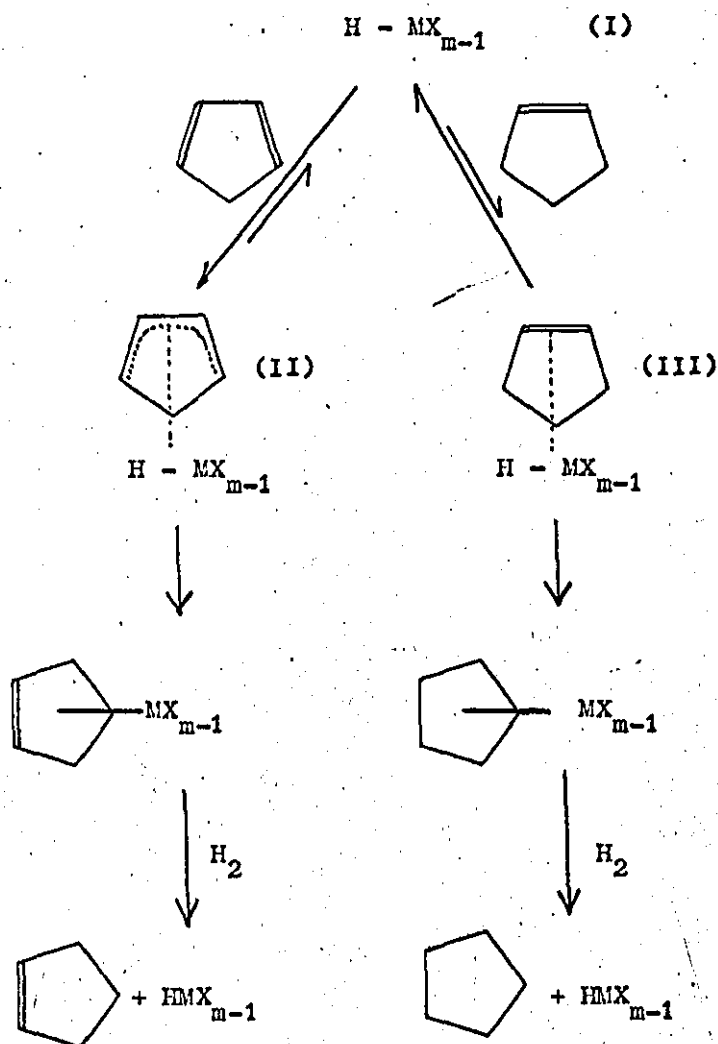
1. ALKYLATION.



2. HYDROGENOLYSIS.



3. HYDROGENATION.





### 3.2. POLYMER HYDROGENATION.

#### 3.2.1. General.

##### 3.2.1.1. Choice of catalyst.

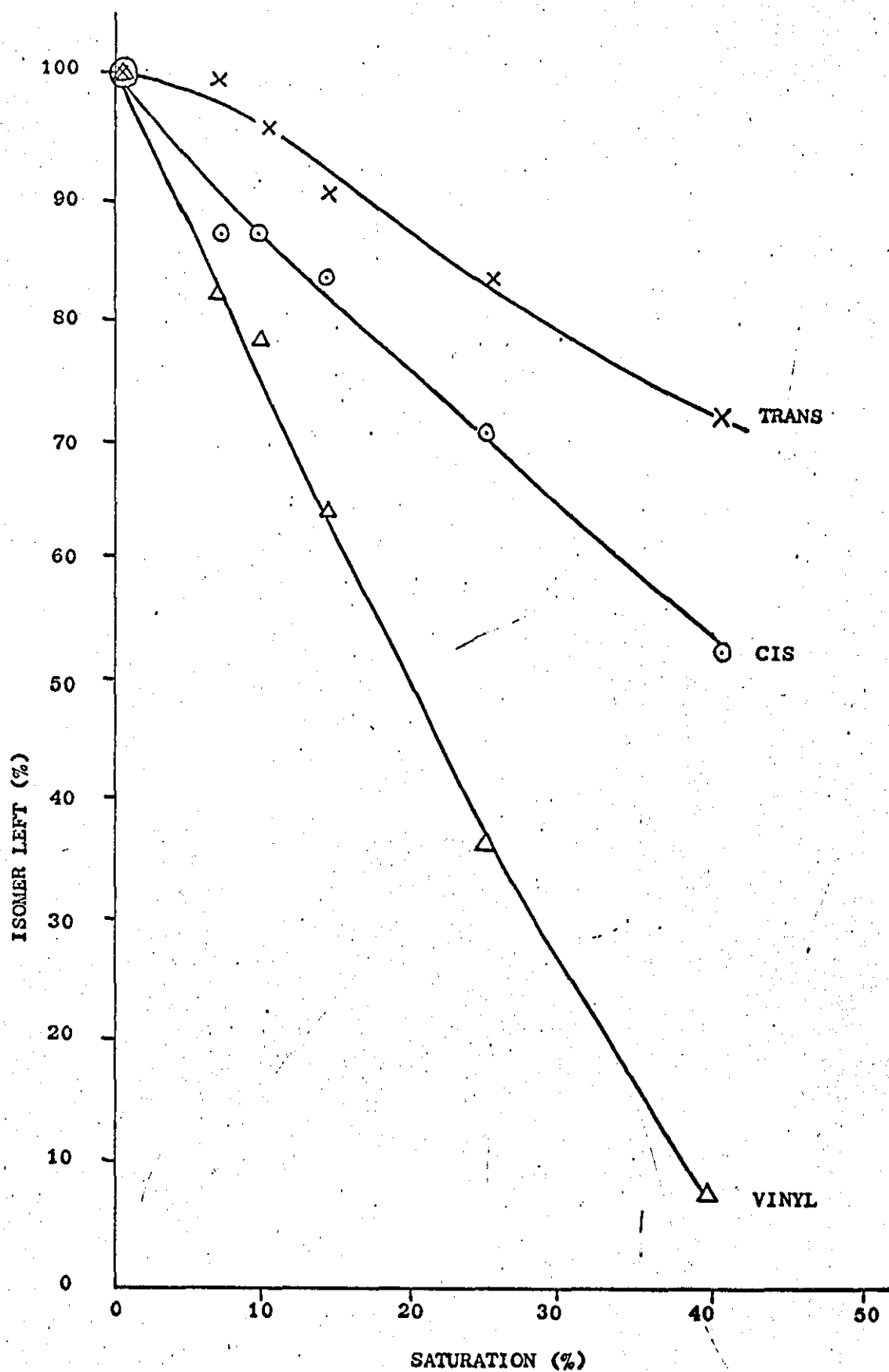
In the catalyst studies section it was shown that the triisobutylaluminium NiDIPS catalyst was superior in activity to the n-butyllithium NiDIPS catalyst, but as the techniques for the polymer hydrogenation were somewhat different for those previously described a check was made on their relative suitabilities in this context.

To simplify procedure, catalysts were premixed under hydrogen just prior to addition to the polymer solution. The premixing was carried out in a pressure compensating dropping funnel attached directly to the hydrogenation vessel. The two catalysts were compared under similar conditions, chosen for their ease of operation, by hydrogenating a solution of polybutadiene (10% vinyl) at 60°C for 3 hr using 1 m.mole NiDIPS/20g polymer. The polymers were then isolated and the extent of hydrogenation determined by iodine number. It was found that the polymer hydrogenated with the aluminium alkyl catalyst was 90% hydrogenated and the other 85% hydrogenated. There was evidently no great difference between catalysts under these conditions and as n-butyllithium was much more easily handled due to it being supplied as a dilute solution rather than neat and hence being non-flammable it was chosen for the subsequent studies.

##### 3.2.1.2. Polymer composition effects.

The hydrogenation of non-polymeric olefins (section 3.1.2.2.) showed that terminal double bonds were reduced at a faster rate than internal double bonds. This suggested that the vinyl groups of a polydiene would be hydrogenated in preference to the cis or trans isomers. Figure 3.2.1. shows that this was indeed the case. Samples of polybutadiene with microstructure 9% vinyl, 51% cis, 40% trans were

FIG. 3.2.1. PED HYDROGENATION.

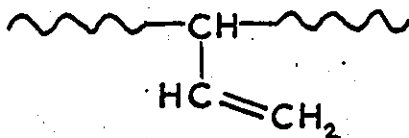


hydrogenated to various extents and the product microstructure determined. As shown when 40% of the double bonds had been reduced only 7% of the original vinyl groups remained whereas 53% of the cis and 72% of the trans remained. This figure also shows that the cis double bonds were hydrogenated at a faster rate than the trans. The relative rates of hydrogenation were therefore



These results are in agreement with those of Tikhomirov et al.<sup>(62,63)</sup>

It should be pointed out however, that Witt and Hogan<sup>(70,71)</sup> using an n.butyllithium, nickel octoate catalyst, found that isomerisation of polyethylene vinyl groups occurred during hydrogenation. This isomerisation <sup>was unlikely to</sup> ~~would not~~ have occurred in the present study for two reasons. Firstly, isomerisation of a polybutadiene vinyl group to an internal double bond <sup>was unlikely to</sup> ~~could not~~ occur, without chain scission, due to the tertiary -carbon,



and no such depolymerisation was found. Secondly, they state the reason for the isomerisation was that the nickel catalyst site was completely shielded from hydrogen as long as vinyl groups remained in the system. This occurred in their system because the catalyst components were not premixed under hydrogen. The active catalyst hydride had thus not been formed before contact with olefin.

The preferential hydrogenation of vinyl groups was of interest for two reasons. Firstly it meant that the vinyl groups in hydrogenated polymers with measurable tensile strengths had virtually

all been reduced to ethyl groups since generally, the onset of measurable strength did not occur until about 45 to 50% hydrogenation. Secondly it indicated that hydrogenation must have occurred to a large extent in a random manner. All of the macromolecules of the original polymer can be considered to have been equal in structural composition so at the end of hydrogenation of the vinyl groups all of the macromolecules must have taken place in the reaction and all parts of the chains attacked.

It was previously found (section 3.1.2.2.) that these catalysts, under the conditions employed, did not reduce the aromatic function of ethylbenzene, thus implying that the styrene units in a styrene butadiene copolymer would not be reduced and indeed no evidence was found for their hydrogenation. This result is again in agreement with earlier workers<sup>(60,67)</sup>. Lapporte and Schuett<sup>(57)</sup> have hydrogenated aromatics using similar catalysts but found it necessary to employ a pressure of 1000 p.s.i. and temperatures in the region of 150-210°C. Under these conditions it is possible that metallic Ni was formed, having a quite different activity from the presumed monatomic species.

#### 3.2.1.3. Method of investigation of variables.

The main aims of this investigation were to produce a good thermoplastic elastomer through a systematic study of the effects of the variables involved, and to gain some insight into the nature of the products.

The two main variables were the extent of hydrogenation and the composition of the polymer. The polymers selected were prepared by anionic polymerisation viz. polybutadiene and styrene butadiene copolymer. This method of polymerisation produced linear, well-defined polymers, the compositions of which could be varied with respect to vinyl content, molecular weight and styrene content. As only one of these variables could be sensibly investigated at a time, three series of polymers were prepared:-

1. Polybutadienes having similar molecular weights but different vinyl contents.
2. Polybutadienes of constant vinyl content but different molecular weights.
3. Styrene butadiene copolymers with constant molecular weight and vinyl content but of various styrene content.

The first series was prepared by the addition of various amounts of diglyme (diethyleneglycoldimethylether) to the n-butyllithium initiator<sup>(75)</sup>, microstructure being determined by infra-red spectroscopy.

Samples of polybutadiene having different molecular weights were prepared by the removal of polymer at various stages during a typical n-butyllithium polymerisation of butadiene, the number average molecular weights being determined by osmometry.

The series of polymers containing various styrene contents was prepared again using n-butyllithium initiator but including potassium t.butoxide to randomise the distribution of styrene without increasing the vinyl content.<sup>(76)</sup>

Samples of each of the polymers were hydrogenated to different extents and then evaluated.

The assessment of products had, at first, to be fairly simple because of the large number of samples involved. The properties of prime interest were ultimate strength, elasticity and thermoplasticity. The ultimate tensile strength was determined using the standard method and a dumb-bell specimen cut from a compression moulded sheet. Elasticity was determined as elongation set; test pieces were extended to 300% elongation, held for 10 mins., released, allowed to relax for one minute. The residual strain was then calculated as a percentage of the original length. A perfect elastomer would have zero elongation set.

The thermoplasticity was not initially investigated as all samples were sufficiently thermoplastic to permit high temperature moulding into thin sheets; the melt flow indices of some materials were determined later.

Most of the samples were also examined for crystallinity. This was determined by X-ray diffraction. The levels of crystallinity measured were generally low and absolute measurement was therefore inaccurate, however comparative estimates could be made and these were found to correlate very closely with product properties. It was therefore a very useful aid in the investigation into the nature of the products.

#### 3.2.1.4. Molar polymer compositions.

The standard method of quoting styrene butadiene copolymer compositions is to use weight percent for styrene content and weight/mole percent of butadiene fraction for vinyl content. For example an SBR could be quoted as having a composition of 25% styrene and 10% vinyl. This means that it contains 25 weight percent styrene and that 10% of the butadiene segments have been polymerised 1,2 instead of 1,4. The extent of reduction of a polymer is often quoted as degree of hydrogenation, that is the percentage of the butadiene segments which have been hydrogenated. This is simple in some respects but can lead to confusion if structures are to be drawn or envisaged. In the present study it was considered expedient that all values should be quoted as mole percentages.

The relationship between mole percent and weight percent styrene contents can be seen in figure 3.2.2.

The conversion of vinyl content to mole percentage depended on the styrene content of the polymer. The relationship between mole percent and percentage of polybutadiene was therefore calculated for different styrene contents and set out as in figure 3.2.3., which permits ready conversion of one quantity to the other.

The concept of mole percent saturation, instead of degree of hydrogenation, was employed to overcome the difficulty of comparing hydrogenated polymers with different styrene contents. For example an SBR containing 25 mole percent styrene would have 25% of the polymer chain monomer units saturated without being hydrogenated at all. It therefore seemed more logical to consider the styrene units as substituted ethylene units and to include them with the hydrogenated butadiene units in the overall mole percent saturation. The mole percent saturation was therefore calculated from the ratio,

$$\frac{\text{styrene content} + \text{saturated PBD content}}{\text{styrene content} + \text{total PBD content.}}$$

All values are quoted as mole percentages, the saturated polybutadiene content being calculated from iodine values determined before and after hydrogenation. In fact, for polymers substantially hydrogenated with moderately low styrene contents, which were those of main interest, there was little difference between mole percent saturation and degree of hydrogenation (figure 3.2.4.).

FIG. 3.2.2. STYRENE CONTENT CONVERSION.

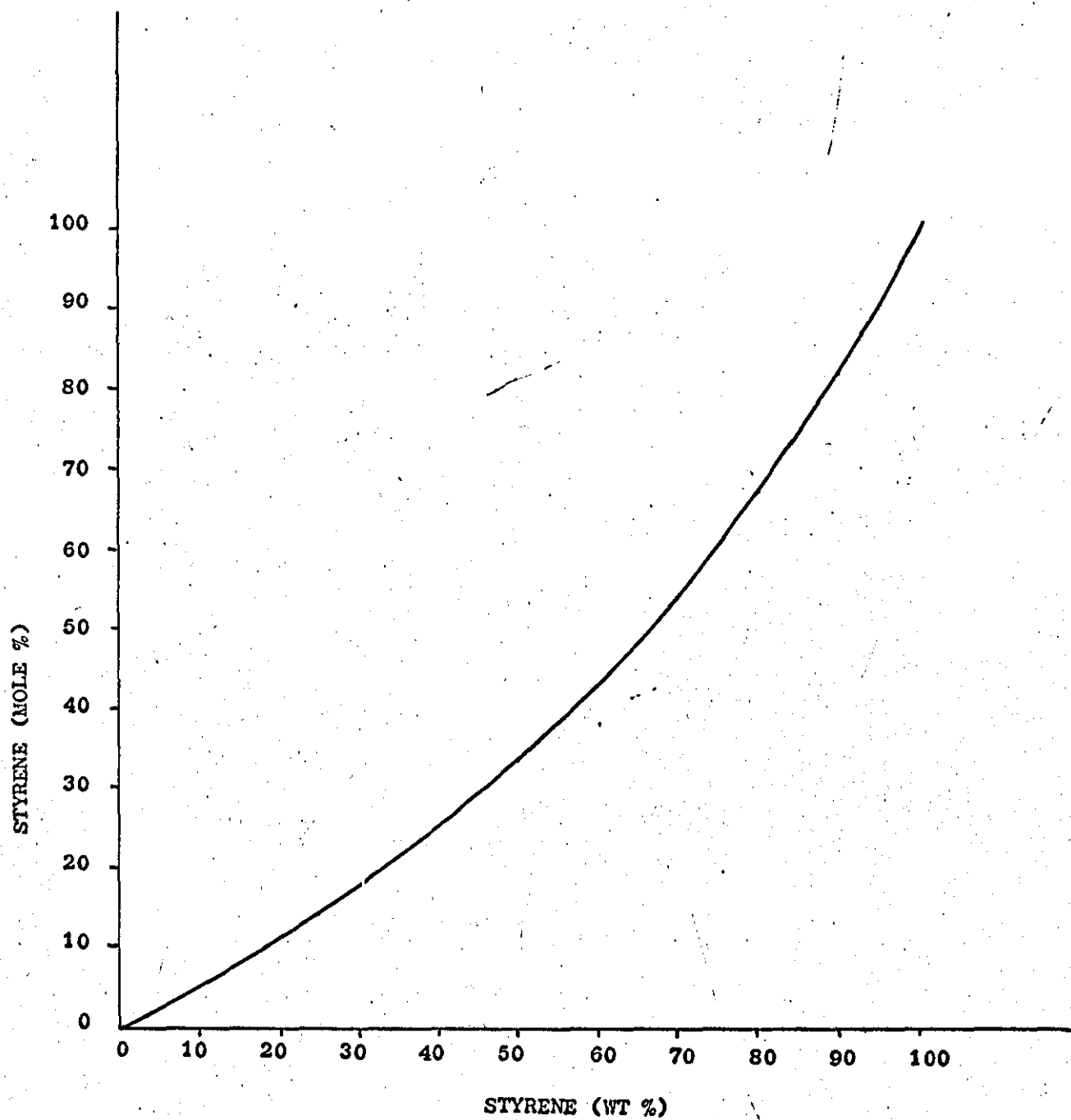
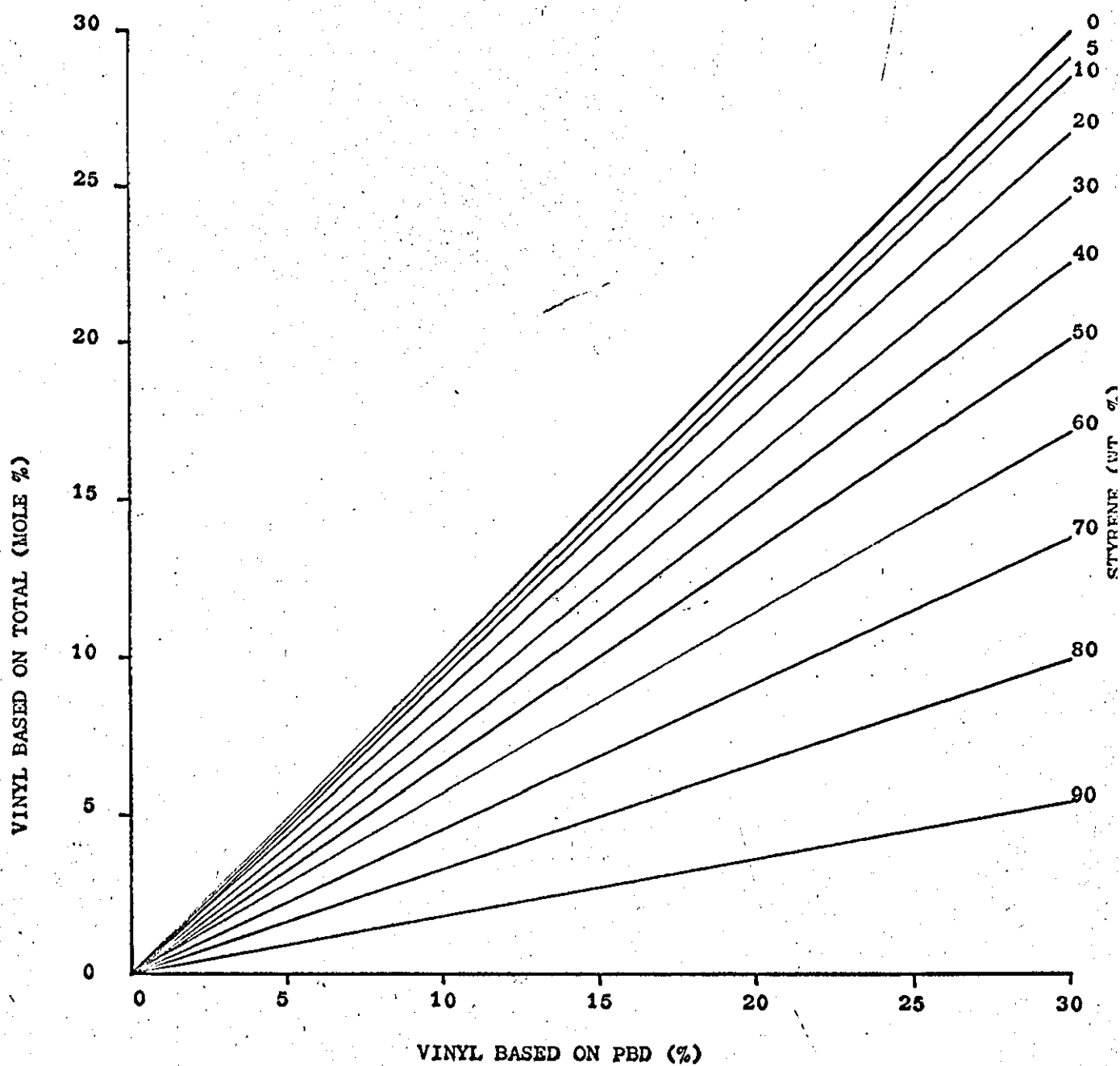
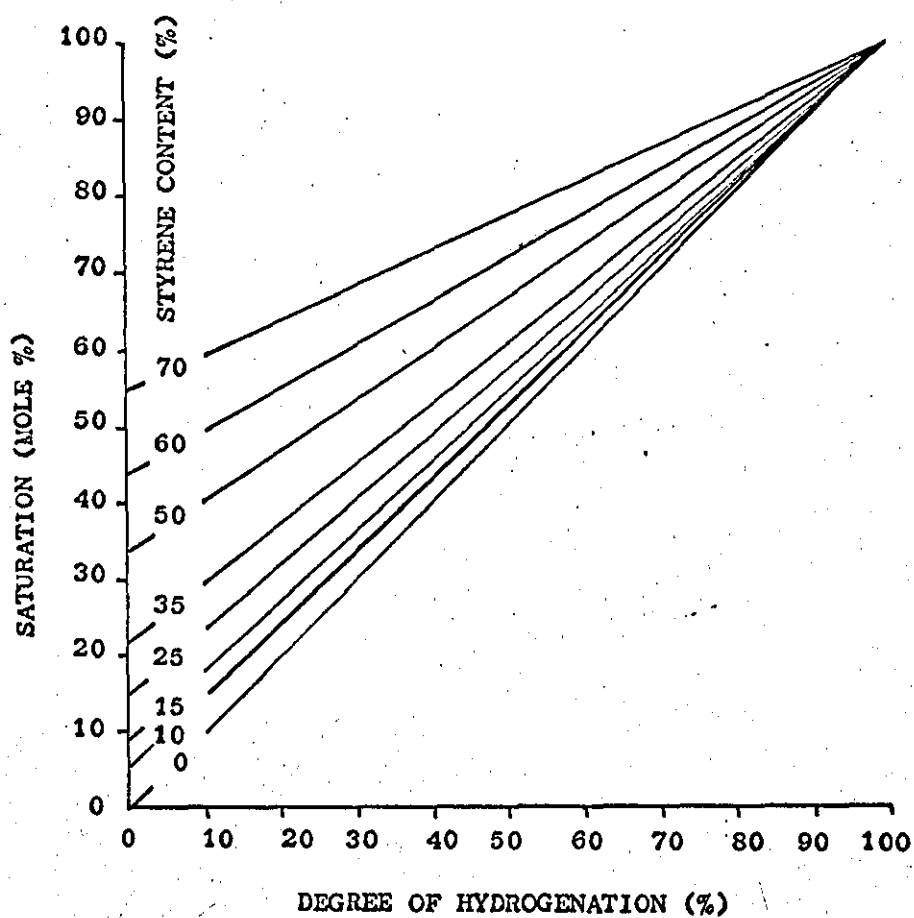




FIG. 3.2.3. VINYL CONTENT CONVERSION.



**FIG. 3.2.4. DEGREE OF HYDROGENATION CONVERSION.**



### 3.2.2. Polybutadienes.

#### 3.2.2.1. The effect of Mole percent saturation.

The general section (3.2.1.3.) described how two series of polybutadienes were prepared having,

1. Various vinyl contents and constant molecular weight.
2. Various molecular weights and constant vinyl content.

Each polymer was hydrogenated in toluene solution using a n-butyllithium, NiDIPS catalyst, samples being reduced for varying lengths of time. The maximum reduction was about 96%, accomplished in about 4 hours.

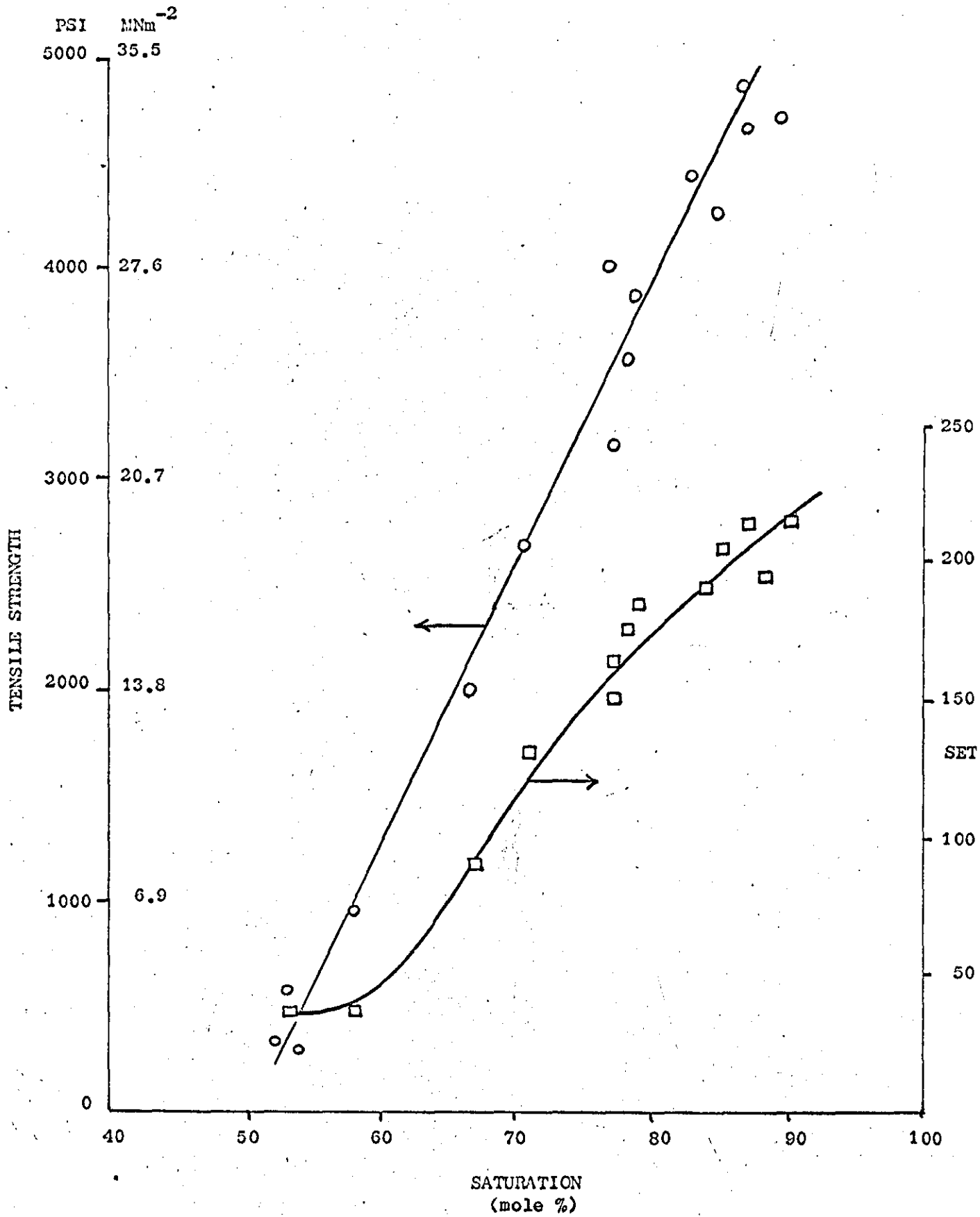
After the reaction, the catalyst was destroyed by addition of methanol and the polymer was then isolated by precipitation with acetone and dried. The hydrogenated samples, up to fifteen with different degrees of saturation for each starting polymer, were then compression moulded without further treatment into thin sheets and tested.

The effect of increasing the degree of saturation was generally similar for each of the polymers investigated. At low levels there was little apparent effect, products retaining the properties of an unvulcanised rubber. However after a certain value had been reached, usually above 40%, further increases in saturation resulted in a rapid increase in green tensile strength. This is illustrated with a polymer containing initially 8 mole percent vinyl (figure 3.2.5). At 50% saturation the tensile strength was too low to be measured, but as saturation was increased so the tensile strength increased markedly up to a value of  $34\text{MNm}^{-2}$  (5000 p.s.i.) at 90% saturation.

Generally, at degrees of saturation less than about 40%, products were not strong enough to permit the measurement of elongation set, however as saturation was increased elongation set went through a minimum then increased so that at high levels of saturation products were generally non-elastomeric, being more akin to flexible thermoplastics. The position of the minimum elongation set and its value proved to be very important in the selection of compositions for optimum properties. Ideally the minimum

FIGURE 3.2.5.

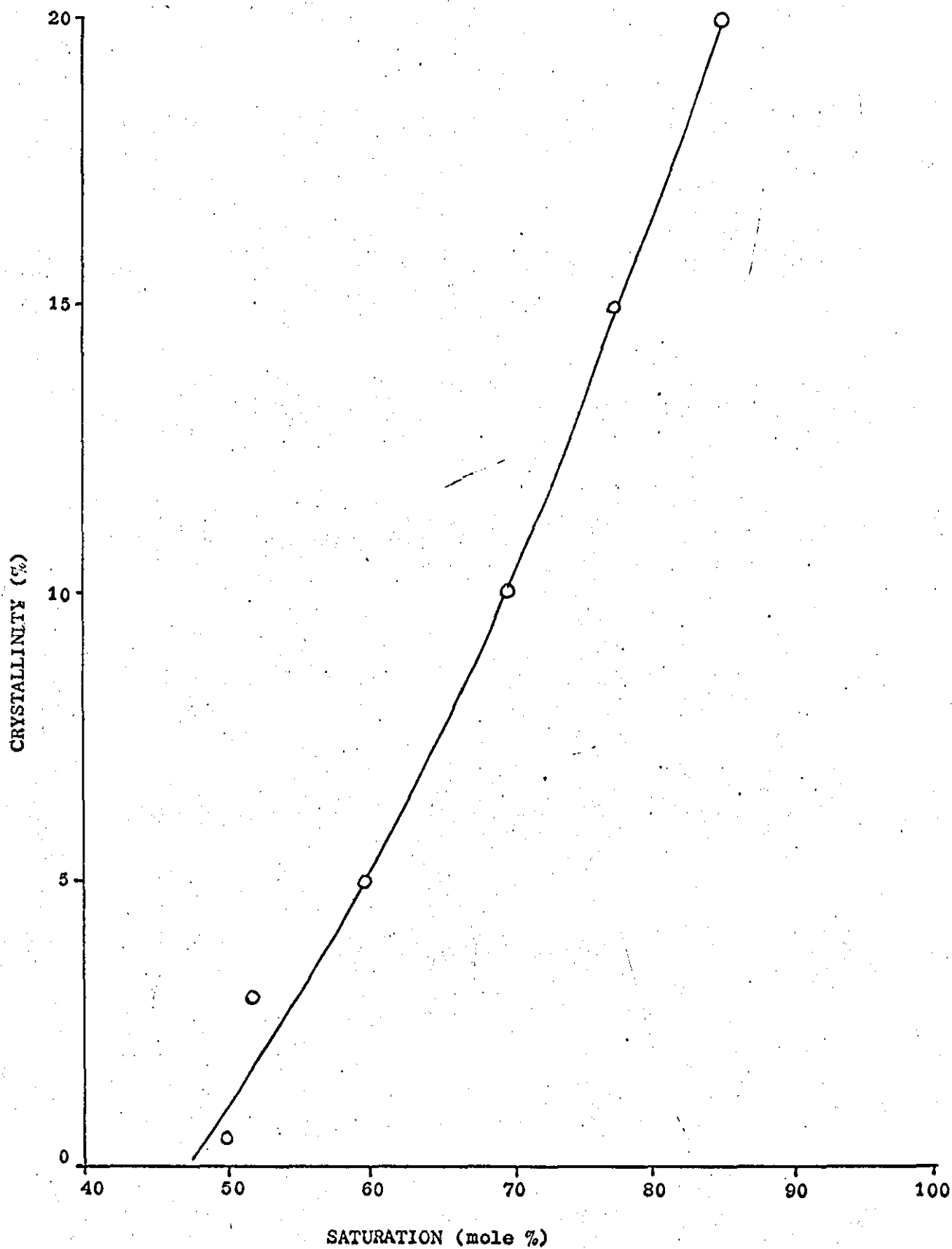
P.B.D.  
8% VINYL



elongation set had to be as low as possible and the tensile strength as high as possible. For 8 mole % vinyl polybutadiene the minimum value can be seen (figure 3.2.5) to be about 30% which corresponds to a tensile strength of about  $6\text{MNm}^{-2}$  (900 p.s.i.), - not very good properties for a thermoplastic elastomer.

The crystallinity of the hydrogenated polymers followed very closely the tensile strength, being too low to measure up to 40-50% saturation and then increasing almost linearly with further increase in saturation. For 8% vinyl polybutadiene (figure 3.2.6) measurable crystallinity was detected at saturation levels greater than 50% and reached a value of 20% at 90% saturation. Polymers saturated to less than 50% were practically amorphous and behaved as non-vulcanised rubbers whereas polymers with high degrees of saturation were more akin to low density polyethylene, both in composition and properties.

FIG. 3.2.6.    Polybutadiene 8% Vinyl.



#### 3.2.2.2. The effect of vinyl content.

Samples of polymers containing 14%, 22%, 31% and 40% vinyl contents and having similar molecular weights of about 200,000 were hydrogenated to various extents and tested for ultimate tensile strength. The results were combined with those from the 8% vinyl polybutadiene and are displayed in figure 3.2.7. It can be seen that for each of the polymers, other than that containing 40% vinyl, tensile strength increased with increase in degree of saturation above a value of 40-50%. The rate of increase, in general, fell away with increasing vinyl content, the ultimate being reached at 40% vinyl content, which was too weak to be measured even at 85% saturation.

The effect of vinyl content is further illustrated in figure 3.2.8. This was constructed from figure 3.2.7. to enable the effect of vinyl content on tensile strength to be determined at constant degrees of saturation. It shows that as vinyl content increased so the ultimate tensile strength continually decreased.

The measurement of the degree of crystallinity in each of the samples enabled the effect of vinyl content on crystallinity to be determined at constant degree of saturation. Figure 3.2.9. shows that at 90% saturation, crystallinity decreased with increasing vinyl content in a similar manner to the tensile strength. Generally, similar trends were found at lower degrees of saturation but the crystalline contents of the higher vinyl content polymers were too low to permit accurate comparison.

To summarise, the tensile strength of these polymers has again been shown to be related to their crystalline content, the highly saturated low vinyl content polymers being comparable to low density polyethylene and the highly saturated high vinyl content polymers being essentially ethylene-butene copolymers with properties similar to the commercially available ethylene, propylene copolymer rubbers.

FIGURE 3.2.7.

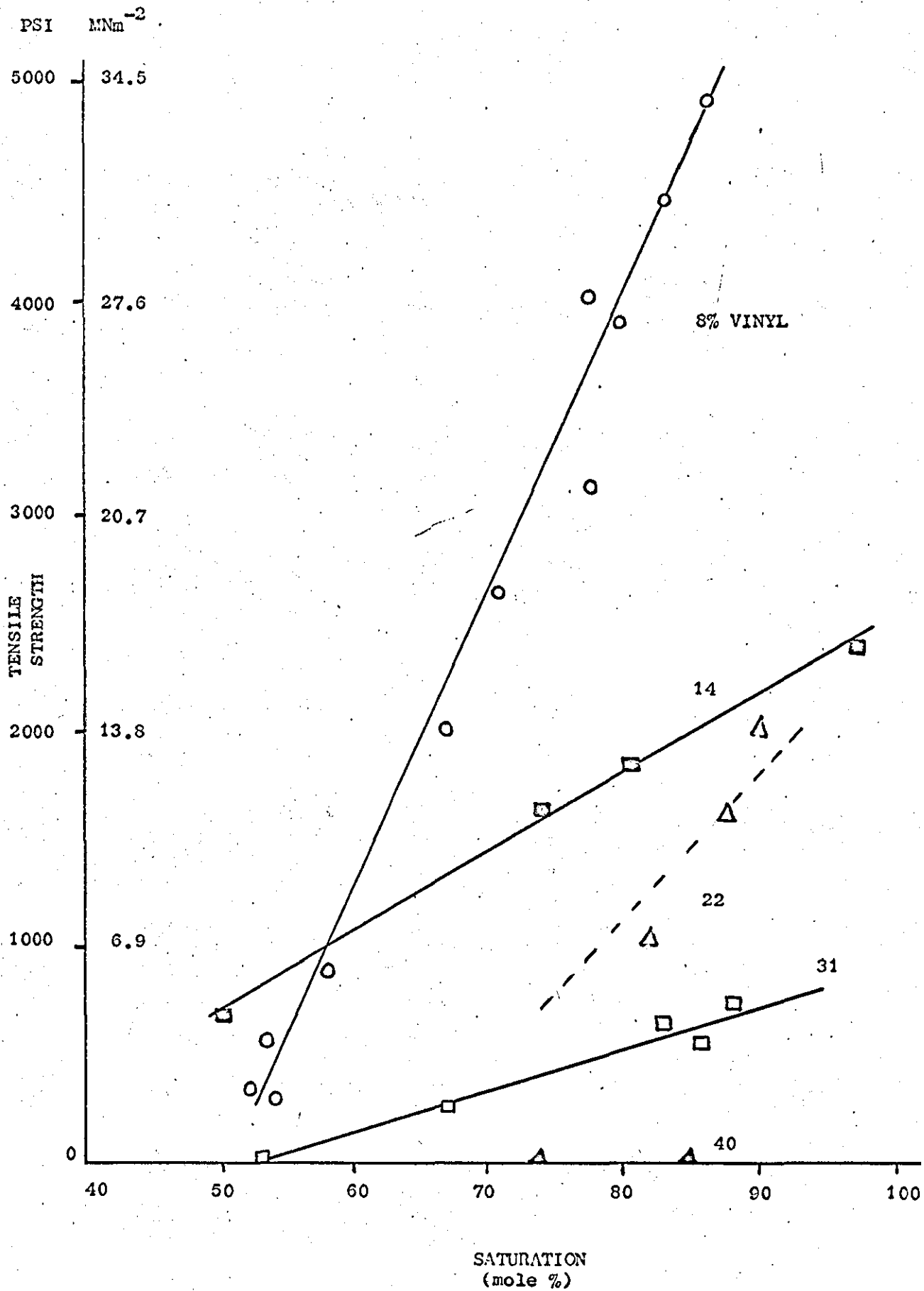




FIGURE 3.2.8.

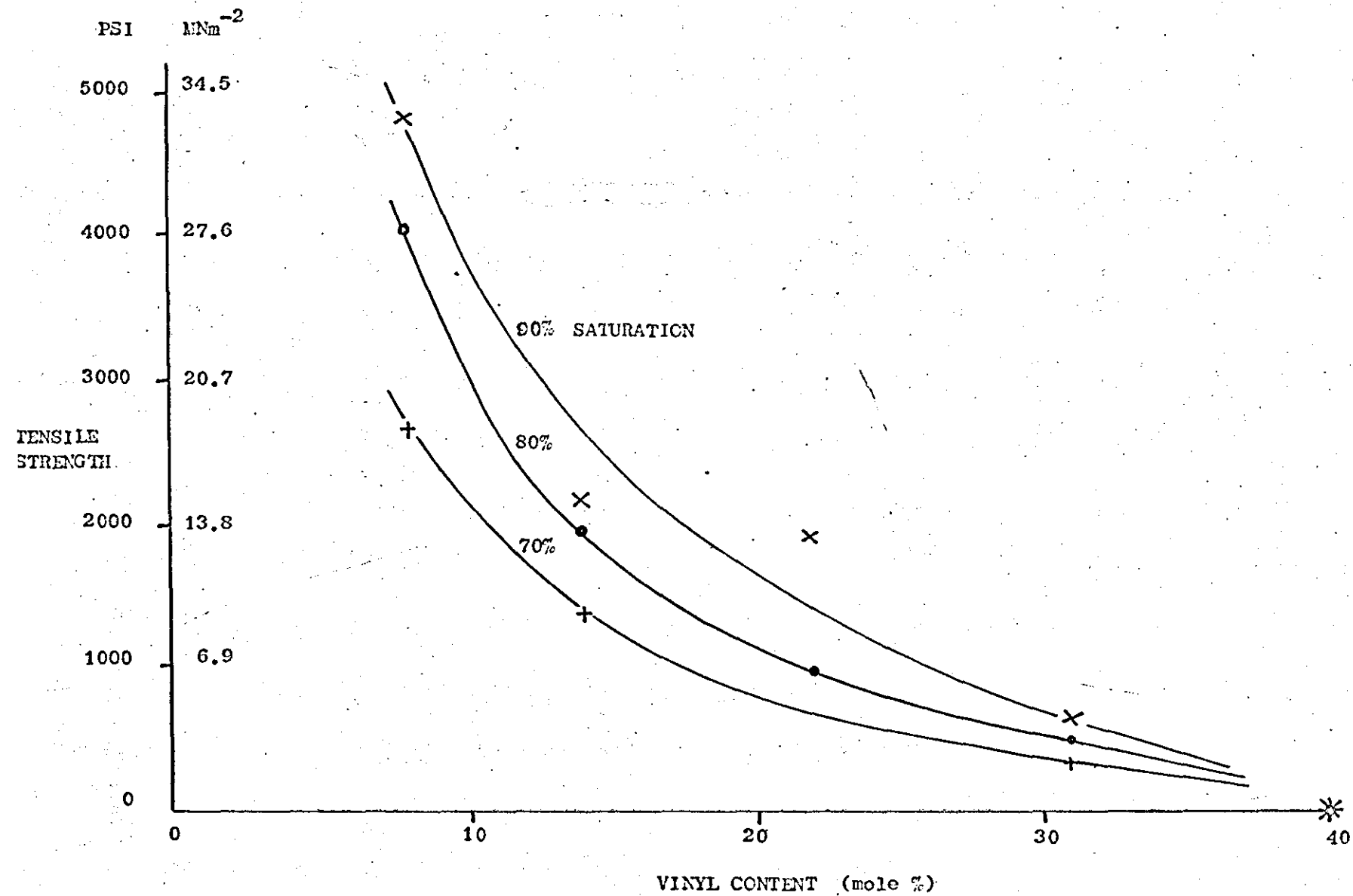
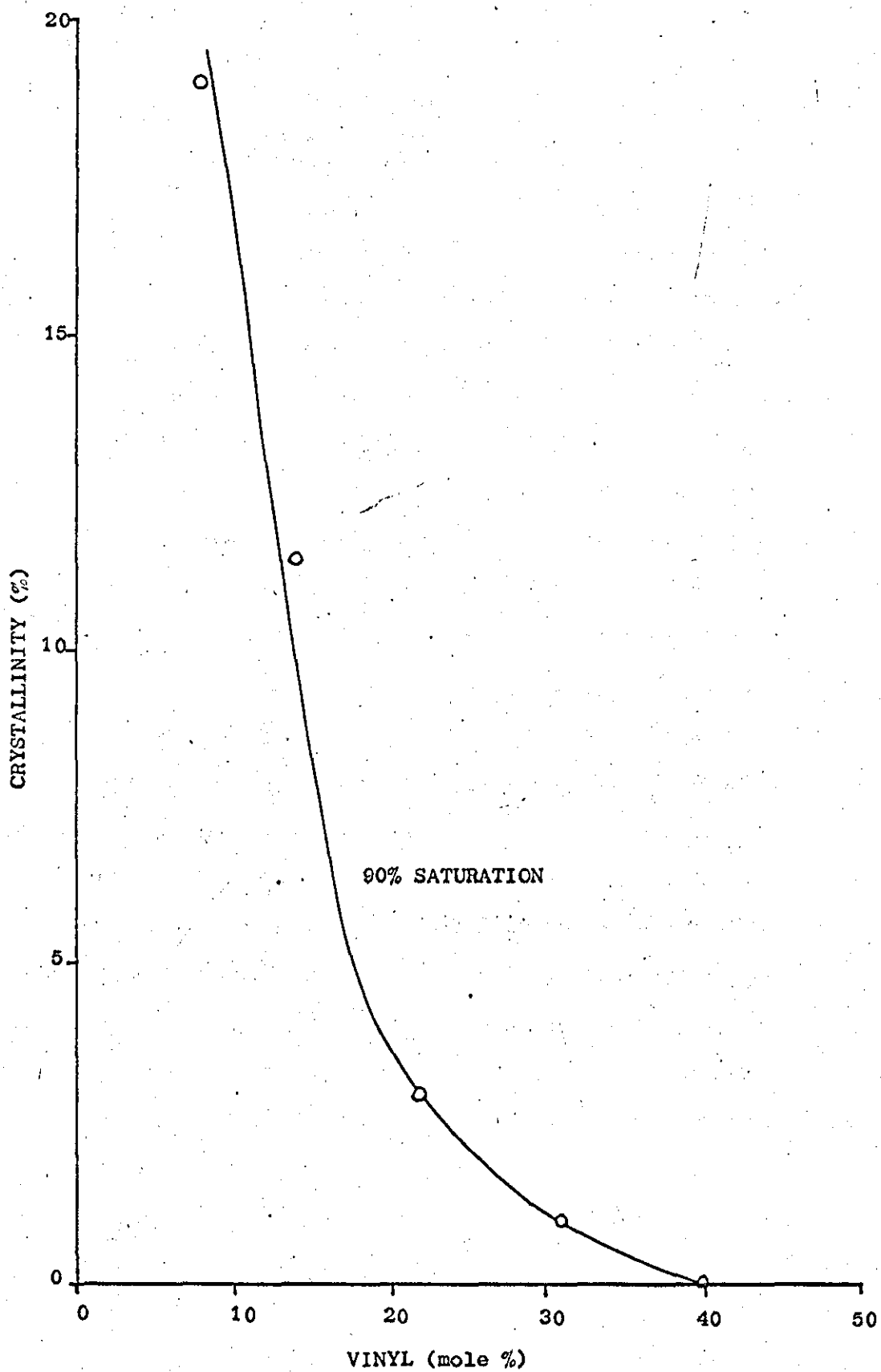


FIGURE 3.2.9.



#### 3.2.2.4. The effect of molecular weight.

Samples of polymers with different molecular weights but similar vinyl contents (8-12%) were hydrogenated to various degrees and their tensile strengths and crystallinities were measured. Each exhibited the expected increase in tensile strength with increase in degree of saturation but, as in the case of the vinyl content effect, the rate of increase was found to be different for each polymer. This is demonstrated in figure 3.2.10 which illustrates also that the lower molecular weight polymers had to be saturated to a higher extent before measurable tensile strengths were obtained.

The effect of molecular weight on tensile strength at constant degree of saturation can be seen more clearly in figure 3.2.11, this being constructed from figure 3.2.10. It shows that the tensile strength initially increased with increase in molecular weight but that the rate of increase decreased above molecular weights of about 150,000. In fact at degrees of saturation greater than about 70% there was no further increase in tensile strength when molecular weight was increased above about 200,000.

It might be thought, by analogy with the results previously discussed, that the crystallinity of the polymers would again be related to their tensile strength. However this was not the case, crystallinity showed no trend with molecular weight variation depending only on the degree of saturation. This is illustrated in figure 3.2.12 which shows that the relationship between crystallinity and degree of saturation falls within a similar range for all of the polymers. Each curve displayed in figure 3.2.11 at constant degree of hydrogenation is thus also at constant degree of crystallinity. In this case it is seen that the tensile strength increase is not accompanied by a corresponding increase in crystallinity. An explanation for this can be found from a more detailed consideration of the function and nature of the polymer crystallinity.

FIGURE 3.2.10.

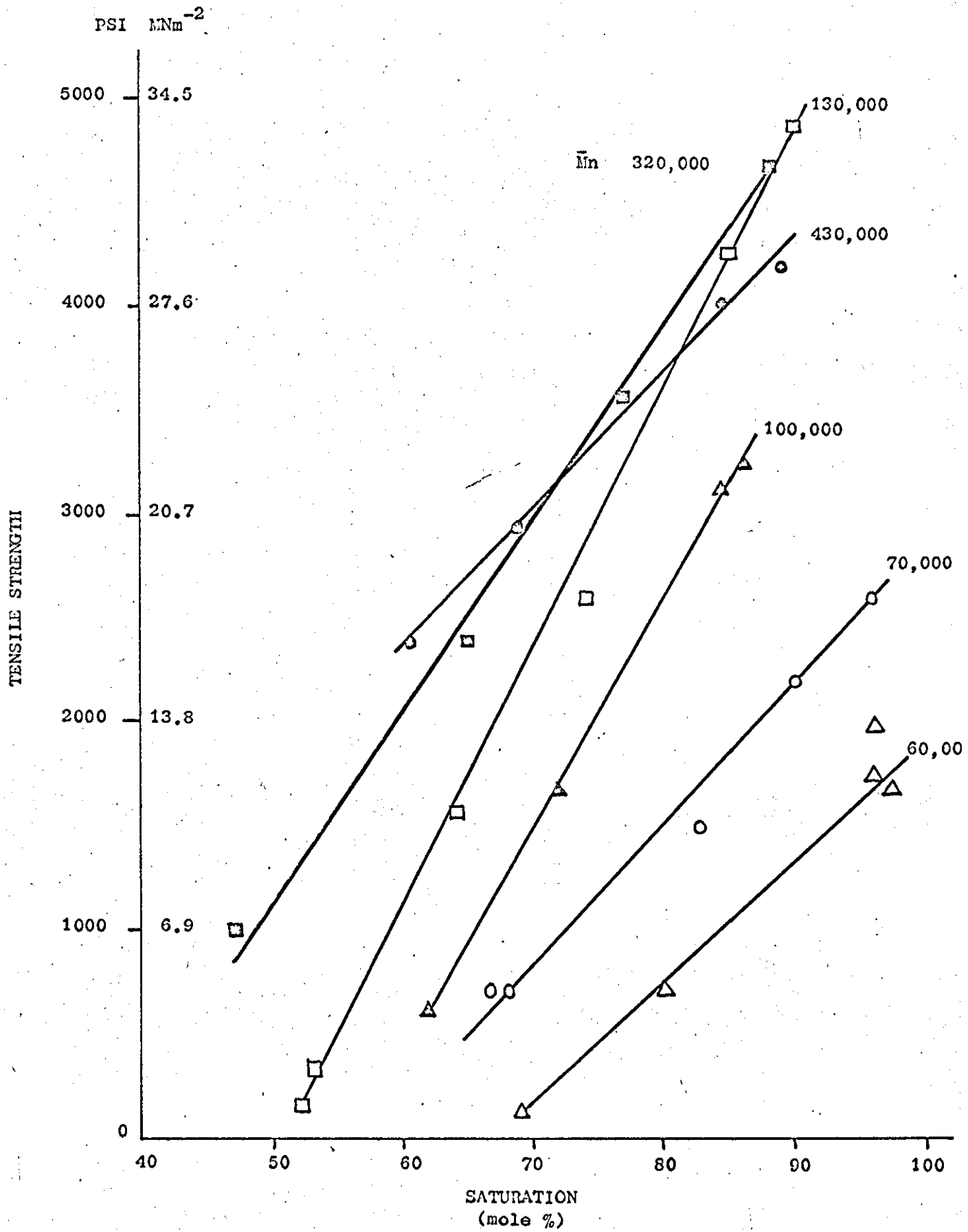


FIGURE 3.2.11.

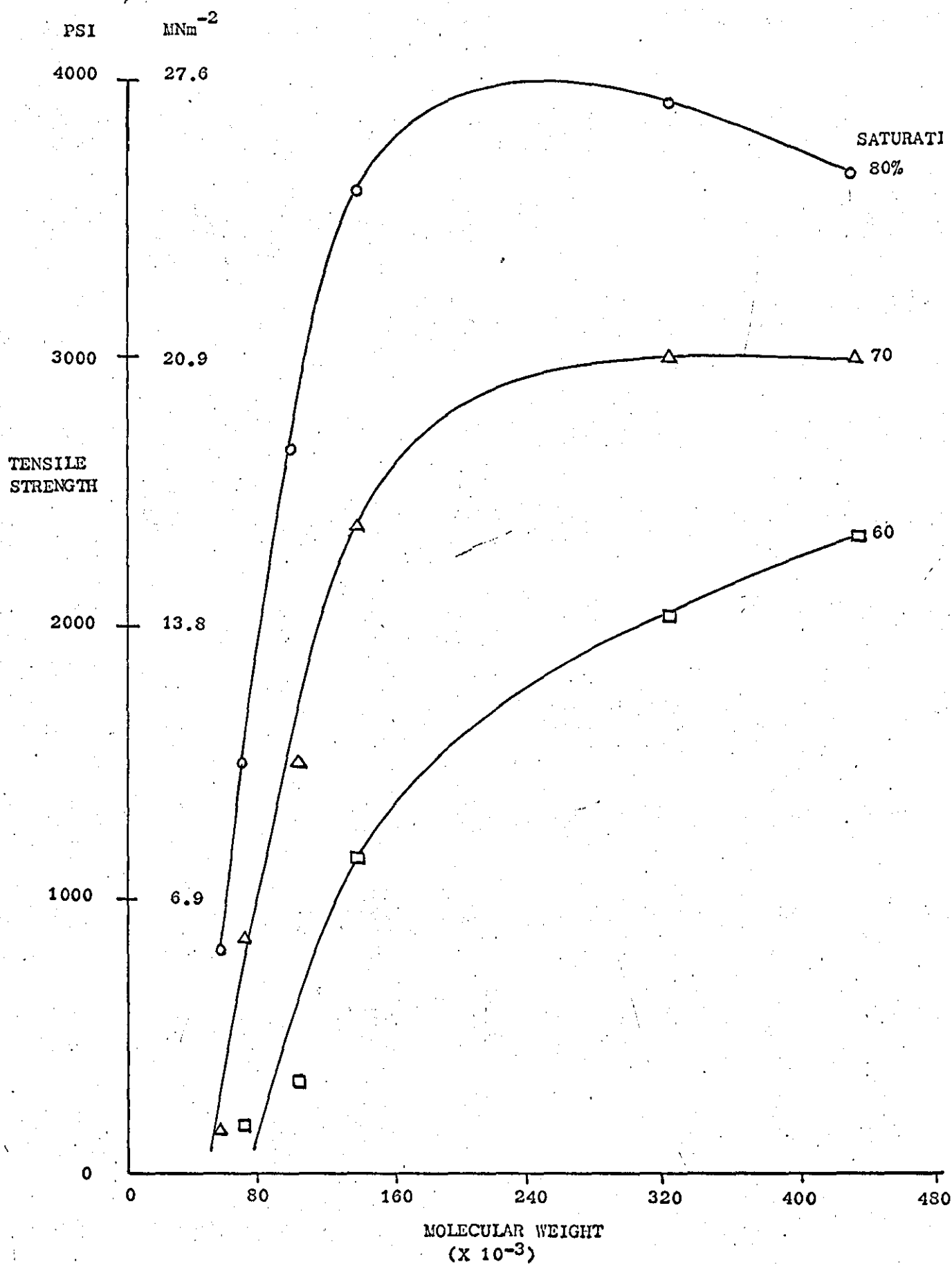
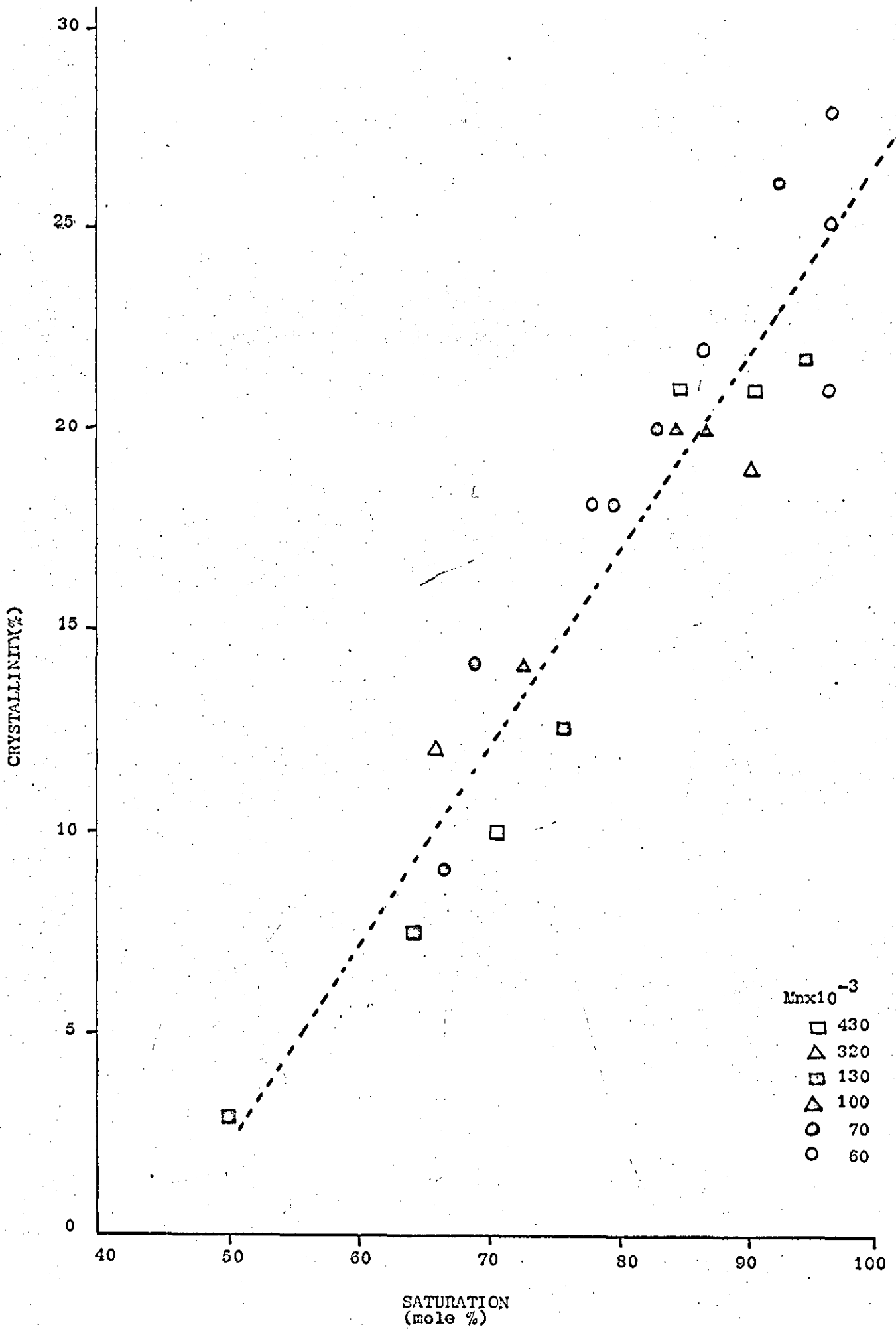


FIGURE 3.2.12.



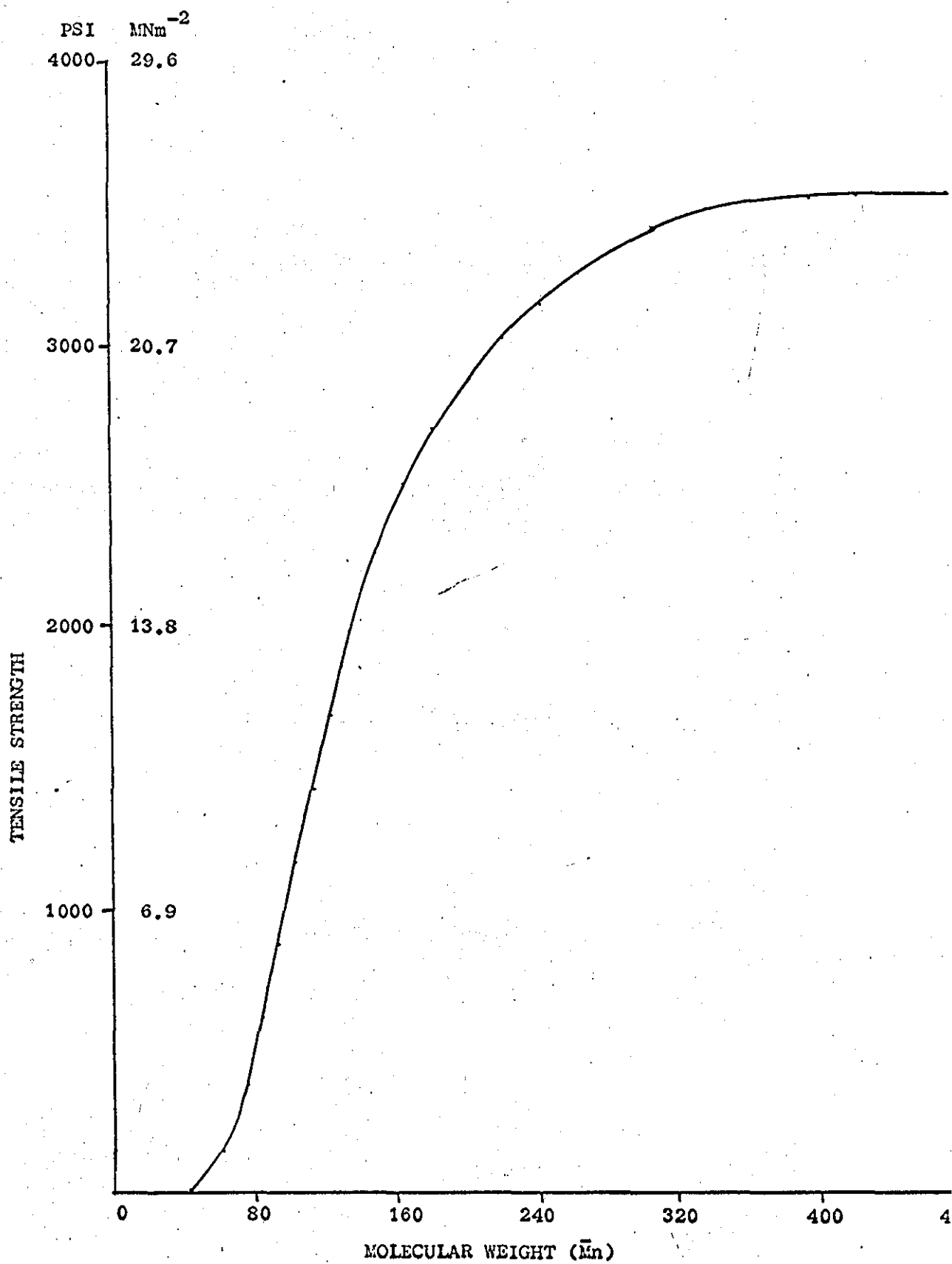
It is well known<sup>(88-91)</sup> that polymers having a small proportion of polyethylene type crystallinity contain small crystallites, formed by intermolecular crystallisation, dispersed within an amorphous matrix. The exact structure of these crystallites is at present not important, they can be considered simply as small crystalline particles bound to the amorphous phase by the non-crystallisable segments of the same chains.

An analogy can be drawn between this situation and that which exists in filler reinforcement of rubbers. The crystallites can be considered to be similar to filler particles which are chemically bound to the rubber matrix, an ideal form of reinforcement. They therefore function both as filler particles and as multifunctional crosslinking agents. The important point for the moment is their crosslinking ability. The degree of crystallinity can therefore be taken as analogous to crosslink density and an increase in the latter, within a certain range, of course increases tensile strength.

The effects of degree of saturation and vinyl content on tensile strength are thus easily understood as an increase in the former and a decrease in the latter caused an increase in crystallinity and hence an increase in crosslink density.

However, in the case of the molecular weight effect the tensile strength was found to vary without change in crystallinity. The tensile strength therefore altered without alteration in crosslink density. A similar effect is well known in normal rubber vulcanisation; at constant crosslink density tensile strength increasing with increase in molecular weight up to a maximum above which there is little further change. To illustrate this point some of the results obtained by Flory in 1946<sup>(92)</sup> have been reproduced in figure 3.2.13. These were obtained from the evaluation of sulphur vulcanised high unsaturation butyl rubber. In this case the crosslink density was held constant since the maximum number of crosslinks attainable was determined by the unsaturation level of the rubber. The similarity between these results and those obtained

FIGURE 3.2.13. Flory's results with vulcanised Butyl rubber.





in the present study are quite remarkable considering the differences between the polymers together with differences in the nature of the crosslinking systems.

The reasons for the increase in tensile strength with molecular weight in the present study are two-fold. Firstly, the increased molecular weight causes a decrease in the number of free chain ends and hence a reduction in the number of flaws in the network. Secondly, if at low molecular weight there are a number of chains present which are not involved in the crosslinked network system then the increase in molecular weight will reduce this number and hence again reduce the number of flaws in the system.

### 3.2.3. Styrene butadiene copolymers.

#### 3.2.3.1. The effect of styrene content.

A series of polymers was produced containing 10 mole percent vinyl polybutadiene, molecular weights of approximately 150,000 and random styrene contents varying from 0 to 30 mole percent. Samples were hydrogenated to various extents and each was then compression moulded and tested for ultimate tensile strength, elongation set and degree of crystallinity. The relationships between mole percent saturation, tensile strength and elongation set are displayed in graphical form in figures 3.2.14-18. Except for the polymer containing 29% styrene the curves appear somewhat similar both to each other and to the polybutadiene series in that no useful strength was attained until the saturation had reached the region of 40-60%, after which there was a steep increase in strength with further saturation. The elongation sets also show a similar trend for each polymer, going through a minimum and then rising with increased saturation. The main differences between the polymers lay in the positions of these curves. Essentially, the greater the styrene content, the higher the saturation required to produce the effect until at 29% styrene the effect was hardly observable. The overall picture can be seen more clearly by referring to figure 3.2.19. This was constructed in a similar manner to that produced to display the effect of vinyl content on the polybutadiene series, viz. points were selected from the individual polymer curves so that curves could be constructed for constant degrees of saturation. The results for the zero styrene content polymer were taken from the 10% vinyl polybutadiene graph (figure 3.2.5) and for convenience are duplicated in figure 3.2.14. Figure 3.2.19 brings out the rather surprising nature of these results, showing the distinct maxima which were obtained at the lower styrene levels. Before discussing the effect

FIGURE 3.2.14.

P.B.D.  
8% VINYL

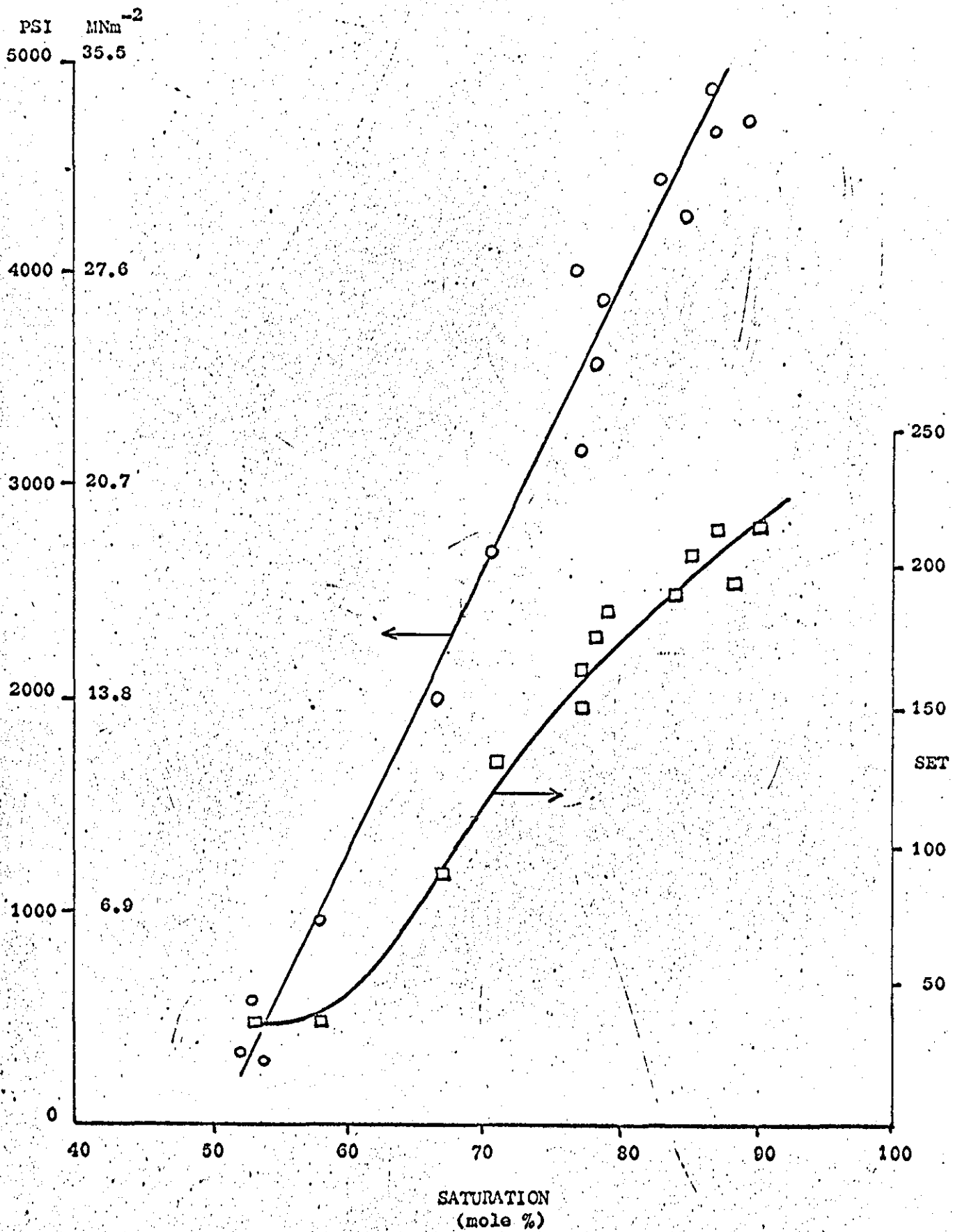


FIGURE 3.2.15.    3% Styrene, 10% Vinyl.

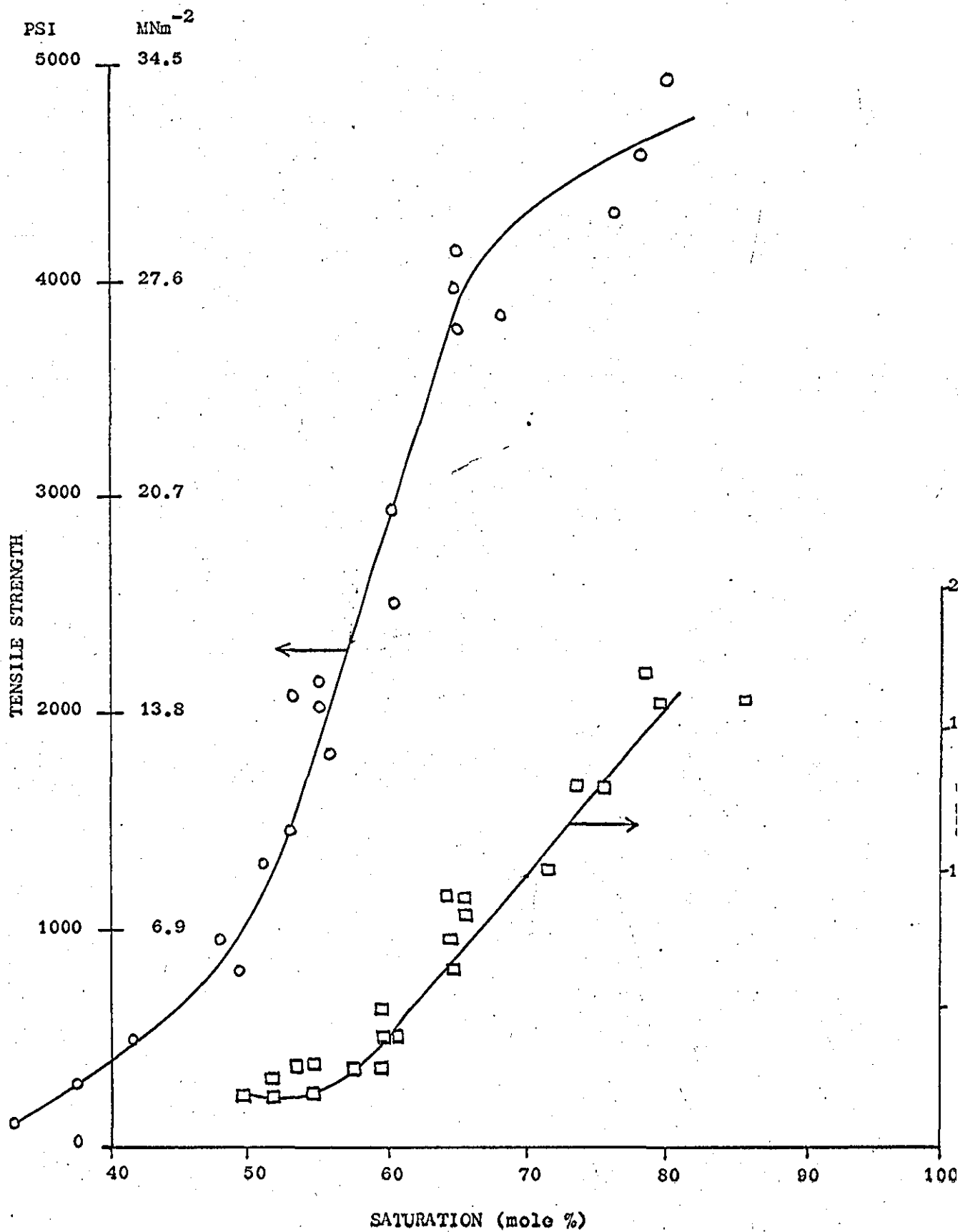


FIG. 3.2.16. 7% Styrene, 10% Vinyl.

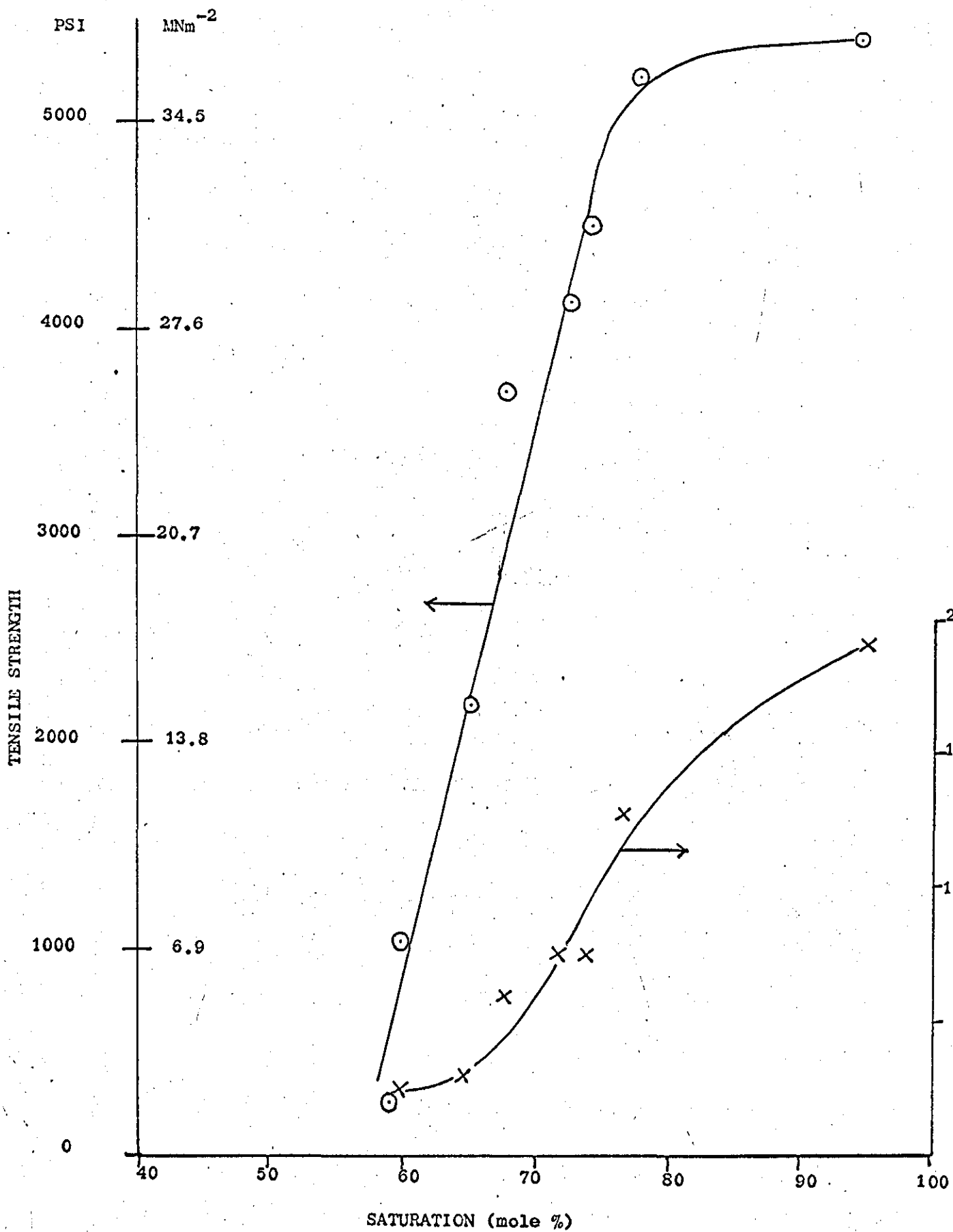


FIG. 3.2.17.     15% Styrene, 10% Vinyl.

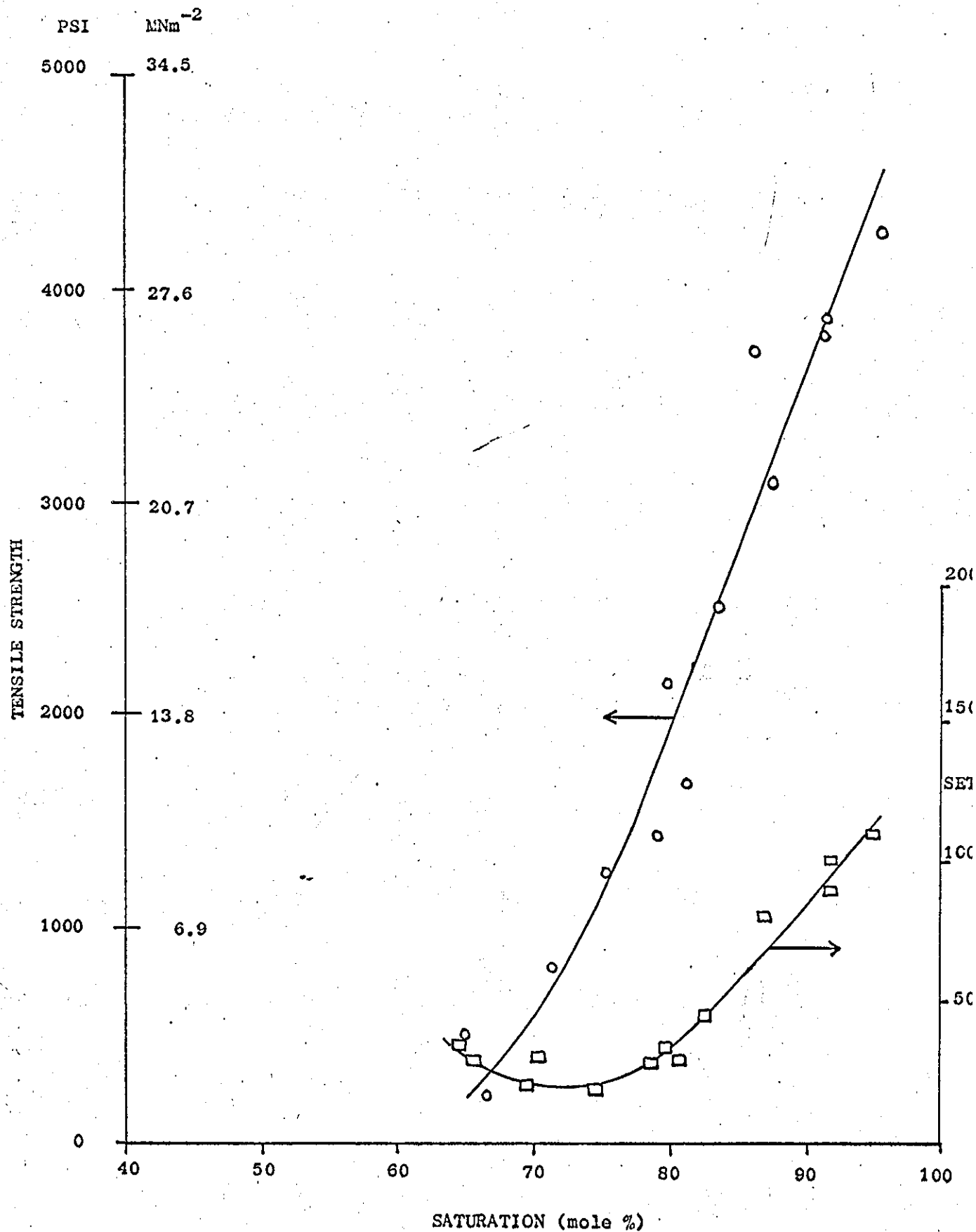


FIGURE 3.2.18. 29% Styrene.

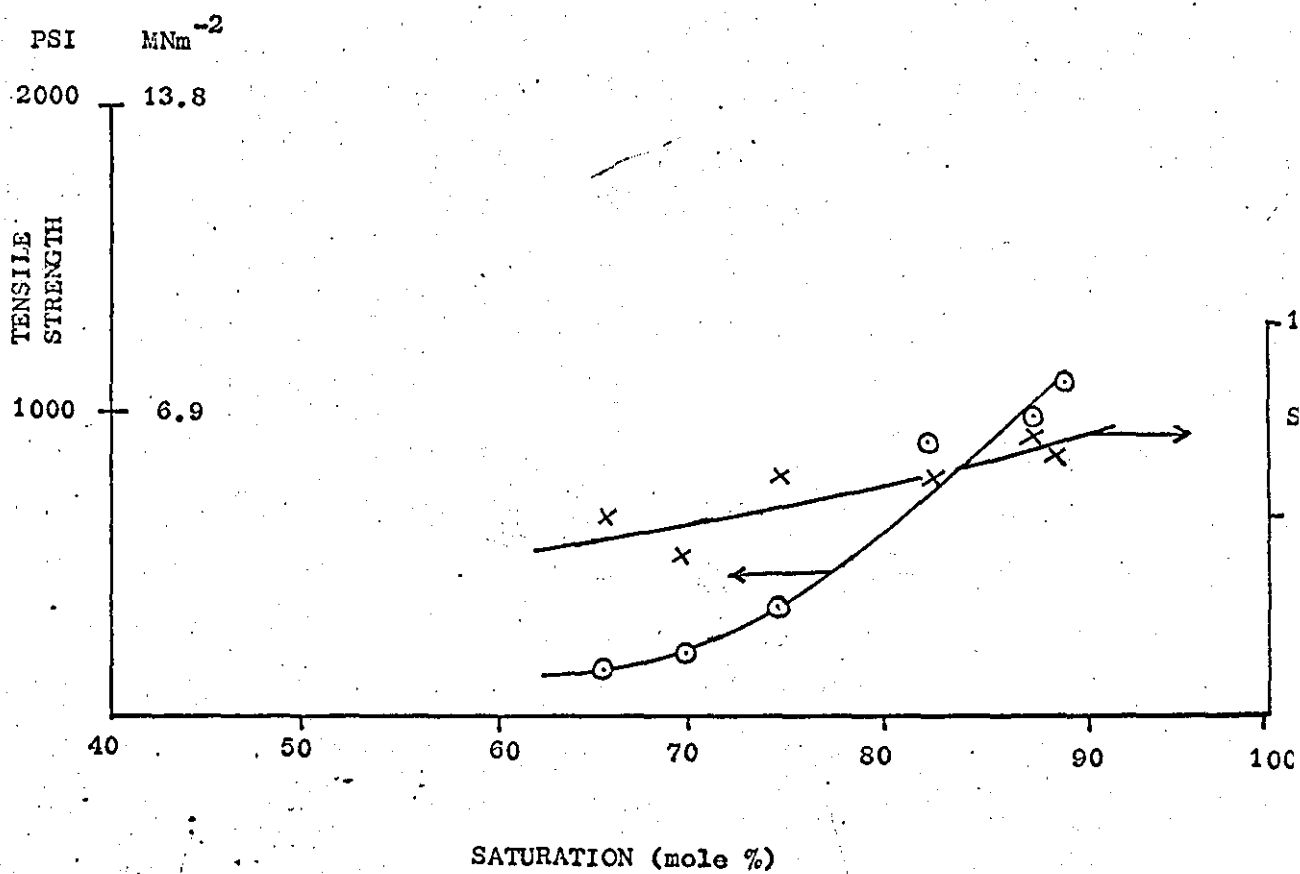
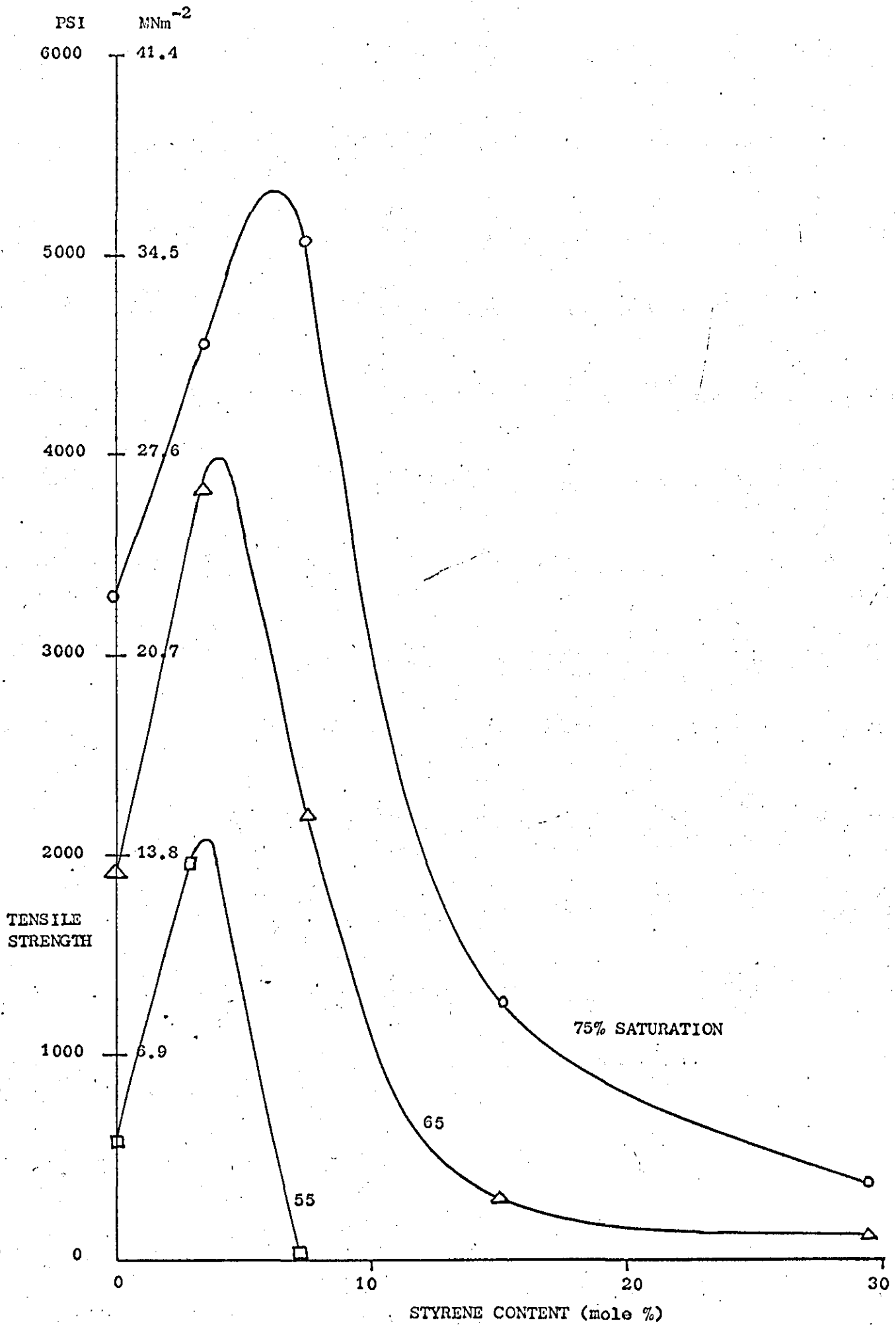


FIGURE 3.2.19.



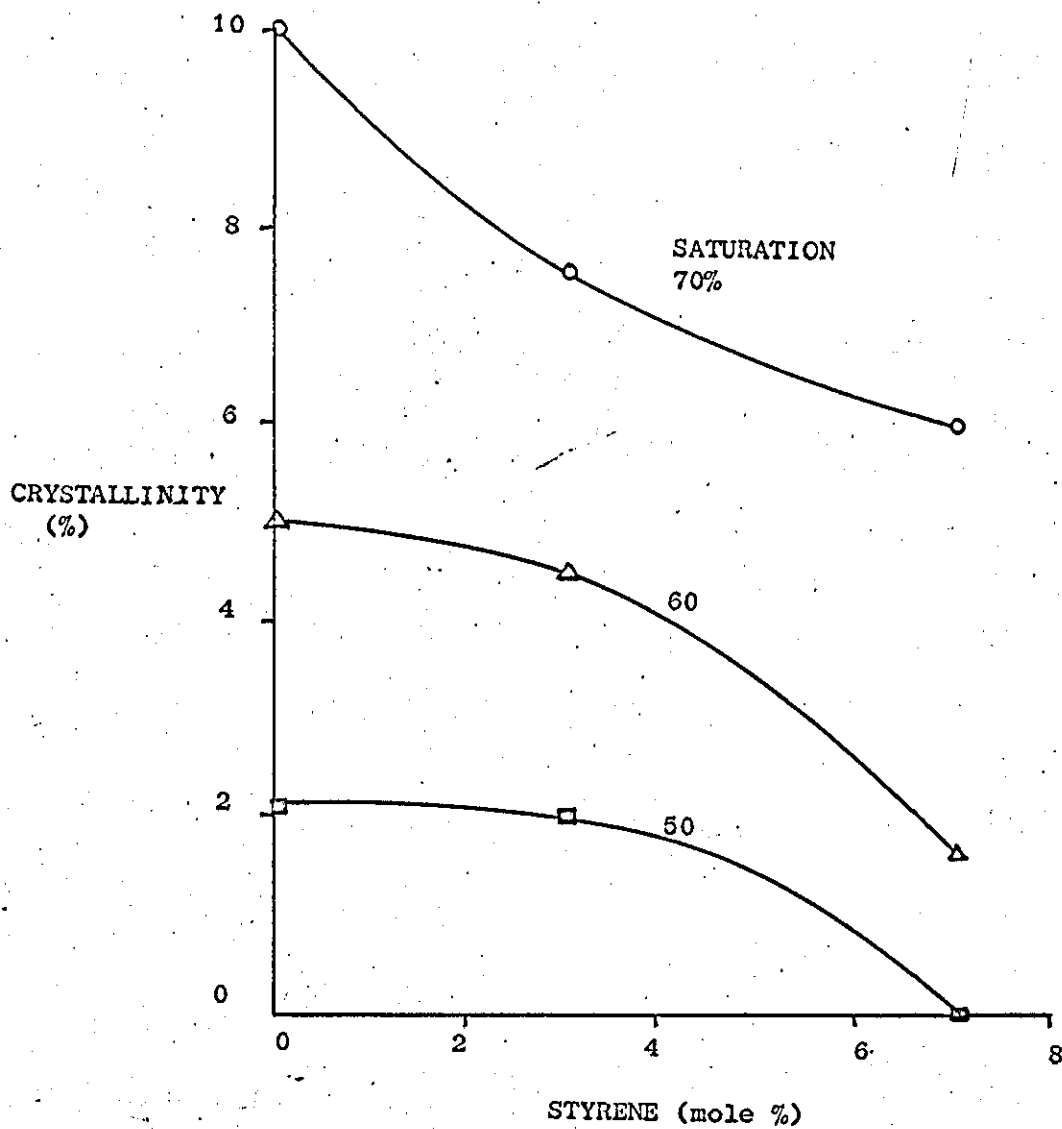


of styrene on elongation set consideration needs be given to this marked effect of styrene on tensile strength.

The explanation to the previous effects has, except for molecular weight, always been found by a consideration of the degree of crystallinity, and in similar fashion the present results would be explained if hydrogenated polymers with styrene contents in the region 3-8 mole % had higher crystallinities than polymers with either lower or higher styrene contents. It might be expected that crystallinity would show maxima in a similar manner to tensile strength, though it is difficult to see why this should necessarily happen. The results show that in fact this did not occur. Figure 3.2.20 shows the effect of styrene content on degree of crystallinity at constant degrees of saturation, the curves being constructed from the crystallinity vs. saturation curves for the individual polymers. Allowing for the inaccuracies of the actual values of crystallinity it can be deduced that there was very little difference in degree of crystallinity between polymers containing 0 to 5% styrene when similarly hydrogenated. Certainly no maxima were found and if anything the general trend over this range was a decrease of crystallinity with increase in styrene content. The question cannot therefore be answered on a basis of crystallinity.

Previous effects have been explained in terms of polyethylene crystallites acting as filler particles and/or multifunctional crosslinks. The present system, consisting of two distinct phases, was therefore somewhat similar to other types of thermoplastic elastomer and an answer to the present problem might be found by a consideration of these materials as a whole. In general, they contain thermoplastic domains, either crystalline, glassy or ionic which link the surrounding rubbery chains. One must

FIG. 3.2.20.



therefore consider how it might be possible to modify a system such as this so that improved tensile strength would result, without altering the overall thermoplastic content and without changing the polymer molecular weight.

Consider the two phases separately, theoretically the amorphous rubbery phase could be modified in such a way that the chains linking the domains could be made more equal in length. This would enable the stresses produced in the network to be distributed more equally and would result in an improvement in ultimate tensile strength. In fact, in the production of the styrene-diene-styrene block copolymer thermoplastic elastomers by Shell (93), great care is taken to obtain polymers with a polydiene segment of narrow molecular weight distribution so that this condition of chain length equality might be approached. However, in the present situation the essentially random nature of both the polymer and the hydrogenation meant that the crystallisable segments of chains must have been randomly distributed and hence the chain segments linking crystallites would have had a very wide molecular weight distribution. It is difficult to see how it would be possible to change this situation merely by including a few styrene groups into the polymer chains. It seems unlikely therefore that the effects under discussion can be explained in this way.

The thermoplastic phase could be modified in such a way as to decrease the size of the domains. This would increase the number of domains present as long as the overall thermoplastic content was not reduced. This would be impossible with the ABA block copolymers as the size of the domains is controlled by the length of the A blocks and any decrease in length would cause a corresponding decrease in thermoplastic content. However, in the case of the hydrogenated polymers an increase in the number of crystallites without increasing the crystalline content would be expected to have a substantial effect, as it would effectively increase both the "crosslink density" and decrease the distance between crystallites, both of these causing an improvement in ultimate tensile strength.

It is not too difficult to see how this situation might have arisen. The phenyl groups on the chain styrene units would have been of sufficient size to have been excluded during the crystallisation process. Their presence would therefore have had the effect of limiting the length of polymer chain that could enter a crystallite and hence the crystallites formed would have been of a smaller size. If only a small proportion of phenyl groups were present then one could envisage them limiting the crystallite size without decreasing the overall crystalline content to any great extent. This situation would then explain the increased tensile strength of the low styrene content SBRs compared to the polybutadienes.

A further increase in styrene content above about 6% has been shown to cause a decrease in both degree of crystallinity and ultimate tensile strength, the decrease in crystallinity clearly causing the decrease in strength. At these levels the phenyl groups would have limited the crystallite size to such an extent that the crystallinity would have been reduced.

This hypothesis explains the effect demonstrated in figure 3.2.19 fairly satisfactorily, though it might be argued that if this held true then one would expect the variation in vinyl content of the polybutadiene series (figure 3.2.4) to cause a similar maximum in tensile strength. The reason that this was not found is likely to be due to the fact that the pendant ethyl groups (formed by hydrogenation of the vinyl groups) were small enough to have been incorporated into the crystallites, causing flaws in the process and not altering the size of the crystallites. This idea is supported by other workers<sup>(94,95)</sup>; they have shown that ethyl groups can be incorporated into polyethylene crystals by an expansion of the unit cell dimensions. The presence of flaws in the present system would have caused a reduction in the measured crystallinity and might also have acted as sites for failure within the crystallites. As the vinyl content was increased so the crystallites would have contained

more flaws, causing a progressive decrease in crystallinity and thus a decrease in ultimate tensile strength to the stage where crystallisation was completely prevented.

We can now proceed to a discussion of the effect of styrene content on the elongation sets of the hydrogenated polymers. It has previously been stated (Section 3.2.2.1) that in order to obtain optimum elastomeric properties, it is necessary to select a polymer which, when it is hydrogenated to the optimum extent, gives a product with both a high ultimate tensile strength and a low elongation set. Thus in a scan of the effects of variables on elongation set one is interested in any trend which might help in this selection.

The effect of styrene content on minimum elongation set values alone can be demonstrated by replotting the values given in figures 3.2.14-18. Figure 3.2.21 was obtained in this way and shows that polymers containing between 2 and 7 mole % styrene can be hydrogenated to an extent such that lower elongation set values can be obtained than with any of the other polymers investigated. However this does not necessarily mean that a polymer with a styrene content within this range will be the optimum as the figure gives no indication of the tensile strengths corresponding to these elongation sets.

Another graph was therefore constructed (figure 3.2.22) to combine all the effects required. Curves were plotted of ultimate tensile strength versus styrene content at various, constant elongation sets. Clearly the curves for the lower set values could not extend over the full styrene content range as these could only be obtained from polymers with the lower styrene levels. The figure shows that hydrogenated polymers containing around 5 mole % styrene could be produced which had tensile strengths of about  $12.4 \text{ MNm}^{-2}$  (1800 psi) and elongation sets of about 20%. With polymers containing no styrene this tensile strength was not reached even at an elongation set of 45%. Furthermore if an elongation set of 45% was

FIG. 3.2.21.

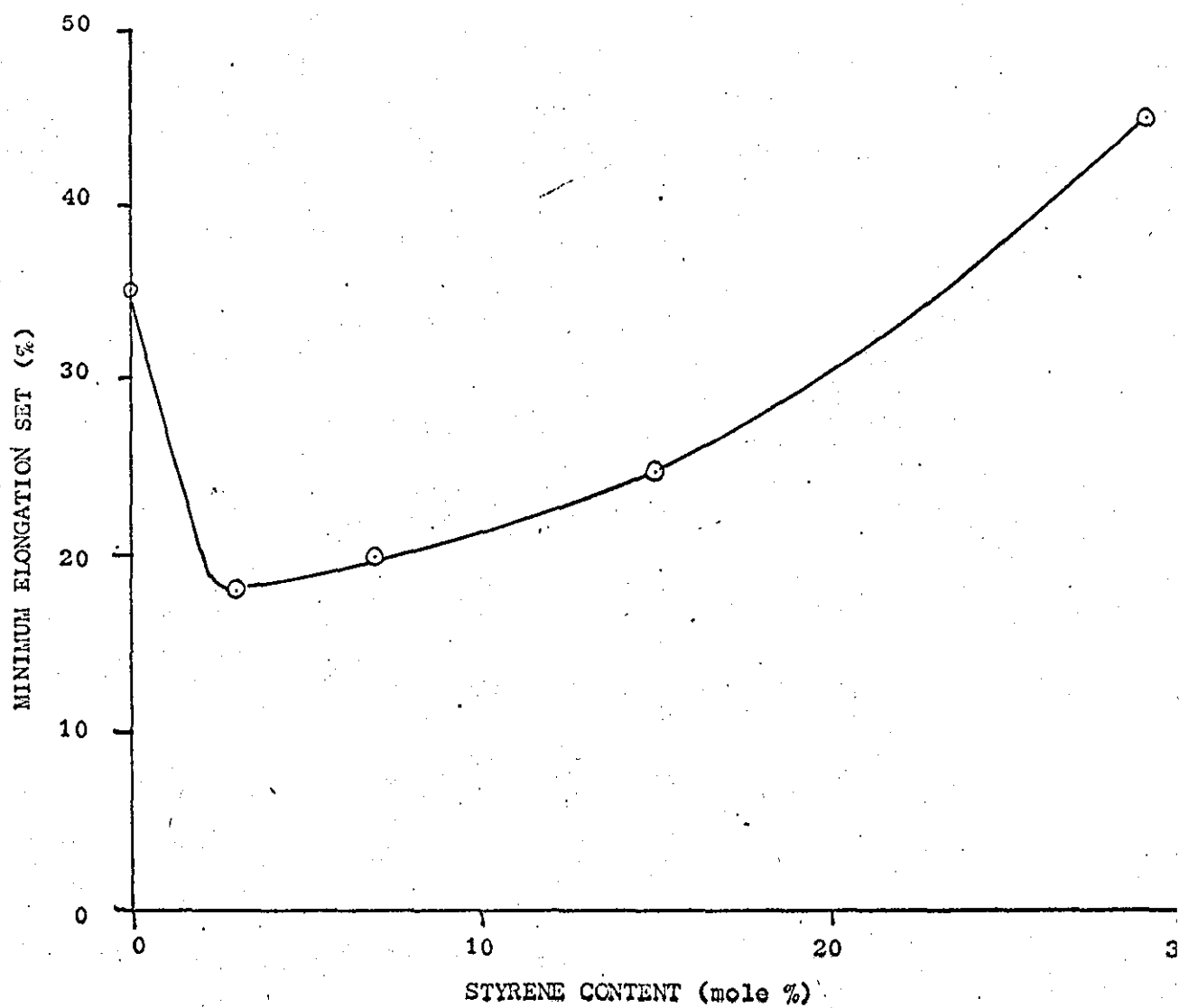
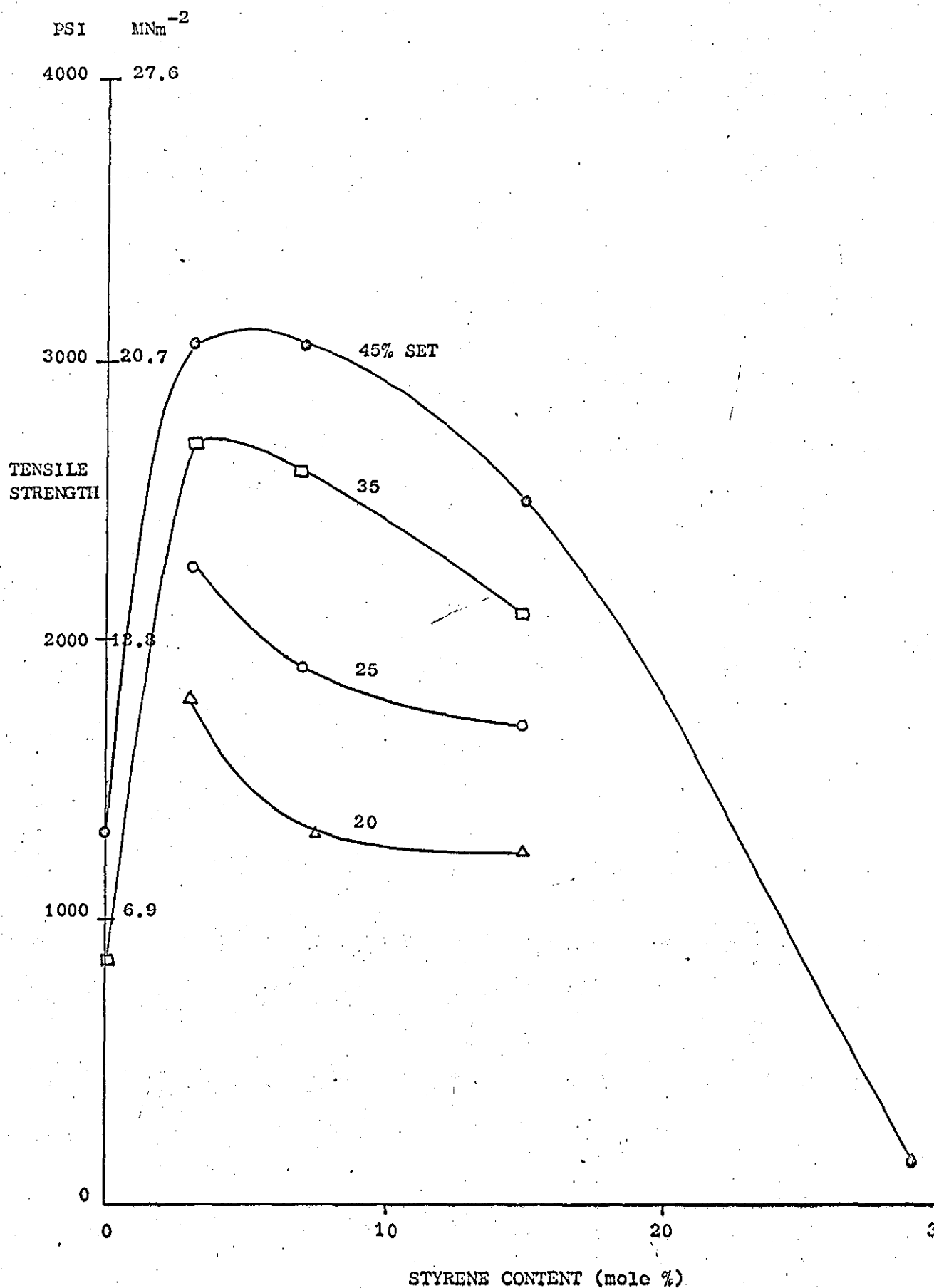


FIG. 3.2.22.



acceptable the maximum tensile strength ( $21\text{MNm}^{-2}$ ) could be obtained only by using a polymer containing again about 5% styrene. Clearly, the optimum balance of strength and elasticity was obtained with polymers containing this level of styrene.

These results can be explained quite satisfactorily in terms of the hypothesis proposed for the tensile strength effect, that is to say that at low styrene levels the crystallite size was limited such that effectively an increased crosslink density was caused. This increase in crosslink density would be expected to cause an increase in elasticity as well as the increase in tensile strength.

#### 3.2.3.2. Stress-strain properties.

No systematic investigation was carried out on the influence of variables on moduli and elongation at break. However, a few results will be given as examples of the ranges within which these values lie.

The stress-strain curves generally were similar in shape to those of reinforced, vulcanised rubbers viz. an initial steep increase of stress, followed by a levelling off and then a further steep increase to break. Some examples are given in figure 3.2.23. This set of curves was obtained from a styrene butadiene copolymer containing 10% vinyl and 15% styrene and each curve represents the results obtained at a particular degree of saturation. It can be seen that at 55% and 63% hydrogenation little reinforcement was achieved and hence little stress developed. The curves for 79% and 89% hydrogenation were however typical of reinforced rubbers, high stresses being developed at moderate strains.

As might have been expected the moduli of these rubbers followed very closely the trends of the ultimate tensile strength. An example can be seen in figure 3.2.24. This shows the effects of degree of saturation on 300% and 100% moduli together with ultimate tensile strength for a rubber containing 15 mole % styrene. The ratio of tensile strength to modulus was of a similar order for all of the rubbers investigated.



FIG. 3.2.23. TYPICAL STRESS-STRAIN  
CURVES.

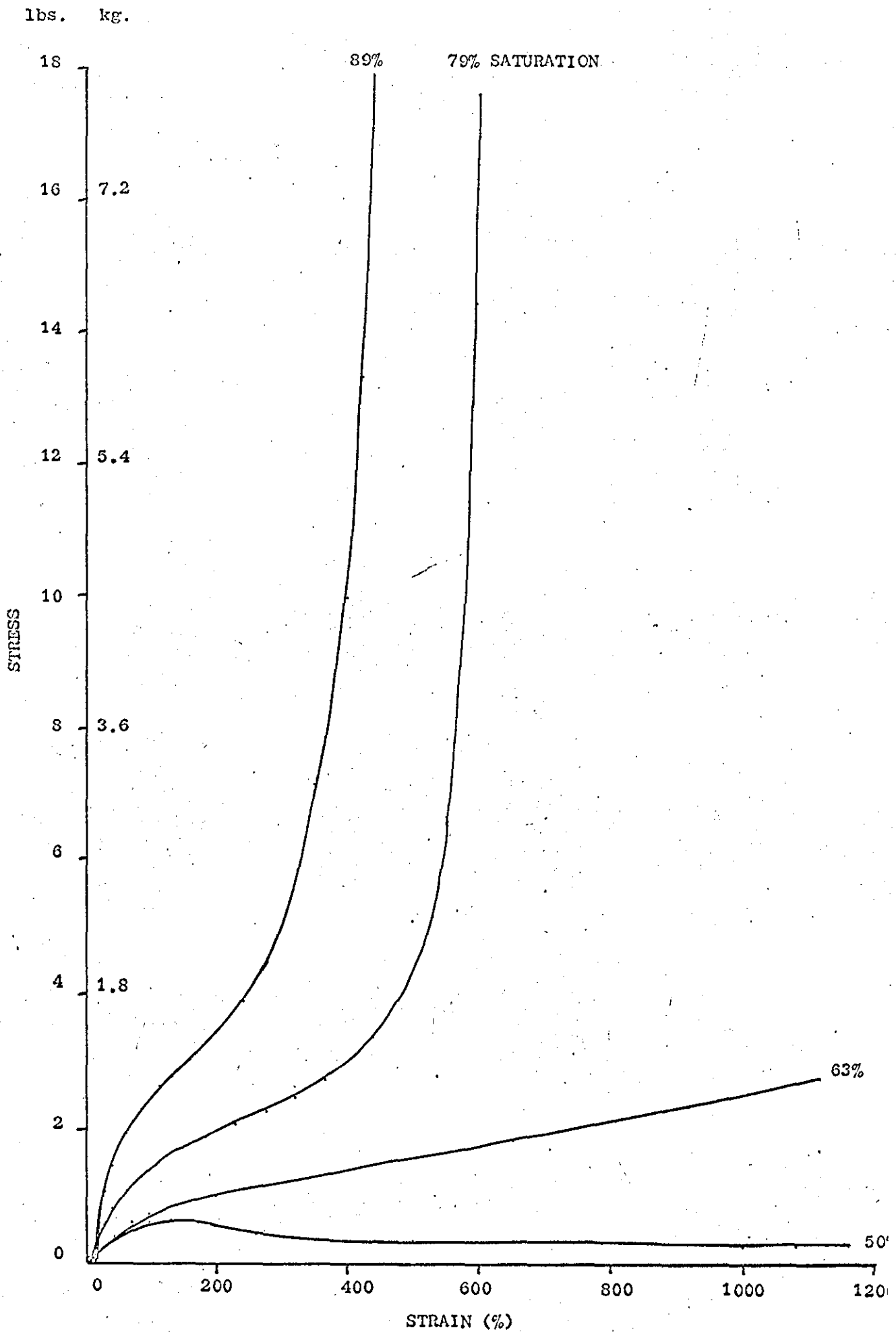
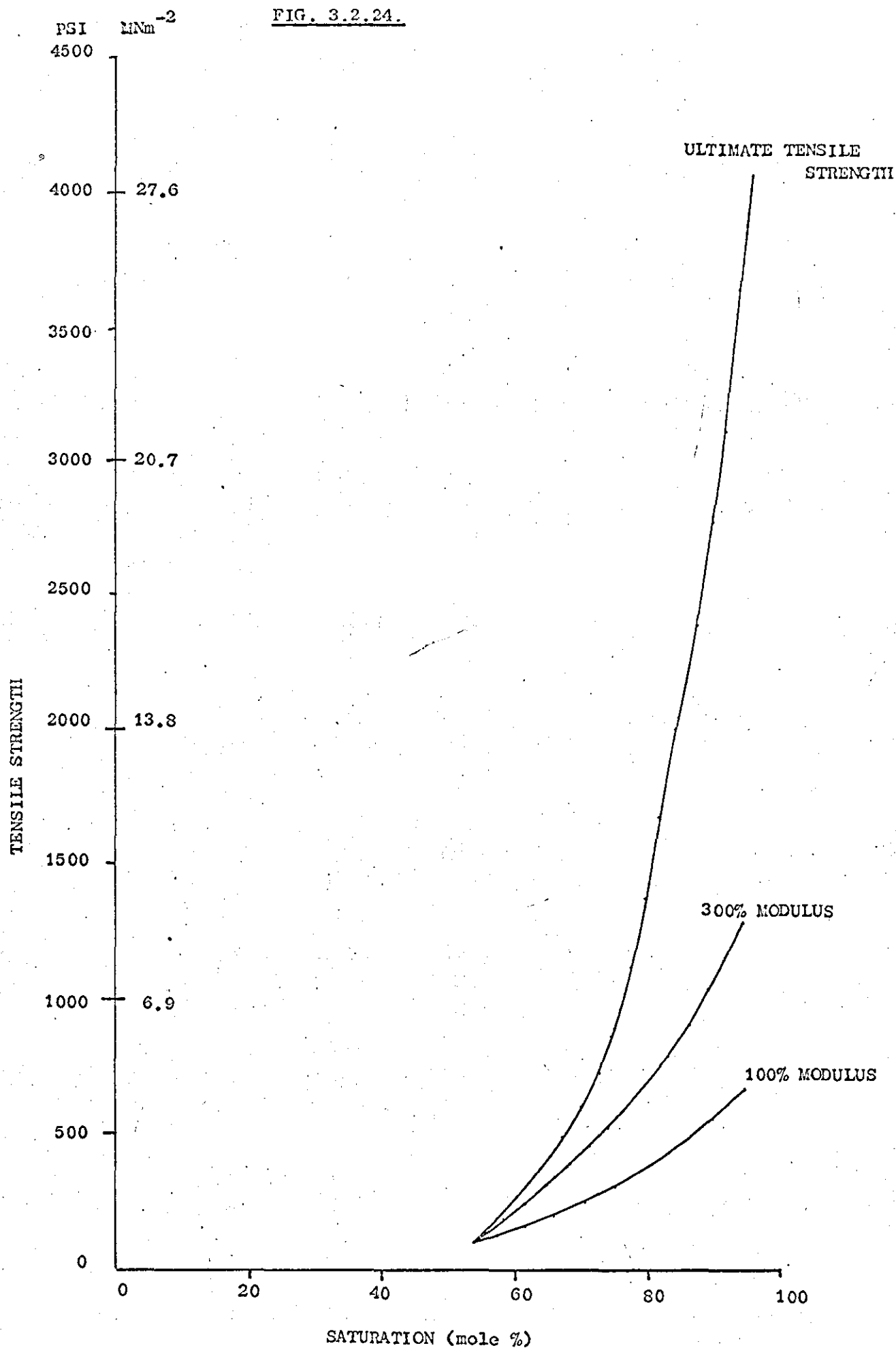


FIG. 3.2.24.



The elongation at break decreased with increase in saturation so that polymers with high tensile strength tended to have lower elongations at break. However, even at high strengths the elongations at break (E.A.B.) were still quite substantial and fairly typical results were:

Tensile Strength	MNm <sup>-2</sup>	27.6	20.7	13.8	6.9
	P.S.I.	4000	3000	2000	1000
E.A.B.	%	400	480	570	740

These stress-strain results are entirely consistent with the ideas proposed earlier suggesting that as saturation is increased so the effective crosslink density is increased, resulting in a tighter network system and hence higher moduli and lower E.A.Bs.

### 3.2.3.3. Melt Index.

Again no systematic investigation was carried out but some melt indices were measured for samples of 15% styrene polymer with differing degrees of saturation. No correlation was found with degree of saturation, the values, measured at 230°C with a load of 12.5 Kg., falling within the range 1-5g/10 mins. These values were comparatively low for a thermoplastic material but were sufficient to allow compression moulding and would probably also be sufficient for screw preplasticised injection moulding.

A reduction in molecular weight of the polymer would improve the flow but if carried too far this would also worsen other physical properties.

The addition of plasticisers was tried in an attempt to improve flow behaviour. Phthalate and naphthenic oils were found incompatible but extension could be achieved with up to about 20 phr paraffin oils or waxes. This resulted in improved flow but again there was a worsening in other properties. In practice a balance of the desired properties could

probably be achieved by the incorporation of the appropriate amount of plasticiser.

#### 3.3.3.4. Aging.

Hydrogenated polymers appeared to remain remarkably unaffected by aging at room temperature. A 60% saturated sample of the 3 mole % styrene polymer was remoulded after 1 month and the properties were found to have changed very little.

		Initial Results	1 month Aged
Tensile Strength	MNm <sup>-2</sup>	18.5	16.5
" "	psi	2700	2400
EAB	%	760	780
300% Modulus	MNm <sup>-2</sup>	2.8	3.1
	psi	410	450
100% Modulus	MNm <sup>-2</sup>	1.6	1.3
	psi	235	195
Elongation set	%	30	20

Samples which were remoulded 1 year after preparation still appeared to be much the same.

### 3.2.3.5. Glass transition temperature.

The glass transition temperatures were determined by differential scanning calorimetry of two polymers each hydrogenated to various levels. One was a polybutadiene containing 10 mole % vinyl groups and the other was a styrene butadiene copolymer containing 10 mole % vinyl and 15 mole % styrene. The results are shown in figure 3.2.25. Three facts were apparent from the results:

1. A single Tg peak was obtained for each polymer.
2. Tg increased with increased degree of saturation.
3. The Tg's for the hydrogenated styrene containing polymers were higher than for the polybutadienes.

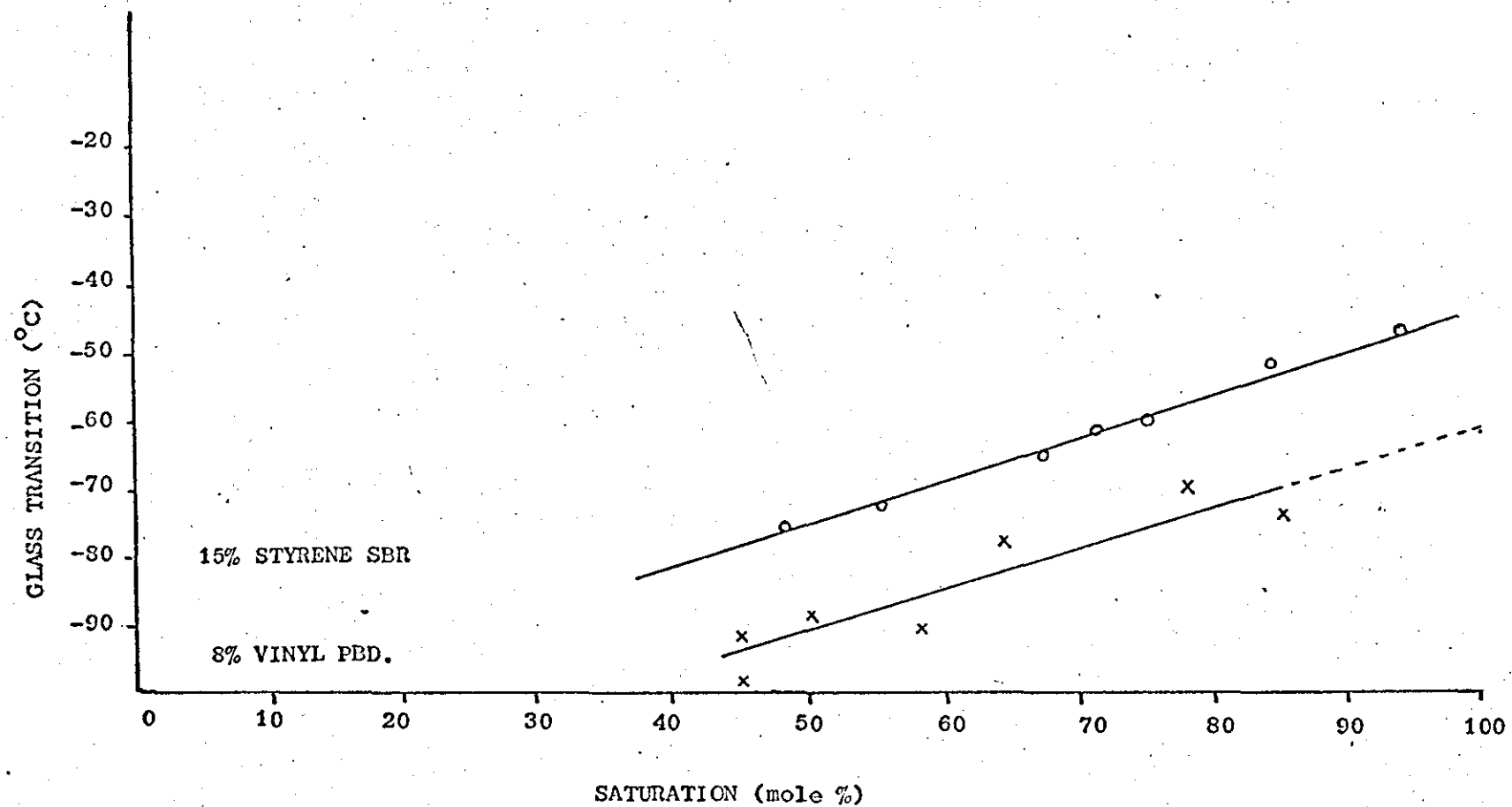
The first fact helps to substantiate the previously mentioned view (section 3.2.1.2) that hydrogenation must have occurred in a random fashion. If it had been non-random then two Tg's would have been apparent, one corresponding to that of the unhydrogenated polymer and the other to that of polyethylene, the former occurring at  $-95^{\circ}\text{C}$  for 10% vinyl polybutadiene or  $-87^{\circ}\text{C}$  for 15% styrene copolymer and the latter, despite some controversy probably occurring at  $-110^{\circ}\text{C}$ <sup>(96)</sup> or  $-125^{\circ}\text{C}$ <sup>(97)</sup>.

Previous studies of the Tg's of hydrogenated polymers have given generally similar results. Illers<sup>(98)</sup> used a dynamic-mechanical method to investigate a polybutadiene containing 24% 1,2 isomer. Before it was hydrogenated he found a single Tg of  $-82^{\circ}\text{C}$  and after hydrogenation, to an unknown extent, he found it had increased to  $-35^{\circ}\text{C}$ .

Yakubchik et al<sup>(92,93)</sup> studied the Tg's of hydrogenated sodium polymerised (68.7% vinyl) and high cis polybutadienes and also natural rubber and synthetic cis 1,4 polyisoprene. Except for the first mentioned polymer he found that Tg increased with increasing saturation. In the case of the sodium polymerised polybutadiene he found a small drop in Tg.

NOTE crystallinity increases at sub-ambient temperatures (99)

FIGURE 3.2.25.



It is therefore generally accepted that polymers with a low side group content exhibit an increase in  $T_g$  when hydrogenated and it is well known that an increase in side group content causes an increase in  $T_g$ . The reason for the latter is that chain mobility is reduced by the steric hindrance of the side groups. This explains the higher  $T_g$  found in the present work for the styrene containing hydrogenated polymers. However, an explanation for the increase in  $T_g$  with increasing saturation is not so evident. Illers proposed no explanation for his results. Yakubchik suggested two possible reasons for the reduced chain mobility on hydrogenation. The first was that a decrease in the double bond content in the chains diminishes the number of single bonds adjacent to double bonds and it is known that these single bonds facilitate internal rotation. The second reason was that conversion of vinyl side groups into ethyl groups, which have larger volume, also hinders rotation. It is thought that these explanations were far from satisfactory. A double bond would be expected to reduce chain mobility, rather than increase it, due to its rigidity and it is proposed that any reduction in number would be more likely to cause a decrease in  $T_g$  rather than an increase. With regard to the other point, in the present work the vinyl content was quite low and analyses previously quoted showed that they were virtually all reduced at about 50% saturation. Although it is accepted that ethyl groups might well hinder rotation to a greater extent than vinyl groups there would be no effect due to this at saturations greater than 50% yet the  $T_g$  still increased. A more suitable explanation for the phenomenon was therefore sought.

Crystallisation would tend to occur along lengths of chain free from side groups; the non-crystalline segments of chain would therefore tend to have an above average side group content. The crystallisation process would therefore result in a side group concentrating effect, the amorphous polymer containing an increasing side group content as degree of saturation and crystallinity are increased. This process would

clearly cause an increase in  $T_g$  with increase in saturation. One can envisage a situation where, for the 10% vinyl polybutadiene, at high degrees of saturation the only non-crystalline portions of chains were very short and contained a very high percentage of pendant ethyl groups.

This idea would explain another previously puzzling fact, viz. the  $T_g$  of polyethylene is generally accepted as being in the region of  $-120^{\circ}\text{C}$ ; the process of polybutadiene hydrogenation produces a material more and more like polyethylene as saturation is increased; therefore one would expect the  $T_g$  to decrease gradually from  $-95^{\circ}\text{C}$  to  $-120^{\circ}\text{C}$  rather than to increase. The side group concentrating effect however predicts that as crystallisation increases and the overall properties of the polymer become more like polyethylene, the amorphous portion in fact becomes more like polybutene and this has a  $T_g$  of  $-20^{\circ}\text{C}$ <sup>(96)</sup>. The  $T_g$  would therefore be predicted to increase from  $-95^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$  and this more nearly approaches the results obtained. In fact, the amorphous portion can be considered to be more like ethylene butene copolymer rather than pure polybutene and this of course would have a  $T_g$  lower than  $-20^{\circ}\text{C}$ . A rather dubious extrapolation of the polybutadiene  $T_g$  curve (fig. 3.2.25) gives a figure of about  $-60^{\circ}\text{C}$  for a 100% saturated polymer but this is in the right region for the present theory to be correct.

If the  $T_g$  curve for the styrene butadiene copolymer is extrapolated to 100% saturation then a figure of  $-45^{\circ}\text{C}$  is obtained. The side group concentrating effect would predict that the amorphous phase would consist of ethylene butene styrene terpolymer and this would be expected to have a  $T_g$  in this region.

The idea of crystallisation causing a side group concentrating effect therefore explains the results obtained much more adequately than the theories proposed by Yakubchik et al.



### 3.2.3.6. Product nature.

The crystallinity of hydrogenated polymers, as measured by X-ray diffraction, has been discussed in the previous sections and the effects on this of a number of variables has<sup>ve</sup> been considered. Although the crystallite size limitation of styrene units has been proposed, as yet no suggestion has been put forward of actual crystallite size and structure. Ideally, one requires a microscopic investigation of these materials. However when an optical microscope and crossed polarises<sup>r were</sup>~~es were~~ used, no detail could be distinguished in polymers containing low levels of crystallinity. A similar result was obtained by Tikhomirov<sup>(88)</sup> et al when studying hydrogenated high cis polybutadiene. They found though that at high levels of crystallinity spherulites could be detected and that with increase in degree of hydrogenation their structure became more clearly defined. They suggested that at lower levels of crystallinity the spherulites were too small to be resolved. In the present work, a limited investigation was carried out using an electron microscope. Samples of hydrogenated polymers were cast as thin films and then reacted with osmium tetroxide to stain regions of high unsaturation. However, little heterogeneity was observed. It is possible that, with more practise in the techniques involved, this method might prove more useful.

A good idea of crystallite size can be gained by an approximate calculation. A polymer containing 40 mole % styrene has no measurable crystallinity, even when fully hydrogenated, due to interference by the phenyl groups. This material has on average one styrene unit to one and a half butadiene units and hence each phenyl group will be an average separated by 8 C-C bond lengths, i.e. approximately  $10\text{\AA}$ . If the styrene content is reduced sufficiently crystallisation may commence.

Good elastomeric properties were obtained with a polymer containing 3 mole % styrene. In this case the phenyl units were separated by approximately 100 C-C bond lengths, i.e. approximately  $125\text{\AA}$ . The average maximum dimension of crystallites must therefore have been of a similar order.

These two calculated limits therefore place the average size of the crystallites as being between  $10\text{\AA}$  and  $125\text{\AA}$ . This treatment does not, of course, preclude the possibility of there being present crystallites of greater size, however it does seem unlikely that there would be any smaller than  $10\text{\AA}$ . This minimum size limitation is in good agreement with results published by Davison and Taylor<sup>(91)</sup>. They used a rather lengthy procedure and complex calculation to come to the conclusion that for alpha-olefin terpolymers crystallisation did not occur with monomer sequence lengths less than approximately 20 carbon atoms, a figure in a similar order to that proposed in the present work.

Further support for these size limitations was found in the work of Tuminello<sup>(92)</sup>. He used DSC to investigate the melting point transitions, of materials prepared in the present work supplied to him by the author. He found that melting occurred over a wide range of temperatures indicating a wide variety of crystallite sizes. It was calculated that the minimum crystallite size present at room temperature was approximately  $40\text{\AA}$ , smaller crystallites only forming at lower temperatures and that crystallites melting at  $90^{\circ}\text{C}$  would be approximately  $150\text{\AA}$ .

One can therefore conclude that the crystallite dimensions present in the materials under discussion must have been in the region of  $20\text{\AA}$  to  $200\text{\AA}$ .

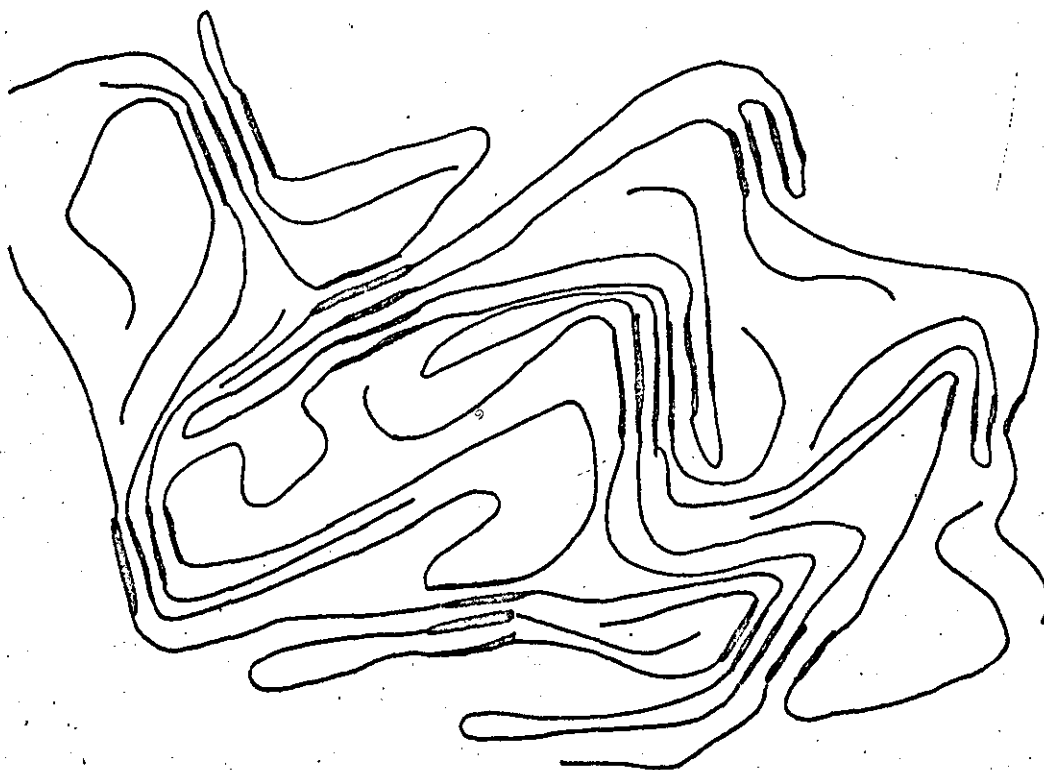
One further point that should be made concerns stress crystallisation. Attempts were made to measure crystallinity on stretched samples. The techniques employed were probably far from ideal but they did indicate that crystallite orientation occurred rather than further crystallisation.

The system investigated in the present study can be represented as in figure 3.2.26, the bold lines denoting crystalline segments of chains within crystallites and the ~~higher~~<sup>lighter</sup> lines the amorphous, rubbery chains linking the crystallites. The picture has been simplified by not including chain entanglements but these are clearly important. The crosslinking effect of the crystallites prevents the entanglements from disengaging and they therefore function as additional crosslinks. Holden<sup>(100)</sup> proposes that in the case of the ABA block copolymers the entanglements play a more important role in crosslinking than do the thermoplastic domains. However, in the case of the hydrogenated polymers it might be argued that this was not the case. The block copolymers contain only two thermoplastic segments per chain and thus can only have two domain crosslinks per chain, a situation which might be expected to produce very poor elasticity unless one invokes a large number of entanglement crosslinks to increase effectively crosslink density. An approximate calculation for hydrogenated polymers indicates that the number of crystallites per chain is rather greater than two.

If one considers the polymer having most nearly the optimum properties, it contained 3 mole percent styrene, had a molecular weight of 150,000, was hydrogenated to 60% and had a 4% crystalline content. If an average crystallite size is taken as  $100\text{\AA}$  then the number of crystallites per chain can be found.

The average chain length is calculated as  $15000\text{\AA}$ , from the molecular weight, using a carbon-carbon bond length value of  $1.25\text{\AA}$  and assuming a C<sub>4</sub> monomer unit molecular weight of 50. If the polymer was 4% crystalline then each chain will be crystalline along a total length of  $600\text{\AA}$ . With each crystallite having an average size of  $100\text{\AA}$  this means that each chain must take part, on average, in 6 crystallites. With this

FIGURE 3.2.26. Polymer Crystallites.



number of crystallite crosslinks per chain it might be expected that entanglement crosslinks, although important, might be less important than in the case of the block copolymers.

Figure 3.2.26 illustrates two reasons why this random type of system can never be ideal. Firstly, it contains a large proportion of free chain ends and secondly, the chains linking the crystallites have a wide distribution of lengths. However in a comparison with the ABA block copolymers these deficiencies have been offset somewhat by the comparatively high number of crystallite crosslinks present in each chain.

#### 4. CONCLUSIONS.

##### Catalyst Studies.

Two Ziegler-type catalysts were investigated, n.butyllithium, NiDIPS and triisobutylaluminium, NiDIPS. Both catalysts were first optimised with respect to the ratio of their two components. This was found to be 5 : 1 for the former and 3 : 1 for the latter, results which were in general agreement with those published by other workers. It was found that the activity of these catalysts was enhanced when they were contacted with hydrogen prior to mixing with olefin, a feature that does not seem to have been recorded by other workers.

The rate of hydrogenation was found to be dependent on catalyst concentration and temperature up to 70°C but was apparently independent of pressure.

The two catalysts were compared with respect to their hydrogenation efficiency towards both polymeric and non-polymeric materials. The organoaluminium catalyst proved to be the more effective in both cases but for polymer reduction the difference was not great. The organolithium catalyst was much more easily handled and was therefore selected for general use despite its lower activity.

The activity of the catalysts towards various olefins was investigated. It was found that the rate of hydrogenation decreased with increasing substitution of the double bond. It was further found that, under the conditions employed, reduction of the aromatic nucleus did not occur. In the case of the styrene butadiene copolymers therefore, only the ethylenic unsaturation was reduced. The catalysts were also found to be highly selective in reducing conjugated double bonds in the presence of isolated double bonds. In particular, cyclopentene was produced from cyclopentadiene in yields up to 90% and the selectivity was still preserved even at a temperature of 80°C. These results formed

the basis of a successful patent application for the production of cyclopentene (British Patent No. 1,357,318).

Evidence was obtained which supported the contention that these catalysts were truly homogeneous rather than colloidal in nature, a point which has caused a certain amount of controversy in the literature.

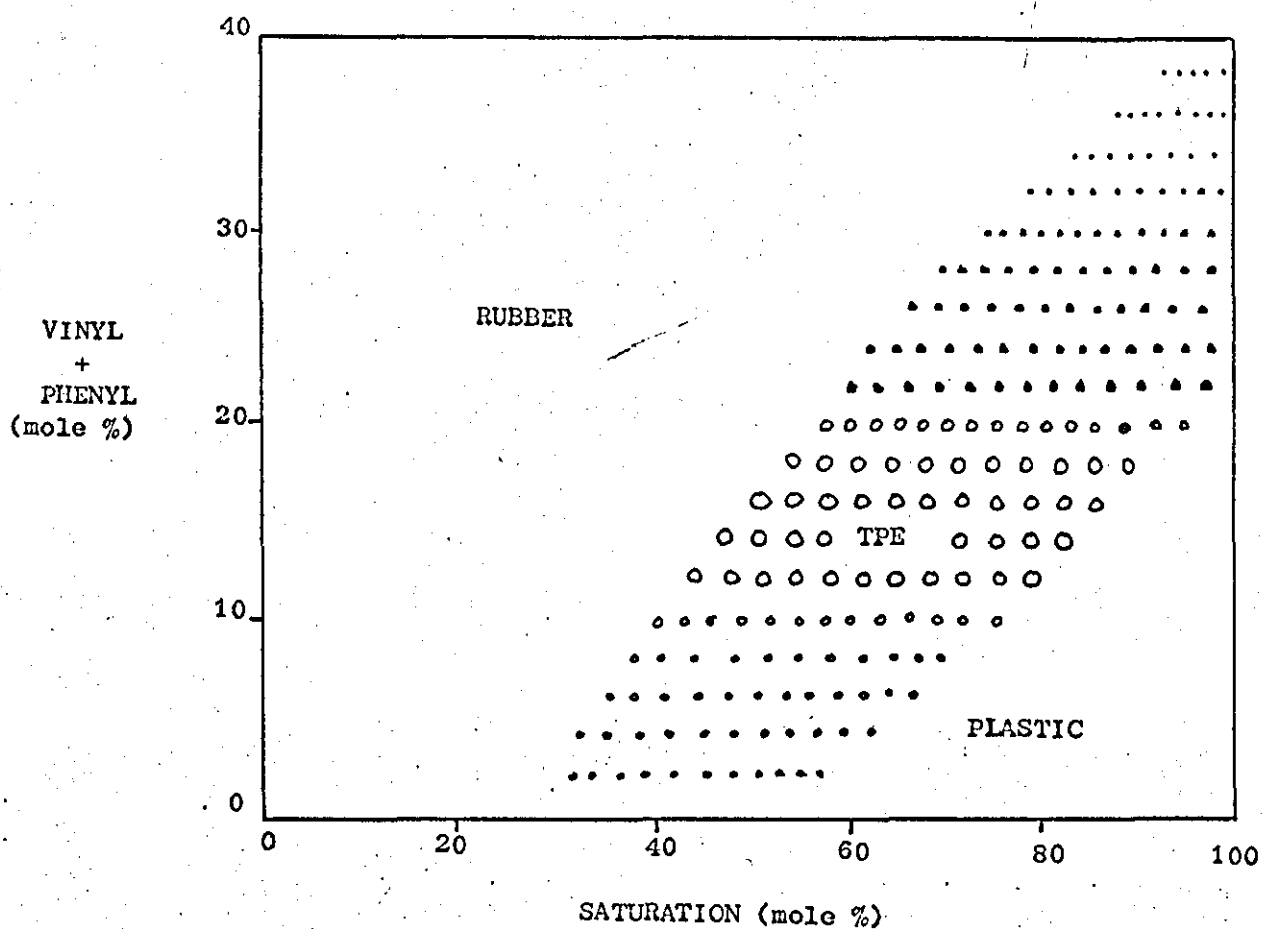
Their mode of operation was explained in terms of the generally accepted Sloan and Matlock mechanism, a modification being made to incorporate selectivity with respect to conjugated double bonds.

#### Polymer hydrogenation.

A systematic study was carried out of the influence of polymer composition on properties. To this end a variety of butadiene homopolymer and copolymers with styrene were produced, hydrogenated to varying levels and then evaluated.

It was found that thermoplastic elastomer properties were obtained within a specific range of compositions, as illustrated in figure 3.2.27. The two main compositional variables were side group content, either vinyl or phenyl, of the starting polymer and extent of saturation. Molecular weight also influenced properties but only when values were less than about 120,000 and in this region there was a general worsening of properties. The figure below shows that with low degrees of saturation and high side group contents, products were generally weak and rubbery whereas at high degrees of saturation and low side group contents, products were tough and plastic. The compositions in between gave products which could be termed thermoplastic elastomers and the best properties were obtained in the area represented by the largest spot size. The figure does somewhat oversimplify the situation as it was found that low styrene content styrene butadiene copolymers gave generally better products on reduction than did the polybutadienes.

FIGURE 3.2.27.





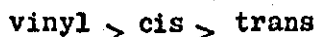
The ultimate aim of the study was to find the composition which would give the best thermoplastic elastomer commensurate with the given system and this aim was substantially achieved. The ideal starting polymer was selected as one containing 4 mole % styrene, 10 mole % 1,2 butadiene, 86 mole % 1,4 butadiene and a number average molecular weight of about 150,000. The ideal extent of hydrogenation is really dependent on the requirements of a particular application, the more saturated products having higher tensile strengths but lower elasticity, however a good balance of properties was obtained with a degree of saturation in the region of 55 to 60%.

Products with fairly good properties were also obtained by the hydrogenation of copolymers with styrene contents in the range of 10-15 mole percent. This is of interest as it is polymers such as these that are already being produced in large tonnages for use in tyre fabrication, they are therefore available comparatively cheaply.

The study does not include a comparison between properties of the hydrogenated polymers and commercially produced thermoplastic elastomers but published data indicate that they are similar in many respects to the Shell ABA block copolymers. A discussion of the relative merits of the two systems has been carried out in the introduction.

The results obtained in the polymer hydrogenation study have provided a good insight into the nature of these materials. In particular crystallinity values could be correlated very closely with most of the effects on properties of the compositional variables. Thus the increase in tensile strength when either side group content was decreased or degree of saturation was increased was found to be accompanied by an increase in crystallinity. These effects were by no means unexpected having been reported previously as occurring in a number of polymeric systems, however they did lead to the hypothesis which explained other, novel, effects.

The literature indicated that the crystalline phase consisted of polyethylene-type crystallites and an approximate calculation and a consideration of results from other sources led to the conclusion that these had dimensions of between  $20 \times 10^8 \text{ \AA}$  and  $200 \times 10^8 \text{ \AA}$ . It was proposed that these crystallites acted in the dual role of filler particles and multifunctional crosslinks in a similar manner to the thermoplastic domains of the Shell block copolymers. A point which was of interest was whether these crystallites were randomly distributed or occurred in blocks and this was clearly dependent on the degree of randomness of the hydrogenation itself. Two pieces of evidence led to the conclusion that hydrogenation was indeed essentially random. The first was that it was found in a study of the relative rates of hydrogenation of double bonds with different configurations in non-polymeric configurations that ease of reduction was in the order,



and this was also found to hold true in polymer hydrogenation. In fact a polybutadiene containing 10 mole percent vinyl groups had virtually all the external double bonds reduced to ethyl by the time the degree of saturation had reached about 50%. It is well known that the vinyl groups in a polymer such as this are randomly distributed along the polymer chains so the hydrogenation must clearly have taken place randomly. Further evidence for random hydrogenation was obtained from measurement of glass transition temperatures. Non-random hydrogenation would have led to the presence of blocks of both non-crystalline polyethylene-type chain segments and also unreduced polydiene segments and this would have led to two glass transition temperatures. In fact only one was detected and this behaved on increased degree of saturation in a manner consistent with random hydrogenation.

The novel effects mentioned above as having been explained by the crystallite filler particle/crosslink hypothesis were those due to variation in polymer molecular weight and styrene content. An increase in the former led to an increase in tensile strength up to a maximum above which there was no further increase. This was explained by the increase in molecular weight causing an increase in the number of crystallites per chain and also a decrease in the number of free chain ends. The effect was shown to be remarkably similar to that discovered by Flory in an investigation of the sulphur vulcanisation of butyl rubber. The improved tensile strength and elasticity of hydrogenated low styrene content styrene butadiene copolymers was explained by proposing that the phenyl groups on the styrene units exerted a size limiting effect on the crystallites resulting in an effective increase in the number of crystallite crosslinks per chain. The fact that the styrene units would have limited crystallite size enabled a calculation to be made which resulted in the conclusion that in the case of the best product obtained each polymer chain, on average, would have participated in five crystallites. Hence each chain was linked through five crosslinks, a situation somewhat more satisfactory than the ABA block copolymers which only have two per chain.

The effects discovered were therefore satisfactorily explained in terms of a two phase system and a schematic diagram was drawn to illustrate this fact.

This study resulted in a successful patent application<sup>(101)</sup> concerning the production of thermoplastic elastomers via polymer hydrogenation.

PART 2.

EPDM MODIFICATION VIA ANIONIC METALATION.

## 1. INTRODUCTION.

The work on ethylene, propylene, diene terpolymers (EPDM) comprised metalation, styrene grafting and carboxylation with the object of suitably modifying the characteristics of the base polymer. These three aspects of the work are treated separately as far as possible and it is convenient to first consider the reasons for employing a metalation technique in preference to any other method of grafting or carboxylation. This will be followed by a consideration of the work previously carried out on metalation reactions.

### Graft Polymerisation.

The literature on grafting techniques has been extensively reviewed (8,102, 103 ) and the main methods may be summarised as:

- 1) Radical
- 2) Photochemical
- 3) Radiation (irradiation)
- 4) Mechanochemical
- 5) Addition
- 6) Condensation
- 7) Cationic
- 8) Anionic

For reasons already stated a specific reaction was desired, firstly to give products of predictable composition and secondly because of the extreme practical difficulty of separating mixtures should the reaction give undesirable by-products.

In EPDM the natural choice is a reaction involving, or adjacent to the double bond as this has a different order of reactivity to the saturated portion (which comprises the bulk) of the polymer and the level of this functional group can be controlled as desired.

The first four methods listed are all free radical in nature and can be discarded for the reasons that graft chain length is uncontrollable, homopolymerisation of the graft species is inevitable and chain scission or crosslinking might occur.

Methods 5 and 6 involve reaction between polymers bearing chemically reactive functional groups which, if specificity is desired, must not be capable of self condensation. A number of elegant syntheses have been achieved but the basic techniques require fairly lengthy procedures and in a commercial context it was felt that these should not be pursued. A point of considerable importance is that each grafting chain has only one addition function and thus the concentration of reacting sites is extremely small. If complete reaction of the sites on the base polymer is to be achieved then long reaction times or a large excess of the graft species is required.

The cationic technique has been employed to graft styrene onto chlorinated butyl rubber<sup>(104)</sup>. It involves the introduction of halogen into the base polymer, reaction with a Lewis acid to generate cationic sites then polymerisation of the monomer. In a similar way isobutylene<sup>(105)</sup> and butadiene<sup>(106)</sup> have been grafted onto polyvinylchloride.

There are a number of reasons why this method is not very suitable for EPDM modification. The EPDM would first have to be halogenated and this would need to be conducted in chlorinated solvent to avoid the formation of side products. The process would result in the presence of Lewis acid residues and these would have to be removed, presumably by water washing. Cationic processes often involve the difficulties mentioned as occurring in the other methods, viz. poor control of product composition and undesirable side reactions.

The last method to be considered, anionic synthesis appeared to be the most attractive for the present study. If a suitable metalating agent could be found it should be possible to produce carbanions on the EPDM chains in a one-step process. These carbanions should not only function as styrene graft polymerisation initiators but also facilitate the introduction of carboxy functionality.

#### EPDM Carboxylation.

As the metalation reaction appeared suitable for both graft polymerisation and carboxylation there was no need to search for an alternative method for the latter. However it is interesting to consider briefly what other methods are available.

The chemical reactions of polymers have been reviewed in a book of that name edited by Fettes<sup>(107)</sup>. Considering only reactions capable of producing carboxyl groups on unsaturated polymers without degradation then the number of possibilities are very few. The free radical addition of thiol acids to unsaturated polymers is well known, the author having carried out some work in this field<sup>(108)</sup>, however though the reaction proceeds quite satisfactorily with polydienes, it does not work very well with EPDM, due to the very low level of unsaturation.

Ozonolysis appears quite interesting. Normally of course the decomposition of a rubber ozonide results in chain scission due to the unsaturation generally being present in the rubber in an internal position. EPDM though is unusual in that all unsaturation is external to the main chains and ozonide decomposition in this case would only result in the

introduction of functionality and not in polymer break down. It is possible that EPDM could be ozonised and the resulting ozonide decomposed under oxidative conditions, with for example hydrogen peroxide, so that a carboxylated product is produced. As far as is known this has not been attempted, possibly due to the fact that a commercial process might prove somewhat hazardous due to the unstable nature of ozonides.

Apart from the possibility of ozonolysis, the methods available for the introduction of carboxy functionality into EPDM appear to be very few and generally unsuitable. The anionic metalation method therefore seems to be not only more convenient but probably also the most suitable.

#### Metalation Reaction.

This type of reaction is by no means novel, metalation being defined in 1934 as the replacement of hydrogen by metal to yield a true organometallic compound and fluorene being metalated with ethyl lithium in 1928<sup>(109)</sup>. In the early days only non-polymeric compounds with fairly acidic hydrogen atoms could be metalated. The work with organolithium compounds has been reviewed by Gilman<sup>(111)</sup> and Morton who state that benzene could only be metalated to the extent of about 5%. The use of sodium and potassium alkyls resulted in increased reactivity and permitted the metalation of substituted aromatics<sup>(112)</sup>, cyclopentene and cyclohexene<sup>(113)</sup> to be carried out. The discovery that organometallics could be activated by chelating polyamines led to a revival of interest starting about 1967. In the next few years reports were made of n.butyllithium, NNN'-tetramethylethylenediamine (TMED) complexes metalating toluene<sup>(114-117)</sup>, benzene<sup>(116,118)</sup> and metallocenes<sup>(118,119)</sup>. A symposium on "Polyamine Chelated Alkali Metal Compounds" was held in New York in 1972 and the



papers presented have recently been published in book form<sup>(120)</sup>. This covers the structure of these complexes and their use in a number of different fields as well as metalation. The discovery of these complexes enabled work to begin on the metalation of polymers, a field previously excluded due to the relative inactivity of earlier metalating agents.

During 1968 and 1969 a number of papers were published dealing with polymer metalation. Chalk, Hay and Hoogeboom<sup>(121-124)</sup> metalated aromatic polyethers with n.butyllithium, TMED complex and used the products to prepare carboxylated and graft polymerised polymers. Some Russians<sup>(125,126)</sup> carried out similar work and also used an indirect method involving the reaction of n.butyllithium with chlorinated polyolefins to produce for example metalated polyethylene. The use of anionic techniques to prepare graft copolymers was reviewed in 1972 by Heller<sup>(127)</sup> but again this dealt mainly with the metalation of aromatic polymers. During this time work on the direct metalation of polydienes was published by two groups of workers, the Japanese Minoura and Harada<sup>(128,129)</sup> and Tate and Halasa of Firestone<sup>(130)</sup>. In these cases metalation was carried out at the olefinically unsaturated sites present in polydienes rather than at aromatic sites. The results obtained were very good, high levels of metalation being achieved and good graft efficiencies. It therefore seemed that the metalation of EPDM might be carried out using a similar reagent so work was commenced to verify this. Before long it became apparent that n.butyllithium, TMED complex was not sufficiently active to operate with the very low levels of unsaturation present and in a patent published later by Dunlop<sup>(131)</sup> a similar conclusion is mentioned.

Potassium t.butoxide had been shown<sup>(76,132)</sup> to behave in a similar manner to TMED when added to the n.butyllithium initiated polymerisation of butadiene, both of them causing an increase in rate of polymerisation, and in vinyl unsaturation. Alkali metal alkoxides generally had been shown<sup>(133)</sup> to increase the yields from metalations of aromatics carried out with n-amylsodium. Accordingly, work commenced using n.butyllithium, potassium t.butoxide as a metalating agent for EPDM. A considerable amount of work had been completed when two relevant patents were issued to Firestone. One<sup>(134)</sup> claimed the use of n.butyllithium, potassium t.butoxide as a metalating agent for unsaturated polymers and mentioned EPDM in the preamble though the examples quoted dealt only with polybutadiene. The other<sup>(135)</sup> dealt with a vulcanisable carboxylated polymer prepared via metalation. In this case metalation was carried out with n.butyllithium, TMED complex and EPDM was not mentioned.

In 1972, in conjunction with some colleagues, the author published a paper<sup>(136)</sup> summarising some of the work that is discussed in this thesis. This mentioned the metalation of EPDM with n.butyllithium, potassium t.butoxide and covered the use of the metalated polymer in the preparation of carboxylated, styrene grafted and butadiene grafted products, the latter section of the work having been carried out by colleague Dr. A.J. Amass. A patent<sup>(137)</sup> was also granted covering the butadiene grafted EPDM in use as a covulcanisation improver. Later in the year the author presented a paper dealing with these topics at the Groupe Francais d'Etudes et d'Applications des Polymers Colloque, "Copolymeres Sequences et Greffes", Mulhouse, France and this was subsequently published<sup>(138)</sup>.

In 1973 Falk and Schlott published a series of three papers; the first<sup>(139)</sup> dealt with the metalation of polydienes using s.butyllithium TMED chelate and subsequent graft polymerisation of vinyl aromatics; the second<sup>(140)</sup> with the styrene grafting of EPDM using the same metalating agent; and the third<sup>(141)</sup> covering the hydrogenation of polydienes grafted with vinyl aromatics. The results quoted for the styrene grafting of EPDM indicate that although in some cases high graft efficiencies were obtained the number of grafts per chain was low. This was possibly due to either insufficient metalating activity or the moderate levels of unsaturation in the EPDM's used.

## 2. EXPERIMENTAL PROCEDURES.

### 2.1. METALATION REACTION.

For the metalation reaction to succeed it was essential to ensure the absence of substances which might react preferentially with the metalating agent. The most common contaminants likely to give trouble are oxygen, moisture, oxygenated compounds in the solvent and aromatics, the last being present in commercial solvents in appreciable amounts.

The general procedure was to purify the solvent and dry the rubber, then make up the solution and subject this to a final purification.

#### 2.1.1. Hexane Purification.

The hexane used was a commercial grade which contained a certain proportion of unsaturated compounds mainly benzene and these were of course capable of competing with the polymer for metalation. Two methods were tried for their removal. The first was the well known sulphuric acid washing technique which however proved wholly unsatisfactory and the second was the method developed by Murray and Keller<sup>(42)</sup>. After the metalatable species had been removed, the solvent was dried.

#### 2.1.1.1. Determination of Aromatics.

Gas/liquid chromatography methods can be used for the determination of aromatic contents but in the case of commercial hydrocarbons, peak assignment is very difficult due to the large number of components. In general therefore U.V. analysis was used, this being supplemented by the quick check I.R. method described in section 3.3.2.

The major aromatic present in commercial hexane is benzene so this was used as the standard for the U.V. analysis. Solvent spectra were recorded using a Pye Unicam SP700 spectrometer and 1 cm cells. Benzene absorbs very strongly in the region of 255 nm the band being resolved into a sextuplet. The determination was carried out on the 0-1.1 absorbance scale using the height of the highest peak (255 nm) as the measure of benzene concentration. The extinction coefficient was first calculated using hexane containing known amounts of benzene,

$$\text{extinction coefficient (E)} = \frac{\text{Molecular weight (M)} \times \text{absorbance (A)}}{\text{concentration (mg/gm)}}$$

and found to have a value of 200.

Samples for analysis were first diluted as necessary in order to obtain an on-scale reading and the absorbance determined. The concentration of benzene was then calculated from the equation,

$$\text{Concentration (\%)} = \frac{M.A.D.}{10E}$$

where M is the molecular weight of benzene

A is the absorbance

D is the dilution factor

E is the extinction coefficient (200).

#### 2.1.1.2. Sulphuric acid washing.

The usual method is to shake the hydrocarbon in a separating funnel with concentrated sulphuric acid and then wash with water to remove the sulphonates and sulphuric acid. It was found that with hexane containing ~0.2% benzene, 2½ l of sulphuric acid were required (in ~700 ml batches) to reduce the aromatic in 1 litre of hexane to 0.003%, and that considerable contact time (~1 week) between the sulphuric acid and hexane was required. Another difficulty with this method was that if the water washing was not carried out extremely thoroughly then sulphonated aromatic impurities could be left.

#### 2.1.1.3. Column dearomatisation.

This method, developed by Murray and Keller,<sup>(142)</sup> produced hexane with no detectable (by U.V.) aromatics, in a comparatively dry state in a one-step process.

The column material was prepared in the following manner:

360g alumina (Spence U.G.2) were mixed with 500 ml of approx. 2M nitric acid. This slurry was filtered off in a Buchner funnel then washed with deionised water until neutral. 40g silver nitrate were dissolved in 20 ml. of deionised water and 350 ml of methanol added. This solution was used to wash the alumina into a Buchi flask and the solvent was then removed on a rotary evaporator. The resulting solid (white or very pale grey) was then air dried at 140°C for 24 hr. The dried material was then packed into a dried, glass column.

Using double quantities in a 50mmx1m packed column about 1 l/hr. of aromatic (and olefin) free hexane could be collected. This size of column was adequate to purify about 25 l. of hexane containing about 0.2% aromatics.

In order to ensure complete removal of water the exit end of the column was packed with molecular sieve and the eluant was collected in a nitrogen flushed receiver.

#### 2.1.1.4. Solvent drying.

Even though the column dearomatisation process produced a dry solvent it was considered desirable to effect further drying. This was carried out by distillation under nitrogen at atmospheric pressure, from n.butyllithium.

In some cases solvents were not dearomatised prior to use, however the were still dried by distillation.

## 2.1.2. Polymer solution preparation and purification.

### 2.1.2.1. Polymers.

Three different ethylene propylene diene terpolymers were used in these experiments.

- (a) Intolan 155, manufactured by The International Synthetic Rubber Company and having ethylidenenorbornene as termonomer,
- (b) Nordel 1040, produced by Du Pont and having 1,4 hexadiene as termonomer,
- (c) A sample prepared in the laboratory by other workers at I.S.R. and having endomethylenehexahydronaphthalene as termonomer.

The structure of these termonomer units is given in section 3.1.5.

The polymers were not especially purified prior to use as it was known from experience that all impurities could be removed effectively by the treatment of the polymer solution described in section 2.1.2.4, they were however crumbed and dried in a vacuum desiccator.

### 2.1.2.2. Solution preparation.

Polymer solutions were made up in large batches so that a number of reactions could be carried out on uniform material. Purified and dried hexane (4 l.) was added to a 5 litre round bottomed, flanged neck flask, fitted with a stirrer, a nitrogen dip pipe and a condenser protected with a calcium chloride drying tube. Nitrogen was purged through the stirred hexane and the polymer was then added in small lumps. The amount of polymer added depended on the end use. On metalation, the polymer solutions tended to increase in viscosity (see section 3.1.3) depending on the extent of metalation. In order to

keep solution viscosity within reasonable limits fairly low concentrations were employed, generally in the region of 1-3% w/v.

The polymer was stirred in solvent, under nitrogen purge warming as necessary, until solution was complete. This solution was then generally pre-scavenged with n.butyllithium prior to passing through the purification column.

#### 2.1.2.3. Scavenging level determination.

Scavenging the polymer solution with n.butyllithium prior to the addition of metalating agent was found to improve reactivity greatly and as it was important to have only a very slight excess of organo-metallic present after scavenging it was necessary to develop a method for the determination of scavenging level i.e. the amount of n.butyllithium needed to leave a slight excess after reaction with all impurities. The method incidentally was also used to measure the effectiveness of different methods of purification (see section 3.3.3).

The method was based on that developed by Gilman and Schulze<sup>(143)</sup> to detect the presence of Grignard reagents. They found the detection limit for EtMgBr to be 0.037M whereas in the present study the sensitivity of n.butyllithium appeared to be much higher at about 0.0004M.

The reaction is based on the reaction of Michler's ketone  $\text{NMe}_2-\phi-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\phi-\text{NMe}_2$  with a metal alkyl to produce ultimately a dyestuff. The quantitative nature of the reaction was irrelevant in the present context as an indication of any free n.butyllithium was sufficient.



The reagents employed were:

Michler's ketone, approximately 1% in dry benzene. The fresh reagent has a very pale blue colour, any yellowness indicating deterioration.

Iodine, approximately 0.2% in glacial acetic acid

n-butyl lithium of known strength.

All solutions were manipulated using dry syringes and test reactions were conducted in 100 ml conical flasks, sealed with Suba-Seals and nitrogen flushed.

Approximately 0.5 ml of the Michler's ketone solution was syringed into one of the conical flasks through a rubber Suba-Seal. About 1 ml of the test solution was added to this and the mixture then shaken. 1 ml of water was then added together with about 0.5 ml of the iodine solution and the mixture shaken again. If butyllithium was present at the start then the water layer turned green and the solvent layer violet. If there was no butyllithium present initially then the water layer was coloured yellow and the solvent layer pink. Incremental additions of butyllithium were made to the solution to be scavenged, and the test repeated after each addition, until a positive reaction was obtained. With experience, the approximate scavenging level of a particular solution was known before testing, which facilitated the estimation of the amount of BuLi to be added. In this way only a few tests were needed.

#### 2.1.2.4. Solution purification.

Several different methods were tried before a suitable purification technique was found; these are discussed in the results and discussions sections 3.1.3. and 3.3.3.

Initial experiments were carried out using solutions prepared as in section 2.1.2.2., however it was soon found that these were quite unsatisfactory due to the presence of impurities. Improvements were achieved by scavenging these with n.butyllithium prior to use but even then results were not very good. The best method found was to treat the solutions with n.butyllithium then pass them through a column of activated alumina and silica gel before scavenging again with n.butyllithium.

The final procedure was:

A glass column, 1m in length with an internal diameter of 25mm was plugged at the bottom with dried glass wool then half filled with freshly activated ( $400^{\circ}\text{C}$ , 16 h.) 50 mesh alumina. The column was then topped up with coarse, fresh silica gel. A dropping funnel was fitted to the top of the column and the bottom was fitted with a tap adaptor equipped with a wide bore syringe needle. The needle was then introduced into a  $\frac{1}{2}$  pint, rubber sealed, crown-capped bottle fitted with another syringe needle to act as a vent. The whole apparatus was flushed for two hours with pure nitrogen.

The pre-scavenged polymer solution (section 2.1.2.2) was transferred directly from the 5 l. flask under a slight positive pressure of nitrogen via a dip pipe and dry polythene tubing to the dropping funnel. After several minutes the purified solution eluted from the base of the column. The first 100 ml. eluted were often a little cloudy due to suspended particles from the column packing in which case the collecting

sample  
bottle was disconnected and/discarded. The reactor in which metalation was to be carried out was then directly connected to the column outlet and filled to the required level whilst being flushed with pure nitrogen.

In general, carboxylation reactions were carried out in 1 l. flange-necked flasks and styrene graft polymerisations in 1 pt. crown-capped bottles. Final scavenging was then carried out with n.butyllithium.

### 2.1.3. Metalating Agent Preparation.

#### 2.1.3.1. n.Butyllithium.

This was used as supplied by Metall G.S. as a 1.5 molar solution in n.hexane. 1 pt. rubber sealed bottles fitted with two-holed crown caps were dried, flushed with nitrogen, then filled directly from the pressurised container via a syringe needle adaptor. Aliquots were then transferred from this bottle by syringe.

#### 2.1.3.2. NNN'N' tetramethylethylenediamine (TMED).

This was obtained from B.D.H. The contents of a fresh bottle (100 ml) were transferred to a dried, nitrogen flushed  $\frac{1}{2}$  pt. bottle containing about 1" of fresh 4A mole sieve. The bottle was then sealed with a rubber disc, fitted with a two-hole crown cap and purged through the liquid layer with pure nitrogen for 4 hrs. Aliquots were transferred by syringe.

#### 2.1.3.3. Potassium t.butoxide.

This was prepared by a standard method. Potassium was reacted with a four-fold excess of sodium dried t.butanol in cyclohexane. The cyclohexane and excess t.butanol were removed by vacuum distillation. The product from this process was a 1 : 1 complex of potassium t.butoxide with t.butanol and in some cases this complex was used, without

further treatment, as a metalating agent together with n.butyllithium. However a more satisfactory metalating agent was obtained after the removal of the coordinated t.butanol. This was effected by vacuum sublimation at 180°C and 0.5 mm pressure.

To facilitate handling, the reagent was slurry ground with hexane in  $\frac{1}{2}$  pint glass bottles containing a few glass beads. A suitable quantity of potassium t.butoxide was weighed into the bottle and a measured volume of hexane added by syringe. After roll milling for a few hours a fine dispersion of known concentration was obtained. The entire weighing operation and transfer were carried out in an atmosphere of nitrogen using a dry-bag.

#### 2.1.3.4. Preparation of Metalating Agent.

The two components of the metalating agent were premixed before being added to the polymer solution. The required amount of TMED or potassium t.butoxide slurry was syringed into a dried, nitrogen flushed,  $\frac{1}{2}$  pt. bottle having a rubber seal and fitted with a two-holed crown cap. An equivalent amount of n.butyllithium solution was then added and the mixture was shaken. The TMED complex was a very pale yellow colour and entirely soluble whereas the potassium t.butoxide complex was a pale pink-brown colour and only partially soluble. Both complexes were added to the polymer solution almost immediately after mixing.

#### 2.1.4. Metalation Reaction Procedure.

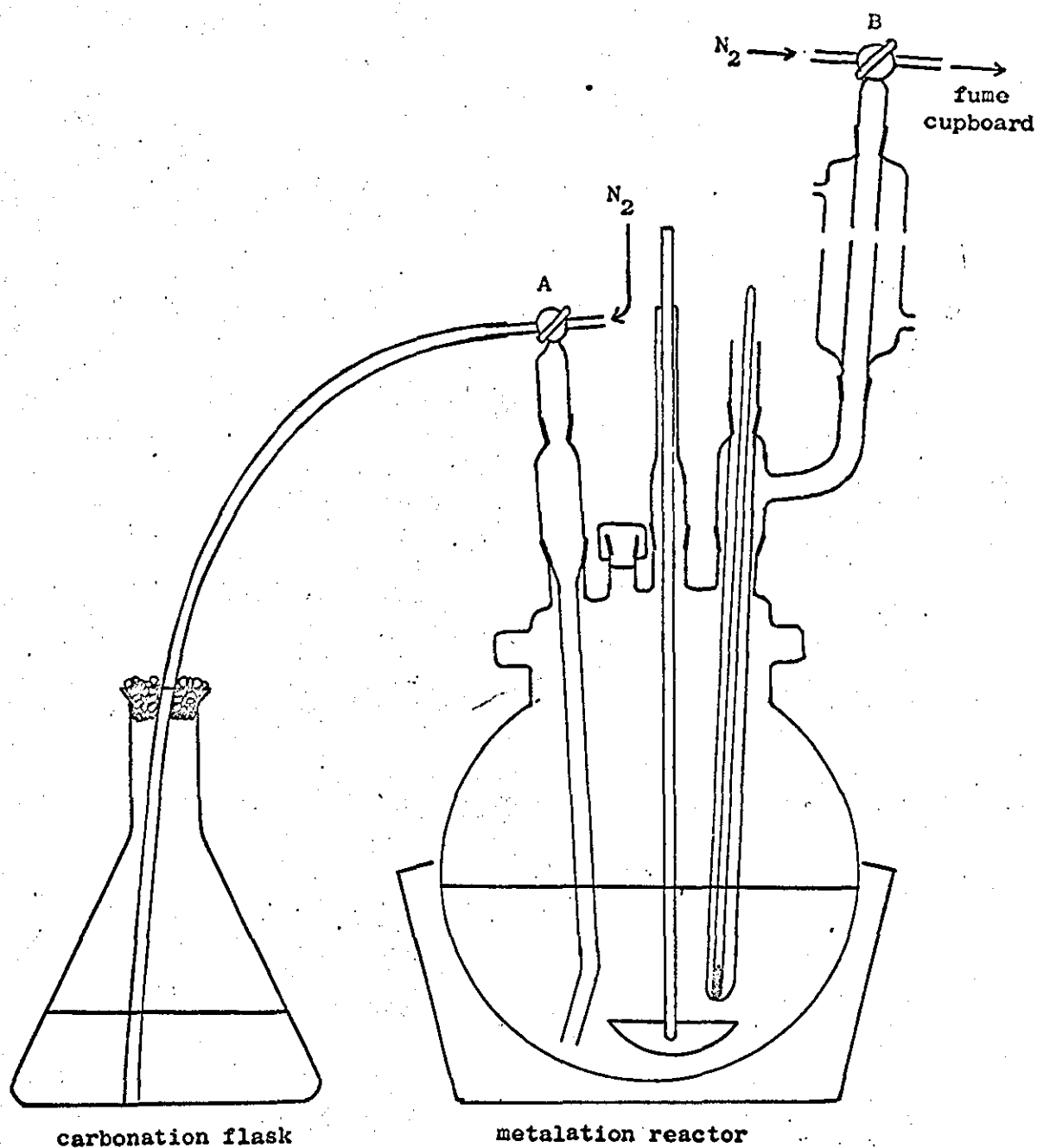
Styrene grafting was carried out simply by adding monomer after metalation, as detailed below, and this operation did not present any special difficulties. Carboxylation however required transfer of the metalated polymer solution and as this was viscous (and jelly-like) preparation was conducted in an apparatus that facilitated handling.

##### 2.1.4.1. Metalation for carboxylation.

The reaction was carried out in a 1 litre flange-necked flask fitted with a four-necked lid as shown in figure 2.1. All glassware was dried overnight in an oven at  $140^{\circ}\text{C}$  and assembled hot. The lid was then fitted to the flask together with the stirrer, nitrogen dip pipe, three-way tap on the dip pipe, and rubber suba-seal. A stopper was fitted initially where the two-way adaptor is shown. The flask was placed just below the polymer solution purification column and purged with nitrogen which was vented through a syringe needle inserted in the suba-seal. until the apparatus was cold. The needle at the bottom of the purification column was then inserted through the suba-seal and polymer solution forced into the flask under  $\text{N}_2$  pressure until it reached a measured mark (700 mls) on the side of the flask. Both needles were then withdrawn from the flask and the three-way tap A was turned so that the flask was sealed.

The flask was then placed in an isomantle and a nitrogen supply connected to the three-way tap. This was opened to purge the tap assembly then turned to admit nitrogen to the flask; at the same time the stopper was removed and the thermometer pocket condenser assembly connected. Prior to the connection of the condenser to the flask tap B directed nitrogen through the condenser and over the thermometer pocket.

FIGURE 2.1. Metalation and Carboxylation Apparatus.



N.B. Each joint was fitted with springs to prevent opening whilst transferring polymer solution into carboxylation flask.

As soon as the condenser had been connected, this tap was turned so that effluent from the flask was directed through polythene tubing to a nearby fume cupboard. The polymer solution was then stirred and warmed slowly until the required temperature was reached. During this time a final scavenging with n.butyllithium was carried out. Metalating agent was then syringed in through the suba-seal and the mixture was allowed to react for the requisite time. As metalation progressed, the polymer solution turned a deep red colour.

#### 2.1.4.2. Metalation for graft polymerisation.

Reactions were carried out in oven dried, nitrogen flushed 1 pt. bottles which had been marked to indicate the 500 ml level. These were fitted with rubber seals and three-holed crown caps and were flushed with dry nitrogen introduced and vented by means of syringe needles. Polymer solution was introduced by inserting the needle on the bottom of the purification column into the third hole in the crown-cap. Solution was added up to the 500 ml. mark on the bottle. This method of introducing the required volume was checked by weighing and found to be sufficiently accurate. The solutions were then usually scavenged with n.butyllithium before addition of the required aliquot of metalating agent. The bottles were shaken, pressurised to 10 p.s.i. with nitrogen then fixed on to a rotating arm situated in a temperature controlled water bath. They were then rotated for the required length of time at the desired temperature.

The level of metalating agent used for the styrene graft polymerisation was generally less than for the carboxylation work and solutions did not therefore assume such a deep-red colour on metalation but were usually orange-red.

## 2.2. POLYMER CARBOXYLATION.

### 2.2.1. Carboxylation Procedure.

The development of this procedure will be partly described in section 3.2.2. For the carboxylation reaction to be effective it is necessary to contact the polymer solution rapidly with a large excess of dry carbon dioxide. In early experiments carbonation was carried out by transferring the solution from the reactor into a flask containing powdered solid carbon dioxide. This proved to be rather unsatisfactory as ice tended to form very quickly on the surface of the solid  $\text{CO}_2$ , also contact between the lumps and the polymer solution was not very good. The final procedure adopted is illustrated in figure 2.1.

A fairly fine slurry (~300 mls) of solid carbon dioxide in dry petroleum ether (100-120°C) was made up in a 2 l. conical flask in a dry bag. A polythene tube was then connected to the three-way tap A on the nitrogen inlet to the metalation reactor. The metalated polymer solution was cooled to room temperature and taps A and B were set in the all-open position to allow nitrogen to pass over the top of the condenser and the top of the dip pipe. The flask containing the carbon dioxide slurry was then placed so that the polythene tube reached inside to the bottom. Tap B was then turned to direct nitrogen into the metalation reactor and tap A was turned to shut off the nitrogen but allow solution to be passed out of the reactor into the slurry. The metalation reactor was thus under a slight positive pressure of nitrogen from the top of the condenser, which forced the metalated solution out of the reactor through the dip pipe and tube into the solid carbon dioxide slurry. The flask containing the slurry was vigorously shaken



by hand to ensure thorough mixing. As the polymer contacted the carbon dioxide the red colour was destroyed. After all the solution had passed into the carboxylation flask the solid carbon dioxide was allowed to evaporate. The flask contents were then processed to isolate and purify the polymer.

#### 2.2.2. Product Purification.

As will be described in section 3.2.2, two methods were developed for purification. The precipitation method was suitable for polymers with acid values up to about 15 but for polymers with higher acid values, difficulty was experienced in redissolving the polymers after precipitation so a column method was developed which removed the byproducts without requiring isolation of the polymer.

##### 2.2.2.1. Precipitation method.

The free acid form of the carboxylated polymer was obtained by adding a few drops of concentrated hydrochloric acid to the solution formed after carboxylation. This dispersed the loose gel of the metal salt solution and the polymer was then precipitated by adding acetone. The solvent was decanted and the polymer squeezed to remove loose solvent. The recovered polymer was purified by twice dissolving in carbon tetrachloride and precipitating with acetone and was then vacuum dried at 60°C. The product was apparently free of non-polymeric acid compounds following this treatment as acid value determinations conducted before and after a further re-precipitation gave the same results.

#### 2.2.2.2. Purification on column.

A 25mm internal diameter, 1m long glass column was filled with coarse alumina and carboxylated polymer solution was filtered through it after acidification. This was a fairly lengthy procedure because of the viscosity of the solution. The eluant was found to be completely neutral to moist<sup>t</sup> indicator paper indicating that all non-polymeric acid compounds had been removed by this treatment. The acid value determination or subsequent neutralisation could then be carried out directly on the eluted solution. The effectiveness of the column treatment was checked by passing some purified solution through a second column, no change in acid value was detected.

#### 2.2.3. Preparation of Metal Salts of Polymers.

In some instances the crude salt formed by carboxylation was isolated without acidification by precipitation with acetone then drying in a vacuum oven at 60°C. In this way wholly neutralised carboxylate polymers were obtained but these inevitably still contained some of the side products from carboxylation, mainly valeric acid salts formed by carboxylation of excess metalating agent. These could not be removed as the polymer in its salt form would not redissolve.

The best method of producing the pure metal salts was either to dissolve the purified free acid form of the polymer, or use solution directly from a purification column and then react this in solution with a solution of e.g. sodium methoxide in methanol. The amount of sodium methoxide added was calculated from the acid value of the polymer. In some instances 100% neutralisation of the acid groups was carried out and in others only 75%. The neutralised polymers remained semi-soluble provided the solution concentrations were kept fairly low (~1%) and the proportion of hexane to methanol was above about 2 : 1.

The reactants were stirred together for about 2 hrs. to ensure complete reaction; the polymer was then isolated by precipitation with methanol and dried via vacuum oven at 60°C.

#### 2.2.4. Product Analysis and Evaluation.

##### 2.2.4.1. Iodine Number.

The level of unsaturation in the EPDM's employed in this work was determined by the method of Lee, Kolthoff and Mairs<sup>(80)</sup>. A solution of the polymer was treated with iodine monochloride in at least a 60% excess. The mixture was allowed to stand for half an hour in the dark to allow reaction to occur. (It was kept in the dark to ensure that reaction occurred via addition rather than free radical substitution). Potassium iodide solution was added to liberate iodine from the excess iodine monochloride and the free iodine was titrated with standard thiosulphate solution using a soluble starch indicator. The result was quoted as an iodine number, that is, the equivalent number of grams of iodine which had reacted with 100 g. of polymer.

##### 2.2.4.2. Acid Value.

The carboxyl content of the polymers was determined by a standard acid-base titration. The polymer was dissolved in toluene/ethanol or hexane/ethanol mixture then titrated with standard potassium hydroxide in ethanol. The end-point was determined using a pH meter and results calculated as acid value, this being the number of milligrams of potassium hydroxide required to neutralise one gram of polymer.

#### 2.2.4.3. Infra-red Analysis.

Infra-red analysis was carried out using a Unicam SP 200 Spectrophotometer. The samples were prepared by casting thin films from solution onto sodium chloride discs. Some of the spectra obtained are illustrated in section 3.2.6.

#### 2.2.4.4. Differential Scanning Calorimetry.

The ionic dissociation temperature of the salt of a carboxylated polymer was investigated using a Perkin Elmer DSC 1B differential scanning calorimeter. A sample of polymer of approximately 10-15 mg was placed in an aluminium dish and sealed by crimping. An empty aluminium dish was used as the reference. The temperature was increased at a rate of 16 deg. C/min and any imbalance between the energy input to the two aluminium dishes was displayed graphically.

#### 2.2.4.5. Physical testing of products.

Test sheets of polymer were compression moulded at 200°C under a pressure of 2000 p.s.i. The polymer was cooled to about 100° before release of pressure and was obtained in a sheet about 0.5 mm thick. Test dumb-bells were cut using a standard cutter and pulled on an Instron tester, using the standard conditions employed for rubber compounds, to determine ultimate tensile strength and elongation at break. The method used is described in detail in part 1. section 2.2.4.2. and generally accorded to the British Standard test procedure<sup>(81)</sup>.

## 2.3. STYRENE GRAFT POLYMERISATION.

### 2.3.1. Grafting procedure.

A discussion of some of this work is presented in section 3.3.4., where some of the problems which arose in the preparation of pure styrene and in the dispersion of the styrene in the metalated polymer solution are discussed.

#### 2.3.1.1. Styrene purification.

The styrene as supplied contained a phenolic stabiliser which had to be removed along with moisture, air and any polymer that might be present. The method adopted was a simple distillation under reduced pressure using a 6" reflux column containing pellets of 4A molecular sieve. The receiver adapter was fitted with a syringe<sup>needle</sup> connection to a dried nitrogen flushed,  $\frac{1}{2}$  pint, rubber sealed, crown capped bottle. After a suitable amount of styrene had been distilled, the receiver bottle was disconnected, cooled in an ice bath, flushed for 1 hr with pure nitrogen and finally pressurised with 20 p.s.i. nitrogen.

In early experiments the distilled styrene was stored in a deep freeze at  $-20^{\circ}\text{C}$  and aliquots were withdrawn as required. However, it was found that even at this temperature some polymerisation could occur over a period of time. To avoid this eventuality styrene was distilled immediately before use.

#### 2.3.1.2. Graft polymerisation.

The basic procedure was to add styrene by syringe to a bottle containing the metalated polymer. Dispersion of the styrene throughout the rather viscous solution proved somewhat difficult and if the styrene was added to the bottle at room temperature then polymerisation commenced immediately, before dispersion could occur. This inhomogeneity showed as opaque, pale pink particles within the clear red solution.

The problem was overcome by cooling the bottle of metalated solution to  $0^{\circ}\text{C}$  before adding the styrene. The bottle was then shaken and fixed on to a rotating arm situated in a water bath cooled to about  $5^{\circ}\text{C}$ . It was then rotated for about 1 hr to disperse the styrene. During this period very little polymerisation occurred. The temperature of the water bath was then raised to  $70^{\circ}\text{C}$  and polymerisation was carried out for 2 hr to ensure complete conversion. At the end of this period the solution appeared quite homogeneous, being slightly opaque and pinkish-red in colour.

#### 2.3.1.3. Product purification.

At the end of the graft polymerisation 5 ml of 10% conc. HCl in methanol were added to terminate the chain ends. The product had then to be isolated and any ungrafted homopolystyrene extracted, this was generally carried out by a simple precipitation technique. The polymer was first precipitated from solution using acetone, the solvent was decanted and the polymer then redissolved by carbon tetrachloride. It was then reprecipitated twice using  $\text{CCl}_4$  and acetone. The product was then dried in a vacuum oven at  $60^{\circ}\text{C}$ . The decanted liquors from each precipitation were collected together and evaporated so that the ungrafted homopolystyrene could be collected.

This extraction procedure was clearly effective for poorly grafted materials, as in a few cases, all the styrene added was removed as ungrafted homopolystyrene, a check was necessary to see if it was also satisfactory for highly grafted polymers. Styrene contents were determined on samples purified as described and the polymers were then further extracted for 4 h. in a Soxhlet apparatus using an acetone/hexane mixture. No change in styrene content was detected after the further extraction.

## 2.3.2. Product analysis and evaluation.

### 2.3.2.1. EPDM molecular weight.

The molecular weight of Intolan 155 was determined before grafting was carried out to enable a calculation of the number of grafts per chain to be made (section 3.3.1.). This was measured using a Mechrolab membrane osmometer according to the method of Steele et al.<sup>(144)</sup>

Solutions of the polymer were made up in toluene with concentrations varying between 1g and 10g/l. . . The osmotic pressure of each of these solutions was measured in terms of cm. of toluene at 25°C. A plot was made of osmotic pressure divided by concentration ( $\pi/c$ ) versus concentration. The resulting curve was extrapolated to zero concentration and the number average molecular weight then calculated using the formula,

$$\bar{M}_n = \frac{R.T.}{\langle \pi/c \rangle_c = 0}$$

The temperature T was 298°K, and the gas constant R, in pressure units, was taken as 2.91 cm<sup>3</sup> toluene °K<sup>-1</sup> mole<sup>-1</sup>.

### 2.3.2.2. Styrene Content.

The determination of styrene content was carried out by refractive index measurement, other methods being unsuitable (see section 3.3.1). This required that the refractive index be determined of the unmodified EPDM, some ungrafted polystyrene and the styrene grafted EPDM. These were measured using an Abbé refractometer at 25°C using sodium light. Films of the polymers were pressed at 150°C to a thickness of approximately 0.5 mm and these were then clamped onto the refractometer prism, ensuring that a good contact was made.

The styrene content of the grafted polymer was calculated from the following formula.

$$\text{Styrene content (weight \%)} = \frac{\mu_{\text{graft}} - \mu_{\text{EPDM}}}{\mu_{\text{PS}} - \mu_{\text{EPDM}}} \times 100$$

#### 2.3.2.3. Polystyrene molecular weight.

This was determined by gel permeation chromatography using a Waters Associates chromatograph.

G.P.C. is a form of sieve or exclusion chromatography in which separation of polymer molecules is effected on the basis of hydrodynamic volume. The column is packed with a material of controlled microporosity in the present instance a cross linked polystyrene gel, in which the pore size lies within the range of molecular diameters of the mixture to be separated. In the case of polymer analysis it is usual to use several columns in series, each having a different pore size in order to effect a reasonable degree of selection. Molecules excluded from the packing pass through the column at the same speed as the eluant solvent whereas those capable of diffusing into the packing elute at a slower rate. Thus in contrast to gas chromatography the highest MW fraction appears first, followed by fractions of successively lower MW.

For the present work the instrument was operated with toluene solvent and differential refractometer detector. Conditions were:

Column temperature 65°C; 4 x 4 ft columns in series, each approx. 480 TP/foot.

Detector temperature 53°C.

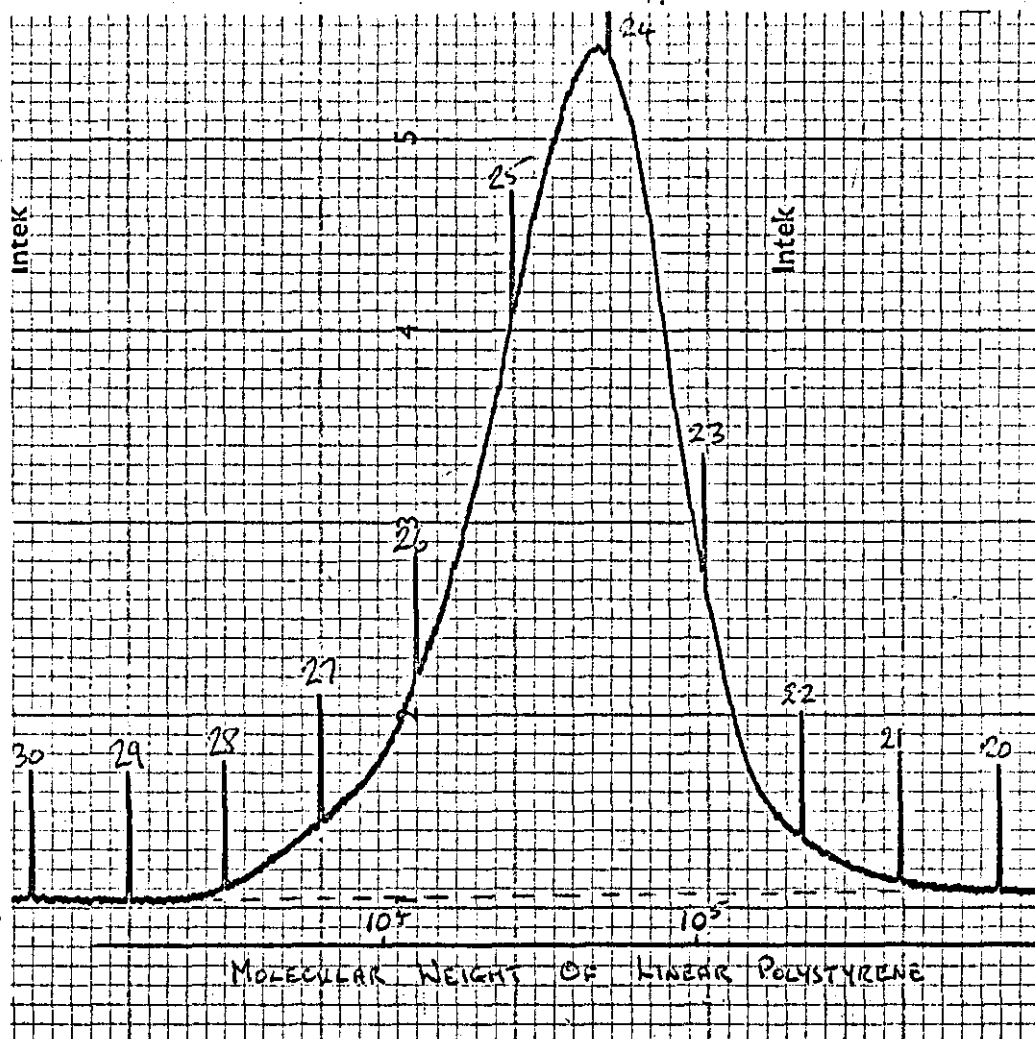
Injection port and eluate volume syphon were operated at ambient temperature as there was no problem of polymer precipitation.

Polymer sample concentration 0.25% w/w; sample size 0.25 ml.

A typical chromatogram is presented in Figure 2.2. The numbered



FIGURE 2.2. Polystyrene Gel Permeation Chromatograph.



pulses represent 5 ml increments of eluant, these being recorded automatically by means of pulsed signals from the eluant volume syphon. The number average molecular weight calibration with standard polystyrene is indicated along the horizontal axis. For the present work it was found sufficiently accurate to take the peak position as indicating the number average molecular weight of the polystyrene sample.

#### 2.3.2.4. Infra-red analysis.

This was carried out as described in section 2.2.4.3. Examples of spectra are given in section 3.3.9.

#### 2.3.2.5. Physical testing of products.

Test sheets were compression moulded at 150°C and 2000 p.s.i. Test dumb-bells were cut from this using a standard cutter and tested according to the British Standard test procedure<sup>(81)</sup>. This is discussed in more detail in the experimental section of the hydrogenation study.

### 3. RESULTS AND DISCUSSION.

#### 3.1. METALATION REACTION.

##### 3.1.1. General.

The aims of this study of metalation were:

- (i) To find a suitable method for the metalation of EPDM rubbers.
- (ii) To evaluate the effect on the metalation reaction of a number of variables.
- (iii) To achieve optimum thermoplastic and elastomeric properties by the variation in the degree and type of modification.

An essential part of this programme was the development of a reliable method for estimating the extent of the metalation reaction. A standard procedure for the estimation of organometallic compounds is the "Gilman double titration"<sup>(145)</sup>. This however is lengthy and does not distinguish between organometallics of high molecular weight, i.e. metalated polymer, and unreacted metalating agent.

The best method for determining the extent of metalation was found to be to carry out the subsequent modification, i.e. carboxylation or styrene grafting and then analyse these products for either carboxyl content by titration or for styrene content by a refractive index method.

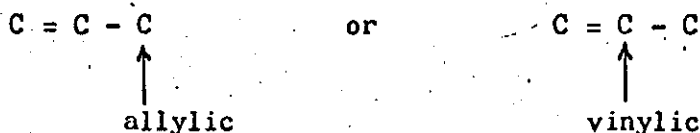
It is difficult therefore to discuss the factors affecting the metalation reaction without consideration of the subsequent modifications. For this reason, only a brief resume of the combined results will be given in this section and the more detailed results will be dealt with under the separate carboxylation and styrene grafting sections.

The general procedure adopted in the present work for carrying out the metalation reaction was to add the appropriate organometallic reagent to a suitably purified solution of an unsaturated polymer, and then heat this mixture, with stirring, under nitrogen, for a few hours. A polymer product having "live" anionic sites distributed along the chains was thus obtained. In the present study these products were further treated by the addition of either carbon dioxide to give carboxylated products or styrene to give grafted polystyrene products.

The mechanism of hydrocarbon metalation has been investigated by a number of people. (113, 116, 122, 133) The earlier work was conducted using potassium or sodium, alkyls with non-polymeric substrates but more recently the (128) metalation of polybutadiene and polyisoprene has been investigated using n-butyllithium, N, N, N', N' - tetramethylethylenediamine (TMEDA) complex as metalating agent.

In general, there are two possible alternative metalation sites, either allylic or vinylic.

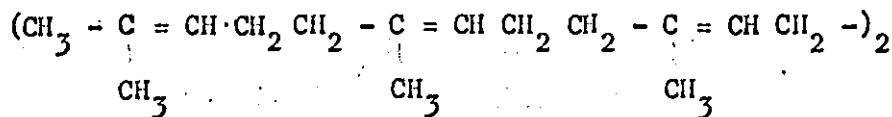
i.e.



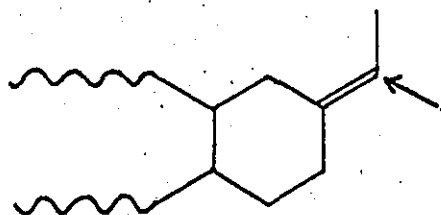
Alkylpotassium compounds have been shown to favour attack at the allylic position and alkylsodium compounds favour the vinylic position. However in the case where the vinyl positions are adjacent to alkyl substituents then reaction favours the allylic position even in the case of the alkylsodium compounds.

The investigation into the metalation of polydienes was carried (128) out using squalene as a model compound. Squalene is a liquid having

the following formula,



It can be seen that all of the vinylic positions have adjacent alkyl substituents and so it is perhaps not surprising that investigation lead to the conclusion that using n-butyllithium, TMED, as metalating agent, substitution occurred at the allylic position. These results do not therefore indicate which position would be substituted in the case of an unsubstituted olefinic linkage such as occurs in polybutadiene, for this reason, squalene is not the ideal model for all polydienes. However, the majority of the present metalation work was carried out on an EPDM having ethylidenenorbornene as termonomer,



~~~~~ representing the polymer chain. In this case, it can be seen that the <sup>vinylic</sup> ~~allylic~~ position, arrowed, is adjacent to an alkyl substituent and it is therefore safe to say that metalation will occur at an allylic position.

### 3.1.2. Solvent selection and purification.

The modified polymer products from this study are potentially very useful commercially. For this reason the selection of operating conditions and choice of solvents always involved a consideration of their commercial suitability. In the choice of solvent the factors involved are, availability; low cost; reasonably low boiling point to enable the use of low pressure steam for recovery; inertness with respect to the desired metalation reaction.

Hexane was regarded as fulfilling all these conditions; it is in fact extensively used as a solvent for solution polymerisation. However, when commercial hexane was used in preliminary experiments it was found, surprisingly, that although the catalyst complex produced a deep red colour characteristic of delocalised carbanions no polymer metalation had in fact been achieved. Investigation revealed that the hexane contained aromatics (mainly benzene) in amounts sufficient to react with all the available catalyst and it was found later from the literature that other workers had made the same discovery. For example, the metalation of benzene by n-butyllithium, tetramethylethylenediamine complex has been reported by a number of people, <sup>(116,118,146)</sup> a typical reaction being the conversion <sup>(116)</sup> of benzene to phenyllithium in thirty minutes at 80°C.

In an attempt to remove the aromatics from the hexane, sulphuric acid washing was tried but was found to be most unsatisfactory, at least at the levels relevant to the present work. Not only was the procedure itself unattractive, the amount of acid required to effect a reduction from 0.2% to 0.033% was of the order 4:1 with respect to hexane. Furthermore, prolonged contact was necessary and extensive washing with water was subsequently required to remove the sulphonated products.

An alternative procedure, described by Murray and Keller<sup>(142)</sup>, was therefore tested. This was found to be entirely practicable and effective. It involved treatment of the hexane with alumina impregnated with silver nitrate. The treated alumina was made up into a column and the hexane then passed through it. The eluted hexane was found to be totally free of unsaturated compounds and thus completely inert towards the metalation reaction. This procedure had the added advantage in that it produced a comparatively dry product.

However, from a commercial standpoint such a process would be impracticable and in this case, hydrogenation or selective adsorption on an 'X' type zeolite sieve would be considered.

### 3.1.3. Polymer solution preparation.

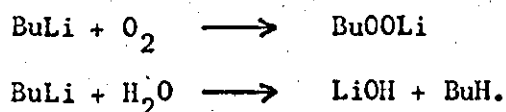
As a "living", anionic polymer system was being dealt with, measures had to be taken to ensure that the reaction was carried out in the total absence of water, air and other impurities. This was most important when attempts were being made to produce a thermoplastic elastomer by styrene grafting. In this case it was desirable that a very specific product be obtained with, if possible, 100% graft efficiency; a selected number of grafts per chain; and grafts having a specific molecular weight. The presence of any impurities would have made this objective impossible.

The methods first tried to dry the polymer solutions were found to be quite inadequate and numerous modifications had to be made before a suitable system was obtained. The procedure used at first, involved drying the hexane solvent and rubber separately and then making up the solution under nitrogen. This gave very poor results but was improved by

scavenging the solution with n-butyllithium prior to the addition of the metalating agent. The scavenging procedure was monitored using the Michlers ketone colour reaction. This had been used previously<sup>(143)</sup> to detect the presence of Grignard reagents but was found, in this case, to be very suitable for the detection of n-butyllithium.

The solution to be metalated was first treated with a small known amount of n-butyllithium; a small aliquot was then taken and tested with the Michlers ketone. The addition of n-butyllithium was continued until a positive test was obtained. In this way a solution was obtained containing a very slight excess of n-butyllithium, most of the impurities having been neutralised.

The two main impurities were oxygen and water, reacting thus:



Both products might be expected to react further with n-butyllithium and its reaction with lithium hydroxide has in fact been reported<sup>(147)</sup>. The significance of further reaction is that, if slow, it may not occur during this quick scavenging process and may therefore lead to depletion of active metal alkyl during the metalation reaction itself. It is probably for this reason that although a considerable improvement in results was obtained using this technique, consistency was still not achieved.

In an attempt to further reduce the level of polar impurities, the polymer solution was passed through activated alumina and de-oxygenated prior to treatment with n-butyllithium. This reduced the scavenging level but not to the desired extent.



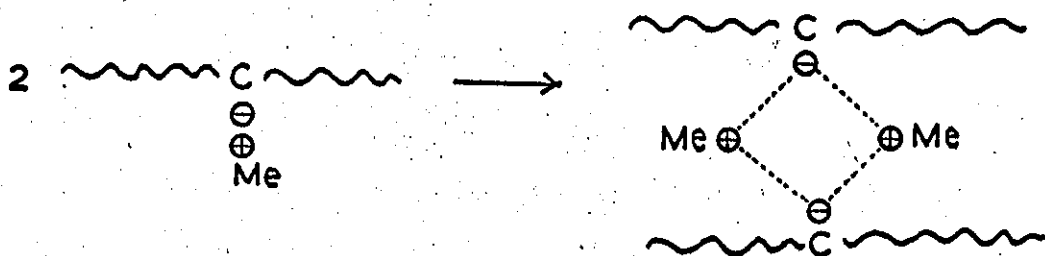
The method finally adopted was to pretreat the polymer solution with n-butyllithium and then pass it through a column containing silica gel and alumina directly into the reactor to be used. This procedure removed the products of scavenging very efficiently and left a solution which required the addition of only a very low level of n-butyllithium before a positive Michlers ketone test was obtained.

In this way, very pure, dry polymer solutions were obtained and when dearomatised hexane was used as the solvent, an excellent medium for metalation resulted.

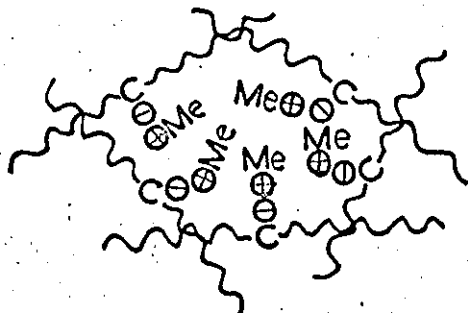
The concentration of polymer solution used was dictated by the extent of metalation that was required. In general, as the degree of metalation was increased, so the solution viscosity increased. If high levels of metalation were required as in the carboxylation study then low starting concentrations had to be employed so that the viscosity of the treated solution was kept within a reasonable limit.

This phenomenon of increased solution viscosity on metalation was found to be due to ionic association of the polymer chains. This was demonstrated by the fact that if the metalated sites were destroyed by the addition of, for example, concentrated hydrochloric acid, then the solution viscosity reverted to the same level obtaining before metalation.

The ionic association probably occurred either through pair formulation,



where  $\ominus$  is a chain carbanion produced by metalation and  $\oplus$  is the associated metal cation, or by cluster formation such as,



A metalated polymer solution probably contained both types of species, the ionic cluster structure predominating at high levels of metalation and the pair structure at low levels of metalation.

#### 3.1.4. Metalating Agent.

Detailed discussion of the effects of different metalating agents is presented in Sections 3.2. and 3.3.

The initial choice of metalating agent was of course determined by information available in the literature where much of the work reported involved the use of the n-butyllithium, tetramethylethylenediamine (TMED) complex.<sup>(121,128,129,148)</sup> Some work was undertaken to determine its suitability but it was found that although, as reported, it was remarkably effective with highly unsaturated polymers, reaction efficiency toward EPDM was disappointing.

A search for a more active metalating agent led to consideration of the n-butyllithium, potassium t.butoxide complex. Potassium t.butoxide had been shown to act in a similar manner to polar ethers and TMED, when used in the n-butyllithium polymerisation of dienes<sup>(132)</sup> and the copolymerisation of butadiene and styrene<sup>(76)</sup>. In the former case it substantially increased the rate of polymerisation and vinyl unsaturation in polybutadiene and in the latter case it allowed the preparation of random copolymers with various amounts of vinyl unsaturation and various

degrees of randomness.

In the metalation of t-butylbenzene with n-amylsodium, sodium t.butoxide had been shown to give a much higher yield than could be achieved in its absence.<sup>(133)</sup>

At first the only direct reference found to the use of n-butyllithium, potassium t.butoxide in metalation was in a paper published by Schlosser<sup>(149)</sup>. This discussed the metalation of aromatics and furan and stated that potassium alkoxides enhanced the reactivity of organolithium compounds even more than polar ethers.

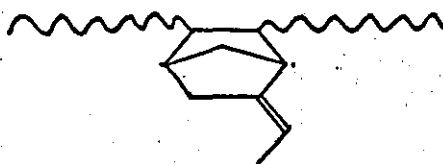
After the start of the present work a patent was published by Firestone<sup>(150)</sup> disclosing the use of organolithium - metal alkoxide reagents for the metalation of polymers. EPDM was mentioned in the claims but no examples were given of its use.

An investigation of the n-butyllithium - potassium t.butoxide metalation of EPDM was therefore carried out. Unfortunately, all of the methods investigated for the preparation of potassium t.butoxide resulted in the formation of a 1:1 complex with t.butanol. The pure butoxide could only be obtained from this complex by a vacuum sublimation technique. The butoxide used by Schlosser was prepared using this procedure however, before this was adopted in the present work an evaluation was carried out using the 1:1 complex. It was found, perhaps surprisingly, that nBuLi - KOt.Bu:tBuOH was a very efficient reagent for the metalation of EPDM and the results obtained with this material were far superior to those obtained using nBuLi - TMED complex. However, the disadvantage with this reagent was that it contained an unknown number of active metalating species. Clearly, some of the butyllithium would have reacted with the t butanol to form lithium t.butoxide. This product could then have complexed with more butyllithium to form species having no metalation activity. Only the remaining butyllithium could have complexed with the potassium t.butoxide to form active metalating agent.

In order to avoid this complication it was decided to purify the potassium t.butoxide by vacuum sublimation. The complex with n-butyllithium was found, as expected, to be extremely efficient with the advantage that it was certain that all the butyllithium added could form active metalating agent.

### 3.1.5. Polymers.

It was hoped that useful products might be obtained by the modification of cheap, commercially available polymers especially those made by the rubber industry. Practical considerations also required that a single material of known and reproducible characteristics be used for a large proportion of the work. Intolan 155, manufactured by The International Synthetic Rubber Company was therefore selected as fulfilling these requirements. This was a copolymer of ethylene and propylene containing ethyldenenorbornene (ENB) to introduce a controlled amount of unsaturation. The molar ratio of ethylene to propylene was 60:40 and the iodine number was 18-20. The monomer unit was polymerised through its least substituted double bond being incorporated thus,



The monomer units were randomly distributed throughout the polymer, a chain sequence can therefore be represented as,

- E - E - E - P - E - P - P - T - E - E - P - E - P - P - E - E - T - E

where the units are,

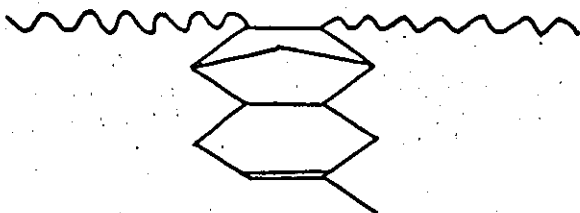
E - ethylene

P - propylene

T - ethylidenenorbornene

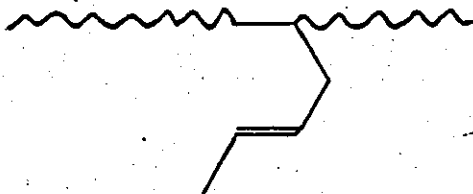
Two other ethylene propylene terpolymers, having similar E:P ratios, were investigated but not to the same extent as the ENB polymer. These were;

1. A laboratory prepared rubber containing endomethylenhexahydronaphthalene (EMHN) as termonomer, incorporated thus,



Unfortunately, the method of preparation was limited in that an iodine number of 10 was the maximum that could be achieved.

2. Nordel 1040, commercially produced by Du Pont, having 1,4 hexadiene (HD) as termonomer. This had an iodine number of 18 and the termonomer was incorporated thus,



The polymers were not especially purified prior to use in metalation reactions as it was known from experience that all impurities could be removed effectively by the treatment of the polymer solution outlined above. Samples were however dried in a vacuum dessicator before use.

### 3.1.6. Reaction Conditions.

The effects of reaction conditions will be discussed in detail where appropriate. However, it may be noted that in order to obtain a satisfactory degree of reaction, temperatures in the region 40-80°C were necessary and reactions were allowed to proceed for up to 5 h. The level of metalating agent chosen was determined by the degree of modification being attempted. In general, levels used for the carboxylation process were much higher than for the styrene grafting.

### 3.2. CARBOXYLATION.

#### 3.2.1. General.

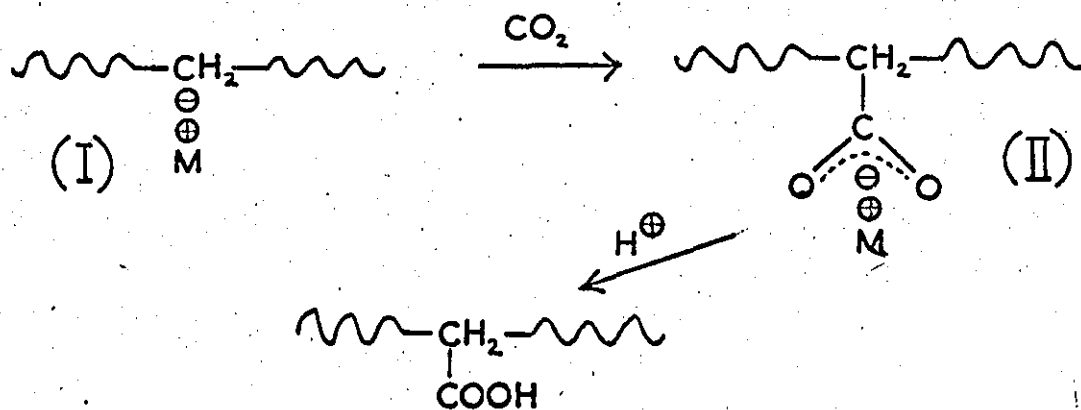
The aims of this part of the study were:

1. To develop a suitable procedure for the preparation of carboxylated EPDM via metalation.
2. To obtain a thermoplastic elastomer product crosslinked through ionic metal carboxylate linkages.

Before these aims could be achieved the following had to be investigated:

- (a) The development of procedures for the carboxylation reaction, the purification of products and the preparation of the metal carboxylate products.
- (b) The choice of a suitable metalating agent and polymer substrate.
- (c) The selection of reaction conditions and metalating agent levels to optimise the properties of the products.

The results obtained from these investigations are given and discussed in the following sections; however, one point to be brought out here is that the carboxylation procedure used in this work results in the immediate production of a metal carboxylate polymer product, the free acid polymer only being obtained after neutralisation with acid. This process can be represented as follows,



Where (I) represents a metalated segment of polymer chain,  $\text{M}^{\oplus}$  being the metal cation. The product ultimately desired from this study was a metal carboxylate polymer rather than a polymer containing free carboxyl groups and it might be thought that isolation of the intermediate (II) would result in the desired product. This would of course be highly attractive from the commercial point of view but in the present study this was unsatisfactory for the following reasons.

- (i) The metal counter ion could not be varied as it was determined by the metal ion in the metalating agent.
- (ii) The effect of only partial neutralisation of the acid groups would have been very difficult to determine.
- (iii) It was found very difficult to remove free metal salts which had been formed by carboxylation of excess metalating agent.
- (iv) For most of this work it was necessary to determine the acid value of the carboxylated polymer so that an estimate could be made of the extent of reaction.

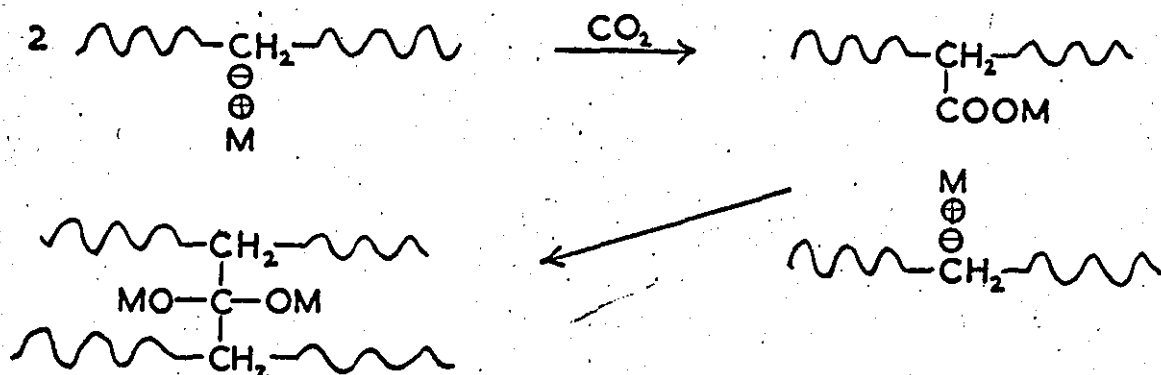
In commercial practice these difficulties might be overcome, however for the present it was desired that the products be isolated as the free acid.



### 3.2.2. Technique Development.

Two techniques required development. The first was the actual carboxylation procedure wherein the metalated polymer solution was reacted with carbon dioxide. The second was the purification procedure during which by-products were removed from the carboxylated polymer.

A prerequisite of the carboxylation technique was that the metalated polymer should be brought rapidly into contact with a large excess of carbon dioxide. This was to avoid crosslinking reactions of the type:-



caused by the reaction of a metalated site with the carboxylated site  
(121,148)  
of another polymer chain.

This possible side reaction precluded the use of the simplest technique i.e. passage of dried carbon dioxide gas through the metalated polymer solution, so alternative procedures had to be investigated.

(116,151)

The standard technique mentioned in the literature was to pour the metalated solution onto crushed, solid carbon dioxide. This had to be modified for the reasons that moisture very quickly condensed on the surface of the  $\text{CO}_2$ , from where it could react preferentially, also it was very difficult to achieve good contact between the polymer solution and the solid. The latter difficulty was aggravated by the fact that the polymer solution formed a loose "gel" on carboxylation. These difficulties were overcome by using a slurry of solid carbon dioxide powder in petroleum spirit. This was made up in a dry bag flushed with nitrogen;

the metalated polymer solution was then blown, with nitrogen, out of the reactor through a tube directly into the vigorously stirred slurry. After the solid carbon dioxide had sublimed the carboxylated polymer was obtained as a solution, often in the form of a loose ionic gel due to the association of chains through the metal carboxylate groups. This "gel" was broken by the addition of a few drops of concentrated hydrochloric acid.

The product had then to be isolated in pure form. The main impurities to be removed were those formed by the hydrolysis of products formed by the carboxylation of excess metalating agent viz. LiCl, KCl t-butanol and valeric acid. Removal of the valeric acid was especially important as this interfered with the determination of the degree of carboxylation. Initially it was found quite satisfactory to precipitate the polymer from solution using acetone, redissolve in carbon tetrachloride then effect a further precipitation with acetone. The valeric acid could be recovered from the precipitant liquor and the sufficiency of this procedure could be proved by redissolving and precipitating the polymer once more. In this case, no more valeric acid could be detected in the precipitating liquor. This procedure worked well with polymers having a low degree of carboxylation but with material having an acid value in excess of 15 difficulty was experienced in redissolving the polymer, in non acidic solvents, after the initial precipitation. Acid value determinations could not then be carried out as the procedure required the sample to be in solution for titration against sodium methoxide solution. A method was therefore sought whereby the highly carboxylated polymer could be purified without isolation from solution.

The final procedure adopted was to pass the acidified polymer solution through a column of activated, granular alumina. This proved extremely successful in removing the by-products of metalation and produced a polymer solution that could be directly titrated for acid value or treated by any other process such as neutralisation to form polymer metal carboxylate or the addition of processing aids.

### 3.2.3. n-Butyllithium/TMED. as metalating agent.

Initial metalation experiments were carried out using n-butyllithium/N, N, N', N' tetramethylethylenediamine (TMED)<sup>(128)</sup>. The conditions chosen were similar to those described by Minoura<sup>(128)</sup>. Reactions were carried out on a laboratory prepared EPDM (207/128) with endomethylenhexahydronaphthalene (EMHN) termonomer and iodine number 10. 10g of polymer was dissolved in 700 ml of hexane, various ratios of n-butyllithium/TMED<sup>3</sup> were added and then reacted for 5 h. at temperatures of 60°C or 80°C. The results obtained are summarised in Table 3.1.

TABLE 3.1: n-BUTYLLITHIUM/TMED.

| BUTYLLITHIUM<br>AMOUNT<br>(m.moles) | TMED<br>AMOUNT<br>(m.moles) | REACTION<br>TEMPERATURE (°C) | PRODUCT<br>ACID<br>VALUE |
|-------------------------------------|-----------------------------|------------------------------|--------------------------|
| 10                                  | 10                          | 60                           | 0.7                      |
| 10                                  | 10                          | 80                           | 0.5                      |
| 10                                  | 5                           | 60                           | < 0.5                    |
| 10                                  | 2.5                         | 60                           | 0.7                      |
| 10                                  | 3.3                         | 60                           | < 0.5                    |
| 10                                  | 20                          | 60                           | < 0.5                    |
| 20                                  | 20                          | 60                           | 0.5                      |

It can be seen that very little success was achieved under any conditions.

According to the literature a 1:1 ratio of n-butyllithium to TMED should give the most active complex<sup>(114,118,128)</sup> but from these results the equimolar complex is seen to be no more effective than the others. Similar difficulty in the metalation of EPDM was apparently experienced by Pope et al. In their patent<sup>(152)</sup> on polymer grafting and metalation using this reagent the only example given of the metalation of EPDM shows a very low level of efficiency. An attempt to graft styrene to this product could not have been very effective judging from their statement, "The amount of grafted polystyrene was difficult to measure, probably owing to the comparatively small amount present".

This is probably not surprising when one compares polybutadiene which can be easily metalated with this reagent,<sup>(128,130,152)</sup> and a typical EPDM.

Both have similar reactive sites i.e. ethylenic double bonds but the concentrations are widely different since EPDM generally has an iodine number in the region of 10-20 whereas the value for polybutadiene is approximately 470, a factor of thirty greater.

#### 3.2.4. n-Butyllithium/potassium t.butoxide.

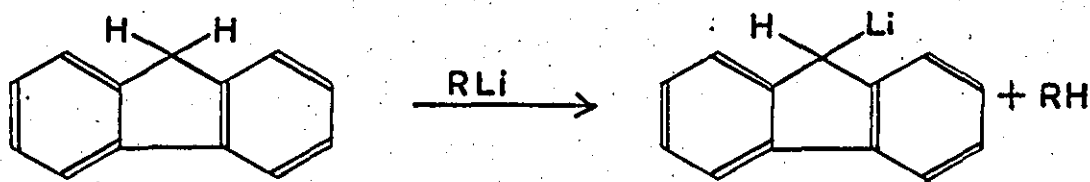
It was mentioned in section 3.1.4. that metalation reactions had been carried out using butyllithium in conjunction with either pure potassium t.butoxide or potassium t.butoxide, t.butanol 1:1 complex. In the carboxylation work, results were only obtained using the pure potassium t.butoxide. A comparison of the two metalating agents is given in the section on styrene grafting (3.3.4).

The polymer metalated with this reagent was the same as that discussed in the previous section (3.2.3.) and attempts were made to metalate and carboxylate to as high a level as possible. Metalation reactions were

carried out for either  $2\frac{1}{2}$  h. or 5 h. and various levels of metalating agent were employed.

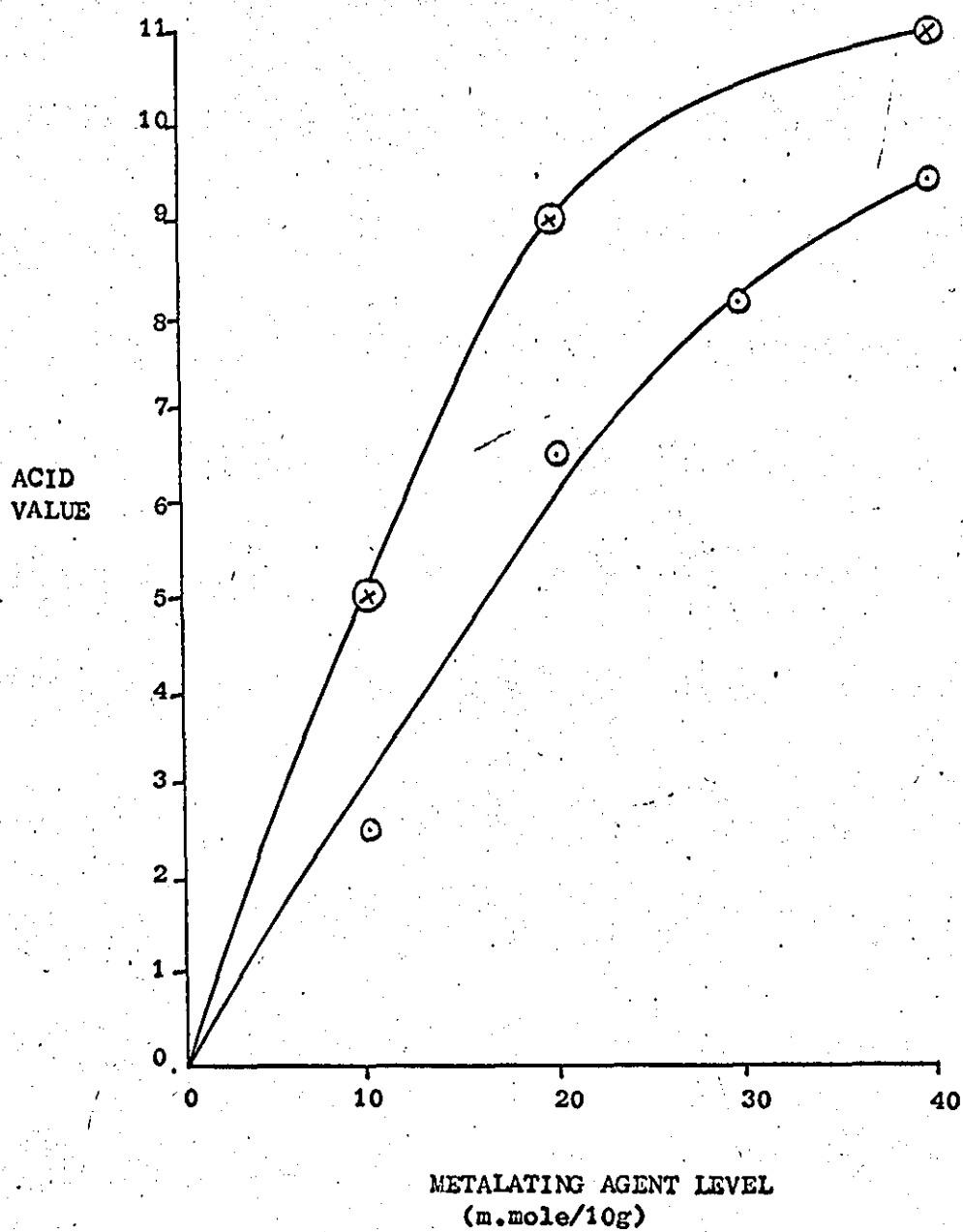
The results obtained by carboxylation of the metalated polymers are shown in figure 3.1. It can be seen that the extent of metalation increased with increasing metalating agent level up to a maximum at which a carboxylated product with an acid value of about 11 was obtained.

The extent of metalation can also be seen to be affected by the length of time for which the reaction was carried out, 5 h. periods giving products with higher acid values than those carried out for  $2\frac{1}{2}$  h. However at high levels of metalating agent, reactions carried out for both periods of time gave products which tend towards a similar maximum in acid value. Reaction periods longer than 5 h. were found to give no further improvement in degree of carboxylation. If these results are compared with those obtained using n-butyllithium/TMED<sup>1</sup> as metalating agent (Table 3.1) it is obvious that the potassium t.butoxide complex is far more effective. A possible reason for this is as follows. Alkyl lithium compounds on their own are poor metalating agents for hydrocarbons though they will react provided they contain a sufficiently acidic hydrogen atom as for example in fluorene and similar materials<sup>(153)</sup>.



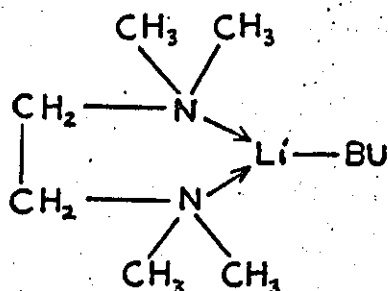
The reactivity of alkyl lithium is considerably increased if they are made more polar by reaction with electron donors or indeed using a polar medium. Thus the complex of n butyllithium with the bidentate electron donor TMED<sup>(146,151)</sup>

FIGURE 3.1. THE EFFECT OF REACTION CONDITIONS  
ON ACID VALUE.



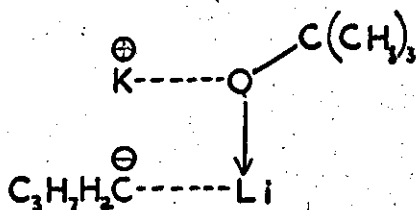
○ 2½ h. REACTION

⊗ 5 h. REACTION.



has considerably enhanced activity and will allow the substitution of hydrogen atoms far less acidic than would be required for n butyllithium on its own. Clearly the more ionic the complex the greater the reactivity, and this would seem to be the case when n butyllithium is complexed with potassium t.butoxide.

Lochmann, Pospisil and Lim<sup>(155)</sup> have made a study of the interaction of organolithium compounds with sodium and potassium alkoxides and state that if n-butyllithium is reacted with potassium t.butoxide in an equimolar ratio then a 1:1 adduct is formed. Schlosser<sup>(149)</sup> postulates the structure as being,



If this is correct the active portion of the complex is probably dissociated n butylpotassium rather than n butyllithium. However whatever the case the fact remains that this complex is highly ionic in nature and this would explain it acting as an excellent metalating agent.

### 3.2.5. Metalation of different terpolymers.

The previous section discussed the results obtained from the metalation and carboxylation of a laboratory prepared terpolymer having endomethylene-hexahydronaphthalene (EMHN) as termonomer and an iodine number of 10. The highest degree of carboxylation that was achieved with this polymer was equivalent to a polymer acid value of 11 and the appearance of this product suggested that a higher carboxyl content was needed in order to achieve the desired properties. Two other EPDMs were therefore selected for study on the basis of their comparatively high levels of unsaturation. These were commercial polymers, Intolan 155, manufactured by the International Synthetic Rubber Company using ethylidenenorbornene (ENB) as termonomer, and Nordel 1040 manufactured by Du Pont using 1,4-hexadiene (HD) as termonomer. The iodine numbers of these polymers were in the region of 18-20. Metalations were carried out on 10g polymer with various levels of n-butyllithium/potassium t.butoxide metalating agent, at 60°C for 5 h and the products then carboxylated. The acid values of these polymers were then compared with those previously obtained using the EMHN terpolymer.

The results show (Table 3.2.) that with similar levels of metalating agent, much higher degrees of carboxylation were achieved with the higher iodine number polymers. Higher levels of metalation were attempted with Intolan 155 and Nordel 1040 but it was found that polymers more highly carboxylated than those shown were extremely difficult to purify and analyse due to their insolubility in non-acidic solvents. It is therefore possibly coincidental that the acid value results quoted for each of these polymers correspond to carboxylation of approximately 50% of their unsaturation.

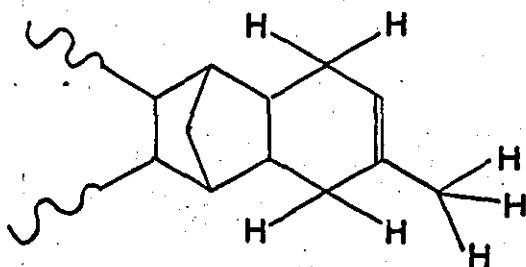


TABLE 3.2: METALATION OF VARIOUS EPDM's.

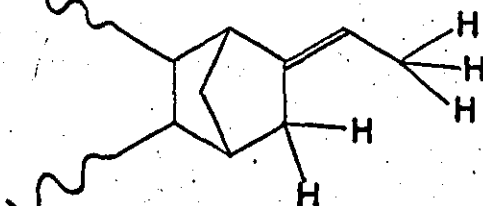
| METALATING AGENT<br>AMOUNT<br>(m.moles) | EPDM       |            | PRODUCT<br>ACID<br>VALUE |
|-----------------------------------------|------------|------------|--------------------------|
|                                         | TERMONOMER | IODINE NO. |                          |
| 10                                      | EMHN       | 10         | 5                        |
| 20                                      | EMHN       | 10         | 9                        |
| 15                                      | ENB        | 20         | 22                       |
| 15                                      | HD         | 18         | 18                       |

It is difficult to draw any conclusions from these results as to whether the type of termonomer has any effect on the degree of metalation and carboxylation as unfortunately the polymers that were available had differing iodine numbers as well as termonomer type. One way in which the termonomer units might be expected to have different reactivity towards metalating agents is the variation in the number of allylically situated hydrogen atoms which are available for substitution. A consideration of the structure of these units,

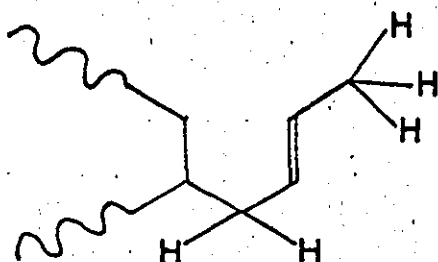
EMHN.



ENB.



H.D.



shows that EMIIN has seven allylic hydrogen atoms, and both ENB and H.D. have five and therefore if one considers just the number of reactive sites in each of these termonomer units the conclusion would be that a polymer containing EMIIN termonomer would be the most suitable for metalation.

However it does appear that, in this investigation, any effect due to the termonomer type must be outweighed by the effect due to differences in termonomer level.

### 3.2.6. Properties of the metal salts of carboxylated EPDMs.

Ideally, after neutralisation of the free carboxyl containing polymer with a suitable metal <sup>compound</sup> an ionically crosslinked product with elastomeric properties should be obtained. These ionic linkages will be sensitive to heat and above the salt dissociation temperature the linkages should become diffuse allowing the polymer to exhibit plastic flow. A product similar at service temperatures to that of a normal sulphur vulcanisate would thus be obtained but having the advantage that thermoplastic forming can be applied.

These properties of elasticity at room temperature and thermoplasticity at elevated temperatures can be shown to be present in these metal carboxylate crosslinked polymers.

A sample of crude metal carboxylate was isolated, after carboxylation but without acidification, by precipitation with methanol. This was dried then pressed at 200°C under a pressure of 2000 p.s.i. The polymer was cooled to 100°C before removal from the press and was thus obtained as a thin sheet. Test pieces were cut from this and tested, under standard conditions for rubber compounds, for ultimate tensile strength and elongation at break. The average results obtained from a sample of Intolan 155 carboxylated to give an acid value of 20 as shown in Table 3.3.

Another sample was similarly carboxylated but then acidified and purified as in Section 3.2.2. so that it was finally obtained in a pure free carboxyl state in hexane solution. A solution of sodium methoxide was then added so that products with 100% and 75% of the acid groups neutralised were obtained. These were then precipitated, dried and tested in the same way as the crude carboxylate. The tensile strength and elongation at break results are given in table 3.3.

TABLE 3.3: PROPERTIES OF NEUTRALISED PRODUCTS.

| SAMPLE *          | TENSILE STRENGTH |                   | EAB<br>% |
|-------------------|------------------|-------------------|----------|
|                   | P.S.I.           | MNm <sup>-2</sup> |          |
| CRUDE CARBOXYLATE | 1200             | 8.3               | 350      |
| 100% NaOMe        | 1600             | 11                | 400      |
| 75% NaOMe         | 1300             | 9.0               | 250      |

It can be seen that the results for the sample 100% neutralised with sodium methoxide are better than those for the crude carboxylate. This is probably due to the fact that the presence of impurities in the crude carboxylate caused early failure. Also, when only 75% of the acid groups are neutralised then a reduction in property values was obtained. However, these results are exceptionally good for an unreinforced rubber and can be certainly said to fulfil all the requirements of an elastomer. It seems likely that the ultimate tensile strength can be improved by the incorporation of a suitable reinforcing filler such as carbon black.

The highest acid value that was obtained for a polymer in this investigation was approximately 20 and it is interesting to calculate from this the crosslink density that would be obtained if the subsequent neutralisation resulted in 100% formation of ionic crosslinks.

\* samples were all prepared free from water.

A polymer of acid value 20 requires, by definition, 20mg of potassium hydroxide to neutralise 1g of polymer. This is equivalent to,

$$\frac{20}{56 \times 1000} \quad \text{moles of carboxylic acid per gram of polymer.}$$

If one takes the average molecular weight of the polymer as being 200,000 then the number of carboxyl groups per chain is,

$$\frac{20}{56 \times 1000} \times 200,000$$

i.e. approximately 80 carboxyl groups/chain. From this the approximate crosslink density can be calculated.

The ethylene, propylene ratio of these polymers is approximately 60:40 and if one neglects the effect due to the comparatively low monomer content then a section of the polymer chain containing 10 monomer units would have, on average, 6 units of ethylene and 4 of propylene. The molecular weight of this section would therefore be,

$$(6 \times 28) + (4 \times 42)$$

$$\text{i.e. } 336$$

and the length of a section such as this would contain 20 carbon atoms.

If the polymer contains 80 carboxyl groups in each chain of 200,000 molecular weight then a section of 336 molecular weight would contain,

$$\frac{80 \times 336}{200,000} \quad \text{groups}$$

and this number of groups would be situated along a chain segment containing 20 carbon atoms. Therefore, the number of chain carbon atoms between each carboxyl group would be,

$$\frac{20 \times 200,000}{80 \times 336}$$

$$\text{i.e. approximately } 160.$$

If neutralisation resulted in all carboxyl groups forming ionic linkages then there would be on average 160 carbon atoms separating each crosslink. A polymer having an acid value of only 10 would have crosslinks twice this

distance apart i.e. a chain segment of 320 carbon atoms separating them. It has previously been shown in this work that a polymer such as this has very poor elastomeric properties. This is perhaps not surprising as the optimum crosslink density for a standard rubber sulphur vulcanisate is in the region of one crosslink per 100-200 chain carbon atoms.

These results also agree very closely with those obtained by H.P. Brown and C.F. Gibbs<sup>(56)</sup>. They prepared copolymers of butadiene and unsaturated acids and investigated metal salt crosslinking. The conclusion was, that to obtain optimum elastomeric properties the separation of each carboxyl group should be in the region of 65-230 carbon atoms.

In the present work very little investigation was carried out on the behaviour of the ionically crosslinked carboxylated EPDM's at elevated temperatures. However, the fact that they do exhibit thermoplastic flow is demonstrated in that they could be moulded into thin sheets by the application of pressure at 200°C. Sheets thus formed could then be reformed after cooling by repeating the treatment. The melt flow properties of these polymers were however generally poor and were probably not good enough to enable standard thermoplastic injection moulding techniques to be carried out. This situation could probably be improved somewhat either by the incorporation of a suitable plasticiser or by starting with a lower molecular weight EPDM.

These results demonstrate clearly that the polymers prepared behaved in the manner expected. The following results obtained using differential thermal analysis and infrared analysis give additional evidence that the properties of these polymers are due to the presence of heat labile, metal carboxylate crosslinks.

IR analysis of the carboxylated polymers can demonstrate the presence of both free carboxyl and ionic, carboxylate groups. Figure 3.2. is the IR spectrum obtained from an unmodified EPDM and shows very little absorption over the range 1500-1800cm<sup>-1</sup>. Figure 3.3. is the spectrum of a carboxylated polymer (acid value 15) after the polymer had been acidified

and purified. It shows a peak at  $1710\text{ cm}^{-1}$  which is characteristic of free carboxyl. After neutralisation of this polymer with sodium methoxide the IR spectrum in figure 3.4 was obtained. This shows the absence of free carboxyl, the peak at  $1710\text{ cm}^{-1}$  having disappeared, and the presence of carboxylate as evidenced by the peak at  $1600\text{ cm}^{-1}$ .

Differential thermal analysis was carried out on an Intolan 155 polymer which had been carboxylated to an acid value of 20 then 100% neutralised with sodium methoxide. A sharp transition temperature at  $153\text{--}154^\circ\text{C}$  was detected which was absent in the unmodified polymer. This transition occurred in the same temperature region at which the polymer commenced viscous flow and might therefore be assigned, tentatively, to the dissociation of the ionic crosslinks.

Evidence has been given that the ionic crosslinking of EPDM has been achieved via its metalation, carboxylation and metal salt neutralisation and a description has been given of the properties of the products. Two interesting questions are raised by these results which merit further discussion.

1. How does the univalent sodium ion effect chainlinking?
2. Why are these polymers so strong?

The first is prompted by the expectation that in order to effect a crosslink between two polymer chains one would require a polyvalent ion reacting with a carboxyl group on each chain in the manner

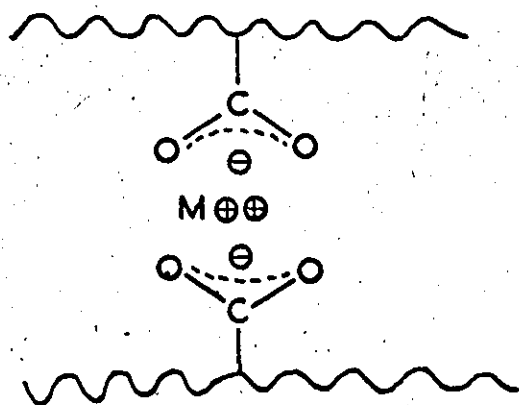


FIGURE 3.2. Intolan 155 EPDM.

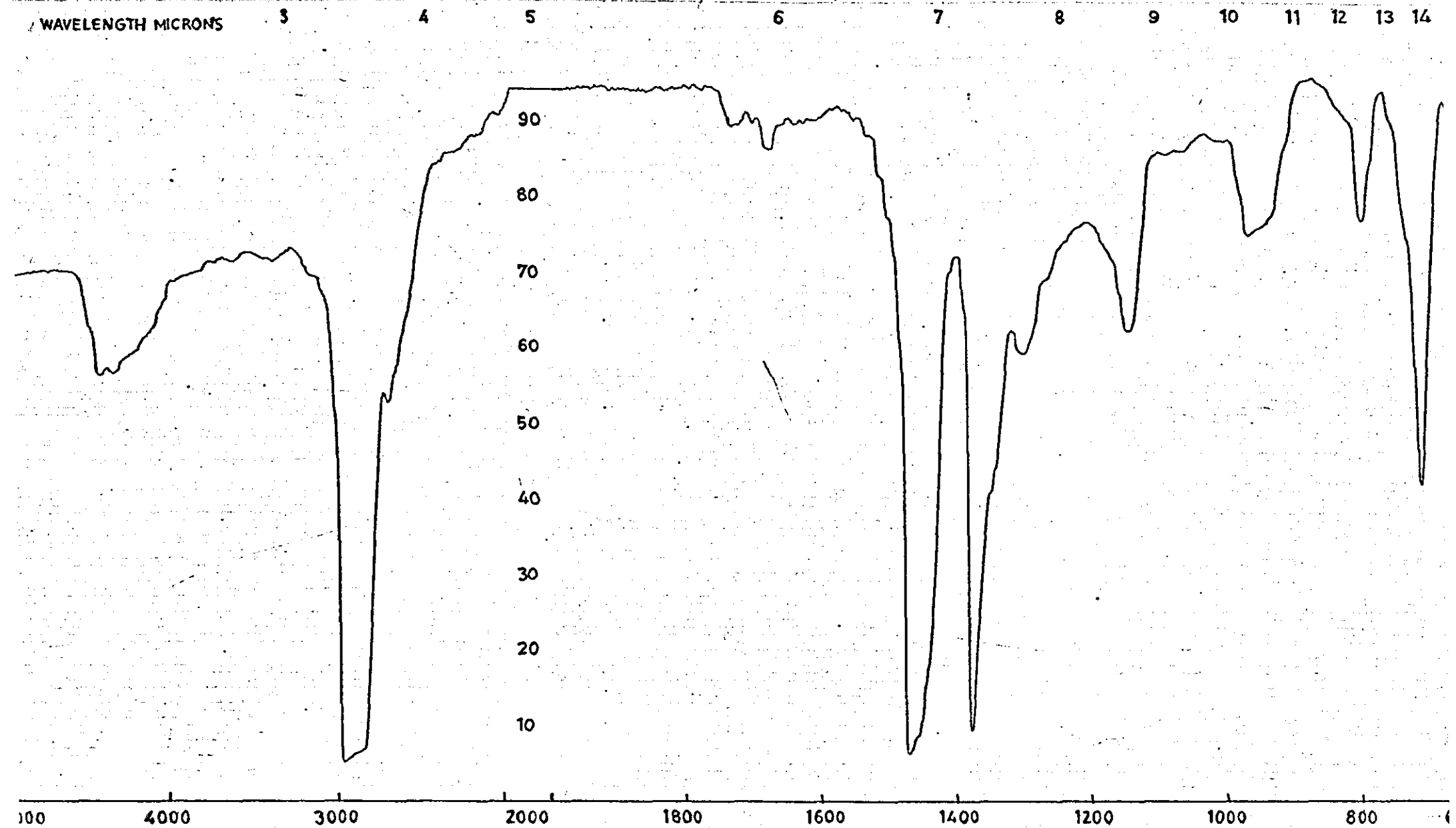


FIGURE 3.3. Carboxylated Intolan 155 - Free acid.

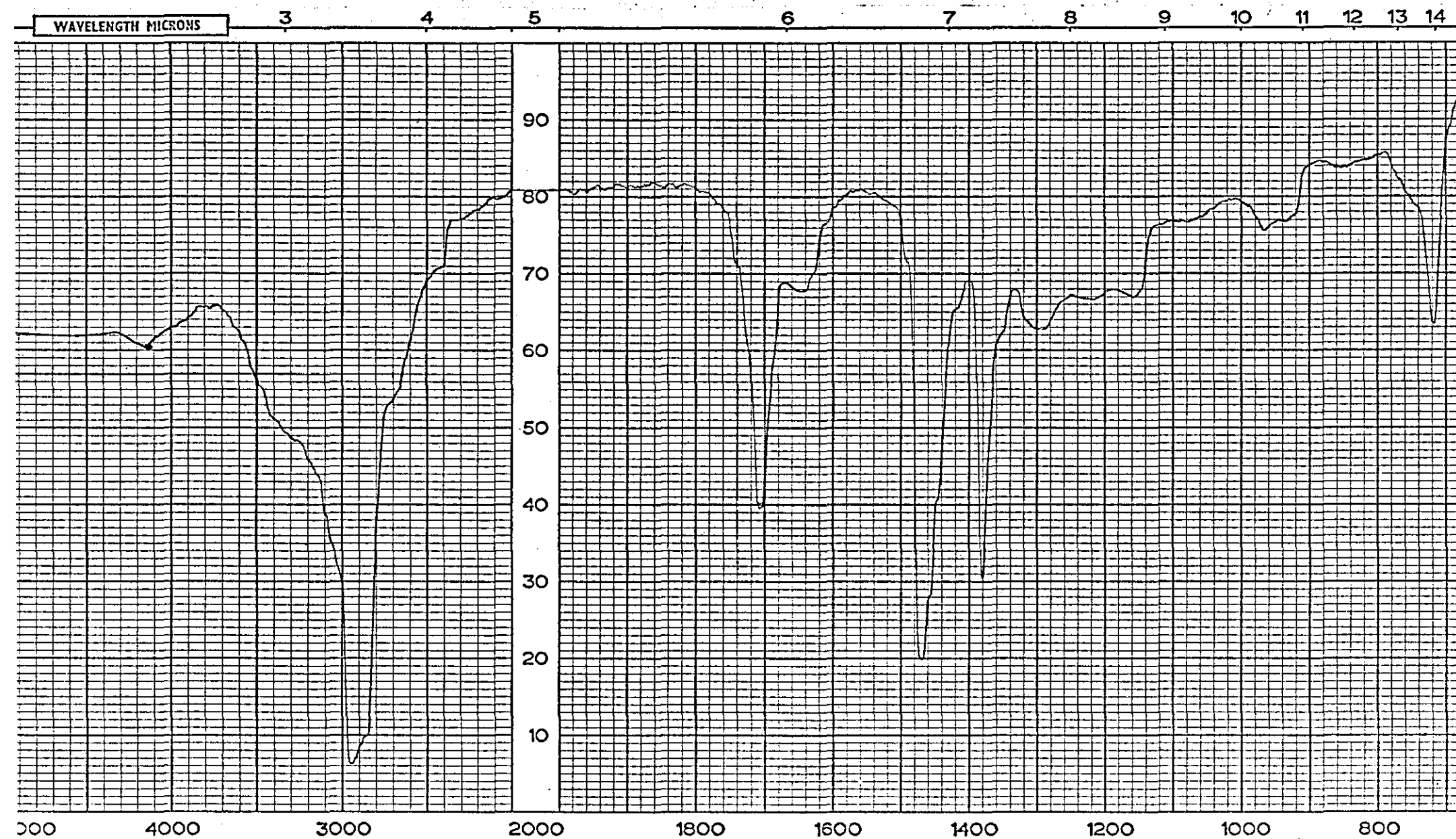
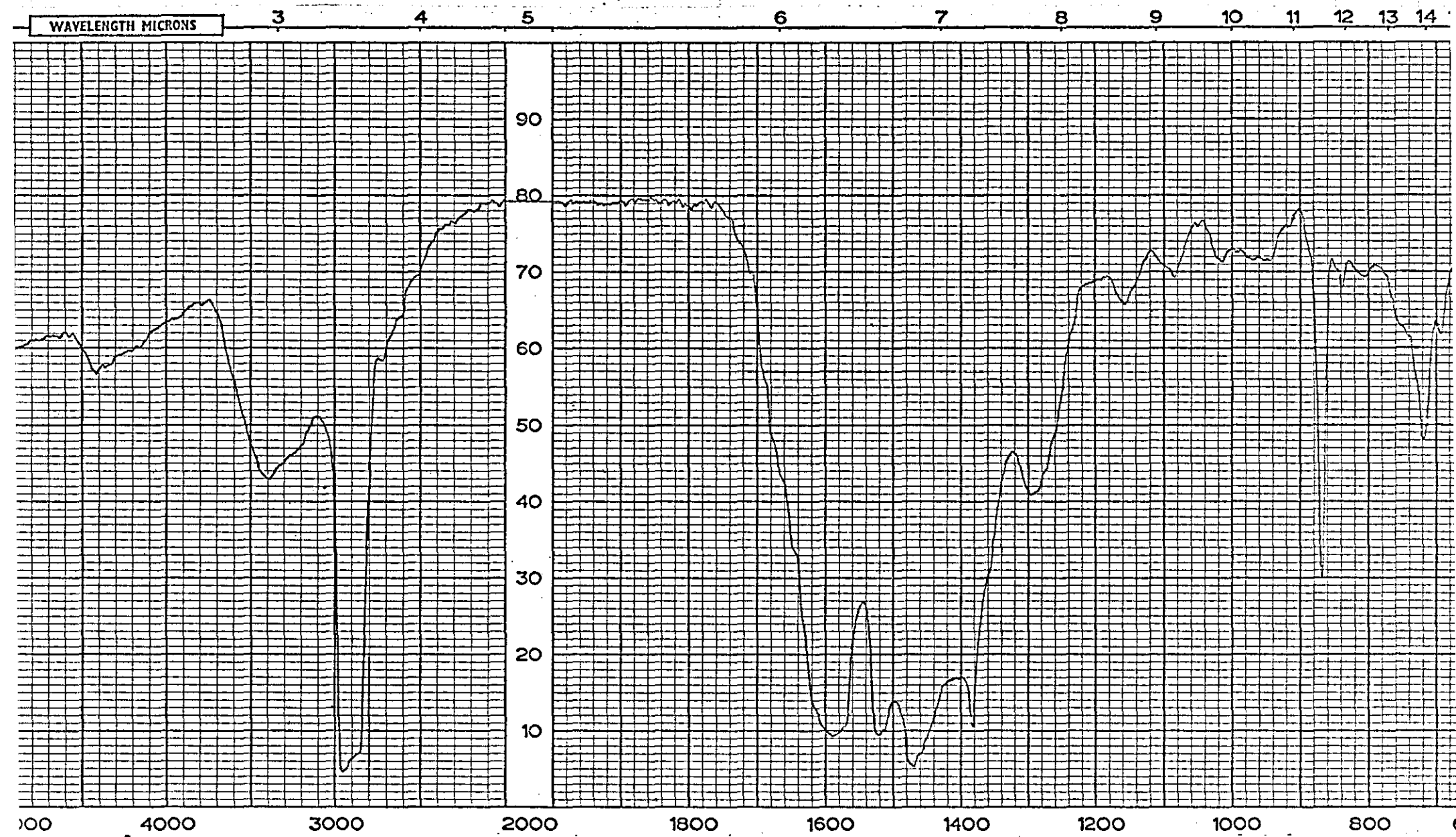




FIGURE 3.4. Carboxylated Intolan 155 - Neutralised.



where  $\sim$  represents a chain segment and  $M^{\oplus\oplus}$  a divalent metal ion.

The second arises from the fact that a standard EPDM, gum sulphur vulcanisate has a tensile strength only in the region of 100-200 p.s.i. i.e. typical of any non-crystallising rubber gum vulcanisate, whereas the strengths exhibited by the ionically linked polymers are very much higher and in the region of the strengths exhibited by reinforced rubber vulcanisates.

It should first be mentioned that the reason that a univalent metal alkoxide was chosen for this work was because previous work by the author at I.S.R.<sup>(157,158)</sup> showed that a univalent ion would give similar effects to those obtained with divalent ions. This earlier work involved the metal salt crosslinking of carboxylated polymers prepared by the free radical reaction of thioglycollic acid with polybutadiene and results showed that similar properties were exhibited by polymers neutralised in solution with methoxides of lithium, sodium, potassium and magnesium.

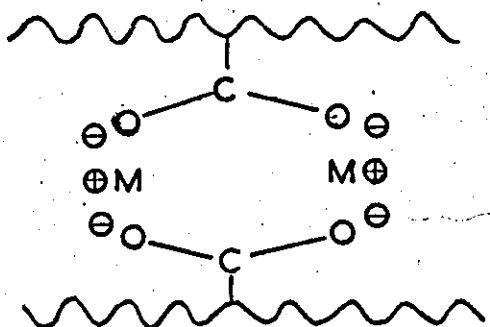
Other investigators in this field appear to present a variety of views, particularly about the behaviour of divalent metal ions. Some said that they produced infusible products similar to covalently crosslinked polymers<sup>(156, 159-162)</sup> and others that thermoplastic products could be obtained which had considerable creep at room temperature.<sup>(163-166)</sup> The views generally expressed about monovalent ions<sup>(156, 159, 160, 163, 164, 167, 168)</sup> was that they caused crosslinking, but the products, although strong, were generally weaker than those prepared with divalent ions. Bonotto and Bonner<sup>(169)</sup> however, came to the conclusion that there was little difference between monovalent and divalent salts when they were used at levels giving similar degrees of ionisation.

It is perhaps not surprising that there is such a divergence of opinion when it is appreciated that the carboxyl containing polymers used by these investigators were often considerably different from each other.

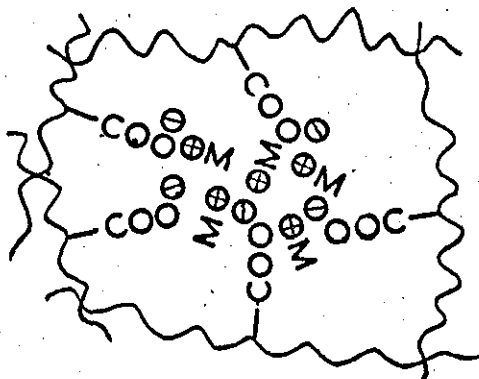
Another contributory factor might well be that, in general, the neutralisation process employed outside of ISR involved the physical blending of metal salts with polymers, using for example a two-roll mill. This is not a very efficient method for mixing materials on a molecular basis and is likely to lead to a variation in results depending on the particular conditions and techniques employed. This effect was probably accentuated when, as in the majority of investigations, even that of Bonotto and Bonner, valency comparisons were carried out using hydroxides such as sodium hydroxide to supply the univalent ions and oxides such as zinc oxide to supply the divalent ions. It seems hardly likely that the mechanical blending of polymers with materials so dissimilar as sodium hydroxide and zinc oxide, would give products differing only in the valency of the ion neutralising the carboxyl groups. It is therefore suggested that the method employed by the author of neutralisation of carboxyl polymers in solution, with monovalent and divalent alkoxides probably gives a fairer idea of the effects of ion valency. However, notwithstanding this divergency of opinion, it is generally agreed that both monovalent and divalent metal ions cause the crosslinking of carboxyl containing polymers. The simple picture of an ionic crosslink as given above therefore needs modification to accommodate this fact.

In the literature there are two groups of workers holding fundamentally different ideas on this subject. The first group<sup>(166,167,170)</sup> retain the idea of an isolated ionic crosslink and the second group<sup>(163,164,169,17)</sup> invoke a conglomerate link. Thus the former propose a divalent metal ion

link similar to that previously given and a monovalent ion link such as,



The conglomerate ion link proposed by the second group has the same structure irrespective of ion valency and can be pictured as,



The investigators proposing the isolated link argue<sup>(167)</sup> that a conglomerate type of linkage is very unlikely to be formed due to the comparatively low concentration of carboxylate groups, it being unlikely that more than two would meet at any one time. This was countered by the opposing camp<sup>(171)</sup> by the proposal that there was a positive motivation to form conglomerate links. This would arise from the highly unfavourable thermodynamic situation of ionic salts essentially dissolved in a hydrocarbon medium. The aggregation of the ionic groups into clusters would relieve this energetically unfavourable condition and the long-range coulombic interaction would assist in the setting up of the clusters.

These two different ideas, concerning the nature of the crosslinks, for an inherent part in the discussion of the theories proposed to answer the question "Why are these polymers so strong?", so it is worthwhile

at this point to go on to an appraisal of these theories.

There are of course two different theories, depending on which of the two proposed crosslink structures is thought to be true.

The first was proposed by Cooper,<sup>(166)</sup> who suggested that the great strength of these polymers was due to the ability of the networks to relax by exchange reactions between crosslinks on different chains, thus preventing the development of local stress.

The second theory, described by Tobolsky et al<sup>(171)</sup>, proposed that the high strength was due to the presence of ionic clusters which gave rise to a two-phase, reinforced structure. The ionic vulcanisation would result in the formation of an internally relaxed network structure with the ionic clusters acting as a reinforcing "filler" and quasi-crosslinks.

Cooper of course explains the strength of the polymers in terms of isolated crosslinks and Tobolsky explains it in terms of conglomerate links. It therefore appears as though there are two completely opposite explanations proposed to explain the properties of these polymers and that only one can be true. However, this is not necessarily so. It is possible that both theories may be true but under different circumstances. It is likely that with a comparatively low degree of carboxylation the frequency of carboxylate ions, along the polymer chains, would be too low to enable the formation of ionic clusters despite the thermodynamic motivation. However, a polymer such as this could still exhibit strengths two or three times that expected for an unreinforced rubber, say of the order of  $7.0 \text{ MNm}^{-2}$  (1000 p.s.i.). In this case the Cooper theory plus the isolated crosslink structure could apply. However, as the degree of carboxylation is increased, so the frequency of carboxylate groups would increase and the formation of ionic clusters would become more and more likely. It is suggested that, from this work and others<sup>(168)</sup>, before polymers exhibit tensile strengths greater than about  $7.0 \text{ MNm}^{-2}$ , the frequency of carboxyl groups must be greater than about one per 200

carbon atoms and this would be sufficient to allow the formation of a high proportion of ionic clusters. The proportion of carboxylate groups in linkages containing more than two ions would therefore increase with increasing degree of carboxylation.

One other piece of evidence which helps to substantiate the proposal that the ionic cluster theory is more valid at high degrees of carboxylation is in fact presented by Cooper. He states<sup>(166)</sup> that although the high creep of these polymers would be expected from the stress relaxation by ionic exchange theory, the permanent set exhibited by them is much lower than would be anticipated. The ionic cluster theory can however provide for an explanation of both properties. The ionic aggregates would be likely to deform fairly easily under applied stress, thus giving high creep, but on release of the stress they would be expected to return to the shape giving a more optimum neutralisation of charge.

It is therefore thought that the more highly carboxylated of the EPDMs, at present under discussion, contain both isolated and conglomerate ionic crosslinks but the majority of the carboxylate groups are more likely to be contained within the latter type of linkage. The properties are thought to be mainly due to these conglomerate ionic bonds acting in the dual role of crosslinks and filler particles.

### 2.3.3. STYRENE GRAFTING.

#### 2.3.3.1. General.

The aims of this part of the study were to develop techniques for the grafting of styrene onto EPDM via metalation and then to optimise conditions so that a thermoplastic elastomer could be obtained.

In practice, the first objective was so difficult that only moderate success was achieved with the second.

By analogy to the ABA block copolymers, the desired product was an EPDM in which all polymer chains contained at least two polystyrene grafts. A further requirement was that there should be a complete absence of any ungrafted polystyrene. The development of procedures was accordingly directed towards obtaining a system which would result in high graft efficiencies with as large a number of grafts per chain as possible.

It is appropriate at this point to describe how approximate values for graft efficiencies and the number of grafts per chain were obtained. To enable values to be calculated the following had to be determined.

- a. The number average molecular weight of the EPDM.
- b. The styrene content of the grafted polymer.
- c. The number average molecular weight of the grafted polystyrene.

The first was determined quite simply by membrane osmometry but the others posed certain problems. In the case of styrene-diene-styrene block copolymers these had been found by degrading the polydiene chain segments with osmium tetroxide and t-butyl hydroperoxide and recovering the polystyrene.

This gave the styrene content of the grafted polymer and also enabled the polystyrene molecular weight to be determined. This procedure could not be used for the EPDM grafted polymers as the ethylene propylene copolymer portion could not be degraded, it was therefore necessary to develop other methods.

A suitable procedure for the determination of styrene content was finally found. This entailed refractive index measurements and full details are given in the experimental section. Briefly, it consisted of measuring the refractive index of; the unmodified EPDM; the grafted EPDM; polystyrene. The refractive index of the grafted polymer was the sum of the effects of the EPDM and the polystyrene. The percentage of styrene could thus be calculated using the following formula.

$$\text{weight \% styrene} = \frac{\mu_{\text{graft}} - \mu_{\text{EPDM}}}{\mu_{\text{PS}} - \mu_{\text{EPDM}}} \times 100$$

The reasonable assumption was made that the molar volume of the graft co-polymer was the arithmetic mean of the components.

The molecular weight of the grafted PS was estimated by assuming that it would be similar to that of the ungrafted polystyrene. This seemed reasonable as the initiation of both would be by similar species and the propagation would occur via identical chain end structures. This assumption was adopted and the molecular weight of the ungrafted polystyrene determined by Gel Permeation Chromatography. It was found that even when very high graft efficiencies were obtained, sufficient free polystyrene could be isolated to enable the molecular weight to be determined.

The three determinations having been made, the graft efficiency and the number of grafts per chain could be calculated.

The graft efficiency was found, as a percentage, by substitution of values in the following formula.



$$\text{Graft Efficiency} = \frac{\text{actual styrene content}}{\text{theoretical styrene content}} \times 100$$

The number of grafts per chain was calculated from a comparison of the mole ratios of EPDM and polystyrene i.e.

$$\text{Number of grafts/chain} = \frac{\text{Styrene content}}{\text{PS.}\bar{M}_n} \div \frac{\text{EPDM content}}{\text{EPDM } \bar{M}_n}$$

In the earlier section dealing with the metalation reaction (3.1) the techniques that had to be developed before reproducible metalation was achieved were discussed. In the following two sections (3.3.2 and 3.3.3) of the grafting study some of the results obtained during this time will be given to illustrate the need for this development work.

The third of the following sections (3.3.4) will deal with the problems found during the development of procedures used in the grafting of styrene onto the metalated polymer.

The later sections will deal with the results obtained from styrene grafting under different conditions and then go on to discuss the properties of the products.

### 3.3.2. Solvent purification.

The impurities of major concern were those which would compete with the polymer in the metalation reaction. In general these were unsaturated compounds, benzene being the most important.

The determination of aromatics in the solvent was mainly carried out by U.V. analysis, however, it was found that I.R. analysis enabled a quick estimate to be made. Figures 3.5, 6 and 7 show the I.R. spectra obtained for hexane analysed by U.V. as containing 5%, 0.2% and zero benzene. A comparison of figures 3.5 and 3.7 show that the benzene contributes in the main to the absorption at four positions  $675\text{cm}^{-1}$ ,  $1035\text{cm}^{-1}$ ,  $1800\text{cm}^{-1}$ ,  $1960\text{cm}^{-1}$ . When the benzene level was reduced to 0.2%

FIGURE 3.5. Hexane + 5% Benzene.

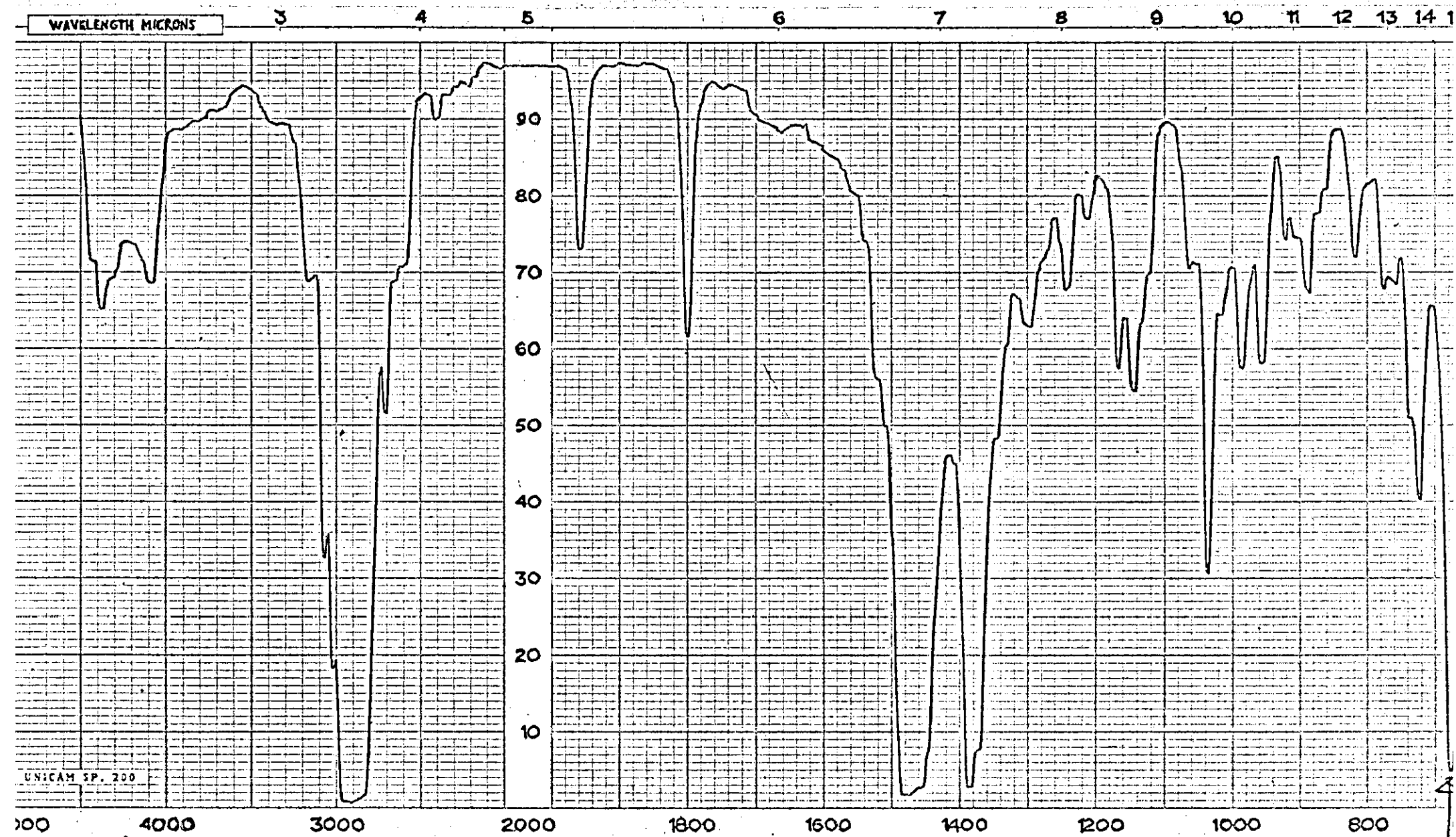


FIGURE 3.6. Hexane + 0.2% Benzene.

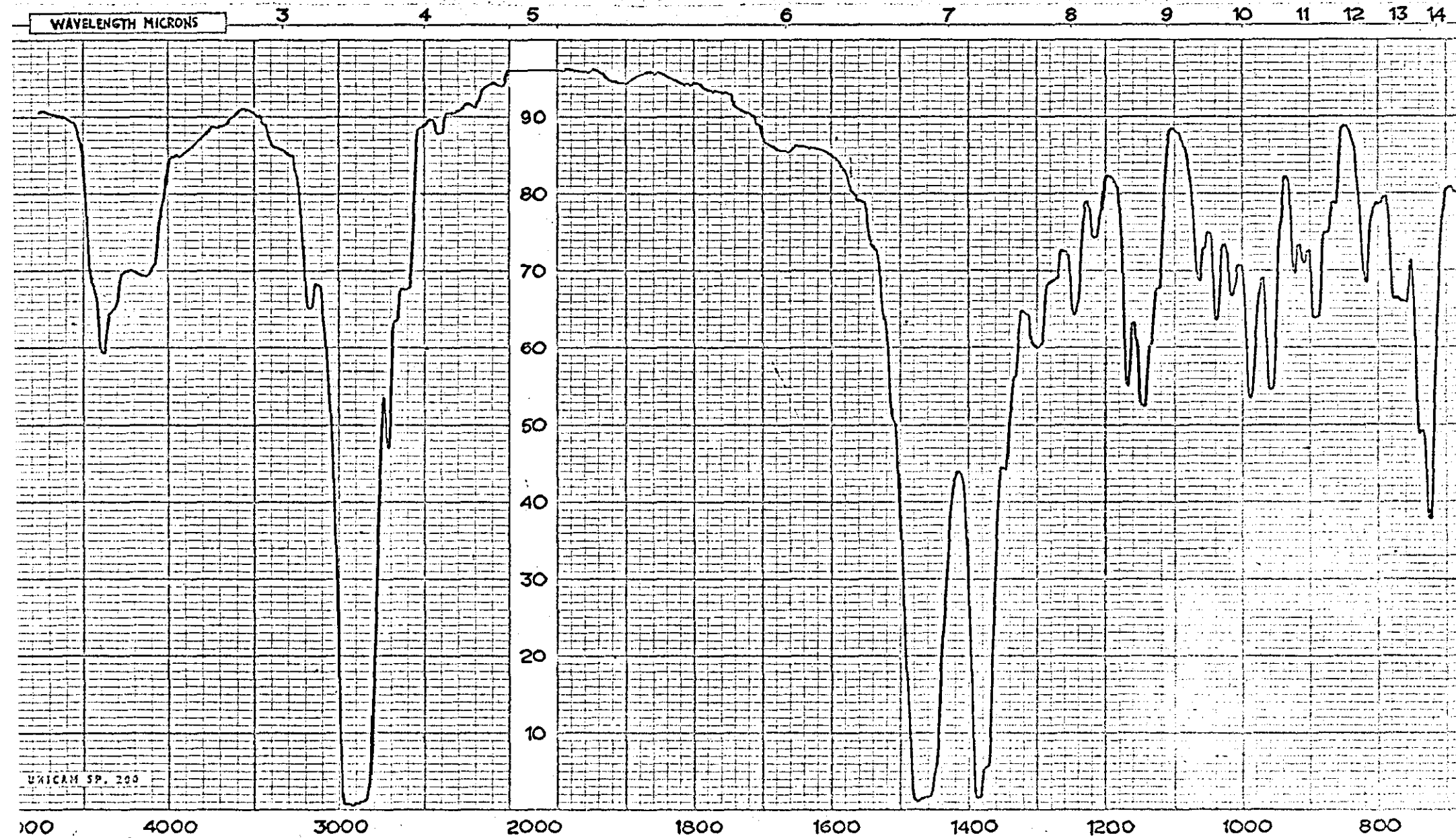
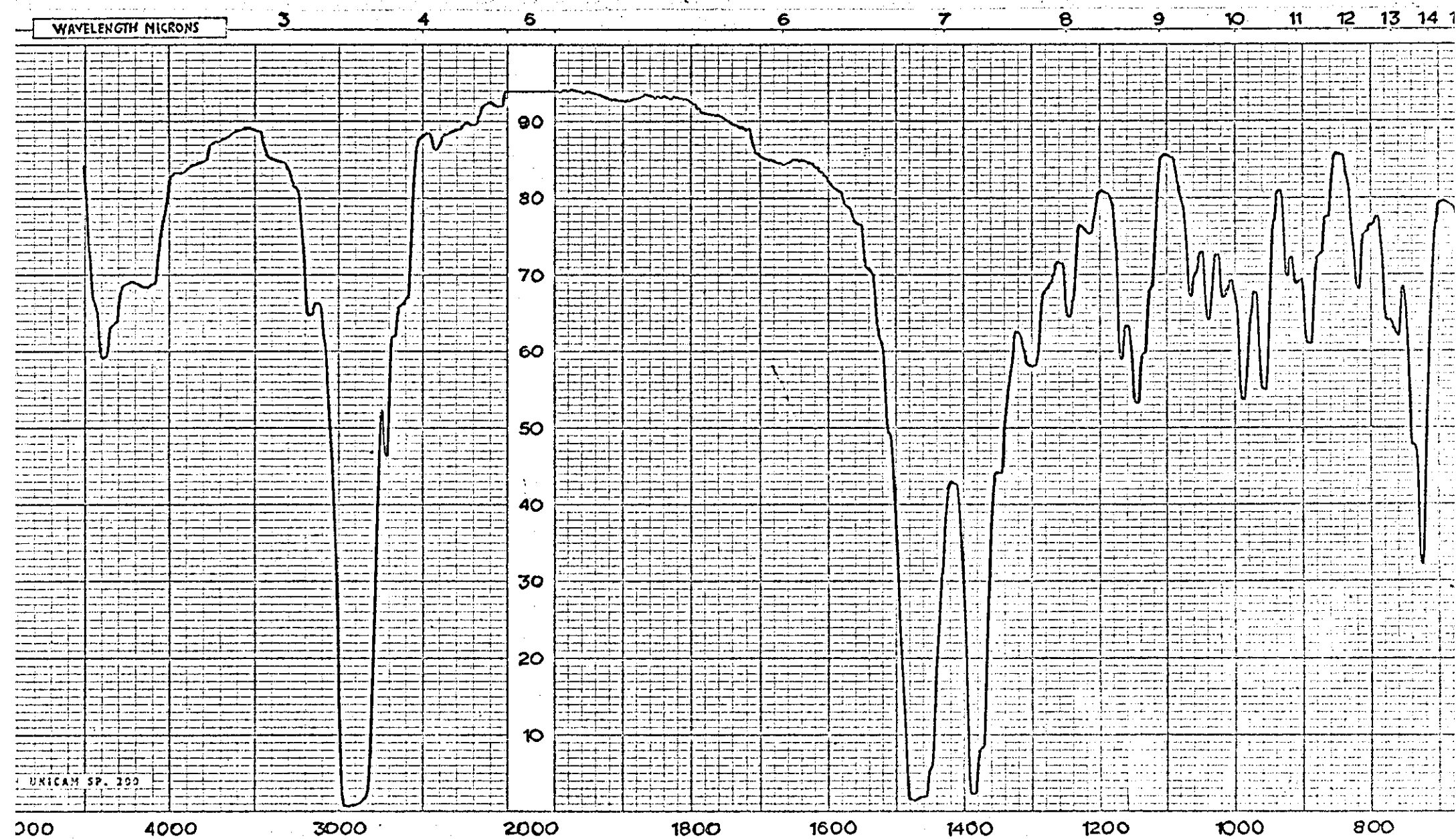


FIGURE 3.7. Hexane - free from aromatics.



(figure .3.6) it was found that although three of the peaks had disappeared, that at  $675\text{cm}^{-1}$  was still visible. In fact, this absorption was still detectable at much lower levels of benzene. Thus by running just the very first section of the spectrum of a particular sample of hexane a check could be made as to its suitability for metalation reactions.

Hexane was obtained with various levels of benzene and used as solvent for metalation and styrene grafting reactions.

Table .3.4 shows the effect of even low levels of aromatics when present during EPDM metalation. The metalation reaction was carried out at  $70^{\circ}\text{C}$  for 5 h. using the butyl lithium, sublimed potassium t.butoxide 1:1 complex as metalating agent at a level of  $2/\text{m.mole}$  per 10g EPDM. Pure styrene was then added and polymerisation carried out for 2 h at  $60^{\circ}\text{C}$ . It can be seen that at aromatic levels of 1.2% and 0.2% no styrene was grafted onto the EPDM. At a level of 0.08% a graft efficiency of 30% was achieved and only when all the aromatics were removed were high graft efficiencies achieved.

TABLE .3.4: THE EFFECT OF AROMATICS ON STYRENE GRAFT EFFICIENCY.

| HEXANE AROMATIC<br>LEVEL<br>(%) | STYRENE<br>CONTENT<br>(%) | GRAFT<br>EFFICIENCY<br>(%) |
|---------------------------------|---------------------------|----------------------------|
| 1.2                             | 0                         | 0                          |
| 0.2                             | 0                         | 0                          |
| 0.08                            | 7                         | 30                         |
| Zero                            | 23                        | 90                         |

### 3.3.3. Polymer solution drying.

Before metalation could be carried out, the polymer solution had to be treated so that it was as free as possible from substances such as water and oxygen which could have caused deactivation of the metalating agent. The determination of scavenging levels, using n-butyllithium and Michler's ketone, has been shown previously (3.1.3) to be a useful method for determining the suitability of solutions for metalation. Table 3.5. gives a list of methods employed for drying the solutions and the corresponding average scavenging levels. It was found that when these solutions were used in metalation-styrene grafting reactions the variability in the results obtained decreased as the scavenging level decreased.

The treatment as described in (e) proved to be very suitable and enabled highly efficient styrene graft polymerisations to be carried out.

TABLE 3.5. SCAVENGING LEVELS OF POLYMER SOLUTIONS PREPARED  
BY VARIOUS METHODS.

| METHOD OF PREPARATION                                                                      | SCAVENGING LEVEL<br>(m.moles/300ml soln.) |
|--------------------------------------------------------------------------------------------|-------------------------------------------|
| a. Polymer dried in desiccator.<br>Hexane distilled from nBuLi under N <sub>2</sub>        | 2.0                                       |
| b. Solution as a. passed through alumina<br>under N <sub>2</sub> .                         | 1.4                                       |
| c. Solution as a. passed through activated<br>(400°C/16 h.) alumina under N <sub>2</sub> . | 1.0                                       |
| d. Solution as a. passed through act. alumina/<br>silica gel under N <sub>2</sub> .        | 0.9                                       |
| e. As d. but prescavenged with 3.0 m.moles nBuLi<br>300ml soln.                            | 0.5                                       |

### 3.3.4. Grafting techniques.

The polymerisation reaction of styrene with metalated polymer presented two problems viz. the preparation of pure, dry, deaerated styrene and the homogeneous dispersion of this in the metalated polymer solution.

The styrene was distilled under reduced pressure through a molecular sieve column into a nitrogen flushed, crown-capped bottle. At first, this was stored in a deep-freeze at  $-20^{\circ}\text{C}$  and aliquots were taken, as required, with a syringe. However, it was found that on continued use of this material, the calculated number of grafts per chain and the graft efficiencies, obtained in grafting reactions, gradually decreased. This was because even when stored at this temperature, a certain amount of polymerisation still occurred and hence, when this was used for grafting, an apparent decrease in graft efficiency was obtained. The reduction in the number of grafts per chain was due, presumably, to the introduction of impurities into the styrene during the syringing out of aliquots. The procedure was therefore modified and the styrene was distilled just prior to use, after purging with dry nitrogen to remove any air.

The difficulty of dispersing the styrene in the metalated polymer solution arose due to the "jelly" like nature of this solution, and the rapidity with which the styrene graft polymerised to form a partially hexane insoluble product. The high viscosity of the metalated polymer solution was reduced somewhat by diluting to 1% w/v though even at this concentration the solution was still somewhat jelly like.

When styrene was added to the metalated polymer solution at room temperature then there was a tendency for the styrene to polymerise, virtually immediately, as it reached the metalated polymer. This inhomogeneity showed itself as opaque, pale pink particles within the clear red polymer solution. The problem of dispersion was overcome

by cooling the metalated polymer solution to  $0^{\circ}\text{C}$  before addition of the styrene. The bottles were then rotated at  $0^{\circ}\text{C}$  for 1 h before increasing the temperature to  $70^{\circ}\text{C}$  for the polymerisation stage. The styrene was thus well dispersed before any significant amount of polymerisation occurred. A well dispersed product was indicated by the polymer solution appearing homogeneous, slightly opaque and red in colour. As long as the dispersion was carried out correctly the grafted polymer remained in solution in the hexane.

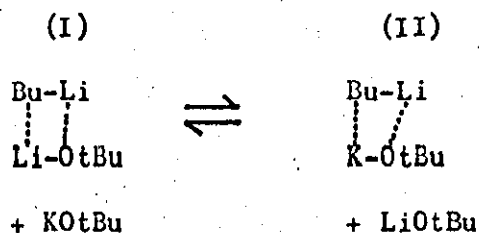
### 3.3.5. nButyllithium/potassium tbutoxide.

All the styrene graft results presented here were obtained using Intolan 155 as the polymer and nbutyllithium-potassium t.butoxide as the metalating agent. Other EPDM's were tried with this metalating agent and Intolan 155 was also tried with n-butyllithium, tetramethylethylene diamine, as metalating agent, however, as in the carboxylation study, little success was achieved with these other combinations.

Experiments were carried out using either  $\text{KOtBu}$  or  $\text{KOtBu.tBuOH}$  in conjunction with butyllithium. However, although good graft efficiencies could be obtained with either of them as metalating agent, when  $\text{BuLi/KOtBu.tBuOH}$  was used there was as stated elsewhere an uncertainty as to what quantity of active species was present. This made it difficult to control the molecular weight of the polystyrene grafts and the number of grafts per chain. Because of this uncertainty it was also impossible to make a direct comparison of the two metalating agents. The use of  $\text{KOtBu}$  in equimolar proportions with  $\text{nBuLi}$  resulted in an excellent metalating agent giving close to 100% graft efficiency but if  $\text{KOtBu.tBuOH}$  was used in similar proportions an inactive product resulted, due evidently to the reaction of  $\text{BuLi}$  with the available  $\text{tBuOH}$ . It seemed that in this case a 2:1 ratio of  $\text{nBuLi}$  to  $\text{KOtBu.tBuOH}$  would be satisfactory but it was found that <sup>this</sup> gave graft efficiencies of only about 70%. The



highest graft efficiencies were in fact achieved using a ratio around 1.5 nBuLi : 1 KOtBu tBuOH. This indicated that there was an equilibrium present of the type,

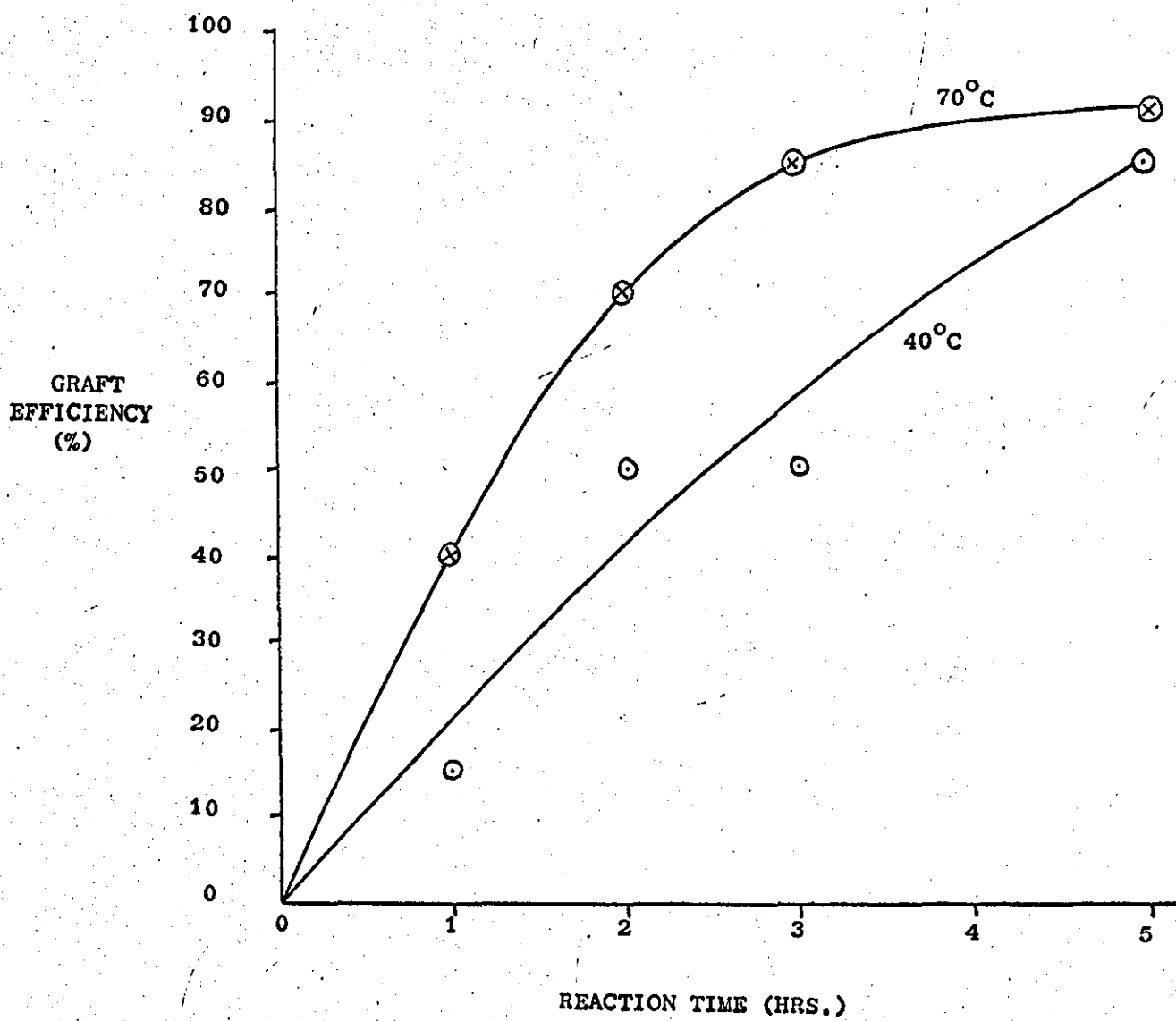


Complex I being inactive towards metalation but capable of polymerising styrene and complex II being highly active towards metalation. The proportion of each present must have depended on the amount of n.butyl lithium present. Thus at the 2:1 ratio a comparatively high proportion of complex I would have been present giving low graft efficiencies whereas at the 1.5:1 ratio very nearly all the n.butyl lithium would have been present in a complex such as II giving high graft efficiencies. Because of the uncertainty of the exact behaviour of this metalating agent it was decided that pure potassium t.butoxide should be used instead. This was a pity as the sublimation procedure required to produce the pure alkoxide was rather difficult and tedious.

### 3.3.6. Metalation conditions.

Metalations were carried out at 40°C or 70°C for varying lengths of time and the effects on polystyrene graft efficiency were studied. The results shown in Fig. 3.8 were obtained using a metalating agent level of 3.0 <sup>m.moles</sup> per 10 g of polymer and styrene was added to give a theoretical 30% polystyrene content. As can be seen from the figure, when metalation was carried out at 40°C there was a gradual increase in graft efficiency with reaction time until an efficiency of 85% was achieved after 5 h. With a reaction temperature of 70°C the graft efficiency increased much more rapidly at first so that an efficiency of 85% was achieved after only 3 h reaction. However, during the subsequent 2 h the efficiency was only increased by a further 5%.

FIGURE 3.8. REACTION TEMPERATURE/TIME  
VS. GRAFT EFFICIENCY.



A temperature of 70°C and reaction time of 5 h was therefore adopted as being suitable metalation reaction conditions. These conditions are fairly typical for a polymer reaction; in general they take considerably longer than equivalent reactions with similar low molecular weight olefins due possibly to the low mobility of the polymer chains.

### 3.3.7. Styrene Level.

After metalation had been carried out, various levels of styrene could then be graft polymerised to produce materials with a wide range of properties. As in this study the objective was to produce elastomeric products. Styrene levels were kept within the 25-45% limits found to be optimum by Shell<sup>(93,100,172)</sup> in their general investigations of ABA block copolymers.

The effects were investigated of styrene level on graft efficiency. Metalations were carried out using n.butyllithium/potassium t.butoxide at 70°C for 5 h. The results given in Table 3.6. show that, as might be expected, the amount of styrene added to variously metalated polymers has little effect on graft efficiencies. The spread of results for similarly metalated polymers was within the range expected and shows the difficulty of obtaining truly reproducible results even with a carefully prepared system.

The Table also shows that if the metalating agent was increased above a level of about 2.0m.mole/10g polymer then graft efficiency decreased. This is shown in more detail in the next section.

TABLE 3.6: THE EFFECT OF STYRENE LEVEL ON  
GRAFT EFFICIENCY.

| METALATING<br>AGENT<br>(m.moles/10g<br>EPDM) | STYRENE CONTENT<br>ATTEMPTED<br>(%) | GRAFT<br>EFFICIENCY<br>(%) |
|----------------------------------------------|-------------------------------------|----------------------------|
| 1.5                                          | 30                                  | 95                         |
| 1.5                                          | 45                                  | 100                        |
| 2.0                                          | 30                                  | 90                         |
| 2.0                                          | 45                                  | 100                        |
| 3.0                                          | 30                                  | 85                         |
| 3.0                                          | 45                                  | 70                         |

### 3.3.8. Metalating Agent Level.

The level of metalating agent level used not only determined the number of grafts per chain but also, in conjunction with the styrene level, determined the molecular weight of the grafted polystyrene.

The published work on ABA block copolymers<sup>(93,100,172-174)</sup> suggested that as well as a styrene content in the region of 25-45%, an optimised product should have a graft polystyrene molecular weight in the range 10,000 to 50,000 and at least two grafts per chain. The level of metalation had therefore to be balanced with the styrene level, in order to obtain products conforming to these limits. It was found difficult to achieve the correct balance as can be seen from the results given in Table 3.7. These were obtained from products having as near the desired composition as could be achieved, and were produced using the standard metalation procedures.

TABLE 3.7: THE EFFECT OF VARIATION IN METALATING AGENT LEVEL.

| METALATING<br>AGENT LEVEL<br>(m.moles/10g<br>EPDM) | PRODUCT STYRENE<br>CONTENT<br>(%) | GRAFT<br>EFFICIENCY<br>(%) | POLYSTYRENE<br>$\bar{M}_n$<br>( $\times 10^{-3}$ ) | AVERAGE GRAFTS<br>PER CHAIN |
|----------------------------------------------------|-----------------------------------|----------------------------|----------------------------------------------------|-----------------------------|
| 1.0                                                | 40                                | 90                         | 50                                                 | 1.0                         |
| 1.5                                                | 45                                | 100                        | 45                                                 | 1.4                         |
| 2.0                                                | 45                                | 100                        | 48                                                 | 1.3                         |
| 3.0                                                | 38                                | 70                         | 23                                                 | 1.9                         |
| 4.0                                                | 36                                | 65                         | 32                                                 | 1.3                         |

Clearly high graft efficiencies were only obtained with low levels of metalating agent and this underlines the difficulties that are experienced when modification of a polymer is attempted with such a low level of active sites.

Two other facts that are apparent from the table are, that polystyrene molecular weight only shows a general trend towards decreasing with increase in metalating agent level and, the number of grafts per chain does not show much of a trend towards increasing with increase in metalating agent level. The absence of positive trends was probably due to variations in the numbers of available initiating species due to variability in the levels of impurity.

The product obtained with 3.0<sup>m.moles</sup> metalating agent had a composition very near to that desired though it would have been better if the number of grafts per chain could have been increased. The work on the carboxylation of EPDM showed that higher levels of metalation could be achieved by increasing the metalating agent level. However, styrene grafting results show that this would have caused a further decrease in graft efficiency due to the increased level of free metalating agent. This decrease in graft efficiency would in turn have caused a decrease in the styrene content of the grafted product. There was of course the further complication that the increase in metalating agent level would have caused a reduction in the molecular weight of the polystyrene.

These effects could have been partially overcome by increasing the level of added styrene at the same time as increasing the metalating agent level. However, the increase in styrene required to maintain the molecular weight constant would not have been the same as that required to balance the decrease in graft efficiency.

Because of these difficulties this line of research was not pursued any further. It is likely that a more ideal product could have been obtained but only at the expense of producing a large proportion of

ungrafted polystyrene.

### 3.3.9. Product nature.

The styrene contents already quoted established the fact that the graft polymerisation of styrene had been accomplished, however additional evidence was gained from infra-red analysis of the samples. Figure 3.9. shows a typical spectrum of a grafted material which can be compared with the spectra of unmodified EPDM (figure 3.2.) and polystyrene (figure 3.10). It can be seen that the spectrum of the grafted polymer would be similar to that which would be formed by combining the spectra of EPDM and polystyrene. In particular it contains peaks at  $645\text{cm}^{-1}$ ,  $760\text{cm}^{-1}$  and  $1600\text{cm}^{-1}$  which are characteristic of polystyrene. Further attempts to extract free polystyrene by Soxhlet extraction using acetone/hexane mixture gave products with unaltered spectra and confirmed that the polystyrene was indeed grafted.

In general, the grafted products behaved rather more as flexible thermoplastics than elastomers, resembling polyethylene. Their thermoplasticity was demonstrated by their ability to form into thin, coherent sheets when pressed at  $150^{\circ}\text{C}$  and then be able to reform under similar conditions. The tensile strengths of some of the best of these sheets <sup>were</sup> in the range of  $7.0\text{--}10.5\text{ MNm}^{-2}$  (1000–1500 psi). This was a considerable increase over the  $0.7\text{--}1.4\text{ MNm}^{-2}$  (100–200 psi) obtained from the unmodified EPDM and very good compared with a non-reinforced rubber vulcanisate, though well below the values which can be obtained from reinforced rubber vulcanisates and commercial thermoplastic elastomers.

Two other properties were rather worse than anticipated. These were melt index and elasticity. In general, melt flow characteristics were very poor. Compression moulding was just possible but injection

FIGURE 3.9. Polystyrene grafted EPDM.

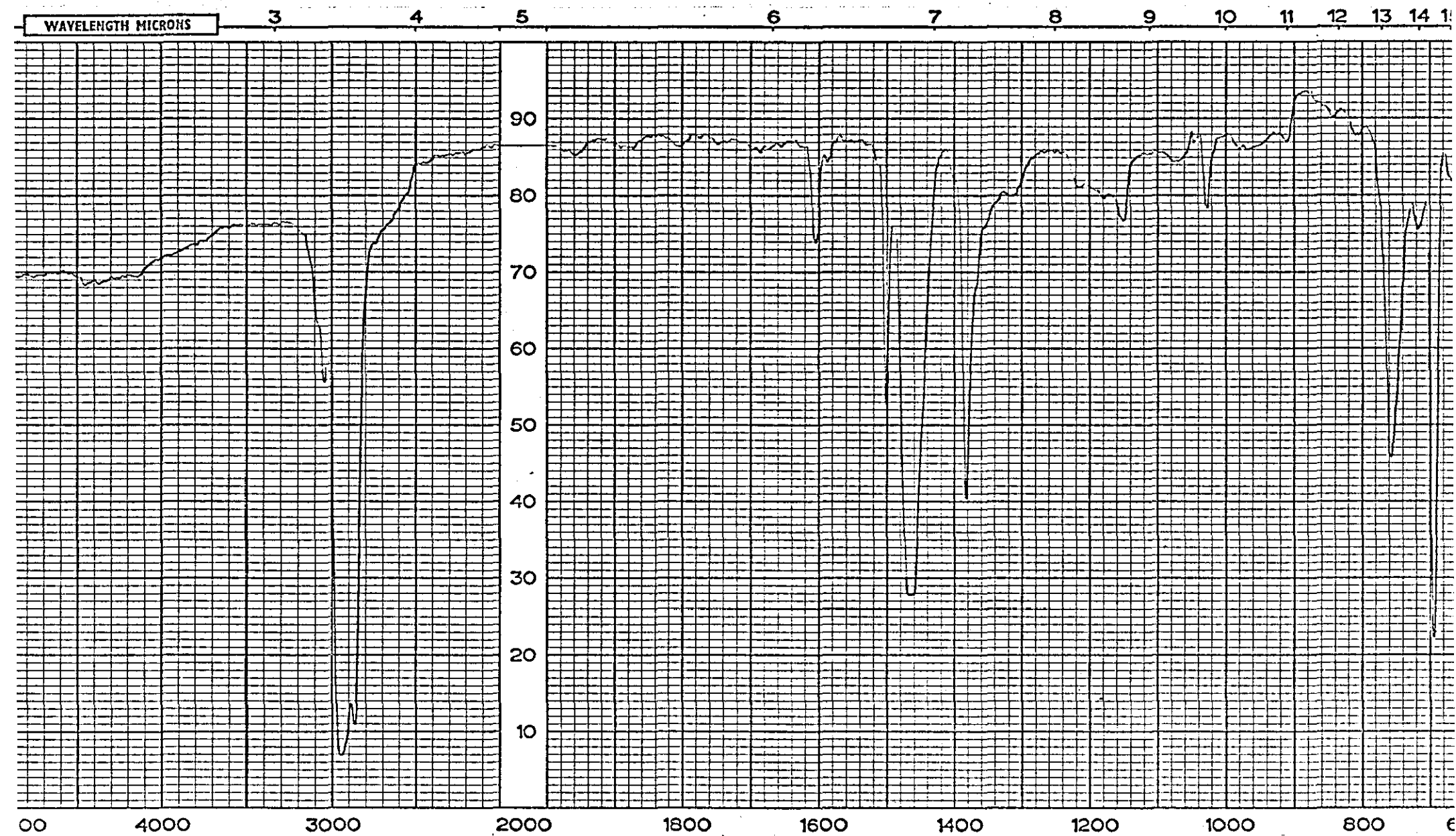
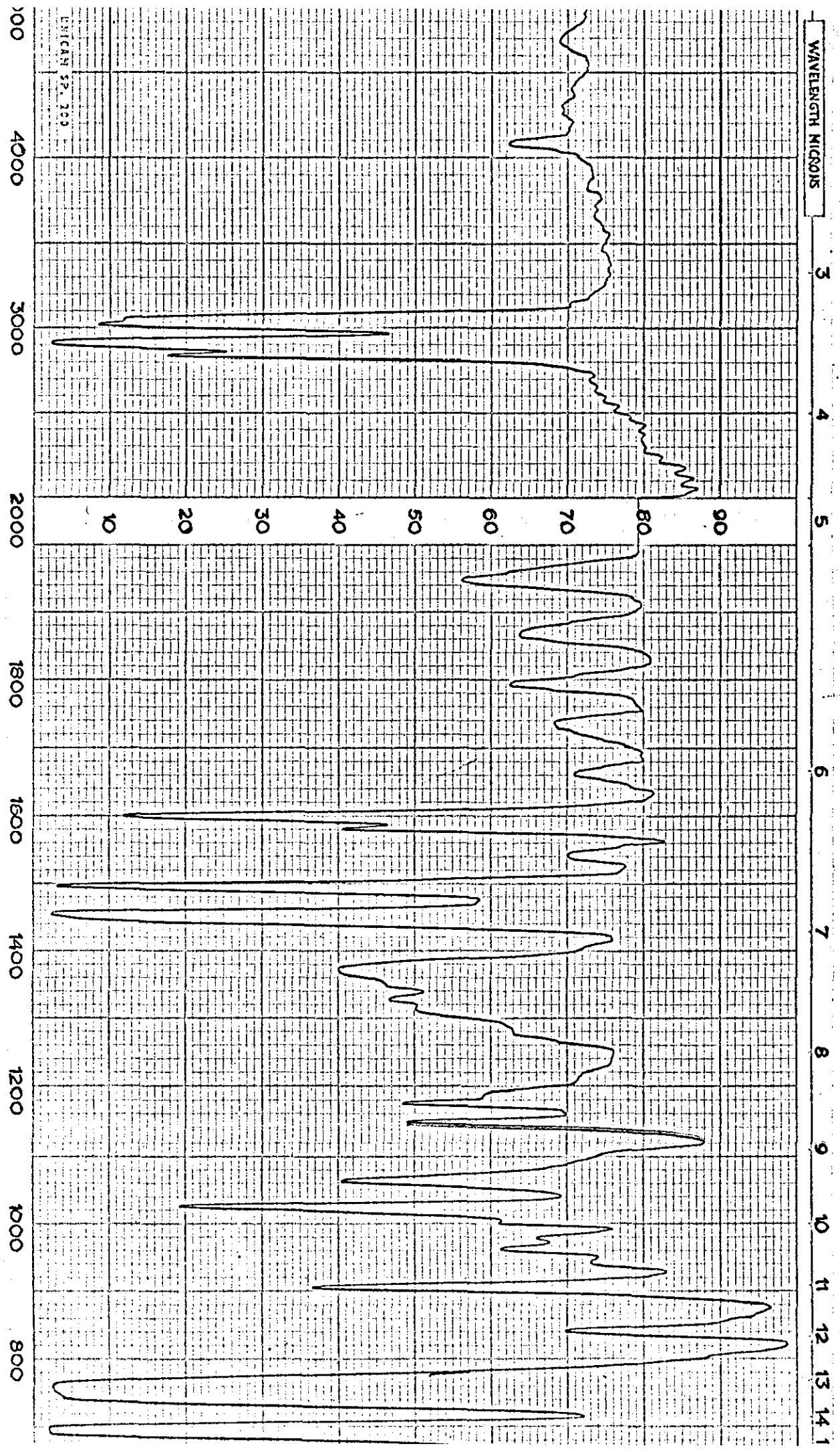




FIGURE 3.10. Polystyrene.



moulding was not possible under normal conditions. Elastic properties were poor and did not meet the requirements of the ASTM definition of a rubber viz. "a material which will, within one minute, retract to less than 1.5 times its original length, after being stretched to twice its length and held for one minute before release".

The properties of these materials can, in general, be accounted for by comparison with those of the ABA block copolymers.

For these polymers structure-property relationships can be summarised as follows.

1. The thermoplastic A block should have a molecular weight  $>7,000$ . Blocks of lower weight tend not to give complete phase separation and a drastic reduction in tensile strength results. (93,172,174)
2. An increase in the polydispersity of either of the blocks can cause a reduction in tensile strength. (14,93,172)
3. Block copolymers with A block contents below about 15% are very weak; (14,100) those with A block contents greater than about 35% exhibit a yield point on extension (14,93,100,173) due to the thermoplastic blocks forming a semi-continuous phase rather than discrete domains, yield being caused by thermoplastic deformation.
4. The presence of polymeric impurities such as free B block or AB diblock can greatly depreciate properties (172). The presence of free A block appears to have a minimal effect but free B block acts as a diluent and causes a reduction in tensile strength and worsening of elasticity. However, the most important of the impurities is the AB diblock, as little as 1-2% causing a noticeable reduction in tensile strength. This is due presumably to the introduction of "network defects", one end of the elastomeric segment being free. These network defects also cause a worsening of the elasticity of these materials.

5. Increase in overall molecular weight increases the viscosity and reduces the melt index.

Clearly in order to obtain optimum strength elasticity properties the composition of these polymers must lie within a well defined range. Generally, any deviation from specification causes a worsening of properties. This is evidently the reason why the EPDM grafted materials exhibited generally poor properties in comparison. In particular two of the above deviations from ideality are applicable to the EPDM grafted materials, viz. the polydispersity of the elastomeric block and the presence of polymeric impurities. The very nature of the metalation reaction means that essentially random grafting must occur and hence the polydispersity of the EPDM segments between grafts must be high. It follows that block copolymers prepared by this method can probably never be ideal, though this effect in isolation would probably not cause too large a worsening in properties.

In consideration of the likelihood of polymeric impurities being present, the best product that was obtained in this study was that containing a calculated average of 1.9 grafts/chain. It is most likely that this average figure was formed from polymer chains having a fairly wide distribution of number of grafts and probably a considerable proportion of chains may have had only one graft per chain. Further, some would probably have been completely ungrafted. This would have been balanced by chains having more than two grafts per chain. By analogy with the ABA block copolymers, this is the most likely cause of the poor strength/elasticity properties of the grafted polymers. If however the average number of grafts per chain could have been increased to 3 or 4 the proportion of chains with less than 2 grafts would have been significantly reduced and an improvement in properties would have been expected. Had it been

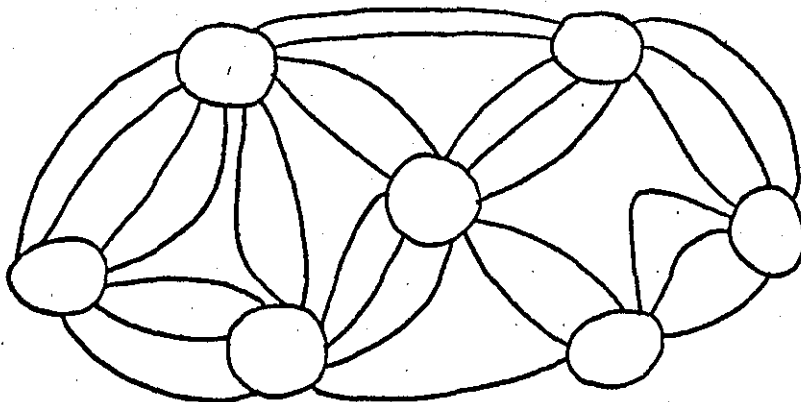
possible in addition to use a lower molecular weight EPDM then an improvement in melt flow properties might also have been obtained.

There is, however, a limit to the number of grafts per chain that can be obtained if the other parameters found for the ABA block copolymers are adhered to, i.e. a polystyrene block molecular weight of about 10,000 and an overall styrene content of below 35%. This limit can be calculated if an EPDM of molecular weight say 100,000 is considered, the maximum number of grafts per chain,  $x$ , can then be calculated from,

$$\frac{35}{100} = \frac{10,000 x}{100,000 + 10,000 x}$$

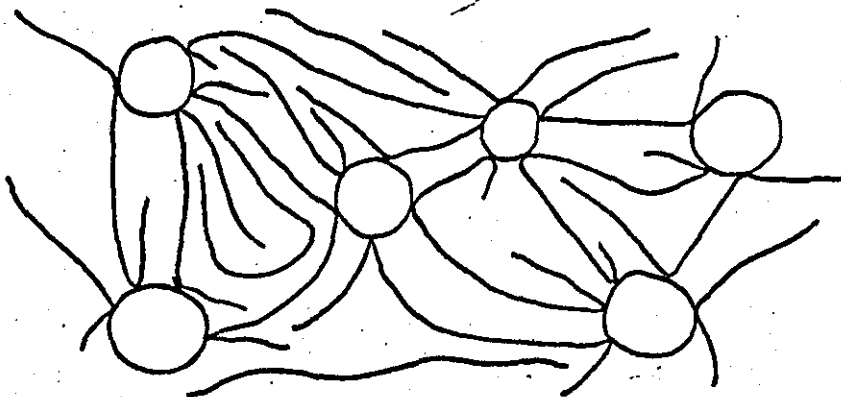
which gives a value of 5. Therefore 5 grafts per chain is the maximum allowable if the limits discussed are observed. If a polymer such as this could be produced it is reasonable to suppose that its properties should be fairly good.

The structure/property correlations for these styrene grafted EPDM's are thus seen to be analagous to those for the ABA block copolymers. The properties of the latter have been explained in terms of thermoplastic domains having the dual function of crosslinks and filler particles and although there is disagreement over the exact shape of these domains, whether spheres, rods or lamellae (14,19-25), the idealised structure can be illustrated thus,



Where the circles represent the thermoplastic domains formed by the A block and the lines represent the rubbery B blocks. In this case there are no free chain ends and the lengths of the B blocks are all very similar.

This picture can be contrasted with that which could represent the grafted polymers prepared in this study.



Here the thermoplastic domains are still present and linked by rubbery chain segments, however, there is a high "free end" content, there are some rubber chains wholly unattached and the lengths of the chain segments linking the domains are variable. The system is thus far from ideal and it is therefore not surprising that the elastomeric properties exhibited were not as good as hoped for.

#### 4. CONCLUSIONS.

##### Metalation reaction.

Before metalation could be carried out, techniques had to be developed which would produce polymer solutions suitably free of impurities. The three impurities of importance were unsaturated compounds capable of metalation, oxygen and water. The first was present in the hexane solvent and consisted mainly of benzene. A purer solvent could have been used but hexane was chosen due to its commercial suitability. The standard method for removal of unsaturated compounds from solvents involves repeated washing with concentrated sulphuric, but this procedure was found to be wholly unsatisfactory for the present study. An alternative method, due to Murray and Keller, was therefore investigated and this proved to be remarkably effective. The importance of this purification stage was realised when it was found that the presence of as little as 800 ppm of benzene caused a substantial reduction in graft efficiency when the graft polymerisation of styrene on to EPDM was being attempted.

Despite careful preparation of the polymer solutions they still contained significant amounts of oxygen and moisture. These were removed by reacting with n.butyllithium, however the products from this reaction were also found to be deleterious to the metalation reaction and therefore these <sup>too</sup> had to be removed. This was effected by passing the treated solutions through columns of activated alumina and silica. Subsequent treatment with small quantities of n.butyllithium resulted in the presence of a slight excess of metal alkyl and solutions such as these were found to be quite satisfactory for the metalation reaction.

The n.butyllithium, tetramethylethylenediamine metalating agent initially chosen for study proved unsuitable being virtually unreactive towards the polymer. Previous workers had found that it metalated polydienes but the level or type of unsaturation in the ethylene propylene terpolymers proved to be too low for it to operate. An alternative, n.butyllithium, potassium t.butoxide was therefore investigated and found to be highly reactive. The reason for its greater activity compared with the TMEDA complex was proposed as being due to its increased ionic nature. A complication was found in that the potassium t.butoxide as normally prepared forms a 1 : 1 complex with t.butanol and it is only with difficulty that the pure material is prepared by sublimation. Both sublimed and unsublimed materials were found to give very good metalating agents in conjunction with n.butyllithium but as the exact composition of the complex with unsublimed butoxide was unknown, it was decided to use the purified material.

Several ethylene propylene terpolymers were studied and it was found as expected that the polymers having the highest unsaturation were most suitable for metalation. Intolan 155, having the highest iodine number of about 20 and manufactured by the International Synthetic Rubber Company was therefore selected for the majority of studies.

Metalation was found to take place to a substantial degree when polymer solutions were stirred with metalating agent, under nitrogen at temperatures of about 70°C for periods up to 5.

A study of the literature and a consideration of the double bond situation in the ethyridenenorbornene termonomer unit of Intolan 155 led to the conclusion that metalation occurred via allylic hydrogen substitution.

Polymer carboxylation.

Two techniques had to be developed before carboxylation to a high degree could be carried out and the products analysed. The first was the carboxylation procedure, the other, purification of highly carboxylated material.

The usual method of carboxylating by pouring metalated polymer solution onto powdered, solid carbon dioxide proved unsuitable due both to the quick formation of ice on the surface of the carbon dioxide and the difficulty in contacting the polymer with the carbon dioxide. A method which proved satisfactory was to make up a slurry, in a dry bag, of powdered carbon dioxide and dry petroleum spirit, the metalated polymer solution was then added slowly to this with vigorous stirring.

Carboxylated polymers had to be obtained, in solution, free from the products of carboxylated excess metalating agent in order that the extent of carboxylation could be determined. Although moderately carboxylated polymers could be purified by acidification followed by precipitation from solution and then redissolving, polymers with acid values greater than about 15 proved to be very difficult to redissolve in non-acidic solvents. An answer to this problem was found by developing a method which enabled the side products to be removed whilst the polymer was kept in solution. The solution was first acidified and then passed through a column of activated, granular alumina the eluant proved to be free of any unbound acidic material and could be used directly for acid value determination.

The development of these techniques led to the production of polymers with acid values up to 20 and products such as these were neutralised with metal salt, and then tested as thermoplastic elastomers. The neutralisation was carried out by reacting, in solution, purified polymers containing free carboxyl, with sodium methoxide solution.



In this case the neutralising salt could be selected at will and the extent of neutralisation varied; however, a completely neutralised product could be obtained by isolating from solution the direct product of carboxylation, the metal cation being determined by the metalating agent used. It was found that products such as these could satisfy the two main criteria for thermoplastic elastomers viz that they should exhibit high tensile strength and elasticity at service temperatures but also be processable at elevated temperatures. Tensile strengths of up to  $11 \text{ MNm}^{-2}$  (1600 psi) were obtained and although the melt flow characteristics were not very good, sheets could be formed by compression moulding.

Only a modest investigation was carried out into the nature of these materials but the results obtained did enable some tentative conclusions to be made. Infra-red analysis showed that in polymers treated with a stoichiometric quantity of metal alkoxide, all carboxyl groups were present as metal carboxylate. Differential thermal analysis indicated a transition at  $153\text{--}154^{\circ}\text{C}$ , a region in which the dissociation of polymer metal carboxylate might well occur. Calculation of crosslink density yielded the information that if all the metal carboxylate groups took part in the network system then there would be approximately 160 chain carbon atoms separating each crosslink, a result in good agreement with those published by other workers. These results and the properties of the polymers were consistent with those which would be expected from a reinforced polymer crosslinked through heat labile, ionic linkages, however this simple postulate did not explain how a monovalent metal ion could link two chain carboxyl groups and it also left unexplained what the form of reinforcement was, as no conventional reinforcing agent was present.

A consideration of the literature on polymers of a similar type showed that there were two, apparently contradictory, explanations of these phenomena. The first suggested the presence of isolated crosslinks, monovalent metal ion crosslinks occurring by the association of metal carboxylate groups from two neighbouring chains and reinforcement being caused by the relief of local stresses by chain slippage and bond exchange. The second explanation invoked a conglomerate ionic crosslink, each link being formed by the association of a number of metal carboxylate groups from different chains. In this case reinforcement was said to occur by the conglomerate links forming a separate dispersed phase and functioning in a similar manner to conventional rubber bound reinforcing filler particles. A consideration of these two explanations led to the conclusion that they were not mutually exclusive but were probably both true albeit under slightly different circumstances. The essential difference between the two was the number of carboxylate groups taking part in each crosslink and it was thought that the higher the degree of carboxylation the greater was the likelihood of more than two groups being present. The more highly carboxylated polymers of the present study were therefore likely to have contained a greater proportion of conglomerate linkages than the less carboxylated materials. Reinforcement of the strongest products obtained would therefore have occurred mainly through conglomerate linkages acting as bound filler particles. The system would therefore have been essentially similar to that proposed for the hydrogenated polymers in the first part of the present study.

### Styrene grafting.

Using the metalation technique, styrene was successfully graft polymerised onto EPDM with very high graft efficiencies. A polymer could be obtained with virtually any styrene content, the level depending only on the amount added.

Attempts were made to produce a polymer with thermoplastic elastomeric properties and a consideration of the Shell ABA block copolymers, a fairly similar system, led to the conclusion that the product composition had to be kept within very strict limits. The realisation of this aim in the present system was complicated by the fact that the three main compositional variables, the styrene content, the polystyrene molecular weight and the number of grafts per chain were interdependent and thus rather difficult to control. A further complication arose through the graft efficiency being dependent on the level of metalating agent used. Thus if the level was raised above a certain value in an attempt to increase the number of grafts per chain then the graft efficiency decreased. As one of the main requirements for the system was that virtually 100% graft efficiency should be achieved this imposed rather severe limitations and the highest average number of grafts per chain obtained was only 1.9. However this product had a composition very close to that desired having a styrene content of 35% and a grafted polystyrene number average molecular weight of 23,000.

The best products obtained had properties somewhat more akin to flexible thermoplastics than elastomers and could not even be said to fulfil the rather limited requirements of the standard definition of an elastomer. However the products could be pressed into thin sheets at elevated temperatures and tensile strengths in the region of  $7-10.5 \text{ MNm}^{-2}$  (1000-1500 psi) were obtained, the latter being a big increase over the negligible strength of the starting material.

The reason the properties were not more satisfactory was ascribed

to the fact that the number of grafts per chain was just not high enough. The value of 1.9 was only an average and the product must have contained a fair proportion of chains with only one graft and some with none at all. This situation would have resulted in a great number of flaws in the network system and hence a loss in strength and elasticity. The system inherently had one unavoidable disadvantage in that no matter how high the number of grafts per chain there would still have been free EPDM chain ends and hence again a large number of flaws. However, it was calculated that the compositional limitations of styrene content and polystyrene molecular weight would have allowed a theoretical 5 grafts per chain and if this could have been realised a vastly improved product might well have resulted.

The aim of this section of the study was therefore only partially realised but a product was obtained which approached the desired composition and its properties indicated that the system did behave in the manner hoped for.

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