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CROSSLINKED POLYESTERS

INVESTIGATION OF THE STRUCTURE OF COMMERCIAL POLYMERS BASED ON TEREPHTHALIC ACID

by

Dimosthenis Kyriacos, B.Sc. (Hons), M.Sc.

- Doctoral Thesis -

Submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of the Loughborough University of Technology

May 1977

Supervisors

.

Professor A W Birley, M.A., D.Phil, F.P.R.I. Institute of Polymer Technology

J V Dawkins, B.Sc., Ph.D. Department of Chemistry

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SYNOPSIS

The thesis describes the characterisation of the polymeric components of crosslinked unsaturated polyesters; that is the saturated prepolymer synthesised from terephthalic acid and excess propylene glycol, the alkyd resulting from the condensation of this prepolymer with maleic anhydride and finally the styrene cured product.

The poly (propylene terephthalate) prepolymer has been characterised qualitatively as well as quantitatively by high resolution nuclear magnetic resonance spectroscopy. A method has been developed which permits the determination of the molecular weight, free propylene glycol content and the amount of glycol lost during polyesterification, from the integrated nmr spectrum.

The prepolymer, has also been resolved into its chain components by low pressure gel permeation chromatography. The species eluting from the chromatographic column were detected by an infrared spectrophotometer and displayed as sets of curves on a time-response recorder. The lowest molecular weight diol, dihydroxypropyl terephthalate, assumed to be a member of the distribution, was synthesised and used for the identification of the same compound present in the prepolymer. The isomeric forms of this component have been estimated statistically by nmr.

Furthermore, a method, has been developed which enables the quantitative interpretation of the chromatograms and the subsequent determination of the prepolymer chain distribution. The effect of the concentration of the starting materials on the distribution has also been studied. In addition the molecular weights as deduced by this method were in very good agreement with those estimated by nmr.

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This project also includes attempts of splitting the double bonds of unsaturated terpolyesters; the aim being the determination of the sequence distribution of the saturated segments. However, ozonolysis, phase transfer catalysed oxidation as well as preferential hydrolysis of some ester bonds failed to give unambiguous results.

Finally, the sequence distribution of the styrene crosslinks in the cured 13 polyester has been studied by C nmr and infrared spectroscopy. The first method involves the degradation of the crosslinked polyester into a styrene-fumaric acid copolymer and the assignment of the styrene quaternary carbon atom absorptions to styrene sequences the length of which is determined from the spectra of standard styrene-diethyl fumarate copolymers.

In the second method the whole crosslinking process is followed spectrophotometrically. The styrene sequences are determined through the statistical treatment of the spectral changes occurring during curing.

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CHAPTER I

ASPECTS OF UNSATURATED POLYESTER CHEMISTRY

1 INTRODUCTION

A simple esterification process is well known to every chemist. The synthesis of ethyl acetate from acetic acid and ethyl alcohol provides a common example.

When a dihydric alcohol such as ethylene glycol is allowed to react with a dibasic acid such as phthalic acid, a linear polyester is produced. Conversely if a trihydric alcohol such as glycerol replaces the diol a tridimensional polyester is the result. Therefore the products of polyesterification reactions largely depend on the functionality of the starting materials.

Therefore polyesters are condensation products of dibasic or polybasic acids and dihydric or polyhydric alcohols. This definition comprises saturated polyesters such as poly (ethylene terephthalate) (Terylene), polyesters modified by fatty acids, used in the paint industry as well as unsaturated polyesters, produced when one of the reactants contains an olefinic unsaturation.

Commercial unsaturated polyesters are produced by reacting a glycol such as ethylene or propylene glycol with an aromatic (or saturated) dicarboxylic acid and an unsaturated dicarboxylic acid (or anhydride), e.g. fumaric acid or maleic anhydride. The polymeric product is dissolved in a liquid polymerisable monomer, usually styrene. The resulting viscous solution can be transformed into a hardened product by means of catalysts which generate a free radical copolymerisation reaction between the monomer and the unsaturation sites present in the polyester backbone. Crosslinked products with outstanding mechanical properties are obtained through a glass fibre reinforcement. The resulting materials are called glass reinforced polyesters (GRP)⁽¹⁾.

2 HISTORICAL DEVELOPMENT

The pioneering work in the polyesterification field dates back to 1847 when Berzelius synthesised a polycondensate by reacting tartaric acid and glycerol. His contemporary Laurenzo, prepared poly (ethylene succinate) by heating ethylene glycol and succinic acid. This was followed by Kraut's investigations on the polymer formed by heating acetyl salicylic acid and the introduction of a chain structure to describe it.

Chain formula assignments were undertaken later on by Blaise and Marcilly on polyesters prepared from hydroxypivalic acid.

Academically, the first unsaturated polyesters were introduced by Vorlander in the synthesis of glycol maleates. A more practical aspect of polyesterification was W J Smith's production of poly (glyceryl phthalate) from glycerol and phthalic anhydride; this discovery led GEC and BTH, in 1913, to develop surface coatings by modifying the resin with various vegetable oils.

With the advent of Staudinger's⁽²⁾ polymer concept, Carothers⁽³⁾ was the first to prepare polyesters with well-defined polymeric structures. He synthesised poly (ethylene maleate) and poly (ethylene fumarate) by performing the condensation reactions in the presence of nitrogen. By his explorations, Carothers introduced a solid basis to the modern chemistry and technology of polyesters. This was followed by Kienle's⁽⁴⁾ theory of functionality. He is also credited with creating the word Alkyd (from Alcohol and Acid). Further developments in the technological area are due to C Ellis. His work covers the reaction products of dihydric alcohols, dibasic acids and acid anhydrides for use as lacquers.

It is in the late thirties that Bradley, Kropa and Johnson⁽⁵⁾ reported the conversion of maleic anhydride based polyesters into infusible products upon heat treatment; thus introducing the concept of crosslinking unsaturated polyesters.

The landmark in the technological development of unsaturated polyesters was Ellis⁽⁶⁾ second publication describing the copolymerisation of maleic polyester resins with monomeric styrene in the presence of a peroxide catalyst referred to as drier. Muskat⁽⁷⁾ then, introduced phthalic anhydride along with maleic anhydride and ethylene glycol to produce polyesters compatible with styrene. These last two discoveries led to the commercial application of unsaturated polyesters in 1941. The earliest alkyd resins were cured only at a temperature of about 100°C, in the presence of benzoyl peroxide. By 1944, however, it was found that curing can take place at room temperature by the use of a tertiary amine as an Accelerator in the presence of the peroxide. Furthermore, the applicability of unsaturated polyester resins was boosted when the United States Rubber Company discovered that glass fibres convey a good deal of reinforcement to plastics of the polyester type.

3 PREPARATION OF UNSATURATED POLYESTER RESINS

3.1 Synthesis of Unsaturated Polyesters

3.1.1 Single Stage Process

In this method, all the ingredients i.e. the saturated and unsaturated acids (or anhydrides) are allowed to react simultaneously and esterification is completed in one step.



In a typical dry laboratory synthesis⁽⁸⁾ all ingredients are introduced in a three necked round bottomed flask fitted with a stirrer, inert gas inlet, thermometer and reflux condenser. The latter is topped with a thermometer and receiver for collecting the water, by-product of the reaction. The high boiling point glycol condenses and returns to the kettle with minimum loss. A low vacuum may also be applied for the separation of water.

The heating programme varies. The reaction can be carried out at one temperature, generally $200-210^{\circ}$ C or at 180° C for several hours then at 210° C. ICI start the reaction at 105° C, and as a result of the exothermic formation of the half esters, the temperature reaches 165° C. In the final stages of the process the temperature is increased to 210° C. The course of the reaction is followed titrimetrically i.e. samples of the reaction mixture are titrated against a standard solution of alkali and the quantity of the latter, expressed in milligrams, required to neutralise one gram of the sample is calculated. The result expresses the acid number. The lower the acid number, the higher the molecular weight. The reactions are usually stopped when the acid number reaches the value ~10.

An alternative, laboratory synthesis⁽⁸⁾ of unsaturated polyesters, consists of carrying out the reaction in the presence of 10% xylol, which, forms an azeotrope with water. In the reflux line, a Dean Stark trap is inserted so that the water present in the heterogeneous condensate can be separated.

3.1.2 Two Stage Process

In this process the saturated acid is esterified with all the glycol to form an essentially neutral ester, basically a polymeric diol.

 $\begin{array}{c} 0 \\ + \text{HO-CH}_2 - \text{CH}_3 \\ \text{OH} \end{array} \xrightarrow{\text{pressure}}_{\text{temperature}} \text{HO-CH-CH}_2 - \begin{array}{c} 0 \\ 0 - \text{C} - \begin{array}{c} 0 \\ 0 - \text{C} - \begin{array}{c} 0 \\ 0 - \text{C} + \begin{array}{c} 0 \\ 0 \end{array} \end{array} \end{array} \right)}$ 2.2 moles 1 mole

In a second stage, the unsaturated component is added and the reaction is carried out to completion i.e. until a low acid number is reached.

O=C C=O O-CH₂-CH-OH + CH=CH _____ unsaturated polyester СН₃ но-сн-сн₂-1 mole

This process has originally been developed to allow a smoother reaction for low reactivity acids such as isophthalic ⁽⁹⁾ and terephthalic acids. The latter is insoluble under ordinary laboratory conditions; its dissolution is brought about only by the severe first stage conditions. The polyesterification has been successfully attempted at atmospheric pressure in the presence of a titanium, tin or silicate catalyst ^(10,11). Another alternative to avoid the use of pressure in the first stage is the transesterification of dimethyl terephthalate with the glycol in the presence of a basic catalyst ⁽¹²⁾.

The isophthalic acid^(33, 35, 36) based unsaturated polyesters may be synthesised by both methods; the two stage process, however is more advantageous and its credits will be discussed later on. Another method, not very much in use, introduces a modified second stage operation⁽¹³⁾. The maleic anhydride is not condensed directly to the neutral saturated polyester, but it is allowed to react, in a separate operation, with the glycol. The resulting, mainly acidic low molecular weight polymer is then brought into contact with the ester synthesised in the first stage and polyesterification is carried out into completion at high temperatures. The process is, perhaps, more complex since it involves an extra operation but again it is credited with producing alkyds of better quality than those produced by a single stage process.

3.2 Preparation of Polyester Resins (9,14)

The polyesters, obtained by each of the synthetic methods described before are solid materials with a pale straw colour. It should be mentioned that considerable decomposition as well as crosslinking, leading to the darkening and insolubility of the polyester, could be the result of a poor temperature control and inefficient agitation.

The dissolution of the alkyd in the monomer, styrene for example, may be carried out by two methods.

In one method the alkyd is pulverised and then slowly dissolved in styrene at room temperature. In the other, the hot liquid alkyd, in the final stage of the polycondensation (temp. 100-120°C), is slowly poured in styrene (25°C) with vigorous agitation. The last procedure is the most effective and more rapid. Room temperature dissolution of the solid alkyd is sometimes inadequate and results in cured products bearing the signs of undissolved particles. In both cases extra stabilisation of the monomer prior to dissolution is needed. This is usually carried out by the addition of 50-100 ppm of inhibitors such as hydroquinone or tertiary butyl cathechol.

Inhibitors are reducing agents capable of donating hydrogen atoms, thus absorbing free radicals and preventing the premature gelation of the resins.

4 THE CROSS-LINKING MECHANISM

This is essentially a free radical copolymerisation between styrene and the unsaturation sites of the polyester chain. The initiation of the cross-linking or curing process is carried out by an accelerator-catalyst system. The catalyst is a free radical generator. At ordinary temperatures its effectiveness is enhanced by the presence of an accelerator which activates its splitting. The system cobalt naphthanate or octoate - tertiary butyl hydroperoxide⁽⁸⁾ is widely used. In this reaction the cobaltous cobalt is oxidised to cobaltic cobalt, thus:

$$R0.0H + Co^{++} = R0.0. + OH^{-} + Co^{+++}$$

The cobaltous cobalt is then regenerated, leading to a chain decomposition of the hydroperoxide

 $R0.OH + Co^{+++} R0.0.+ H^++ Co^{++}$

The cycle is repeated until all the hydroperoxide has been decomposed. Other important catalysts are cyclohexanone peroxide, methyl ethyl ketone peroxide, and benzoyl peroxide. Amines such as dimethylaniline and diethylaniline are also effective accelerators.

The radicals generated attack a polyester or monomer double bond and therefore initiate a free radical reaction, leading to the cross-linking and hardening of the resins. This process may be schematically represented as follows:

S From Former Former Former www.F.S.F.F.F.S.F.S.F.S. S Fun Fun Frank Frank Frank initiation S Fun Fun Frank Frank Frank R-S F F F F

S = styrene F = fumarate R = radical



Because of the increasing viscosity of the medium, complete curing is brought about only by heating the product at elevated temperatures.

The kinetics of the cross-linking process were followed dilatometrically⁽¹⁵⁾ as well as by infrared spectroscopy and refractometry⁽¹⁶⁾. All methods indicate, perhaps as expected, a first order dependence of the rate on the overall unsaturation; the activation energy being of the order of 20 kcal/mol.

5 EFFECT OF COMPOSITION ON PROPERTIES

The physical properties of polyester resins are affected to a great extent by the chemical composition of the polyester. This aspect of unsaturated polyester technology will be briefly reviewed in this section. For a more extensive survey reference (17) is recommended. For a specialised review on corrosion resistant polyesters we recommend reference (18).

5.1 Effect of Saturated Acids

The effect of terephthalic, isophthalic, phthalic, adipic and diglycolic acids on the physical properties of unsaturated polyesters⁽¹⁹⁾ cured with 30% by weight of styrene, is illustrated in the series of graphs displayed in figure I.1.

The flexural strengths follow the sequence aromatic acids > diglycolic > adipic. The tensile strengths follow roughly the same sequence. Isophthalic acid showing slightly higher values in the aromatic series. Terephthalic acid has the highest heat distortion temperature, while water absorptions of the isophthalics are uniformly slightly lower than those of the others. Furthermore, the heat distortion point curve for diglycolic acid is well below that of adipic acid and both acids lead to poor water absorption results.

The superiority of terephthalic acid based unsaturated polyesters, over other acids, as far as corrosion resistance and heat resistance are concerned is well exemplified in references (10) and (20). In addition terephthalic acid leads to polyester resins exhibiting a very low shrinkage on curing.

From a structural point of view aromatic acid based polyesters result in the so called rigid polyesters because of their higher tensile and flexural strengths over aliphatic acid based polyesters which are called flexible. The hardness, on the other hand decreases as the aliphatic chain of the diacid becomes longer. Aromatic acids giving the hardest products; a similar behaviour is found when considering heat distortion temperature. On the contrary the impact strength increases with increasing chain length and is minimum in the case of aromatic







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acids. In addition they increase the compatibility of polyesters with styrene monomer and avoid crystallisation.

5.2 Effect of Glycols^(8,17,21)

The most common glycol used in unsaturated polyester synthesis is propylene glycol. It is a low cost raw material and, at the same time imparts to the cured product excellent physical and chemical properties. A wide range of properties may be obtained by modifying the glycol composition. For example, the greater flexibility and impact resistance of propylene glycol based polyesters, may be enhanced by co-condensation with other glycols such as diethylene or triethylene glycol which produce phthalate-fumarate castings with higher tensile and flexural properties than propylene glycol does.

The effect of some glycols on the flexural strength, flexural modulus , impact strength and heat distortion temperature of cured polyesters is shown in figure I.2. Accordingly, some structural features, specific to each glycol may be roughly used to predict their influence on the performance of cured resins. For example, pendant methyl groups seem to impart higher heat distortion temperatures whereas the oxygen ether linkages tend to reduce the heat distortion temperatures generally, flexible products have much lower heat distortion temperatures than the rigid. On the other hand, glycols contributing to the flexibilisation of cured polyesters, such as the long chain ones and those containing ether oxygen linkages and pendant groups, tend to promote water absorption. Furthermore, the highest impact strength is achieved in compositions containing long chain unbranched alcohols, generally when used in conjunction with aromatic The trend is sometimes reversed when aliphatic acids are used. acids. Similarly, the ether oxygen bond should tend to increase impact strength because of its flexibilising nature but yet reduce it because of the crystallinity it induces. The latter may be avoided through glycols co taining pendant groups.

Glycol type	Flex strength b.s.	Flex.mod. D. sic 10	Glycol type	Unnotched Imp str.	slycel type	Hed Dist.Temp C
Picpylene glycol	18.7	6.1	1,5 Rentane diol	11.2	2.3 Butane dist	81
bielhylene glycol	17.5	5.D	1,4 Butane dicl	3.7	Propylene glycol	73
Elhylene Ropylene gly.	F.U	5.9	Dipropylene glycol	3.7	1.3 Butane diol	62
Trimethylene glycol	13.3	3.6	Repylene glycol	2.4	1.4 Butane diol	59
Ethylene Dicthylene	12.1	3.1	2.3 Butane diel	1.9	Dipropylene glycol	below room temb
			1,3 Butane did	1.5	Diethylane alucol	
			,	(it.16/in)		

Figure I.2 Effect of glycol type on properties of cured polyesters

5.3 Effect of Unsaturated Acids

Two types of unsaturated components are industrially employed in the manufacture of unsaturated polyesters. These are fumaric acid and maleic anhydride. In most cases the latter is preferred since it isomerises to the former under polyesterification conditions hence a difficulty in comparing the properties of entirely maleate based polyesters to fumarate based.

In the following comparison, the work of Parker et al⁽²²⁾ is exposed since they synthesised both fumarate and maleate based polyesters in solution at low temperatures (xylene solvent) avoiding thus, in our opinion a complete isomerisation of maleates to fumarates.

The properties of the products cured with 30% by weight of styrene are shown on the graphs displayed in figure I.3.

Fumarate based polyesters react much faster and much more effectively with styrene (see Chapter II, subsection 3.1.1).

5.4 Effect of Monomers^(17,23)

In the early stages of unsaturated polyester technology, the alkyds were converted into hardened products by a heat treatment in the presence of a catalyst. Crosslinking was the result of a free radical addition between the olefinic components of the polyester chains. The practical difficulties associated with this curing method are obvious. The breakthrough in unsaturated polyester technology was the use of alkyds as solutions, of considerable viscosity, in polymeris able monomers, the main functions of which are two-fold: a) to act as solvent carriers for the unsaturated polyester thus facilitating

its handling and processing, and

b) to provide a rapid means of reacting with the unsaturation sites to yield completely crosslinked copolymers. Styrene is by far the most widely used monomer. It has a fast copolymerising capability and yields cured products with very good properties. <u>Vinyl toluene</u> having a higher boiling point than styrene permits cure at higher temperatures in short time. It also gives less loss of



<u>Figure I.3</u>. Effect of type and content of unsaturated acid on properties of polyesters

monomer during mixing and storage. The low volume shrinkage of the vinyl toluene cured products contributes to a good cracking resistance. It has the tendency to shift the haze colour towards red, especially in the presence of acrylic monomers. The corrosion resistance it confers to the final product is comparable to that of styrene, but the weatherability is poorer. The advantages of chlorostyrene over styrene are its high boiling point, low polymerisation shrinkage and high heat distortion of the final products. Also, the laminates have higher strength as well as better surface smoothness and greater resistance to burning. In addition, it provides faster cure rates than styrene. Alpha Methyl styrene, on the other hand, enhances the storage stability and allows the control of the exothermic heat of polymerisation in large section castings. Meta divinyl benzene, because of its tetrafunctionality, results in highly crosslinked and therefore harder, more temperature resistant and more brittle products than those obtained with styrene. In addition to styrene monomers, acrylates are often used as monomers, mostly in conjunction with styrene. For example, methyl methacrylate, enhances the transparency of laminates as well as their resistance to weathering. But, its poor copolymerisation characteristics and low boiling point lead to the poor durability and the large shrinkage of the cured products. The presence of styrene is therefore almost inevitable. Methyl acrylate also suffers from its low boiling point. However, it improves the clarity, gloss retention as well as the resistance of laminates towards discoloration.

Finally, allyl derivatives are also used as monomers. <u>Diallyl phthalate</u>, for example, is employed in applications where high exotherm temperatures are undesirable, because it copolymerises slowly with a low exotherm. In addition it leads to cured products with very good impact resistance as well as flexural strength. Both <u>triallyl cyanurate</u> and <u>triallyl isocyanurate</u>, improve the heat stability of unsaturated polyesters. Despite the difficulties associated with their copolymerisation characteristics, the products have a high heat distortion temperature and a good strength retention at 500°F.

5.5 Special Purpose Components (8,24)

This subsection will deal primarily with the production of self-extinguishing resins. This may be achieved either by the physical addition of a special filler to the resin or by the modification of one of its chemical constituents.

The most common fire retardant filler is antimony trioxide which is used together with a highly chlorinated paraffin. Chlorinated waxes are rarely _ used on their own since they tend to sweat out and result in a rapid deterioration of the laminates.

A simple chemical method of conferring some degree of fire retardance to a polyester resin is to replace the acids by chlorinated ones. Thus the degree of fire retardance of phthalic anhydride based polyesters can be increased when tetrachlorophthalic anhydride is used instead. A higher chlorine content and therefore better self extinguishing properties can be built up into the polyester by the use of chlorendic acid produced by the Diels-Alder reaction of hexachloropentadiene and maleic anhydride $^{(40)}$



Chloromaleic acid based polyesters, on the other hand, contain insufficient chlorine to be self-extinguishing without the addition of antimony trioxide.

Quite good self-extinguishing resins can be made by replacing all or part of the styrene by diallyl benzene phosphonate and dichlorostyrene.

Cost reduction, on the other hand, is achieved through the incorporation of cheap mineral fillers such as chalk or china clay. Mouldings with reinforced structures are obtained when short glass fibres (12-55 mm) are added to the resin (20-35% by weight). This mixture is very often called sheet moulding compound (SMC) in contrast to the dough moulding compounds (DMC) which contain, in addition to calcium carbonate and other special purpose fillers shorter glass fibres $(3-12 \text{ mm})^{(24)}$. The viscosity of the resin itself is altered by the addition of thixotropic materials such as silica aerogels and treated bentonite clays. Finally the light stability of the castings is improved by the incorporation of phenyl salicylate, acetyl salicylic acid and other UV absorbers.

6 EFFECT OF STRUCTURAL VARIABLES ON THE PROPERTIES

Besides the contribution of the chemical nature of the components to the final properties of the cured polyesters, lies the effect of some variables related both to the structure of the polyester backbone and to the crosslinking process itself⁽²⁵⁾. These variables as well as their influence on the properties of crosslinked polyesters will be briefly exposed in the following subsections.

6.1 Concentration of Components

This is perhaps a vital point for the production of polyester castings exhibiting optimum properties, and its importance may be visualised from the experiments of Parker et al⁽²²⁾, which describe the effect of varying the amounts of styrene and degree of unsaturation on the physical properties of poly (propylene maleate phthalate) styrene resins. The ratio of maleic anhydride to saturated acid, in the base polyester, was varied in mole % steps and each member of the resulting polyester was mixed with 20,30,40 and 50% styrene in order to obtain the effect of varying the quantity of styrene as well as the degree of unsaturation. The results are shown in figure 1.4

Since most commercial polyester resins contain 50% by weight of styrene reference will be made to the graphs in order to find the corresponding molar concentration of maleic anhydride which would result in cured products with optimum properties. Thus the elongation at break is minimum at~100% unsaturation, the water absorption at 20%, the heat distortion point is maximum at~100% unsaturation, the exotherm is minimum at 20%, the tensile strength is maximum at 45%, the flexural strength at 60% and the moduli in tension and flexure at 30 and 35% unsaturation respectively. It is obvious that no one polyester resin can fill adequately all the commercial needs. The selection, therefore, should be made, on the basis of the application requirements.



<u>Figure I d</u>. Effect of varying amounts of styrene and degrees of unsaturation on properties of polyl propylene maleale philholate)

6.2 Distribution of the Components along the Polyester Chain

The importance of the distribution of the chemical constituents along the polyester backbone may be well examplified by the superior properties of polyesters synthesised by the two stage process.

The first "two stage" polyesters were produced on a laboratory scale by Carlston et al⁽⁹⁾. The starting materials were isophthalic acid, propylene glycol and maleic anhydride. The authors proved that their new synthetic method results in polyesters with higher softening points, their solutions in styrene are much more viscous and the styrene cured polyesters have higher heat distortion temperatures and improved impact strengths compared with the same polyesters made by charging all ingredients to the kettle at once.

Bockstahler⁽¹³⁾ has also described a slightly different two stage process. Accordingly in a first stage adipic acid and propylene glycol are condensed to yield a saturated polyester which when freed from unreacted matter had an acid number of 1.1. Separately, maleic anhydride was allowed to react with propylene glycol again, to yield rather a large quantity of the monoester with acid number 350. Both products were then brought together under pressure and at high temperature to give an unsaturated polyester. The styrene cured product had better physical and electrical properties than the cured one stage polyesters. Although no scientific explanation was given by the authors to account for these differences, it is very apparent that the two sets of polyesters should differ in their skeletal structure.

A Szayna⁽²⁶⁾ interpreted these differences in terms of the location of the double bonds. He suggested that a two stage process is conducive to polymeric chains bearing unsaturation sites at their ends. Commenting Carlston's results he suggested that in the first step, the low melting maleic anhydride reacts first, forming the spine, and the high melting and difficultly soluble isophthalic acid reacts later and adds toward the terminals of the chain.

This assumption was proved experimentally by means of low molecular weight polyesters based on succinic anhydride, maleic anhydride and ethylene glycol. Polyesters with double bonds located towards the end of the chains (endenes) were prepared by first esterifying two moles of succinic anhydride with three moles of diethylene glycol for eight hours and then adding to the saturated spine unsaturated terminals in the form of maleic acid monoester. The corresponding centrene polyester was prepared by first reacting the maleic anhydride with the glycol until a fully hydroxylated polyester is obtained and then adding succinic anhydride. The styrene cured endenes had a higher tensile and impact strengths and larger elastic modulus than the corresponding centrenes. The same assumption was proved experimentally by Mikhailova et al^(27, 34) as well as by Mleziva et al⁽²⁸⁾.

In addition to the above evidence, Jedlinski and Penczek⁽²⁹⁾ attributed the better physical properties of polyesters prepared in two stages to the regular distribution of the unsaturated units along the polyester chain. In their synthetic method however, the first stage polyester was freed from all unreacted propylene glycol, emphasising thus that side reactions may also affect the properties.

Sedov et al⁽³⁰⁾ acknowledged the influence of the regularity of the saturated segment distribution on the mechanical properties of cured polyesters based on triethylene glycol, maleic anhydride and sebacic acid, but added that another advantage of the two stage process is the absence of side reactions between the unsaturated components and propylene glycol; The larger part of the latter having reacted with the saturated acid in the first stage. The side reactions, leading to doublebond losses will be discussed in Chapter II.
6.3 Other Variables

In the following paragraphs some important factors expected to affect the properties of cured unsaturated polyester resins will be briefly discussed. Their details will be considered in the next chapter which deals with the characterisation of unsaturated polyesters.

For example, an increase in the molecular weight of the polyester chains leads to cured products with higher heat distortion temperatures and improved chemical resistance.

On the other hand, it is known that maleates isomerise to fumarates on heating and therefore, because of the better performance of the fumarate based polyesters, it is expected that the extent of this isomerisation, during polyesterifications involving maleic anhydride, will affect the properties of the final product.

Finally, the degree of crosslinking^(37,38,39) described qualitatively in subsection 6.1, as well as the occurrence of side reactions, leading to the loss of double bonds and to the disturbance of the polyester chain distribution are variables influencing the structure and therefore the properties of the crosslinked polyester resins.

7 "IMPOLEX" UNSATURATED POLYESTER RESINS⁽³²⁾

"Impolex" is the brand name of the unsaturated polyester resins produced by Imperial Chemical Industries Limited.

Of particular interest, to this research project, are the T400 and T500 series. Both are terephthalic acid based polyesters, synthesised by the two stage process. The T400 polyesters are the result of the polycondensation of one mole of terephthalic acid, 2.2 moles propylene glycol and one mole of maleic anhydride. The monomer is styrene, added in 50% by weight. The main characteristic of the resulting cured products is their excellent resistance to attack by dilute acids and aqueous solutions of inorganic salts. Generally, they exhibit a high degree of chemical resistance. The T500 polyesters are synthesised from one mole of terephthalic acid, 3.3 moles of propylene glycol and two moles of maleic anhydride. Their styrenated solutions result in laminates with excellent heat stability and chemical resistance.

The work exposed in this research project, will be mostly related to the investigation of the structure of the T400 and T500 polyesters.

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CHAPTER II

ASPECTS OF UNSATURATED POLYESTER CHARACTERISATION

1 INTRODUCTION

The identification of the chemical components of an unsaturated polyester of unknown composition examplifies the term characterisation in its simplest form. However, with polymers, essentially those of practical importance, more details on their structures are needed for their development to progress. Characterisation, therefore, embraces the whole range of identification processes leading to an understanding of the structural variables which affect the properties of the polymer. These variables as well as the effect they have on the properties of the cured polyesters, have been exposed in the previous chapter. The present chapter is a literature review of the different methods of characterising the variables cited in Chapter I. In essence, the following sections will include the identification of the chemical components of unsaturated polyesters, as well as the characterisation of the structural changes occurring during the synthesis and the crosslinking of polyesters.

2 METHODS OF UNSATURATED POLYESTER CHARACTERISATION

In this section, the different methods of identification of unsaturated polyesters will be reviewed. Little emphasis will be given to the elucidation of structural problems. These will be fully discussed later in the chapter.

2.1 Infrared Spectroscopy

The infrared analysis of polymers in general and of polyesters in particular is well examplified in papers (1,2) and standard textbooks (3). Basically, these mention the specific absorptions of a variety of diacids and diols used in polyester synthesis. Analysis of the styrenated resin itself is also possible thus eliminating the need for any prior chemical treatment.

The most important infrared absorptions as far as the structural characterisation of polyester resins is concerned are those caused by the various olefinic components. These are:

- a) The C=C stretching vibrations of the vinyl group of styrene and those of the polycondensate unsaturation at 1629 cm^{-1} and 1639 cm^{-1} respectively.
- b) The =CH out of plane deformation vibrations at the fumarates and maleates at 982 cm⁻¹ and \sim 700 cm⁻¹ respectively.
- c) The =CH₂ wagging vibration of the styrene vinyl group at 910 cm⁻¹.
- d) The fumarate double bond absorption at 775 $\rm cm^{-1}$.

In addition to the straightforward identification of the polyester components infrared spectroscopy has been successfully used in monitoring the various structural changes that occur during the synthesis as well as during the crosslinking of polyesters. Examples of these changes, which will be reviewed in later sections of this chapter are the isomerisation of the maleate double bonds to fumarates as well as the disappearance of these bonds during crosslinking.

24[.]

2.2 Gas Chromatography (3,4,5)

The method involves the separation of the monomer followed by the methanolysis of the alkyd. Isolation of the alkyd from the monomer solution can be achieved either by successive precipitations and purifications from petroleum ether/acetone or by direct vacuum distillation in the presence of a small quantity of hydroquinone to prevent polymerisation.

The isolated alkyd is then subjected to methanolysis either in the presence of sodium methoxide or by means of boron trifluoride and sulphuric acid. After completion of the esterification process a small portion of the methanolic solution is injected in the chromatographic column where separation of the various components occurs. Packing materials such as Carbowax 20M on Chromosorb W and methylsilicone gum E30 on Fluoropak 80 have been used for successful separations. Furthermore, temperature programming is often needed for the resolution of the liquid components (mixture of two glycols) and the acceleration of the appearance of the esters.

For identification purposes, the retention times of the components are compared to those of standards estimated under the same experimental conditions. A better identification can be achieved by examination of the infrared spectra of the trapped fractions.

The components can be determined quantitatively by means of a flame ionisation detector provided that calibration diagrams are constructed for each of the components; The area under the chromatogram peak being proportional to the concentration. In this method fumaric acid is not distinguished from maleic acid, since under the methanolysis conditions employed both are converted to dimethyl methoxy succinate⁽⁶⁾.

Dibasic acids and polyols could also be quantitatively identified according to the procedures of Esposito and Swann⁽⁷⁾ and Esposito⁽⁸⁾.

Pyrolysis gas chromatography has also been used for the identification of saturated polyesters such as poly (ethylene adipate). Despite the presence on the chromatogram of some unidentifiable products, results of the pyrolysis conditions, it is claimed that the method can be used to identify two and three components of polyesters as well as some of their structural units⁽⁹⁾.

2.3 <u>Nuclear Magnetic Resonance Spectroscopy</u>(10, 11, 12)

This is perhaps the quickest method of analysing unsaturated polyesters both qualitatively and quantitatively. Analysis can be carried out either at 30-35°C by dissolving the alkyd in a deuterated nmr solvent (acetone, chloroform, DMSO) or at 125°C by working directly on the styrenated solutions. However, it is recommended to isolate the alkyd from the monomer to avoid any interference of the latter with the components absorptions.

The most important nmr absorptions, as far as the structural characterisation of unsaturated polyesters is concerned, are those corresponding to the olefinic hydrogens of the fumarates and maleates; they occur mostly as singlets at \sim 7 ppm and 6.5 ppm (delta values from TMS internal standard). An important observation concerns the splitting of these singlets. For example, the olefinic protons of fumaric acid in the nmr spectra of poly (ethylene fumarate) and the copolyesters of fumaric and sebacic acids with ethylene glycol consist of three peaks the intensity of which varies with time during esterification. These three peaks have been assigned to the free fumaric acid, its half ester and its diester⁽¹³⁾.

Furthermore, ethylene glycol units are sensitive to the linking acid units; in an nmr experiment, identically diesterified ethylene glycol gives rise to a single methylene absorption while two are the result when ethylene glycol is esterified to two different acids at both ends. This observation has been applied in the determination of the chain composition of some polyesters⁽¹⁴⁾.

2.4 Other Methods of Unsaturated Polyester Identification

A considerable amount of effort has been put in the determination of polyester components by polarography (15,16). However, the method is not of universal value since its application is limited mainly to the detection of fumaric, maleic and phthalic acids. Thus, the polyester is hydrolysed with potassium hydroxide solution in the presence of acetone. When hydrolysis is completed acetone is evaporated and the product is neutralised with hydrochloric acid and diluted. An aliquot of the solution, in the presence of ammonium chloride and hydrochloric acid is polarographed after deoxygenation. The half wave resolution of the polarographic waves of each constituent largely depends on the pH of the medium. Furthermore quantitative estimates can be reached by constructing calibration graphs of concentration of standard solutions against wave height.

Another interesting characterisation method, though not as important as nmr, is Raman spectroscopy (17). Although not very much applied for polyester characterisation it offers, by being a light scattering technique, the possibility of analysing cured polyesters; an advantage in some respects over infrared spectroscopy.

3 TOPICS IN UNSATURATED POLYESTER CHARACTERISATION

This is the first of two sections in which the application of the techniques described earlier, on the elucidation of some structural problems related to unsaturated polyesters, will be exposed.

This section will deal exclusively with the structure of the alkyds only and the different changes they suffer during their formation from their chemical constituents. In the following we shall discriminate between the terms structural and chemical in the sense that structural changes will mean alterations in the configuration of the polyester chains, including the chemical processes leading to these alterations, while chemical changes will concern those processes which destroy the actual chemical consistency of the polyester components.

3.1 Structural Changes taking place during Polyesterification

3.1.1 Isomerisations

This is one of the most extensively investigated topics in the field of unsaturated polyester characterisation. It concerns the isomerisation of the maleate unsaturation to fumarate during the synthesis of polycondensates starting from maleic anhydride. The reason is obvious, especially from a technological point of view, since the fumarate based polyesters exhibit better properties but maleic anhydride is much more easily esterified and also much cheaper than fumaric acid.

From a scientific point of view the superior properties of the fumarate type polyesters are mainly attributed to the ease with which the fumarate double bonds react with the crosslinking agent, styrene. This is obvious from the reactivity parameters ⁽¹⁸⁾ of ethyl fumarate (r_f) and ethyl maleate (r_m) with respect to styrene r_s

 $r_s = 6.52$ $r_m' = 0.005$ at $60^{\circ}C$ (19) $r_s = 0.3$ $r_f = 0.07$ at $60^{\circ}C$ (20)

indicating that if two polyesters one containing only fumarate double bonds and the other an equivalent amount of maleate bonds, were crosslinked with

the same quantities of styrene, the former will have much shorter styrene crosslinks than the latter. The logical consequence would be, if a quantity of monomer enough to react with all the fumarate bonds of the first polyesterwere used to cure the maleate polyester, a good deal of its unsaturated sites would remain unreacted contributing thus to the deterioration of its properties.

Carothers first observed this cis-trans isomerisation when maleic acid was esterified at 200[°]C. Temperature assists therefore the isomerisation. However, the contribution of several other factors, especially those encountered in polyesterifications is also of considerable importance. These factors, as well as the methods applied in their study will be reviewed in the following paragraphs.

a) Type of glycol used in the polyesterification process

This topic has been investigated by a team of Hungarian researchers⁽²¹⁾. They esterified maleic anhydride with equivalent amounts of various glycols in melts, without catalyst at 160-175°C for 12-14 hrs. Aliquots taken from the reaction mixture during polymerisation were subjected to cold saponification. The maleic and fumaric acid content of the decomposed polyesters was determined by polarography. The graph below shows the extent of isomerisation as a function of molecular weight, for different glycols.



l Ethylene Glycol

2 1,2 Propylene Glycol

3 1,3 Butylene Glycol

4 Diethylene Glycol

It is apparent that the extent of isomerisation is influenced by the structure of the glycol used. The authors claimed that the effect of propylene glycol is more pronounced because it provides polyesters with densest structures, and as a result the trans configuration is, in this case, energetically more stable. This view has been confirmed by Sedov⁽²²⁾ who noticed that polyesters synthesised from poly (ethylene glycols), of various molecular weights, and maleic anhydride were getting poorer in trans unsaturation as the molecular weight of the polyethylene glycol used increased. For example the fumarate unsaturation decreased from 59% to 37% on changing from a polyethylene glycol of molecular weight 300 to a polyethylene glycol of molecular weight 1000 despite any increase in reaction temperature.

Curtis et al⁽²³⁾ investigated the same topic by nuclear magnetic resonance; based on the fact that the maleic proton resonance occurs at higher field strengths than the fumaric proton resonance; the relative concentration of each unsaturation type being proportional to the area under the absorption peak. These authors had recourse to the nmr technique arguing that the polarographic method could induce some isomerisation because of the hydrolysis step it includes. Their method of synthesising the polyesters was the same as the one the Hungarians used, the only difference being that the reaction was conducted under a nitrogen atmosphere. The effect of the glycol type on the extent of isomerisation is shown on the graph.





PG = Propylene glycol EG = Ethylene glycol NPG = Neopentyl glycol DEG = Diethylene glycol TMPD = Trimethyl pentane diol CHDM = 1,4 Cyclohexane dimethanol Basically, both methods lead to the same results but nmr is much quicker and more versatile than polarography. Commenting on their results, these authors attributed the higher extent of isomerisation of propylene glycol and the substituted pentane diol maleic anhydride based polyesters to steric hindrance adding that the less accessible secondary hydroxyl groups prefer to react with the trans isomer during the polyesterification process.

b) Type of saturated acid

It has also been observed that the presence of a saturated acid, in addition to the glycol and maleic anhydride, during polycondensation, influences the extent of isomerisation; this effect is shown on the following graph.



It is apparent that isomerisation is faster and more effective in polyesters containing aromatic components. The authors suggested that the intramolecular strain induced by phthalic anhydride is compensated by the trans isomerisation; succinic acid has little effect because its structure corresponds to the trans configuration, it seems therefore that, in this case only the glycol contributes to the isomerisation.

The effect of the saturated acid has also been studied by nmr.



Degree of Polymerisation

Phthalic	anhydride	(1.0	mole)
Hmaleic	11	(1.0	mole)
+glycol		(2.2	moles)



Degree of Polymerisation

Isophthalic acid (1.0 mole) +maleic anhydride (1.0 mole) +glycol (2.2 moles)

Because of its insolubility isophthalic acid was first allowed to react, for one hour with propylene glycol at 200°C. These results again favour that the more sterically hindered the reacting functional groups are the fastest cis-trans isomerisation takes place.

Furthermore Zalmanski⁽¹¹⁾ has found that when maleic anhydride is condensed with poly (propylene phthalate) of acid number 50 the resulting unsaturated polyester contains 99% trans unsaturation. But, if phthalic anhydride is condensed with poly (propylene "maleate") of acid number 50 the resulting polyester contains 85% trans unsaturation

c) Effect of temperature

In a subsequent paper the Hungarian researchers investigated the influence of temperature on the cis-trans isomerisation. This is shown on the following graphs.



In order to give more light on the rate this isomerisation takes place the same authors expressed the fumarate conversion as a function of the average number of ester bonds; graphically this is represented as follows.



These results favour the isomerisation prior to diester formation in the case of propylene glycol; this again is due, as molecular models suggest, to the strained structure of the cis monoester which prefers to assume the trans configuration prior to diester formation. The less strained the structure is, as in the case of 1,6 hexamethylene glycol isomerisation takes place to a lesser extent.

In addition, the authors expressed the isomerisation rate constant in terms of a second order equation; they also found that the activation energy for the isomerisation to occur is $20^{\pm}4$ kcal/mole. The effect of temperature on its own on a maleate free of extensive steric hindrance can be better visualised from Turunens ⁽⁴³⁾ experiments. A commercial grade dioctyl maleate was heated at 180° C- 200° C, its extent of isomerisation (the method will be described later) as a function of time is shown below.



3.1.2 Transesterifications

The importance of synthesising polyesters with a statistically tailored backbone has been discussed in Chapter I. However some experimental evidence suggests that the transesterification reactions which would most probably accompany the two stage polyesterification process lead to a completely random distribution of the components along the polyester chains.

P Kresse⁽²⁵⁾ first reported that a mixture of two kinds of homopolyesters changes gradually to a random copolyester through transesterification reactions when heated for several hours at temperatures higher than the melting points. R Yamadera and M Murano⁽²⁶⁾ studied the extent of the transesterifications by high resolution nuclear magnetic resonance spectroscopy. They heated a mixture of two different saturated polyesters and estimated the degree of randomness brought about by the interchange reaction from the variation in the intensity of specific proton absorptions. For example, the ethylenic protons of poly (Ethylene Terephthalate) and poly (Ethylene Sebacate) have different chemical shifts assigned to the T-E-T and S-E-S units respectively. When these two polyesters are heated together at 276°C under nitrogen a third absorption, assigned to the newly formed S-E-T units develops. By treating statistically the changes in intensities of the nmr absorptions with the progress of the heating treatment, the authors concluded that an entirely

random structure is reached after three hours under the experimental conditions cited above. The same technique was applied by Khramova et al⁽²⁷⁾ again on polycondensates of ethylene glycol, dimethyl terephthalate and dimethyl sebacate; they concluded that the copolymerisation is non statistical in nature, on the basis of their calculation of the average length of homogeneous sequences. On the same basis, the above mentioned researchers, compared the chain composition of copolymers of fumaric acid, sebacic acid and ethylene glycol⁽²⁸⁾ produced by one or two stage syntheses and found that whatever the synthetic method, the resulting polyesters have approximately the same chain structure.

V Korshak et al⁽²⁹⁾ applied the same nmr procedure to estimate the randomness in copolyesters synthesised from terephthaloyl chloride and two diols or a diol and a bisphenol of different reactivities. The reaction was carried out in solution at low temperatures and in the presence of a catalyst such as triethylamine. It has been found that even when one of the comonomers is thirty times more reactive than the other, the resulting polyester has its components randomly distributed along the macromolecular chains. In an attempt to produce block copolycondensates the acid chloride was allowed to react, in a first stage, with the more reactive comonomer. After the comonomer had practically completely reacted the second comonomer was added. However, the method did not result in block copolymers. Block copolymers were effectively produced only by gradual introduction of the intermonomer (the acid chloride) into the reaction zone. The extent of randomness and, accordingly the length of the blocks depended both on the monomer reactivity ratio and on the rate of introduction of the intermonomer into the reaction zone.

3.2 Chemical changes taking place during Polyesterification

In this subsection, the reactions accompanying each polyesterification stage of a two stage polycondensation (Chapter I, section 3) will be dealt with separately. The chemical changes that occur during a single stage polyesterification are inevitably the same.

Some of the following paragraphs will be mainly concerned with "Impolex" type polyesters i.e. based on terephthalic acid, propylene glycol and maleic anhydride.

3.2.1 <u>First stage side reactions</u> a) <u>Cyclisations</u>

Most of the investigations found in the literature concern the isolation of cyclic compounds formed during the synthesis of high molecular weight poly (ethylene terephthalate).

Ross et al⁽³⁰⁾ isolated 1% of a cyclic trimer by extracting poly (ethylene terephthalate) with trichloroethylene. The isolated solid had a melting point of $325-327^{\circ}$ C. Commenting on the low concentration of the cyclic compound the authors suggested that the phenyl ring introduces enough strain to reduce the probability of cyclisation. Goodman et al^(31,39) on the other hand, extracted and identified 1.5% of cyclic oligomers from poly (ethylene terephthalate) with dioxane or mixed xylenes. These authors put forward several mechanisms in order to explain the formation of these cyclic materials. They concluded, however, that cyclisations are caused by interchange reactions among ester groups within or between high molecular weight polymer chains.

e.g.

Furthermore, they showed by means of molecular models, that the structures of the oligomeric cyclics are strain free, and that a sort of equilibrium exists between cyclisation and straight chain polycondensation. Thus, once poly (ethylene terephthalate) freed from cyclics by extraction with solvents is remelted equivalent quantities of oligomeric cyclics are formed.

These authors have excluded the possibility of cyclisation through a dehydration reaction taking place between two terminal hydroxyl groups belonging to the same chain, based on Zahn's (33, 34) work; the latter has extensively investigated the structures of oligomeric poly (ethylene terephthalates) (maximum number of segments = 9) and concluded that cyclisations do not take place.

Goodman et al have also related their experimental results to the ones derived from the Jacobson-Stockmayer⁽³⁵⁾ and Boissonas-Schuman⁽³⁶⁾ equations. These are tabulated below:

<u>No. of Segments</u>	<u>% Cyclic Spec</u> Jacobson	<u>ies (theoretical)</u> <u>Boissonas</u>	<u>% Cyclic</u> (<u>Experimental</u>)
2	2.76	3.4	-
3	1.00	1.00	1.00
4	0.49	0.42	0.08
5	0.09	0.22	0.02

The evidence provided by the research work summarised above, examplifies the triviality of cyclisations, of low molecular weight terephthalate based polyesters, as side reactions.

b) Glycol Losses

During polyesterification glycols suffer from a number of dehydration processes, the extent of which is catalysed by the acidity of the reaction mixture. Thus butanediol-1,4 decomposes into tetrahydrofuran, 2,2,4 Trimethylpentane diol-1,3 decomposes into a complex mixture of low boiling products. Propylene glycol undergoes similar side reactions, their effect being more pronounced in the presence of a catalyst. The simplest evidence for the occurrence of such reactions is that the quantity of water eliminated, during polyesterification, exceeds the theoretical amount by as much as 30%⁽³⁷⁾.

A literature survey on the various reactions leading to the dehydration of propylene glycol revealed the following:

ref (38) Et CHO propionaldehyde NaH,POL SiO, но-сн-сн,-он phthalic anh ation exchange PhSO₂h $150^{\circ}C - 165^{\circ}C$ (5 hrs)

Εt Me

2 ethyl 4 methyl dioxalane ref (39)

EtCHO (23%) + CH₂=CH-CH₂OH (14%)

2,6 dimethyldioxane ref(40)

СНЗ

+ 2,6 dimethyldioxane ref (41)

Some of these products have been identified in the organic layer topping the water eliminated during polyesterification. Their yield is increased under the severe conditions of pressure and temperature required by the process. This is examplified by the following experiment. Runs of poly (propylene terephthalate) carried out with C^{14} labelled propylene glycol and followed by analysis of all the products including those isolated in two $CO_2/MeOH$ traps accounted for 93.5% of the activity. When the same experiment was carried out at atmospheric pressure 98.4% of the activity is accounted for $^{(37)}$.

3.2.2 Second stage side reactions

a) Free radical addition of double bonds to each other

Since the early stages of unsaturated polyester development, it has been known that when alkyds are heated in the presence of oxygen the result is a hardened and insoluble product⁽⁴²⁾ indicating that a crosslinked network has been generated as a result of the polymerisation of the unsaturated sites with each other. L Turunen⁽⁴³⁾ studied the interaction of these double bonds based on a model ester "dioctyl fumarate". This model was subjected to the conditions generally encountered in polyesterification processes i.e. high temperatures and a nitrogen atmosphere; any loss of double bonds was detected by changes in refractive index. The validity of the results was also checked by polarography. The results obtained from the above experiments showed that oxygen could have deleterious effects on the stability of the double bonds. This effect is represented diagramatically as follows:



It is evident that 0.4 parts per thousand of oxygen is capable of causing the loss of 10 to 20% of the double bonds under the usual heating conditions.

Complementary information to the above is shown on the graphs describing the change of the rate constant with the oxygen concentration in carbon dioxide (used as inert atmosphere) and with temperature.





The rate constant of the reaction of O_2 with the double bonds is a linear function of the square root of O_2 concentration

The reaction rate constant increases with temperature according to the Anheuius equation.

It is apparent that there is a threshold oxygen concentration below which reaction does not occur. Furthermore it has been found that a purely thermal polymerisation is unlikely to take place at least at temperatures below 200°C, in addition the authors have shown that the severity of the reaction is not altered by the type of the model ester and, therefore should occur during the synthesis of unsaturated polyesters.

Fortunately the adverse effect oxygen has on the double bonds can be suppressed or at least markedly reduced if a small quantity of an inhibitor, hydroquinone for example, is added during the esterification process. More specifically 0.01% of hydroquinone is able to reduce the loss of double bonds of dioctyl fumarate to less than 3% at 200°C for a heating period of eight hours.

The experimental evidence provided by the author lets us assume that polyesterification reactions involving fumaric acid or maleic anhydride should be conducted at temperatures in the range of 200°C under an oxygen free

atmosphere and for more safety in the presence of an inhibitor.

b) Glycol addition to the double bond

This side reaction has received a good deal of attention, since its occurrence, will deprive the crosslinking agent of reaction sites and, therefore lead to an inadequately cured end product.

Z Ordelt^(44,45) prepared unsaturated polyesters by heating one mole of maleic anhydride and 1.1 moles of ethylene glycol at 197^oC under a nitrogen atmosphere. From a study of the balance of double bonds and hydroxyl groups he found that besides limited dehydration of the glycol the latter is added to the double bonds. The decrease in number of double bonds has been found equal to twice the decrease in neighbouring hydroxyl groups. The reaction results in the formation of esters of 1 (2 hydroxy ethoxy) ethane 1,2 dicarboxylic acid, the latter being isolated, on hydrolysis, in the form of the lactone or identified by paper chromatography.

The severity of this side reaction is examplified in the table below:

Reaction time (hrs)	3	5½	10	13
Extent of reaction %	61.4	77.8	84.7	87.3
Extent of glycol addition %	9.8	10.5	12.6	13.0
Mol weight (ebul.)	800	850	1250	-
Mol (end grp analysis)	610	734	1090	-

Z Ordelt also found that the degree of addition increases with increase of the reaction temperature and on addition of excess glycol, and falls with increase in degree of conversion of the maleates into the fumarates. The addition proceeds according to the following mechanism:



The polyesters, modified by this reaction leading to the formation of branched chains and network structures, cause the discrepancy between the molecular weight as determined by physical methods and as calculated from end group $\binom{46}{}$ analysis. Knodler et al, on the other hand, studied the effect some glycols have on the extent of the addition; they concluded that when one mole of fumaric acid is condensed with one mole of propylene glycol 15.7% of the double bonds are lost.

Furthermore, Felici et al⁽⁴⁷⁾ studied the effect of glycol addition on the double bonds of poly (propylene fumarate phthalate) and poly (propylene maleate phthalate) synthesised from 2.2 moles of propylene glycol 1.0 mole of fumaric acid or maleic anhydride and 1.0 mole of phthalic anhydride, at 200°C under a nitrogen atmosphere containing 0.1% of oxygen. The polyesters were hydrolysed and analysed for fumaric acid content by polarography. It has been found that except the complete cis-trans isomerisation of maleic anhydride, a portion of the double bonds is lost. This is examplified graphically below:







Accordingly 14.2 to 10.5% of the double bonds are lost as a result of glycol addition. The dashed line shows an additional double bond loss when polyesterification is carried out in a nitrogen atmosphere containing 0.6% of oxygen.

4 TOPICS IN THE CHARACTERISATION OF CURED POLYESTERS

This aspect of characterisation has received extensive attention since the early stages of unsaturated polyester technology. Conventional instrumental as well as chemical methods have been applied to follow the crosslinking process with the aim of elucidating the structure of the crosslinked product. These studies are in fact complementary to the different physical tests used to assess the performance of the cured polyesters since they are able to offer a scientific reason for their physical behaviour.

4.1 <u>Residual Unsaturation</u> (degree of cure)

4.1.1 Detection by infrared spectroscopy

Hayes et al⁽⁴⁸⁾ first examined by infrared spectroscopy the variation in the double bond content during the curing of poly (propylene fumarate) and poly (propylene fumarate-phthalate) with styrene.

The infrared spectrum of the styrenated solution was first recorded. A thin film was then cured and re-examined. The decrease in the intensity of the band at 775 cm⁻¹ was used, after correction for overlapping styrene absorption, to estimate the reduction of double bond content on curing.

The relationship between styrene content and polyester double bond content of the cured poly (propylene fumarate) copolymer is shown on the following diagram:



% Styrene in resin

Accordingly, increasing the amount of styrene beyond the value where the molar proportions of styrene and double bonds are equal has no significance in reducing the double bond content.

A more accurate procedure consists of using the polyester carbonyl groups, the concentration of which is not affected by the curing process, as internal standards⁽⁴⁹⁾.

For example, if D_1 and D_2 denote the optical densities of the i.r. bands corresponding to the double bond and to the carbonyl in the polyester resin, before crosslinking and correspondingly D_3 and D_4 after curing, then the ratio D_1/D_2 will correspond to a 100% content of unreacted double bonds and the ratio D_3/D_4 to the number of unreacted double bonds in the cured product. The proportion of unreacted polyester bonds (A) expressed as a percentage of all the bonds going into the copolymer, will be given the expression:

$$A = \frac{D_3 \cdot D_2}{D_4 \cdot D_1} \times 100$$

Learmonth et al⁽⁵⁰⁾, introduced a correction to the above equation, and followed the crosslinking of Beetle 4116 (a BIP polyester) at 45° C. They assigned the band at 985 cm⁻¹ to fumarate unsaturation and the one at 915 cm⁻¹ to the styrene double bond. In a similar study, Alekseyeva et al⁽⁵¹⁾ followed the disappearance of the band at 1654 cm⁻¹ also attributed to the fumarate double bonds. Similar studies were also undertaken by Imai⁽⁵²⁾ and Fijolka et al⁽⁵⁵⁾. According to Learmonth's results, 4.1% of the fumarates unsaturation and 10.6% of the styrene remain unreacted. This suggests, that under normal curing conditions, all the double bonds react, allowance being made for the quantity of styrene lost by evaporation.

4.1.2 Detection by Refractometry

During the crosslinking process the refractive index increases as a result of the reaction of styrene with the fumarate unsaturation. Both Spasskii et al⁽⁵³⁾ and Learmonth et al⁽⁵⁰⁾ applied this method to estimate the degree of cure of unsaturated polyesters.

A drop of catalysed resin is placed between the prisms of a precision Abbé refractometer equipped with a sodium lamp and a thermostatted bath; the increase of refractive index with time is then recorded. Methods for avoiding damage of the prisms are described by Dannenberg⁽⁷³⁾ generally a plastics film or silicone fluid are used as release agents and the edges of the prisms are sealed with plasticine to prevent the loss of styrene.

The increase I in refractive index is calculated from the equation

$$I = aM_s + bM_f$$

where Ms and Mf represent the mole fractions of styrene and fumarate respectively which have reacted, a and b are constants for a particular resin and are independent of crosslinking conditions. The insertion into the equation of experimental values of I, M_s and M_f from chemical measurements allows the constants to be obtained.

The value of I at completion of the reaction can be calculated from the mole fraction of styrene and fumaric acid present in the uncured polyester and compared to the experimental value for the estimation of the degree of cure. It has been found that both infrared spectroscopy and refractometry give very close results.

4.2 Average Length of Styrene Crosslinks

4.2.1 Determination by infrared spectroscopy

The method consists in degrading the styrene cured polyester, usually by an alkaline solution of benzyl alcohol and analysing the methyl ester of the styrene-fumaric acid copolymer produced by the action of diazomethane on the hydrolysate by infrared spectroscopy. Other degradation procedures also developed by Funke et al^(54,55) involve the use of benzylamine with ammonium chloride as catalyst and hydrazine hydrate in dioxan. The analysis is achieved with the aid of reference standards containing specific groups present in the copolymer. For example, the concentration-absorbance relationship of the phenyl and carbonyl absorptions of ethyl benzene and phenyl ethyl propionate respectively, is first determined, and then used to estimate the corresponding concentrations of the phenyl and carbonyl groups of the degradation products. This in fact leads to the molar ration of styrene to fumaric acid units which constitute the copolymer.

Several researchers applied this method of analysis. Funke et al^(5.6) and Learmonth et al^(5.8) suggested 1-5 styrenes, and Koenig^(1.8) suggested an average of two styrenes per crosslink. It is obvious that this average largely depends on the initial quantity of styrene monomer^(5.9) as well as on the extent of cis-trans isomerisation of the maleate double bonds, since the molecular weight of the degraded copolymer varies from 2000 to 14000 in styrene rich polyesters.

4.2.2 Determination by elementary analysis

The results obtained by the method described previously were compared to those estimated by elementary analysis. This method consists in the carbon-hydrogen analysis of the degraded product and the subsequent estimation of the molar ratio of styrene to fumarate units. Both infrared and this method give similar results. The data obtained by Hayes et al⁽⁴⁸⁾ are shown in the table below:

% Styrene in Resin	No. of Styrenes/Reacted Double Bond
20.0	1.31
35.5	2.48
37.4	1.57
45.9	2.0
50.0	2.27

4.2.3 Determination by isotopic labelling

N Ghanem⁽⁶⁰⁾ determined the average length of the styrene crosslinks using labelled maleic anhydride. He synthesised an unsaturated polyester from 14 l.1 mole of 1,4 butanediol and one mole of C labelled maleic anhydride. The styrene cured product was hydrolysed to give the styrene-fumaric acid copolymer. The latter was oxidised to a certain extent and the evolved CO₂ was detected by a gas counter. The same experiment was repeated on an equivalent quantity of labelled maleic anhydride only.

According to this technique, the counter counting rates are directly 14 12 proportional to the C/C ratio in the samples. The lowering of the counting rates is therefore effected solely by the extent of incorporation of styrene units in the copolymer. This can be expressed by the equation:

$\frac{\text{counts/minute for maleic anhydride}}{\text{counts/minute for copolymer}} = \frac{(x + 4)}{4}$

where 4 is the number of C atoms in 1 molecule of maleic anhydride and x is the number of C atoms which dilute 1 molecule of maleic anhydride. As one molecule of styrene contains 8 carbon atoms, the number of styrene units per fumaric acid unit in the copolymer can be determined. The average length of the styrene crosslinks is plotted against the resin styrene content in the following figure:



4.3 <u>Presence of Free Styrene, Polystyrene, Homopolymerised and</u> <u>Unreacted Polyester Chains</u>

K Sakaguchi⁽⁶¹⁾ noticed that fully cured samples of commercial unsaturated polyester resins yield traces of polystyrene, unsaturated polyester chains as well as free styrene, when treated with chloroform for 24 hours at room temperature. Ghanem (60) claimed the presence of less than 2% of free polystyrene in a cured product in contrast to Funke et al⁽⁶²⁾ who suggested that free polystyrene is only formed in polyester resins containing a large quantity of styrene and that the turbidity which sometimes develops in cured products is the result of long styrene crosslinks. Solvent extractions followed by the gravimetric estimation of the solid extracts have also been attempted by Gordon et al⁽⁶³⁾, Wright⁽⁶⁴⁾ and Vaughan⁽⁶⁵⁾. In all cases, however the amount of extract is so trivial that its effect on the properties of the crosslinked product can be probably disregarded. On the other hand, Alexeyeva $\binom{66}{6}$ showed, on the basis of chemical analysis of the hydrolysed polyester, that the polyester double bonds react not only with the crosslinking agent but also On the contrary, Funke et al observed that such an interaction with each other. does not take place.

The above set of observations prove, in fact, the point of view that at the early stages of the curing of commercial, fumarate based polyesters, the fumarate and the styrene double bonds tend to alternate. Longer styrene crosslinks are formed when the viscosity of the medium increases.

5 CONCLUSIONS

One of the most extensively investigated but still not yet fully understood topics concerns the advantages of polyesters synthesised by the two stage polycondensation process. Two inter-related approaches have been suggested, and tentatively proved, to account for the fact cited above. These approaches concern the position of the double bonds and the distribution of the saturated segments in the polyester chains. However, experimental, as well as theoretical evidences (Chapter III), suggest that the distribution, aimed at by the two stage technique is lost during the second stage and the resulting polyester is structurally similar to the one synthesised by a single stage operation insinuating that some side reactions, especially the glycol addition to the double bonds, which is more pronounced in a single stage polycondensation, could play a rather important role in that respect.

The crosslinking process itself is better understood. Additional techniques such as $DTA^{(67)}$, $TMA^{(72)}$, $NMR^{(68,69,70)}$ and light scattering⁽⁷¹⁾ have been successfully applied to monitor it. However, the actual microstructure of the poly (styrene-fumaric acid) copolymer resulting from the degradation of the hardened polyester still needs characterisation, especially the distribution of the styrene n-mers along its backbone.

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CHAPTER III

MATHEMATICAL DESCRIPTION OF THE POLYESTERIFICATION AND CROSSLINKING PROCESSES INVOLVED IN UNSATURATED POLYESTER TECHNOLOGY

The various esterification and crosslinking reactions involved in the synthesis and curing of unsaturated polyesters have been described mathematically. Most of the mathematical expressions will be reviewed and commented upon in the present chapter. This, in fact, comes to reviewing perhaps more analytically the basic mathematical concepts of polymer chemistry, since the system under consideration is the result of a step reaction polymerisation followed by a free radical copolymerisation taking place during the crosslinking stage. Under the terms mathematical description, both the statistical and kinetic aspects of the treatments will be considered.

1 Polycondensation Reactions

The treatments dealing with these reactions aim at the determination of the molecular weight distribution of the polycondensate macromolecular components at various stages of the reaction. This distribution is calculated by two The statistical assumes that the distribution is a function of the methods. state, and it dependson several simple variables such as conversion, reaction efficiency, stoichiometry and in some cases the ratio of rate constants of propagation. The other methods of calculating molecular weight distributions are based on kinetic equations. These approaches also assume the system to be homogeneous and that end group reactivities are independent of chain length. However, both P J Flory⁽¹⁾ and L C Case⁽²⁾, pointed out that the reactivity of an acid or hydroxyl radical, in the condensation of a diacid with a diol, is greatest when the radical is on an unreacted monomeric unit. The reaction rate is 10 to 20% slower when the radical is attached to a larger molecule. These research workers also suggested that the rate is an assymptotic, monotonic function of the molecular weight of the attached chain. However, the rates for very long chains are not much less than for a chain in which only one unit has been added

to the original monomeric unit i.e. the reactivity of a group attached to a half reacted unit can be assumed independent of the length of the attached chain, but is significantly less than the reactivity of a group attached to an unreacted unit. This fact, is expected to influence the kinetics of the reaction and as it might be anticipated, its effect would be more pronounced in the case of low molecular weight polymers.

In the following sections, only some specific theories of polycondensation reaction will be discussed, essentially those illustrating better the ICI process. Schultz's $^{(3,4)}$ work on polycondensation equilibria and random degradations of polycondensates as well as Stockmayer's $^{(5)}$ classical work will only be mentioned as general references.

1.1 <u>Chain Distribution of the First Stage Condensate in a Two Stage</u> Polyesterification Process

1.1.1 <u>P J Flory's Treatment</u>(6)

The first stage polycondensation process could be described mathematically by Flory's statistical treatment.

Because of the extensive application of the derived equations to some of the work included in this report, the treatment will be analytically reviewed. It is based on the fact that during the condensation of a glycol (B-B) with a dibasic acid (A-A), three types of macromolecules are present in the polymeric mixture, their relative population depending on the number of reactant molecules (x) combined in the polymer molecule. The classification is the following:

> (i) If X is an even integer, the resulting chain is a hydroxyacid

 $x/2 A-A + x/2 B-B \rightarrow A.A-(B.B-A.A)(x-2)/2-B.B$

(ii) If x is odd, the resulting macromolecule can either be a diol or a dicarboxylic acid depending on which reactant is present in excess

i.e. $(x+1)/2 A.A + (x-1)/2 B.B \rightarrow A.A-(B.B-A.A)(x-3)/2^{-B.B-A.A}$ or $(x-1)/2 A.A + (x+1)/2 B.B \rightarrow B.B-A.A(B.B-A.A)(x-3)/2^{-B.B}$

The molecular size distribution of these linear condensation polymers, when prepared from equivalent amounts of reactants is given by the equation

$$P_{(x)} = p^{x-1}(1-p)$$

where $P_{(x)}$ is the mole fraction of every x-mer i.e. a polymer composed of x reactant molecules or segments. p is the extent of reaction or the fraction of the total number of A (or B groups) which have reacted at time t; therefore, if N_o is the original number of A (or B) groups and N the number of unreacted groups after time t, then

$$p = (No-N)/No$$

However, when an excess of one reactant, the glycol for example, is used separate functions are derived for each of the three kinds of molecules. The derivation includes the following terminology:

 N_A and N_B represent the number of A and B groups in the initial feed. N_A^{\prime} and N_B^{\prime} are the numbers of the respective unreacted functional groups after condensation.

If an excess of B-B (glycol) is used

 $N_B - N_A = N_B - N_A = excess of B-B segments$

On the other hand, the probability p that an A group has reacted is

$$p = (N_A - N_A^*)/N_A$$

Similarly, the probability q that a B group has reacted is

$$q = (N_B - N_B)N_B$$

By defining $r = N_A / N_B$

p = r.q

Now, let us select, randomly, a segment S from the sequence of segments

 $\begin{array}{c} p \quad q \quad p \quad S \quad p \quad q \quad p \\ -B-A.A-B.B_{\overrightarrow{b}}A.A_{\overrightarrow{b}}B.B_{\overrightarrow{b}}A.A_{\overrightarrow{b}}B.B_{\overrightarrow{b}}A.A_{\overrightarrow{b}}B.B.\dots A_{\overrightarrow{b}}B.B_{\overrightarrow{b}}A_{\overrightarrow{b}}B_{\overrightarrow{b}}$

and let us assume that the chain molecule is a hydroxyacid i.e. one of the terminal groups is A and the other B.

It follows that, for this specific case, described by the chemical equation (i), x is an even integer.

If the segment S happens to be A-A, the probability that there is a linkage at b_1 is p, at b_2 is q, at b_3 it is p again. Therefore p is the probability of linkage where n is odd and q the probability where n is even.

For each of the x configurations which will include S in the even x-mer, there will be x/2 links the probability of occurrence of each is p and (x/2-1) links with probability q each. On the other hand, the probability of finding a terminal A is 1-p and a terminal B is 1-q. It follows that the probability that any given A.A segment is a component of an even x-mer is

$$M_{x}^{A} (even) = x.p^{x/2}. q^{x/2-1} (1-p) (1-q)$$
$$= x.p^{x-1}. r^{x/2-1} (1-p) (1-rp)$$

If a B.B group had been selected as the segment S, the same considerations would apply with p and q interchanged. Hence the probability that any given B.B segment is a component of an even x-mer is

$$M_{x}^{B}$$
 (even) = x.p^{x-1} r^{x/2}. (1-p) (1-rp)
or M_{x}^{B} (even) = r. M_{x}^{A} (even)

If N (even) is the number of even x-mer molecules then the total number of segments in even x-mers is

$$x N_x$$
 (even) = $\frac{NA}{2} \cdot M_x^A$ (even) + $\frac{NB}{2} \cdot M_x^B$ (even)

By substitution and rearrangement

$$N_x (even) = N_A M_x^A (even)/x$$

= $N_A p^{x-1} r^{x/2} (1-p)(1-rp)r^{-1}$

The fraction of the total number of both kinds of segments which are contained in x-mers is

$$M_{x} \text{ (even)} = \frac{xN_{x} \text{ (even)}}{\frac{1}{2}(N_{A}+N_{B})}$$

Since

$$N_A + N_B = N_A (1+r)/r$$

 $M_x (even) = xp^{x-1}r^{x/2} \frac{2(1-p)(1-rp)}{(1+r)}$

Then 🔬

 M_x (even) is the approximate weight fraction of an even x-mer. For the mole fraction of even x-mers

$$P_{x} \text{ (even)} = \frac{N_{x}}{\text{Total no. of molecules}} = \frac{N_{x}}{\frac{1}{2}(N^{*}A + N^{*}B)}$$

Hence

$$N'' = (1-p)N_{A}$$

$$N'' = (1-q)N_{B} = (1/r-p)N_{A}$$

$$Px (even) = p^{x-1} r^{x/2} \left[\frac{2(1-p)(1-rp)}{(1+1/r-2p)r} \right]$$

In a similar way the mole fraction of dicarboxylic acids P_x (odd A) and the mole fraction of glycol can be derived. The corresponding equations are

$$P_{x} (odd A) = p^{x-1} \cdot r^{x/2} \left[\frac{(1-p)^{2}r^{-1/2}}{(1+1/r-2p)} \right]$$

$$P_{x} (odd B) = p^{x-1} \cdot r^{x/2} \left[\frac{(1-rp)^{2}r^{-3/2}}{(1+1/r-2p)} \right]$$

and

The above treatment rests upon the following assumptions:

a) The reactivity of a functional group is independent of the size of the molecule to which it is attached.

b) Reverse reactions e.g. hydrolysis, do not occur.

c) Formation of cyclic compounds does not occur.

On the other hand, the application of these equations does not pose any problem. The term r is the molar ratio of the reactants and p can be easily determined.

1.1.2 L C Case's Treatment⁽⁷⁾

L C Case derived several statistical equations describing the chain distribution of polycondensates resulting from the combination of a large number of reactive species. The simplest system of terephthalic acid (A-A) reacting with ethylene glycol (B-B) will be first considered, in the following paragraphs, since it offers the simplest way of comparing Case's statistics with Flory's.

Accordingly, if N_{AA} and N_{BB} represent the number of original AA and BB units respectively, then

$$No = N_{AA} + N_{BE}$$

To each of the functional groups is assigned a separate reaction probability, e.g. a for A and b for B, defined as the number of groups that have reacted

$$\cdot \cdot aN_{AA} = bN_{BB}$$

Hence No = $N_{AA}(1+\frac{a}{b})$

Whereas Flory's treatment is based on the random selection of a unit in the macromolecule, Case assumes that a chain is built starting from an AA (or BB) segment onto which are linked alternately BB (or AA) units, the reaction proceeding in one direction

$$a \longrightarrow b \longrightarrow a \longrightarrow b \longrightarrow a$$

i.e. $AA \longrightarrow BB \longrightarrow AA \longrightarrow BB \longrightarrow AA \longrightarrow BB$

On the assumption that the products are the same as the ones dictated by Flory, the number of free ends will be

$$2N_{AA}(1-a) + 2N_{BB}(1-b)$$

or $2 N_{AA}(1-a) + 2 \frac{a}{b} N_{AA}(1-b)$

The number of molecules after polymerisation, being half the number of free ends, is equal to

$$N_{AA}(1-a) + \frac{a}{b} N_{AA} (1-b)$$
$$\frac{No}{a+b} (a+b-2ab)$$

or

By following the same reasoning as for the derivation of Flory's equation, the number distributions of the different types of molecules can be found.

Starting at A =
$$\frac{No}{1+\frac{a}{b}} \left[(1-a)^2 a^{n-1} b^{n-1} \right]$$
 for n AA units and (n-1) BB

$$\frac{No}{1+\frac{a}{b}} \left[(1-a)(1-b)a^{n}b^{n-1} \right] \text{ for n AA units and n BB}$$

Starting at B =
$$\frac{No\frac{a}{b}}{1+\frac{a}{b}}$$
 [(1-a)(1-b)bⁿaⁿ⁻¹] for n AA units and n BB

=
$$\frac{No\frac{a}{b}}{1+\frac{a}{b}}$$
 [(1-b)²bⁿaⁿ] for n AA units and (n+1) BB units

The number distribution function of these molecules or their mole fractions are obtained by dividing each of the above equations by the total number of molecules after polymerisation. This is equal to

$$\frac{(1-a)^2 a^{n-1}b^n}{a+b-2ab}$$
 for n AA units and (n-1) BB

$$\frac{2(1-a)(1-b)a^{n}b^{n}}{a+b-2ab}$$
 for n AA units and n BB units

$$+ \frac{(1-b)^2 a^{n+1} b^n}{a+b - 2ab}$$
 for n AA units and (n+1) BB units

If the system terephthalic acid - propylene glycol (BC) is considered two different reaction probabilities are assigned to the glycol; these are b for B and χ for C, and the number distribution functions are

$$(1-a)^2 \frac{(2ax)}{b+x}/(1-2a + \frac{2a}{b+x})$$
 for n AA units and (n-1) BC

+
$$2a(1-a)(1-\frac{2a}{b+a})(\frac{2a}{b+a})^{n-1}/(1-2a+\frac{2a}{b+a})$$
 for n AA units and n BC

+ $(1-\frac{25}{b+5})^2 a^2 (\frac{2a5}{b+5})^{n-1} / (1-2a+\frac{2a}{b+5})$ for n AA units and (n+1) BC

+ $\frac{2a}{b+\delta}$ (1-b)/(1-2a+ $\frac{2a}{b+\delta}$) for unreacted BC units

It is obvious that whereas Flory represented both cases by a single statistical treatment, Case accepts that due to the different reactivities of the chemical groups involved, the resulting distributions should be different. In other terms, the extent of reaction, designated by the term p, in Flory's equations, is split in Case's treatments into two or three parameters depending on the number of different reactive groups.

Although these assumptions seem to be very plausible, no experimental evidence exists to substantiate the difference between the two theories. An advantage however, of Flory's, is that it is easily applicable since all the parameters involved can be estimated in the simplest way.

1.1.3 Other Treatments

Perhaps the easiest, but nevertheless the most elementary statistical treatment is T M Gritsenko's⁽⁸⁾. The assumptions involved are similar to Flory's i.e. equality and invariability of the relative reactivities of the functional groups. However, this treatment describes the distribution of a polymer only at the completion of the reaction, furthermore, it assumes that one of the reactants should be present in excess. Accordingly, if m (m < 1) mole of a dicarboxylic acid (B) is allowed to react with one mole of a glycol (A), then in a macromolecule of the type BA-BA-(BA)_n-B, the probability of finding B as the end unit is equal to 1-m. On the other hand, the number distribution function that the macromolecule chosen at random from the system will contain n units of A and n+1 units of B is expressed by the equation

$$N_{n} = m^{n}(1-m)$$

At n=0 this function gives the probability of finding unreacted B particles in the system.

The author further assumes that $\sum_{n=1}^{\infty} N_n = 1$ and hence expresses by N_n the mole fraction of each macromolecular constituents of the polymeric mixture.

The above equation may be compared to Flory's equation expressing the mole fraction of the glycol terminated components P_x (odd B) (section 1.1.1) provided that p=1, x=n and r=m; under these circumstances

$$P_{(x)}$$
 odd $B = \frac{m^{n/2} \left[(1-m)^2 m^{-3/2} \right]}{(\frac{1}{m} - 1)}$

or
$$P_{(x)}$$
 odd $B = m^{(n-1)/2}(1-m)$

Since m < 1 it is obvious that for n=0,1 Nn $> P_{(x)}$ odd B, but for integral values of n larger than unity $P_{(x)}$ odd $B > N_n$, suggesting that Flory's and Gritsenko's distributions are different. In other terms, if the parameter n, in the simplified Flory equation is replaced by n' the relation

Nn =
$$P_{(x)}$$
 odd B is satisfied when
 $(n^{*}-1)/2 = n$
 $n^{*} = 2n+1$

٥r

meaning that the unit sequences derived from Gritsenko's distribution function correspond exactly to those of the (2n+1)-mers derived from Flory's equation.

Attempts have also been made to determine the molecular weight distribution of polycondensates by means of kinetic treatments. Kilkson⁽⁹⁾, first introduced the use of generating functions to solve the resulting kinetic equations. This work has been followed by Bamford's⁽¹⁰⁾, Herman's⁽¹¹⁾ and Nekrasov's⁽¹²⁾.

Bamford defined the generating function

 $G_{(s)} = \sum_{r}^{P} S^{r}$

where P_r is the concentration of the rth polymer. Use of this function reduces the set of kinetic equations to a finite set which in some cases may be solved analytically for $G_{(s)}$ which can be expanded into the appropriate series to give the concentration of each species in the mixture. A review on the work performed with the aid of these functions is given by Amundson and Luss⁽¹³⁾.

1.2 <u>Statistical Treatment of the Second Stage of a Two Stage</u> Polyesterification Process

Such a statistical treatment is expected to describe the types as well as the number of diols, already obeying the distribution functions cited in the previous section, which condense with the unsaturated acid to form a macromolecule of a chain length.

L C Case⁽⁷⁾, dealt with the distributions arising when a given linear polymer is allowed to react with a difunctional agent. He acknowledged that if a statistical copolymer is the result of the reaction, the "coupling distributions" are not the same as the distributions arising if the same components are reacted together as in a single stage polyesterification process. Since polymer chains of a certain distribution are the building units, this author regarded the formation of a coupled polymer like the generation of a Markov type of chain. However, the various distribution functions derived by Case lack experimental backing, and the models studies do not include a type similar to the ICI resins. Nevertheless, a parallel derivation for this specific case

is not an impossible task provided that the parameters involved can be estimated experimentally.

However, as shown in Chapter II, experimental evidence suggests that the second polyesterification process leads to condensates with randomly distributed units along the chains.

H Sawada⁽¹⁴⁾ treated the problem of randomness statistically and also reached the conclusion that the melt polycondensation methods employed industrially yield copolymers with random distributions.

This confirms a theoretical observation which arises from Gritsenko's⁽⁸⁾ statistical treatment of the two stage polyesterification process. This author concluded that despite of the exchange reactions that are taking place, there is always a distribution of the difference sequences of units along the polymeric chains. This distribution is determined only by the molar concentration of the comonomers irrespective, even of differences in their relative reactivities and is similar to the distribution of units in a polyester synthesised in two stages.

Actually, Gritsenko replaces the widely used expression of randomness by assuming the existence of a finite distribution.

1.3 <u>Mathematical Treatments of a Single Stage Polyesterification Process</u> Such treatments are expected to describe the intrinsic polydispersity of an unsaturated polyester chain i.e. the sequences of saturated and unsaturated units constituting the macromolecule. However, the fact that the theories put forward by several research workers to solve this problem, are still being reviewed and corrected, favours the point of view that the complete answer to the question has not yet been found.

L C Case⁽⁷⁾, derived the first statistical equations describing the distribution of the macromolecules resulting from the condensation of two diacids of different reactivities with a symmetrical diol by assigning, to each reactive group, separate reaction probabilities. The mathematical treatment is similar to the one explained before; for example the expression of the number distribution function of those polymer chains containing n glycol units, i units of one type of acid and terminated at both ends by hydroxyl groups is:

$$F(n) = (1-a)^2 a^{n-1} \left(\frac{b^2}{r \sqrt{2}}\right)^i \left(\frac{r \sqrt{2}}{b+r \sqrt{2}}\right)^{n-1} \frac{(n-1)!}{i!(n-1-i)} / \frac{1-2a+a}{b+r \sqrt{2}}$$

Where a is the reaction probability of the -OH group, b and y are the reaction probabilities of the acids, the molar ratio of which is equal to r. The most probable combination of n and i is expected to depend on the rate of reactions of each group as well as on the extent of reaction. Unfortunately, there is no strong experimental evidence to back these mathematical derivations, although, these equations, offer only a tentative assessment of the fine structure of an unsaturated polyester chain. Furthermore, the derivation method may be applied to a model system involving an unsymmetrical glycol, propylene glycol for example, which is very common in unsaturated polyester formulations.

A different statistical treatment, but perhaps less complex but not sufficiently explicit to satisfy the requirement of the ideal solution, was proposed by L F Beste⁽¹⁵⁾. Accordingly, probabilistic equations have been derived to express the population of the mixed molecules, i.e. those in which both acids and the glycol are present, as well as the population of the chains consisting solely of one acid and the glycol. This treatment implies that the glycol and the acids are present in equimolar amounts.

Theoretically predicted results are represented on the graph.



Relative Number of Molecules throughout the Reaction

It is assumed that 0.5 moles of each of the saturated acids, the rate constants of which are in the ratio 1:2, are allowed to condense with one mole of a symmetric glycol. Basically, this treatment helps in obtaining the distribution functions of the unit sequences in a macromolecule but does not allow the deduction of their length. Similarly N Shito⁽¹⁶⁾ calculated the distribution of saturated chains in a polyester composed of maleic anhydride, adipic acid and propylene glycol. The number of polymer molecules containing no maleic anhydride and their proportion by weight were plotted as a function of maleic anhydride content.

V Z Nikonov et al⁽¹⁷⁾ examined the relation between macrocomposition, and extent of reaction, composition of the initial monomer mixture and activities of the functional groups in a system involving two dibasic acids and a glycol, by formulating a set of kinetic equations, and solving the resulting differential equations with theoretical and experimental values by means of a computer. The kinetic equations involved the early stages of condensation

and their rate constants were assigned to different values even for the further condensation of the two same groups. The results of the integration gave the concentration of the unreacted groups as well as the molar content of the esterified acids present in the polymeric chains at different stages of the reaction. In addition, the authors compared their results with those deduced from Beste's equations and found a fair agreement between them.

A more analytical treatment of the distribution of components in condensation interpolymers is Kuchanov's^(18,19) who described the composition of the macromolecules in terms of the coefficient of microheterogeneity (K); accordingly K = $\frac{P_{RS}}{P_{RS}+2P_{RR}}$ + $\frac{P_{RS}}{P_{RS}+2P_{SS}}$

where P_{RS} , P_{SS} and P_{RR} are the fractions of heterotriads (RIS) and homotriads (S-I-S & R-I-R) constituting the copolymer -I-R-I-R-I-S-I-R-I-S- for a mixture of two homopolymers $P_{RS}=0$ and consequently $K_m=0$, whilst for a strictly alternating copolymer $P_{RR}=P_{SS}=0$, to which the value $K_m=2$ corresponds. Between these two extremes, which correspond to a fully ordered position of units in the copolymer, all possible values of K_m are situated, $K_m=1$ corresponding to a completely random distribution. Consequently from the absolute value of deviation of K_m from unity the degree of ordering of the units in the copolymer may be evaluated quantitatively. By assuming proportional activities of the first and second groups of the intercomponent (I) in reactions with different comonomers, the authors deduced theoretical relations between K_m , the proportions of these comonomers, their reactivities as well as their effect on the activity of the intercomponent. Alternation is generally encountered when the reactivities of the comonomers towards one group of the intercomponent, greatly differ.

A much simpler and explicit enough treatment is Gritsenko's⁽⁸⁾. The model considered involves the reaction between two comonomers e.g. two dicarboxylic acids $(B_1 + B_2)$ and an intermonomer e.g. a glycol (A). This can be represented as follows:

 $A + (M_1B_1 + M_2B_2 + \dots + M_1B_1 + \dots) \rightarrow \dots AB_1AB_2AB_1AB_1AB_2 \dots (AB_1)_n$

where M_1 and M_2 are the mole fractions of the comonomers with respect to their total quantity i.e. $\sum_{i=1}^{j} M_{i} = 1$. The distribution function of units of one species can be found on the assumption that the formation of the copolymer occurs as a result of the simultaneous reaction of all the components and under conditions of equality and invariability in the course of the reaction of relative reactivities of the functional groups. It is also assumed that the reaction takes place under homogeneous conditions. Accordingly, the probability of unit AB, taken at random from the copolymer, will be AB_i will be equal to M_i and the probability that the sequence chosen at random will contain n units of the i-th type is equal to M_i^n and the probability that after these n units there will be found A connected with any other than the i-th component B

$$N_{i}(n) = M_{i}^{n}(1-M_{i})$$

where $N_i(n)$ is the number distribution function of sequences $(AB_i)_n$ according to lengths.

2 CROSSLINKING REACTIONS

Ideally, the crosslinking mechanism occurring during the curing process of an unsaturated polyester resin, may be considered as a free radical copolymerisation between the monomer, styrene (S) for example, and the unsaturation sites of the polyester backbone e.g. fumarate groups (F). The composition of the copolymer being formed at any instant is given by the copolymer equation (20, 21, 22)

$\frac{d[S]}{d[F]} = \frac{[S] \cdot r_S[S] + [F]}{[F] \cdot r_f[F] + [S]}$

The monomer reactivity ratios r_s and r_f are the ratios of the rate constant for the radical, styrene or fumarate, adding its own monomer to that for its adding to the other monomer. For example, in the system considered in this paragraph $r_s = 0.3$ and $r_f = 0.07^{(23)}$, the styrene radicals prefer to add to their own monomers approximately four times faster than fumarate homopolymerises.

The copolymer equation has been extended to the description of a three component copolymerisation⁽²³⁾. This could be applied to a polyester system containing both fumarate and maleate (M) unsaturation. The relevant equations are

$$\frac{d [S]}{d [F]} = \frac{1 + \frac{r_{sf}[S]}{F]} + \frac{r_{sf}[M]}{r_{sm}[F]}}{\frac{d [S]}{d [M]}} = \frac{1 + \frac{r_{sm}[S]}{M]} + \frac{r_{sm}[F]}{M]}}{\frac{d [F]}{d [M]}} = \frac{r_{sm}[F]}{r_{sf}[M]}$$

The applicability of the copolymer equation to a polyester system was first pointed out by Leavitt and coworkers (24). Similarly, Bohdanecky et al (25) calculated the gross composition of the copolymerisates formed in a cured polyester and showed that the values obtained experimentally during the initial phase of the crosslinking reaction agreed satisfactorily with the

calculated values. Gordon^(26,27) calculated the final compositions of the cured product obtained from a poly(ethylene fumarate) containing methyl methacrylate, by means of the integrated copolymerisation equation. He also calculated the concentration of the unreacted unsaturation sites on the polyester chain after crosslinking by developing. They also calculated the concentration of the unreacted unsaturation sites on the polyester chain after crosslinking by developing the following statistical treatment.

If p is the probability of a fumarate carboxyl having become esterified during polycondensation, then according to Flory's statistics⁽¹⁾ the most probable distribution of the number fraction Mn of n-meric condensation chains is

$$Mn = p^{n-1}(1-p)$$

with a number average chain length

$$DPnc = 1/(1-p)$$

If q is the probability of a fumarate double bond not having become polymerised during polyaddition, then after crosslinking the distribution of chains all of whose double bonds have escaped polyaddition, is given by

$$M'n = p^{n-1}(1-p)q^n$$

Multiplying by Foc, the concentration of crosslinked fumarates can be obtained i.e. $V = Foc p(1-q)^2(1-pq)$ Foc is the number of moles of original fumarate double bonds per liter.

Funke, Knodler and Feinauer⁽²⁸⁾ determined experimentally the composition of a cured polyester containing only fumarate unsaturation in the polymeric chains that had been crosslinked via styrene monomer. The theoretical gross composition of the cured product was obtained from the equation⁽²⁹⁾

$$V_{s} = \frac{f_{s} \circ - \frac{f_{s} (1 - A_{m})}{(1 - f_{s} \circ) - (1 - \frac{f_{s}}{s})(1 - A_{m})}$$

where Vs represents the mole ratio [S]/[F] of the polymerised monomer units, f_s the molar fraction of F styrene units before crosslinking, and f_s the molar fraction of non polymerised styrene after a relatively complete conversion A_m of both unsaturated species.

The value f_s can be both calculated and derived graphically from the integrated copolymerisation equation and from the experimentally established value for the total conversion A_m . The authors employed Skeist's integrated equation ⁽³⁰⁾

$$\ln(1-A_{\rm m}) = \int_{\rm fs}^{\rm fs} \frac{\rm dfs}{Fs - fs}$$

to determine fs graphically. The copolymerisation equation is inserted into this equation in the form

$$\frac{d[s]}{d([s] + [f])} = \frac{\binom{r_s - 1}{s^2 + f_s}}{(r_s + r_f - 2) + (2 - 2r_f)f_s + r_f}$$

By summation of M'n, the fraction of the original chains remaining free is

$$\sum M'n = q(1-p)\sum (pq)^{n-1} = q(1-p)/(1-pq)$$

The concentration (moles per liter) of original condensation chains is given by

$$Foc/DPnc = Foc (1-p)$$

Hence the concentration of free condensation chains is

$$W_{\rm F} = Foc \ q(1-p)^2/(1-pq)$$

To find the concentration of crosslinks a fumarate unit F is selected at random, this comes to determining the probability that this unit should be polymerised, and that proceeding from F along the condensation chain in one direction another polymerised fumarate double bond is found. The total contingency of this event is made up of four probabilities, thus: the probability of F being polymerised is (1-q), that of finding n fumarates below is p^n . There is also a probability q^{n-1} that the first (n-1) of these are unpolymerised and a chance (1-q) that the n^{th} is polymerised. Combining the whole set of probabilities

$$(1-q)p^{n}q^{n-1}(1-q) = p^{n}q^{n-1}(1-q)^{2}$$

To determine the fraction z of all the original fumarate double bonds which have given rise to a crosslink, the above equation is summed over all values of n

The experimental results obtained by these authors were in good agreement with the theoretical values.

3 CONCLUSIONS

Most of the statistical treatments of the first stage polyesterification process fail to justify, from a theoretical point of view, one experimental fact, that is the higher reactivity of the monomer compared to the n-mers. Apparently, this point is crucial especially as far as low molecular weight polyesters are concerned. Perhaps Case's treatment, is the most complete statistical treatment but, nevertheless not the simplest.

The difference in the activities of the functional groups have been taken into consideration in Babur's (31) kinetic treatment.

There is strong theoretical evidence that in a two stage polyesterification process, the chain distribution of the first stage polyester is lost during the second stage reaction.

Although the mathematical aspect of the polycondensation reaction is still being reviewed and renewed, the investigations on the theoretical treatment of the crosslinking stage do not follow the same rate. On the contrary these investigations are rather rare.

However, the few experimental evidences that exist suggest that there is a fair agreement between the predicted values of some crosslinking parameters and the experimental.

Taking into consideration the information exposed in Chapter II it becomes obvious that most of the work concerned with the crosslinking reactions of unsaturated polyesters, is experimentally orientated and the equations are developed to suit a particular parameter studied by a specific technique.

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CHAPTER IV

CHARACTERISATION OF LOW MOLECULAR WEIGHT POLY (PROPYLENE TEREPHTHALATES) BY HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

1 INTRODUCTION

In this chapter, the structure of the first stage polyesters synthesised by Imperial Chemical Industries Limited is investigated by proton nuclear magnetic resonance spectroscopy. The term prepolymer will be very frequently used to refer to these low molecular weight saturated polyesters. The present research work is concerned exclusively with the characterisation of those prepolymers utilised as intermediates in the production of the T400 and T500 unsaturated polyesters of the "Impolex" series and, therefore, they will be referred to as T400 and T500 prepolymers. The former are synthesised from one mole of terephthalic acid and 2.2 moles of propylene glycol while 3.3 moles of glycol are used in the synthesis of the latter.

The first stage of the ICI polyesterification process involves two operations. For a start all the ingredients are charged in the reactor and condensed under high temperature and pressure to give poly (propylene terephthalate) and water as byproduct. The vigorous reaction conditions employed as well as the subsequent water distillation step involved in the process lead to the loss of a certain quantity of glycol which should remain unreacted because of the non-stoichiometry of the feed. In order to compensate for the losses, an additional amount of propylene glycol is introduced in the reaction mixture and polycondensation is continued for a further period of time until the final acid value reaches a low figure or, in other terms, until the extent of reaction tends to one. The resulting polyester is in the form of a transparent, viscous liquid and upon further condensation with maleic anhydride yields an unsaturated polyester.

Most of the experimental work described in this project is performed, unless cited, on a T400 prepolymer ready for further condensation with maleic anhydride and we shall refer to it as prepolymer T400-A to differentiate it from the prepolymers T400-B and T400-C which have been isolated prior to excess glycol addition.

According to the reaction scheme put forward by J P Flory (see Chapter III) the polymeric constituents of the various ICI poly (propylene terephthalate) prepolymers should be $P(TP)_x$, $(PT)_y$, $T(PT)_z$, where P describes the propylene glycol segment and T the terephthalate segment. The subscripts x, y and z represent the number of propylene terephthalate repeat units.

However, because of the large amount of propylene glycol used in the synthesis which, in fact, aims at the formation of hydroxylated chains, and following the experimental evidence provided in the next chapter, the prepolymers will be regarded as being constituted mainly of low molecular weight $P(TP)_{y}$ units.

2 QUANTITATIVE ANALYSIS OF POLYMERS BY NMR

The use of nmr spectroscopy in the characterisation of unsaturated polyesters has already been discussed in an earlier chapter.

The application of this technique in the polymer field in general is well exemplified in Slonim's⁽¹⁾ and Bovey's⁽²⁾ books. Both combine an extensive literature survey up to 1971, the former has also a chapter on quantitative analysis including ¹⁹F and wide line nmr.

Of more interest to the present work is Kasler's (3) succinctsurvey on the quantitative analysis of polymers, an account of which will be given later in this section.

As stated previously, this part of the project deals with the characterisation, by proton nuclear magnetic resonance spectroscopy, of the poly (propylene terephthalate) prepolymers. The method involved makes use of simple chemical reactions which, in conjunction with the very basic assumptions of nmr spectroscopy $^{(4,5)}$ lead to the elucidation of the spectrum without any reference to specific literature data.

Of particular interest is the quantitative information that can be deduced from the integrated trace of an nmr spectrum. The published articles (6,7,9)in that respect, deal with the derivation of the polymers molecular weights. The method, however, is not applicable to very high molecular weight polymers.

Spragg⁽³⁾ deduced the molecular weight of p.octyl novolak, prepared from an excess of phenolic reagent, from its spectrum in acetone or pyridine. According to the polymer general formula,



the average number of methylene bridge protons, absorbing at 3.9 ppm, is (2n + 2) per chain, and the average number of the aromatic protons, showing a peak at ~7 ppm is (2n + 6). From the peak areas, the ratio of the proton types can be measured and n determined. This, since the formula is known, gives the molecular weight.

Urman et al ⁽⁶⁾ synthesised plasticisers by the transesterification of dibutyl adipate with different glycols and determined their molecular weight by comparing the area of the butoxyl end group triplet with the proton area of a specific group present in one repeat unit. A fair agreement was found between the values obtained by NMR and those determined by conventional ebullioscopy methods. It is worthwhile mentioning that the latter method requires a very pure sample since it is sensitive to impurities.

The molecular weights of poly (ethylene) and poly (propylene) glycols were determined by Page and Bresler ⁽⁷⁾ in terms of the shift that distinguishes the groups attached to the etheroxygen and those attached to the oxygen of the hydroxyl group. A very good resolution was obtained when pyridine heated with a small amount of HCl gas was used as NMR solvent. The molecular weight of polyethylene glycol was calculated from the equation $\frac{44Y}{X} + 62$ where X is the resonance area of the $-CH_2$ -OH protons and Y, the resonance area of the $-CH_2$ -O protons. For the calculation of the molecular weight of poly (propylene glycol), the integrated traces of the absorptions of all the groups have been considered which is rather tedious compared to the much easier repeat unit method. The authors also suggest a way of estimating the molecular weight of poly (diethylene glycol succinate), which could be useful in following the kinetics of the esterification process since it takes into consideration the contribution of the free carboxyl groups.

In addition to pyridine, the resolution of the near end group multiplets can be improved in the presence of benzene and alpha chloronaphthalene⁽⁸⁾. Superior, however, in that respect, is the effect of shift reagents such as $Eu(dpm)_3$, tris(dipivalatomethanato) europium. This reagent has actually been used by Ho⁽⁹⁾, to distinguish between the doublets of the end and internal methyls of poly (propylene glycol). The end methyls are shifted downfield from the interior methyls and by comparison of the areas, Aend and Aint, the number average molecular weight is obtained as:

$$M\bar{n} = \frac{Aint}{Aend} \times 116 + 134$$

Finally, of importance to insoluble polymers is the pulse and wide line NMR technique as used by Liepins and Crist (10) for the determination of Mn.

3 EXPERIMENTAL PROGRAMME

3.1 <u>Characterisation of T400-A Prepolymer by NMR Spectroscopy</u> The 90 MHz spectra of T400-A in CDCl₃ and DMSO-d₆ (30-40% wt/vol), recorded at room temperature on a Perkin-Elmer R-32 spectrometer are shown in figures IV 1 and IV 2 respectively, (peak assignments should be disregarded at this moment). Additional spectra under examination have been recorded under the same instrumental conditions. The spectra can be subdivided into three distinct regions, which, expressed in terms of § values from the tetramethyl silane internal standard are:

a. 1.0 - 1.6 ppm
b. 3.1 - 5.8 ppm
c. a singlet at 8.01 ppm

In order to assign the absorptions occurring in these regions to hydrogen atoms belonging to specific groups, the polymer will be represented by the following structural model, the different segments of which will be numbered: (2) (1) (3)



The various groups expected to give rise to nmr signals are: methyl, methylene, methyne, phenyl and hydroxyl.

It is well known that the methyls of such a spin system, will absorb radiofrequency at high fields i.e. in the 1.0 - 1.6 ppm region, the methylene and methyne groups in region b, while the phenyl groups absorb in the lowest field region. The hydroxyl groups are expected to give rise to singlets in the 3.00 - 5.00 ppm region.

In the following discussion, the nmr absorptions of each group will be treated separately.





3.1.1 Methyl Absorptions

and

Because of their vicinity to methyne groups, the methyls of the polymer as well as those of the glycol are expected to give rise to doublets in the high field region of the spectrum. Since more than one doublet appears in this region it is evident that the methyls are present in different magnetic environments. It is assumed, at this stage, that the inductive, -I effects, exercised by the hydroxyl and the ester groups on their neighbouring methyl groups are responsible for the different chemical shifts of the doublets; at first glance, two types of electronically different methyls can be distinguished, these are:

> CH_3 (beta to hydroxyl group) CH_{-CH-OH} (beta to hydroxyl group) CH_3 (beta to ester group)

Consequently, the stronger -I effect of the ester group⁽¹¹⁾, will result in a lower field absorption of the neighbouring methyl compared to the methyl beta to the hydroxyl group. In support to this claim, the following experimental evidence is provided:

The methyl doublet in the NMR spectrum of isopropanol (figure IV. 3a) appears at 1.15 - 1.23 ppm whereas it occurs at 1.32 - 1.4 ppm in the spectrum of the derived benzoate (figure IV. 3b), showing the stronger deshielding effect of the ester group. Accordingly, the spectrum of the polymer should show only two doublets in the high field region; however, this is not the case. It is apparent (figure IV. 1) that this region comprises:

a. a doublet at 1.09 - 1.16 ppm
b. a triplet (like) at 1.25, 1.32, 1.40 ppm
c. a doublet at 1.45 - 1.53 ppm



The triplet will be regarded as being composed of two doublets, since the same spectrum taken from a DMSO-d6 solution (figure IV. 2) shows four methyl doublets. It follows that four magnetically different methyls are present in this region.

If the combined inductive effects of the hydroxyl and ester groups on the methyl are considered, then logically, the four methyls, in order of decreasing inductive influence are:

CH, R-O-CH-CH₂-O-R > R-O-CH-CH₂-OH > R-O-CH₂-CH-OH > HO-CH₂-CH-OH

Complete benzoylation of the prepolymer should convert all those segments bearing free hydroxyl groups i.e. 2, 3 and 4 to the form of 1, and the result should be a single doublet giving the exact chemical shift of the methyl group of segment 1.

In fact, the spectrum of the benzoylated prepolymer in $CDCl_3$ (figure IV.4), shows one doublet only, at 1.43 - 1.50 ppm which when transposed to the spectrum of the prepolymer (figure IV. 1) corresponds to the lowest field doublet at 1.46 - 1.53 ppm. As a further proof, the only high field doublet of propylene 1,2 dibenzoate (figure IV. 5) occurs at 1.44 - 1.51 ppm. These observations lead to the conclusion that the doublet at 1.46 - 1.53 ppm is due to the methyl of segment 1.

Vacuum distillation of the unreacted propylene glycol leaves behind a glassy mass, the nmr spectrum of which is shown in figure IV 6. It is evident that the doublet at 1.09 - 1.16 ppm of figure IV 1 is absent. In addition, examination of the nmr spectrum of the distillate confirms that it consists of propylene glycol only (figure IV. 7a, b). Therefore, the highest field doublet is due to the methyl group of propylene glycol. Furthermore, when the propylene








glycol free prepolymer has its spectrum taken in the presence of the shift reagent, $Eu(fod)_3$, europium 1,1,1,2,2,3,3 heptafluoro 7,7 dimethyl-4,6 octanedione, three distinct sets of doublets appear, clarifying thus the nature of the triplet of figure IV 1. In the presence of this europium complex, the polymer molecules interact with the paramagnetic center by coordination through the hydroxyl groups at either end. The strong magnetic moment from the unpaired electron spin is felt by the molecule so that the protons closest to the coordinating hydroxyl group are shifted downfield.

In addition, bis (2 hydroxy propyl) terephthalate

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the methyl groups of which are of type 3 gives, in DMSO-d₆, a doublet at 1.18 - 1.25 ppm (figure IV.9) which corresponds exactly to the doublet next to the propylene glycol one on figure IV 2.

On the basis of these three assignments, it becomes obvious that the electronegativity trend cited above holds. Therefore, the doublet at 1.3 - 1.36 ppm in figure IV. 2, will be assigned to the methyl of segment 2.

3.1.2 Methylene Absorptions

The CH₂ groups of the prepolymer, should give rise to doublets because of their proximity to methyne groups.

Referring to the nmr spectrum of the propylene glycol free prepolymer and comparing it to the spectrum of the benzoylated derivative as well as to the spectrum of the benzoylated propylene glycol, it is obvious that the methylene doublet of segment 1, in the sequence cited previously, occurs at 4.52 - 4.57 ppm. In addition, the corresponding integrated trace, 1.8 cm (figure IV. 1) is equal to two thirds of that of the methyl doublet of 1, 2.7 cm, confirming that both groups belong to the same segment.





On the other hand, the methylene group of bis (2 hydroxy propyl)terephthalate results in a doublet at 4.15 ppm which corresponds to the doublet at 4.25 ppm on figure IV 1. The shift (0.1 ppm) is due to a solvent effect, since the spectrum of T400-A in DMSO-d₆ (figure IV. 2) shows the same doublet at 4.18 ppm. Therefore the latter will be assigned to the methylene group of segment 3. To support this claim, two experimental evidences are provided. First, the integrated trace of this doublet, overlapping with a -CH multiplet and therefore corresponding to three hydrogen atoms (figure IV. 6) is approximately equal to the integrated trace of the methyl doublet of the same segment. In addition when the CDCl₃ solution of the propylene glycol free prepolymer is treated with Eu(fod)₃, the doublet at 4.3 ppm is strongly shifted to lower fields, showing that it belongs to a segment bearing a free hydroxyl group.

The only doublet to interpret, now, is the one occurring at 3.78 - 3.84 ppm (figure IV.6). The only possibility is that it is caused by the methylene group of segment 2. It has an integrated trace which corresponds to the neighbouring methyl group and also shifts strongly downfield upon treatment with the europium derivative.

The methylene doublet of free propylene glycol can be identified unambiguously by superimposing the spectrum of free propylene glycol (figure IV. 7a) with the spectrum of T400-A.

The relative position of each doublet favours again the combined inductive effects of the ester and the hydroxyl group on the chemical shifts of the methylene groups. The order of decreasing inductive influence being:

CH2 CH Roch_2 -ch-or > $\operatorname{R-och}_2$ -ch-oh > $\operatorname{Roch-ch}_2$ oh > $\operatorname{Hoch-ch}_2$ oh

3.1.3 Methyne Absorptions

Being in the vicinity of a methyl and a methylene group, the methynes of the model structure are expected to give rise to a sextet. The methyne group of segment 1 is illustrated in figure IV. 1 by a multiplet centered at 5.58 ppm. This allocation has been done with the aid of the spectra of the benzoylated prepolymer and propylene glycol dibenzoate, the -CH group of which is centered at the same region. In addition, the integrated trace of this absorption, 1.4 cm in figure IV. 6, is approximately equal to the integrated trace of the methylene absorption (2.9 cm), and the methyl group doublet (4.2 cm) of the same segment after taking into consideration the relative populations of hydrogen atoms.

The methyne group of bis (2 hydroxy propyl) terephthalate, on the other hand, absorbs at 4.00 ppm and the multiplet partly overlaps with the neighbouring methylene doublet at 4.15 ppm. The same pattern exists in the spectrum of T400-A in DMSO at 4.00 ppm and is assigned to the methyne of segment 3.

The only multiplet left is the one at 5.27 ppm (figure IV. 6) which will be assigned to the methyne of segment 2. Its integrated trace, 0.8 cm, is half the integral of the neighbouring $-CH_2$ group (1.6 cm) at 3.8 ppm and approximately equal to one third of the integral of the methyl group doublet of the same segment (3.9 cm).

By superimposing this spectrum with the spectrum of propylene glycol it is found that the -CH multiplet of the latter overlaps with the doublet of the methylene group of segment 2.

3.1.4 Phenyl Absorptions

The phenyl hydrogen absorption of bis(2 hydroxy propyl)terephthalate occurs at 8.11 ppm and gives rise to a sharp and well defined peak accounting for the magnetic equivalence of the four hydrogens of the terephthalate ring (figure IV. 10a). On the other hand, the phenyl peak on the nmr spectrum

of a mixture of bis (1 hydroxypropy), bis (2 hydroxypropy)) and 1,2 Bis hydroxypropyl terephthalates, isolated from the prepolymer itself by GPC (see Chapter VI, Section 4.1) shows a fine splitting (figure IV. 10b). This is accounted for, without any further experimental backing, by a slight loss in magnetic equivalence of the phenyl hydrogens caused by the position of the electron repelling methyl group with respect to the ester oxygen.

More fine splitting of the phenyl absorption is noticeable in the spectrum of the prepolymer, attributed this time to the different dispositions of the diesterified segments at either sides of the terephthalate ring (figure IV. 10c).

3.1.5 Hydroxyl Hydrogen Absorptions

The hydroxyl hydrogen nmr absorptions of the prepolymer (figure IV 11a) are concentration dependent and their exact position in the spectrum is hard to localise. Roughly, they appear in the 3-4 ppm region as shown in figures IV. 11 b & c, where portions of the NMR spectra of the prepolymer containing additional amounts of propylene glycol and bis (2 hydroxy propyl) terephthalate are displayed.

3.2 <u>Chemical Methods Involved in the NMR Experiments</u> The single chemical reaction involved in the above experiments is benzoylation⁽¹²⁾.

Thus, propylene glycol (0.13 moles) was mixed with 25 ml of pyridine in a three necked round bottomed flask equipped with a condenser, a thermometer and a dropping funnel. This contained benzoyl chloride (0.3 moles) and it was added dropwise, at room temperature, under continuous magnetic stirring. After complete addition, the solution was left to stand overnight. Separation of the product involved dissolution of the reaction mixture in chloroform, followed by washings with dilute sodium bicarbonate solution and water. After drying over anhydrous sodium sulphate, propylene glycol

Figure IV. lo

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Phenyl hydrogen absorptions

Figure IV.11

Hydroxyl hydrogen absorptions







1,2 dibenzoate was isolated by distillation under reduced pressure, b.p. 232^oC/12 mm Hg⁽¹³⁾. The nmr spectrum shown in figure IV. 5, confirms its structure. A similar procedure was applied to synthesise isopropyl benzoate from isopropanol and benzoyl chloride.

The benzoylation of the prepolymer itself was carried out in a chloroform solution in the absence of pyridine. The addition of benzoyl chloride was carried out at 40-50°C with continuous stirring and then, the mixture was refluxed for a further hour. Only the solvent was distilled off, and the nmr spectrum of the benzoylated prepolymer was recorded in the presence of traces of benzoyl chloride, its nmr absorptions not interfering with those of the prepolymer parafinic segment.

On the other hand distillation under reduced pressure of the free propylene glycol from the prepolymer was carried out initially at $120^{\circ}C$ (bulk). The temperature was then raised to $190^{\circ}C$, to ensure that all volatile products which might be present (e.g. dipropylene glycol b.p. $232^{\circ}C/760$ mm Hg) have been distilled off.

4 QUANTITATIVE ANALYSIS OF THE PREPOLYMER BY NUCLEAR MACNETIC RESONANCE SPECTROSCOPY

The integrated trace of the already elucidated nmr spectrum of the T400-A prepolymer offers an accessible path towards quantitative estimations, since it is proportional to the areas beneath the corresponding peaks of the spectrum which, in fact, give a quantitative measure of the number of protons contributing to a specific resonance.

This proportionality has been used to estimate the number average molecular weight as well as the free propylene glycol content of the prepolymer.

4.1 Molecular Weight Determination

Following the argument exposed in the introduction of this chapter the terephthalate based prepolymer constituents are:

$$P(TP)_1, P(TP)_2, P(TP)_3 \dots, P(TP)_n, \dots$$

If each of these esters were analysed separately by nmr, then the integrated traces of the phenyl hydrogens (four in number) and those of the methyl hydrogens (three) should be in the ratio

 $\frac{4}{6}$, $\frac{8}{9}$, $\frac{12}{12}$,, $\frac{4n}{3n+3}$, respectively

the general expression being:

$$\frac{4n}{3(n+1)}$$

On the other hand, the molecular weight of each of these esters may be expressed by the formula

$$M_{\bullet}W_{\bullet} = 282 + 206 (n-1)$$

where 282 is the molecular weight of $P(TP)_{l}$, and 206 is the molecular weight of a -TP- repeat unit.

Since the nmr integrated trace of the polymer represents an average number of protons then, n will take an average value \bar{n} , to represent the species $P(TP)_{\bar{n}}$ the molecular weight of which will represent the number average molecular weight of the terephthalate based components.

If the spectrum of the prepolymer is considered without including the propylene glycol methyl protons then

> $\frac{4\bar{n}}{3(\bar{n}+1)} = \frac{6.3}{7.3}$ (figure IV 2) $\bar{n} = 1.833$

and therefore the molecular weight can be calculated

$$M.W. = 282 + 206 (1.833-1)$$

= 454

Hence

The above \bar{n} value is used for the calculation of the number average molecular weight of the terephthalate containing units only. If propylene glycol is to be included, then its representative formula will be P(TP) and in this particular case the subscript n defined above will take the values 0, 1, 2, 3, ..., n, ...

The expression for the molecular weight will not be altered since when n = 0, M.W. = 76 which is the molecular weight of propylene glycol. Only the value of \bar{n} will change, since, this time, the integrated trace of the whole methyl region will be considered

i.e. $\frac{4\vec{n}'}{3(\vec{n}+1)} = \frac{6.3}{9.4}$ $\therefore \quad \vec{n} = 1.0107$ M.W. = 284

This molecular weight (284) can be used in the determination of the hydroxyl number, since it represents the weight of one mole of $P(TP)_{\overline{n}}$ which is associated with two moles of -OH.

Therefore

284 grams of $P(TP)_{fi}$ are equivalent to 2 x 56x10³ mg KOH 1 gram " is " X " "

X = 394 mgr KOH/g

compared to 340 by end group analysis.

The NMR method can be extended for the calculation of the quantity of free propylene glycol, since the latter has characteristic nmr absorptions.

4.2 Estimation of Excess Propylene Glycol

If we assume that the prepolymer consists essentially of two species namely propylene glycol and $P(TP)_n$ of molar concentrations x and y respectively, then these should be in the ratio of the methyl protons of the constituents

i.e.
$$\frac{x}{y} = \frac{2.1/3}{7.3/3(\tilde{n}+1)}$$

y, can be calculated from the integrated trace of the phenyl hydrogens the population of which is $4\overline{n}$

 $\frac{2.1(\bar{n}+1)}{7.3}$

$$v = 6.3/4n$$

since n = 1.833then y = 0.859 moles and x = 0.7 moles

consequently the weight percent of propylene glycol in the prepolymer is

PG % =
$$\frac{0.7 \times 76 \times 100}{0.7 \times 76 + 0.859 \times 454}$$
 = 12% by weight

The same result can be obtained from $\mathbf{n'}$ = 1.0107

In this case the parameter y will be replaced by z to express the molar concentration of the prepolymer plus the propylene glycol; its corresponding integrated trace will therefore be 7.3 + 2.1 = 9.4 cm

Hence
$$\frac{x}{z} = \frac{2.1}{9.4} (1.0107+1)$$

Since all the phenyl integral is regarded as corresponding to a single component of molecular weight = 284

$$z = 6.3/4n' = 1.558$$

and x = 0.699 = 0.7 (as previously)

But this time

PG
$$7 = \frac{0.7 \times 76 \times 100}{1.558 \times 284} = 127$$

The x and y values may also be used in the determination of the number average molecular weight of the prepolymer by means of the equation

$$M.W. = \frac{\sum_{i} M_{i}}{\sum_{i} N_{i}}$$

Where Ni is the number of moles of the component of molecular weight Mi

lence M.W. =
$$\frac{0.7x76 + 0.859x454}{0.7 + 0.859}$$

= 284

which is in agreement with the value derived previously.

A further proof, supporting the validity of the method is the calculation of the hydroxyl number by means of the quantity of free glycol. Since, it is known that the weight percent of propylene glycol is 12% then 12/76x100 moles of free propylene glycol are present in one gram of prepolymer; the corresponding molar concentration of free -OH groups will be

 $2 \times 12/76 \times 100 = 0.316 \times 10^{-2}$ moles per gram Similarly, the weight percent of P(TP) is

$$100 - 12 = 88\%$$

and the molar concentration of free hydroxyl groups

$$\frac{2x88}{454x100}$$
 = 0.387 x 10⁻² moles per gram

The total -OH group molar content is

 $0.316 \times 10^{-2} + 0.387 \times 10^{-2} = 0.703 \times 10^{-2}$ moles per gram On the other hand

> One mole of -OH is equivalent to 56 x 10^3 mg KOH . 0.703 x 10^{-2} moles are to Y Hence Y = 394 mg KOH/g

which is in accordance with the value derived previously.

4.3 Determination of the Quantity of Propylene Glycol Lost During the Polyesterification Process

It has already been shown that the polymer can be regarded either as being composed of a mixture of two components, $P(TP)_{\overline{II}}$ and propylene glycol, or as a single component having the general formula $P(TP)_{\overline{II}}$. Both expressions may be used for the determination of the total quantity of propylene glycol, free and esterified, present in the final product. By comparison to the quantity of glycol in the original feed, the amount that has been lost during the polyesterification process may be calculated.

It has been found that $\bar{n} = 1.833$. Therefore, one mole of P(TP)_{\bar{n}} consists of 1.833 moles of terephthalic acid and 1.833+1 = 2.833 moles of propylene glycol.

It has also been found that the molar concentration, y, of $P(TP)_{\overline{II}}$ is 0.859; it follows that the actual concentration of terephthalic acid is 0.859x1.833 = 1.575 moles.

On the other hand, the molar concentration of esterified propylene glycol is 0.859x2.833 = 2.434 moles. Since the molar concentration, x, of free propylene glycol is 0.7 then the total concentration of glycol units (reacted and free) in the reaction product

2.434 + 0.7 = 3.134 moles.

Since the T400 series of prepolymers are synthesised from one mole of terephthalic acid and 2.2 moles of propylene glycol, then the theoretical quantity, N, of glycol corresponding to 1.575 moles of terephthalic acid is

$$\frac{N}{2.2} = \frac{1.575}{1}$$
 (Assuming no propylene glycol loss during the reaction)

...N = 3.465 moles

It follows that the quantity of propylene glycol lost during the polyesterification process, expressed in mole percent is

$$\frac{3.465 - 3.134}{3.465} = 9.6\%$$

However, the amount of propylene glycol lost during the actual polyesterification should be much higher than 9.6% since to this particular prepolymer T400-A, an excess glycol has been added at the end of the condensation reaction in order to compensate for the losses. But it is very obvious, that the glycol which has been added is still less than the quantity required for the complete compensation of these losses.

The same result can be obtained from $P(TP)_{\hat{n}}$, where n = 1.0107 meaning that one mole of $P(TP)_{\hat{n}}$ is associated with 1.0107 moles of terephthalic acid and 2.0107 moles of propylene glycol. As before, stoichiometric quantity, N, of propylene glycol should be

$$\frac{N}{2.2} = \frac{1.0107}{1}$$

N = 2.224

and this corresponds to a loss of

 $\frac{2.224 - 2.0107}{2.224} \times 100 = 9.6\%$

4.4 Result Reproducibility

The reproducibility of the nmr integrated trace, and therefore of the results, has been verified on three more samples of T400-A collected from the same batch and analysed under similar experimental conditions as before. The phenyl and methyl absorption regions of the spectra are shown in figure IV. 12. The number average molecular weights of the terephthalate based components (MWT), that of the polymer itself propylene glycol included (MW), the free glycol content as well as the glycol losses are shown in table 1.

It is obvious that the more sensitive figure to slight variations in the nmr trace is the one expressing the free glycol.

Further research aimed at the improvement of the agreement between these values has not been performed. It is thought, however, that analysis of less concentrated DMSO solutions will improve the resolution and therefore the consistency of the results.

	Figure IV. 12	Result reproducibility
8 1		8 2 8 3 1
	Figure 3V. 12	Result reproducibility

In this particular set of experiments, the interference of shoulders at the bases of nmr peaks with the actual integrated trace has been avoided by defining the boundaries of the trace. For example, the methyl absorption region of the esterified propylene glycol segments was limited to 1.6 - 1.4 ppm and the propylene glycol methyls to 1.14 - 1 ppm.

In addition to sample concentration factor, the consistency of the trace is largely affected by the performance of the integrator itself, a point that has not been investigated prior to taking measurements.

Nevertheless, these factors which most probably led to only a fair agreement between the results cited in table 1, are experimental and may easily be alleviated.

Table 1

Sample	MWT	MW	Excess PG Wt %	% Deviation from mean (11.1)	PG Lost Mo1 %	% Deviation from mean (10.8)
1	450	284	10.7	3.6	11.5	6.5
2	450	299	10.4	6.3	12.6	16.7
3	430	284	11.3	1.8	9,6	11.1
Figure IV. 2	454	284	12	8.1	9.6	11.1

5 CONFIRMATION OF THE NMR RESULTS BY OTHER METHODS OF ANALYSIS

5.1 <u>Estimation of Free Propylene Clycol by Gas Liquid Chromatography</u> In order to verify the validity of the nmr results, the content of unreacted propylene glycol in the prepolymer was determined quantitatively by GLC. The internal standardisation method (14) was applied for calibration purposes. It involves the chromatographic resolution of standard solutions of propylene glycol and an internal standard in a volatile solvent followed by the construction of a graph relating the ratio

<u>Peak area of propylene glycol</u> Peak area of internal standard

to the known concentration of propylene glycol.

By means of resulting calibration graph, the glycol concentration in the prepolymer may be estimated provided the experimental conditions are not altered.

The GLC experiments described in this section were carried out with the aid of a Pye Unicam 104 gas chromatograph equipped with a flame ionisation detector and connected to a calibrated CR100 - JJ time-response recorder.

The glass columns (4ft x $\frac{1}{2}$ ") used were packed with 10% Carbowax 20M on 60-80 mesh Chromosorb W.

The chromatographic separations were carried out under the following conditions:

Nitrogen flow rate	100 ml/min
Hydrogen pressure	12 lb/in ²
Air pressure	20 lb/in ²
Amplification	$\times 10^3$

The standards were prepared by weighing accurately propylene glycol samples in 5 ml volumetric flasks; 0.1 ml of m-cresol, used as internal standard was then added by a 1 ml syringe and the contents were made up to the mark of the flask with acetone. All the chemicals were redistilled prior to use.

One microliter of each solution was injected in the chromatographic column with a Hamilton microsyringe; the process was repeated thrice. Under the experimental conditions cited above the retention time of m-cresol with respect to propylene glycol was 7 minutes (figure IV. 13).

The areas under the propylene glycol and m-cresol peaks were then computed geometrically and themean value of their ratios was plotted against the corresponding concentration (weight) of propylene glycol in the standard solutions (figure IV. 14).

For the dermination of the free glycol, 1.0937 g of T400-A were weighed directly in a 5 ml volumetric flask and an acetone solution, including 0.1 ml of m-cresol was made up as before. After chromatographing l microliter, the ratio of propylene to m-cresol peak areas was determined in triplicate.

Area propylene glycol peak Area m.cresol peak = 0.539 (0.55% deviation) From the calibration curve, the above area ratio corresponds to 0.103 g of glycol, which are contained in 1.0837 g of prepolymer, therefore the percentage of glycol is

$\frac{0.103}{1.837} \times 100 = 9.5\%$

This value is slightly lower than the ones obtained by nmr but, nevertheless the fact that its deviation from the mean of the spectroscopic result by $\sim 6\%$, shows that it is within the limits of experimental errors involved in these experiments.

5.2 Hydroxyl Number Determination

The most common method, applied for the determination of the hydroxyl group content of a compound, involves its treatment with an excess of an acetylating reagent followed by the titrimetric determination of the unreacted reagent. The hydroxyl number represents the weight of alkali, in milligrams, equivalent to the quantity of the acetylating reagent that has reacted with one gram of the compound.



figure. [V. 13

GLC chromatogram



The actual acetylation of T400-A was carried out with a mixture of dry pyridine (4 volumes) and acetic anhydride (1 volume).

About one gram of the polymer was accurately weighed in a glass stoppered 250 ml Pyrex Erlenmeyer flask; 10 ml of the acetylating solution were added by pipette and the flask was connected to an air condenser. A blank of the reagent was treated similarly. The flasks were heated on an electrical heater with occasional shaking till complete dissolution of the sample. Then 20 ml of neutral benzene were added and the flasks were stoppered and shaken vigorously. After the addition of 75 ml of distilled water, the solutions were titrated with a standard sodium hydroxide solution using about twice the normal amount of phenol phthalein indicator.

The results are shown in Table 2.

Ta	Ъ	1	e	2
_		-		

Weight of sample (g)		Vol. NaOH used to titrate excess reagent		
A:	1.1586	9.0 ml		
в:	1.3390	8.45		
	•			

Normality NaOH 1.958N (standardised against benzoic acid)

Volume NaOH required to neutralize 10 ml of acetylating mixture: 12.6 ml. This was determined from the blank experiment.

Therefore, the acetic acid used in the actual acetylating procedure corresponds to 12.6 - 9.0 = 3.6 ml NaOH (for A)

. Hydroxyl No = $\frac{3.6 \times 1.958 \times 4.0}{1.1586}$ (molecular weight NaOH)

= 243.3 for A and 242.7 for B (expressed in milligrams NaOH per gram of prepolymer)

In terms of KOH these values lie around 340 mg KOH/g compared to 394 as determined by nmr.

The above experimental results may also lead to the determination of the molecular weight of the prepolymer, propylene glycol included. Accordingly: 1 gram mole NaOH = 1G.Mole CH₂COOH = 1 OH group

36 m1, 1.958N NaOH \$3.6 x 1.958/1000 OH groups

1.1586 grams of prepolymer # 3.6 x 1.958/1000 OH groups

Number average molecular weight 2 OH groups (assuming all end groups are hydroxy) It follows that the number average molecular weight is 329 compared to 284 as calculated by nuclear magnetic resonance. However, because of the probable presence of traces of water in the polymer analysed, the hydroxyl number as determined by titration is expected to be much higher than the one estimated by nmr, since water absorptions are not considered in the calculations by the latter method, and, consequently the titrimetric molecular weight should be lower. But since the opposite has happened, we must assume that either the acetylation reaction has not proceeded to completion or the phenol phthalein end point has been surpassed in both cases.

In the above argument, the spectroscopic method has been regarded as the standard or reference method because it does not involve personal errors.

Despite this discrepancy, it is worthwhile considering, the simple treatment of the combined GLC-titration results, for the determination of the molecular weight of the terephthalate based components only of T400-A is

 $1.1586 - \frac{1.1586 \times 9.5}{100} = 1.0486 \text{ grams}$

the rest being free propylene glycol.

Since one gram mole of propylene glycol = 2 gr moles NaOH it follows that $\frac{1.1586 \times 9.5}{100} = 0.11 \text{ grams of the free propylene glycol are equivalent to}$

 $\frac{2 \times 40 \times 0.11}{76}$ = 0.1158 grams NaOH

102.

These are present in 1.48 ml of a 1.958N NaOH solution, therefore only 3.6 - 1.48 = 2.12 ml of alkali are equivalent to the hydroxyl groups of the terephthalates.

Again, since 1 G. Mol. NaOH \equiv 1 G. Mole CH₃COOH \equiv 1 OH group

. 2.12 ml. 1.958N NaOH 至2.12 x 1.958/1000 -OH groups

1.4086 gr of terephthalates # 2.12 x 1.958/1000 -OH groups

and Molecular weight ≡ 2 -OH groups

It follows that the number average molecular weight of the terephthalate based components of T400-A is 505 in contrast to 450 by nmr.

Both the GLC and the titrimetric methods show the advantage of nmr as a rapid and reliable analytical tool for the estimation of the molecular weights and the concentration of the unreacted components of the prepolymer.

6 QUANTITATIVE ANALYSIS OF SOME OTHER PREPOLYMERS BY NMR

The molecular weight, free propylene glycol content and glycol losses during polyesterification of T400-B, T400-C and T500 have also been determined by the nmr method.

All the spectra were recorded under the same experimental conditions as T400-A, i.e. 30-40% solutions in DMSO-d₆ at 90 MHz.

The representative phenyl and methyl nmr peaks as well as their integrated traces are shown in figure IV.15; the arithmetic analysis of each spectrum separately is described below. The terms are the same as the ones used in the previous analysis.

6.1 <u>T400-B</u>

6.1.1 Molecular Weight of Terephthalate Based Components

 $\frac{4n}{3(n+1)} = \frac{6.2}{6.8}$... n = 2.165

Therefore the molecular weight is

M.W. = 282 + 206 (2.165 - 1)

= 522

6.1.2 Molecular Weight of Prepolymer Including Propylene Glycol

$\frac{4n^{2}}{3(n+1)}$	=	<u>6.2</u> 8,6
. n'		1.179

Therefore the molecular weight is

$$M.W. = 282 + 206 (1.179 - 1)$$
$$= 319$$

6.1.3 Free Propylene Glycol Content

$$\frac{X}{Z} = \frac{1.8 (n'+1)}{8.6}$$

Since n' = 1.179, then

$$\frac{x}{z} = 0.456$$

Also Z = $\frac{6.2}{4n'}$

= 1.315



Figure IV. 15

Hence X = 0.6

Therefore, the free glycol content is

$$\frac{0.6 \times 76}{1.315 \times 319} \times 100 = 10.86\%$$

The free glycol was also determined by GLC as for T400-A. Thus one microliter of a 5ml solution of 1.0837 g of the prepolymer in acetone containing 0.1 ml m-cresol was injected in the chromatographic column. The mean area ratio of the glycol to cresol peaks was 0.504 (0.8% deviation) which, according to the calibration graph (figure IV. 14) corresponds to 0.096 g of glycol. This figure, when translated into a weight percentage gives 8.86%.

6.1.4 Propylene Glycol Losses

Since n' = 1.179, then one mole of $P(TP)_{\bar{n}}$ is associated with 1.179 moles of terephthalic acid and 2.179 moles of propylene glycol. On the other hand, the stoichiometric quantity, N, of propylene glycol should be

$$\frac{N}{2.2} = \frac{1.179}{1}$$

Hence

$$N = 2.59$$

Therefore, the quantity of glycol lost is

$$\frac{2.594 - 2.179}{2.594} \times 100 = 16\%$$

6.2 <u>T400-C</u>

6.2.1 Molecular Weight of Terephthalate Based Components

$$\frac{4n}{3(n+1)} = \frac{5.3}{5.8}$$

. . . n = 2.175

Therefore the molecular weight is

$$M.W. = 282 + 206 (2.175 - 1)$$

= 524

6.2.2 Molecular Weight of Prepolymer Including Propylene Glycol

$$\frac{4\bar{n}'}{3(\bar{n}+1)} = \frac{5.3}{6.7}$$
$$\bar{n}' = 1.457$$

Hence the molecular weight

$$M_{\bullet}W_{\bullet} = 282 + 206 (1.457 - 1)$$

= 376

6.2.3 Free Propylene Glycol Content

However

Z = 5.3

X =

 $\frac{X}{Z} = \frac{0.9(n+1)}{6.7}$

Hence

Therefore, the free glycol content is

0.3

$$\frac{0.3 \times 76}{0.909 \times 376} \times 100 = 6.7\%$$

The free glycol was again determined by GLC exactly as before.

0.33

The mean area ratio of propylene glycol and m-cresol was 0.278 (0.7% deviation) which corresponds to a glycol content of 5%.

6.2.4 Propylene Glycol Losses

Since n' = 1.457, then one mole of P(TP)_n is associated with 1.457 moles of terephthalic acid and 2.457 moles of propylene glycol. The stoichiometric quantity, N, of propylene glycol should be

$$\frac{N}{2.2} = \frac{1.457}{1}$$

Hence

$$N = 3.2$$

Therefore, the quantity of glycol lost is

$$\frac{3.2 - 2.457}{3.2} = 23.4\%$$

6.3 T500

6.3.1 Molecular Weight of Terephthalate Based Components

$$\frac{4\bar{n}}{3(\bar{n}+1)} \approx \frac{2.9}{3.6}$$

... $\bar{n} \approx 1.528$

Hence the molecular weight

$$M.W. = 282 + 206 (1.528 - 1)$$
$$= 391$$

6.3.2 Molecular Weight of Prepolymer Including Propylene Glycol

$$\frac{4\bar{n}'}{3(\bar{n}+1)} = \frac{2.9}{5.8}$$
$$\therefore \bar{n} = 0.6$$

It follows that the molecular weight is

 $M_{\bullet}W_{\bullet} = 282 + 206 (0.6 - 1)$

= 200

6.3.3 Free Propylene Glycol Content

$$\frac{X}{Z} = \frac{2.2(n+1)}{5.8}$$

Since $\bar{n}' = 0.6$ Then $\frac{X}{Z} = 0.607$

However $Z = \frac{2.9}{4\bar{n}}$

= 1.208

Hence X = 0.733

Therefore the free glycol content is

 $\frac{0.733 \times 76}{1.208 \times 200} \times 100 = 23.06\%$

The same estimation has been carried out by GLC, with a rough alteration in the calibration procedure. Thus one microliter of a 5 ml solution of 1.0837 g of the prepolymer in acetone containing 0.1 ml m-cresol was injected in the chromatographic column. The mean area ratio of the glycol to cresol peaks was 1.313 (2.4% deviation) which is not represented on the calibration graph; but the concentration, found to be 23.24%, was calculated by comparing this area ratio to the area ratio and percent glycol content of T400-C on the assumption that the linear proportionality between area ratio and glycol content is valid at high free glycol concentrations.

6.3.4 Propylene Glycol Losses

One mole of $P(TP)_{fi}$ is associated with 0.6 moles of terephthalic acid and 1.6 moles of propylene glycol.

The stoichiometric quantity, N, of propylene glycol should be

$$\frac{N}{3.3} = \frac{0.6}{1}$$

Since 3.3 moles of propylene glycol are used in the synthesis of the T500 prepolymers

$$N = 1.98$$

It follows that the quantity of glycol lost is

$$\frac{1.98 - 1.6}{1.98} = 19.19\%$$

7 DISCUSSION

The work described in this chapter shows clearly the importance of the qualitative as well as quantitative aspects of nuclear magnetic resonance spectroscopy as far as the characterisation of low molecular weight polyesters is concerned.

In this work, the value of the technique is enhanced by the fact that the polymer under consideration is an important intermediate in the synthesis of the "Impolex" unsaturated polyesters, since it offers a quick way of evaluating and monitoring the reproducibility of the process. Of particular interest is the estimation of the free hydroxyl group content by means of which the stoichiometric quantity of the unsaturated acid component to be added in the second polyesterification stage can be calculated. The possibility of estimating the free glycol as well as the glycol losses do not lack of interest since they appear to vary from batch to batch. A valuable observation concerning the ICI first stage polyesterification process is that no signs of propylene glycol homopolymerisation are present; this is on the basis of the following experimental evidence. Had homopolycondensation proceeded to a small extent, then dipropylene glycol should have been formed and consequently detected in conjunction with propylene glycol on the nmr spectrum of the distillate, methyl groups beta to an ether oxygen being expected to have different chemical shifts than methyl groups beta to a hydroxyl oxygen. Furthermore, no dipropylene glycol has been detected throughout the gas liquid chromatography experiments carried out in this project. On the other hand, if the extent of homopolycondensation was high enough for the reaction to proceed far beyond the dipropylene glycol stage then the spectrum of the benzoylated polymer should have shown signs of methyl groups beta to ether bonds, which is not the case.

It is worthwhile mentioning that at the present development stage of the nmr technique, its importance is limited to the characterisation of the final product only since it has been assumed that carboxyl group terminated species are absent, therefore a previous knowledge of the extent of reaction, through a simple acidimetric titration is certainly required.

It is obvious that the development of the method has been facilitated by the fact that the polymer is almost fully hydroxylated on one hand and, on the other that its molecular weight is low.

Application of the technique to polyesters of higher molecular weight may be hampered by a lack of sensitivity in the integration of the spectrum. However, Urman et al claimed that a fair reproducibility (10-15%) is reached with polymers of molecular weights up to 5000, which suggests that the method could be extended to the unsaturated polyesters resulting from the condensation of the T400 prepolymers with maleic anhydride, the molecular weight of which is much lower than 5000.

In this case, the macromolecular components are: $\left[P(TP)\vec{n}-F\right]_1-P(TP)\vec{n}', \left[P(TP)\vec{n}-F\right]_2-P(TP)\vec{n}', \dots, \left[P(TP)\vec{n}-F\right]_n-P(TP)\vec{n}'$ Where F stands for fumarate. (Assuming that the maleate - fumarate isomerisation is complete).

It is assumed that the alkyd is hydroxyl group terminated, the alcoholic component being $P(TP)_{\overline{n}}$.

The ratio of fumarate hydrogens (two in number) to phenyl hydrogens (four in number) for each particular component of the system is

 $\frac{2 \times 1}{4\bar{n}' \times 1 + 4\bar{n}'} \quad \frac{2 \times 2}{4n \times 2 + 4\bar{n}'} \quad \dots \quad \frac{2 \times n}{4n \times n + 4\bar{n}'}$

The general term being

where \mathbf{n}' is the value determined in section 3.1

The general expression for the molecular weight of each component is

M.W. = M(n+1) + 82n

Where M is the molecular weight of $P(TP)_{\overline{n}}$ and 82 the molecular weight of the -OC-CH = CH-CO- segment.

The molecular weight of the unsaturated polyester itself will be derived by substituting n by \hat{n} as obtained from the integrated spectrum.

If the ratio of fumarate to methyl hydrogens is considered then \bar{n} will be calculated from the general expression

At this point, the discussion will be shifted towards a rather more technological level especially concerned with the use of a nuclear magnetic resonance spectrometer next to a polyester plant for checking the reproducibility of the process essentially as far as the prepolymer manufacture is concerned.

It is well known that an nmr spectrometer is an expensive and rather delicate tool; and the author's opinion is that at the present development stage of the "Impolex" resins, such process control method should only be used to satisfy meticulously the reproducibility of the synthetic method only, since there is not enough information accounting for the effect of slight molecular weight changes as well as variations in free propylene glycol concentrations on the different properties of the final polyesters. If the effect of these variables proves to be significant then the importance of the NMR as a quality control tool is obvious. Intuitively, it may be suggested that a high propylene glycol content will impart to the standard T400 resin properties perhaps not very different to those of a T500 resin which contains a rather large quantity of free propylene glycol.
8 CONCLUSIONS

The sensitivity of the isopropyl group hydrogens towards slight electronegativity changes may be used advantageously in the nmr characterisation of low molecular weight, propylene glycol based polyesters.

The reproducibility of the results as well as the ease and rapidity with which they are obtained make nmr spectroscopy a valuable technique for the quantitative analysis of polymers.

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CHAPTER V

CHARACTERISATION OF LOW MOLECULAR WEIGHT POLY (PROPYLENE TEREPHTHALATES)

BY GEL PERMEATION CHROMATOGRAPHY

1 INTRODUCTION

In the last chapter it has been assumed that although polymerisation statistics predict the formation of three different species during the polycondensation of terephthalic acid and 1,2 propylene glycol i.e. P(TP), (PT), and T(PT), the poly (Propylene Terephthalates) under investigation in this research project mainly consist of P(TP), units. This is also a statistical prediction since the reaction is carried out to completion in the presence of an excess of glycol. The first stage polyesterification process, also aims at the synthesis of hydroxyl group terminated species for further esterification with maleic anhydride and the subsequent formation of unsaturated polyesters. The prepolymers exhibit a slight acidity, which presumably arises from the monocarboxylic acids (PT), rather than from the dicarboxylic acids T(PT), the concentration of which is assumed to be extremely low because of the non stoichiometric quantities of the starting materials. The scope of the work described in this chapter is the study of the chain distribution of the prepolymers. Here again most of the work will be performed on T400.A.

It is obvious, therefore, that a quantitative method of fractionating the polymer into its macromolecular components has to be applied.

It has been found that gel permeation chromatography in conjunction with the detection method used is very versatile, practical and quantitative in contrast to other fractionation techniques which are tedious and which necessitate additional experimentation for the characterisation of the fractionated species.

To emphasise the advantages of gel permeation chromatography, some of the various polymer fractionation methods will be briefly described and discussed in the following section.

2 METHODS OF POLYMER FRACTIONATION^(1,2)

2.1 Bulk Fractionation by Non-Solvent Addition

The polymer sample is dissolved at a constant temperature in a liquid in which all its fractions are completely soluble. The result is a clear homogeneous solution, to which a non solvent is added gradually while mixing thoroughly, until a stable turbidity appears. To ensure the establishment of equilibrium, the mixture may be warmed until it is homogeneous and allowed to cool slowly back to the required temperature, which should thereafter be carefully maintained. Two phases form, one of them is the highest molecular weight fraction, precipitated as a result of the decrease in solvent power of the medium. The liquid phase is a solution containing a mixture of all the other polymer fractions. After separation of the precipitate more non solvent is added and the process is repeated until all the fractions are precipitated. Among the requirements of this technique is that the solvent and the precipitant should be chosen so that precipitation occurs over a wide range of solvent composition to avoid any mechanical entrainment of macromolecules of a different molecular weight while precipitating any given fraction. Refractionation is often used to achieve better separation.

2.2 Direct Extraction

This consists of the extraction of a polymer sample, as a thin film coating on glass beads in a column. Generally, a column of 4 cm internal diameter and 60 cm in length is used for the fractionation of 1g of sample. A uniform column temperature is maintained and elution is carried out by passing solvent non-solvent mixtures of increasing solvent power. The chain constituents of the polymer are thus eluted in the order of increasing molecular weight. The method requires that soluble low molecular weight species diffuse through the swollen matrix of higher molecular weight polymer, however inversion in the molecular weight sequence of the fractions frequently occurs, and it is desirable to precede this method of fractionation by the following procedure.

2.3 Extraction Following Selective Deposition

This method requires the selective deposition of the polymer chain constituents onto glass beads. The deposition method consists in pouring a 1 to 2% solution of the polymer on the packed column which has been previously heated. The solution should contain sufficient non solvent to bring the system close to phase separation at elevated temperatures, thereby assuming almost complete precipitation of the sample on cooling the column to room temperature.

With decreasing column temperature the highest molecular weight species are expected to precipitate first and would be overlayered by progressively lower molecular weight polymer. After solvent elimination and drying stepwise elution is carried out by means of a solvent non solvent system.

2.4 Precipitation in a Thermal Gradient

This involves the precipitation of the polymer from solution, in a column packed with glass beads, with a thermal gradient produced by maintaining the top of the column at a higher temperature than the bottom. When the polymer solution, adjusted to the point of near precipitation at the higher temperature, is passed down the column, the highest molecular weight species are retained at the top of the column while the lower molecular weight species are precipitated on the cooler zones further down the column. Solutions containing 1 gr of polymer are applied on the column and the packing is extruded and cut into sections for analysis of the deposited fractions.

2.5 Precipitation Chromatography

By this method, separation is achieved through the combined use of thermal gradient and solvent. The thermal gradient is applied as before but the polymer coated beads occupy a uniform temperature region at the top of the column which is the highest temperature zone. The lower three quarters of the column is filled with uncoated beads and the sample is extracted by a gradually solvent enriched solvent-non solvent system. As the extracted

polymer is carried down the column into the cooler zones it undergoes a partial reprecipitation and this precipitated polymer is reextracted by further enriched solvent. From an effectiveness point of view this method is comparable to the one described before (subsection 2.4).

Essential requirements in the above methods are that the samples remain in position on the support and undergo displacement only when extracted by the solution, and that physical interaction with the glass support is suppressed.

2.6 Turbidimetric Titrations

May be used for the rough assessment of the molecular weight distribution. Estimation of the turbidity increase during the precipitation from an extremely dilute solution provides an optical means of weighing the polymer precipitated at a given volume fraction of non solvent. Other fractionation methods include thermal diffusion, ultracentrifugation as well as rheological fractionation.

3 BACKGROUND TO GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC) was developed by J C Moore⁽³⁾ in 1964. He described it as "a mechanism of fractionation through which solute molecules are separated by their permeation into a gel which offers different internal volumes to molecules of different sizes over an extended range."

The separation process is schematically represented as follows:

00

Molecular sizes

Ge1







Figure V.1 Fractionation by GPC

A dilute solution of a polymer is applied at the top of a columm (e.g. 1 m long, 1.5 cm diameter) containing a swollen gel continuously irrigated with solvent. The gel itself has pores of various sizes. At this moment of sample application the different chain constituents of the polymer are uniformly distributed throughout the cross section of the tube (figure V.1a). As the solvent flows through the column, the small molecules penetrate the gel pores and their downward motion is retarded, while the large molecules which have a larger volume than the pores are not captured by the gel network or in other words stay in the void volume and, therefore are transported by the solvent (figure V.1 b & c). Intermediate size molecules, on the other hand, are barred from entering the smaller pores only. Hence the net result is a separation in order of decreasing molecular weight i.e. the elution volume is a diminishing function of the molecular size.

In fact, under these circumstances, the word chromatography is used to describe the experimental procedure involved rather than the separation mechanism itself; since classically, the term chromatography refers to a fractionation mechanism related to differences in the interaction between the various solutes and the surface of the chromatographic medium. In gel permeation chromatography, adsorption has almost no contribution to the fractionation process.

The source of the concept dates back to 1959, when Porath and Flodin⁽⁴⁾ first used the term gel filtration to describe the separation of solutes of different sizes by means of hydrophilic gels. The same term was applied by Vaughan⁽⁵⁾ to describe the fractionation of polystyrene by means of highly crosslinked polystyrene gels.

Typical polystyrene beads used in gel permeation chromatography consist of styrene copolymerised with divinyl benzene. A detailed description of preparation of gels of this type is given by Moore⁽³⁾ and Altgelt⁽⁶⁾. Briefly the procedure is to mix 11 grams of polyvinyl alcohol stabiliser with 500 ml of hot water. The solution is stirred at 80° C and 50 ml of a divinyl benzene mix (53.5% divinyl benzene, 41.9% vinyl ethyl benzene, 3.5% diethyl benzene), 50 ml of styrene, 100 ml of toluene, 50 ml of n-dodecane and 1g of azodiisobutyronitrile are added. The mixture is stirred for 24 h and the gel suspension is filtered.

The polymer precipitation conditions as well as the reaction medium and the concentration of monomers play an important role in controlling the porosity of the gel⁽³⁾. For example, styrene (92% by weight) copolymerised with divinyl benzene (8%) in the absence of solvent and precipitant yields a copolymer with a molecular weight exclusion limit of 1000. But when 30% styrene and 10% vinyl benzene are polymerised in 15% toluene and 45% n-dodecane the exclusion limit or porosity reaches 2,000,000.

Successful separations have also been achieved on support materials such as spherical silica beads (7), porous glass (8,9) and swollen crosslinked rubber of molecular weight $18000^{(10)}$. Several theories have been put forward to explain the mechanism of this particular chromatographic process.

Some authors emphasised the role of preferential exclusion of large molecules from small pores. Porath⁽¹¹⁾ described the gel pores as being conical in shape, thus accommodating better the small spherical molecules and excluding those which have a radius larger than the cone radius. Another mechanism is based on the principle of restricted diffusion⁽¹²⁾. Accordingly, the gel phase consists of cylindrical pores in which free diffusion of the molecules is hindered both sterically (molecular size) and by friction; consequently the elution volume of molecules of different sizes is dependent on their rate of diffusion in the gel phase. On the other hand the downward motion of the entrapped molecules is the result of an exchange of solvent and solute molecules between the mobile and the stationary phases. The rate of exchange depends on the equilibrium distribution of the species between the two phases. Furthermore, the dependence of the retention or elution volume, Ve, of solutes which are neither completely excluded nor able to diffuse freely is represented by the equation

$Ve = Vo + KV_{i}$

where K stands for the fraction of the pore volume V_i , accessible to a solute of a certain size and Vo is the volume of the mobile phase i.e. void volume. The sum of these last two volume parameters plus the volume of the gel matrix represents the total volume of the

gel bed. The final product from a GPC analysis is the recorder trace of the chromatogram, which in the case of a monomeric compound appears not as a straight line but as a bell shaped gaussian curve. This is due to the occurrence of a certain amount of mixing and dilution of the sample



also expressed as instrumental or peak broadening. The width of the peak (W) and the elution volume (Ve) are used for the determination of the efficiency of a gel column in terms of the height equivalent to one theoretical plate (HETP). The number of plates constituting a gel bed is calculated from the equation

$$N = \left(\frac{4.Ve}{W}\right)^2$$

By dividing the length of the gel bed by the number of plates, one obtains the length of the column that corresponds to one plate (HETP). The smaller the base of the elution curve the lower the value for the HETP and the greater the efficiency of the gel bed.

A general review on gel chromatography and its applications is given by Determan⁽¹³⁾ and some further developments are reviewed in reference (14).

Several mathematical methods have been developed to describe the chromatogram shape. These have been reviewed and compared experimentally by Hamielec⁽¹⁵⁾. Tung's⁽¹⁶⁾ equation, for example takes the form

$$F(V) = \overline{A} \int_{m}^{h} \exp \left[-h(V - V_{O})\right]^{2}$$

where F(V) represents the observed chromatogram height at elution volume V; Vo is the eluent volume at the peak of the curve, A is a constant related to the concentration the compound and h is a resolution factor. For infinitely high resolutions h approaches infinity and the curve reduces to a straight line. Methods of solving this equation have been proposed by Smit et al⁽¹⁷⁾. Smith⁽¹⁸⁾ on the other hand, described the chromatogram shape in the similar form

$F(V) = F(V_0) \exp \left[-(V_0 - V)^2/2\epsilon^2\right]$

The exponential form of the equation is very similar to the normal distribution function; Vo representing the mean of the population and 6^{2} its variance. A moderate agreement has been found between the two equations at low average molecular weights, basically these equations have been developed for the elucidation of the chromatograms of high molecular weight polymers for which a single peak is regarded as an envelopeof several elution curves each

corresponding to a macromolecule of a specific molecular weight. We have confined ourselves to those equations describing the elution curves of monodisperse compounds.

Furthermore, several approaches have been put forward to relate the elution volume to a molecular size parameter of the eluting species. Edwards et al⁽¹⁹⁾ related linearly the elution volume to the logarithm of the molar volume of model compounds. Their calibration curve was found satisfactory for the description of the elution behaviour of low molecular weight compounds.

The elution volume V has also been empirically related to the molecular weight M of the solute by the equation (20)

$\ln M = a - bV$

where a and b are constants for a particular column and their values may be established by experiments with materials of known molecular weight.

Because of the extensive GPC work done on polystyrene and its fractionation into samples of very narrow distribution, hence of well defined molecular weight, attempts have been made to derive from it a calibration for less tractable polymers, by finding an independently derivable parameter that is related uniquely to elution volume.

The extended chain length, Lmax, was first introduced as a universal parameter (21), in the Q factor form

$$Q = \frac{M}{Lmax}$$

where M is the molecular weight at the peak elution volume.

Since M = Mo Lmax

where Mo is the molecular weight of a repeat unit of length 1, then $Q = \frac{Mo}{1}$, which can be easily calculated for different polymers. The calibration relationship taking the form If the relation M_1 versus elution volume, of a standard, is known then M_2 can be calculated.

However, from a GPC point of view, the resolution is effected with respect to molecular volumes rather than to linear dimensions which may be visualised from the fact that the above relationship stands well for polymers of different backbones but with similar intrinsic viscosities⁽²²⁾, [n]; i.e. the Mark-Houwink equation, $[n] = KM^{\circ 4}$, where K and are constants for a particular polymer-solvent system, must be taken into consideration.

Dawkins⁽²³⁾ suggested the root mean square end to end distance, $\overline{L_o^2}^2$, as a universal parameter. This is expressed in terms of the A factor, where $A = \frac{\overline{L_o^2}}{M}$

The calibration relationship being

$$\frac{M}{M_2} = \frac{A}{A_1}^2$$

 $\frac{M}{M_2} = \frac{Q}{Q_2}$

However, the most successful universal calibration for GPC is based on the postulate that the elution volume, v, of a solute reflects its hydrodynamic volume⁽²⁴⁾ i.e. (v) = [n] M. The method itself has been developed by Dawkins^(25,26), the calibration equation being

$$\frac{M}{M_2} = \begin{bmatrix} \mathbf{n} \\ \mathbf{n}_2 \end{bmatrix}$$

4 PREPARATIVE GPC SET UP

This section deals with the description of the equipment set to study the molecular weight distribution of the poly (propylene terephthalate) prepolymers. The techniques and recommendations of Mulder and Buytenhuys⁽²⁷⁾ as well as those of Bio Rad Labs⁽²⁸⁾ have been found very useful.

In essence, the equipment consists (figure V.2) of a glass column packed with gel. The top of the column is connected to a solvent reservoir while the bottom end is connected to the cell of an infrared detector, which in turn is connected to a time response recorder.

4.1 Gel Materials and Swelling Agents

The GPC experiments described in this project were carried out on polystyrene gels. The polystyrene beads, commercially known as Bio-beads, were purchased from Bio-rad laboratories. Two different grades have been selected; these were the Bio-beads SX-1 and the Bio-beads SX-2 of molecular weight exclusion limit 3500 and 2700 respectively.

The beads were swollen in various solvents. In all cases they were soaked for 24 hours in an excess solvent and were degassed on a water pump before packing.

The solvents used were of analytical grade purchased from Fisons Ltd, BDH or supplied by ICI Ltd. They were directly used without further purification or degassing.

The most suitable solvent was selected on the following basis:

- Its effectiveness to dissolve completely the polyesters under examination.

- Its swelling power for the polystyrene beads.

- Its infrared absorptions not interfering with the absorptions of the main polyester groups, namely the carbonyl stretch at $1715-1720 \text{ cm}^{-1}$ and phenyl hydrogens out of plane bending at 730 cm⁻¹.



Solvent	≪value (29)	Clear i.r. region	Bp (30)	Refractive index (20 [°] C)
CHC13	0.76	1715-1720	61.7	1.4459
THF	0.72	730	65	1.407-8
Dioxan	0.694	730	101	1.4224
Benzene	0.78	1715-1720	80.1	1.5011

The above considerations lead to the choice of the following solvents.

The alpha value is the exponent of the Mark-Houwink equation, and represents a measure of the polystyrene-solvent interaction. The more alpha tends to unity the better the swelling power of the solvent.

On the other hand, THF and dioxan do not show any infrared absorptions in the carbonyl group region, however such absorptions develop with time despite the presence of inhibitors thereby making this region inadequate for GPC purposes. In addition, these two solvents are difficult to obtain moisture free.

Dichloroethane which has a relatively clear infrared spectrum has been recently used for the spectroscopic analysis of the eluting species in solution⁽³⁴⁾

4.2 Columns and Plungers

The columns used were made of glass since the system operated under very low pressures only. In addition, glass columns offer an advantage over steel columns, because cracks and channels, which sometimes develop in the gel bed can be observed.

The column dimensions ranged from 100 cm - 110 cm in length and from 1 cm to 1.25 cm in diameter; these proved to be adequate for the resolution of the polyester under examination.

The plungers, manufactured from steel are schematically represented in figure V.3. These are adapted in the columns in the following way: by turning the horizontal ring of the plunger, the polyethylene ring is pushed down over the oblique bottom part until the gap is sealed.

On the other hand, the bottom end of the glass column is drawn until the inner diameter of the capillary formed matches, approximately the outer diameter of the coupling plastic tubing.

4.3 Coupling

Stainless steel capillaries and serum needles (No.1 or No.0) of about 3 cm in length were used to interconnect the valve, plunger, column and detector with the intermediate of either PTFE or polyethylene flexible tubing. For example, to the drawn end of the glass column a 2 cm capillary, half covered with plastic tubing, was inserted to constitute the column outlet; similarly, the plunger and its tubing were connected by means of a short steel capillary present in the plunger bore and by means of serum needles with Luer connections to a Hamilton three way valve.

Before using the column, a small wad of glasswool is pushed into the drawn end of the glass column above the stainless steel connecting piece, followed by a flat thin layer of sand in order to avoid irregularities in flow at the end of the separation and for supporting the gel itself.

4.4 Column Packing

The adequacy of a chromatographic resolution largely depends on the packing of the gel bed. Many packing procedures are described in the literature (2,13,31); we have not adopted any special method.

Packing was started by keeping the column outlet shut and filling to a quarter of its length with solvent. The gel slurry was poured with the aid of a glass rod in a funnel topping the column. In order to avoid gel splashing, the slurry



was allowed to reach the solvent surface by sliding along the walls of the column.

When the solvent reached a considerable height, the column outlet was opened and packing was continued under flow. During the packing operation the gel must not be allowed to settle otherwise a separating zone is formed when more gel is added; in addition the gel should be always topped with 15-20 cm of solvent except, of course, when the gel bed has reached the required height. The plunger is then placed in position and the gel is allowed to settle under the required working pressure. Very often a solvent gap develops between the plunger and the gel. This is alleviated by pushing the plunger down until it meets again the gel surface.

The described packing procedure can be carried out by using reasonably thick gel slurries in solvents such as tetrahydrofuran, dioxaneand benzene whereas with chloroform, in which the gel floats, we have experienced that a dilute gel is easier to handle. Packing with gel swollen in THF, followed by chloroform washings as a means of avoiding flotation of the gel, has also been suggested. In our opinion, this method is time consuming and uneconomical since a good gel performance is attained when chloroform is used on its own.

4.5 Solvent Flow and Sample Application

The flow rates ranged from 15 to 25 ml/h since the system operated under gravity. The average duration of a GPC experiment was 5h. The sample (0.015g) was dissolved in 0.5 ml of solvent, in an ignition tube, and was applied to the column, through the three way valve, under the effect of the solvent flowing through the column. After complete suction of the solution followed by solvent washings, the column was again connected to the reservoir by means of the valve. The whole "injection" sequence lasted for 4-5 min. approximately.

4.6 Detection

The most widely used method of detection of the eluting species is differential refractometry. Accordingly the refractometer response is proportional to the concentration of the solute. Other methods of detection include flame ionisation⁽³²⁾, ultraviolet and infrared detection⁽³³⁾.

In the experiments described in this project a: 459 Perkin Elmer infrared spectrophotometer has been used as detector.

The column outlet was connected, with a plastic tubing to a steel capillary inserted in the PTFE plug of a sodium chloride cell of the detector. The cell crystals were separated by a 0.07 mm Teflon spacer. The experiments to follow will show that this path length allows an adequate differentiation between the different species that flow through the cell. The outlet of the latter consisted again of a PTFE plug equipped with a steel capillary, connected to a plastic tubing. The effluent solvent was collected in a graduated cylinder.

The infrared spectrophotometer read throughout the experiment a single wavelength where a specific group of the eluting component absorbed. The exact position of the absorption maximum was obtained from the spectrum of a dilute solution of the solute under examination. Once the maximum is found, the infrared pen is brought to its base line (100% transmittance) by attenuating the reference beam either with an attenuator or with a NaCl reference cell containing pure solvent. In other terms when solvent only passes in the sample cell the infrared pen must not move from its base line.

Furthermore, the detector was connected to a JJ type time-response recorder which is also used to amplify the infrared signal several times.

As the eluting species flow through the cell they cause the detector pen to deflect vertically. These deflections are converted into sets of curves by the recorder. Typical chromatograms will be found throughout this chapter. Their quantitative interpretation is based on a detection theory exposed in the following section.

5 DETECTION THEORY

5.1 Meaning of the Area Under the Elution Curve

Infrared detectors, as already mentioned, have been and are being used in line with GPC columns for the detection of the eluting species. Of particular importance to this project, is the understanding of the meaning of the area under the chromatogram curve in terms of the infrared spectroscopy basic theory.

To elucidate this point the following simple treatment has been introduced:

The process of formation of a GPC elution curve may be considered as the result of a series of separate infrared spectroscopy experiments, whereby the NaCl cell is filled with solutions of concentrations determined by the GPC spread and, their transmittance, at a wavelength where only solute absorbs, plotted against an arbitrary linear scale. As expected, the resulting plot will be a curve equivalent to the chromatogram curve.

On the other hand, the transmittance, T, is related to the concentration, C, expressed in moles per liter, according to Beer's law

$$\log \frac{1}{T} = E.c.l.^{(35)}$$

T = e^{-E.c.l.}

 $T = e^{-kC}$

Since the extinction coefficient, E, is constant for a given compound at a constant wavelength, and 1, the path length, does not change provided the same cell is used, then,

where
$$k = E_1$$

or

However, calculating the area under the curve in terms of the linear transmittance scale plotted as the ordinate i.e. Area = $T.\Delta x/2$, on the assumption that the curve is almost triangular in shape, is irrelevant since

the zero of the metric scale corresponds to unity on the transmittance scale.

Therefore, the relevant linear expression for the calculation of the curve height in terms of a metric scale is 1-T, and its relation to the concentration is obvious,

i.e.
$$1-T = 1-e^{-kC}$$

By expanding the exponential factor

$$1-T = 1 - (1-kc + \frac{k^2c^2}{2!} - \frac{k^3c^3}{3!} \dots)$$
$$= kc - \frac{k^2c^2}{2!} + \frac{k^3c^3}{3!}$$

If the concentration is low enough for the second and third terms to be disregarded, then

$$1-T = kc$$

This means that the spectrophotomer deflections or the chromatogram heights, measured in centimeters, for example, are linearly proportional to the solute concentration in moles per liter.

It follows that the area under the GPC curve will be represented by the sum of these deflections, each being the result of an independent experiment

i.e.
$$S = kc_1 + kc_2 + kc_3$$

 $= k \sum_{i=1}^{c} k$

Hence the area under the GPC curve, as far as infrared detection is regarded, is proportional to the concentration of the eluted component in moles per liter.

It is essential that the concentrations are very low otherwise Beer's law, on the validity of which this treatment has been based will be no longer applicable because of possible associations leading to deviations from the proportionality. The severity of the error which could be introduced by the concentration factor may be visualised if the same derivation is achieved by having recourse to the absorbance (A), which is exponentially related to the transmittance

i.e.
$$A = \log \frac{1}{T}$$

Calculation of the area under the chromatogram curve in terms of the absorbance will again be irrelevant since the latter is represented by a logarithmic scale. However, figure V.4, shows that the region between the units of the semi-logarithmic plot are linear functions; it follows that in these regions and specifically in the 0 to 0.1 region, there is a linear relation between absorbance and recorder deflection (D) and, eventually between the latter and the concentration

$$D = KA$$

where k is a proportionality factor depending on the amplification levels used.

Hence

$$\mathbf{D} = \mathbf{K} \cdot \mathbf{E} \cdot \mathbf{c} \cdot \mathbf{I}$$

= K.c

The area under the curve will be represented by

$$S = D_1 + D_2 + D_3 \cdots$$
$$= Kc_1 + Kc_2 + Kc_3 \cdots$$
$$= K \sum c_i$$

Hence, provided the concentrations or at least the maximum concentration, is low enough to give an infrared pen deflection in the linearity region, the area under the GPC curve is proportional to the concentration expressed in moles per liter. It is obvious that this description of the concentration does not represent the actual concentration of the solution applied to the GPC column, but the quantity, preferably in moles, of the solute.



The linear relationship between quantity of material applied to the GPC column and the corresponding area under the curve has been verified experimentally by injecting dilute solutions (2-5%) of Bis (2 hydroxy propyl) terephthalate (Chapter VI) in a column running on chloroform and determining the areas under the curves of the recorder chart. The results are shown in figure V.5.

5.2 <u>Relation Between the Chromatogram Areas of Macromolecular Isomers</u> Of particular interest to this work is the deduction of a proportionality between the area under the GPC curve and the number of chemical groups present in a macromolecule.

To reach this expression, Beer's law will be applied separately to two possible components of the prepolymer, namely $P(TP)_1$ and $P(TP)_2$. The former comprises two carbonyl groups and one phenyl while the latter four and two respectively.

A preliminary experiment has therefore been carried out to verify the applicability of Beer's law on solutions of $P(TP)_1$. Thus dilute chloroform solutions of bis (2 hydroxy propyl) terephthalate, the synthesis of which is fully discussed in Chapter VI, had their maximum absorbance at 1715 cm^{-1} , determined by means of a Perkin Elmer 459 infrared spectrophotometer using chloroform as reference. The cell path was 0.07 mm. The plot of absorbance against concentration gave a straight line (figure V.6).

Therefore, for P(TP) solutions

 $A_1 = E.1.C_1$

where ℓ_1 is an arbitrary point on the abscissa of the graph.

The term C_1 also describes the molar concentration of the -PT- units. If Beer's law had to be written in terms of the carbonyl group concentration then





Absorbance (logscale)

2

1

0.2

0.1

6

8 10 12 14 Concentration (moles/liter × 10³)

If the same, infrared spectroscopy experiment, were repeated on $P(TP)_2$, which contains two -PT-units, then C_1 moles of the solute would have been equivalent to $2C_1$ moles of $P(TP)_1$ or $4C_1$ moles in terms of carbonyl group concentration. The corresponding absorbance would have been $2A_1$

glycol,

i.e.
$$2A_1 = 4E_2 1.C_1$$

 $A_1 = 2E_1 1C_1$

where E_2 is the extinction coefficient of $P(TP)_2$ at 1715 cm⁻¹.

The ratio of the last two equations shows that

$$E_2 = 2E_1$$

Similarly $E_n = 2nE_1$ where E_n is the extinction coefficient of $P(TP)_n$. Therefore, the extinction coefficient will be regarded as a property of a single carbonyl group, i.e. the maximum absorbance at 1715 cm⁻¹, of C_1, C_2, \ldots, C_n , moles of $P(TP)_1 P(TP)_2, \ldots P(TP)_n$ respectively per liter of chloroform would be

$$A_1 = 2 E1C_1, A_2 = 4E1C_2, \dots, A_n = 2nE1C_n$$

If, now, a gel permeation chromatography experiment were run on a mixture of these species, the areas under the corresponding chromatogram curves would be

$$S_1 = 2K \sum_{i=1}^{k} c_i, \quad S_2 = 4K \sum_{i=1}^{l} c_i, \quad \dots, \quad Sn = 2nK \sum_{i=1}^{k} c_i \text{ respectively.}$$

Hence, the concentrations of the components in moles per liter

$$\xi c_{i} = \frac{S_{1}}{2R}$$
; $\xi c_{i} = \frac{S_{2}}{4R}$,, $\xi c_{i} = \frac{S_{n}}{2nK}$

Therefore by dividing the areas under the GPC curve of each component in the mixture by the corresponding number of carbonyls an expression for the concentration is found from which the mole fraction of each component can be calculated.

6 EXPERIMENTAL PROGRAMME

6.1 <u>Chromatographic Resolution of T400-A with a single-column system</u>. The gel permeation chromatogram of the T400-A prepolymer is shown in figure V.7.a.

The experiment was run on a 95 cm long, 1.12 cm diameter column packed with Biobeads SX1 swollen in chloroform. A solution of 0.016 g of prepolymer in 0.3 ml chloroform was applied and the infrared signal was amplified 4.3 times. Since the spectrophotometer is set at 1715 cm⁻¹ (carbonyl stretch), it follows that propylene glycol is not represented on the chart. On the other hand, the elution volume of the lowest molecular weight component is 74 ml whilst the highest molecular weight component, starts eluting at 30 ml.

According to the GPC principles and Flory's polycondensation scheme each of the chromatogram peaks could be assigned, in an increasing molecular weight sequence starting from the right, to the various hydroxyl group and carboxyl group ended species cited in the introduction.

However, following the assumptions, also cited in the introduction of this chapter, the main constituents are of the $P(TP)_i$ type and a minority of the (PT)_i type. The population of the latter, may be roughly estimated through an acid number determination⁽³⁶⁾.

Therefore 2 grams of the prepolymer were accurately weighed in a 100 ml conical flask and were dissolved in 10 ml neutral acetone (AR). The solution was titrated against a 0.182N methanolic solution of KOH using bromothymol blue indicator. The KOH solution was standardised with benzoic acid (AR) dissolved in ethanol using the same indicator as before.

The titration trials are shown in table 1.

Weight of Sample (g)	Vol. KOH Soln.(ml)	Acid Number
2.0289	2.18	10.95
2.2271	2.37	10.85

Table 1: Acid Value: of T400-A

Approximately, therefore, the acid value of the T400A prepolymer is 11, which is an expression of the number of free carboxyl groups present in one gram of prepolymer. Its magnitude can be better visualised, when compared to the acid number of the original feed which can be calculated theoretically since it is known that the mixture (166 g terephthalic acid + 2.2 x 76 g propylene glycol = 333.2 g) is neutralised by 2 x 56 g potassium hydroxide. Therefore one gram of the mixture will be neutralised by

112/333.2 = 0.336 g or 336 mg KOH

It follows that 3.3% of the carboxyl groups remain unreacted.

This observation, in conjunction with the low molecular weight of the polymer, suggests that the majority of the prepolymer constituents consists of $P(TP)_i$ species. Another way of confirming this assumption is that if the acidity were mainly contributed by $(PT)_1$ or monohydroxypropyl terephthalate, the molecular weight of which is 224, than 11 mg KOH would be equivalent to $224x11/56x10^3 = 0.044$ g of $(PT)_1$, or, in other terms T400-A would contain 4.4% by weight $(PT)_1$, had only these species been formed.

Therefore, following these acidity measurements, the component eluting at 74 ml could be tentatively assigned to $P(TP)_1$, its neighbour to $P(TP)_2$, the next to $P(TP)_3$... etc.

6.2 <u>Identification of a Prepolymer Component by a GPC Peak Enhancement</u> <u>Technique</u>

This is based on the chromatographic evidence that under identical experimental conditions the elution volume of a compound is constant. Therefore, $P(TP)_1$ or bis (hydroxy propyl) terephthalate has been synthesised (Chapter VI) and 0.003 g of it were added to 0.017 g of prepolymer; a chloroform solution of the mixture was applied to the chromatographic column and the resulting chromatogram (figure V.7.b) had its last peak enhanced, definitely the one corresponding to $P(TP)_1$. In addition to this peak enhancement technique, 0.0057 g of the synthesised compound was applied on its own to the column.

The retention volume of the eluent (figure V.7.c) corresponded to the last peak of the prepolymer chromatogram.

These experimental observations back the assumption made earlier on that the first chromatogram peak, corresponds to $P(TP)_1$, its neighbour to $P(TP)_2$, the next to $P(TP)_3$... etc., provided that the contribution of -COOH terminated components to the chromatogram pattern is trivial, which remains to be proved.

6.3 <u>Detection of Carboxyl Group Ended Components of T400-A-</u> Addition with Carbodiimides

For the detection of the acidic components of the prepolymer, the free carboxyl group is condensed with a high molecular weight compound which reacts rapidly and preferentially with the -COOH groups. As a result the acidic prepolymer constituents will have their molecular weight increased and, accordingly, their chromatogram peaks will be shifted to lower elution volumes or, in other terms, their position, relative to the peaks of hydroxyl group terminated chains will be altered.

Advantage has, therefore been taken of the reaction between carbodiimides and carboxylic acids, the course of which is described as follows (37, 38)





+ R'COOCOR' Anhydride

The carboxylic acid first adds to the carbodiimide to form o-acylisourea(i). The latter either isomerises into N-Acyl urea (ii) or interacts (side reaction) with a free carboxylic group to give an acid anhydride and a urea derivative.

Compound (ii) predominates with diaryl carbodiimides and should therefore be our reaction product since the carbodimide we have used, commercially known as Daltogard PR, has the following structure

Its molecular weight is 390.

Therefore, a chain bearing a terminal carboxyl group will have its molecular weight increased by 390 if the aroyl urea is formed and by at least 206 if the anhydride of monohydroxy propyl hydrogen terephthalate were formed; an appreciable increase to displace a peak from its original position on the chromatogram of the untreated sample.

Samples of T400-A were accurately weighed in 50 ml round bottomed flasks. From the initial acid value of the prepolymer, the stoichiometric quantity of Daltogard to be added has been calculated and a 20% excess has been used. The samples were dissolved in 20 ml of tetrahydrofuran and refluxed for various time intervals. At the end of each period the acid number was determined by titration with standard methanolic KOH, using bromothyImol blue indicator. The results are shown in table 2.

Reflux time (hours)	Weight of T400A (g)	Weight Daltogard (g)	Acid No.
0.0	2,2427	-	10.52
0.5	2.1972	0.1870	7.8
1.0	2.3040	0.1960	6.8
2.0	2.2234	0.1980	5,26
3.0	2.4723	0.2148	3.8
5.0	2,2719	0.2115	2.0
6.0	2.7586	0.2606	1.5
6.0	2.8884	-	10.47

Table 2: Treatment of T400A with Daltogard PR

On the other hand a sample free from Daltogard PR was refluxed for the longest time period (6 hours) and its acid number was determined; the fact that no alteration occurred indicates that further condensation of the carboxyl groups with the free -OH groups under these experimental conditions does not occur.

In addition, the course of the reaction has been followed by infrared spectroscopy.

The most characteristic absorption of Daltogard is the one corresponding to the assymmetric stretching vibration of the carbodiimidegroup. It is a very strong band occurring at 2170 cm⁻¹ (39)(figure V.8.a). The weaker symmetric

vibration at 1360 cm⁻¹, is not of any interest since it is overshadowed by the much stronger deformation vibrations of the methylene and methyl groups of the prepolymer.

As a result of the reaction between carbodiimides and carboxyl groups the strong band should gradually disappear, although not entirely from our spectra, since the films cast from THF on the NaCl discs contain 20% more Daltogard than the stoichiometric quantity (figure V.8.b). In addition the weak C-N, N-H and C=O absorptions of the products will be shadowed by the strong C-O, OH and carbonyl absorptions of the prepolymer appearing at $1050-1200 \text{ cm}^{-1}$, 3400-3500 cm⁻¹ and 1720 cm⁻¹ respectively.

The most prominent change, however, in the spectrum of the sample treated with the carbodiimide for six hours is the presence of strong band at 2290 cm⁻¹, which falls in the absorption region of the isocyanate group; N,N^* disubstituted ureas as well as anhydrides not having specific absorptions in this infrared region.

We shall not try to comment on this change at the present moment, but merely accept the fact that as a result of the interaction between the carboxylic groups of the prepolymer and Darltogard PR the acid number of the former has fallen from 11 to 1.5.

The absence of any interaction between the hydroxyl groups and the carbodiimide has been verified again by infrared spectroscopy; it is known that carbodimides react with alcohols according to the following path:

 $R-N=C=N-R + R'-OH \rightarrow RNHC=N-R$

Such reaction generally occurs at high temperatures, and proceeds quantitatively when base catalysed i.e. in the presence of an alkoxide.


Thus propylene glycol (2.7 g) and Daltogard PR (0.234 g) were refluxed in 20 ml tetrahydrofuran for six hours. The presence of the strong assymetric absorption at 2170 cm⁻¹ on the infrared spectrum (figure V.8.c) excludes the possibility of any interaction between the carbodimide and the hydroxyl groups.

Summing up, the commercial carbodiimide, Daltogard PR, reduces the acid value of the prepolymer and furthermore does not interact with the free hydroxyl groups. Had the last reaction occurred then a quantity of Daltogard PR corresponding to the hydroxyl number of the prepolymer should have been used.

For the chromatographic assessment of this effect, the following experiments have been carried out.

0.11 g of untreated T400-A was applied to the THF column. The infrared spectrometer monitoring the appearance of terephthalate groups at 730 cm⁻¹. The chromatogram is shown on figure V.9.a. This was followed by 0.5 ml of the prepolymer solution in THF treated with Daltogard PR for six hours. The volume used contained approximately 0.11 g of prepolymer, the acid number of which is 1.5. The chromatogram is shown in figure (V.9.b).

It is apparent that no difference exists between the basic peaks of the two chromatograms; the elution volumes being the same indicates that the chromatogram pattern is caused by hydroxyl group ended components having different molecular weights.

The only variation is caused by the appearance of a small peak at high elution volumes and therefore corresponding to a low molecular weight component. We shall leave this peak aside for the moment to draw our attention to the infrared absorption at 2290 cm⁻¹ which, intuitively should correspond to a group present on the reaction product. By monitoring the appearance of this group the chromatogram should give evidence on the distribution of the acidic chains. However, this was not the case (figure V.9.c). Only one peak appears, the elution volume of which is the same as the elution volume of the species giving rise to a low intensity peak in

figure V.9.b. In view of its position it cannot be attributed to a carbodiimideadduct since the molecular weight of the latter exceeds 282 (molecular weight of $P(TP)_1$). The alternative is that the peak corresponds to a reaction byproduct. However, despite this ambiguity it is known that the molecular weight of the carboxyl group ended chains has been increased but this alteration has no effect on the chromatogram pattern.

Several assumptions may be put forward to account for the absence of "acidic peaks". The simplest assumption is that the concentration of the -COOH terminated components, essentially that of (PT)₁ is far too low for these species to be detected by the present detection system.

The question also arises on the position of the carbonyl absorption of this monoester which could be different from that of the diester. This assumption, however, is disproved by the fact that no $(PT)_1$ peak occurs when the phenyl absorption at 730 cm⁻¹ is monitored. Dimethyl terephthalate and terephthalic acid both having an out of plane bending vibration of the phenyl hydrogens exactly at 730 cm⁻¹. Finally, another assumption is that the acidic species are intramolecularly bonded to all the other species and therefore do not give rise to any specific chromatogram peak. This assumption, although plausible is, in fact, weak because the same interaction could have taken place between the hydroxyl ended components, and the result would have been a disturbance of the chromatogram pattern, which is not the case (sub-section 6.6). An alternative possibility is the interaction between the gel and the -COOH groups.

To account for the appearance of the low molecular weight peak in figure V.9.c as well as for the formation of a strong infrared absorption band at 2290 cm^{-1} the following mechanism is suggested.

11 V 100 60 10

chromatogram of the prepolymer <u>a</u>.

Figure V.9

Detector Response 8

8o 107 112 **6**9 70 90 ICO.

<u>b.</u> Chromatogram of the prepolymer treated with Dautogard PR 1035 106 110 85

trepolymer treated with Daltogard PR. Monitoring in Land at 2293 au



6.4 Identification of a Prepolymer Component by Nuclear Magnetic Resonance Spectroscopy

The method involves the isolation of the component giving rise to the second chromatogram peak, most probably $P(TP)_2$, followed by its nmr analysis.

The same isolation procedure, as the one to be described in Chapter VI, subsection 4.1, has been applied. The procedure will be briefly reviewed here to avoid reference to a later chapter. Accordingly 0.15 gram of prepolymer in 2 ml chloroform was applied to the chromatographic column and the eluting solvent containing the component giving rise to the second chromatogram peak, was isolated. The solution was concentrated and was reapplied to the column for further purification of the component from higher and lower molecular weight isomers. A part of the eluting solvent, assumed to contain the pure component was isolated. After complete evaporation of the solvent, the clear liquid residue left was subjected to nmr analysis. The phenyl and methyl nmr absorptions are shown in figure V.10. The fact that the ratio of their integrated traces is equal to $\frac{7 \cdot 1}{8 \cdot 2} = 0.87$ suggests that the component is P(TP)₂ since it contains 8 phenyl hydrogens and 9 methyl hydrogens the ratio of which is $\frac{8}{9} = 0.89$. This observation leads to the conclusion that each chromatogram peak corresponds to a P(TP)₄ component where i = 1, 2...n.

This could also be regarded as an indication that the acidic components are not bonded to other species.



Figure V.10

Low and high field regions of the HNHR spectrum of the fraction corresponding to P(TP)2

6.5 Quantitative Interpretation of the Chromatogram

It has been shown experimentally that each chromatogram elution curve corresponds to a $P(TP)_n$ macromolecule where n is the number of phenyl groups of the component or half the number of carbonyl groups.

Provided that no solute-solvent or solute-solute interactions interfere with the chromatogram pattern, the area, S, under each elution curve is proportional to n and the ratio S/n represents the molar concentration of $P(TP)_n$ in the prepolymer.

In the following sub-sections the numerical results will be tabulated as follows

Prepolymer Components	Molecular Weight(M _i)	Chromatogram Areas	Molar Concent'n	Mole Fraction (N _i)	N _i M _i
Р(ТР) ₁	M ₁	s ₁	s ₁	$s_1 \sum_{i=1}^{n} (s_i/i)$	M ₁ S ₁ /Ž(Si/i)
P(TP) ₂	M ₂	s ₂	s ₂ /2	s ₂ /2 ⁿ (Si/i)	$M_2S_2/2\sum^n(Si/i)$
P(TP) ₃	M ₃	s ₃	S ₃ /3	s ₃ /3 Ž (Si/i)	M ₃ S ₃ /3 Ž (Si/i)
P(TP) _n	Mn	Sn	Sn/n	$\frac{n}{\sum}(Si/i)$	$MnSn/n \sum_{i=1}^{n} (Si/i)$
	6 · · · · · · · · · · · · · · · · · · ·		n (Si/i) 1	$\left[\sum_{i=1}^{n} \sum_{j=1}^{n} (s_{i/i}) \right]$	$\sum_{n=1}^{n} \sum_{j=1}^{n} \sum_{j$

The letter "B" represents the molecular weight of the terephthalate based components. The mole fractions, as given in the table above, do not represent the actual composition of the prepolymer but rather translate the relative content of the various propylene terephthalate isomers, since under the detection conditions employed, the free propylene glycol is not represented on the chromatogram. It is after its introduction in the calculations, that the

distribution of the various species will be meaningful and representative of the prepolymer analysed.

The free propylene glycol content expressed in weight percent, W, as estimated by nmr (Chapter IV) is fitted in the above distribution as follows. If Wg propylene glycol are associated with (100-W)g of $P(TP)_n$ species then Xg " " will be " " Bg " " " The molar concentration of propylene glycol will, therefore, be X/76, where 76 is its molecular weight.

It follows that the mole fraction of the free glycol, in the prepolymer is equal to X/76/1+X/76

Hence the mole fraction of each $P(TP)_i$ component in the system containing propylene glycol, will be

$s_{i'_{i}} \left[\left(\sum_{j=1}^{n} s_{i'_{i}} \right) \left(\frac{1+x}{76} \right) \right]$

6.6 Effect of the Solvent on the Distribution of T400-A

Under this heading, the distribution of the prepolymer constituents in chloroform, tetrahydrofuran, dioxane and benzene will be investigated. This aims at the elucidation of any possible solute-solvent or solute-solute interaction leading to variations in the chromatogram patterns, since it is known that in a non polar solvent, such as benzene for example, intramolecular hydrogen bonds will result in molecularaggregates which would have retention volumes different from those of the free prepolymer constituents or those bonded to polar solvent molecules.

The chromatograms of T400-A in the solvents cited above as well as the experimental conditions employed are shown in figure V.11. The areas under the chromatogram peaks were used to calculate the distribution of the terephthalate based components only. However, owing to the extensive overlap between the different peaks, especially in the high molecular weight region, the representative areas have been confined to triangles drawn in such a way that overlap could be avoided. The representative areas are shown on the figures while the mole fractions are shown in table 3.





C	Мо	le Fractions		
species	Chloroform	Tetrahydrofuran	Benzene	Dioxan
р(тр) ₁	0.557	0.526	0.532	0.533
P(TP) ₂	0.276	0.272	0.297	0.277
P(TP) ₃	0.097	0.111	0.099	0.1
P(TP) ₄	0.036	0,050	0.042	0.045
P(TP) ₅	0.016	0.02	0.015	0.023
Р(ТР) ₆	0.009	0.012	0.008	0.011
р(тр) ₇	0.006	0.007	0.004	0,005
P(TP) ₈	0.003	0.002	0.002	0.004
	and the second sec			

Table 3 Distribution of P(TP), species of T400-A in different solvents

It is apparent, that the values expressing the mole fractions of the high molecular weight components, show a pronounced deviation from solvent to solvent. This can be better visualised from table 4, indicating the percent absolute deviation of each value from the arithmetic mean of the four mole fractions in each row.

	Maan	% Devia	ation from	the Mean	
Species	Mean	CHC13	THF	Benzene	Dioxan
P(TP) ₁	0.537	3.7	2.0	0.9	0.9
P(TP) ₂	0.280	1.4	2.8	6.0	1.0
P(TP) ₃	0.102	4.9	8.8	3.0	2.0
P(TP) ₄	0.043	16.2	16.2	2.3	4.6
P(TP) ₅	0.0185	13.5	8.1	18.9	24.3
P(TP) ₆	0.01	10.0	20.0	20.0	10.0
P(TP) ₇	0.0063	4.0	12.0	36.0	20.0
P(TP) ₈	0.0028	8.3	27.2	27.2	45

Table 4

It is clearer now that in the region of high overlap i.e. the high molecular weight region the deviation from the mean becomes more and more pronounced. This is attributed to a poor resolution of the chromatographic column rather than to a solvent effect. Had the latter happened then its effect would have been more pronounced on the low molecular weight components.

It is also apparent from the values in the first four rows, that variation either of the solvent or the monitoring of the infrared absorption viz. suitable solvent has no effect on the resolution; The values showing a satisfactory agreement.

In order to effect a better resolution, which would enable a thorough comparison between the experimental results and the theoretical ones, a twin column system has been set up.

6.7 <u>Chromatographic Resolution of the Prepolymers with a Twin Column System</u> The twin GPC column system is schematically represented in figure V.2. The main difference from the one used in the previous experiments is the additional column connected in series to the original one. The first column (1.05 cm long, 0.9 cm diameter) was packed with Bio-beads SX2 while the second (95 cm long, 1.12 cm diameter) with Bio-beads SX1. It is assumed that the lower exclusion limit of Bio-beads SX2 will allow a better separation of the high molecular weight components from the low molecular weight ones. This in conjunction with the length of the column system, the low flow rates and the minute quantities of sample under analysis will lead to reasonably well resolved chromatograms permitting, thus, a more accurate calculation of the areas under the curves.

The solvent used was chloroform and, therefore, the infrared spectrophotometer was monitoring the carbonyl groups at 1715 cm^{-1} .

6.7.1 Fractionation of Prepolymer T400-A

The chromatogram of T400-A is shown in figure V.12.a. The resolution, as expected, is far better than the one obtained with the single column system, especially in the high molecular weight region.

The areas under the curves were estimated manually by subdividing the curves into triangles. The numerical results are tabulated in the way described in sub-section 6.5, and are shown in table 5.

Species	M.W.	Area	Molar Concentration	Mole Fraction	NIMI	Complete Distribution
PG	76					0.426
P(TP) ₁	282	7.405	3.702	0.531	149.742	0.3045
P(TP) ₂	488	6.975	1.744	0.250	122	0.1433
P(TP) ₃	694	5.175	0.863	0.124	86,056	0.0711
P(TP) ₄	900	3.24	0.405	0.058	52.2	0.0332
P(TP) ₅	1106	1.595	0.16	0.023	25.44	0.0132
P(TP) ₆	1312	0.78	0.065	0.009	11.81	0.0052
P(TP)7	1518	0.44	0.031	0.004	6.072	0.0023
			6.971		453.32	

Table 5: Experimental Distribution of T400-A

At this stage the most obvious deduction is that the molecular weight of the terephthalate based components is 453 compared to 454 as determined by nmr (Chapter IV).

On the other hand, the last column represents the chain distribution of the prepolymer after the introduction of the free propylene glycol content, which has been found to be equal to 11.1% wt. by wt.

The method of calculating the new distribution is described in sub-section 6.5 of this chapter, will be applied numerically below.

Since the free propylene glycol (abbreviated PG) content is 11.1% then 11.1 g PG coexist 88.9 g of terephthalate based components. It follows that X g PG will coexist with 453.32 g of terephthalates

Hence X = 56.60 g. Expressed in moles $= \frac{56.6}{76} = 0.744$ moles and the corresponding mole fraction

$$\frac{0.744}{1+0.744} = 0.426$$

The mole fractions of the $P(TP)_i$ species are obtained by normalising the values in the fifth column of table 5 against 1.744.

From these results, the molecular weight of the prepolymer, propylene glycol included, can be obtained since

Number average molecular weight = $\frac{\sum NiMi}{\sum Ni}$

where Ni is the mole fraction of those species having molecular weight Mi. By substituting the values of columns 2 and 7 in the above equation the molecular weight is found to be equal to 292 compared to 284 by nmr.

6.7.2 Fractionation of Prepolymer T400-B

The prepolymer was resolved into its chain components with the chromatographic twin column system described previously. A solution of 0.0196 gram of T400-B in 0.5 ml of chloroform was applied. The resulting chromatogram is shown in figure V.12.b. The mole fractions of the component, calculated from the areas under the curves, are shown in table 6, column 5.

In order to calculate the complete distribution of this prepolymer the concentration of free propylene glycol was estimated by nuclear magnetic resonance spectroscopy (Chapter V) and was found to be equal to 10.86% weight by weight.

The method of fitting the propylene glycol concentration in the distribution of the terephthalate based components will be described once more. It is known that 10.86 g of glycol coexist with 89.14 g of $P(TP)_n$

therefore X g of glycol will coexist with 474.34 g of $P(TP)_n$ 474.34 is the molecular weight of the terephthalate based components only. It follows that X = 57.79 g.

The corresponding molar expression is 57.79/76 = 0.76

Hence the mole fraction of propylene glycol in the prepolymer is

Species	M.W.	Peak Area	Molar Concentration	Mole Fraction	Nimi	Complete Distribution
PG	76			· · · · · · · · · · · · · · · · · · ·		0.432
P(TP)	282	7.81	3.905	0.514	144.95	0.292
P(TP) ₂	488	7.2	1.8	0.237	115.66	0.1347
P(TP) ₃	694	5.99	0.998	0.131	90.91	0.0744
P(TP)4	900	4.025	0,503	0.066	59.4	0.0375
P(TP) ₅	1106	2.38	0.238	0.031	34.29	0.0176
P(TP) ₆	1312	0.9	0.075	0.010	13.12	0.0057
P(TP) ₇	1518	0.665	0.048	0.006	9.11	0.0034
P(TP) ₈	1724	0.425	0.027	0.004	6.9	0.0023
			7.594		474.34	

 $\frac{0.760}{1+0.760} = 0.432$

Table 6: Experimental Distribution of T400-B

By normalising the mole ratios of column 5 against 1.76, the actual distribution of the T400-B constituents is obtained (column 7).

On the other hand, according to the tabulated results, the molecular weight of the terephthalate based components is 474, compared to 522 determined by nmr. Furthermore, the molecular weight of the polymer including propylene glycol is obtained with the aid of the familiar equation $M.W. = \frac{2NiMi}{2Ni}$ by substituting the Mi and Ni values of columns 2 and 7 (table 6).

The result is 302 compared to 319 obtained by nmr.

In addition to the above evidence an essential differencebetween T400-B and T400-A should lie in their acid value since T400-A is the result of the reaction of T400-B and an amount of glycol added near the end of the polyesterification process.

Therefore acetone solutions of samples of T400-B were titrated against a standardised 0.0845N methanolic KOH solution, for the determination of the acid number. The trials and results are tabulated below

Sample Weight (g)	Vol. KOH added (ml)	Acid Number mgKOH/g
1.2330	4.2	16.119
3,3820	11.4	15.95
3.064	10.4	16.06

It follows that the acid number of T400-B is 16 compared to 11 of T400-A.

6.7.3 Fractionation of Prepolymer T400-C

The chromatogram of the prepolymer is shown in figure V.13.a it is the result of the resolution of 0.020 gram of T400-C in 0.5 ml of chloroform.

The unreacted propylene glycol was estimated quantitatively by nuclear magnetic resonance spectroscopy (Chapter V) and was found to be equal to 6.7% weight by weight, which corresponds to 0.48 moles. The normalisation factor, on the

other hand is equal to 1.48. Therefore by normalising the values in column 5 of table 7 against 1.48, the chain distribution of the prepolymer under consideration can be found (column 7).

Species	M.W.	Peak Area	Molar Concentration	Mole Fraction	NiMi	Complete Distribution
PG						0.3242
P(TP) ₁	282	4.73	2.365	0.4576	129.04	0.3092
P(TP) ₂	488	5.51	1.378	0.2666	130.1	0.1801
P(TP) ₃	694	4.18	0.696	0.1347	93.48	0.0910
P(TP) ₄	900	3.06	0.383	0.0741	66.69	0.0500
P(TP) ₅	1106	1.485	0.1485	0.0287	31.74	0.0194
P(TP) ₆	1312	1.21	0.1	0.0194	25.45	0.0131
P(TP) ₇	1518	0.7	0.05	0.0097	14.72	0.0066
P(TP) ₈	1724	0.45	0.028	0.0054	9.31	0.0036
Р(ТР) ₉	1930	0.35	0.019	0.0037	7.141	0.0025
		· · · · · · · · · · · · · · · · · · ·	5.1675		507.671	

Table 7: Experimental Distribution of T400-C

The molecular weight of the terephthalate based components is 507.67 (508) compared to 524 obtained by nmr. Furthermore, the molecular weight of the polymer including propylene glycol obtained with the equation $M.W. = \sum NiMi / \sum Ni$, where Mi and Ni are the values in columns 2 and 7 of table 7. The result is 368 compared to 376 by nmr. Furthermore the acid number of this prepolymer was found to be equal to 13 mg KOH/g.

6.7.4 Fractionation of Prepolymer T500

The gel permeation chromatogram, result of the fractionation of 0.022 gram of prepolymer in 0.5 ml chloroform is shown in figure V.13.b. The free propylene glycol content was determined experimentally by nmr spectroscopy, and was found to be 23.06% weight by weight. Its corresponding normalisation factor, calculated by the method described earlier is 2.577 and the glycol mole



fraction is 0.6120 which leads to the establishment of the experimental distribution (table 8).

Species	M.W.	Area	Molar Concent- ration	Mole Weight Fraction N ₁ M ₁		Complete Distribution
PG					- - -	0.6120
Р(ТР) ₁	282	11.61	5.805	0.6276	176.98	0.2435
P(TP) ₂	488	8,925	2.2313	0.2413	117.75	0.0936
Р(ТР) ₃	694	4.582	0.764	0.0826	57.32	0.0325
P(TP) ₄	900	2.282	0.286	0.0309	27.81	0.012
P(TP) ₅	1106	1.35	0.135	0.0146	16.15	0.0057
P(TP) ₆	1312	0.33	0.0275	0.003	3.936	0.0012
			9.2488		399.946	
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Table 8: Experimental Distribution of T500

Because of the high propylene glycol content, the number average molecular weight of the T500 prepolymer is expected to be low. In fact, substitution of the Mi and Ni values of columns 2 and 7 in the formula $M.W. = \sum NiMi / \sum Ni$ gives 202 compared to 200 as estimated by nmr.

On the other hand the molecular weight of the terephthalate based components is 399.9 (400) compared to 391 as determined by nmr. Furthermore the acid number of this polymer was found to be equal to 9.6 mg.KOH/g.

6.8 Detection of the Carboxyl Group Ended Components of T400-B - GPC Resolution of the Esterified Prepolymer

In subsection 6.4 it has been assumed that the carboxyl group terminated macromolecules are either of very low concentration or physically bonded to hydroxylated chains or to the gel. The last assumption will be examined for T400-B, because of its relatively high acidity.

The expected position of the "acidic peaks" can be determined through the linear relationship between elution volume and log. molecular weight the validity of which is exemplified in figure V.14.

Since the molecular weight of monopropylene glycol terephthalate, $(PT)_1$, is 224, then, from the graph, its elution volume should be 150 ml. However, examination of the chromatogram of T400-B, which, theoretically, contains the largest quantity of $(PT)_1$ units, clearly suggests that no peak exists at that particular elution volume.

In order to eliminate all the association effects brought about by the free carboxyl groups, and also to shift their -COOH carbonyl absorption to lower wavenumbers, the T400-B prepolymer was treated with diazomethane which converts all carboxyl groups into their methyl esters.

6.8.1 Esterification Procedure

a) <u>Preparation of Diazomethane</u>⁽⁴⁰⁾

The laboratory set up used is shown in figure V.15. In the round bottomed flask are introduced 6 grams of potassium hydroxide dissolved in 10 ml of water, 35 ml of ethanol, 10 ml of ether and a PTFE coated magnetic stirrer. In the dropping funnel is placed a solution of 21.5 g of p.tolyl sulfonyl methyl nitrosamide in 125 ml of ether. The distilling flask is heated at 70-75°C, the stirrer is started and the nitrosamide solution is added at a regular rate during 15-20 minutes. When all the nitrosamide solution has been added more ether is introduced at the previous rate until the distillate is colourless. The ethereal solutions recovered in the Erlenmeyer flasks are stoppered and stored in a refrigerator.



A4.



Figure V.15 Laboratory set up for the preparation of diazomethane

b) <u>Diazomethane Standardisation⁽⁴¹⁾</u> and Prepolymer Esterification The standardisation method consists in treating 10 ml of the solution with an excess of an ethereal solution of benzoic acid at 0° C and neutralizing the unreacted acid with a standard solution of KOH in methanol, using bromothymol blue indicator. The titration trials are tabulated below.

Wt. Benzoic (gr)	Vol.KOH (ml.) (0.16N)	% CH ₂ N ₂ (wt/v)
0.4520	5.0	1.22
0.476	6.3	1.22

Before treating a prepolymer sample with the diazomethane solution, the effectiveness of the esterification procedure has been checked as follows: "Since the acid number of T400-B is 16 mg KOH/g then the equivalent quantity of diazomethane is 12×10^{-3} g; one mole of KOH being equivalent to one mole of CH₂N₂. In other terms one milliliter of the ethereal solution is needed to esterify completely one gram of T400-B. For the quantitative determination, 1.5427 g of prepolymer dissolved in redistilled chloroform were treated with 1.7 ml of diazomethane solution at 0° C. This solution was titrated with the standard alkali solution prepared before. Only a single drop (0.02 ml) was needed to turn the initial pale yellow colour of bromothymol blue into dark blue indicating that esterification had proceeded to completion.

6.8.2 GPC Fractionation of the Esterified T400-B

0.0258 g of the same prepolymer, dissolved in 0.5 ml of chloroform, were treated with 0.03 ml (micropipette) of diazomethane solution at 0° C. The solvents were then evaporated by means of a stream of cold air and the residue was dissolved once again in 0.5 ml of chloroform. The solution was then applied to the twin chromatographic system operating under the same conditions as for the previous experiments, the only difference, this time, being that the quantity of solute used is higher (25%) and the amplification level has been increased to 6. We had recourse to these alterations in order to enhance the intensity of those peaks corresponding to the acidic (now esterified chains). This effect is obvious when the chromatogram of this sample

(figure V.16) is compared to the chromatogram of the unesterified T400-B prepolymer (figure V.12.b). The former shows, beside the familar pattern, two more peaks. One appearing at 150 ml and corresponding to a low molecular weight component while a higher molecular weight one elutes at 128 ml.

The semilogarithmic plot indicates that the molecular weights of the polyester components eluting at these volumes are 223 and 410 respectively which correspond to the molecular weights of the methyl esters of (PT)₂

[M.W.430] and $(PT)_1$ [M.W. 238] with a 5% error.

The results show that the acidic components can be detected by the chromatographic system provided that the experiment is run on the fully esterified prepolymer.

Therefore, the most probable cause for the absence of peaks of acidic components from the chromatograms of the non esterified prepolymer could be well due to a physical interaction between the carboxyl groups and the gel.



7 DISCUSSION

7.1 <u>Comparison between Theoretical and Experimental Distributions</u> Our initial aim was to compare the experimental distributions as obtained by gel permeation chromatography with the Flory distribution (Chapter III). For this purpose the Flory equations have been written in the form of a Fortran IV computer program (pages 158 & 159). For these equations to be solved the necessary data are the extent of reaction p and the ratio of the molar concentration of terephthalic acid to propylene glycol. The latter is known, while the former can be calculated from the acid number, A, determined by an acidimetric titration.

In sub-section 6.1, it has been shown that, the acid number of a mixture consisting of one mole of terephthalic acid and 2.2 moles of propylene glycol, is 336 mg KOH/g; it follows that the number of reacted carboxyl groups and therefore, the extent of reaction of the carboxyl groups is

$$p = \frac{336-A}{336}$$

For T400-B, A = 16, therefore p = 0.952.

The computer output, for these values, is shown in table 9. A graphical comparison between the experimental and the theoretical P(TP)_i mole fractions only is shown in figure V.17. The lack of agreement between the theoretical values and the experimental is obvious. However, this discrepancy cannot be used to disprove Flory's theory because the reaction conditions under which the prepolymers are synthesised do not comply with Flory's model i.e. during the ICI polyesterification process the water, by-product of the reaction is continuously distilled off; the distillate, however contains free propylene glycol also. Therefore initial stoichiometry of the system is lost and the resulting prepolymer cannot be described theoretically or at least not by the Flory equations.

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Table 9: Theoretical distribution of T400-B

However, it may be tentatively suggested, on the basis of the similarity between the shapes of the curves in figure V.17, that there is a fair chance for the theoretical treatment to describe adequately the experimental distribution of a low molecular weight polycondensate synthesised under controlled conditions. Further research in that respect has not been undertaken.

7.2 Comparison between the Experimental Distributions of T400-A, T400-B, T400-C and T-500

The experimental distributions of the four prepolymers studied in this project (Tables 5, 6, 7 & 8, column 7) are compared graphically in figure V.18.

It is obvious that little is gained from the further treatment of T400-B with excess glycol to convert it into a T400-A; basically a reduction of the acid number, from 16 to 11 and a few ester interchange reactions at the expense of the high molecular weight components.





It would be very interesting to know whether the variations of these distributions have any effect on the properties of the cured resins, and if so which is the distribution which results in products with optimum properties.

Furthermore the T-500 prepolymer, constitutes in fact a class on its own because it has been synthesised from 3.3 moles of glycol instead of 2.2. It is obvious that the major constituent is propylene glycol and a comparison between the properties the resulting cured resin to those of a poly (propylene fumarate) will clearly show the role contributed by the low content of terephthalate components.

7.3 Conversion of a T400 Prepolymer to a T500

Instead of synthesising separately T400 and T500 prepolymers, ICI makes T400 and converts it to a T500 prepolymer through the addition of excess propylene glycol. This is on the basis that the T500 poly (propylene terephthalate), synthesised from one mole of terephthalic acid and 3.3 moles of propylene glycol has its terephthalate based components diluted because, as it has been shown, a large amount of glycol remains unreacted.

The aim from the following paragraph is to find out how similar, the distribution of a T500, originating from a T400, is to a standard T500 as characterised in this chapter.

For this purpose, the factor, 2.577 (sub-section 6.7.4) which corresponds to a 23.06% free glycol, will be used to normalise the mole ratios of the terephthalate based components of T400A, T400B and T400C. This will result in a distribution having a mole fraction of free glycol equal to that of T500 i.e. 0.6120. The distributions of the T400 prepolymers converted, theoretically, into T500 are shown alongside with the distribution of the standard T500 (Table 8 column 7) in table 10.

	T400-A	Т400-В	Т400-С	т500
PG	0.6120	0.6120	0.6120	0.6120
р(тр) ₁	0.2061	0.1995	0.1776	0.2435
P(TP) ₂	0.097	0.092	0.1035	0.0946
P(TP)3	0.0481	0.0508	0.0523	0.0321
р(тр) ₄	0.0225	0.0256	0.0288	0.012
P(TP)5	0.0089	0.012	0.0111	0.0057
р(тр) ₆	0.0035	0.0039	0.0075	0.0012
р(тр) ₇	0.0016	0.0023	0.003	-
р(тр) ₈		0.0016	0.0021	· -
P(TP) ₉	-		0.0014	- .

Table 10

The distributions tabulated above suggest that a fair agreement, is reached between a T400 converted into a T500 and a standard T500. An assessment on the success of this conversion may be reached only if the physical properties of the resulting styrene cured unsaturated polyesters are considered. If no difference exists between the properties of a polyester resulting from a standard T500 and one resulting from a converted T400, it can be certainly claimed that the process has been successful.

7.4 <u>Application of Gel Permeation Chromatography in the Study of the</u> <u>Microstructure of Ter-polycondensates</u>

In the following paragraphs a method is suggested for the determination of the composition of the chain constituents of polyesters synthesised from three components e.g. terephthalic acid, fumaric acid and propylene glycol. The discussion will be restricted to low molecular weight polyesters i.e. result of the condensation of one mole of acids and 2.2 moles of glycol, for a good chromatographic separation of the chain components to be obtained.

The experimental procedure will involve two steps:- first the application of a sample solution to the chromatographic column and the detection, with the infrared spectrophotometer, of the phenyl groups only. This would result in a chromatogram as the one represented in figure V.18.a. The second experiment will involve the chromatographic resolution of exactly the same quantity of sample but this time the infrared detector will be monitoring the fumarate double bonds. The resulting chromatogram would be similar to the one represented in figure V.18.b. The area, under each chromatogram peak will be proportional to the number of terephthalate (or fumarate) present in each macromolecular constituent. In addition, the elution volumes of the mixed molecules will remain the same in both chromatograms, only the $P(TP)_i$ and $P(FP)_i$ species will have different elution volumes and will therefore be easily picked up, on the assumption that the resolution allows so.

A quantitative interpretation of the resulting chromatograms and consequently a clear picture on the copolymer microstructure may be easily obtained on the basis of the treatment exposed in sub-section 5.1.

For example if the area under the elution curve of a mixed molecule on chromatogram -a- is D_{T} (T standing for Terephthalate) then

$$D_{T} = E_{T}C_{T}k1$$

On the other hand if D_F is the area under the same curve on chromatogram b, (F standing for Fumarate) then

$$D_F = E_F C_F k1$$

Since, the areas under the curves are proportional to the concentration of each component in moles per liter, then the mole ratio of terephthalates to fumarate groups in the mixed molecule under examination can be determined provided that the extinction coefficients $E_{\rm p}$ and $E_{\rm p}$ are known

i.e.
$$\frac{D_T}{D_F} = \frac{E_T C_T}{E_F C_F}$$

As far as the relative concentration of all the components is concerned, then this may be easily found by running a third GPC experiment, the detector monitoring, this time a particular group of the intercomponent (figure V.18.c) and interpreting the chromatogram in the usual way.

The final results may be used for the verification of the mathematical treatments developed to describe theoretically the composition of terpolymers.



Figure V. 19 Microstructure of poly (probylene fumarate terephthalate) by GPC

I mixed molecules

Poly(propylene junarates)

Poly(propylene terephthalates)

8 CONCLUSIONS

Both NMR and GPC techniques agree quite well in their reading of the prepolymers molecular weight, supporting thus, the idea behind the experimental method.

A method has been developed for the quantitative estimation of the chain constituents of low molecular weight polymers. This method can be extended to the study of the microstructure of low molecular weight terpolycondensates.

The detection method can be used in the verification of the Flory statistics provided that the model polymer is synthesised under controlled experimental conditions.

The various T400 prepolymers are different from a statistical point of view. This, in conjunction with the fact that they should have different hydroxyl numbers (Chapter IV) suggests that, the final resins should have different structures; if the cured products prove to differ in their physical properties, then it is necessary to define the prepolymer structurally for optimum final properties to be obtained.
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CHAPTER VI

SYNTHESIS AND IDENTIFICATION OF BIS(HYDROXYPROPYL) TEREPHTHALATE

1 INTRODUCTION

Reference to the title compound has been repeatedly made in earlier chapters. The interest in synthesising it has been limited to the characterisation purposes involved in this research project, although the literature suggests that its use has been extended in the technological field and especially in the synthesis of saturated polyesters.

The bulk of the work is dealt with in the patent literature emphasising perhaps, the quality of the final products as well as the techniques required by the esterification process mainly applied to overcome the insolubility and low reactivity of terephthalic acid on the one hand and, on the other, to avoid the formation of high molecular weight esters since the process involves the condensation of two difunctional components.

In essence the synthetic methods involve the reaction between equimolar quantities of terephthalic acid and propylene oxide in the presence of a solvent and a basic catalyst, under a nitrogen atmosphere. The use of high pressures is very often mentioned. The reaction times are short compared to polycondensation times and the temperatures rarely exceed 130°C.

Solvents such as water⁽¹⁾, Dimethyl formamide⁽²⁾, benzene⁽³⁾, xylene⁽⁴⁾ and ethyl methyl ketone⁽⁵⁾ have been reported. The chemical nature of the catalysts used varies from conventional bases such as triethyl amine, Nmethylpiperazine, pyridine⁽⁶⁾, tripropyl amine⁽⁵⁾, phenyldiethylamine⁽⁷⁾, to ammonium salts such as Et_3NCH_2Ph Cl⁻⁽¹⁾, $Et_4NBr^{-(6)}$ and the rather nonconventional MeCN⁽⁸⁾, (Me₂N)₃PO⁽⁹⁾, triphenyl phosphine⁽⁶⁾, ferric acetyl acetonate⁽³⁾, hexamethyl phosphoric triamide⁽¹⁰⁾ as well as porous particles⁽⁴⁾

Yields vary from very good (75%) to excellent (98%) when water is the reaction medium.

The product itself, referred to as Bis (2 hydroxypropyl) terephthalate is a white solid melting at $130-131^{\circ}C$.

2 LABORATORY PREPARATION OF BIS(HYDROXYPROPYL)TEREPHTHALATE

An account will be given on the unsuccessful and successful attempts made to synthesise the title compound. None of the methods described in the introduction has been applied.

2.1 Ester Interchange Reactions

$$\begin{array}{c} & & & & \\ & & & \\ & & & \\ & &$$

Owing to the high melting point and poor solubility of terephthalic acid $(sub > 300^{\circ}C)$, direct esterification with glycols under ordinary laboratory conditions, is a difficult process. On the other hand, transesterification of dimethyl terephthalate with propylene glycol in the presence of a catalyst offers a more accessible path.

Hence, one mole of dimethyl terephthalate and 20 moles of propylene glycol, were allowed to react in the presence of a catalytic amount of sodium metal, in a three necked round bottomed flask equipped with mechanical stirrer, air condenser, thermometer and nitrogen inlet. The flask was heated on an electric mantle.

Dissolution of the solids started at 80°C. However, no reaction took place at this temperature even after 4 hrs. On cooling a white precipitate resulted which proved to be dimethyl terephthalate (m.p. 141°C, absence of -OH absorption band from the infrared spectrum).

Similar attempts were made at 105° C, 120° C but no reaction occurred. Finally the experiment was repeated at 160° C for 3 hrs. and, separately, at 175° C for 3 hrs. and at $185-190^{\circ}$ C for half an hour.

In all cases, the product consisted of unreacted dimethyl terephthalate suspended in a syrupy mixture of propylene glycol and, apparently polymeric products. However the time consuming fractionation procedures as well as the possibility of obtaining a poor yield led us to give up any further attempt by this method.

2.2 Condensation Reactions with Disodium Terephthalate

 $\begin{array}{c} 0 \\ -C \\ 0Na \end{array} + 2 \begin{array}{c} CH_{3} \\ -CH_{2} - CH_{2} - OH \end{array} \xrightarrow{-2NaC1} \\ HO-CH_{2} - CH_{2} - CH_{2} OH \\ HO-CH_{2} - CH_{2} OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \\ CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array} \xrightarrow{0} \begin{array}{c} 0 \\ CH_{2} - CH_{2} - OH \end{array}$

An attempt was made to synthesise bis(hydroxypropyl)terephthalate from the disodium salt of terephthalic acid and 1,2 propylene chlorohydrin. The reaction was carried out under various conditions but without success. Thus one mole of disodium terephthalate and 2.1 moles of propylene chlorohydrin were allowed to react successively in dimethyl formamide, pyridine, dimethyl sulphoxide and dioxane⁽¹¹⁾ at reflux temperatures. No reaction took place even in the absence of a solvent but with a large excess of propylene chlorohydrin and a catalytic amount of pyridine.

The isolation procedure involved the distillation of the solvent and excess liquid reactant under reduced pressure followed by dissolution of the unreacted salts in water which in our opinion, shouldn't dissolve the diester. No precipitate was formed.

A similar set of reactions was carried out with bromoacetone instead of propylene chlorohydrin. Had it been successful, the procedure would include a further reduction of the carbonyl group. But this was not the case.

2.3 From Terephthaloy1 dichloride

C1-C- C-C-C1 + HO-CH-CH₂-OH (excess) \rightarrow CH_3 HO-CH - CH₂-O о сн₃ с-о-сн₂-сн-он

2.3.1 In Absence of Solvent

Terephthaloyl dichloride (0.02 moles) supplied by ICI Fibres Division was allowed to react with 0.2 moles of redistilled propylene glycol. The stirred mixture was warmed at $55-60^{\circ}$ C for two hours on a water bath. The resulting clear solution was mixed with a slight excess of diethyl ether and washed successively with a dilute (1%) solution of Na₂CO₃ and water. The ethereal extracts were dried over a small amount of anhydrous sodium sulphate. After the ether has been distilled off, a viscous material was left behind. However, the presence of more than one peak on the gel permeation chromatogram of the reaction product suggested a polymeric composition.

2.3.2 In Tetrahydrofuran

Propylene glycol (0.4 moles) and pyridine (20 ml or 0.02 moles) were mixed with tetrahydrofuran (20 ml) in a 100 ml three necked round bottom flask equipped with mechanical stirrer, reflux condenser, a thermometer and dropping funnel. The last contained 5g (0.02 moles) of terephthaloyl dichloride dissolved in 20 ml dry tetrahydrofuran. The solution was added dropwise to the stirred mixture over a period of two hours, the reaction being carried out at room temperature. After the addition was completed, the mixture was warmed up to 45° C on a water bath for one hour. The resulting clear solution was then poured in ice cold water and the precipitated solid was filtered off and dried in a vacuum oven at 50° C. After two crystallisations from water the pH of which was adjusted to 8 with Na₂CO₃, the melting point of the product was 129-131°C. A~50% yield was obtained. The compound also gives tiny crystals from 1,2 dichloroethane; it is sparingly soluble in chloroform, ether and benzene but readily soluble in tetrahydrofuran, methanol, dioxane and dimethyl formamide.

Although this method leads to the product which, most probably is the desired one, doubts arise however of a possible polymerisation of tetrahydrofuran by the hydrogen chloride evolved during the reaction despite the presence of a large amount of pyridine (12). A further attempt, therefore was made using a different solvent.

2.3.3 In Diethyl Ether

The same reaction was carried out in dry ether instead of tetrahydrofuran. The equipment is shown in figure VI 1. After the complete addition of the ethereal solution of terephthaloyl chloride, the reaction mixture was stirred for a further 10 hours at room temperature. Two layers appeared on standing. The bottom propylene glycol layer contained a white dispersion which resulted in a white precipitate after separation of the ether and addition of ice cold water containing a small quantity of Na₂CO₃.

During crystallisation from water (pH=8) of approximately twenty grams of the vacuum dried product, the larger part of it dissolved in hot water while the remainder formed a heavy oily layer. Upon filtration of the clear aqueous solution and subsequent cooling a crystalline compound precipitated. The latter was recrystallised from boiling water; its melting point as determined by an electrothermal melting point apparatus was $131^{\circ}C$ (compound A). The oily layer was isolated from the bottom of the container and washed repeatedly with small quantities of boiling water. It was then crystallised from a large quantity of water to give a compound melting at $124^{\circ}C$ (compound B).

Figure VI.1 2.5 0.03 molies 20 mis снь но-сн-сна С Его 20mls 10molto 0.4 moles 4

3 IDENTIFICATION OF THE REACTION PRODUCT

3.1 Purity of the Compound

A solution of compounds A and B in tetrahydrofuran was applied to a GPC column. The presence of a single peak on the chromatogram suggests that components of higher or lower molecular weight of the synthesised compound are absent (figure VI.2).



It is obvious, however, that under this peak could be included three possible isomers formed because of the assymetric nature of propylene glycol. These isomers are:

$$CH_3^{CH_3}C-$$

bis (1 hydroxy propyl) terephthalate



bis (2 hydroxy propyl) terephthalate



1,2' (bis hydroxy propyl) terephthalate

3.2 <u>Mass Spectrometry</u> (13, 14, 15)

The spectra were obtained on a MEI.MS12 type mass spectrometer the ion source of which was maintained at 148°C for compound A and at 130°C for compound B.

The m/e values of the most important fragment ions (population exceeding 2%) appearing in the spectra as well as their relative abundance are tabulated below. The most intense peak (base peak) was assigned the value of 100 percent.

m/e	Relative Abundance			Relative Abundance	
	Comp ¹ d A	Comp'd B	m/e	Comp ¹ d A	Comp [*] d B
282	1.8	Visible at high resol- ution	134	21	25.7
238	17.5	17.14	121	14	20.0
225	3.5	14.3	104	29.8	48.6
207	100	100	76	19.3	31.43
180	-	8.6	65	-	25.7
162	57.9	82.9	58	15.3	17.1
149	-	14.3	45	31.6	34.3
			31	15.8	14.3

The molecular ion peak is not significant showing the instability of the compound under the conditions the spectra were taken. Nevertheless it denotes that the molecular weight of the compound is 282 which corresponds to the molecular weight of bis (hydroxy propyl) terephthalate ($C_{24}H_{18}O_6$). The formation of the ions giving rise to the values tabulated above may be explained by the following fission mechanism.



Furthermore a double rearrangement may lead to the following



In the above mechanism consideration has been given to one of the possible isomers, namely bis(2 hydroxypropyl)terephthalate. The assignment is favoured by the presence of a peak at m/e = 45 corresponding to CH_3 -CH = OH and a parent peak at m/e 237. However, the occurrence of a peak at m/e = 31 suggests the presence of a terminal -CH₂-OH group, but the absence of the parent peak at m/e = 251 which is more stable than the one at m/e 237 because of the stabilising effect of the methyl group, indicates that a single compound is present; the m/e = 31 fragment ions arising from a different source, possibly from the ions at m/e 75 and m/e 76 (corresponding to propylene glycol).



3.3 Nuclear Magnetic Resonance Spectroscopy

The proton nmr spectra of both compounds (figures VI.3 and VI.4) were recorded at room temperature on a Perkin Elmer R32 type spectrometer operating at 90 MHz. 30 to 40% DMSO-d₆ solutions were used into which CDCl₃ was added to dissolve the tetramethyl silane internal standard.





The spectral characteristics of both compounds (A and B) are identical i.e. a doublet, in the 1.2 - 1.3 ppm region indicates the presence of a methyl group neighbouring a methyne. The latter, being in the neighbourhood of a methylene and a methyl group gives rise to a sextet overlapping with the methylene doublet at 4 - 4.3 ppm.

On the other hand, the ratio of phenyl to methyl plus methylene, to methyl hydrogens, in both spectra, follow approximately the stoichiometric sequence 4:6:6 of Bis(hydroxypropyl)terephthalate.

The hydroxyl hydrogen absorption of compound A occurs at 4.85 ppm while that of compound B at 4.95 ppm, since it disappears following a D_2^0 exchange. This shift difference is the result of slight variations in the concentrations of the solutions analysed.

The main conclusion, drawn from these observations is that both A and B represent a single and the same isomer.

A closer examination of the nmr absorptions, especially their chemical shifts may lead to the elucidation of the exact structure of the compounds; if three isomers were represented then two methyl doublets would have been expected to appear in the spectrum, each representing one of the following two segments:

CH3 R-O-CH-CH_OH Ι

R-O-CH2-CH-OH

ĊH3

and

11

Such an expectation arises from the evidence given in an earlier chapter, according to which the methyl groups of isopropanol absorb at higher fields than the methyl hydrogens of isopropyl benzoate. However, the key to the elucidation of the exact chemical structure of the isomer is the overlap of the methylene doublet with the methyne sextet. The argument is the following. The methyme multiplet of propylene glycol occurs at 3.8 ppm in CDCl₃ (figure VI.5a) while its methylene hydrogens absorb at higher yields 3.45 ppm. Furthermore, the methyne sextet of isopropanol occurs at 4 ppm (figure VI.5b) while the methyne of isopropyl benzoate appears at 5.3 ppm (figure VI.5c) showing the effect of the more electronegative ester group in increasing the chemical shift expressed in delta values from TMS.

In addition, the fact that both methyne and methylene absorptions of the synthesised compounds overlap at around 4 ppm indicates that while the methyne is almost magnetically equivalent to that of propylene glycol and isopropanol, the methylene doublets appear at lower fields than those of propylene glycol indicating that the group in their vicinity is more electronegative than the -OH; the only alternative arises from the presence of an ester group.

It follows therefore that the terephthalate is composed of type II segments, its structure being that of bis (2 hydroxypropyl) terephthalate



3.4 Infrared Spectroscopy

Infrared analysis of both compounds in the form of KBr discs provides the basic information characterising them as propylene glycol esters of terephthalic acid, mainly by:

a) The -OH stretching vibration ($\sqrt{-}$ OH) at $\sim 3400 \text{ cm}^{-1}$ b) The aromatic -CH stretching vibration ($\sqrt{-}$ CH) at $\sim 3050 \text{ cm}^{-1}$ and the corresponding aliphatic vibrations at $\sim 2850 - 3000 \text{ cm}^{-1}$.



- c) The carbonyl stretching (VC = 0) at 1710 and 1715 cm⁻¹ for compound B and A respectively; and the ester stretching (C-O-) at 1100 cm⁻¹ and 1270 cm^{-1} .
- d) The methyl and methylene scissoring vibrations in the 1380 1460 cm⁻¹ region.
- e) The -CH (phenyl) out of plane bending vibrations (X -CH) at 730 cm⁻¹.

Whereas the nmr and mass spectra of both compounds showed the same features, their infrared spectra have the following differences:

- (i) The ratio of the absorbance of the methylene assymmetric deformation at 1410 cm⁻¹ to that of the methyl deformation at 1450 cm⁻¹ is 1.138 for compound A and 1.779 in compound B (figure VI.6 c & d).
- (ii) Whereas the methylene rocking vibration at 918 cm⁻¹ of compound B has a rather broad band of medium intensity, the absorption corresponding to compound B is sharper but shows a shoulder at 930 cm⁻¹ (figure VI.6 e & f). These band broadening features can be observed in the -CH stretching region at 2900 cm⁻¹ (figure VI.6 a & b).

The information given in paragraph 3.4 of this chapter dismisses the possibility of these compounds having different chemical formulae or even different molecular weight, had this been the case, then the nmr spectra would have been different. The alternative therefore is that their crystalline structures are different which results in slight variations in their infrared spectral characteristics.



Figure VI.6 I.R. spectral differences between compounds A+B

3.5 Microscopic Examination

The crystals of both compounds were examined under a microscope as suspensions in cedar oil the refractive index of which is 1.533. Compound A consisted of needle like crystals, fibrillar in places, having a straight extinction i.e. only parallel to the direction of the polarised light. Their birefringence was very high and the refractive index in the transverse direction of the crystal matched that of the suspending medium while the same index in the longitudinal direction was slightly lower, perhaps 1.5. Their crystallographic appearance can be roughly described as orthorombic, hexagonal or triclinic. Furthermore, examination of the melting behaviour under a precalibrated kaufler hot stage microscope, showed that whilst a very small quantity melted at 125°C the bulk of the crystals melted at 129 - 133.5°C.

The crystals of compound B, on the other hand, were found to consist mainly of plaques, two to three times longer than the needles described above and, whereas the refractive index in the longitudinal direction matched that of the medium the other had a far greater index. In addition the extinction was not straight and from a crystallographic point of view the shape can be described as monoclinic.

The presence of some needle like crystals could not be disregarded.

Their melting behaviour, examined under the Kaufler microscope, revealed that the plaques melted at 125° C while the fibrils at $128-130^{\circ}$ C.

4 <u>CONTENT OF BIS (HYDROXY PROPYL) TEREPHTHALATE ISOMERS IN POLY (PROPYLENE</u> TEREPHTHALATE) PREPOLYMERS

Since the analysis of the synthesised title compound suggests that the secondary hydroxyl group remains free, it is our aim now, to find out whether this isomer is the predominant one in the polymer itself or, if the replacement of terephthaloyl chloride by the parent acid in the synthesis of the prepolymer, gives rise to the three possible isomers and if so in what proportions.

4.1 Isolation of P(TP)

Bis (hydroxy propyl) terephthalate was isolated from the T400-B prepolymer by means of our standard GPC column containing polystyrene beads swollen in chloroform.

Thus a solution of 0.15 grams of prepolymer in 2 ml of chloroform were first applied on the column and the eluting solvent containing the last component i.e. $P(TP)_1$ was isolated (figure VI.7a). The solution was then concentrated by means of a stream of cold air, until approximately 2 ml were left behind. This solution was then reinjected in the same column, for further purification of the component, and a part of the solvent, thought to contain uncontaminated $P(TP)_1$ has been isolated (figure VI.7b). Again, the excess solvent was evaporated, completely this time, with cold air and the residue was subjected to analysis. It consisted of a colourless liquid in which crystals developed with time.

Following the work of Heitz et al^(16, 17) who achieved preparative separations on a one gram scale, using glass columns of 200 cm length and 50 cm diameter, an attempt has been made to isolate $P(TP)_1$ from 1 gram of prepolymer. A 20% THF solution was first applied to a 1 m long, 2.75 cm diameter column containing biobeads SX1. The solvent containing the last component was isolated, and after concentration on a water bath, the solution was reinjected in a 1 m long, 2 cm diameter column containing biobeads SX2 of low exclusion limit, for the better separation of the low molecular weight components. Both columns were



<u>Figure VI.7</u>

Isolation of PLTP)



running on THF. The isolation seemed to be adequate but the contamination of the compound with THF impurities and decomposition products rendered its analysis doubtful.

4.2 Analysis of the Isolated Component

The compound isolated from chloroform, has only been subjected to NMR analysis. The spectrum (figure VI.8) taken from a 20% solution in DMSO can be easily elucidated by means of the information given in Chapter IV (the lack of resolution, in CDCl₃, is apparent). The fact that the ratio of phenyl to methyl hydrogens is approximately equal to 4/6 ($\frac{4.6}{6.8} = 0.67$), as well as because of the absence of absorptions characteristic of diesterified propylene glycol segments, indicate that the compound is P(TP)₁.

It is apparent that in addition to the absorptions due to Bis (2 hydroxy propyl) terephthalate, other multiplets are also present. These are caused by Bis (1 hydroxy propyl) terephthalate. The contribution of the mixed isomer also, cannot be overlooked.

4.3 Statistical Analysis of the Results

For the calculation of the relative population of the above mentioned isomers, advantage has been taken of the presence of two distinct methyl doublets at 1.14 and 1.25 ppm characterising the primary esterified hydroxyl groups (p) and the secondary esterified -OH groups (s) respectively; Their integrated traces being in the ratio

$$\frac{2}{5} = \frac{4.1}{2.7}$$

In statistical terms, the probability of esterification of a primary hydroxyl group, denoted P(p) is 4.1/6.8 and that of esterification of a secondary -OH, P(s), is 2.7/6.8.



Since the synthesis of the polymer is carried out in the presence of excess glycol, then the formation of a p ester bond will have no effect on the formation of an s bond, both events being independent⁽¹⁸⁾. It follows that the probability of formation of a p-p diester, (Bis 2 hydroxy propyl terephthalate), denoted by P(p-p) will be equal to $\frac{4.1}{6.8} \times \frac{4.1}{6.8} = \frac{16.81}{46.24}$ on the same basis

$$P(s-s) = \frac{2.7}{6.8} \times \frac{2.7}{6.8} = \frac{7.29}{46.24}$$

and

$$P(p-s) = \frac{4.1}{6.8} \times \frac{2.7}{6.8} = \frac{11.07}{46.24}$$

However, in the last case allowance must be made for P(s-p) which is equal to P(p-s). Therefore, the probability of formation of the mixed isomer is

$$P(ps) = 2 \times \frac{11.07}{46.24} = \frac{22.14}{46.24}$$

It follows that the ratio of p-p to p-s to s-s isomers in the poly (propylene terephthalate) prepolymer is equal to

2.3 : 3.1 : 1

or

The faster esterification rate of the primary hydroxyl groups ⁽¹⁹⁾ with the carboxyl groups is clearly shown from the ratio of the methyl group integrals

$$\frac{P}{S} = \frac{4.1}{2.7}$$

i.e. primary hydroxyl groups are esterified 1.5 times more effectively than secondary hydroxyls.

5 DISCUSSION

e.g.

Bis (2 hydroxy propyl) terephthalate offers an example of a compound existing in two different crystalline forms; these are the low melting plaques and the needles with a higher melting point.

In the experimental part of this chapter, it is not claimed that the different crystals have been successfully isolated despite repeated crystallisations, meaning that each form, although chemically pure and satisfactory enough for characterisation purposes, is slightly contaminated by the crystals of the other thus causing probably some discrepancies in the true melting points.

The contamination can be easily understood from the fact that both "compounds" as obtained through the synthetic method described earlier on coexist and both crystallise from water. The high melting one however being more soluble in the mother liquor, which, nonetheless is not entirely free from the low melting crystals, despite their much lower solubility. Other solvents, suitable for the crystallisation of the compounds, such as dichloroethane, have the ability to dissolve both types of crystals with the same ease thus making their separation practically impossible. Further attempts aiming at the isolation of the pure crystalline forms, followed by more extensive crystallographic studies are being considered by other researchers⁽²⁰⁾.

The formation of these two types of crystals may be explained in terms of possible arrangements, or packings, the molecules can assume through hydrogen bonding; thus the plaques may result from molecules associated parallel to each other

O-CH-CH -CH

while the needles could be the result of a preferentially longitudinal arrangement

e.g.



In the synthetic method, described in sub-section 2.3.3, 20 moles of propylene glycol have been used on the basis that they correspond to a "large excess" which will prevent the formation of high molecular weight polyesters. This quantity can be gradually reduced and the reaction conditions may be changed provided that under the new conditions the stage of esterification of the glycol at both ends is not reached and this can be monitored by nmr since, as shown in Chapter IV, 0 CH_3 H_3 H_3 H_3 segments such as RC-0-CH-CH₂-0-C-R show specific nmr absorptions.

Whilst the kinetics of polyesterification have not been studied in this work it should be possible to apply nmr examination to this field when the following considerations apply; large scale syntheses still with considerable excess of acid chloride⁽²⁰⁾ revealed the presence of relatively small quantities of the mixed isomer (primary-secondary) as well as of bis (1 hydroxy propyl) terephthalate, supporting the fact that acid chlorides react much faster with the primary than with the secondary hydroxyl groups.

NMR evidence, on the other hand, shows that the rate of reaction of terephthalic acid with the secondary hydroxyl cannot be disregarded. A comparative study of their relative reactivities towards a large excess of primary and secondary -hydroxyl groups can be achieved by means of nmr spectroscopy and the following general kinetic treatment.

If Po represents the initial concentration of the primary hydroxyl groups and P their concentration after a reaction time t, then

$$\frac{d}{dt} \begin{bmatrix} P \\ P \end{bmatrix} = kp \begin{bmatrix} P \end{bmatrix} \begin{bmatrix} A \end{bmatrix}$$

where kp is the rate constant and A the concentration of the acid or acid chloride.

By rearranging, and integrating between limits

$$-\int_{0}^{P} \left[\frac{P}{P} \right] = kp \left[A \right]_{0}^{t} dt$$

Similarly

$$-\ln\left(\frac{s_0}{s}\right) = ks[A] t$$

Where S stands for secondary

The ratio of the two logarithmic equations is:

$$\frac{\ln [P]/[Po]}{\ln [S]/[So]} = kp/ks$$

Since $[Po] = [So] = [G_o]$, where G_o is the initial glycol concentration,

then

$$\frac{\ln \left[P\right] / \left[G_o\right]}{\ln \left[S\right] / \left[G_o\right]} = kp/ks$$

On the other hand

$$[G_o] = [G] + [P] + [S]$$

Where G is the concentration of the free glycol at the end of the reaction. The ratio [P] / [S] can be determined as explained in sub-section 4.3, by means of the corresponding methyl integrated traces \bar{p} and \bar{s} whilst the individual values of [P], [S] and [G] may be estimated by the method described in Chapter IV i.e. $[P] + [S] = \frac{phenyl integral}{4}$

and with their already known ratio, [P] and [S] can be calculated.

where \bar{g} is the nmr integrated trace of the free glycol methyls. Once [G] and [G] calculated, the ratio kp/ks may be determined.

Similarly $\frac{[p] + [s]}{[c]} = \frac{(\overline{p} + \overline{s})/6}{\overline{c}/3}$

From a technological point of view, bis (2 hydroxy propyl) terephthalate is an aromatic diol and subsequently a source for the development of novel unsaturated polyesters. It is obvious that the ratio of styrene molecules to ester bonds in a repeat unit of cured product, will be lower than in the case where the prepolymer, P(TP) is used as the original diol, provided that both unsaturated polyesters contain equivalent amounts of fumarate unsaturation as well as styrene; therefore a theoretical prediction would be the enhancement of the hydrolytic stability of the P(TP), based polyesters. In addition, because of the short distance which will separate the double bonds a reduction of the flexibility of the final product is to be expected. However, owing to the lower molecular weight of bis (hydroxy propyl) terephthalate compared to the poly (propylene terephthalate) prepolymer, the resulting alkyd will consequently have a lower molecular weight and therefore its styrenated solutions will have their viscosity reduced, when equal styrene levels are used to dissolve both polyesters. Nevertheless, lower styrene quantities than those used in the 'Impolex' resins could be tried to reach the required viscosity and the properties of the cured polyester tested and compared to those of the 'Impolex' types.

6 CONCLUSIONS

A novel simple method has been introduced for the synthesis of bis (2 hydroxy propyl) terephthalate, a diol which has not yet been used in unsaturated polyester technology.

Nuclear magnetic resonance spectroscopy can be used in following the kinetics of the reaction as well as in improving the reaction conditions.

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CHAPTER VII

SEQUENCE DISTRIBUTION OF SATURATED SEGMENTS IN UNSATURATED

POLYESTERS

1 INTRODUCTION

Experimental evidence suggests that unsaturated polyesters synthesised in two stages result in cured products with better properties than those originating from one stage alkyds. Two reasons have been given for the explanation of this fact; the first is that the two stage polyesters have their double bonds located at the end of the chains thus allowing a closer packing of the macromolecules during crosslinking, and the second reason lies in the influence of the distribution of the saturated segments determined by the first stage. The effect of side reactions has also been mentioned in that respect (Chapters I and II).

However, it seems hard to believe that the terminal double bond has such an effect on the properties especially when the molecular weight of the polyesters is in the 3000 to 4000 range with an acid number of 7-10; in addition to the fact that more than 50% of the prepolymer population consists of low molecular weight species of the order of 450 as shown in Chapter IV indicating that at least four double bonds are present in the polyester spine besides the terminal. Furthermore the occurrence of a hydroxylated end in the bulk of the unsaturated polyester chains is unavoidable since they are synthesised from equimolar amounts of maleic anhydride and a diol, in the form of a prepolymer.

On the other hand the assumption that the molecular weight distribution of the first stage polyester contributes to the superiority of the properties of the final polyesters can be criticised on the basis that this distribution can easily be lost during the second polyesterification stage through ester interchanges.

In this chapter are described attempts made to dissociate the saturated poly (propylene terephthalate) segments from poly (propylene terephthalate fumarate) chains; The objective being the comparison of their distribution with the distribution of the original prepolymer, described in Chapter V. In fact this exercise aims at the elucidation of whether the prepolymer chain structure suffers from any perturbation during the second polyesterification stage as the result of transesterification reactions.

Basically two routes have been followed in that respect. One, involving the breakdown of the double bonds, including ozonolysis and phase transfer oxidation and the other dealing with the preferential hydrolysis of the fumarate ester bonds. The methods will be detailed in the sections to follow.

2 DOUBLE BOND SPLITTING BY OZONOLYSIS

The reaction of defins with ozone is described in all the standard textbooks of organic chemistry, although specialised reviews (1,2,3) offer a better understanding of the process. The mechanism of ozonolysis is related to the classical work of Criegee; this can be described in the following way:

$$\begin{array}{c} \begin{array}{c} & & \\ & & \\ & \\ & \\ & \end{array} \end{array} \xrightarrow{} \begin{array}{c} & & \\ & \\ & \\ & \end{array} \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ & & \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \end{array}$$

$$\begin{array}{c} & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \end{array}$$

$$\begin{array}{c} & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \begin{array}{c} & & \\ \end{array} \xrightarrow{} \end{array}$$

$$\begin{array}{c} & & \\ \end{array} \xrightarrow{} \end{array}$$

Because of the instability of the zwitterion formed, the following side reactions may occur

$$\dot{c} = 0 = 0^{-0} + \dot{c} = 0 \longrightarrow \dot{c} < 0^{-0} < 0^{-0}$$
 ozonide

and

e.g.

$$-c - 0 - 0^{-0}$$
 \longrightarrow polymeric peroxides + $c = 0 - 0^{-0}$

Since the main purpose of this reaction is the splitting of a molecule bearing a double bond into two products, it is essential to stabilise and decompose the zwitterion and the ozonide respectively; i.e. two paths are available, either to stop the reaction at the stage of the zwitterion formation through its interaction with a reactive medium, usually an alcohol

$$+\dot{c}-o-o^{-} \xrightarrow{R-OH} \dot{c} \stackrel{OR}{\underset{OOH}{\longrightarrow}}$$

followed by the subsequent reduction of the hydroperoxide (4)

$$c \xrightarrow{OR} + (CH_3)_2 S \xrightarrow{OR} c = 0 + ROH + (CH_3)_2 S c$$

or by allowing the ozonization to proceed to the ozonide stage by carrying it in a neutral medium e.g. CCl_A and splitting the ozonide with a reducing agent

$$c \xrightarrow{0} c + RH \longrightarrow 2 c = 0 + ROH$$
Methods of ozonide reduction may be found in reviews and standard organic chemistry books. Examples of typical reducing agents are sodium or potassium iodides and glacial acetic acid (when hydroperoxides are formed)⁽⁵⁾, zinc or magnesium and water or acetic acid, catalytic reduction $(Pd/H_2)^{(6)}$, sodium bisulfite, sodium borohydride and aqueous ethanol^(7,8) as well as triphenyl phosphine^(9,10). The last seems to be particularly attractive because it converts ozonides almost quantitatively to the corresponding carbonyl compounds; it also avoids the formation of oxygen containing bi-products since hydroperoxides, dimeric and polymeric peroxides and polymeric ozonides are all converted to carbonyl compounds

e.g.

The reaction proceeds at room temperature in the absence of oxygen and it is faster in polar media (e.g. ethanol).

From an experimental point of view, the ozonisation reaction is generally followed by infrared spectroscopy; the ozonides as well as the ozonolysis products are generally detected by gas liquid chromatography.

In the polymer characterisation field, ozonolysis has been mainly used in the elucidation of the structure of rubbers^(11,12,13). The preferred technique used is microozonolysis⁽¹⁴⁾, carried out on small samples. This is claimed to eliminate side reaction as well as the potential danger of large scale ozonolysis. On the other hand, triphenyl phosphine is the reducing agent mostly employed.

The ozonolysis of unsaturated polyesters has not been tried before. Therefore of particular interest to the work described in this section is the ozonolysis of fumarate esters which constitute the polyester backbone sites for ozone attack.

The actual ozonisation procedure of diethyl fumarate in CCl_4 has been extensively studied by Briner et al^(15,16,17). The course of the reaction was followed by infrared spectroscopy; the changes in absorption bands were commented in terms of the chemical alterations that occur during the reaction. Particular importance has been given to the carbonyl absorption at 1730 cm⁻¹.

As ozonisation proceeds a strong band, attributed to the carbonyl neighbouring the ozonide cycle, develops at 1766 cm⁻¹. This band bears a shoulder at 1750 cm⁻¹ caused by the carbonyl group of ethyl glyoxylate, formed during ozonolysis. The ozonide group itself has a characteristic absorption at 1105 cm⁻¹.

After prolonged ozonolysis (20 days), the intensity of the absorptions at 1766 cm^{-1} and 1105 cm^{-1} is reduced while two strong bands are formed at about 1747 cm^{-1} and 1732 cm^{-1} . The first is attributed to ethyl glyoxylate while the second to diethyl oxalate resulting from the progressive auto-transesterification of ethyl hydrogen oxalate which is also accompanied by the precipitation of oxalic acid.

A mechanistic approach to the ozonolysis of diethyl fumarate in methanol has been given by Johnson and Bailey⁽¹⁸⁾ accordingly

Etoco-CH=CH-OCOEt $\frac{O_3}{CH_3OH}$

EtOCO- CHO ethyl glyoxylate OOH EtO-CO-C-H

The hydroperoxide itself rearranges by two competitive routes



OCH,

но-о 2 Eto-co-с-н — Etoco-с-о-н – осн₂ бо-н

Etoco-oc-och

Methyl ethyl oxalate

H,0

The reaction was followed quantitatively by gas liquid chromatography. Thus one mole of ozonised diethyl fumarate gave one mole of ethyl glyoxylate, 0.4 mole of methyl formate and 0.6 mole of ethyl methyl oxalate.

Pappas et al⁽⁴⁾, however did not mention the formation of the last two compounds when their diethyl fumarate ozonisation product, in methanol, was treated with dimethyl sulfide. Two compounds were obtained, namely ethyl glyoxylate and methanol hemiacetal in 87-92% yield.

The above experimental evidence will be regarded as valid for the description of the ozonolysis of unsaturated polyesters. In the following sections, it will be assumed that ozonisation in a neutral medium followed by the splitting of the ozonide results in glyoxylates, while in protic solvents such as methanol and treatment with dimethyl sulfide the product will be glyoxylates and methanol hemiacetals. Because of the slight molecular weight difference between these two compounds, it should be expected that the ozonolysis products, in methanol, have a less defined chromatogram.

2.1 Experimental Programme

The experimental approach to the problem involves basically two steps. First the ozone treatment of the double bonds to form the ozonides and their subsequent splitting, followed by a gel permeation chromatography fractionation of the ozonolysis products.

2.1.1 Ozonolysis of T400 alkyd in neutral media

The ozonisation was carried out on 0.2g samples of alkyd dissolved in 3 ml chloroform or dichloroethane, at dry ice temperatures.

The ozoniser used is shown in figure VII.1 Its ozone output, as determined iodometrically⁽¹⁹⁾ was 4.5 millimoles of 0_3 per hour at an oxygen flow rate of 60 ml/min.

Since the alkyd itself has been synthesised from 1 mole of terephthalic acid (M.W.166), 2.2 moles of propylene glycol (M.W.76) and 1 mole of maleic anhydride (M.W.98), then 0.2 grams of it will contain approximately 0.5 millimole of unsaturation. Therefore, if it is assumed that all the ozone formed is consumed by the double bonds without any loss, ozonisation would be completed in

7 minutes.

For a more accurate assessment of the ozonisation process the reaction has been followed by infrared spectroscopy, this of course is based on the fact that absorptions characteristic of the double bonds will have their intensity reduced with time. Specifically these bands are due to:

a The =CH vibration at 772 cm⁻¹ (figures VII.2.a, b&c)

b The =CH out of plane deformation at 980 cm⁻¹ figures VII.3a,b&c)

c The C=C stretching vibration at 1640 cm⁻¹ (figures VII.4a,b&c) The disappearance of the first band as a function of ozonolysis time is shown in figure VII.5; the band at 730 cm⁻¹ (out of plane bending vibration of the phenyl hydrogens) has been taken as internal standard. The graph shows that ozonisation is complete in 75' which is a much longer period than the calculated one indicating that the reaction of these double bonds with ozone is slow.

The fact that maleate double bonds are absent is mainly deduced from the nuclear magnetic resonance spectrum of the alkyd (figure VII.6.a) which exhibits a single absorption at 6.88 ppm, characteristic of the =CH fumarate hydrogen, compared to the two absorptions of a low M.W. poly (propylene-maleate) copolycondensate synthesised at low temperatures (figure VII.6.b). Figure VII. 1 Oz

OZONISER





Figure VII.2

Gradual disappearance of the band at 172 cm¹ during ozonisation of an alkyd



<u>Figure VII.3</u> Gradual disappearance of the band at 98cm⁻¹ during ozonisation of an alkyd.



<u>Figure VII.1</u> Broadening of the carbonyl absorption band and disappearance of the band at 1641 cm⁻¹ during ozonisation of an alkyd.





a. Fumarale hydrogen NHR abscription of an Impolex alkyd

b. Fumarate and maleate 11-NHR absorptions

Furthermore, the formation of the ozonide is translated by a broadening of the carbonyl absorption band (figure VII.4.a,b&c) mainly shifting towards higher wave numbers, as well as by the broadening of the C-O stretch absorption region (figure VII. 7 a,b & c).

It is also interesting to notice a broadening in the region of the OH group absorption (figure VII. 8 a, b&c) mainly attributed to the formation of hydrogen bonds as well as to the possible occurrence of hydroperoxides.

In addition the poly (propylene terephthalate) prepolymer, which constitutes the saturated portion of the alkyd chains, has been subjected to ozonisation on its own. However, its infrared spectrum showed no changes even after two hours of ozone treatment (figures VII. 9 a&b). Furthermore, the same technique was applied to study the effect of pure oxygen on the alkyd. Here again no noticeable effect was detected spectrophotometrically.

Triphenyl phosphine was the reducing agent used to split the ozonides into aldehydes. It has been selected on the basis of its fast and quantitative effect furthermore it reacts without any special treatment in the ozonisation solvent itself without affecting the chemical groups of the rest of the macromolecule.

Therefore the freshly ozonised alkyd solution was first flushed with nitrogen to expel the dissolved ozone and oxygen; it was then treated with 2.5 g twiphenyl phosphine. Because of the exothermic nature of the reaction it is preferable to immerse the tube containing the chloroform solution in cold water during addition of the solid ozonide reducing agent. The solution is flushed once more with nitrogen then the tube is stoppered and left to stand overnight. A colour change to pale yellow is noticeable.











2.1.2 Ozonolysis of T400-alkyd in Dichloroethane/Methanol

In the introductory part of this section, it has been shown that when ozonization is carried out in a reactive solvent such as methanol, the reaction does not reach the ozonide stage but results in a stable carbonyl compound and a hydroperoxide formed by the reaction of the solvent with the intermediate zwitterion.

However owing to the insolubility of the alkyd in methanol, 0.2 g were first dissolved in 2 ml dichloroethane and then alcohol was added till the formation of a slightly persistant turbidity.

The solution was ozonised, as before at dry ice temperatures, until the infrared absorptions corresponding to fumarate unsaturations completely vanished from the spectrum.

The solution was then flushed with nitrogen and treated with 2 ml of dimethyl sulfide at 0° C for 2-3 hr.

2.1.3 <u>GPC Fractionation of the Ozonolysis Products</u> The gel permeation chromatography experiments described in this subsection were carried out on a 95 cm long, 1.12 cm diameter column packed with Biobeads SX1 swollen in chloroform. The infrared detector was set to detect the eluting species containing a carbonyl group absorbing at 1715 cm⁻¹.

Two reference chromatograms were first recorded. The one shown in figure VII.10.a. corresponds to a T400 alkyd. The absence of any resolution clearly suggests that the molecular weight of this unsaturated polyester surpasses the exclusion limit of the gel. The other chromatogram (figure VII.11.b) displays the familiar pattern of a T400 prepolymer.

The chromatograms of the ozonised samples were the result of the application of a quarter of the solution used in the actual ozonisation experiments i.e. ~ 0.5 g/l ml chloroform (or dichloroethane). Because chloroform develops a carbonyl infrared absorption after treatment with ozone, the solvent was evaporated with a stream of nitrogen and replaced with a fresh quantity.





Figure VII.11.c, shows the chromatogram of a T400-A prepolymer subjected to an ozone treatment for one hour. It is obvious that despite the fact that its corresponding infrared spectrum remains unaltered, a good deal of the GPC resolution has been lost especially in the high molecular weight region. No attempt was made to investigate the factors causing the loss of resolution. The chromatogram has been considered as a rough representation of the future chromatogram of the alkyd ozonolysis product had the splitting taken place as anticipated from the basic mechanism of ozonolysis.

The chromatograms of the ozonisation product treated with triphenyl phosphine and dimethyl sulphide are shown in figures VII.lla and figure VII.llb respectively. It is apparent that the chromatographic resolution is entirely lost, in addition to the fact that peaks probably due to low molecular weight products as well as peaks due to high molecular weight components, apparently unaffected by ozone, can be detected.

The most unexpected observation, however emerges undoubtedly from the chromatogram of the ozonisation product (figure VII.11.c) which looks almost like the two previous chromatograms suggesting that the reducing agent hardly affects the ozonides, most of the splitting having taken place beforehand.

It is worthwhile mentioning that all the experiments have been repeated at least thrice. The outcome was always the same.

2.2 Comments on the results

Before drawing any conclusion about the controversial and apparently unhelpful GPC results, some experimental facts will be first enumerated.

a It has been positively shown, by infrared spectroscopy, that the attack of ozone on the polyester double bonds proceeds slowly but quantitatively.



- b The ozonides assumed to be formed in chloroform or dichloroethane are split either during ozonolysis or during their residence in the chromatographic column (3-4 hr) since their chromatogram, expected to ressemble that of the untreated alkyd, indicates clearly the presence of low molecular weight components in amounts suggesting the complete breakdown of the chain structure. Besides, side reactions which could affect the rest of the structure are unlikely to occur to a large extent since the gross features of the prepolymer chromatogram are retained even after 2 h of ozone treatment.
- The intensity of the chromatogram peaks of the very low molecular weight eluants (elution volume 85 ml) is largely increased when the ozonised alkyd is treated with triphenyl phosphine or dimethyl sulfide.
- d The elution volume range of all the prepolymer components is between 40 to 85 ml with two intense peaks, due to $P(TP)_1$ and $P(TP)_2$ at 81 ml and 66 ml respectively. The elution volume range of the components of the ozonised alkyd constituting the large undefined curve is 35 to 80 ml. If a tentative guess on the possible position of the two most intense peaks had to be made then this would be at 65 ml and 68 ml.

Some of the observations cited above seem to contradict basic and widely accepted facts concerning ozonolyses.

Observation b, to start with, insinuates that the decomposition of an ozonide is a spontaneous process. However it is well known that the ozonides of diethyl fumarate have been isolated, characterised and are stable compounds (17). To account for this ambiguity it is suggested that the splitting of the ozonides may be facilitated or promoted by the strain imposed by macromolecular chain as well as by the interaction of the ozonides with the reactive terminal hydroxyl group or carboxyl group hydrogens by a mechanism similar to that proposed by Criegee (reference 3 p.33).

e.g.

This, of course assumes that the interaction of the intermediate zwitterion with the intermediate carbonyl compound leading to the formation of the ozonide ring is much faster than the reaction of the zwitterion with the active hydrogens

e.g.

If it is assumed that the formation of long chain hydroperoxides, through the interaction of the terminal hydroxyl group hydrogen with the intermediate zwitterions predominates then the result would be a chain structure bearing both hydroperoxide and ozonide bonds. The formation of the ozonides is inevitable because the population of the double bonds exceeds that of the hydroxyl groups.

However, as stated before the hydroxyl group population is rather low, and because of their large dilution it may be readily assumed that both mechanisms are competing during ozonization

If it is assumed that the mechanism involving the ozonide splitting which in fact is a catalytic process predominates in neutral media then the resulting products could well account for the chromatogram pattern, the undefined shape of which could arise from hydroperoxides of intermediate sizes as well as from chains the double bonds of which have been lost during the second polyesterification stage. This explanation seems to tie up well with the fact that the chromatograms of the products of ozonolysis in chloroform as well as in dichloroethane/methanol are alike.

To account for the position of the most intense peak on the chromatogram of the ozonide (elution volume 68 ml) the following is suggested: Because of the high concentration of $P(TP)_1$ species in the prepolymer the presence of segments such as

in the unsaturated polyester chains is inevitable. These, upon ozonolysis will most probably yield

of molecular weight 394 which is midway between the molecular weight of $P(TP)_1$ (282, elution volume 81) and $P(TP)_2$ (488, elution volume 66) therefore the expected elution volume, V, assuming similar elution behaviour, can be calculated.

$$\frac{\log 488 - \log 282}{66 - 81} = \frac{\log 394 - \log 282}{66 - V}$$

'. V = 75.5 ml

in contrast to experimental 68 ml, suggesting either a lower molecular weight which seems improbable on the basis of the ozonolysis mechanism or a different elution behaviour. Finally it is suggested that the very low molecular weight peaks are due to the ozonolysis of segments of the type

Further research aiming at the full elucidation of the ozonolysis of unsaturated polyesters has not been carried out beyond this point. However, some interesting suggestions can be found in section 5 of this chapter.

At this experimental stage our concern was to find an alternative method for detaching the saturated segments from the unsaturated polyester chain and to compare its fractionation pattern with those obtained from the ozonised alkyd.

3 DOUBLE BOND SPLITTING BY PHASE TRANSFER CATALYSED OXIDATION

Phase transfer catalysis involves the reaction between two substances located in different phases by the use of small quantities of an agent which transfers one reactant across the interface into the other phase so that reaction can proceed.

This technique was thought to be of particular interest for the oxidation of the unsaturated polyester double bonds with potassium permanganate since it is known that the former is insoluble in water while the latter is soluble.

The transfer of permanganate ions from an aqueous solution to the solution of the alkyd in an organic solvent immiscible with water commonly benzene, is brought about by organic soluble quaternary ammonium cations, Q. The mechanism of the oxidation in benzene is not known but it is speculated that the reaction sequence is similar to that generally accepted for aqueous systems⁽²⁰⁾

i.e.

$$3 \text{ RCH=CHR} + 8 \text{ Q MnO}_4 \longrightarrow 6 \text{ RCO}_2 \text{ Q} + 8 \text{MnO}_2 + 2 \text{ QOH} + 2\text{H}_2 \text{O}_2 \text{OMnO}_2 + 2 \text{ RCH}_2 +$$

The mechanism being

Under the oxidation conditions cited the formation of the aldehyde, unaccompanied by further oxidation to acid, is detected only at very low olefin conversion.

A whole range of reactions can be achieved by phase transfer catalysis; these reactions have been reviewed by $Dockx^{(21)}$ and $McKillop^{(22)}$.

As far as double bond oxidations are concerned, 1 decene for example in benzene, has been oxidised to monanoic acid (91%) by aqueous KMmO₄ using tricapryl methyl ammonium chloride as phase transfer catalyst⁽²³⁾. Similarly, Sam and Simmons⁽²⁴⁾ found that dicyclohexyl-18-crown 6 ether complex of KMmO₄ is effective in oxidising quantitatively internal olefins to diacids e.g. oxidation of pinene to cis pinonic acid with 90% yield. Trans-Stilbene, on the other hand when rolled in a ball mill with solid KMmO₄, the phase transfer catalyst and benzene gives benzoic acid in 97% yield. The same reaction has been attempted with aqueous KMmO₄ solution and tetrabutyl ammonium bromide as catalyst. The yield was again excellent⁽²⁵⁾. The use of other catalysts is also discussed. Finally the use of basic KMmO₄ efficiently hydroxylates the double bonds; for example olefins have been converted to cis 1,2 glycols with improved yields⁽²⁶⁾.

3.1 Experimental Programme

Oxidation of fumarate double bonds by phase transfer catalysis has not been directly attempted on unsaturated polyesters but first on a model compound namely dibenzyl fumarate, the reason being that such a reaction has not yet been carried out on olefinic unsaturations of the fumarate type. Also the reason for choosing the benzyl ester is that if the reaction gives the expected product i.e. benzyl hydrogen oxalate then this would be a solid much easier to isolate and purify on a semimicro scale.

3.1.1 <u>Synthesis of a Model Compound - Dibenzyl Fumarate</u> The title compound has been synthesised by the direct esterification of fumaric acid with benzyl alcohol.

Thus 20 g fumaric acid and 200 ml benzyl alcohol were introduced in a 500 ml round bottomed flask equipped with a reflux condenser and a thermometer. The mixture was heated at 130°C for 15 h. At the end of the reaction period the unreacted benzyl alcohol was distilled off under reduced pressure. The solid residue was dissolved in benzene and then was successively washed with dilute sodium bicarbonate solution and water.

After drying the organic layer over anhydrous sodium sulphate, the benzene was distilled off and the solid was crystallised from diethyl ether. The melting point of the resulting needles was $60-61^{\circ}C$ ⁽²⁷⁾ yield ~85-90%.

3.1.2 Oxidation of Dibenzyl Fumarate by Phase Transfer Catalysts 5 grams of KMnO₄ were dissolved in 50 ml of distilled water present in a three necked round bottomed flask equipped with a reflux condenser, a dropping funnel and a thermometer. The flask, immersed in ice cold water, contained the PTFE coated bar of a magnetic stirrer. To the aqueous solution was added 0.6 g of tertiary butyl ammonium iodide, phase transfer catalyst, a buffer solution to regulate the pH at 7 throughout the reaction and essentially to neutralise the effect of the basic salt (QOH) generated, as well as 30 ml of benzene. Upon stirring the benzene layer assumed a purple colour because of the transfer of the permanganate ions from the aqueous layer by means of the tertiary butyl ammonium cation.

To the magnetically stirred two phase liquid mixture was added dropwise, a 30 ml benzene solution of dibenzyl fumarate (3g) present in the dropping funnel. The addition was completed in 20 minutes and the temperature was kept at 10° C throughout. Stirring was then continued for 2.5 h at room temperature. After completion of the reaction period the precipitated MnO₂ was filtered

off and the two layers were separated. The aqueous layer, the pH of which remained at 7 and containing the reaction product in the form of a salt was first treated with sodium sulfite to destroy the excess KMnO₄.

This was followed by the addition of a cold, dilute solution of HC1 until pH=3. The precipitating compound was extracted with diethyl ether; the ethereal solution, to which were added the other extracts of the water washings of the benzene layer as well as the washings of the precipitated MnO₂, was dried over anhydrous sodium sulphate.

After distillation of the ether on a water bath the oil residue left behind slowly solidified on standing. The melting point of the solid was 42° C-44 $^{\circ}$ C. Crystallisation was carried out from CCl₄; m.p. 48 $^{\circ}$ C yield ~l.o.g. (33%).

In addition, the benzene, constituting the organic layer was distilled off. A yellowish liquid, benzyl alcohol, containing traces of diethyl fumarate was left behind; yield 0.5 g (17%). Both components were identified by infrared spectroscopy.

The crystalline solid recovered from the ethereal extract was identified as benzyl hydrogen fumarate from its integrated nmr spectrum; the ratio of the integrated trace of the methylene hydrogens absorption ($\delta = 5.25$ ppm) to the trace of the phenyl hydrogens absorption ($\delta = 7.35$ ppm) being 2/5 (figure VII.12). Furthermore, upon treatment with a dilute solution of sodium bicarbonate the solid dissolved with effervescence which indicates its acidic nature.

3.2 Comments on Results

Whereas the application of phase catalysed oxidation to olefins, mostly bearing a terminal double bond, results in quantitative yields, its effectiveness in splitting fumarate double bonds is, as shown by the above experimental evidence, reduced considerably. This suggests that the method is not adequate for studying the sequence distribution of the saturated segments in unsaturated polyesters; an almost quantitative splitting being the prime requirement in fulfilling this purpose.

Further investigations in improving the reaction yield e.g. alteration of reaction conditions, as well as the isolation and identification of the remaining 50% of the reaction products, have not been undertaken. However, it is thought that owing to the poor yields obtained by this procedure followed any further improvement will hardly lead to quantitative oxidative cleavages.

Other oxidation methods, perhaps not phase transfer catalysed, but operating in mixed solvents, particularly dioxan/water, where the alkyd is soluble (80% dioxan by volume), can be applied as alternatives to the method described in this section.

These methods are a) Periodate - permanganate oxidation (Lemieux-von Rudloff) $\binom{(28,29)}{30}$ in which the permanganate is reduced only to the manganate stage; it is then regenerated by the periodate which by itself does not attack the olefin. e.g.

 $\begin{array}{c} \text{RCH} \\ \parallel \\ \text{R'CH} \\ \text{NaIO}_4 (25^\circ\text{C}) \\ \end{array} \xrightarrow{\text{R-CH-OH}} \\ \text{R-CH-OH} \\ \text{R'C-OH} \\ \text{R'COOH} \\ \end{array} \xrightarrow{\text{R-CH-OH}} \\ \text{R'COOH} \\ \end{array}$

b) Periodate-osmium tetroxide oxidation (Lemieux-Johnson)⁽³¹⁾ The reagent, periodate catalysed by osmium tetroxide, operates as follows. Osmium tetroxideadds to a double bond to form an osmate ester, and this is oxidised by periodate with cleavage to carbonyl compounds and regeneration of osmium tetroxide

 $RCH=CR_{2} \xrightarrow{4} 25^{\circ}C \xrightarrow{RCH} CR_{2} \xrightarrow{2NaIO_{4}} RCH=0+0=CR_{2}+2NaIO_{3}+0sO_{4}$

e.g.

c) Periodate-ruthenium tetoxide oxidation $(^{32})$, is an alternative to the above method and proceeds quite well in aqueous acetone where the alkyd is soluble. The periodate is the prime oxidant, ruthenium tetroxide functions as a catalyst. The application of the periodate-osmium tetroxide oxidation method has been attempted directly on the alkyd, but the results were not very promising. Thus 0.12 g of T400 alkyd present in a 10 ml volumetric flask were dissolved in 2 ml dioxan, to this solution was

added distilled water till the appearance of a slight turbidity; this was followed by the addition of a few drops of dioxan and 10.2 mg of $0sO_4$. The solution first assumed a yellowish colour which turned to deep brown on shaking. 0.2 g of finely ground $NaIO_4$ were then added over a period of 15 min and shaking at $25^{\circ}C$ was continued for 1 h until the colour of the slurry became pale yellow.

The mixture was extracted with 5 ml chloroform, the extract dried over anhydrous sodium sulphate and 1 ml was injected in the chromatographic column operating on chloroform. However, a greyish colour becoming darker and darker developed with time and spread itself throughout the GPC column. This adverse development led us to give up the method without any further investigation.

4 SEPARATION OF SATURATED SEGMENTS BY PREFERENTIAL HYDROLYSIS

The objective of the experiments described in this section is to detach the saturated poly (propylene terephthalate) segments from the unsaturated poly (propylene terephthalate fugmarate) chains by hydrolysing preferentially the propylene fumarate ester bonds.

The higher rate of hydrolysis of the esters of fumaric acid over similar esters of succinic, maleic and terephthalic acids may be easily deduced from published work.

It has long been known that the rate of hydrolysis of the esters of some of the above mentioned acids increases in the order

benzoates $\boldsymbol{\zeta}$ succinates $\boldsymbol{\zeta}$ fumarates⁽³³⁾ On the other hand, the difference of saponification rates of diethyl fumarates, maleates and succinates in water-dioxan mixtures at 25°C has been investigated by Pekkarinen and Halonen^(34,35); their results are tabulated below.

Reactant	k ₂₅
OOC CH2 CH2 COOEt	0.0177
EtOOC CH ₂ CH ₂ COOEt	0.207
OOC CH=CH COOEt (trans)	0.158
EtOOC-CH=CH-COOEt (trans)	4.47
-OOC CH=CH COOEt (Cis) EtOOC CH=CH COOEt (Cis)	0.00486 0.407

The tabulated results indicate that the rate of alkaline hydrolysis of the three diesters under consideration increases in the order

succinate 🔨 maleate 🎸 fumarate

Furthermore, it has been shown that diesters of terephthalic acid undergo alkaline hydrolysis approximately 1.5 times slower than the diesters of maleic acid⁽³⁶⁾.

This set of observations suggests that during the hydrolysis of an Impolex alkyd the fumarate ester bonds are bound to be separated from the

macromolecules much faster than the terephthalate ester bonds and provide therefore a method of detaching the saturated segments from the unsaturated polyester chains with the subsequent study of their distribution by gel permeation chromatography.

4.1 Experimental procedure

Before making any attempt to hydrolyse a T400 unsaturated polyester, the rate of hydrolysis of fumarates, succinates as well as that of terephthalates in neutral aqueous solutions has first been verified, since the experimental evidence exposed in the previous paragraphs, mainly concerning the hydrolysis in alkaline media, suggests that the rate determining step is the hydrolysis of the sodium salt of the monoester because of the electron repelling nature of the carboxylate group, it follows that in a purely aqueous medium the kinetics should be different since the hydrolysis of the first ester bond gives rise to a -COOH group which on the one hand accelerates the hydrolysis of the second ester bond and, on the other, increases the acidity of the medium and therefore catalyses the hydrolytic process. The actual hydrolysis experiments were not performed on simple diesters but on polycondensates the alcoholic component of which was propylene glycol present in a molarquantity similar to that of a T400 prepolymer.

4.1.1 Synthesis of model polyesters - Poly (propylene fumarate) and poly (propylene succinate)

In a 500 ml three necked round bottomed flask equipped with a mechanical stirrer, a thermometer a nitrogen inlet and a condenser set in a distillation position, were introduced 100 g propylene glycol, 58.6 g maleic anhydride (molar ratio 2.2:1) and a few crystals of hydroquinone. The reaction was carried out at 160°C under a slow stream of nitrogen. Samples taken at various time intervals were titrated against a standard alkali solution for the acid number determination.

The reaction was stopped when the acid value of the polyester reached approximately 20 mg KOH/g. The polymer contained 82% of fumarate double bonds as estimated by nuclear magnetic resonance spectroscopy. The same experimental procedure was applied for the synthesis of poly (propylene succinate). Thus 100 g of propylene glycol and 70.56 g succinic acid (molar ratio 2.2:1) were stirred at 160°C till the acid number of the polycondensate reached 25 mg KOH/g. The poly (propylene terephthalate) model used in the hydrolysis experiment described below was the T400-B prepolymer, the acid number of which was 16 mg KOH/g.

4.1.2 Hydrolysis of model polyesters

Accurately weighed 0.2 g samples of the model polyesters were introduced in 50 ml round bottomed flasks, each equipped with a reflux condenser. The samples, dissolved in 5 ml dioxan and 5 ml water, were heated at 90°C in a temperature regulated oil bath. At various time intervals, a flask was allowed to cool at room temperature and its contents were titrated against a standard KOH solution for the determination of the acid number. The end point was detected with bromothymol blue indicator.

The variation of the acid number of each polyester with hydrolysis time is graphically represented in figure VII.13.

Accordingly the rate of hydrolysis, expressed in mg KOH/g/h, of poly (propylene terephthalate), poly (propylene succinate) and poly (propylene fumarate) is in the respective order of 1:2.3:15.4. Therefore, if a T400 unsaturated polyester hydrolyses with the same gase as the model polyesters above, then its fumarate ester bonds will be hydrolysed well before the saturated terephthalate segments are seriously affected. Ideally, therefore, a curve representing the extent of hydrolysis of poly (propylene fumarate terephthalate) with time should first result in a straight line with a considerable slope denoting the preferential hydrolysis of the fumarate ester bonds. When the latter comes to an end then the slope of the curve should decrease sharply, approximately 15 times, because of the hydrolysis of the

terephthalate ester bonds only which is a much slower process.

The objective of the following experiments is to detect first the point of inflection of the hydrolysis curve and then to isolate the hydrolysate at this point. Accordingly it should consist of poly (propylene terephthalate) segments with a definite chain distribution which could be studied by gel permeation chromatography.

4.1.3 Hydrolysis of a two stage T400 unsaturated polyester

Accurately weighed 0.2 g samples of the alkyd were dissolved in dioxan. The solutions were made up to the mark of a 50 ml volumetric flask. 10 ml samples of the resulting solution were introduced, with a pipette in 50 ml round bottomed flasks equipped with a reflux condenser. This was followed by the addition of 2.4 ml distilled water. More water causes the precipitation of the alkyd. The solution was heated for different time intervals in an oil bath regulated at 90° C. At the end of every interval the contents of a flask were allowed to cool in a refrigerator; they were then transferred quantitatively in a 100 ml beaker and titrated against a standard methanolic solution of KOH (0.0695N). The end point was detected with a calibrated pH-meter. A typical titration curve is shown in figure VII.14. The whole set of results is given in table 1

Time (h)	24	48	72	96	122	146	216
Vol.KOH(ml)	1	2.1	7.5	12	13.7	22.7	35.5

Table 1: Volume of Standard Alcoholic KOH Solution required to Neutralise the Hydrolysate at Various Stages of the Hydrolysis Process

The evolution of the hydrolysis is also represented diagrammatically in figure VII.15. (The experiment has been performed twice). It is obvious that the shape of the curve is not the expected one i.e. first a line with a considerable slope followed by an almost horizontal line. On the contrary, after a 48 h heating period the curve shows a marked increase in slope without any tendency of deceleration.




It is known that a T400 alkyd consists of terephthalic acid propylene glycol, maleic anhydride (converted in the fumarate form) in molar proportions 1:2.2:1; meaning that the alkyd in its fully hydrolysed form (1x166+2.2x76+1x116 = 449.2 g) is neutralised by 4 moles of KOH i.e. 4 x 56 = 224 g. Accordingly 0.204/5 g are neutralised by 0.02 g KOH (0.204 is the total weight of alkyd dissolved in 50 ml dioxan) or 5.14 ml of a 0.0695N KOH solution.

The experiment itself required more than 25 ml indicating thataside reaction proceeds parallel to the hydrolysis of the ester bonds, and its effect becomes very pronounced after 48 b which is actually near the point where the curve should have started to become horizontal since 2.5 ml of KOH solution are required to neutralise all the hydrolysed fumarate bonds. The acidity therefore should most probably arise from the decomposition of the solvent under prolonged heating. In fact 10 ml samples of dioxan containing an additional 2.4 ml water were heated at 90°C for different time intervals and then titrated with the same KOH solution used before. The volumes of alkaline solutions consumed are represented by the dotted line in figure VII.15. (The experiment has been performed once).

Finally a polyester solution was heated for 120 h in the presence of hydroquinone which is an antioxidant. In fact, 0.3 ml of standard KOH solution were required for neutralisation, meaning that under these conditions hydrolysis of the resin hardly takes place.

4.2 Comments on Results

It is very clear that conclusions concerning the results of the hydrolysis experiments cannot be deduced without any difficulties because of the strong interference of the solvent with the acidity of the solute itself. In addition, this observation renders the information initially gained from the hydrolysis of the models not very trustworthy.

However, if the literature data are regarded with faith i.e. if the faster hydrolysis rate of fumarates compared with terephthalates is definitively accepted, then most of the concern should arise from the relative rate of hydrolysis in water only which, as shown experimentally is a very slow process as well as the resistance of the organic solvent used in conjunction with water to withstand prolonged heating periods.

It is worthwhile however, to attempt the hydrolysis in the presence of minute quantities of an alkali on the basis that the fumarates will be hydrolysed much faster. The extent to which the terephthalate ester bonds are affected can be checked by gel permeation chromatography. Then if this proves that the damage may be overlooked then the method could be regarded as promising.

5 DISCUSSION

In this chapter have been exposed attempts aiming at the study of the sequence distribution of the saturated segments in unsaturated terpolyesters.

Out of the three methods it seems obvious that ozonolysis deserves more attention because of the promising, first attempt results it gave and also because of its simplicity which enables its use directly in line with gelepermeation chromatography, whereas the other methods considered require sometimes more than one chemical treatment between the actual double bond splitting or fumarate ester hydrolysis and the GPC fractionation, ozonolysis is carried out in the GPC solvent and it may also be attempted on a microscale. The second choice being hydrolysis with very dilute NaOH solutions. The prime objective of this chapter has not been definitely reached. The work should have involved firstly an investigation on the possibility of double bond losses through the addition of free propylene glycol which, as stated before, could result in saturated segments of intermediate molecular weight compared to those of the prepolymer and consequently creating the broad and undefined curve on the chromatogram of the alkyd ozonolysis product.

Therefore, the first attempt in solving positively the problem of fumarate double bond splitting would be to study the ozonolysis of a model polyester free from any side reaction; for example poly (propylene fumarate) synthesised from propylene glycol in excess and fumaroyl dichloride, the chromatogram of which should be similar to that of the poly (propylene terephthalate) prepolymer.=

On the other hand, if the ozonolysis of the model is effective then two peaks should be represented on the corresponding chromatogram. CH_3 One corresponding to HO-CH-CH₂-OCO-CHO M.W. 132

and the other to OHC-OCO-CH₂-CH-OCO-CHO M.W. 198

Because of their small molecular weight difference, a twin column system should be used to improve the resolution. An ancilliary experiment would be the identification of the eluting components. The second set of experiments would be to synthesise a model two stage unsaturated polyester starting from the prepolymer the chromatogram pattern of which is known, and fumaroyl dichloride. This should be followed by ozonolysis and GPC analysis. Finally the same experiments should be repeated on a one stage model unsaturated polyester synthesised from the acid chlorides of fumaric and terephthalic acids and propylene glycol. The difference in the chromatograms of the last two terpolyesters would show the difference in their structures even if ozonolysis does not proceed quantitatively i.e. >95% reaction.

The published research work concerning the single stage and two stage unsaturated polyesters does not differentiate experimentally between the influence of the distribution of the saturated segments in improving the properties of the two stage alkyds and the effect of the side reactions, essentially the addition of glycol to the double bonds, in deteriorating the properties of one stage polyesters.

However, published experimental evidence suggests that the distribution of two stage polyesters is lost during the second polyesterification stage and, it could be argued that, in fact it matches the distribution of one stage polyesters. On this basis, a perhaps daring assumption for the present experimental stage would be to say that the two stage polyesters are structurally, single stage polyesters the double bonds of which are almost intact because of the low concentration of free propylene glycol present in the first stage prepolymer.

The problem may be also tackled from a different angle; by examining the model resins from a physical point of view i.e. testing and comparing their properties with the properties of similar resins collected from a production line.

This set of experiments will, undoubtedly, reveal, in its own way, the structural factors that influence the final properties of unsaturated polyester resins.

6 CONCLUSIONS

The development of a method of splitting the double bonds of unsaturated polyesters, ozonolysis or hydrolysis for example is an important and necessary step towards the elucidation of their microstructure upon which depend many of their properties. Essentially, its importance, in conjunction with gel permeation chromatography, lies in the determination of the difference in sequence distribution of the saturated segments in one stage and two stage polyesters.

The development of this method should lead to the determination of the structure of the commercial unsaturated terpolyesters.

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CHAPTER VIII

SEQUENCE DISTRIBUTION OF STYRENE CROSSLINKS IN CURED UNSATURATED POLYESTERS

1 INTRODUCTION

The determination of the average number of homopolymerised styrene molecules constituting the crosslinking bridges in a styrene cured unsaturated polyester has been extensively studied over the past two decades. These studies have been reviewed in Chapter II.

This final part of our project may be regarded as a further step towards the structural characterisation of the crosslinks since its scope is the determination of their sequence distribution. Up to the present development stage of unsaturated polyester resin technology no interest has been shown in that respect. However, with the increasing commercial success of SMC and DMC, it is certain that a deeper study of the structure of unsaturated polyester resins is required.

Most of the studies related to the styrene crosslinks involved the conversion of the insoluble cured resin to a soluble easy to handle polymer, without affecting the crosslinks themselves. In an idealised way, the process is represented as follows

i.e.



The resulting poly (styrene-succinic acid) may also be regarded, from a theoretical point of view, as a hydrolysed copolymer of styrene and diethyl fumarate since in the actual crosslinking process of the resin, copolymerisation takes place between the vinyl group of styrene and the double bond of the fumaric acid diester basically diisopropyl fumarate. Ideally, therefore, the copolymer composition may be described by the copolymerisation equation (Chapter III). The instantaneous composition of a styrene diethyl fumarate copolymer as a function of the feed composition is represented graphically in figure VIII.1.

For the analysis of the copolymer in terms of monomer sequence distribution several techniques are available. These techniques have been applied, for the same purpose, to various copolymers and they will be reviewed in the following section.



Figure VIII.1 Copolymerisation curve of the system styrene.

diethyl fumarate at 60°C ...

2 METHODS OF DETERMINATION OF COPOLYMER MICROSTRUCTURE

2.1 Infrared Spectroscopy

The sequence distribution of styrene-methyl acrylate (MA) copolymers has been determined by infrared spectroscopy in terms of the broadening of the carbonyl group absorption with increase in methyl acrylate content⁽¹⁾. The change in half band width was plotted against P_2 and P_3 which are the probabilities for finding the connections MA-MA and MA-MA-MA in a chain, respectively. These probabilities were evaluated from the reactivity ratios for styrene and methyl acrylate.

Naobumi et al⁽²⁾, on the other hand, considered the band intensity rather than the band broadening in the determination of the sequence distribution of styrene units in styrene-acrylonitrile copolymers. Accordingly, the probability, P, for finding the styrene-styrene bonds in a copolymer chain, is calculated by the equation $P = (A_1/A_2-b)/a-b$ where A_1/A_2 is the relative intensity of the -CH out of plane bending vibration band at 760 cm⁻¹ to the out of plane ring deformation band, at 700 cm⁻¹; a and b are constants characteristic of polystyrene and the styrene-acrylonitrile alternating copolymer. The observed P values were in excellent agreement with the calculated.

2.2 Pyrolysis Gas Chromatography

Pyrolysis gas chromatography was applied to elucidate the microstructure of chlorinated polyethylenes, poly propylenes, ethylene-propylene and other copolymers.

Of particular relevance to the work described in this chapter is Tsuge's (3) application of this technique in the determination of the sequence distribution of monomers in high conversion methyl acrylate-styrene copolymers. Thus, copolymer samples ranging from 0.2 to 0.5 mg were pyrolysed under a flow of

nitrogen at 510[°]C. Each cluster of dimer and trimer peaks appearing on the pyrogram was identified by means of mass spectrometry and was interpreted in terms of diad and triad concentrations in the copolymer chain. It has been found that the experimental results for the sequence distributions were fairly compatible with those predicted by the theories of copolymerisation.

2.3 H-Nuclear Magnetic Resonance Spectroscopy

The concept of studying the monomer sequence distribution of styrene copolymers by proton nuclear magnetic resonance spectroscopy, has its source in Bovey's⁽⁴⁾ observation that the nmr spectra of atactic and isotactic polystyrenes show two peaks in the phenyl hydrogen region (figure VIII.2.a). The peak at 7.05 ppm attributed to the para and the two meta protons and the peak at 6.5 ppm to the two ortho protons. Furthermore, Bovey and coworkers studied emulsion butadienestyrene copolymers and estimated that the styrene sequence length must be eight to ten units before the shoulder starts to appear in the main aromatic peak. This figure is backed by Fujishige's⁽⁵⁾ work who recorded the nmr spectra of polystyrene dimers, trimers, tetramers and pentamers isolated by GPC; all of these n-mers show only a single peak in the phenyl proton absorption region, (figure VIII.2.b). Based on this observation Mochel^(6,7) studied the distribution of block styrene in styrene butadiene copolymers. A computer method was introduced to resolve the overlapped aromatic protons nmr peaks. Accordingly, styrene sequences as small as two or three units were detected.

2.4 <u>C-Nuclear Magnetic Resonance Spectroscopy</u>^(8,9)

This technique is becoming more and more useful in the structural analysis of polymers.

The direct observation of backbone nuclei, the broad range of chemical shifts 13 and the simplicity of H-decoupled spectra combine to make C -nmr spectroscopy a more valuable tool than H-nmr in the characterisation of polymers; especially in the copolymer field where comonomer distributions expressed as connecting diads and triads can be determined.





Aromatic-proton spectrum of stactic polystyrene in CCLs at 28%



Figure VIII.2.5 60 MHz H-NMR spectra of pure styrene nomers in COLGS at 50°C

Of particular interest to this research project is the sequence distribution of styrene copolymers, the analysis of which depends on the sensitivity of the quaternary phenyl carbon, C_1 , to both structural and configurational differences. Published spectra of pure polystyrene show the C_1 region (around 145 ppm downfield from TMS) to consist of three peaks corresponding to the isotactic, syndiotactic and heterotactic configurations⁽¹⁰⁾. Since these peaks cover a range of only 2.5 ppm while multiplicities due to structural effects (comonomer distribution) cover~8 ppm, it is assumed that the gross features of the C_1 absorption region is due to different structural units with configurational differences causing broadening of the peaks.

Shaefer⁽¹¹⁾ used¹³ Cnmr to study the monomer distribution in acrylonitrile-styrene copolymers. The relative concentration of styrene triads, and diads was calculated from the areas under the absorption peaks at 145.1 and 139 ppm respectively. A good agreement was found between theoretical and experimental values. Buchak and Ramey⁽¹²⁾, on the other hand, used the same technique to determine the styrene sequence distribution in low molecular weight styrene-maleic anhydride copolymers. The resulting spectra as well as the peak assignments are shown in figure VIII.3. The relative concentration of the styrene triads, diads as well as monads are calculated from the areas under the peaks. The same type of splitting occurs in the carbonyl carbon absorption region, however its use for structural analysis has been ruled out on the basis that assignments are speculative.

Finally, a poor resolution of the phenyl quaternary carbon atom in poly (styrene 13 acrylic acid) copolymers C nmr spectra, led Toppet et al⁽¹³⁾ to study the microstructure of these copolymers in terms of splitting the -COOH carbon atom.

Numerous examples on the use of nuclear magnetic resonance spectroscopy in copolymer characterisation can be found in Bovey's "High Resolution nmr of Macromolecules" (Chapter IV, ref. 2).



<u>Figure VIII.3</u> Downfield region of proton-decoupled natural-abundance ¹³C-NMR spectra of three styrene maleic anhydride copolymers PPM shifts are relative to TMS

3 EXPERIMENTAL PROGRAMME

3.1 Distribution of Styrene Crosslinks by ¹³Cnmr

The method employed for the determination of the distribution of the styrene crosslinks can be summarised as follows:

cured polyester resin <u>hydrolysis</u> styrene-fumaric acid copolymer <u></u>Methyl ester.

The resulting poly (styrene methyl succinate) is analysed by Cnmr and the splitting of the C₁ phenyl carbon absorption region is compared to the splitting of styrene-diethyl fumarate copolymers of known chemical constitution.

The actual experimental procedures are detailed below.

3.1.1 Curing of T400 and T500 Impolex Resins

To twenty five grams of each resin were added 1.0% w/w of methyl ethyl ketone peroxide (Laporte SD2) and 2.0% w/w of cobalt octoate solution (Novadel NL 49/ST). The resins were then cast in petri dishes. Cellophane was used as mould release agent. The curing was allowed to proceed for 5 h at room temperature (20° C), then the moulds were successively heated at 60° C for 2 h, at 80° C for 1 h and finally at 120° C for another hour.

3.1.2 Hydrolysis of the Cured Products

The cured resins were finely ground in a laboratory hammer mill and ten grams of each were introduced in a 500 ml round bottomed flask equipped with a reflux condenser and containing 25 g KOH dissolved in 200 ml of benzyl alcohol.

The hydrolysis scheme may be represented as follows (Chapter II ref. 54,55).



The effectiveness of the hydrolysis is visualised from the absence of infrared absorption bands at 730 cm⁻¹ characteristic of terephthalates (figure VIII.4).

3.1.3 Esterification of the Hydrolysate

0.3 grams of the polycarboxylic acid were dissolved in 3 ml tetrahydrofuran. To the solution was added, with gentle stirring, an ethereal solution of diazomethane (Chapter V, Subsection 6.8.1). The addition was stopped when the evolution of nitrogen gas ceased, then the excess ether as well as the tetrahydrofuran were distilled off and the esterified hydrolysate was dried for two hours at 50° C in a vacuum oven.





Figure VIII. A Part of the i.r. spectrum of the polymeric hydrolysis product. The band characteristic of terephthalates (730cm') is absent.

3.1.4 <u>Synthesis of Poly (Styrene-diethyl Fumarate) Copolymer Standards</u> The copolymer standards were prepared by free radical bulk polymerisation. Styrene (Fison's SLR) was vacuum distilled and used immediately. Diethyl fumarate (BDH chemicals) was used without further purification as well as the free radical initiator azodiisobutyronitrile (BDH).

Polymerisation reactions were carried out in 25 ml stoppered tubes washed thoroughly with H_2SO_4 , distilled water and evacuated before use. The desired quantities of monomers were introduced separately, in the tubes, by 10 ml microburettes. A total volume of 6 ml was used for each reaction. The initiator (0.3% weight by volume) was accurately weighed and then transferred in the tubes.

Nitrogen was then bubbled in the solution for 30 sec. and the tubes were stoppered by a glass ground joint stopper and sealed with PTFE tape.

Polymerisation was allowed to proceed at 60°C in a temperature regulated bath for 5 hours.

In a typical preparation of a copolymer standard, 0.44 ml of styrene (density = 0.905 gr/ml) and 5.56 of diethyl fumarate (density = 1.06 gr/ml) i.e. in a 1:9 molar ratio, were used in conjunction with 20 mg of initiator.

At the end of the polymerisation period, the tube contents were allowed to reach room temperature. The polymers were precipitated from the monomers solution with light petroleum (n-hexane). Purification was carried out by multiple precipitations and dissolutions from light petroleum-dichloromethane non solvent-solvent system.

The absence of monomers occluded in the isolated polymer was verified by gas liquid chromatography as well as by infrared spectroscopy. The chromatographic method consists in injecting a dilute solution of the polymer in a column packed with Apiezon-L on Celite. The absence of peaks corresponding to the retention times of the monomers clearly suggests that the polymers are pure. The purity is also inferred by the absence of infrared absorptions corresponding to olefinic unsaturation.

Finally the polymers were dried for 10 h at 50°C in a vacuum oven.

3.1.5 <u>Quantitative Determination of Copolymer Standards</u> Composition by GLC

A picture on the composition of the copolymers can be easily obtained through a GLC analysis of the reaction mixture before and after the polymerisation process. The method is the following:

0.2 ml of the reaction mixture are transferred into a 5 ml volumetric flask by a l ml pipette, and made up to the mark with a 1% (weight by volume) solution of p.dichlorbenzene in dichlorethane (para-dichlorobenzene being the chromatographic internal standard). 0.5 ml of this solution was injected by a Hamilton microsyringe, in the 4 ft x $\frac{1}{2}$ " column of a 104 Pye chromatograph

Column packing	Apiezon L on Celit
Oven temperature	125 [°] C
Nitrogen Flow Rate	100 m1/min
Air Pressure	20 lb/in ²
Hydrogen Pressure	12 lb/in ²

A typical chromatogram of a mixture of 0.57 mole styrene and 0.43 mole diethyl fumarate is shown in figure VIII.5.a.

styrene. diethyl fumarate (mole ratio 3:2). free monomer content in Ρ polymerisation GLC chromatograms. mixture 0

Figure VIII.5

5.um	ene
(a) Defore polymerisation	
p dichlorobenzenc	
Diethyl-	
funcrate	
3min 2min	min



At the end of the polymerisation period, 0.2 ml of the same mixture were made up to the mark of a 5 ml volumetric flask with the dichlorobenzene solution and the injection procedure was repeated under the chromatographic conditions cited above. The changes that occur are clearly shown on the chromatogram displayed in figure VIII.5.b.

The composition of the copolymer itself can be determined from the areas under the curves. For example if D, F and S represent the areas under the chromatogram curves of dichlorobenzene, diethyl fumarate and styrene respectively, before the initiation of polymerisation and D', F' and S' are the corresponding areas on the second chromatogram, then the extent of conversion of styrene, for example, is:

$$\frac{S/D - S'/D}{S/D} \times 100 = M$$

Therefore the styrene content of the copolymer will be:

M x original feed

The composition of the various standards as determined by GLC is shown in table 1.

Feed (Styrene/Dieth. Fumarate)		Copolymer (Styrene/Dieth. Fum)	
Volumes (ml)	Mole Fractions	Mole Fractions	Expected S Sequences
0.44:5.55	0.1:0.9	0.27:0.73	Monads
1.40:4.60	0.3:0.7	0.5 :0.5	Mainly monads
2.90:3.10	0.57:0.43	0.58:0.42	Monads-diads
3.09:2.91	0.6:0.4	0.68:0.32	Mainly diads
5.19:0.81	0.9:0.1	0.85:0.15	Triads,n-ads
		•	

Table 1: Copolymer Standard Composition

13

13

3.1.6 C -nmr Analysis of Copolymer Standards

The C-nmr spectra of some standard copolymers as well as of the esterified degradation product were recorded on a Varian XL100-15 Fourier Transform nmr spectrometer operating at 25.2 MHz. Proton-noise decoupling was used throughout and a standard VFT-100X Fourier transform system.

The samples were dissolved (20% wt/vol) in d₆-DMSO which also provided the deuterium signal for field/frequency stabilisation; 12 mm OD nmr tubes were used at 130⁰C.

For a full spectrum, that is 200 ppm, the following spectrometer conditions were employed:

Spectral width	5000 Hz
Acquisition time	0.8 sec.
Pulse width	90 ju sec.
8000 points Fourier tra	nsformed
Number of transients	40,000

Expanded spectra were obtained under the following conditions:

Spectral width2500 HzAcquisition time1.0 sec.13

Three copolymer standards were selected for C nmr analysis; one synthesised from a feed containing 90% styrene and thus expected to contain long styrene sequences contrarily to the one synthesised from 10% styrene which should bear short styrene sequences, mostly monads. Finally, the third standard was obtained from a feed leading to an alternating structure. The mole fraction of styrene in this copolymer was found to be equal to 0.45 by 'H-nmr spectroscopy.

The downfield absorption region of the quaternary phenyl carbon, of each of the standard copolymers is shown in figure VIII.6. Whereas the spectrum of polystyrene, in CDCl₃, (figure VIII.8.a) exhibits a single absorption in this region at 147.2 ppm, two of the standards spectra have this absorption split into at least three peaks.

In order to assign these peaks to specific styrene units along the copolymer backbone, the following structural sequences will be first considered.



styrene-diethyl fumarate copdymers. PPM are relative to THS

•



Isomeric forms have been ignored because, as stated in the introduction, they result in trivial chemical shifts.

From a structural point of view, a quaternary phenyl carbon of type 1 (monad) constitutes, by lying between two fumarates, a structural unit on its own. Type (2) and (4), on the other hand will be structurally and magnetically similar, as well as (3) and (6). Both sets of carbon types having a styrene unit on one side and a fumarate on the other, the only difference being the mode of attachment of the last styrene group to the fumarate. Finally, the type (5) carbon constitutes a unit on its own since it is surrounded by two styrene units.

Further, the spectra in figure VIII.6 may be subdivided into four resonance regions each assigned to styrene monomer units according to the sequences shown in table 2.

Table 2

Structural Type	Styrene Sequence	Chemical Shift (ppm)
(1)	Monad (F-S-F)	137.5
(3) + (6)	Diad+n-ad, (F-S _n -F) n>1	139.1
(2) + (4)	Diad+n-ad	142.5
(5)	n-ad (F-S _n -F) n > 2	144

The quantitative analysis of the tabulated assignments is based on two facts. First, that the area under the absorption peak is proportional to the number (moles) of species responsible for the absorption and, secondly, under the resolution power of the spectrometer the triad peaks overlap with the peaks of higher order sequences.

If we assume that a copolymer consists of amoles of $F-S_1-F$ monads, b moles of $F-S_2-S_3-F$ diads and c moles of $F-S_4-(S_5)_n$, $-S_6-F$ poly-ads (the subscripts indicating the styrene type), then the number of moles of each styrene type will be: a moles of type (1), b moles of type (2) and (3), c moles of type (4) and (6) and $(n-2)_c$, moles of type (5). The letter n represents an average number of styrene units in a polyad since the spectrometer resolution is limited to n = 3.

It follows that the peak area at 137.5 ppm is equivalent to a moles of monads, the one at 139.1 ppm to b moles of diads plus c moles of n-ads, the one at 142.5 ppm to b moles of diads plus c moles of n-ads again and therefore its area should be equal to the previous peak area, and finally the peak at 144 ppm is equivalent to (n-2).c moles of n-ads (n > 2).

Accordingly, the number of monads, a, can be easily determined since they give rise to a well defined peak. The values of b and c can be estimated if n = 3otherwise only a tentative guess of their values can be reached.

As a numerical example, the spectrum of the 90% copolymer will be considered (figure VIII.6). The peak areas corresponding specific sequences are tabulated below (the terms will be the same as before)

Peak Area (cm ²)	Hypothetical No. of Sequences
2.56	b + c
9.72	b + c + (n-2)c
9.72-2.56=7.16	(n-2)c
	Peak Area (cm ²) 2.56 9.72 9.72-2.56=7.16

If we assume that S represents the area corresponding to the sum b + c and C' the area corresponding to (n-2)c, then

$$s - \frac{C'}{n-2} > 0$$
 (1)

Hypothetically S can be split into two peaks their areas being B and C attributed to b and c moles

 $\cdot \cdot S = B + C$

By replacing this equality in (1)

$$C = \frac{C^{*}}{n-2} > 0$$

But since

and

Then

 $B + C - \frac{C^*}{n-2} = I$

In the example under consideration

$$B = C = 2.56 \text{ cm}^2$$

C' = 7.16 cm²

$$2.56 - \frac{7.16}{n-2} = B \text{ or } b (2)$$

Hence for n = 3, B = -4.6, i.e. $B \le 0$

and for n > n', where n' is a number satisfying the condition B = 0 in equation (2), B>O, insinuating that diads are formed only when n > n' > 3 which is absurd; therefore diads are absent from the copolymer standard containing 0.9 moles of styrene i.e. B = 0 and the average value of n is

$$\frac{7.16}{2.56}$$
 + 2 = 4.8

The assumption that the quaternary carbon gives rise to two peaks on a C nmr spectrum of styrene n-ads (n > 2) can be proved experimentally if a low molecular weight polystyrene, having n > 2 is first synthesised (this can be checked by GPC) and then copolymerisation with diethyl fumarate i.e. a single synthesis carried out in two stages. The spectrum of the resulting copolymer should show two peaks in the quaternary carbon absorption region, all representing n-ads, where n > 2.

As a general rule, applicable to the type of nmr experiments described in this chapter, if inequality (1) is not satisfied when n = 3, the copolymer is free from styrene diads this of course implies that peaks corresponding to monads are absent. On the other hand, if the inequality is satisfied for n=3, then it will be assumed that styrene sequences of higher order than triads are absent, this of course because of resolution problems.

Furthermore, it is worthwhile considering from a qualitative point of view only, the carbonyl carbon resonances in the 172 ppm region of the copolymer standard spectra, figure VIII.7. Quantitative interpretations would seem ambiguous because of the configurational as well as structural effects which should be considered in elucidating the nature of the multiplets. For example a fumarate monad F-S-F, may assume the following configurations (R denoting the ester group -COO Et).





It is assumed that a phenyl group distant by 3 carbons from an R group has no effect on the magnetic characteristics of this group. It follows that there are six different carbonyl carbons and in fact six singlets (two of which apparently overlap) appear on the spectrum of the copolymer standard synthesised from 90% styrene and which is expected to include fumarate groups mainly in the form of S-F-S monads. Other structures can be interpreted in a similar way.

3.1.7 C nmr Analysis of the Hydrolysis Products

The spectra of the esterified hydrolysis products of T400 and T500 cured Impolex resins are shown in figures VIII.8, b and c respectively. The expanded spectrum of the T500 hydrolysate is represented in figure VIII.8.d. (The corresponding spectrum of the T400 hydrolysate is not available).

It is obvious that the resolution of the spectra is not as good as the resolution of the standards. Initially, the spectra of the standards were recorded at room temperature and they displayed a splitting pattern similar to that of the hydrolysates. However, whereas the spectra of the standards recorded at elevated temperatures (130°C) showed a fine resolution, those of the hydrolysates remained unaffected. This effect might perhaps hamper slightly the accuracy of the numerical results without however, making the analysis an impossible task.

Figure VIII.8 C-NMR spectra of Polystyrene and 7400 A T500 polymeric hydrolysis products Downfield region only represented. PPM shifts are relative

Lo TMS.

1447.4 1447.4



Basically the styrene quaternary carbon of the hydrolysates results mainly in two broad resonance peaks centred at 140.0 ppm and 144.4 ppm. Each of these peaks will be regarded as an envelope of two peaks, specifically the broad peak at 140.9 ppm may be subdivided into a peak centred at 139.7 ppm and caused by styrene monads F-S-F (its area on the expanded spectrum being 4.4 cm^2) and into a peak centred at 140.5 ppm caused by the quaternary carbon types (3) and (6) of diads and n-ads respectively (its area being 6.2 cm^2). No attempt will be made to resolve the peak at 146 ppm, its area being equal to 9.7 cm^2 .

According to the calculation procedure described in the previous subsection and applying the same terminology, it follows that

$$S - \frac{C'}{n-2} > 0$$

Since $S = 6.2 \text{ cm}^2$

then $C' = 9.7-6.2 = 3.5 \text{ cm}^2$

By substituting these numbers in the inequality above

 $6.2 - \frac{3.5}{n-2} > 0$

which is true for all values of n > 3. However, as stated previously, only the value n = 3 will be considered.

Hence the number of diads will be equivalent to

 $6.2-3.5 = 2.7 \text{ cm}^2$

and the monads are equivalent to the area of the first peak, i.e. 4.4 cm^2 . Therefore, the styrene triads, diads and monads constituting the crosslinking bridges in a cured T-500 Impolex resin are in the ratio 3.5:2.7:4.4, the corresponding fractions being 0.33:0.25:0.42.

This result can be interpreted in two different ways; it can either be accepted as it is i.e. that longer sequences than triads are not formed during crosslinking and therefore the reaction does not proceed statistically or that the copolymerisation does proceed statistically and that sequences of more

than three styrene units are formed but are not detected. Roughly, it may be suggested, that the styrene sequences constituting the crosslinked network of a T-500 Impolex resin consists of less than 50% of monads more than 25% of diads and the rest are triads, tetrads etc. in decreasing population.

3.2 Distribution of Styrene Crosslinks by Infrared Spectroscopy

The idea of using infrared spectroscopy in following the crosslinking of unsaturated polyesters, is not new. A survey on the techniques applied has been exposed in Chapter II.

In this section, infrared spectroscopy will be used in a slightly different way for the determination of the sequence distribution of styrene crosslinks formed at different stages of the curing process.

The method is simple and straight forward; it consists in following the disappearance of infrared absorption bands specific to the fumarate and styrene double bonds, and treating these changes statistically aiming thus at the determination of the copolymer structure. The details of the method will be described in the sub-sections to follow.

3.2.1 Sample Preparation and Spectral Analysis

Five grams of T500 Impolex resin were mixed with 0.5 g of catalyst (methyl ethyl ketone peroxide) and 0.05 g of accelerator (cobalt octoate). Immediately after the mixing 0.0148 g of the resin were applied on a NaCl infrared disc. This was topped by a second disc. Both discs, separated by a 0.025 mm PTFE spacer, were clamped in position and were exposed to infrared radiation at different time intervals. The resin level used was sufficient to fill the available space between the discs and therefore to result in a well defined spectrum. Spectra were recorded at different time intervals, on the same chart. (figures VIII.9 a and b).


The exact origin of the bands which decrease in intensity during curing can be easily deduced from the spectra of styrene (figure VIII.10) and diethyl fumarate (figure VIII.11) recorded from thin films between sodium chloride discs. It is obvious that the styrene double bond bands which do not overlap with any other band are the ones at 907 cm⁻¹ (=CH₂ wag) and at 1629 cm⁻¹ (C=C stretch). The fumarate double bonds, on the other hand, have only one characteristic non overlapping absorption on the resin spectrum, at 1640 cm⁻¹ (C=C stretch). It is also obvious that the -CH stretching vibrations, in the 3000 cm⁻¹ region, exhibit some changes during the crosslinking process.

For the quantitative purposes of the present work, consideration will be given to the styrene and fumarate absorptions at 1629 cm⁻¹ and 1640 cm⁻¹ respectively, to which will be assigned a single common base line.

3.2.2 Quantitative analysis of the spectra

The changes in band intensities with time are interpreted in terms of the absorbance difference between the base line and the peak of the absorption band. The results are displayed in table 3.

Time	Fumarate (1640 cm ⁻¹)	Styrene (1629 cm ⁻¹)		
4"	0.145	0.197		
1h 45'	0.095	0.142		
2h 50'	0.065	0.107		
4h	0.050	0.087		
15h	0.020	0.027		
+ 20 h at 80 ⁰ C	0.008	0.002		
		·		

These changes can also be interpreted quantitatively in terms of double bond consumption on the assumption that Beer's law is applicable. Thus, if A is the absorbance of a band at the start of the crosslinking process

•
$$A = E \cdot C \cdot 1$$
.

where C is the concentration of the specific group in moles per liter, 1 the thickness of the resin film and E the extinction coefficient.

If A' is the absorbance after a curing time, t, then

$$A^{\dagger} = E.C^{\dagger}.1.$$

It follows that the amount of unreacted component is

$$\frac{\mathbf{A}^{\bullet}}{\mathbf{A}} \mathbf{x} \mathbf{100} = \frac{\mathbf{C}^{\bullet}}{\mathbf{C}} \mathbf{x} \mathbf{100}$$

Therefore, if C is known, C' can be determined and the amount of monomer consumed can be calculated. The method does not require reference to any standard band since all of them have the same intensity throughout the experiment. In the calculations, the crosslinking process will be regarded as a set of independent copolymerisation reactions, the feed of each of which is estimated spectrophotometrically.

The relative changes in double bond consumption and feed are given in table 4.

	Fumarate (%)			Styrene (%)				
Time	With re to f	spect eed	With respect to amount left free from previous stage		With respect to feed		With respect to amount left free from previous stage	
	Free	Reacted	Free	Reacted	Free	Reacted	Free	Reacted
4'	100	0	100	0	100	0	100	0
1h45	65.6	34.5	65.5	34.5	72.1	27.9	72.1	27.9
2h50	44.8	55.2	68.4	31.6	54.3	45.7	75.4	24.6
4h	34.5	65.5	76.9	23.1	44.7	55.8	.81.3	18.7
15h	13.8	86.2	40	60	13.7	86.3	31.0	69
+20h 80°C	5.5	94.5	40	60	1.0	99.0	7.4	92.4

Table 4: Monomer consumption during curing of a T500 Impolex resin

Figure VIII.10

6,0

TC=C

£.

-1

1600

Intrared spectrum of styrene

:40

1400

1200

WAVENUMBER (CM-1)

12

-CH= out of plane

1000

δ =CH2

=CH

800

4

16

6(

Intra red spectrum of diethyl fumarate Figure VIII. 11 8.0 9.0 10 7.0 6,0 12 14 27 **C**-0 C=O ۸ T C=C -c-H т_С-н 3000 -/H 1800 -1600 1400 T250 1000 WAVENUMBER (CM-1)

16

<u>.</u>

EGO

	Fumarak/Styrene Content					
Time		Feed	Copolymer Network			
	Moles	Mole Fraction	Moles	Mole Fraction		
4ª	2: 2.95	0.4:0.6	-	-		
1h45 ·	1.31:2.13	0.38:0.62	0.69:0.82	0.46:0.54		
2h50	0.90:1.61	0.36:0.64	0.41:0.52	0.44:0.56		
4h	0.69:1.31	0.35:0.65	0.21:0.30	0.41:0.59		
5h	0.28:0.41	0.41:0.59	0.41:0.90	0.31:0.69		
+20h,80 ⁰ C	0.110:0.03	0.79:0.21	0.17:0.38	0.31:0.69		

Table 5: Molar concentration of monomers in feed and copolymer network at various stages of the crosslinking process

These results can be easily translated in molar concentrations of the olefinic monomers, since a T500 Impolex resin is made of one mole of terephthalic acid, 3.3 moles of propylene glycol, two moles of maleic anhydride and 50% by weight of styrene. Therefore, in terms of unsaturated monomers, the resin contains two moles of maleic anhydride and 2.95 moles of styrene (mole fraction 0.4:0.6). It follows that for each row of values present in table 4 the corresponding raw of value shown in table 5.

3.2.3 <u>Determination of sequence distribution of styrene crosslinks</u> The tabulated mole fractions can be used in the determination of the sequence distribution of the styrene units through Bovey's⁽¹⁴⁾ statistical treatment.

Accordingly, if Pss denotes the probability that styrene will add to itself then the probability of addition to a fumarate is (1-Pss). In a styrene-fumarate copolymer, the fraction of styrene triads (fsss) is given by Pss.Pss. Similarly the fraction of monads F-S-F (f_{ssf}) is $(1-Pss)^2$, which is the probability that S will have two F neighbours. The fraction of styrene diads (FSS and SSF) is equal to Pss(1-Pss) + (1-Pss) Pss

$$fsss = P_{SS}^{2}$$

$$f_{ssf} : f_{fss} = 2 Pss (1-Pss)$$

$$f_{fsf} = (1-Pss)^{2}$$

The value of Pss is calculated from the equation

or

$$Pss = r_s f_s / (1 - f_s + r_s f_s)$$

where r_s is the reactivity parameter of styrene with respect to fumarate and f_s is the mole fraction of styrene in the feed. In the following calculations to r_s will be given the value 0.3 of the styrene-diethyl fumarate system at 60° C. On the other hand f_s will be determined from the curve in figure VIII.1. Since the copolymer composition at the end of each copolymerisation stage is known, this will lead to separate Pss values for every stage. The results are tabulated below (table 6).

Crosslinking Stage	Mole frac. S in copolymer	Mole frac. S in feed (from fig.VIII.1)	Pss	f _{fsf}	f ssf	fsss
lh 45	0.54	0.47	0.21	0.624	0.332	0.044
2h 50	0.56	0.53	0.26	0.545	0,385	0.068
4h	0.59	0.6	0.31	0.476	0.428	0.096
15h	0.69	0.8	0.55	0.203	0.495	0.302
+20h,80 [°] C	0.69	0.8	0.55	0.203	0.495	0.302

Table 6: Sequence distribution of styrene crosslinks at various stages of the crosslinking process

The variation of styrene sequences with time is also shown graphically in figure VIII.12. The most obvious deduction is that the concentration of styrene diads and triads increases with time while the concentration of the monads decreases.



The overall mole fractions of the tabulated sequences are compared to those 13

obtained by C nmr in table 7.

	S-Monads	S-Diads	S-Triads
I.R.	0.41	0.43	0.16
NMR	0.42	0.25	0.33
	l		· · · · · · · · · · · · · · · · · · ·

Table 7: Comparison between IR and NMR results

4 DISCUSSION

13

4.1 C nmr Analysis

An important point arising in that respect is related to the interpretation of the quaternary carbon splitting exposed in this chapter compared to Schaefer's and Buchak's interpretation. Both these researchers attributed the quaternary carbon resonances to a particular sequence distribution based on the magnetic environment of a central styrene unit in a triad. Their assignments are given below in table 8.



Table 8: Buchak's assignment of triads in poly (styrene-maleic anhydride) copolymers

The question we are asking is quite simple; why picking up the central styrene group and not its neighbour since both are expected to give rise to an absorption in the same spectral region but most probably of different chemical shift despite their existence in the same sequence for example S_1 and S_2 in M-S₁-S₂-S-M. According to the above scheme S_1 belongs to a MSS triad and S_2 to an SSS triad. We believe that this peak assignment is not quite true, a more realistic approach to the determination of the sequence 13 distribution of monomers in copolymers by C nmr, can be achieved by means of the new assignment as put forward in this chapter.

From an experimental point of view, the method can be used to follow the distribution of the styrene sequences at various stages of the crosslinking process, by hydrolysing samples taken from a resin during its curing cycle, 13 esterifying the resulting copolymers and analysing them by C nmr. Furthermore, the effect of structural variables such as the distribution of the double bonds along the polyester chain as well as the effect of fillers and curing conditions on the sequence distribution of the crosslinks can also be studied by this method. The only drawback being the poor resolution of the resonance peaks corresponding to styrene n-ads (n > 2).

4.2 Infrared Analysis

The method of following the crosslinking process by infrared spectroscopy has been introduced as a rough alternative to the method suggested in the previous subsection.

The accuracy of the method, however is doubtful; first from an experimental point of view since it involves the study of the crosslinking process of a very thin film of resin which might be different from bulk curing because of exotherm variations. From a theoretical angle, the method involves the use of a statistical treatment which assumes that the reactivity parameters of standard monomers can also describe the hardening of the polyester network.

If this assumption is accepted with reluctance (15), since it is known that fumarates in unsaturated polyester chains do not homopolymerise during curing then the fact that these parameters are temperature dependent (16), arises serious doubts about their applicability especially during the early stages of the crosslinking reaction where temperature variations are pronounced.

Furthermore, Bovey's statistical treatment also considers the probability of a fumarate double bond homopolymerisation, which has been overlooked in our calculations. Finally the treatment does not make any allowance for the formation of a fully alternating copolymer i.e. for this condition to be fulfilled.

> $f_{fsf} = (1-Pss)^2 = 1$... Pss = 0 and Pss = $r_s f_s / (1-f_s + r_s f_s) = 0$

which is only true when $r_s \rightarrow 0$

Surprisingly, however, during the first 15 hours of crosslinking (table 5) the reaction between the fumarate and the styrene double bonds proceeds almost as predicted by the instantaneous copolymerisation curve (near the alternating point). But it is not surprising to notice that after this period, the free styrenes, owing to their increased mobility relative to the fumarates already members of a rigid crosslinked network, are consumed faster and probably give rise to long styrene sequences i.e. in the latter stages of the crosslinking process the copolymerisation equation fails to predict the kinetics of the system. As a result the values given in table 7 should shift towards higher concentrations of triads; the formation of n-ads (n) 3) should also be considered.

5 CONCLUSIONS

The sequence distribution of crosslinks in styrene cured unsaturated 13 polyesters can be determined by C nuclear magnetic resonance spectroscopy, through a more realistic absorption peak assignment of the styrene quaternary carbon resonances.

The method can be used to follow the build up of the crosslinks during the curing process.

Infrared spectroscopy is a more practical but less accurate alternative in following the crosslinking process since it involves the use of a statistical treatment which regards the curing reaction as a standard free radical copolymerisation of two monomers.

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