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PREPARATION AND CHARACTERIZATION OF SOME
UNSATURATED POLYESTER ALKYDS BASED ON
TEREPHTHALIC AND ISOPHTHALIC ACIDS

by

AHMED IBRAHIM HAMAD

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Supervisors: Dr J V Dawkins, Department of Chemistry
Professor A W Birley, Director,
Institute of Polymer
Technology

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SYNOPSIS

In this work unsaturated polyesters based on terephthalate acid and isophthalic acid have been prepared by a two-stage process.

In the first stage the prepolymer bis(2-hydroxypropyl) terephthalate (PTP_1) was prepared and purified. PTP_1 was heated at different temperatures within the range 150-180°C, and the changes in molecular weight distribution, on heating, and the considerable ester-interchanges were assessed by gel permeation chromatography (GPC) and nuclear magnetic resonance spectroscopy (NMR). Similar experiments were performed with the prepolymer ($P(TP)_n$) provided by Imperial Chemical Industries and the prepolymer bis(hydroxypropyl) isophthalate (PIP_1) which was synthesised and purified. GPC and NMR were used to compare the temperature dependence of ester-interchange and polycondensation in the three prepolymers.

In order to see the implications of the ester-interchange observed on the mechanism of the reaction between prepolymer and maleic anhydride, unsaturated polyesters produced at various temperatures in short reaction times have been fractionated by preparative GPC. High resolution 300 MHz proton NMR was used for the qualitative and quantitative analysis of the unsaturated polyester and its fractions, structures were assigned to the oligomeric compounds and reaction mechanisms were outlined.

Finally the products of the reaction of (PTP_1), propylene glycol, maleic anhydride (or fumaric acid) in various molar ratios were examined by NMR and GPC, and their results were compared with a study of unsaturated polyesters based on ($P(TP)_n$) and (PIP_1).

CHAPTER 1

INTRODUCTION

1.1 Historical Development

As early as 1847 polycondensates of tartaric acid and glycols, and polyethylene succinate were prepared by Berzelius and Lorenzo respectively⁽¹⁾. Chain formulations were then introduced by the investigations of Kraut⁽²⁾ on polymers formed by heating acetyl salicylic acid and of Blaise and Marcilly⁽³⁾ on polyesters prepared from hydroxypivalic acid.

The earliest investigations of glycol maleates appear to have been made by Volander⁽⁴⁾. Although a number of other workers prepared polyesters of various types, e.g. the poly (glyceryl phthalate) prepared by Smith⁽¹⁾, Carothers⁽⁵⁾ was the first to establish preparation procedures and well defined structures for polyesters, following the establishment of the macromolecular concept of Staudinger⁽⁶⁾. In the work of Carothers with maleic and fumaric acids, the initial condensation reactions were carried out under nitrogen and vacuum was applied in the last phases of the reaction.

In spite of all this the history of the commercial production of unsaturated polyesters is relatively short. The first commercial production unit of maleic anhydride was built in 1933⁽⁷⁾. Maleic anhydride was prepared by the catalytic oxidation of benzene, with vanadium pentoxide as the catalyst. Unsaturated polyesters were in essence, unknown before this as maleic anhydride is the most widely used unsaturated component.

In the late 1930's Bradley, Kropa, and Johnson⁽⁸⁾ reported unsaturated polyesters as being insoluble and infusible (thermoset) after curing, which took place due to unsaturation present in the base resin (free of monomer). Concurrently, Ellis⁽⁹⁾ reported that a substantial increase in cure rates was observed when unsaturated monomers (such as vinyl acetate) were present in the polyester. Following Ellis, Muskat⁽¹⁰⁾ prepared polyesters from phthalic anhydride, maleic anhydride and ethylene glycol, which were found to be compatible with styrene.

In 1941 unsaturated polyesters began to be used in commercial casting applications⁽¹¹⁾. In 1942 the U.S. Rubber Company used glass-

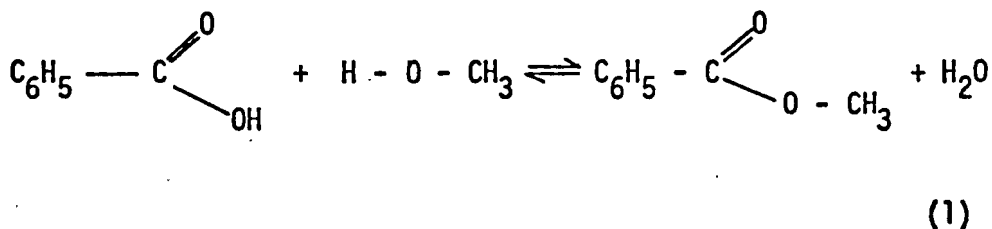
fibre reinforced polyesters for military purposes. After World War II the first large peace time use was in paper laminates, which was followed by corrugated polyester sheeting reinforced with glass mat. In 1946 boat hulls were made of reinforced polyester, this being the major field of application until early 1949⁽¹¹⁾. Since that time a number of companies and patents helped in developing the chemistry and technology of unsaturated polyesters. To mention a few, U.S. Vesicol Corporation⁽¹²⁾ used the adduct of hexahalo cyclopentadiene (Het anhydride) for built-in fire resistance to polyesters. A product of maleic anhydride and dicyclo pentadiene was described in a British patent⁽¹³⁾ to improve air-dry properties. Atlas Company⁽¹⁴⁾ used a diol which is a diether of propylene glycol and bisphenol A to improve the chemical resistance. American Cyanamid⁽¹⁵⁾ produced triallyl cyanurate polyesters of high heat resistance for maximum heat performance. General Electric⁽¹⁶⁾ used moisture containing metal oxides to impart thixotropy, and thixotropy agents are used today in every laminating resin. Owen Corning⁽¹⁷⁾ used chromium complexes to strengthen the bonding at the glass/resin interface.

1.2 Synthesis of Unsaturated Polyesters

1.2.1 Polycondensation reactions

Introduction

The reaction of an acid with an alcohol results in an ester with the elimination of water "esterification". This esterification process is reversible by 'hydrolysis':

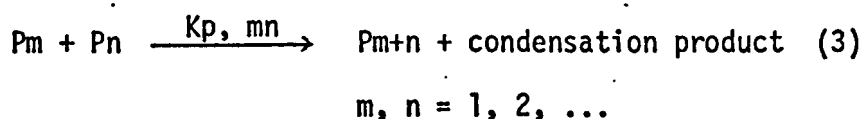


Both reactions are accelerated by hydrogen ions; hydrolysis is also accelerated by hydroxyl ions. The general equation of an esterification-hydrolysis reaction is:



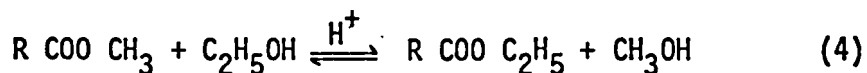
where (P) and (q) are the molar concentrations of alcohol and acid at the beginning of the reaction, X is the molar concentration of ester (and water) at equilibrium, and K is the equilibrium constant. It is clear that for complete conversion of alcohol into ester a large excess of acid must be added. Conversely if it is necessary to convert all the acid to ester a large excess of alcohol must be used. In dicarboxylic acid systems a large excess of glycol leads to the formation of diesters with free hydroxyl ends.

Polycondensation reactions can be represented as an infinite set of elementary reactions:



where (P_m) and (P_n) are molecules having m and n repeat units and $K_{p, mn}$ is the corresponding rate constant. Temperature has a great influence on the speed at which the limit of esterification is reached. In addition, numerous investigations showed that the limit of esterification depends greatly on the structure of the alcohol⁽¹⁸⁾. The limit of esterification of acetic acid, for example, showed a 10% increase with primary alcohols over that of secondary alcohols and ten times that of tertiary alcohols⁽¹⁸⁾.

An important reaction of esters is the ester interchange. The methyl ester of an acid, for example, is converted, to a large extent, into the ethyl ester when refluxed with excess ethyl alcohol containing a few percent of hydrogen chloride or sulphuric acid:

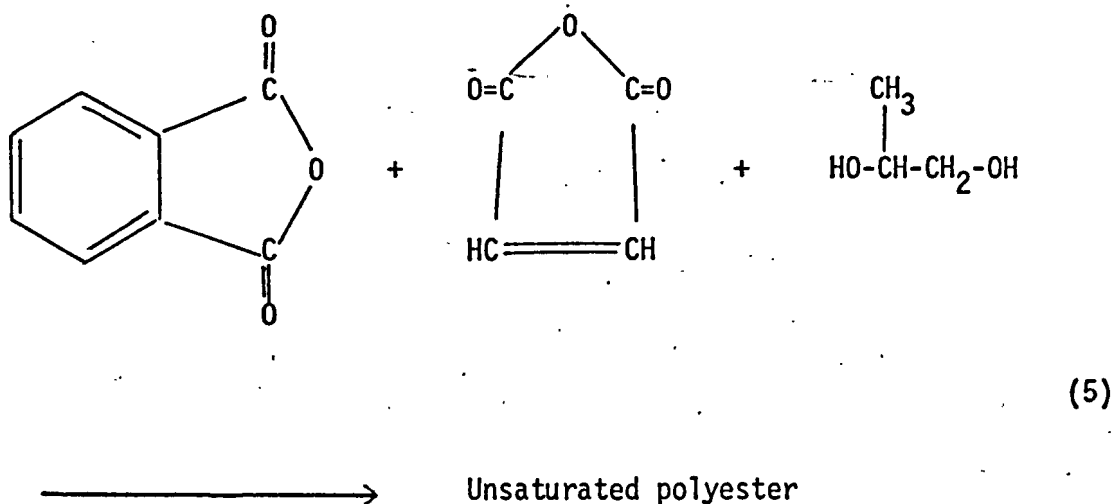


An ethyl ester can be transformed similarly into the methyl derivative by ester interchange. However, an ester can produce by ester interchange another ester either in a reaction with an alcohol, or with a carboxylic acid, or with another ester in a redistribution reaction.

Single stage process:

Unsaturated polyesters are generally prepared by a polycondensation reaction, at elevated temperatures, between glycols, saturated acids

(or esters), and unsaturated acids (or anhydrides). For example, the polyester formed from phthalic anhydride, maleic anhydride and propylene glycol is given by the equation:



Much of the versatility of polyesters hinges on the availability of a number of combinations of acid and glycol components rendering a wide variation in properties. Commercial polyesters contain at least two acid components and one or more glycols. All the monomers are mixed together in the single-stage process and the esterification is completed in one step. The diol is normally added in excess to compensate for the loss of glycol encountered during the reaction.

The reaction is performed under nitrogen (an inert gas) and a free radical inhibitor is used since the unsaturation involved is sensitive to oxygen. The polyester can be prepared in a refluxing solvent to azeotrope the water of esterification or it can be produced in the absence of solvents by use of the fusion method⁽¹⁹⁾. These reactions are normally carried out at temperatures in the range of 200°C - 225°C. Lower temperatures are sometimes used when heat sensitive raw materials are present or when extremely light colour is desired⁽²⁰⁾.

In the production of Impolex resins⁽²¹⁾, (ICI) started their reaction at 105°C. Then the initial stage of the reaction, the exothermic half-ester formation, raised the temperature to 165°C. After this stage the temperature was deliberately raised to 210°C. To follow the extent of the reaction, samples from the reaction mixture were taken at different intervals of time. The acid numbers of these samples were

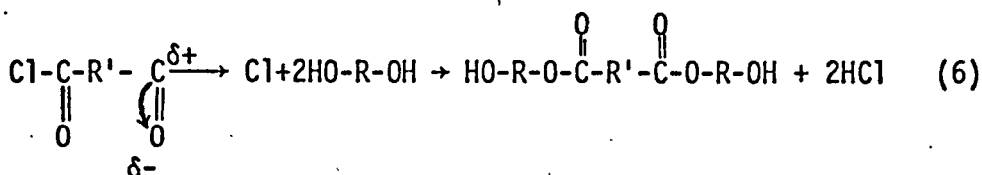
determined and the reaction was stopped when the acid number reached about 10. In these cases where the acid number was required to reach a value of 10, the reaction rate fell off rapidly towards the end of the reaction. The acid in the reaction mixture, which acted as a catalyst in earlier stages, was depleted. Therefore a catalyst can be added. Due to the slow reactivity of these systems they are prepared by a two-stage process.

Two-stage process

In some combinations it is most unlikely that an alternating terpolymer with a regular distribution of components along the polymer chain will be produced in a single-stage process. This is because of the slow reaction of glycol with the commonly used saturated components such as phthalic anhydride, terephthalic acid and isophthalic acid.

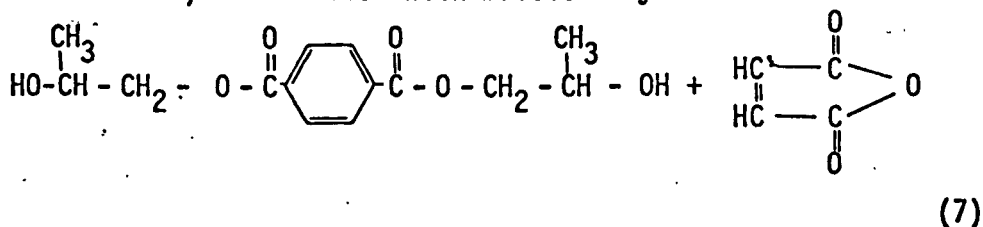
In addition the catalyst does not achieve a regular incorporation of saturated acids in the polymer in the presence of unsaturated acids⁽²²⁾. So in cases where a partially soluble combination, such as terephthalic acid and propylene glycol is used, a two-stage process is used. The two-stage process is meant to give a polymer of more regular structure with a regular distribution of unsaturated units along the polyester chain. It is also hoped in the two-stage process to minimize the losses of unsaturation as all the glycol is esterified in the first stage with the saturated acid⁽²⁰⁾. These two factors are expected to facilitate a regularly spaced copolymerization reaction with styrene in the curing step. Mayer and Gerwig⁽²³⁾ reported that, using a two-stage process, in which maleic anhydride is added after most of the water from the reaction of the glycol and isophthalic acid had been removed, it was possible to produce unsaturated polymer end groups. It was also shown by Szayno⁽²⁴⁾ that unsaturated polyesters having double bonds located towards the ends of the chain have heat distortion and water resistance properties superior to those chains having the double bonds located towards the centre of the chain.

In the first step of the two-stage process all the glycol is esterified with the saturated acid⁽²⁰⁾. When the saturated acid is not very reactive with the glycol, an acid chloride may be used due to the greater electronegativity of the chloride ion rendering a powerful acylating agent.



Another way is to use the anhydride (when possible) or diester or the acid directly with the aid of a catalyst⁽²⁵⁾. Stevens and Gardener⁽²²⁾ have recommended tetrabutyl titanate, tetrabutyl zirconate, zirconium naphthenate, and a mixture of stannous oxalate and sodium acetate as among the most effective catalysts. Their work showed that there appears to be a great deal of specificity between the catalyst used and the system being used so that no one particular catalyst is best in all situations. The catalyst activity was so dependent on the polyester formulation that it was impossible to predict the effectiveness of catalysts from one formulation to another when using different glycols.

In the second stage the unsaturated component is added and the reaction is completed to the required limit. An example is the system used in this work, where a prepolymer based on terephthalic acid (or isophthalic acid) was reacted with maleic anhydride:



—————→ Unsaturated polyester

Another method is to react the ester formed in the first stage with the product of maleic anhydride with glycol in a separate operation. Although this method involves an extra operation it is credited with producing polyesters of better quality than those formed by single stage process⁽²⁶⁾.

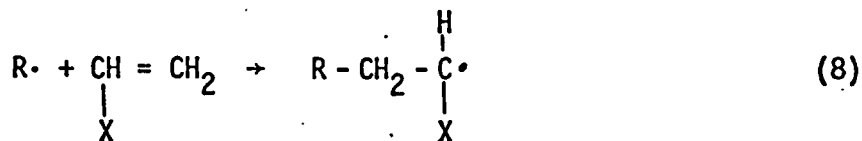
1.2.2 Resin formation

To form the resin the polyester already prepared must be inhibited and dissolved in a monomer. This could be done in the direct or reverse method⁽²⁰⁾. In the direct method the polyester is placed in a stainless steel tank and cooled to a temperature around 100 - 125°C. Inhibitors,

such as hydroquinone or tertiary butyl cathechol, are introduced at the right temperature to prevent premature gelation of resin. The monomer is added and the mixture cooled to room temperature. In the reverse method the monomer is placed in the tank while hot polyester is added to it at a rate such that a homogeneous mixture is obtained⁽²⁰⁾.

Cross-linking

The initiation of the cross-linking reaction can be started in different ways, including thermal and photochemical decomposition of such compounds as organic peroxides and hydroperoxides⁽²⁷⁾. Systems like cobalt naphthenate or octoate-tertiary butyl hydroperoxide are widely used⁽¹⁹⁾. The free radicals formed ($R\cdot$) are relatively unstable, and therefore react readily. They open the double bond of a monomer $CH_2=CH-X$ and generate an unpaired electron, thus preparing the stage for free radical copolymerization with the monomer.



In unsaturated polyester systems where styrene, fumarate, and maleate are present the propagation reaction can proceed theoretically in nine ways. But there is strong evidence that the maleate and fumarate have vanishing rates of self propagation⁽²⁸⁾. It can also be assumed that they do not add to each other under the conditions normally encountered in a polyester cross-linking reaction. The cross-linking is thus initiated by the styrene radical attacking the fumarate (or maleate) double bond. The reverse reactions have vanishing rates⁽²⁸⁾. Therefore the equations relating copolymer composition to the composition of reactants in the original feed are as follows^(28,29,30):

$$S/f = 1 + \frac{r_{sf} S}{F} + \frac{r_{sf} M}{r_{sm} F} \quad (9)$$

$$S/m = 1 + \frac{r_{sm} S}{M} + \frac{r_{sm} F}{r_{sf} M} \quad (10)$$

$$f/m = \frac{r_{sm} F}{r_{sf} M} \quad (11)$$

where S/f, S/m, f/m are the ratios of styrene to fumarate, styrene to maleate, and fumarate to maleate in the polymer; and r_{sm} and r_{sf} are the reactivity ratios of styrene with regard to maleate and fumarate in the system respectively. S, M, F are the ratios of reactants in the original feed.

It appears that the two determining factors in the cross-linking reactions are; the overall unsaturation of the resin⁽³¹⁾ and the reactivity ratio of styrene as compared to maleate or fumarate systems⁽²⁸⁾.

In maleic systems:

$$r_s = 6.52, \quad r_m = 0.005 \quad \text{at } 60^\circ\text{C}$$

In fumaric systems:

$$r_s = 0.3, \quad r_f = 0.07 \quad \text{at } 60^\circ\text{C}$$

The main functions of the monomer are; to act as a solvent carrier for the unsaturated polyester, and to provide a rapid means of reacting with the unsaturation in the polyester to yield a completely reacted cross-linked copolymer. The major monomer in use in polyester resins is styrene. It contributes substantially to the final properties of the cross-linked network of the cured resin because of its fast copolymerizing ability. It does not detract from the normal properties of polyester in any appreciable way⁽³²⁾. Concerning water absorption Smith reported that if the polyester is condensed to a sufficiently high molecular weight, the water absorption properties are not affected significantly over the range 20 - 80% of styrene content.

Parker⁽³³⁾ and Fisher⁽³⁴⁾ suggested an optimum molar ratio of styrene to fumaric species of 2:1. Boenig⁽³⁵⁾ reported that no polystyrene, as such, in a cured system of unsaturated polyesters was detected unless the molar ratio of styrene to fumarate was greater than 9:1. Smith⁽³²⁾ mentioned that the molar ratio of styrene/fumarate of 2:1 enhanced the properties dependent on the degree of cross-linking. These are such as the heat distortion, and elevated temperature strength, whereas high tensile strengths were obtained in resins containing excess of either fumarate or styrene.

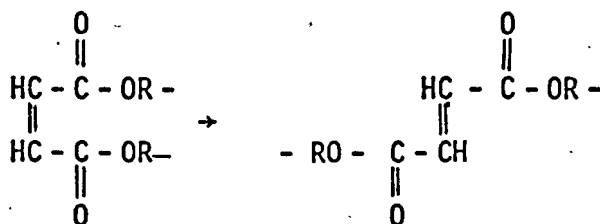
Monomers other than styrene are used in unsaturated resins. Table 1⁽³²⁾ includes some of these monomers and some properties pertinent to their use.

Although all these monomers can be used, styrene still dominates monomer use with unsaturated polyesters, because of its low shrinkage, low volatility, fast coreactivity with polyester unsaturation, and finally because of its low cost.

1.3 Important Side Reactions in Unsaturated Polyester Formation

1.3.1 Maleic/fumaric isomerization

Maleic anhydride is more easily esterified and much cheaper than fumaric acid, so that it is extensively used in unsaturated polyesters. The isomerization of maleic species to fumaric species, during the course of preparation reactions is desired as fumarate based polyesters exhibit better properties.

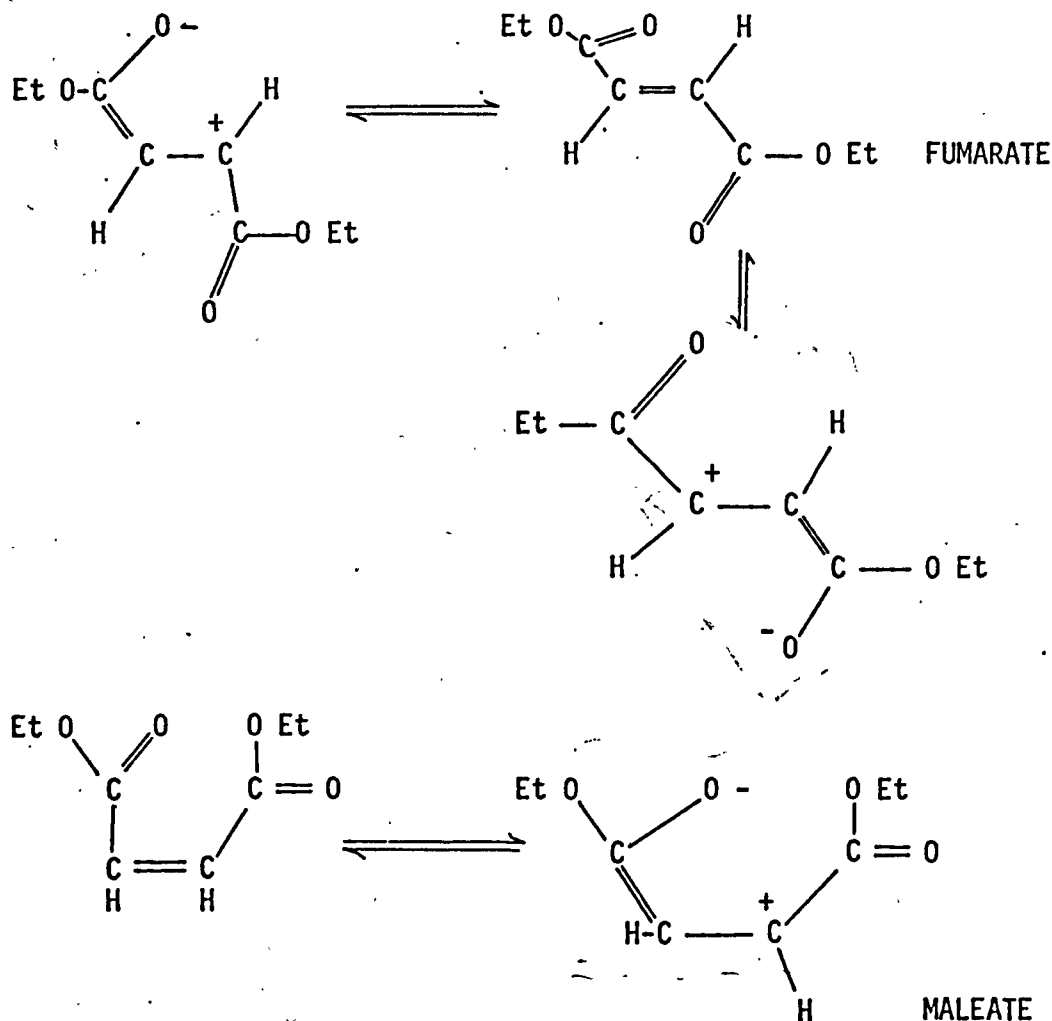


The superiority of fumarate types over maleate types is mainly based on the relative ease of the reaction of the internal fumarate double bonds with the cross-linking agent, e.g. styrene. Price⁽³⁵⁾ studied the copolymerization of diethyl maleate and diethyl fumarate with styrene and found that diethyl fumarate reacts with styrene 12 times as fast as diethyl maleate. Price⁽³⁶⁾ pointed out that the obvious factor lacking in the maleate, which is operative in the fumarate, is the high degree of resonance stabilization in the latter. This stabilization is possible when the molecules are coplanar:

TABLE 1.1

Monomers Used in Unsaturated Polyester Resins

Monomer	Molecular Weight	Boiling Point °C	Specific Gravity	Refractive Index	Volume Shrinkage %	Characteristics
Styrene	104	145	0.902	1.5439	15	Offers low cost, fast coreaction
Vinyl toluene	118	171	0.892	1.5395	12.5	Provides lower volatility, low shrinkage
Chlorostyrene	139	187	1.095	1.5599	12	Provides lower volatility, low shrinkage, very fast coreactivity
Methyl styrene	118	166	0.906	1.5359	...	Controls exothermic heat
Divinyl benzene	131	195	0.913	1.5585	...	Provides extra cross-linking
Diallyl phthalate	246	290	1.12	...	18	Exhibits low volatility, fast cure
Triallyl cyanurate	249	162	1.113	Provides high hot strength
Methyl methacrylate	100	100	0.939	1.412	20	Provides weathering or translucency



In the above diagram the two ester groups in diethyl maleate cannot simultaneously be brought into the same plane as the rest of the molecule due to steric interference of the oxygen atoms in the two carboxylic groups. In diethyl fumarate both ester groups can be coplanar due to the resonance stabilization. Since the approach of the free radical which attacks the double bond is partially negative and in a plane preferentially perpendicular to the plane of the double bond, it will be sterically hindered in the case of the maleate which is not the case in diethyl fumarate.

It is obvious from the reactivities shown above that under the same conditions of cross-linking the maleate based polyesters will have a great deal of unreacted double bonds and longer styrene cross-links as compared with fumarate based polyesters. This will certainly be reflected in the properties of the two types of polyesters. Fumarate

polyesters generally possess higher heat distortion temperatures, greater tensile strength, a higher hardness value, and better chemical resistance characteristics.

Although Hayes et al⁽³⁷⁾ and a number of other workers⁽³⁷⁾ did not find any detectable difference in the chemical composition of polyesters made from maleic anhydride or fumaric acid, Park⁽³⁸⁾ reported that the chemical composition of these polyesters is actually different. He stated: "it is not only that the isomerization of maleate to fumarate is seldom lost, but because of the greater reactivity of the cis double bond, polyesters prepared from maleic anhydride have a substantially higher degree of branching and a lower degree of unsaturation." The recent work of Higgins⁽³⁹⁾ supported these observations. By high resolution ¹H (NMR) and ¹³C NMR some polyesters prepared from terephthalic acid, propylene glycol, and maleic anhydride were proved to form detectable branched structures.

Factors Influencing Isomerization

Glycols and saturated acids:

The factors influencing isomerization were summarised by Vancso-Szmercsanyi⁽⁴⁰⁾ et al as: the type of glycol, the type of aromatic acid, the time of polycondensation and the final molecular weight of the polyester produced. Szmercsanyi et al⁽⁴¹⁾ investigated the effect of different glycols on the isomerization of maleic anhydride polyesters to fumarate polyesters. Their work showed that 1,2 propylene glycol gave better results than ethylene glycol, 1,3 butylene glycol and diethylene glycol. The difference was noticeable even in the early stages of polyesterification but was more remarkable when the molecular weight reached 900 or more, when the fumaric acid percentage induced by each glycol remained constant. They attributed the higher isomerization results of 1,2 propylene glycol to the dense structure of the polyester formed from it which preferred the trans configuration. This assumption was supported by the investigations performed by Sedov et al⁽⁴²⁾ on polyesters based on maleic anhydride and polyethylene glycols of various molecular weights. The results showed that the higher the molecular weight of the polyethylene glycol used, the lower was the isomerization of cis structures to trans configurations. Almost the same results were reached by Curtis⁽⁴³⁾ et al in their study of the effect of glycols on

isomerization using NMR spectroscopy. They believed that the higher isomerization induced by 1,2 propylene glycol was due to steric hindrance. The less accessible secondary hydroxyl group in 1,2 propylene glycol was prompting the trans configuration during the process of esterification. Their results are shown in Table 2 in which the percentage of fumarate increases considerably as the glycol becomes more sterically hindered.

TABLE 2
Isomerization to Fumarate in Polyesterifications

Glycol used	Unsaturated acid	Saturated acid	% Fumarate units
Cyclohexanedimethanol	Maleic anhydride	-	33
Diethylene	Maleic anhydride	-	50
Neopentyl	Maleic anhydride	-	50
Ethylene	Maleic anhydride	-	75
Propylene	Maleic anhydride	-	93
2,2,4-Trimethyl-1,3-pentanediol	Maleic anhydride	-	93
Cyclohexanedimethanol	Maleic anhydride	Phthalic anhydride	52
Diethylene	Maleic anhydride	Phthalic anhydride	52
Neopentyl	Maleic anhydride	Phthalic anhydride	85
Ethylene	Maleic anhydride	Phthalic anhydride	84
Propylene	Maleic anhydride	Phthalic anhydride	94
Diethylene	Maleic anhydride	Isophthalic acid	65
Neopentyl	Maleic anhydride	Isophthalic acid	72
Ethylene	Maleic anhydride	Isophthalic acid	71
2,2,4-Trimethyl-1,3-pentanediol	Maleic anhydride	Isophthalic acid	96
Propylene	Maleic anhydride	Isophthalic acid	95

The results of Curtis et al⁽⁴³⁾ indicated that the introduction of an aromatic dibasic acid into the system enhanced the cis-trans conversion. The inclusion of either phthalic or isophthalic groups as parts of the polyesters contributed more steric effects thereby causing the observed increase in cis-trans conversion. Of further interest and as an added support to these results, two sets of polyesters were prepared in exactly the same manner⁽⁴³⁾. One was based on propylene glycol, isophthalic acid, fumaric acid with maleic anhydride as the unsaturated component in another case. In the other set diethylene glycol was used instead of propylene glycol with isophthalic acid and maleic anhydride in one case and fumaric acid in the other. Styrene solutions (40% styrene content) of these polyesters were prepared and cast. Heat distortion and flexural modulus were measured. No significant differences existed in the properties of the propylene glycol polyesters whether prepared from maleic anhydride or fumaric acid. Conversely, comparison of the data on the two diethylene glycol resins showed significant property differences. This indicated a lower degree of cis-trans isomerization.

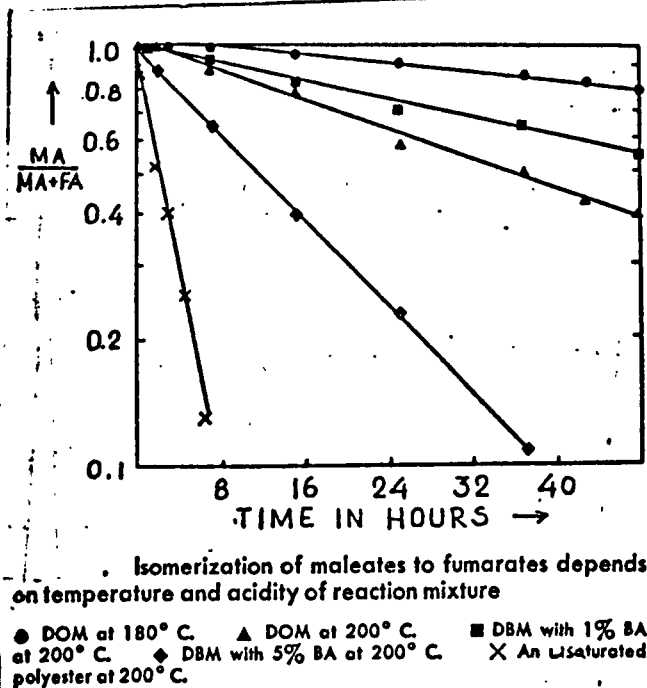
Succinic and sebacic acids (i.e. aliphatic saturated acids) when added to systems of maleic anhydride and glycol gave lower degrees of isomerization as compared to aromatic acids⁽⁴⁴⁾.

Temperature Effect on Isomerization

Model compounds were used by Turunen⁽⁴⁵⁾ to study the isomerization of maleate to fumarate species. He used dioctyl maleate and dibutyl maleate and heated them to 180°C and 200°C in the presence of hydroquinone inhibitor under an inert atmosphere (CO₂). He reached the conclusion that temperature and acidity of the reaction mixture had a remarkable influence on the rate of isomerization.

Because steric hindrance could not explain the higher isomerization rate of dioctyl maleate, its effect was assumed to be due to the slow decomposition during heating which resulted in an increase of the acidity of the reaction mixture. To confirm the acid effect two experiments were carried out with dibutyl maleate, at 200°C, which contained 1% and 5% by weight of benzoic acid respectively. The acidity of the reaction mixture seemed to have a remarkable influence on the rate of isomerization (see Figure 1.1).

FIGURE 1.1



Curtis et al⁽⁴³⁾ in their NMR analysis of unsaturated polyesters found that the rate of cis-trans conversion was accelerated by high temperature, but within the same acid number level.

Because both the isomerization of maleate to fumarate and the destruction of unsaturation are favoured by high temperatures, Parker⁽³⁸⁾ tried to find the optimum temperature for a polyester consisting of 1 mole of maleic anhydride, 1 mole of phthalic acid, and two moles of diethylene glycol. The optimum temperature, at which the highest amount of fumarate would be found without considerable destruction of unsaturation, was reported to be about 210°C. At lower temperatures too little isomerization was obtained and at higher temperatures too much of the fumarate was destroyed by side reactions.

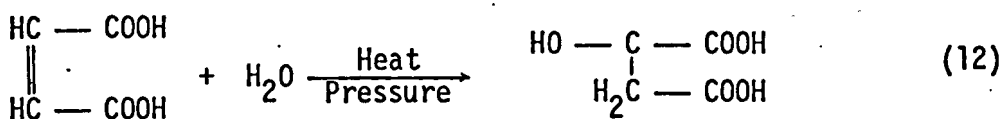
1.3.2 Loss of Unsaturation

Loss of unsaturation in unsaturated polyester systems is widely reported in^{the} literature. These losses result in non-uniform lengths, and an irregular spacing of the cross-links formed between the polyester and the monomer. The objective is to attain short and uniformly spaced cross-links.

These losses can either be encountered through the addition of the glycol (or water) to the maleate or fumarate double bonds, or through the oxidative destruction of the double bonds in the presence of atmospheric oxygen.

Addition of glycols to the double bonds:

The unsaturated bond in maleic anhydride and its derivatives participates in a variety of addition reactions. Water at elevated temperatures and pressure adds to the maleic acid double bond to produce malic acid⁽⁴⁶⁾.



In unsaturated polyester systems Felici et al⁽⁴⁷⁾ showed that about 15% of the unsaturation was destroyed by the addition of glycol to the double bond in the case of a formulation containing maleic anhydride, and that 10% of unsaturation was destroyed in a formulation containing fumaric acid. Knodler⁽⁴⁸⁾ detected a loss of 15.7% of double bonds in a reaction containing fumaric acid and propylene glycol in a molar ratio of 1:1. Sauer et al⁽⁴⁹⁾ reported similar results. Ordelt^(50,51) reacted maleic anhydride with an excess of ethylene glycol (1:1.1 mole) at 147°C under nitrogen. He detected a loss of double bonds and postulated an addition of the glycol to the double bonds resulting in the formation of 1 (2 hydroxyethoxy)-ethane 1,2 dicarboxylic acid, which was hydrolysed and analysed by paper chromatography. Later⁽⁵²⁾ on he suggested that the attack occurred on the maleic anhydride double bond at the beginning of the reaction simultaneously with the ester formation. In subsequent papers^(53,54,55) he reported that, under similar conditions, water produced during the course of the condensation reaction was also capable of attacking the double bond. He stated that the extent of this side reaction resulted in 3% of malate groups. He postulated that these side reactions are reversible involving a cyclic intramolecular mechanism with a carboxylic acid end group in diethylene glycol/maleic anhydride systems.

Oxidative destruction of double bonds:

Loss of unsaturation and the formation of a cross-linked hard insoluble product was noticed by Bradley⁽⁶⁾, when alkyds were heated in the presence of oxygen or exposed to U.V. radiation. This indicated a free radical reaction between double bonds.

Turner⁽⁴⁵⁾ used dioctyl maleate and dibutyl maleate as model substances. He heated the two substances to temperatures between 180°C and 220°C under nitrogen containing various concentrations of oxygen: (0.04%, 0.08%, 0.28%, 0.84%). The loss of double bonds was detected by the change in refractive index. It was found that the loss of double bonds was increased by the increase of oxygen concentration and with temperature for the same oxygen concentration, (see Figure 1.2).

The products of these reactions did not result in a noticeable increase in molecular weights. Molecular weight measurements suggested that the products contained mainly dimers. The low degree of polymerization was also evident from the fact that the increase of viscosity during the reactions was relatively small, and even fully reacted products were liquids.

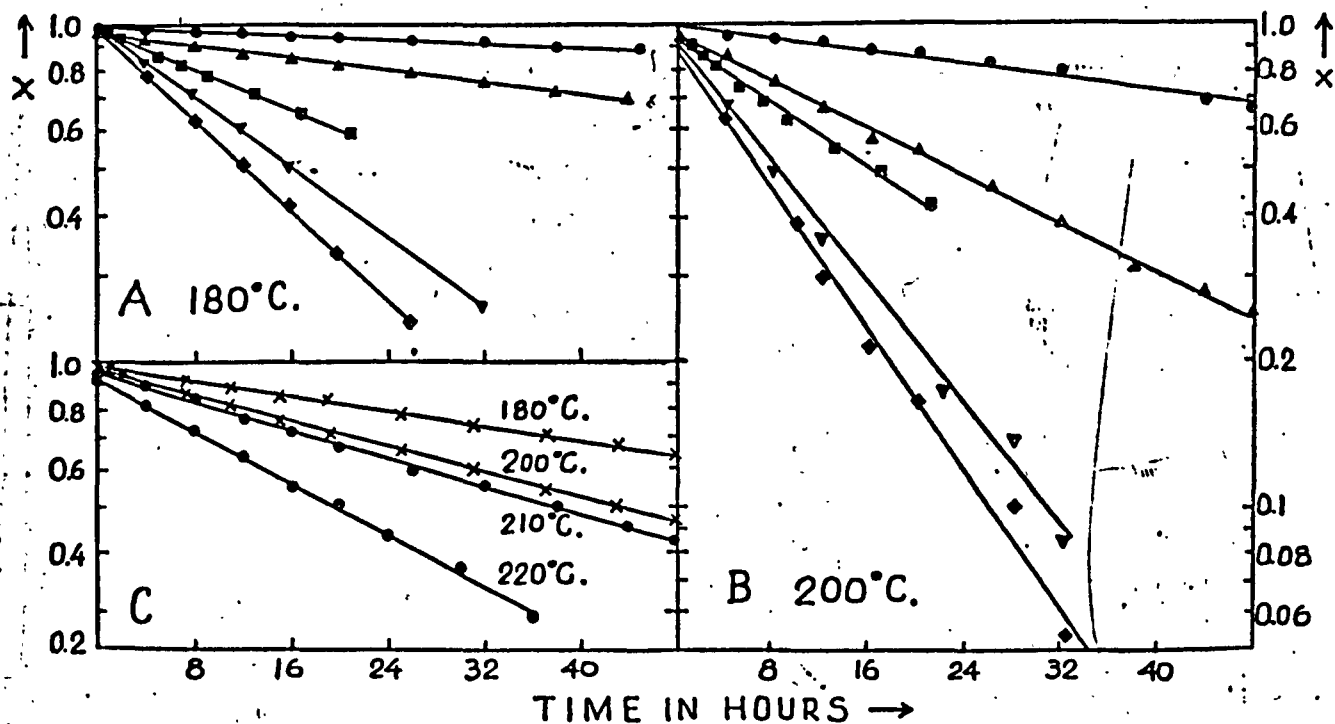


Figure 1.2 The reaction of fumaric double bonds of DOF is of the first order and the reaction rate depends on oxygen concentration in inert gas and reaction temperature

● 0.04% O₂ in CO₂
▼ 0.64% O₂ in CO₂

▲ 0.08% O₂ in CO₂
◆ 1.04% O₂ in CO₂

■ 0.28% O₂ in CO₂
X 0.05% O₂ in N₂

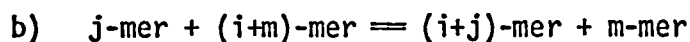
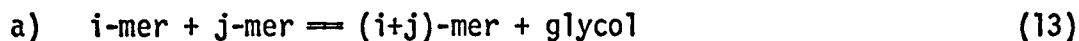
To prevent or to retard the undesirable reaction of double bond homopolymerization, inhibitors such as hydroquinone or benzoquinone were used and investigated. The reaction rate, however, was considerably lower than without an inhibitor. No marked inhibition period was detected and both hydroquinone and benzoquinone acted as retardants. Benzoquinone was reported to be more effective.

1.3.3 Ester Interchange

An important objective of the two stage process is the regular alternation of components along the chain of the polyester produced. This in turn would ensure more efficient cross-linking and regular spacing of components between the cross-links. This advantage of the two-stage process is jeopardized by ester interchange which takes place under the same reaction conditions as the second-stage of this process. The result would be a random rearrangement of components along the polyester chain. This has been proved by the work of Kresse⁽⁵⁶⁾ who reported the formation of a random copolyester on heating for several hours two different polyesters at temperatures above their melting points.

The more recent work of Korshak et al⁽⁵⁷⁾ showed that a random polyester is formed even when one of the comonomers is thirty times more reactive than the other in systems containing terephthaloyl chloride and two diols of different reactivities. It was also stated that block copolymers cannot be obtained by reacting the more reactive glycol with the acid chloride in a first step then followed by the other. Nevertheless, the extent of randomness depends on the reactivity ratio of the monomer and its amount in the reaction mixture. The results of Korshak et al are in agreement with the earlier work of Yomadera⁽⁵⁸⁾ and Murano on ester interchange between poly (ethylene terephthalate) and poly (ethylene sebacate) at 276°C under nitrogen. They reported that random copolymer was reached after only 3 hours. Khramova et al⁽⁵⁹⁾ obtained approximately the same chain structure for polyesters based on copolymers of fumaric acid, sebacic acid, and ethylene glycol produced by either one or two-stage processes.

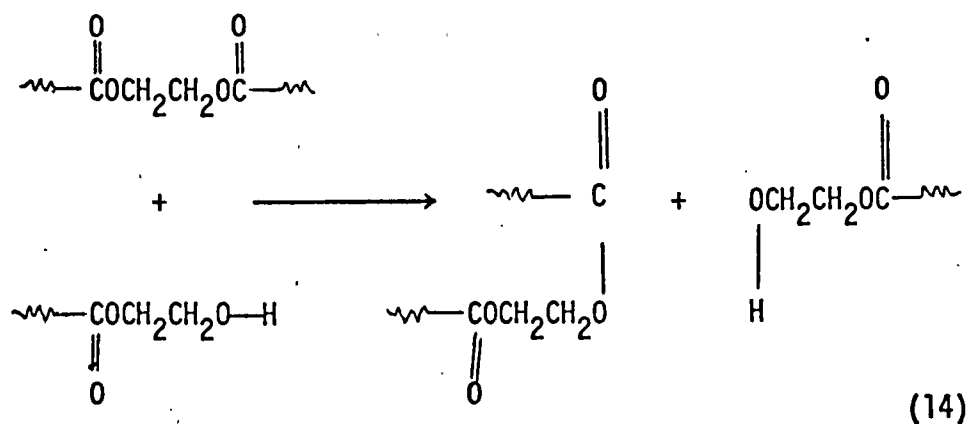
Challa⁽⁶⁰⁾ for the condensation of bis (2-hydroxyethyl) terephthalate to polyethylene terephthalate postulated the following ester interchange reactions which can formally take place:



(a) Proceeds by ester interchange between the hydroxyl group of a 2-hydroxyethyl ester end group and the ester linkage of another 2-hydroxyethyl ester end group, thus eliminating ethylene glycol.

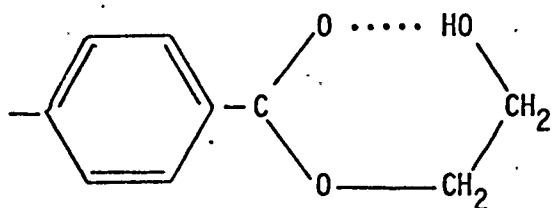
(c) proceeds by ester interchange between two ethylene diester groups situated along polymer chains. As in aliphatic polyesters⁽⁶¹⁾ this reaction can be expected to proceed at an extremely low rate. They attributed the low rate to the lack of active hydroxyl hydrogens in the diester groups along the chain.

(b) This reaction proceeds by ester interchange between the alcoholic hydroxyl group of a 2-hydroxyethyl ester end group and an ester linkage of an ethylene diester group along the polymer chain.



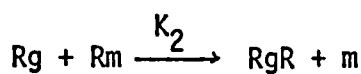
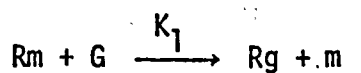
They called this reaction a redistribution reaction as it does not affect the number of molecules or the type of end groups. The rate constant for this reaction at 223°C and 254°C is of the same order of magnitude as the polycondensation and glycolysis rate constants. Owing to the much higher activation energy of the redistribution reaction (31 versus 23 K Cal/mole for polycondensation and glycolysis), the redistribution rate constant will exceed the polycondensation rate at higher temperatures, e.g. 280°C, obtained under manufacturing conditions. Consequently, the redistribution considerably accelerates the attainment of an almost most probable molecular size distribution if one starts from

a product with a very abnormal distribution, e.g. a mixture of two polyethylene terephthalates, one of low and one of higher average molecular weight. Challa hinted that the difference in activation energy of about 8 K Cal/mole between redistribution and glycolysis (both reactions involve an ethylene diester group along a polymer chain) is similar to the energy required to break an intramolecular hydrogen bond in the end group entering into the redistribution process.



The energy of such a bond amounts to about 7 K Cal/mole and the bond has actually been detected in crystalline diethyl terephthalate⁽⁶²⁾.

In the study of polycondensation equilibrium and the kinetics of catalysed transesterification in the formation of polyethylene terephthalate (PET), Fontana⁽⁶³⁾ treated the ester-interchange as two consecutive reactions in the reaction of dimethyl terephthalate and ethylene glycol:



where (G) is glycol, (Rm) methyl ester, (Rg) half esterified glycol, methanol (m), (RgR) fully esterified glycol. He reported that the hydroxyl group reactivity of each of the hydroxyl groups on free glycol is twice the hydroxyl group reactivity of the half esterified glycol. Accordingly the value of K_2/K_1 in the above equations has a value of 0.25.

Another important statement was the appreciable presence of acid ends which resulted from the relatively rapid and reversible dissociation of (PET).

1.4 Composition/Properties Relationship

One of the outstanding characteristics of these polyester resins is their fast rate of cure at low temperatures and pressure. The cured resins are rigid, insoluble solids with good dielectric properties and high structural strength. They are used with glass reinforcement and other reinforcing materials to produce large, rigid mouldings by low-pressure lamination. These reinforced laminates are used in structural building panels, automobile bodies, boats, chemical storage tanks, light weight pipes, furniture, luggage, machinery housings and bath tubs. There is ample evidence that the particular reactants in polyesterification affect the properties of both the polyester and its cross-linked structure, but before considering the effects of different reactants, it should be stated that the distribution of these reactants along the polymer chain and the chain length also affect the properties of these materials.

Starkweather⁽⁶⁴⁾ noticed that the tendency of fumarate polyesters to polymerize readily does not seem to be observed in the low molecular weight species. Wood⁽⁶⁵⁾ showed that some physical properties of polyester castings vary largely with the length of the polyester building block, which he defined as the "*least chain length*", i.e. the smallest chain containing all the elements of the polyester except the styrene. In the cured resins tested, some physical properties such as flexural strength and modulus, coefficient of linear expansion, and heat distortion temperature, were demonstrated to be functions of this least chain⁽⁶⁵⁾.

However, the influence of reactants on properties appeared to depend mainly on the extent of maleate/fumarate isomerization. Sterically hindered glycols and aromatic acids instead of aliphatic acids ensure higher isomerization^(43,66,67,68).

In general purpose resins it is customary to use propylene glycol which imparts a higher degree of compatibility with the commonly used monomers, and it is among the lowest in cost. 1,3-butanediol would be an excellent replacement for propylene glycol were it not for its higher cost. Diethylene glycol can be used as a partial or complete replacement for propylene glycol when greater resilience or flexibility is desired⁽³²⁾. Dipropylene glycol permits higher filler loadings, because it is not adsorbed on common fillers, and enhances flexibility

in polyesters whereas 1,4-butanediol is suitable when higher crystallinity is desired^(20,32).

The propylene glycol-maleate-styrene copolymer is brittle⁽⁴⁴⁾. Flexibility and toughness can be built into the molecule by decreasing the number of double bonds and/or by changing their spatial position. This improvement of mechanical properties can be accomplished by using longer-chain glycols or by substituting phthalic anhydride or a long-chain aliphatic dibasic acid, for part of the maleic anhydride. The use of saturated acids is the most commonly used method^(20,38).

Phthalic anhydride is by far the most widely used of the saturated acid components. The aromatic unsaturation in its benzene ring is inert to the polymerization reaction^(30,38). One of the limitations of phthalic anhydride is the difficulty of preparing high molecular weight polyesters with it. This is due to the strong tendency of phthalic anhydride to form phthalic acid half esters^(20,38). Since terephthalic and isophthalic acid do not form cyclic anhydrides, they are free from this limitation and high molecular weight products can be prepared from them more readily. They also have good compatibility with styrene.

Among the aliphatic acids used, adipic acid which is used to prepare flexible cured polyesters, has usually been less expensive than other dibasic aliphatic acids. Azelaic acid and sebacic acid are more expensive and offer only little improvement in impact strength^(69,70,71). Benzoic acid has also been used to lower the molecular weight of polyesters by acting as a chain stopper⁽³⁸⁾.

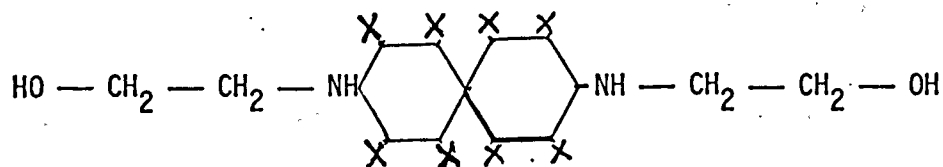
Self-extinguishing polyesters:

The main objectives in this field are to reduce the flammability of the resins as well as the smoke generated when they are burned.

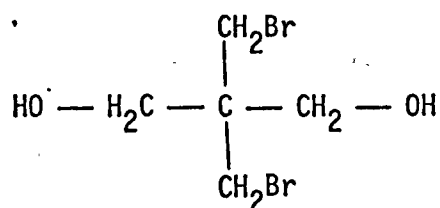
In spite of the fact that the problem of harmful smoke generated upon burning is not completely solved, it was suggested by Lundberg⁽⁷³⁾ and Tsuchiya⁽⁷⁴⁾ that substituting a non-aromatic monomer for styrene, introducing strong char or intumescence, and increasing the non-burning levels, are ways of approaching this goal.

In fire-retardant resins it is usually preferred that the fire-inhibiting component be a part of the reacting portions of the resin, so that heat and solvent resistance is not impaired. For this purpose

halogenated components are extensively used. Among the most widely used halogenated acids are⁽⁷⁵⁾: chlorendic acid, tetrachlorophthalic and tetrabromophthalic acids. Halogenated polyols are also mentioned as halogen containing comonomers i.e.⁽⁷⁶⁾:



bis octa chloro diphenyl diethanolamine. Halogenated glycols are also used⁽⁷²⁾:



Di bromo neopentyl glycol

To attain higher degrees of fire resistance phosphate compounds were incorporated as additives to halogenated polyesters⁽⁷⁷⁾. It was reported by James⁽⁷⁷⁾ that clear fire retardant resins are limited to those containing halogen and/or phosphorous. Antimony oxide (Sb_2O_3) is also used with halogenated polyesters. It is reported that it gives a synergistic effect with halogen compounds and especially bromine⁽⁷⁸⁾. Borates, basic magnesium carbonate, and hydrated aluminium oxide are other fire retardant resin additives⁽⁷⁹⁾.

1.5 Progress in Unsaturated Polyester Studies at Loughborough University of Technology and Objectives of Present Work

The work described in this thesis is a continuation of PhD programmes performed by two research students under the same supervision.

In the first programme, carried out by Kyriacos⁽²¹⁾, poly (propylene terephthalate) prepolymers provided by Imperial Chemical Industries Limited were characterized by gel permeation chromatography (GPC), with an infra-red spectrophotometer detector, and 90 MHz ^1H nuclear magnetic resonance (NMR). The free propylene glycol content, and the amount of glycol lost during polycondensation were estimated by NMR.

From (GPC) chromatograms and NMR spectra, number average molecular weights and molecular weight distributions were determined for the prepolymers. Dihydroxypropyl terephthalate, assumed to be the lowest molecular weight component in that distribution, was synthesised. It was then used to confirm the identification of the same component in the prepolymer.

The investigation of the reaction of dihydroxypropyl terephthalate with maleic anhydride was the subject of the second project performed by Higgins⁽³⁹⁾. He investigated the polymerization reaction of maleic anhydride with three systems: bis (2-hydroxy propyl) terephthalate (PTP₁), propane-1,2-diol, and propane-1,2-diol/(PTP₁). In his results he reported that propane-1,2-diol catalysed maleate/fumarate isomerization. He also suggested that some propane-1,2-diol underwent an addition reaction with maleate groups to produce some alkoxy succinate groups. Higgins⁽³⁹⁾ claimed the detection of these groups in alkyds prepared according to the Impolex (ICI prepolymer) procedure from 220 MHz ¹H and ¹³C spectra. Fractionation of the product of the reaction of (PTP₁) with maleic anhydride was attempted by Higgins and his results will be discussed later.

At the end of the second programme it was evident that an investigation of the extent of the ester interchange involved in the preparation of the (PTP₁) prepolymer and its implications on the polymerization reaction of the prepolymer with maleic anhydride was required. This was a major objective in the present research together with a study in more detail of the polymerization reaction of (PTP₁) with maleic anhydride with and without the presence of free propylene glycol, in various molar ratios. Of prime interest are the maleate/fumarate conversion ratios, the losses in maleate double bonds, and the chemical environment of propylene glycol molecules in the reacted polyester. The results obtained are to be compared with polyesters prepared under similar conditions based on (T400) prepolymer P(TP)_n provided by (ICI Ltd), and a laboratory prepared prepolymer based on isophthalic acid (PIP₁).

The polymerization systems described in the summary of previous work were designed by Higgins to be relatively large scale production polymerizations. It is evident, from the thermal history cited for these reactions, that they were operated with poor temperature control.

Thus it was difficult to obtain reproducible results or to correlate in a definitive way some of the observations to specific reaction conditions. The work performed in this project has the advantage of being carried out at approximately constant temperatures and having access to a 300 MHz ^1H NMR spectrometer.

CHAPTER 2

UNSATURATED POLYESTER CHARACTERIZATION BY GEL
PERMEATION CHROMATOGRAPHY AND HIGH RESOLUTION
NUCLEAR MAGNETIC RESONANCE

2.1 Gel Permeation Chromatography

2.1.1 Introduction

The preparative fractionation methods used to determine the molecular weight distribution (MWD) of polymers have considerable limitations⁽⁸⁰⁾. They rely upon the molecular weight dependence of polymer solubility, they are time consuming "several weeks", and practically inefficient in obtaining monodisperse fractions and in defining the tails of different fractions.

Several attempts were made to replace preparative fractionation methods by new chromatographic methods such as "gel filtration". Polymer molecules of different sizes were separated on the basis of their ability to penetrate the pores of a rigid porous gel. Porath⁽⁸¹⁾ and Flodin⁽⁸²⁾ separated solutes of different sizes by means of hydrophilic gels. Vaughan⁽⁸³⁾ fractionated polystyrene by means of a highly cross-linked polystyrene gel.

Gel permeation chromatography as an analytical technique was developed by Moore⁽⁸⁴⁾. He prepared versatile cross-linked polystyrene gels covering a wide range of porosity suitable for a wide range of polymer-solvent pairs. These gels can be used for polymers of molecular weights up to 10^6 . Moore⁽⁸⁴⁾ also replaced the process of collecting fractions from the column by passing the column eluate through an on-line refractometer where the concentration of solutes was measured continuously.

Gel permeation chromatography (GPC) has become a predominant technique for polymer characterization producing rapid, reliable and reproducible results. The process of separation is started by injecting a dilute solution of sample (0.1 to 1.0%) into a valve leading to a set of columns. These columns are packed with porous gels of various pore sizes. A stream of solvent is then allowed to flow through the column acting as the "mobile phase" while the solvent trapped within

the gel pores is considered as the "stationary phase". As the injected sample passes along the column, those molecules of smaller size than the gel pores will have access to both the mobile and stationary solvent phases. In contrast molecules of very large size cannot enter the gel pores and are, therefore, confined to the mobile solvent phase. It follows that the movement of molecules of smaller sizes than gel pores will be retarded by their penetration into the gel pores while large molecules, protected by their size against this penetration, will travel through the column at the speed of the mobile phase. Molecules of intermediate sizes will be retarded at a rate dependent on their molecular size. When either total exclusion or total penetration takes place, no separation is possible.

Mechanism of separation:

If it is assumed that the time taken for a polymer molecule to diffuse into a gel pore is small with respect to the time spent in the vicinity of the pore, then it can be assumed that the separation process is independent of diffusion processes. In this case for a solute of given size in solution the partition coefficient K_p is dependent on the distribution of pore size and pore shape in the gel and retention volume ' V_r ' can be given by⁽⁸⁵⁾:

$$V_r = V_0 + K_p V_i \quad (2.1)$$

where V_0 is the volume of the mobile phase and V_i is the volume of solvent in the stationary phase.

Molecules of the polymer sample tested will be eluted according to their size in solution. The value of K_p is equal to zero for molecules having sizes larger than gel pores (see Figure 2.1), while molecules of smaller sizes penetrate an increasing fraction of the solvent within the gel pores (stationary phase). Finally, molecules of smaller sizes than the gel pores have free access to both the mobile and stationary phases where K_p value reaches unity⁽⁸⁵⁾ (total penetration, see Figure 2.1).

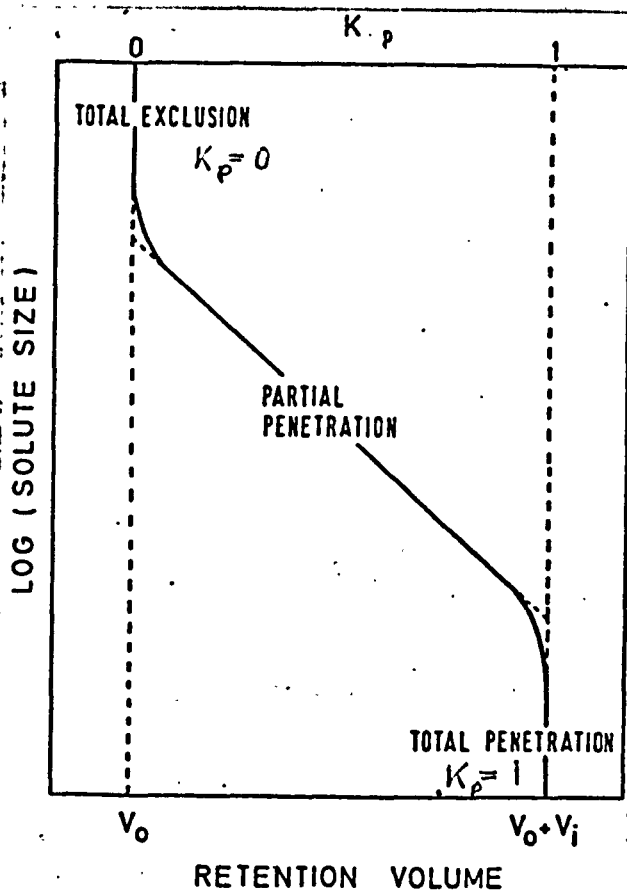


Figure 2.1 Theoretical curve for a steric exclusion separation mechanism

The mechanism described above assumes a separation process at equilibrium in which kinetic effects, particularly those of diffusion, can be neglected. Hence the partition coefficient can be rewritten as:

$$K_p = \frac{V_a}{V_i}$$

where V_a is the fraction of stationary phase accessible to the particular molecule under consideration and V_i is the stationary phase volume. Billingham⁽⁸⁵⁾ reviewed the attempts made by Porath⁽⁸¹⁾ and Laurent⁽⁸⁶⁾ to relate V_a , and hence K_p , to molecular parameters of polymer molecules and reached the conclusion that none of their suggested models is realistic enough to allow the calculation of K_p values for an unknown polymer. Porath⁽⁸¹⁾ considered the penetration of molecules with spherical shape into conical pores and Laurent⁽⁸⁶⁾ assumed the gel as a network of straight rods.

Cassasa⁽⁸⁷⁾ treated K_p as a true equilibrium constant which can be determined from the calculated value of the free energy change " ΔG " accompanying the transfer of a polymer molecule from solution to the pores. He assumed that the only contribution to ΔG is the loss of conformational entropy when the molecules transfer from the mobile phase to a pore where the conformations are restricted. Therefore, the reduction in the number of conformations is determined by the size of the molecule, the unperturbed root-mean-square end-to-end distance. This treatment provided a relationship between K_p , polymer molecule size, and pore size for various models of pore shape. It also advocates the domination of steric exclusion in GPC separations. The Cassasa model is probably the best currently available, but to date, complete agreement between theoretical and experimental values of K_p has not been obtained. Dawkins⁽⁸⁵⁾ attributed this to the simple model employed in which enthalpy and other entropy contributions to ΔG have been ignored, i.e. the neglect of solute-gel interactions. Furthermore Dawkins⁽⁸⁵⁾ added that, although steric exclusion is dominant in influencing solute separation, kinetically controlled mechanisms in a real separation-not at equilibrium, e.g. diffusion processes and transport effects, must contribute to some extent in determining the retention volume of the solute. Yau et al⁽⁸⁸⁾ in their study of the relative importance of steric exclusion and diffusion effects concluded that both steric exclusion and restricted diffusion are involved in GPC separations at high flow rates. They reported that the observed distribution coefficient can be rewritten as:

$$K_p = K_x \cdot K_D \quad (2.3)$$

where K_D is the distribution coefficient resulting from the non-equilibrium process of diffusion of molecules into the gel pores. K_x is the distribution coefficient resulting from equilibrium exclusion of solute from the gel pores. K_D is dependent on the flow rate while K_x is not. On the basis of these findings, it could be concluded that at low flow rates where K_D approaches unity K_p is determined by steric exclusion.

Universal calibration:

It is generally accepted and empirically proved that in the absence of polymer-gel interactions and at sufficiently low flow rates the separation of polymer molecules in GPC is determined by molecular size in solution. Anderson and Stoddart⁽⁸⁹⁾ reported that theoretical values of K_p versus the logarithm of solute size gave a linear relationship in the central region of the curve. They considered the linear relationship to be:

$$K_p = - A \log M + B \quad (2.4)$$

where M is molecular weight and A and B are constants. The expression was found to be dependent on the nature of the polymer and type of gel, which indicated that the use of molecular size was more appropriate than molecular weight. Nevertheless, the relationship gave satisfactory results for polymers made from monomers of similar sizes. Therefore retention volume could be written as:

$$V_r = V_0 + V_i (- A \log M + B) \quad (2.5)$$

If V_0 and V_i are constants, then

$$V_r \propto - \log M \quad (2.6)$$

The earlier observation of Benoit⁽⁹⁰⁾ et al, that a plot of $\log[\eta]M$ versus V_r is the same for all polymers (a universal calibration), was confirmed by the work of Grubisic⁽⁹⁰⁾ and Dawkins⁽⁹¹⁾. So the equations relating molecular size to retention volume were introduced by Dawkins:

$$V_r \propto - \log[\eta]M \quad (2.7)$$

where $[\eta]$ is the intrinsic viscosity for a polymer.

If $[\eta]M$ is proportional to the hydrodynamic volume as suggested by the Einstein and Flory treatments of intrinsic viscosity, Dawkins⁽⁹²⁾ suggested that if the operational conditions remain the same, then at a

given retention volume the relationship:

$$\log M_p - \log M_{ps} = \log[\eta]_{ps} / \log[\eta]_p \quad (2.8)$$

will apply to all polymers. Hence, p refers to the polymer under analysis and ps to an experimental study with polystyrene standards. Equation (2.8) will therefore permit the determination of M_p when the dependences of $[\eta]_{ps}$ and $[\eta]_p$ on retention volume have been established. The above expression may be written as:

$$\log M_p - \frac{1 + A_{ps}}{1 + A_o} \log M_{ps} = \frac{1}{1 + A_p} \log \frac{K_{ps}}{K_p} \quad (2.9)$$

where A is the exponent in the Mark-Houwink equation which is:

$$[\eta] = KM^A \quad (2.10)$$

where K and A are constants.

The dependence of equation (2.9) on the Mark-Houwink equation makes it inaccurate for molecular weights below 50,000 because deviations from the straight line relationship set in as suggested by Billmeyer⁽⁹³⁾. Another theoretical objection⁽⁸⁵⁾ to the above equation (2.9) was based upon the fact that increasing solvent power causes the end-to-end distance of a polymer chain to increase more rapidly than the effective hydrodynamic radius, so that the $[\eta]M$ calibration is only valid for polymers with similar interactions with the solvent. But Dawkins et al⁽⁹⁴⁾ studied the problem extensively and concluded that the objection is invalid.

Resolution:

To achieve satisfactory separation and resolution in GPC, it is important to have instrumentation with the correct type of gel, the proper column packing method, and the right length of gel bed. It is generally suitable to use a length/diameter ratio of 25-100 with a bed volume which is 25-100 times the sample volume⁽⁹⁵⁾.

In the apparatus used here columns of about one metre long and of 1.5 cm diameter were used. An excess of this length was believed

to lead to the compression of the gel beads at the bottom of the bed. When a bed length in excess of one metre was needed two columns, connected in series, were used.

The resolution in GPC is also greatly affected by the sample viscosity and the method of sample application. Too large a sample volume may lead to broad overlapped peaks, while too small a volume of sample may lead, on the other hand, to the loss of some peaks because of the low concentration of some components in the original sample. However, the flow rate effects were not particularly important in the systems used in this work as they were gravity elution systems. The resolution in GPC is given by the equation:

$$R = \frac{\Delta V}{2w} = \frac{V_2 - V_1}{2w} \quad (2.10)$$

where V_1 and V_2 are the elution volumes for the two neighbouring peaks in Figure 2.2, and w is the width of the peak in these,

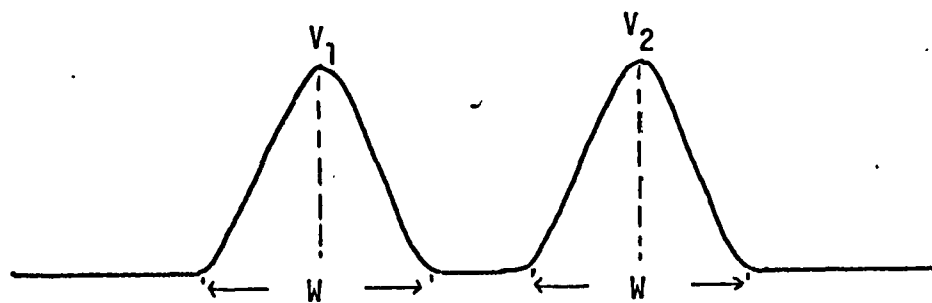


FIGURE 2.2

gravity elution, systems cannot be decreased further and the resolution depends on Δv , which is believed to be optimised when the fully swollen soft beads are used because the ratio V_i/N_0 is large.

2.1.2 Gel Permeation Chromatography Apparatus

Description:

The equipment used in this work is shown in Figure (2.3). A similar set up was used by Kyriacos⁽²¹⁾ and Higgins⁽³⁹⁾. It consists of a single packed glass column (1.5 x 110 cm), or two similar packed columns connected in series in the case of a two-column set up. To

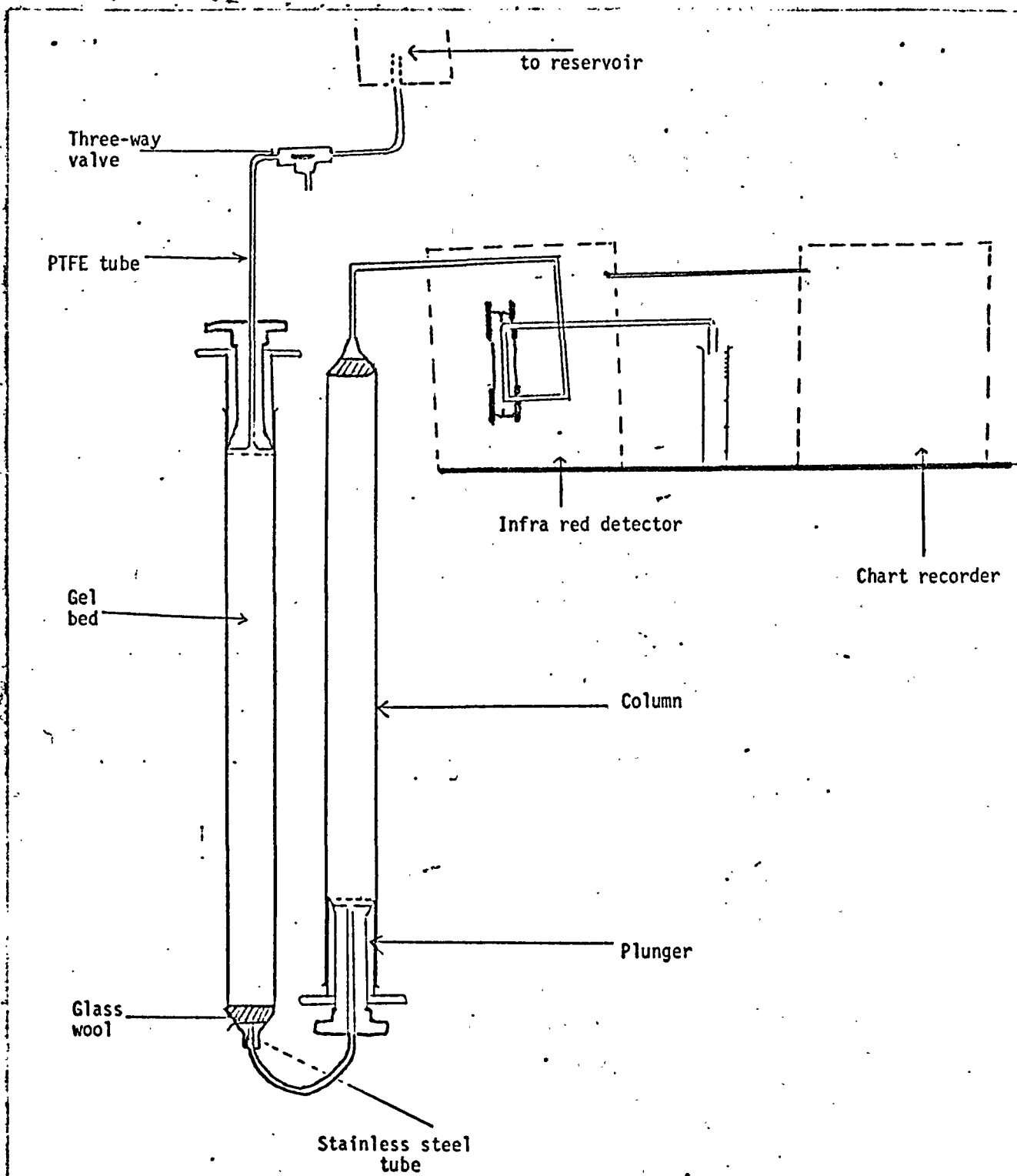


FIGURE 2.3. Two column GPC apparatus

this set of columns the solvent is syphoned by a gravity feed from a reservoir placed above at enough height to give sufficient eluant hydrostatic pressure. A glass delivery tube from the reservoir is connected to the first column by PTFE tubing via a three way valve. When the eluant passes through the glass wool bed support, it goes through a short length of stainless steel tubing (3 cm) tightly fixed into the short drawn end of the column. The eluting solvent is carried with PTFE tubing to the lower port of an infra red solution cell, attached to a Perkin Elmer infra red spectrometer, and finally to a measuring cylinder. A fan is installed to cool the infra red cell and guard against the formation of air bubbles caused by the heat build up in this region.

Gel material and packing procedure:

The gel materials used were Bio-beads SX-1 and Bio-beads SX-2 supplied by Bio-rad Laboratories. Both consist of a copolymer of polystyrene and divinyl benzene but Bio-beads SX-1 are 1% cross-linked and have the exclusion limit of 3500 whilst Bio-beads SX-2 are 2% cross-linked and have the exclusion limit of 2700. In the one column GPC system described in this work Bio-beads SX-1 were used. Bio-beads SX-2 were introduced into the two-column GPC systems to improve the separation power between low and high molecular weight species.

Chloroform is a good solvent for polyesters. Chloroform, a good swelling agent for the beads, was used as it does not interfere with the infra red absorption of the polyester carbonyl groups at $1715 - 1720 \text{ cm}^{-1}$. Kyriacos⁽²¹⁾ surveyed a number of solvents which could be used in GPC systems and found that chloroform is a better swelling agent for the beads than tetrahydrofuran and dioxane. On the other hand tetrahydrofuran and dioxane are difficult to obtain moisture free and they tend to develop, on standing, an infra red absorption in the region of the carbonyl group.

The gel (15g) was swollen in chloroform (350 ml) for at least 15 hours with careful handling, avoiding stirring or vigorous shaking. This time was enough to completely swell the gel and to get rid of the air bubbles trapped in the first mixing of gel and solvent. Many packing procedures are recommended in the literature. The ultimate

aim is to obtain a properly packed gel bed, which presents a low and uniform (with respect to cross-section) resistance to eluant flow, free of air bubbles, channels, and other discontinuities. A good packing procedure is a prerequisite for efficient resolution in GPC.

The column was clamped firmly and the lower third was filled with chloroform while the outlet was closed. The gel slurry was carefully poured to a height of 5 cm above the solvent level. A thin glass rod was used to conduct the slurry along the inner wall of the column in order to prevent splashing. The outlet was then opened after a period of 15 minutes to drain the solvent and ensure a uniform gel bed base. When the top of the gel bed (1.0 mm) started to get dry, more solvent was added to stir the top part of the gel layer followed by the addition of slurry to a height of 5 cm. The packing was then continued in 5 cm increments until the column was packed to the required height. The plunger was then fitted and the packed column was left under a continuous flow of the eluant solvent. A gap was usually found to develop between the plunger and the gel bed which could be removed by pushing the plunger down to meet the top surface of the gel bed. The flow rate, under gravity, was in the range 15-20 ml/hr in one column system and 10-15 ml/hr in two column systems.

Sample application:

To obtain, in single or two column GPC systems, reliable and well resolved analytical chromatograms the dissolved sample should be of reasonably low viscosity. Viscosity of both the sample and eluant must ordinarily be low, since the method depends upon efficient diffusion of solutes within the gel bed. The viscosity of the sample should not exceed the viscosity of the eluant by a factor of 2⁽⁹⁵⁾.

A solution of polyester sample (0.015g) in chloroform (3 ml) was applied to the column through the three way valve. After the solution was syphoned into the column, small volumes of solvent (3 ml each) were applied to the column in the same way. The solvent was then allowed to flow through the system in the normal way to effect the separation process. The solvent eluting from the column was collected in a measuring cylinder to determine the retention volume for each component.

In preparative GPC applications two-column systems were used. The sample applied was 0.1g of solute dissolved in 1 ml of chloroform. The application procedure was essentially the same as described before.

When the different fractional components were eluted from the column, they were collected separately and applied again to the column set after they had been concentrated by evaporating the solvent. This procedure was repeated until a single peak was obtained for each fraction. See Figure 4. 6.

Infra-red detection:

Method:

An on-line Perkin Elmer 457 IR spectrophotometer was used. A normal infra red spectrum was obtained for the sample under consideration to determine the maximum absorption region of its carbonyl groups. That wavelength was monitored throughout the separation time. The pen of the infra red spectrophotometer was restored to the 100% transmittance position, base line position, with an attenuator while the solvent was passing through the cell. The detector response was then relayed to a recorder which converted the detector signals into amplified response-time curves.

Theory of detection:

When a solute fraction passes through the infra red cell, its concentration builds up gradually to a maximum, then gradually decreases as it is washed out of the cell. During this process, the solute molecules absorb at the preset wavelength. Therefore the transmitted light intensity will be reduced to a limit proportional to the concentration of molecules passing through the cell at any point of time. The transmittance is correlated to the concentration of the sample by the Beer-Lambert law:

$$\log \frac{I_0}{I} = E.C.L. \quad (2.11)$$

where I_0 is the intensity of the incident light, I is the intensity of transmitted light, E is the molecular extinction coefficient (molar absorptivity), C is the concentration of sample, L is the path length of sample. Equation (2.11) may be expressed by:

$$T = \frac{I}{I_0} \quad (2.12)$$

$$\therefore \log \frac{1}{T} = E.C.L. \quad (2.13)$$

If the extinction coefficient is constant, i.e. the same group at constant wavelength, and L is constant, i.e. the same cell is used, then

$$T = e^{-KC} \quad (2.14)$$

so that K is regarded as a constant.

As the base line is 100% transmittance, the height of the curve (pen deflection) is $1-T$, so that equation (2.14) becomes

$$1 - T = 1 - e^{-KC} \quad (2.15)$$

$$= 1 - \left(1 - KC + \frac{K^2 C^2}{2!} - \frac{K^3 C^3}{3!} \dots \right)$$

$$= KC - \frac{K^2 C^2}{2!} + \frac{K^3 C^3}{3!} \quad (2.16)$$

At low concentrations where the Beer-Lambert law holds, the second and third terms can be neglected

$$\therefore 1 - T = KC \quad (2.17)$$

It could therefore be concluded that the pen deflection (or GPC curve height) is linearly proportional to the concentration of solute, and the summation of pen deflections for the whole range of the component producing the area under the curve S is:

$$S = K \sum C_i \quad (2.18)$$

To relate the area under the curve to absorbance values, one will be faced by the problem that absorbance A is represented by a logarithmic scale, i.e.

$$A = \log \frac{1}{T} \quad (2.19)$$

However Kyriacos showed that a semi logarithmic plot gives a linear relationship between A and the recorder pen deflection provided that A is in the region (0.0 to 0.1). Higgins reported the limiting value to be very high and assigned a new range (0 to 0.025). Anyhow at low concentrations the relationship of area under the curve to the concentration of solute still holds:

$$S = K \sum C_i \quad (2.20)$$

If the extinction coefficient (molar absorptivity) is regarded as the property of the individual carbonyl group at maximum absorbance, the area under the curve should be related to the number of carbonyl groups in the component under consideration:

For PTP:

$$S = 2 K \sum^{\ell} C_i \quad (2.21)$$

For P(TP)₂ or PTPM, assuming equal values of E for all carbonyl groups the relationship is:

$$S = 4 K \sum^m C_i \quad (2.22)$$

For P(TP)_n or P(TPM)_{n/2} then

$$S = 2n K \sum^h C_i \quad (2.23)$$

Therefore within the concentration range used for analytical GPC systems in this work the areas under the curves can be related to the concentration of different fractional components of the sample.

2.2 Aspects of High Resolution Nuclear Magnetic Resonance Spectroscopy

2.2.1 Introduction

Various methods of physical and chemical analysis are employed to determine the chemical structure and physical properties of polymers. It is intended, from this broad spectrum of methods and techniques, to obtain information which could relate specific parameters in chemical structure to physical properties. Basic to the understanding of structure-property relationships is the necessity of having characterization techniques which permit detailed analysis of polymer structure without affecting this very structure in the measuring process. High resolution nuclear magnetic resonance (NMR) spectroscopy is an excellent technique in delineating the composition sequences, and microstructure of chain molecules. It is unrivalled for the observation of any kind of isomerism, the determination of composition, and the elucidation of minor structural features even when they involve only a few percent of monomer units⁽⁹⁶⁾. The high resolving power in NMR spectroscopy is reflected in the information it provides concerning chemical environmental differences (seen in the form of chemical shifts) caused, for example, by stereochemical configurations which are too subtle to detect by other means.

The application of NMR spectroscopy in the polymer field has expanded in the last decade. Extensive literature surveys on these applications were carried out by McCall⁽⁹⁷⁾, Woodbrey⁽⁹⁸⁾ and more recently by Slonim⁽⁹⁹⁾, Bovey⁽⁹⁶⁾ and Kasler⁽¹⁰⁰⁾.

The use of ^{19}F NMR in fluorine containing polymers has been very valuable particularly with regard to head to head and head to tail isomerism⁽¹⁰¹⁾. The ^{13}C nucleus is common to virtually all polymers and despite its low natural abundance (N 1.1%) and small magnetic moment, it can provide important information about the polymers. In the recent work of Fyfe⁽¹⁰²⁾ et al on aromatic polyesters, they obtained high resolution ^{13}C NMR spectra for insoluble, highly crystalline homopolymers of P-hydroxybenzoic acid, two methyl derivatives of this polymer, and two copolymers with biphenyl terephthalate. The width of the resonance lines obtained was 3-6 times narrower than those obtained by Schaefer et al⁽¹⁰³⁾ under the same conditions for glassy polymers.

This narrow width of resonance lines was attributed to both the rigidity of these aromatic polyesters and the homogeneous local environment associated with crystal habit.

The vast majority of polymer studies, however, have been devoted to proton NMR spectroscopy measurements, as the ^1H nucleus is most amenable to NMR observation. Areas under proton NMR spectrum signals are proportional to the number of protons in those environments, and are automatically measured by the integration of each signal. Integral values are in the form of continuous lines in which steps appear as each signal is measured thus producing step heights proportional to areas under peaks. Quantitative information was derived from the integrals of NMR spectra by Spragg⁽¹⁰⁰⁾ and Urman⁽¹⁰⁴⁾. They determined the molecular weights for P.octyl novolate and dibutyl adipate/glycols respectively. Molecular weights could be determined for prepolymers of known structure from the ratios of the integrals of NMR peaks corresponding to proton types present in one repeat unit.

A conspicuous feature of polymer spectra is the broadening of lines as compared to those of small molecules of analogous structure. In the spectra of high molecular weight polymers the signals of a particular type of proton may consist of many overlapping unresolved lines corresponding to the fact that groups in different positions along the chain will not experience precisely the same average magnetic environment⁽⁹⁶⁾. Bovey⁽¹⁰⁵⁾ suggested that for lower solute concentrations (15-20%), the line width is only weakly dependent on the molecular weight of the polymer and the solution viscosity, indicating that local viscosity (segmental motion) is the determining factor. Despite the line broadening the spectra are usually sufficiently well resolved to provide structural information. For improved resolution high operational temperatures are used together with a proper choice of solvent ensuring low viscosity, an absence of interfering absorption lines, and an absence of impurities. Chemical shift reagents provide the most powerful method of increasing the resolution. Page and Bresler⁽¹⁰⁶⁾, in their determination of the molecular weights of poly(ethylene) and poly(propylene) glycols, obtained better resolution when they used pyridine heated with a small amount of HCl gas as NMR solvent. Benzene and chloronaphthalene were reported to improve

the resolution of groups near the end of the polymer chain⁽¹⁰⁷⁾. The more effective and most widely used shift reagents are the lanthanide complexes which are soluble in NMR solvents. Europium (II) complexes such as those with dipivalomethane (DPM) or those in which the methyl groups are replaced partially or completely by trifluoromethane (fluoroform), are the most frequently used. In these complexes the paramagnetic Europium (III) ion complexes with the compound and induces enormous down field shift in its resonance. This effect is particularly felt by the end groups⁽¹⁰⁸⁾ Up field shifts can also be achieved by using praseodymium instead of Europium⁽¹⁰⁹⁾

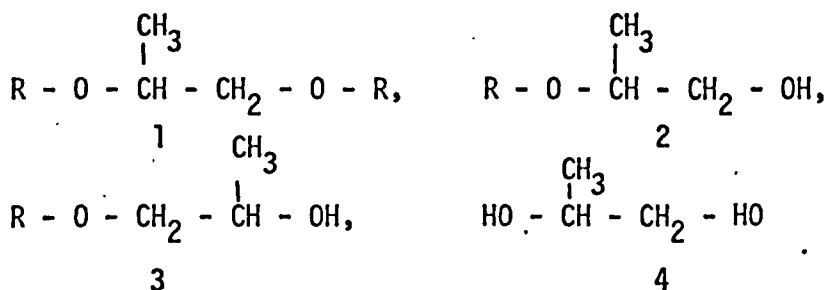
2.2.2 Analysis of Unsaturated Polyesters by Nuclear Magnetic Resonance Spectroscopy

In this work high resolution nuclear magnetic resonance spectroscopy was used to study reactions involved in the synthesis of unsaturated polyesters by a two-stage process. A Perkin Elmer R-30 spectrometer (90 MHz) was utilized to estimate the extent of ester-interchange and polycondensation in reactions performed on the prepolymers, bis (hydroxypropyl) terephthalate and bis (hydroxypropyl) isophthalate, produced in the first stage. Later a Varian Associates SC-300 Fourier Transform (F.T) spectrometer (300 MHz) was employed to follow certain aspects in the second-stage reactions such as the losses in unsaturation, maleate/fumarate transformations, and the type of sequences formed in the polymer chain structure. The 300 MHz Fourier transform (F.T) spectrometer has the advantage of producing well resolved spectra from sample concentrations which were found to be too low for the application of the 90 MHz NMR spectrometer. These spectra revealed useful information on the different environments of the chain protons.

Prepolymer analysis:

Spectra obtained for propylene glycol, bis (hydroxypropyl) terephthalate (PTR) and its higher oligomers (in CDCl_3 , and DMSO-d_6) confirmed the absorption assignments suggested by Kyriacos⁽²¹⁾. He used propylene glycol, isopropanol, propylene 1,2 dibenzoate as model compounds to confirm the assignment of proton groups, i.e. methyl, methylene, methine, to the observed chemical shifts in spectra recorded for $(\text{PTP})_1$ and $\text{P}(\text{TP})_n$. The combined inductive effect of hydroxyl and ester groups

in different possible structures in the prepolymers can be investigated in the following sequences:



Electronegative groups withdraw electron density from the proton groups (inductive effect) and this deshielding effect means that a lower value of the applied magnetic field is needed to bring the protons to resonance. As the electronegativity of the function is increased the protons come to resonance at higher δ values (down field). Experimental results and considerations of the inductive effect made it clear that the absorptions of the methyl groups shift from low to high field in the same order as the structures cited above from 1 to 4, as shown in Table 2.2.1.

TABLE 2.2.1

Structure	Chemical Shifts
1. $\begin{array}{c} \text{CH}_3 \\ \\ \text{R} - \text{O} - \text{CH} - \text{CH}_2 - \text{O} - \text{R} \end{array}$	A doublet at 1.46-1.53 ppm
2. $\begin{array}{c} \text{CH}_3 \\ \\ \text{R} - \text{O} - \text{CH} - \text{CH}_2 - \text{OH} \end{array}$	A doublet at 1.3-1.36 ppm
3. $\begin{array}{c} \text{CH}_3 \\ \\ \text{R} - \text{O} - \text{CH}_2 - \text{CH} - \text{OH} \end{array}$	A doublet at 1.18-1.25 ppm
4. $\begin{array}{c} \text{CH}_3 \\ \\ \text{HO} - \text{CH}_2 - \text{CH} - \text{OH} \end{array}$	A doublet at 1.09-1.16 ppm

Absorptions of methyl protons in $\text{P}(\text{TP})_n$

For the methylene groups the sequence of decreasing inductive effect was proved to be in the order

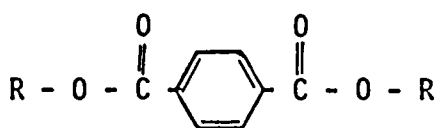
Structure 1 (a doublet at 4.52-4.57 ppm) > Structure 3 (a doublet at 4.15 ppm) > Structure 2 (a doublet at 3.78-3.84 ppm) > Structure 4 (a doublet at 3.4-3.6 ppm).

The order of the methine groups follows the same order as in methyl groups shown in Table 2.2.1.

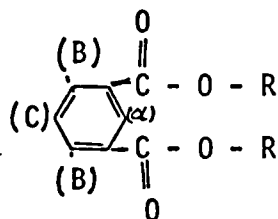
- 1) A doublet at 5.58 ppm.
- 2) A doublet at 5.0-5.2 ppm.
- 3) A doublet at 4.0 ppm.
- 4) A doublet at 3.7-3.9 ppm.

The hydroxyl groups are concentration dependent and are found mostly in the region 3-4 ppm while the phenyl protons signal appears at 8.11 ppm.

In this work the spectra of bis (hydroxypropyl) isophthalate were found to follow the same assignments for all the proton groups (Figure 2.2.1). An exception is the phenyl proton group which lack the magnetic equivalence present in the terephthalic ring.



equivalent protons



non-equivalent protons

The chemical environments for propyl protons are essentially the same for both terephthalic based and isophthalic based prepolymers. The ring protons in the isophthalate prepolymers show three regions of absorption. From the integral traces and inductive effect considerations proton (α) is the most deshielded absorbs at (8.55-8.65 ppm), with an integral value of (1.25 cm), proton (C) is least deshielded and absorbs at (7.45-7.65 ppm) with an integral value of (1.25 cm) and finally protons(B) of equivalent magnetic environment absorb at (8.1-8.3 ppm) with an integral value of (2.5 cm). (Figure 2.2.2).

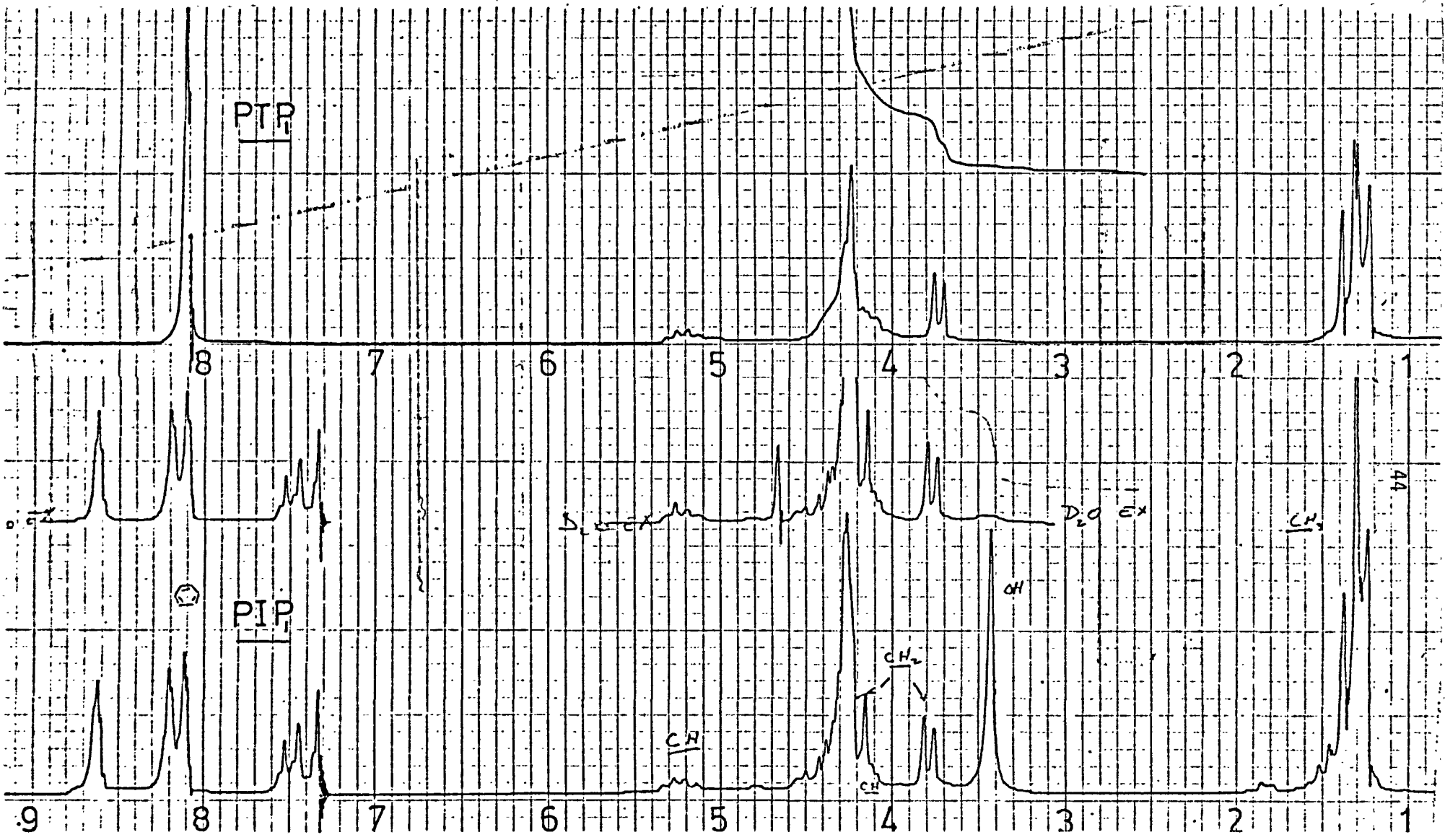


FIGURE 2.2.1 90 MHz NMR spectra of PTP₁ and PIP₁

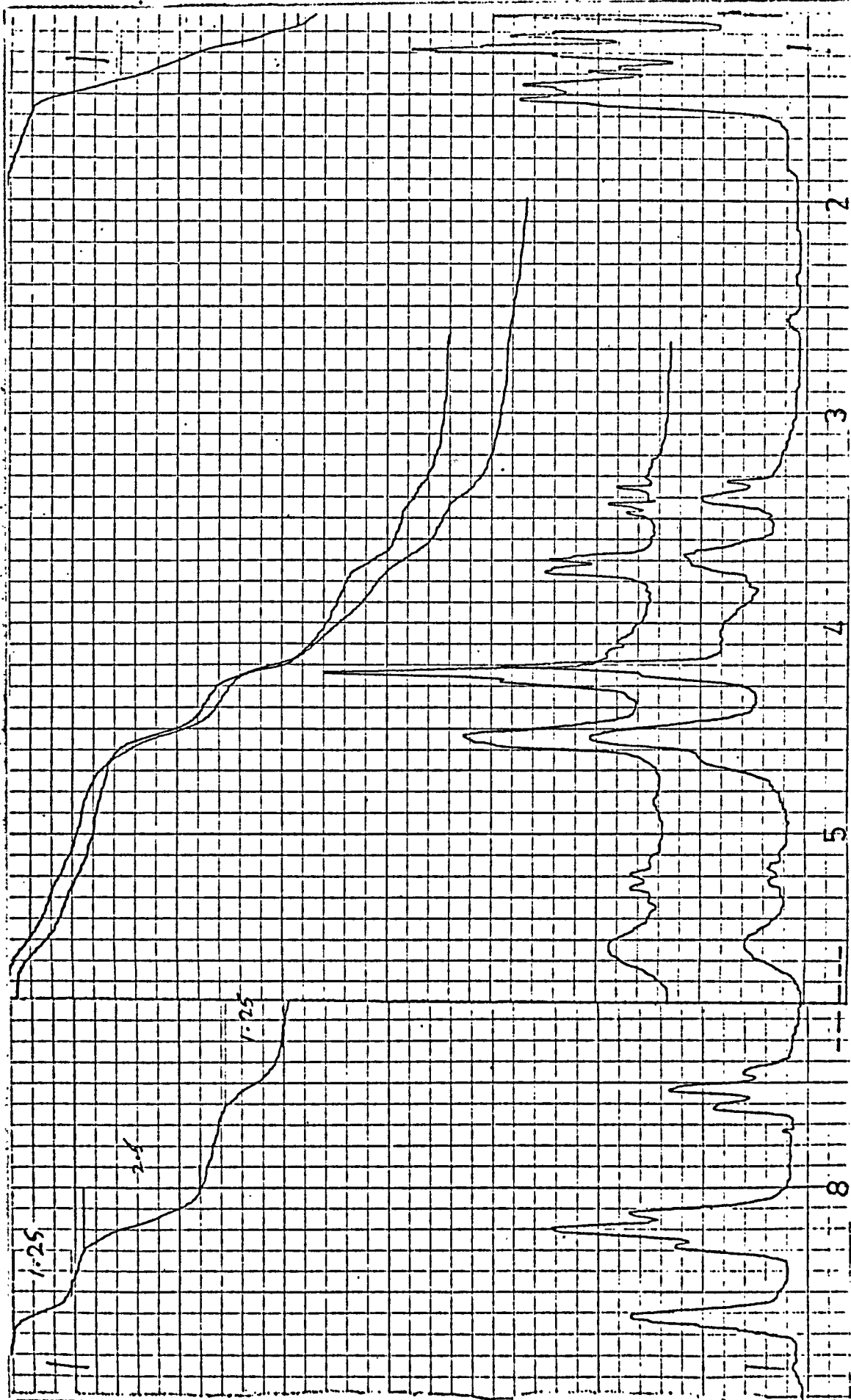


FIGURE 2.2.2 90 MHz NMR spectrum of PIP₇

Unsaturated polyester analysis:

The chemical shifts in unsaturated polyesters follow the same logic presented for the prepolymers. However, the unsaturated polyester spectra are complicated by incorporating into the prepolymer picture an additional unsaturated component. The resulting diversification in chemical shifts is not without its merits in the elucidation of the polymer chain structure. This depends strongly on the differences in the influence of aliphatic and aromatic acids on the chemical shifts of protons in the polymer. The role of the aromatic component in organic compounds analysis by NMR spectroscopy is widely reported in the literature⁽¹⁰⁹⁾. In aromatic compounds the ring π -electrons are delocalized cyclically over the aromatic ring. A circulation of these delocalized electrons, induced by the applied field, produces a substantial electric current (the ring current). The induced field (cyclization effect) is diamagnetic in the centre of the ring (opposing the applied field), whereas the returning reflux is paramagnetic (augmenting the applied field). So protons around the periphery of the ring experience an additional magnetic field and consequently come to resonance at higher δ values (down field). An example of this effect is the resonance of methyl protons in toluene at 2.34 δ whereas a methyl group attached to an acyclic conjugated alkene appears at 1.95 δ . The greater deshielding influence of the ring current in aromatic compounds compared to the deshielding effects of conjugated alkenes is so important that NMR has become one of the principal criteria in deciding whether an organic compound has substantial aromatic character⁽¹⁰⁹⁾.

The effect of the aromatic component was verified experimentally in the NMR spectra of the products of the polymerization of propylene glycol with maleic anhydride (Figure 2.2.3). Methyl, methylene, and methine protons are shifted up field as compared to those in bis (hydroxy propyl) terephthate prepolymers. It is clear that the product giving the spectrum in Figure 2.2.3 has no free propylene glycol (no methylene and methine absorptions of propylene glycol), but, still the methyl groups of lowest δ values give a doublet at 1.1-1.15 ppm. From the basic assumptions of inductive effects, the structure containing these methyl protons should be experiencing the minimum "deshielding effect" in the system:-

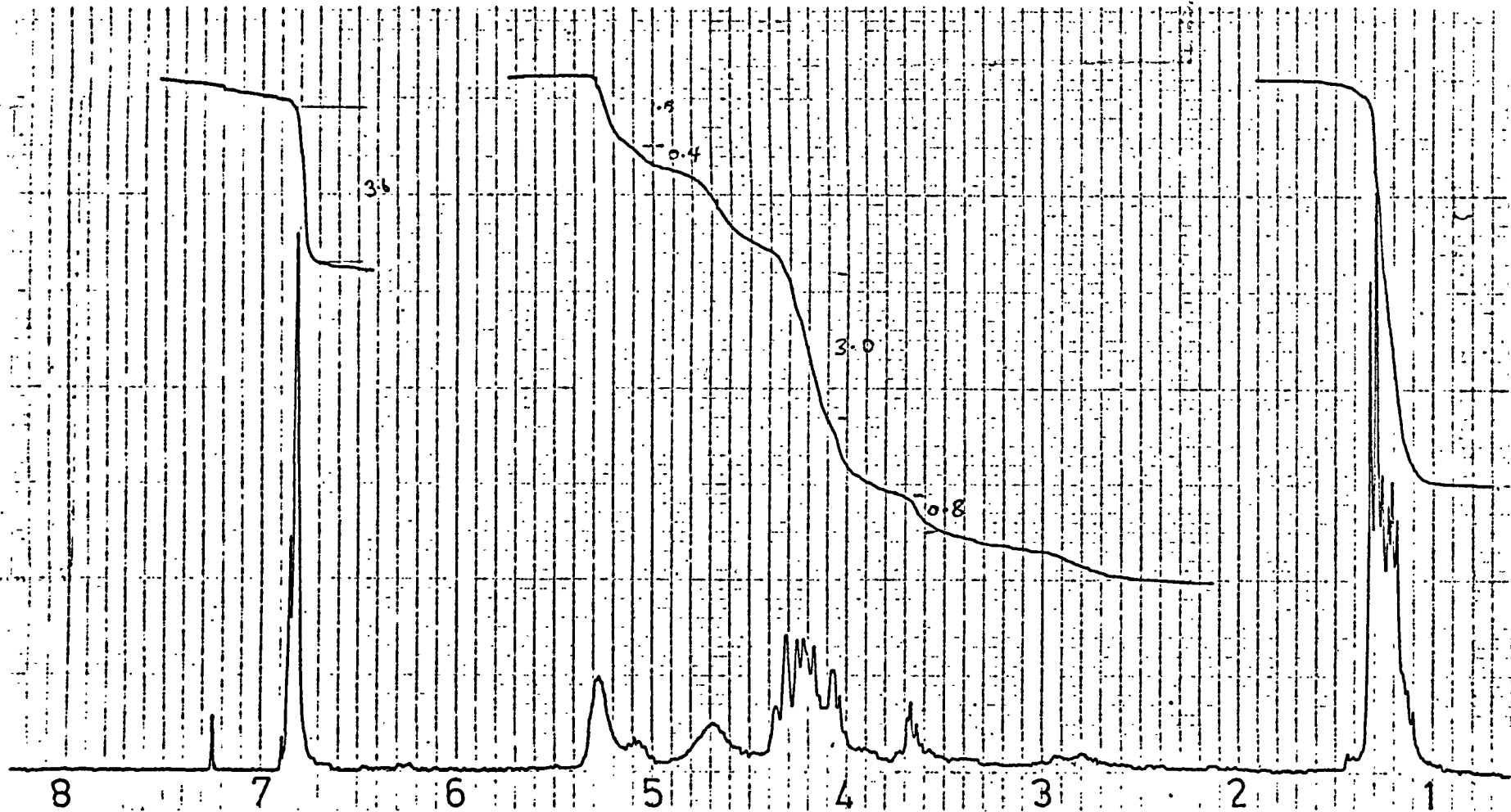
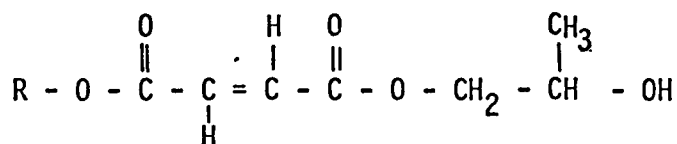
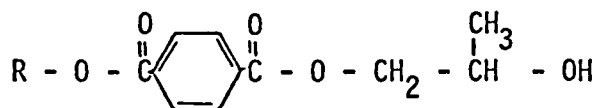


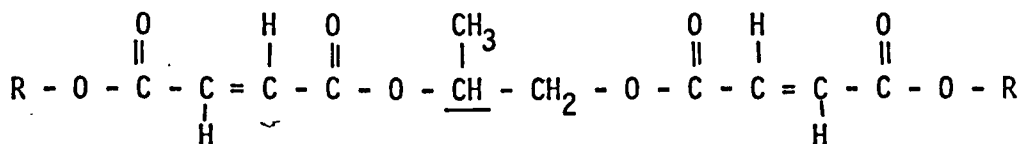
FIGURE 2.2.3 300 MHz NMR spectrum of the product of (1 PG:1M) at 150°C for 5 hours (reduced)



which corresponds, in bis (hydroxypropyl) terephthalate to:



which absorbs at 1.18 - 1.25 ppm. The methylene protons signal in this case are shifted from 4.15 ppm (for PTP₁) to 4.05 ppm in propylene glycol/maleic anhydride system. If the propylene glycol is secondary linked to maleic acid, the methine protons appear at 5.0 ppm while, in terephthalate (or isophthalate) based prepolymer they appear at 5.1 - 5.2 ppm. Even bigger shifts in the absorption of methine protons are shown when the propyl part is flanked between two unsaturated acid species:



In Figure 2.2.3) the integrals of this spectrum suggest that the multiplet at (5.0 ppm) with an integral value of (0.4 cm) is due to the methine protons in secondary-linked propylene glycol to maleic acid, of which the methylene protons absorb at 3.7 ppm with an integral value of 0.8 cm. The peak at 5.2 - 5.3 ppm could therefore be assigned to methine protons (integral 1.5 cm) situated in a propyl part flanked by two unsaturated acid species in which the methylene protons absorb at 4.18 - 4.3 ppm with an integral value of 3.0 cm. A summary of assignments for poly (propylene maleate) in δ values is shown in Table 2.2.2.

TABLE 2.2.2
NMR peaks of poly propylene maleate

Structure	Chemical Shifts		
	Methyl	Methylene	Methine
$\begin{array}{c} \text{O} \quad \text{CH}_3 \\ \parallel \quad \\ -\text{R}-\text{C}-\text{O}-\text{CH}-\text{CH}_2-\text{OH} \end{array}$	1.2-1.3	3.7	5.0
$\begin{array}{c} \text{O} \quad \text{CH}_3 \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{R}-\text{C}-\text{O} \quad \text{CH} \quad -\text{CH}_2-\text{O}-\text{C}-\text{R} \end{array}$	1.3-1.4	4.18-4.3	5.2
$\begin{array}{c} \text{O} \quad \text{CH}_3 \\ \parallel \quad \\ \text{R}-\text{C}-\text{O}-\text{CH}_2-\text{CH}-\text{OH} \end{array}$	1.1-1.15	4.05	4.0

Unsaturated polyester (PTP, 1 PG/MA):

The spectrum of a polyester prepared from PTP₁ and maleic anhydride in the presence of free propylene glycol (Figure 2.2.4) displayed four different peaks in the region 5-5.58 ppm, with the maximum intensities at 5.05 ppm, 5.2 ppm, 5.4 ppm and 5.55 ppm. These are in the resonance region of methine groups. From previous discussions the following assignments in Table 2.2.3, are possible:

TABLE 2.2.3

Chemical Shifts	Methine Protons
At 5.05 ppm	Methine groups of the propylene glycol end, secondary-linked to either acid (5.1 ppm, 5.0 ppm)
At 5.2 ppm	Methine groups in between two unsaturated acid species in the polymer chain (-MPM-)
At 5.55 ppm	Methine groups in between two saturated acid species in the polymer chain (-TPT-)

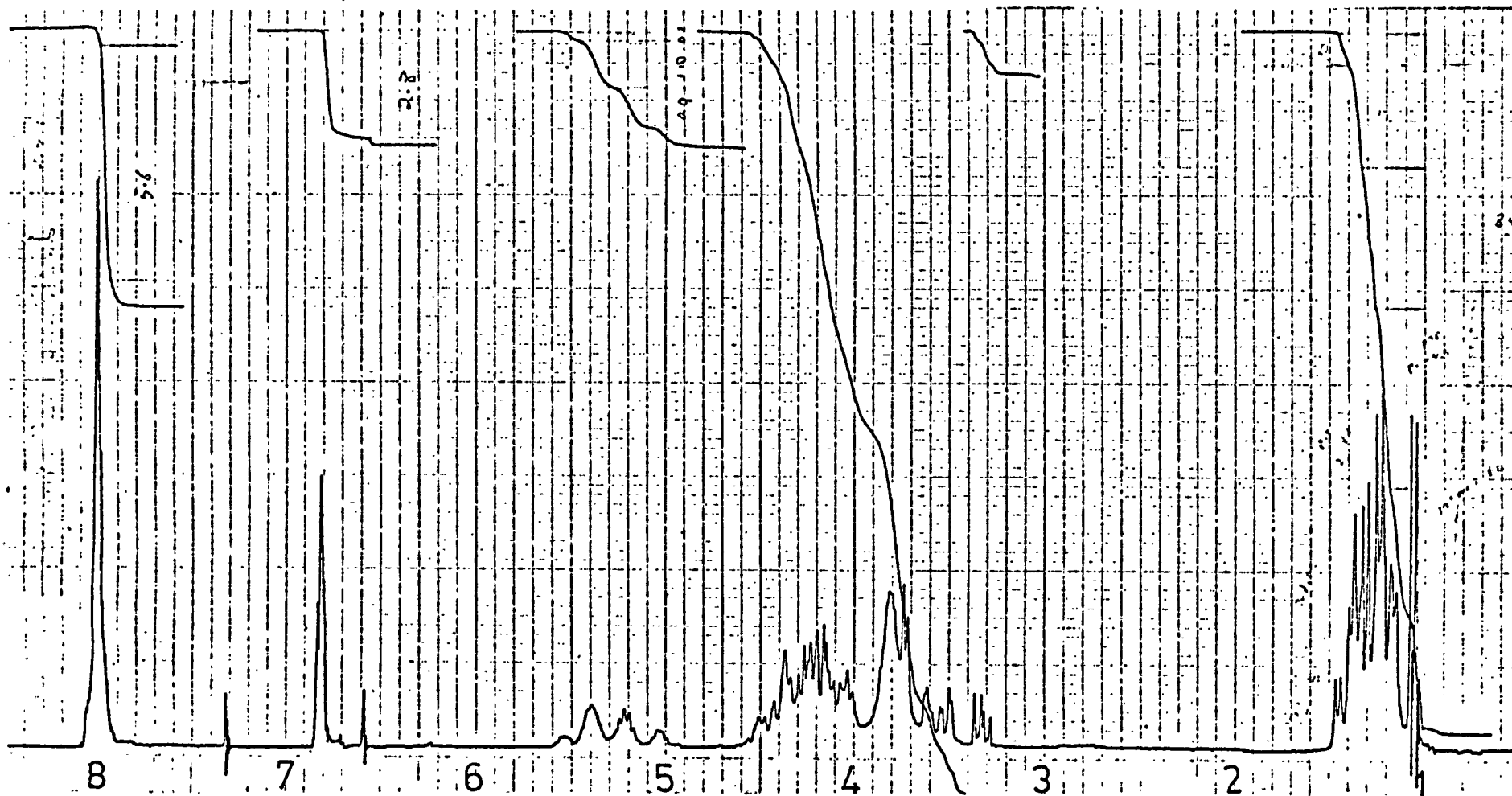


FIGURE 2.2.4 300 MHz NMR spectrum of propylene glycol/PTP₁/maleic anhydride product

We are only left with the peak of greatest integral value (1.1 cm) suggesting that its occurrence is predominant in the polymerization reaction. Its chemical shift (5.4 ppm) suggests that the deshielding effect encountered by this group is greater than the methine groups of free propylene glycol ends or those of methine groups between two unsaturated acid species. It is, however, less deshielded than those methine protons situated between two saturated acid species in the polymer chain (5.55 ppm). The only possible assignment according to these observations is that this peak is due to the resonance of methine groups between a saturated and an unsaturated acid species in the polymer chain (-MPT-). It follows, therefore, that the peak at 4.3-4.45 ppm falling in between methylene groups of (-MPM-) and (-TPT-) is due to the methylene groups of (-MPT-). Consequently, the methyl protons for (-MPT-) are those which absorb at 1.4-1.46 ppm (between -MPM- and -TPT- methyl groups).

The same reasoning holds for polyesters based on isophthalic acid in assigning proton groups to different chemical shifts.

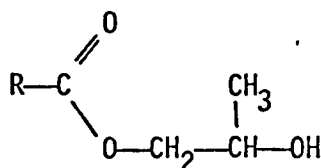
2.2.3 Quantitative Analysis

Quantitative analysis data were based on the utilization of the assignments made for different chemical shifts in NMR spectra of unsaturated polyesters and their prepolymers. The areas under the peaks (in the form of integrated traces) were measured and compared for protons in different environments. A theoretical accuracy of 5% (or less) is normally assigned for those integrals but a number of factors mitigate against this accuracy. In a spectrum of a specific compound the net absorption of radio frequency energy in an NMR experiment depends on relaxation times (which may not be the same for all polymer molecules), and on the rate of scan and the intensity of the radio frequency source⁽⁹⁶⁾. The effects of these factors are minimized if the comparison of integral values in one spectrum is confined to the same spectrum and not stretched to include comparisons with integrals of other spectra. High resolution 300 MHz can add to the accuracy by lessening the overlap of adjacent peaks. However, fair agreements were found by Urmann et al⁽⁹⁴⁾ and Kyriacos⁽²¹⁾ between quantitative results obtained by NMR and other characterization methods,

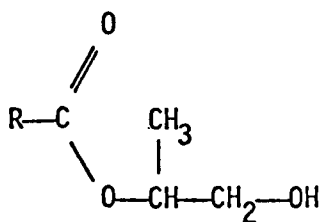
the results from NMR spectroscopy analysis were found to be more reliable and were easy to obtain.

Prepolymer:

In this work the prepolymers used in the synthesis of unsaturated polyesters were bis (hydroxypropyl) terephthalate (PTP₁) and bis (hydroxypropyl) isophthalate (PIP). From the NMR spectra of these prepolymers the ratios of primary to secondary-linked ends were determined according to the absorptions and integrals of their respective methyl protons.



Primary-linked



Secondary-linked

The extent of polycondensation and the loss of propylene glycols, when the prepolymers tended to form higher oligomeric species, were calculated by a simple procedure. The phenyl protons were taken as an internal standard as they are stable at the highest temperatures used (180°C), and virtually inert to the type of reactions taking place. The integral values of methyl protons (or methylenes + methines) were compared to the integral values of the phenyl protons. For (PTP)₁ and (PIP)₁ the integral values for T (or I) to (P) should be in the ratio:

$$4 : 3 (\times 2)$$

when the prepolymers were changed to P(TP)_n and P(IP)_n the extent of polycondensation (and the loss of propylene glycol) was manifested

in a decrease in the integral values of (P). The general expression for the value of n is:

$$\frac{4n}{3(n+1)} = \frac{\text{phenyl integrals}}{\text{methyl integrals}}$$

The molecular weight (M) is determined from n with the relation:

$$M = 282 + (n-1) 206$$

Unsaturated polyester:

The high resolution 300 MHz NMR spectrometer is unmatched in the information it provides about the proportions of protons and their chemical shifts in spectra obtained for unsaturated polyesters. From the integrated traces quantitative estimates of the primary and secondary-isomers ratios of the unreacted prepolymer ends can be obtained offering a clear picture of the reactivity of these isomers especially in polymers of low molecular weights. Also a quantitative comparison can be made between free propylene glycol ends and those incorporated within the chain from the integrals of their methyl protons (or methylene + methine protons). Thus the extent of polymerization can be followed and polymer fractions formulae can be elucidated in conjunction with spectral data discussed before. The integral signals for methine protons give useful information about the ratios of different segments formed along the polymer chain.

Quantitative estimation of the loss of double bonds incurred in the polymerization process can be calculated by comparing the integrals for phenyl protons with integrals of maleic and fumaric double bond protons (6.35 ppm and 6.8 ppm respectively). The ratio of maleate/fumarate transformation can also be obtained by comparing their double bond protons integrals.

Simple expressions for molecular weight determination, similar to those attempted by Kyriacos for these systems assuming an intact prepolymer structure throughout the copolymerization reaction, are not possible. This is because of the big role of side reactions in these

polymerization processes. But, nevertheless, detailed consideration of spectral data yields valuable information about the environment of functional groups and units of unsaturation in these systems. Thus a reasonable picture of the sequence of these structural units in the polymer molecule may be envisaged.

CHAPTER 3

ESTER-INTERCHANGE AND POLYCONDENSATION OF
PREPOLYMERS BASED ON TEREPHTHALIC AND ISOPHTHALIC ACIDS3.1 Preparation of Bis (2-hydroxypropyl) TerephthalateReactants and Method

Analytical grades of propylene glycol and pyridine supplied by Fisons Limited, were used in these reactions without any further treatment. Analytical grade of chloroform, supplied by Fisons Limited, was purified by extracting the ethanol content, used as a stabilizer, from the chloroform using concentrated sulphuric acid. The chloroform was then washed with water to remove all the acid traces and stored over magnesium sulphate overnight before use.

Propylene glycol (313 ml) was charged into a 1 litre flask (Figure 3.1), provided with a stirrer, a condenser, and a dropping funnel, together with purified chloroform (132 ml) and pyridine (44 ml) as an acid-acceptor. The flask was heated on a water bath at 60°C and all the clear solution of terephthaloyl chloride (108g) in chloroform (230 ml) in the dropping funnel was allowed to mix gradually, dropwise, with the propylene glycol solution under continuous stirring. After 2 hours all the terephthaloyl chloride solution had been added and the reaction was left for a further 3 hours under continuous stirring at the same temperature (60°C). It was then left overnight at room temperature.

Purification and Characterization of Product

The same procedure followed here was used by Kyriacos⁽²¹⁾ and Higgins⁽³⁾ except that in the recrystallization of the product chloroform was used in this work instead of dichloroethane.

The reaction product was poured into water to give two layers. The aqueous layer, containing traces of propylene glycol, was separated and extracted twice with chloroform. All the chloroform layers were collected together and then washed with 3N hydrochloric acid to remove the pyridine, and the hydrochloric acid traces were removed

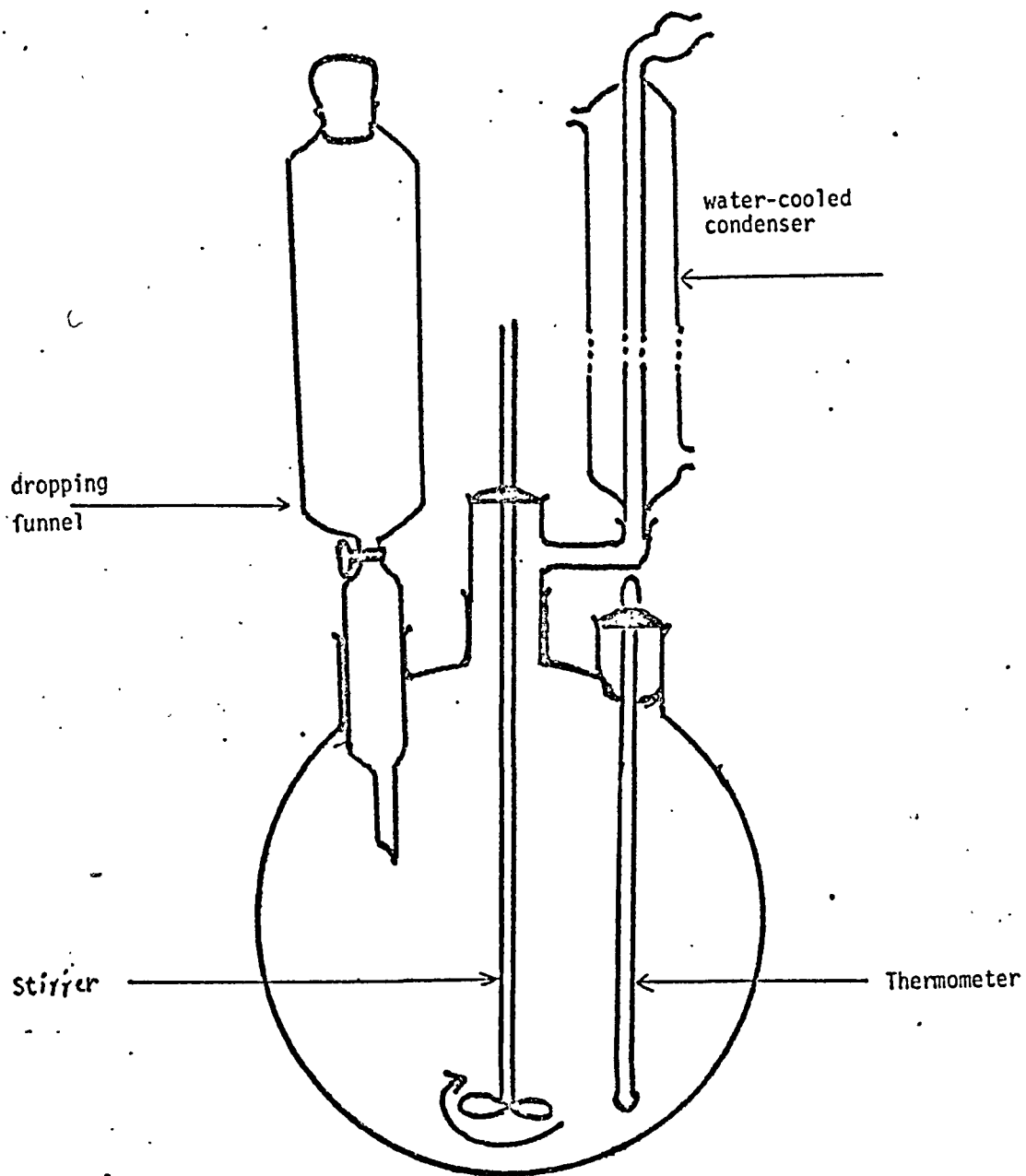


FIGURE 3.1

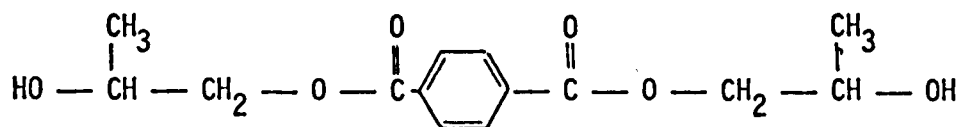
from the product solution by further washing with water until no acidity was found in the final washing. From the wet solution of bis (hydroxy propyl) terephthalate the chloroform/water azeotrope was distilled over. The viscous product was then dried for 5 hours at 70°C in a vacuum oven. The final product was then recrystallized twice from chloroform and dried. The final product was found to have a melting point of 141°C.

When the product was analysed by GPC it gave only one peak at elution volume 120 ml suggesting that the product was constituted of a single component, see Figure 3.2. The 90 MHz NMR spectrum obtained for the product, in Figure 3.3 showed the absorptions listed in Table 3.1.

TABLE 3.1
NMR Absorptions of the Prepolymer

Peaks	Chemical Shifts	Proton Groups
A doublet at	1.15 - 1.2 ppm	CH ₃ groups
A doublet at	4.15 - 4.25 ppm	CH ₂ groups
A multiplet at	3.9 - 4.1 ppm	CH groups
A singlet at	4.95 ppm	OH groups
A singlet at	8.15 ppm	phenyl protons

Following the assignments of NMR peaks as discussed in Section 2.2 in Chapter 2, the final product must have the following structure:



Bis (2-hydroxy propyl) terephthalate (PTP₁).

The isolated isomer prepared as described above will be represented by (PTP₁) and the ICI T400B product will be represented by P(TP)_n.

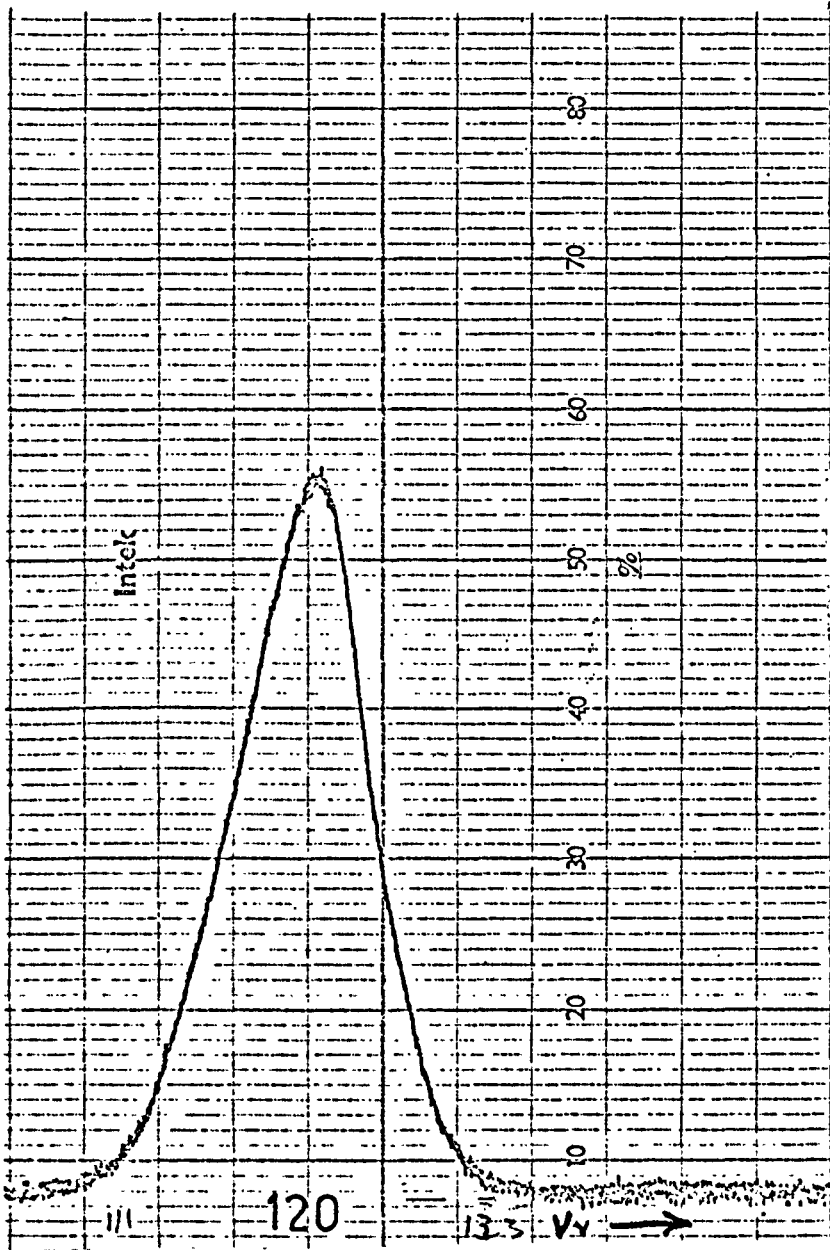


FIGURE 3.2

GPC Chromatogram of PTP₁

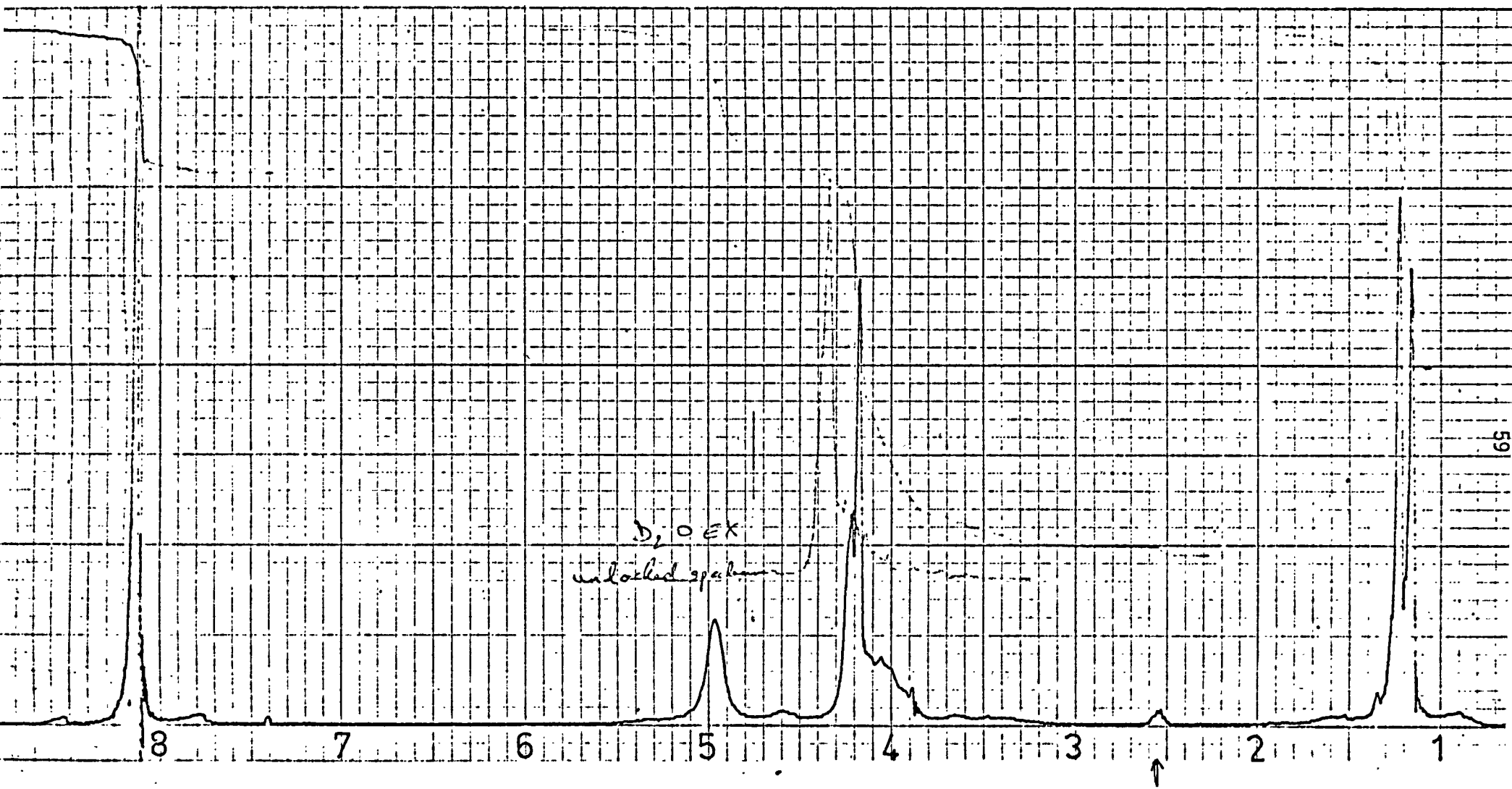


FIGURE 3.3 90 MHz NMR spectrum of PTP₁

peak due to DMSO-d₆

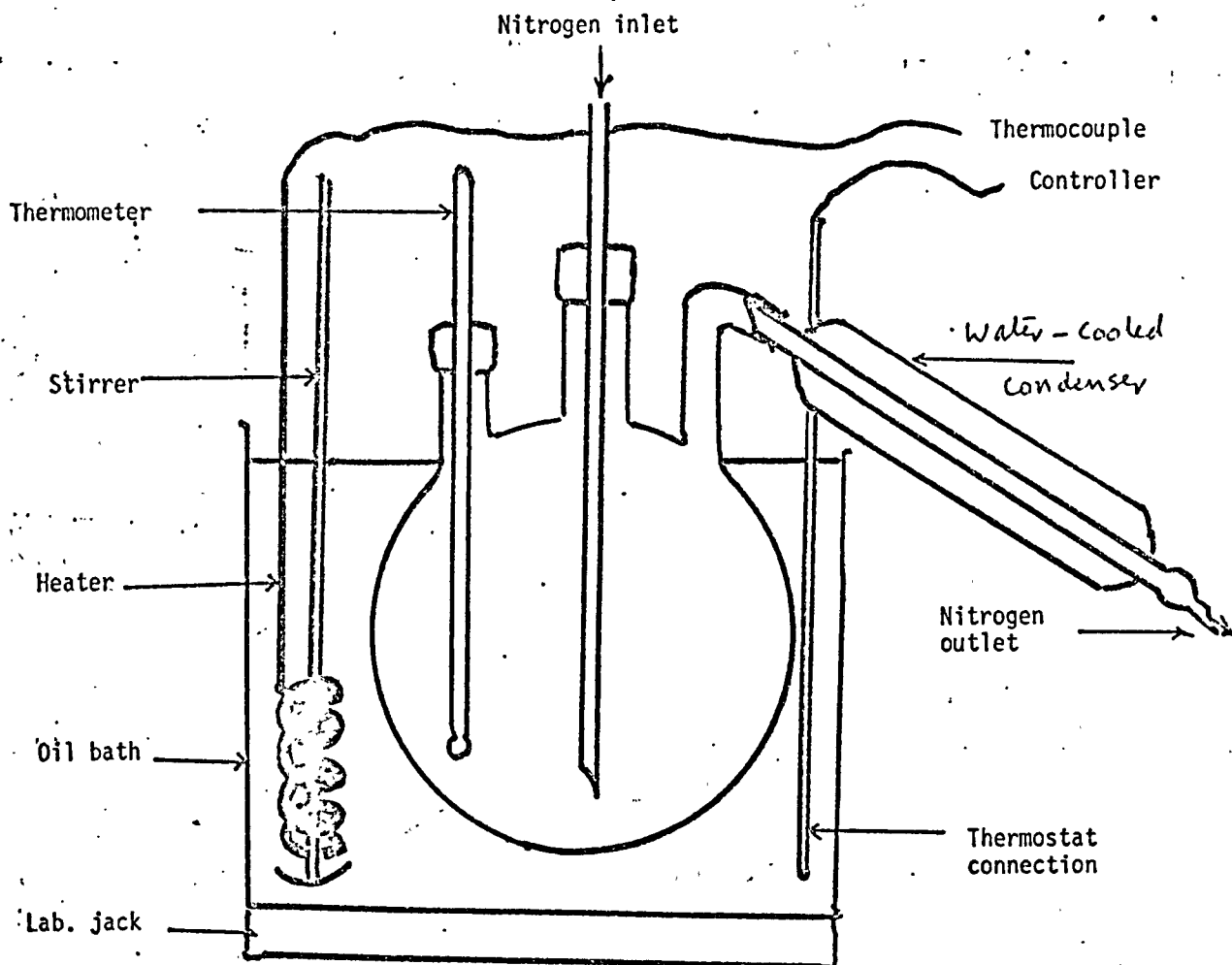


FIGURE 3.4

3.2 PTP₁ Heating Experiments

The aims of these experiments were to see whether PTP₁ will maintain its stereochemical structure under the influence of the intended polymerization temperatures and to investigate the possibility of ester interchange reactions leading to higher oligomers (P(TP)_n).

Apparatus and Method

A simple apparatus was devised to give rapid dissipation of heat and to avoid loss of material through excessive evaporation (Figure 3.4). A small polymerization vessel of 30 ml total capacity was used. It was adapted with ports for: a 250°C thermometer, a nitrogen inlet, a curved nitrogen outlet and a water-cooled condenser.

The characterized isolated PTP₁ in small quantity (2.0g) was placed in the vessel and heated by a thermostated oil bath under nitrogen at different constant temperatures in the range (150°C-180°C) for 5 hours and at particular temperatures for different times. The temperature in all these experiments was controlled within the range of ± 2°C. Also, the same experiments were repeated with ICI T400B (P(TP)_n) to examine the effect of temperature on this product. Both PTP₁ and P(TP)_n were heated for 5 hours at temperatures ranging from 150°C to 180°C. Samples from these products were run through the one column GPC and analysed by 90 MHz NMR spectrometer.

GPC Results of PTP₁ and P(TP)_n Systems

The product of heating PTP₁ for 5 hours at 150°C gave a GPC chromatogram, Figure 3.5, with more than 4 peaks which appear at elution volumes, 85, 90, 104 and 120 ml. The largest peak appears at the highest elution volume, an elution volume similar to that of PTP₁ (Figure 3.2). To confirm this observation, a sample of the same product with a small quantity of PTP₁ was applied to the GPC column. The resulting chromatogram showed an enhancement of the last peak (lowest molecular weight) appearing at 120 ml elution volume in Figure 3.6. This confirmed that the last peak in Figure 3.5 is PTP₁.

Subsequent batches of PTP₁ heated to 160°C, 170°C and 180°C for 5 hours were applied to the column and the chromatograms obtained are shown in Figures 3.7, 3.8 and 3.9 respectively. The chromatograms in

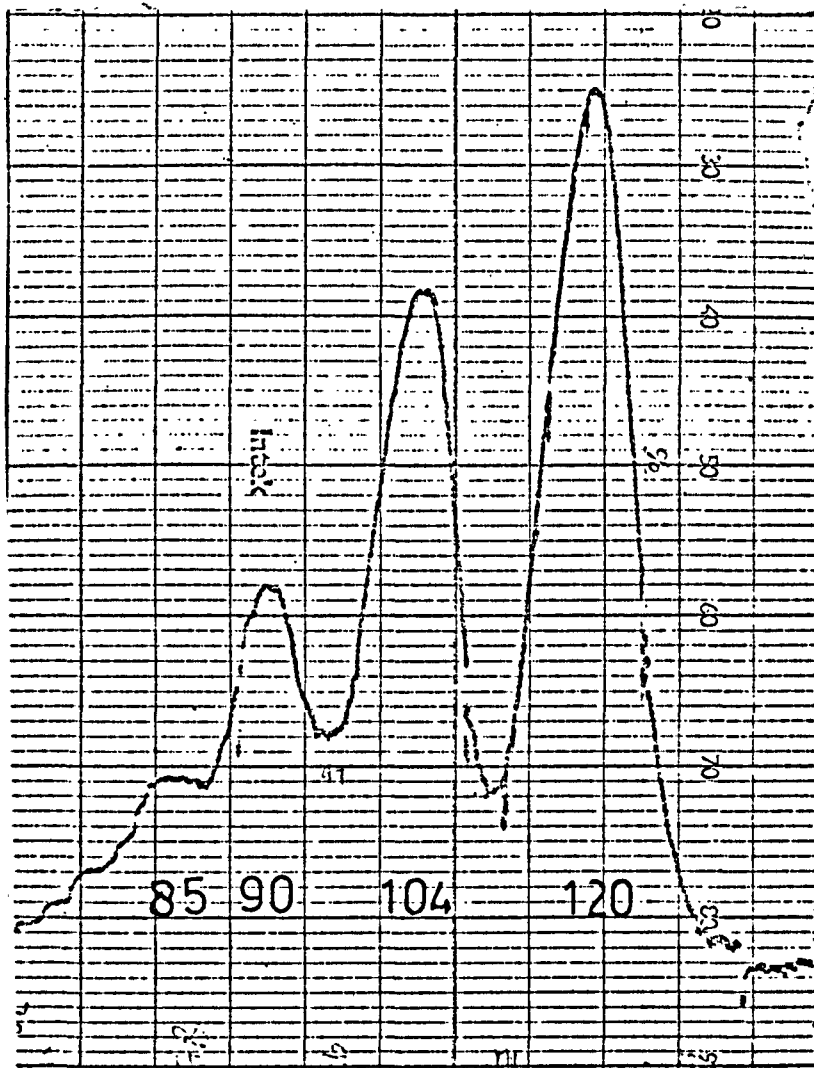


FIGURE 3.5 GPC Chromatogram of the product of PTP_1 at 150°C for 5 hours

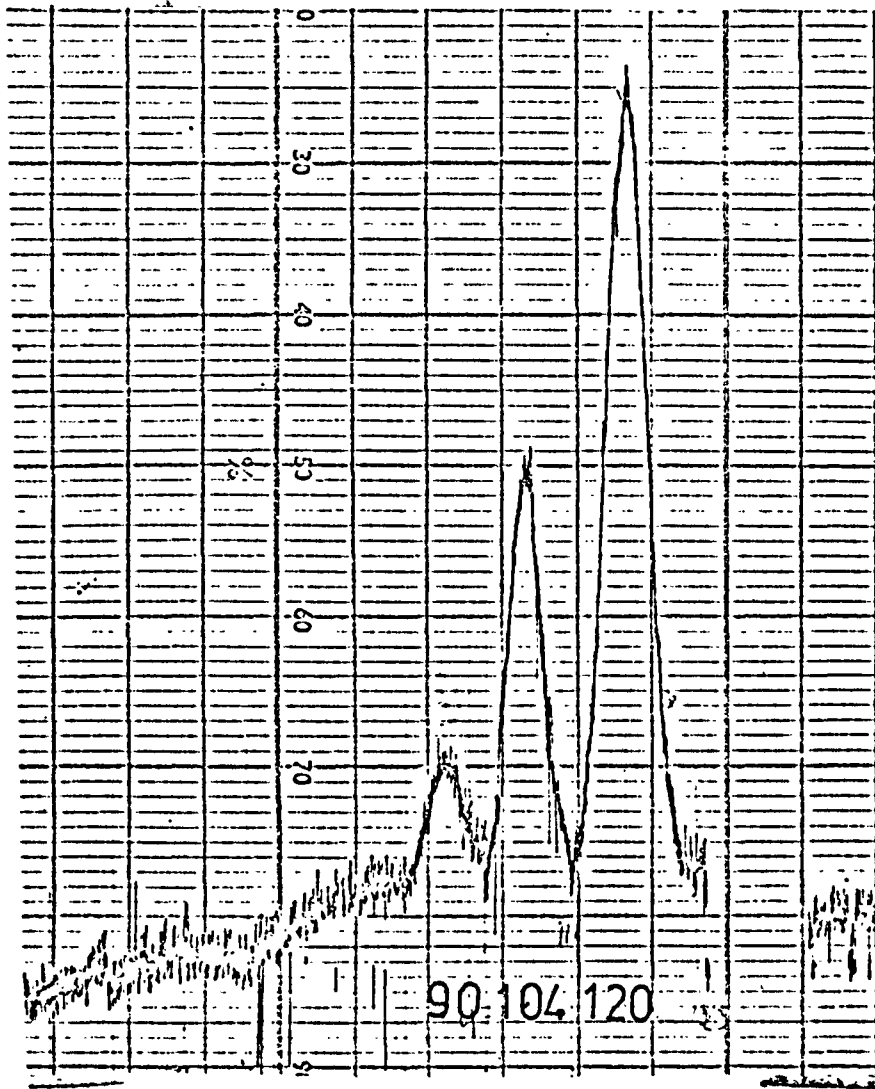


FIGURE 3.6 GPC Chromatogram of the production of PTP_1 at $150^{\circ}C$ for 5 hours + PTP_1

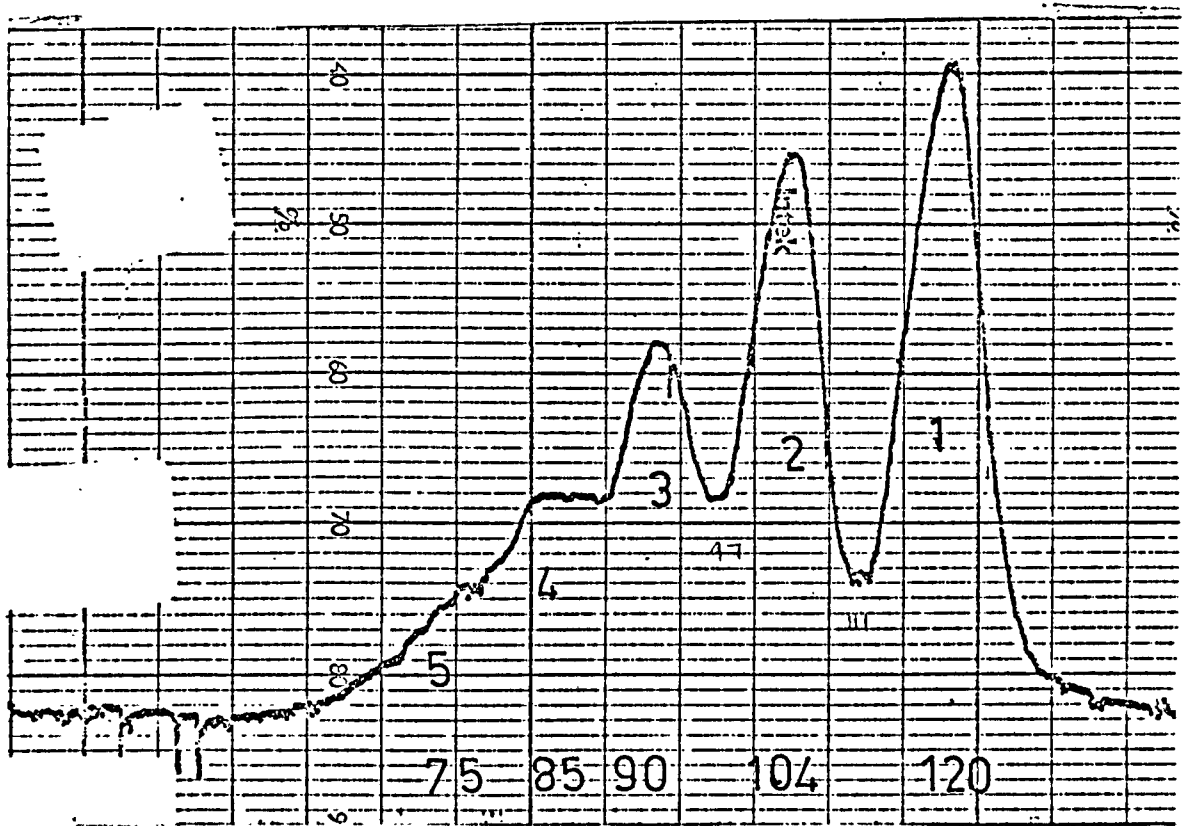


FIGURE 3.7 GPC Chromatogram of the product of PTP_1 heated at 160°C for 5 hours

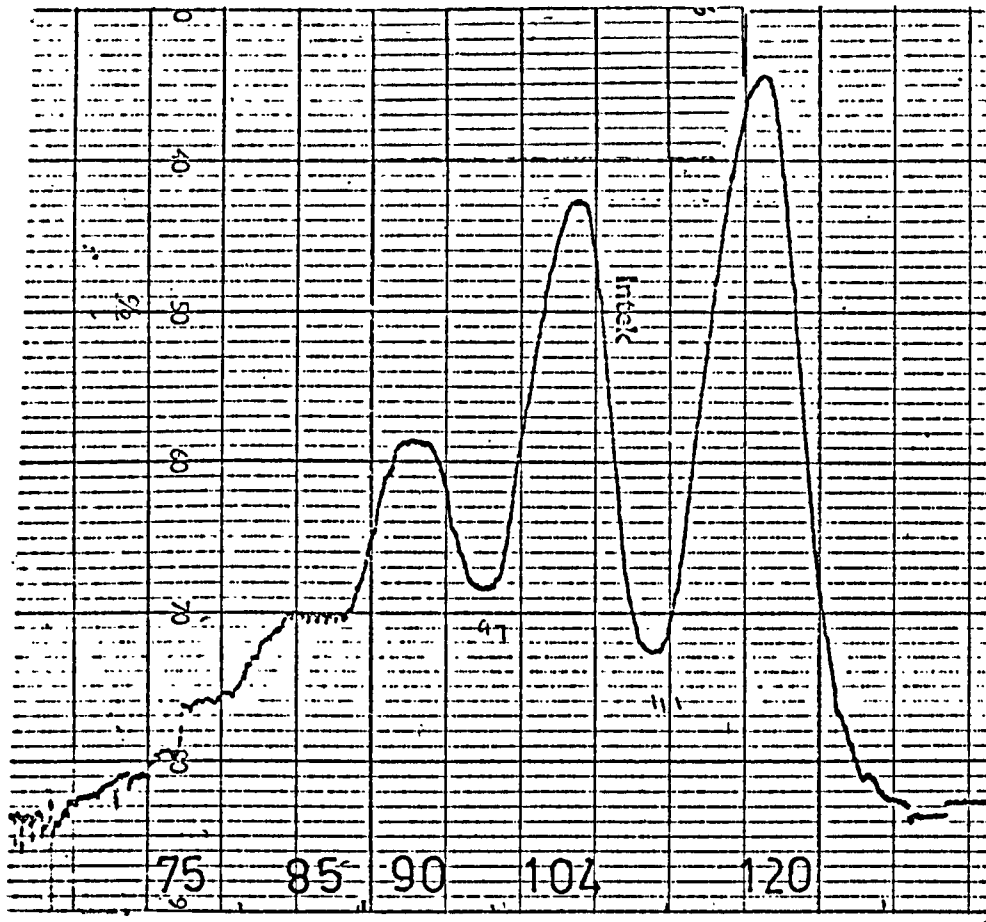


FIGURE 3.8 GPC Chromatogram of the product of PTP₁ heated at 170°C for 5 hours

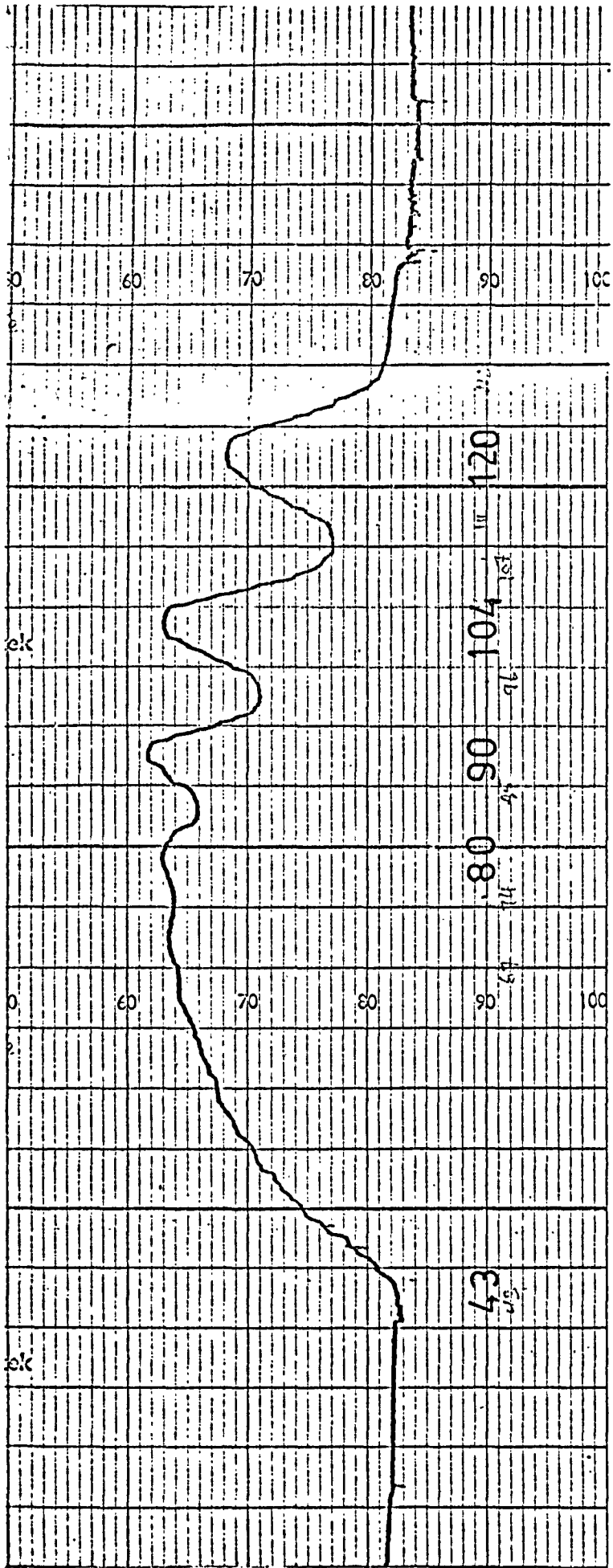


FIGURE 3.9 GPC Chromatogram of the product of PTP₁ heated at 180°C for 5 hours

Figures 3.7 and 3.8 showed the effect of temperature on the polycondensation of PTP_1 in the enhancement of the peaks appearing in the lower elution volumes i.e. 90, 85, and 75 ml. A gradual decrease of the peak corresponding to PTP_1 was noticed in these chromatograms, together with the increase in the number and size of the peaks corresponding to higher oligomers. The gradual change was noticed up to 170°C . However, at 180°C the polycondensation reaction was much faster and a greater change in molecular weight distribution of the product could be noticed. The chromatogram of the product of heating PTP_1 at 180°C can be seen in Figure 3.9. In this figure a broad peak of considerable size appears between the elution volumes range 43 ml and 80 ml. This broad peak appears at elution volumes much lower than the other peaks shown in the other products chromatograms and with considerable size. It could also be noticed that the peaks appearing at higher elution volumes, 90, 104, and 120 ml, are clearly reduced in size, especially the last peak which appears at elution volume similar to PTP_1 .

The ICI T400B product ($P(TP)_n$) was applied to the GPC column as received before any heating, and it produced a chromatogram indicating the presence of oligomers up to $P(TP)_4$, see Figure 3.10. The other samples of $P(TP)_n$ heated to 150°C , 160°C , 170°C and 180°C for 5 hours were applied to the column to give Figures 3.11-3.14 respectively. The chromatograms in these figures show peaks at elution volumes similar to those observed for PTP_1 products. Figure 3.11, chromatogram for the product of heating $P(TP)_n$ to 150°C for 5 hours, showed very little change, i.e. a slight enhancement of the peaks at elution volumes 90 and 85 ml can be noticed together with the appearance of a small shoulder for a fifth peak at elution volumes lower than 85 ml. At 160°C the chromatogram in Figure 3.12, a similar increase in the peaks of lower elution volumes over that of Figure 3.11, could be seen. At 170°C , Figure 3.13, the same gradual increase in the size of the peaks at lower elution volumes is also noticed. At 180°C , the chromatogram in Figure 3.14, showed a considerable change in the molecular weight distribution, greater enhancement was noticed for the peaks at the elution volume 90, 85, 80 ml, with an introduction of a small broad peak for the sixth peak.

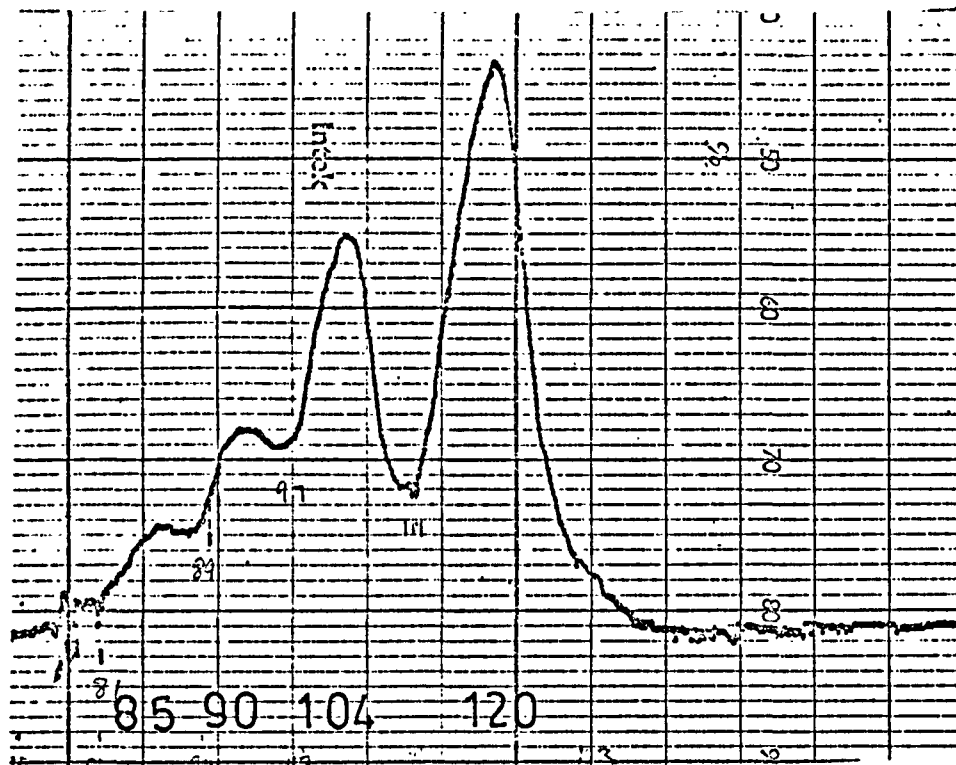


FIGURE 3.10 GPC Chromatogram of $P(TP)_n$ (T400B)

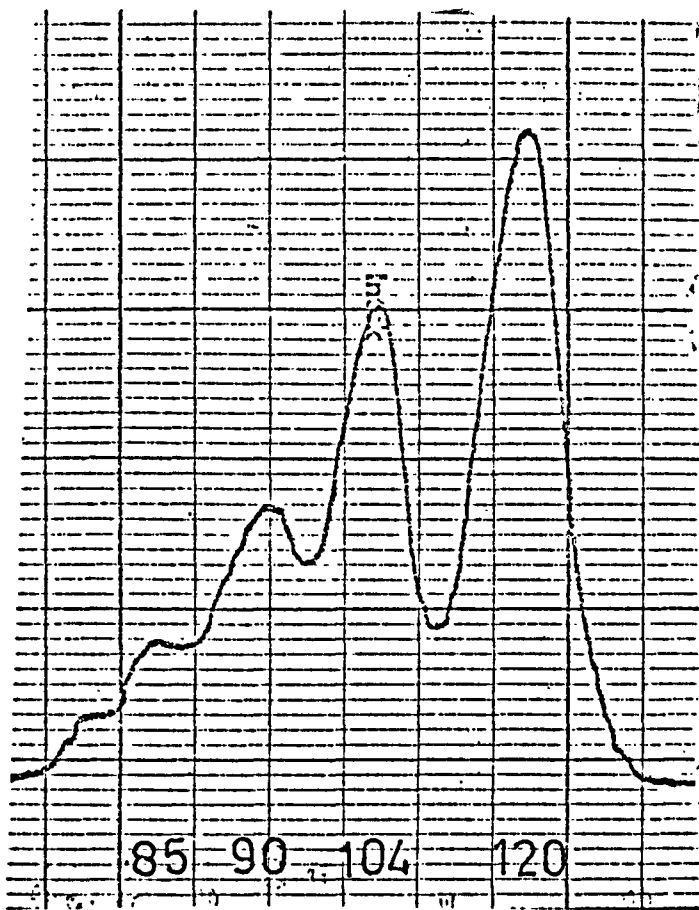


FIGURE 3.11 GPC Chromatogram of $P(TP)_n$ at 150°C for 5 hours

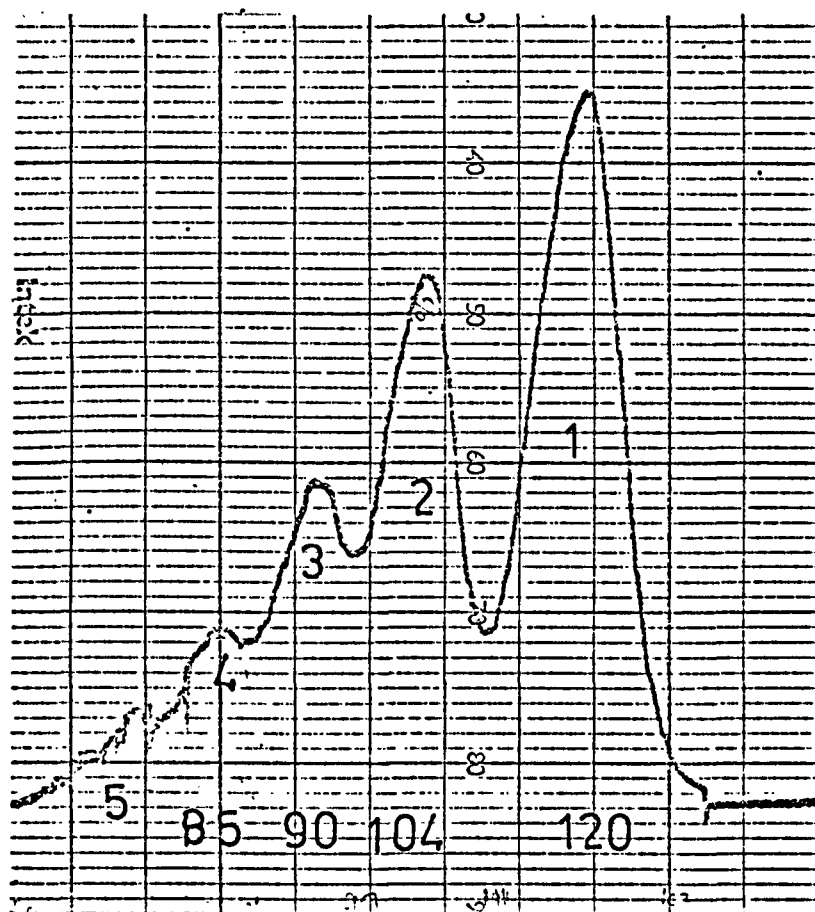


FIGURE 3.12 GPC Chromatogram of $P(TP)_n$ at 160°C for 5 hours

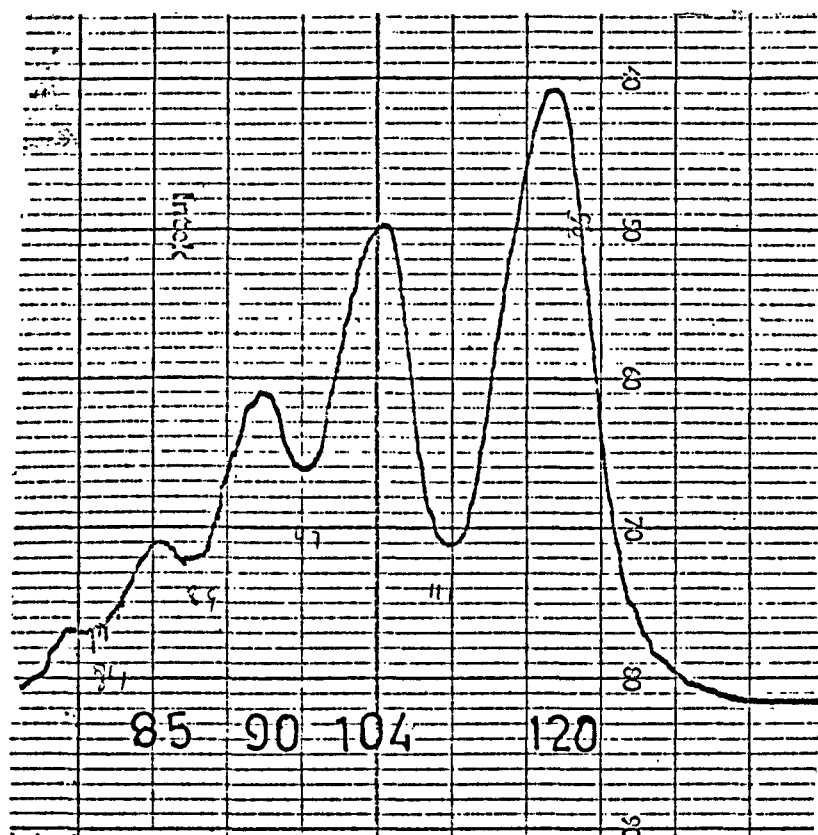


FIGURE 3.13 GPC Chromatogram of $P(TP)_n$ at 170°C for 5 hours

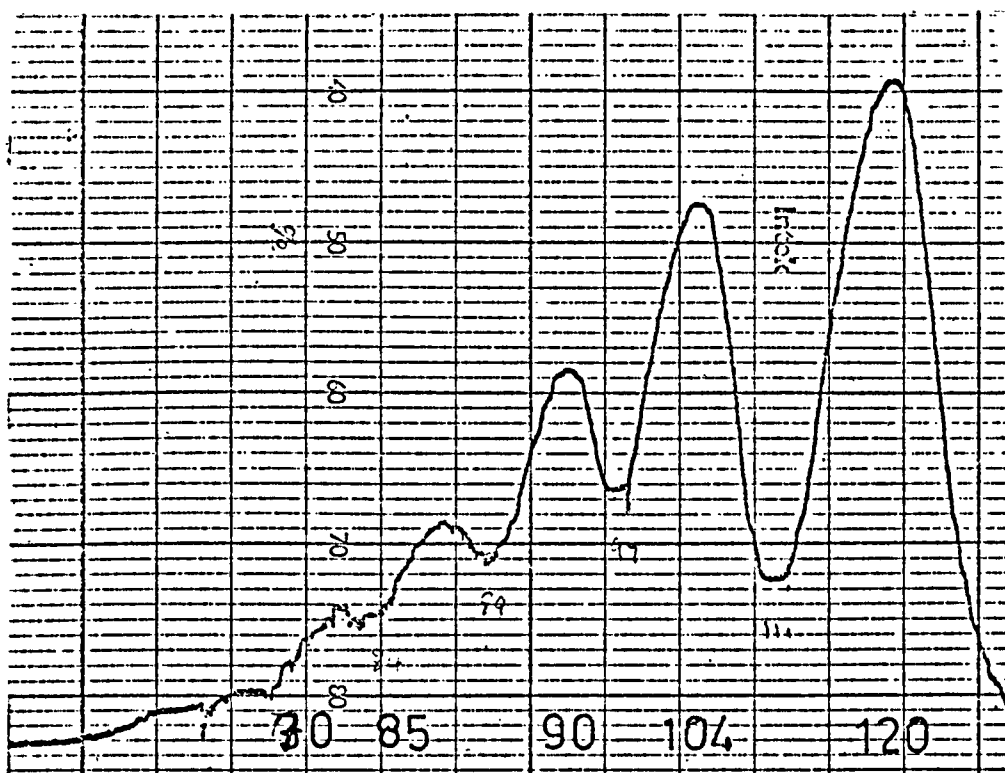


FIGURE 3.14 GPC Chromatogram of P(TP)_n at 180°C for 5 hours

In these chromatograms there was a noticeable increase in the number and size of peaks corresponding to high molecular weight species. But this increase was gradual without the sudden jump in the number and size of these peaks at 180°C as noticed for PTP₁ at 180°C. However, to show the compatibility of PTP₁ and P(TP)_n systems a sample of P(TP)_n heated at 150°C for 5 hours containing a small amount of PTP₁ heated for one hour at 150°C was applied to the GPC column giving the chromatogram in Figure 3.15 which confirmed their compatibility. The chromatogram produced peaks at the same elution volumes seen for these systems in the above described chromatograms. No partial overlapping was noticed and it could be noticed that the PTP₁ sample, which was heated for one hour at 150°C, enhanced the last peak eluted at 120 ml, (PTP₁), and the peak eluted at 104 ml (P(TP)₂). It could be suggested that despite the difference in the methods of preparation used for P(TP)_n and PTP₁, they produced on heating similar products. This implies that all species produced by the GPC have hydroxyl end groups.

In the products of the PTP₁ and P(TP)_n heating experiments there was a significant change in viscosity and a change of colour towards a dark brown colour.

NMR Analysis

Samples from the above PTP₁ heating experiments were examined by NMR. The 90 MHz NMR spectra are shown in Figures 3.16-3.19. From these spectra the following observations can be made.

An expected decrease was found in the prepolymer content of the (CH₃) groups as shown by the integrated traces for all the products of PTP₁ heating experiments. This was detected by measuring the integral traces of the methyl protons at 1.15-1.5 ppm, in the spectra shown in Figures 3.15-3.18. The integral values obtained were compared to the integrals measured for the phenyl protons at 8.15 ppm. The ratio of phenyl protons: methyl protons for the original (PTP₁) is 2:3.

If Figure 3.15, which shows the spectrum of the product of heating PTP₁ to 150°C for 5 hours, is considered, we find that:

The integral value of phenyl protons = 3.075 cm

The corresponding value for methyl protons in PTP₁ is:

$$= \frac{3.075}{2} \times 3 = 4.6125 \text{ cm}$$

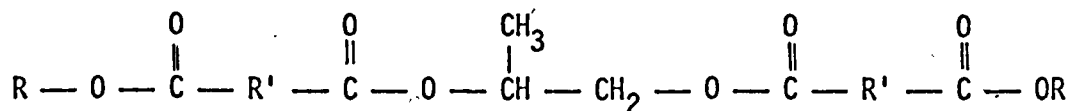
But the integral value measured for the methyl protons was:

$$= 4.15 \text{ cm}$$

The difference = 4.6125 - 4.15 = 0.4625 cm

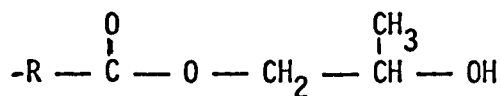
Therefore the loss in propylene glycol = $\frac{0.4625}{4.6125} \times 100 = \underline{10\%}$

The decrease in the methyl protons was also accompanied by an appearance of a new peak in the methyl protons absorption region at 1.5 ppm. According to the assignments of NMR peaks discussed in Chapter 2, this peak represents the methyl protons of the structure:

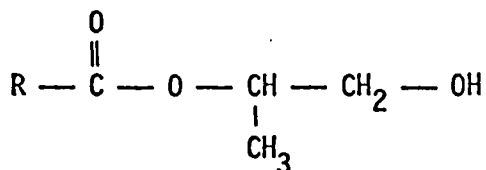


where R' is a terephthalate group.

In the original PTP₁ isomer the terminal propylene glycol ends were all in the primary position:



This was shown in the 90 MHz NMR spectra of this product shown in Figure 3.2. The spectra shown in Figures 3.15-3.18 indicate the presence of the secondary isomer which was brought about by ester-interchange reactions:



This is illustrated by the peaks occurring at 1.3-1.4 ppm for the methyl protons, peaks at 3.7 ppm for the methylene protons, and the methine protons absorptions at 5.1-5.2 ppm. The ratio of primary/secondary ends can be determined from the integral traces in the (methyl) or (methylene + methine) absorption regions. In the methylene and methine region, this can be calculated by comparing the integrals of methylene peaks at 3.7 ppm to the integral value of primary methylene protons. The latter can be related to the integrals obtained for the methylene and methine protons of the primary isomer between 3.9-4.25 ppm by the following ratio:

$$\frac{\text{integral trace (cm)} \times 2}{3}$$

Similarly, the ratio of internal (P) to terminal (P) can be calculated from this region. The terminal secondary isomer methylene protons are estimated from the integrals at 3.7 ppm, its methine protons ratio are estimated from the integral at the chemical shift 5.1-5.2 ppm which should give a value equal to half the value obtained for the methylene protons. The methine protons for internal (P) in these systems can be estimated from the integral of the peaks at 5.5 ppm, which are equal to (all the integral for methine absorptions at 5.0-5.5 ppm - the integral for secondary isomer methine absorptions). To determine the ratios of primary isomer methine and methylene protons: the integral at 3.9-4.25 ppm - 2 x integrals for the internal (P) methine protons

= total integral value for methylene and methine protons in the terminal primary isomer.

These are in the ratio of 2:1 respectively. The ratio of internal to external (P) can thus be determined by summing all the primary and secondary integrals in this region and comparing them to the total integral values of the terminal (P).

The spectra obtained for $P(TP)_n$ systems are shown in Figures 3.20-3.23. These spectra show an increasing intensity for the methyl protons peak at 1.5 ppm with the increase in the reaction temperature.

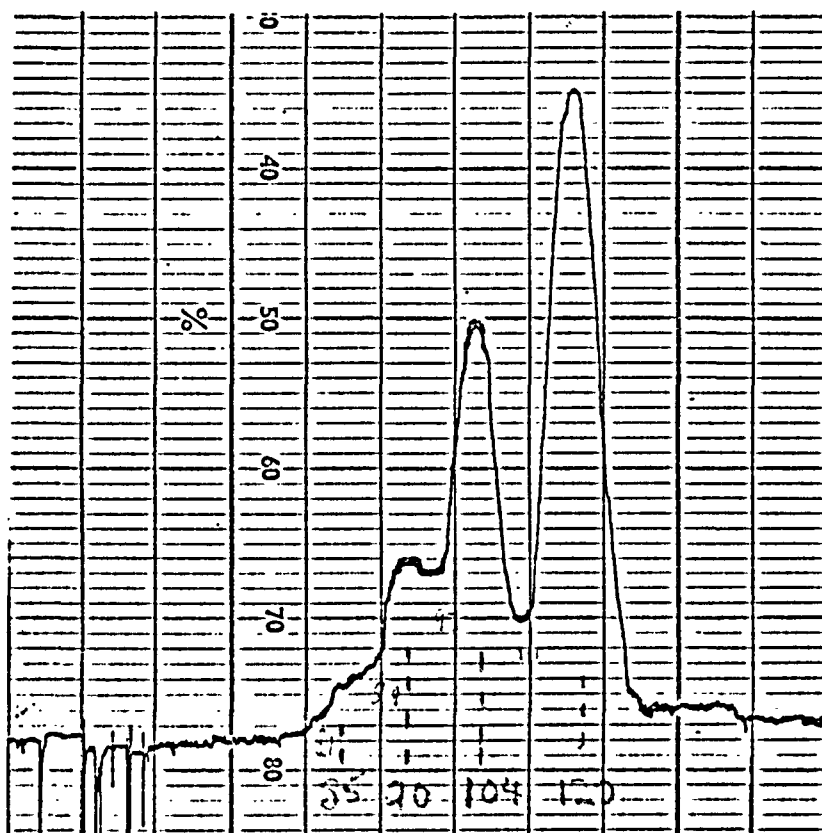


FIGURE 3.15 GPC Chromatogram of $P(TP)_n$ at 150°C for 5 hours + PTP_1 at 150°C for one hour

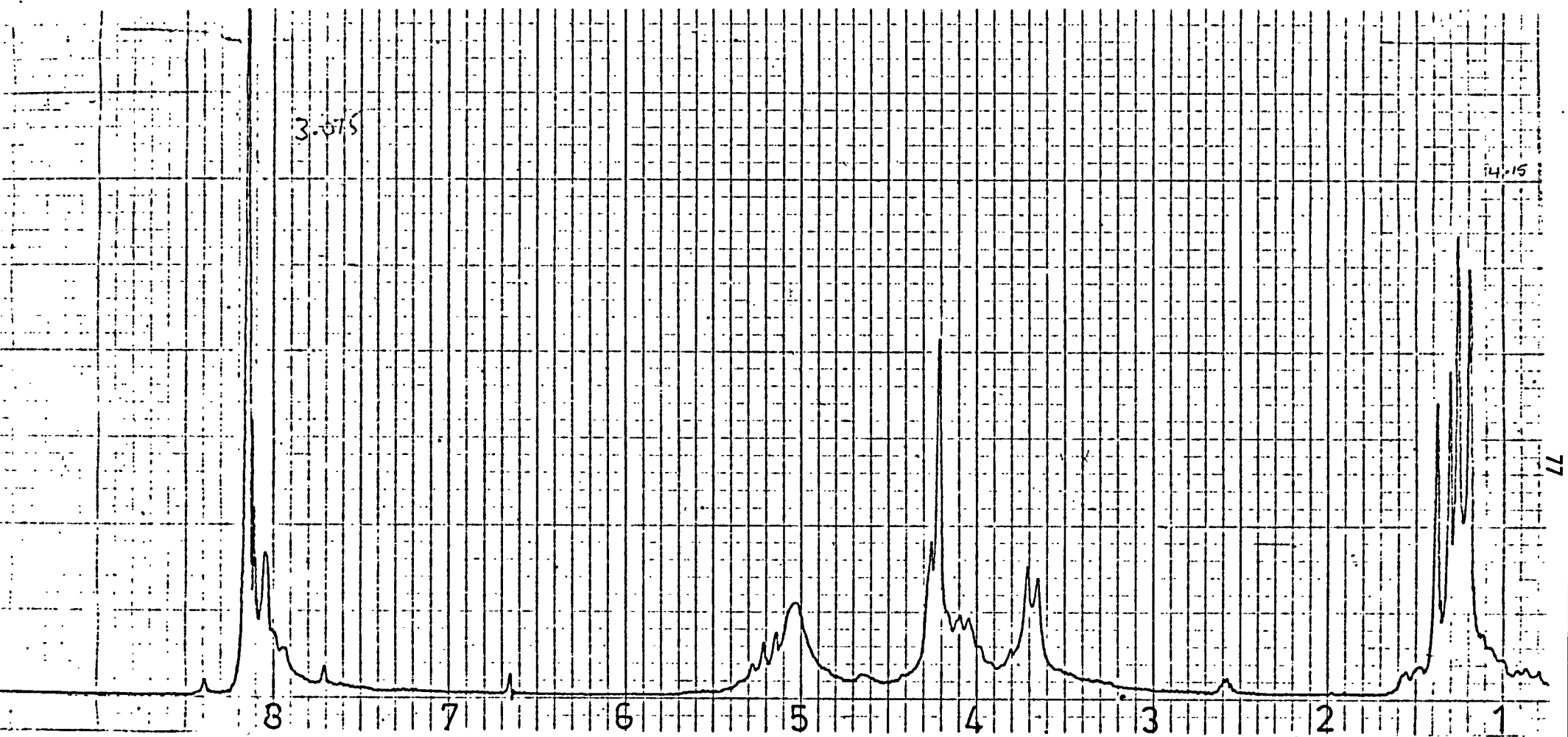


FIGURE 3.16 90 MHz NMR spectrum for the product of PTP_1 at $150^{\circ}C$ for 5 hours

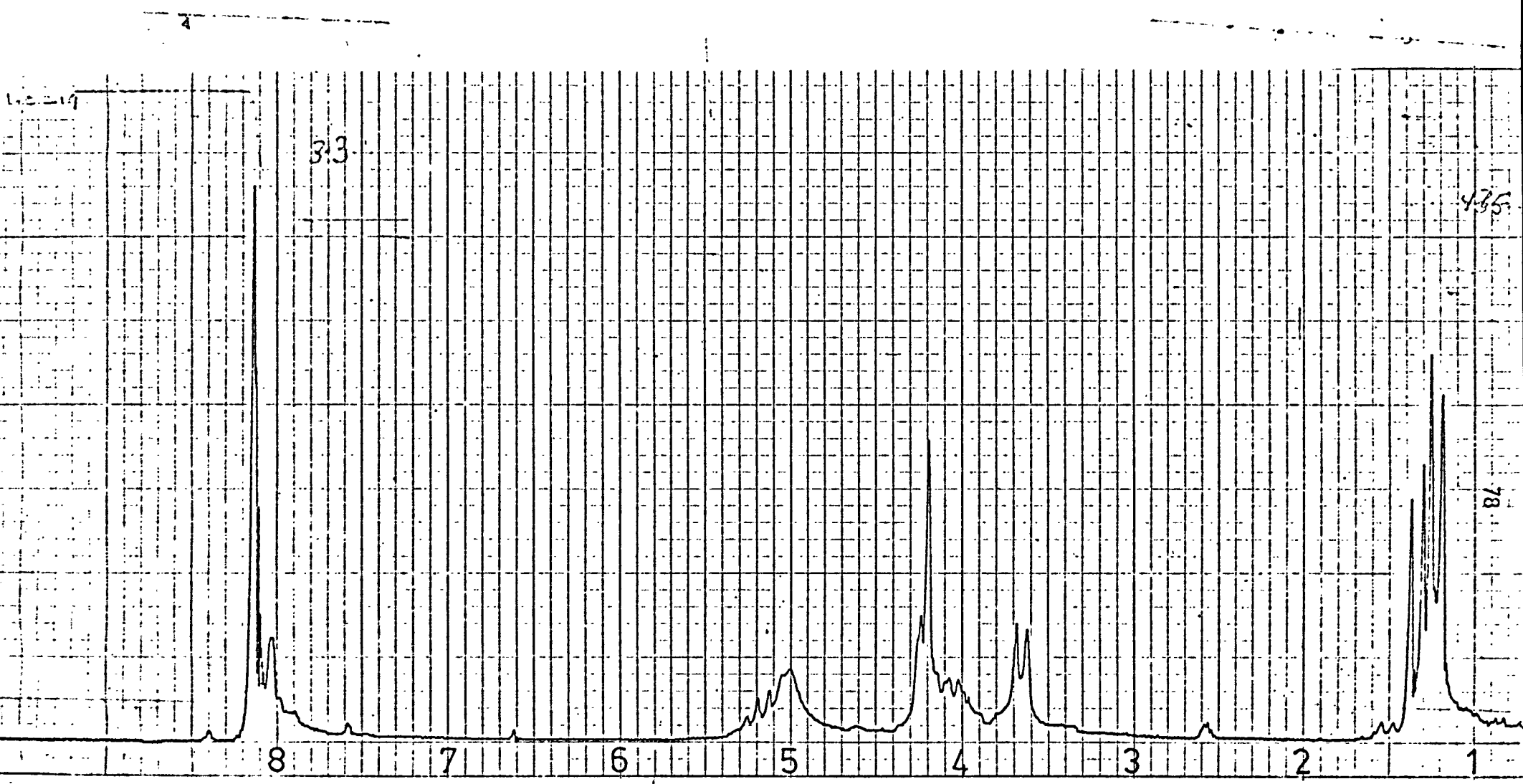


FIGURE 3.17 90 MHz NMR spectrum of the product of PTP₁ at 160°C for 5 hours

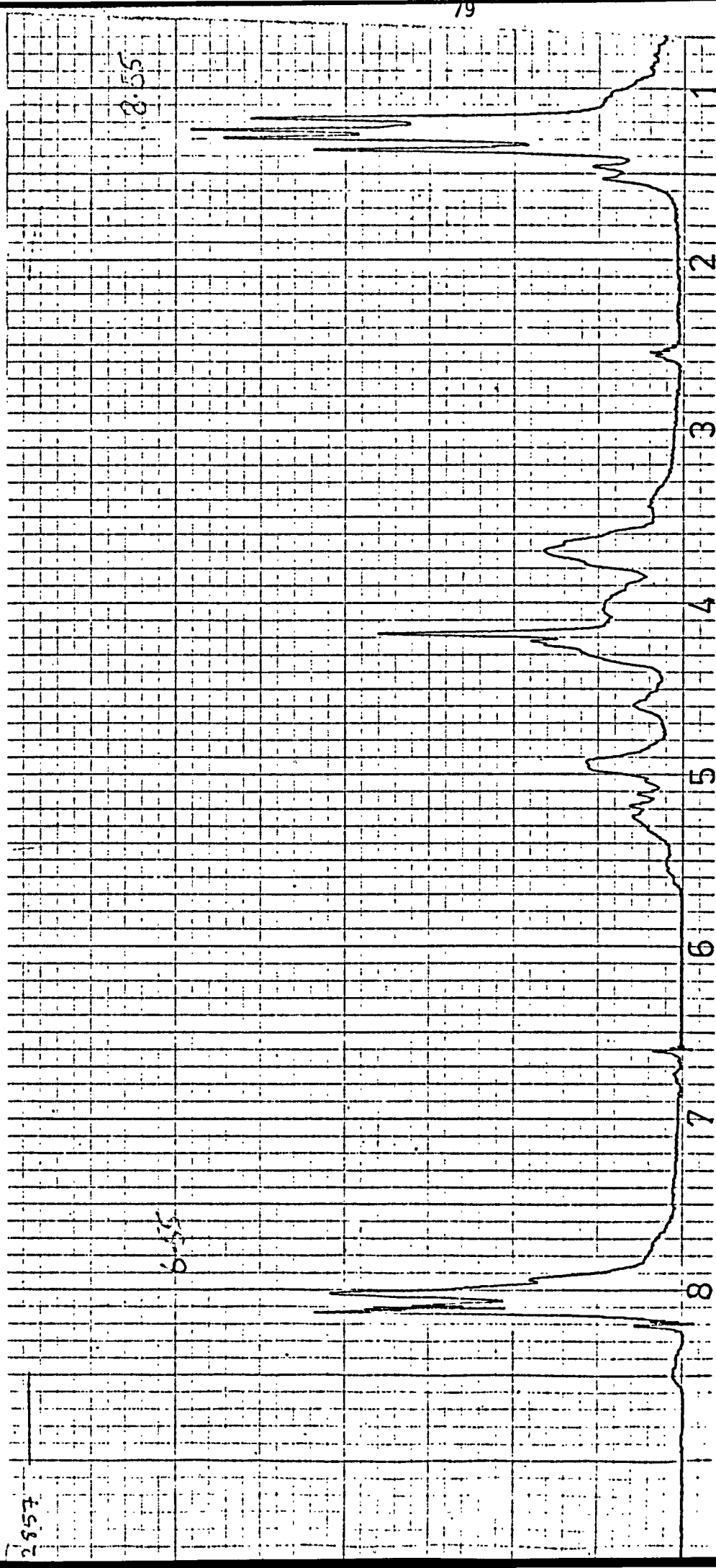


FIGURE 3.18 90 MHz NMR spectrum of the product of PTP₁ heated at 170°C for 5 hours

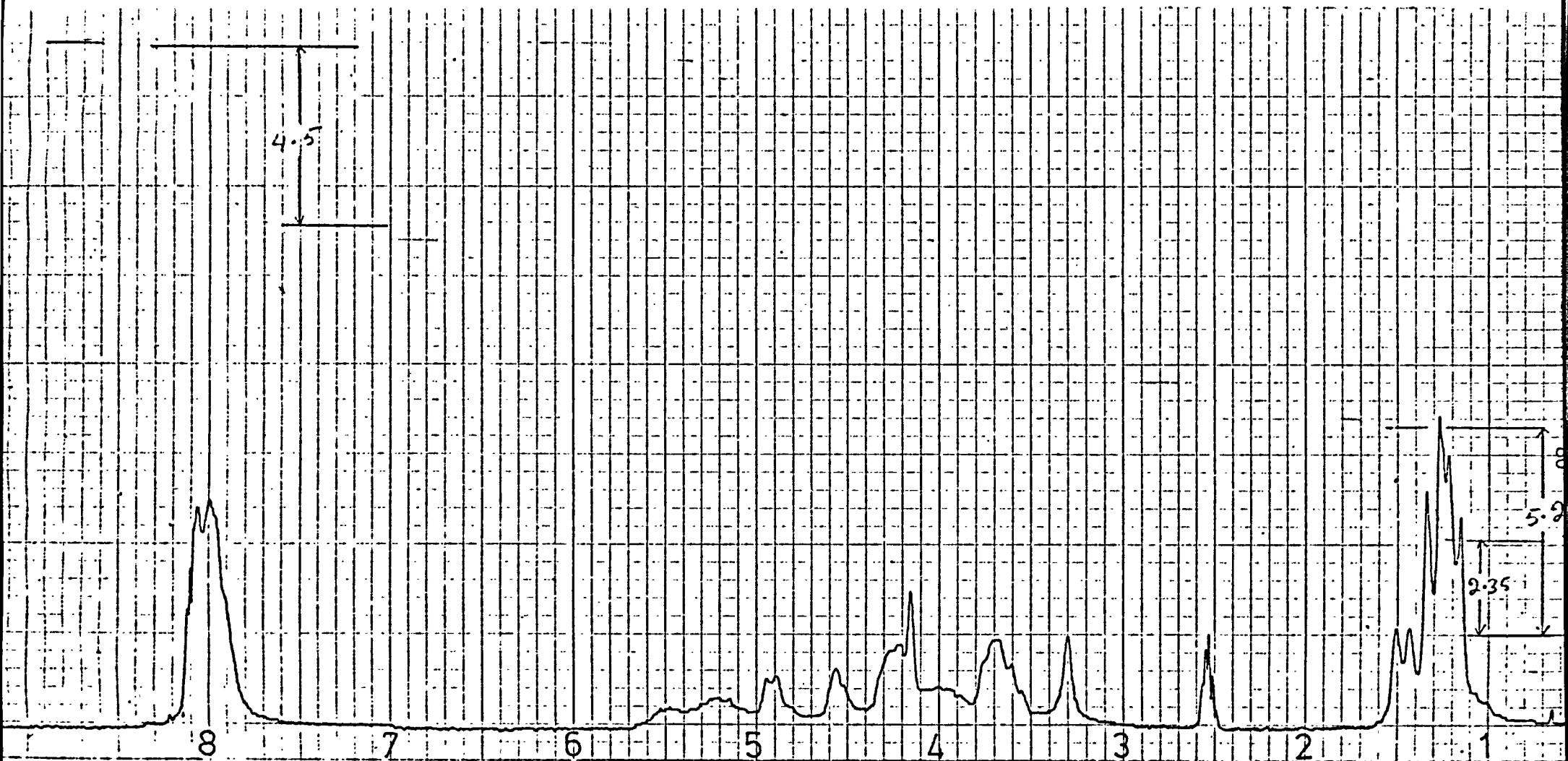


FIGURE 3.19 90 MHz NMR spectrum of the product of PTP_7 heated at 180°C for 5 hours

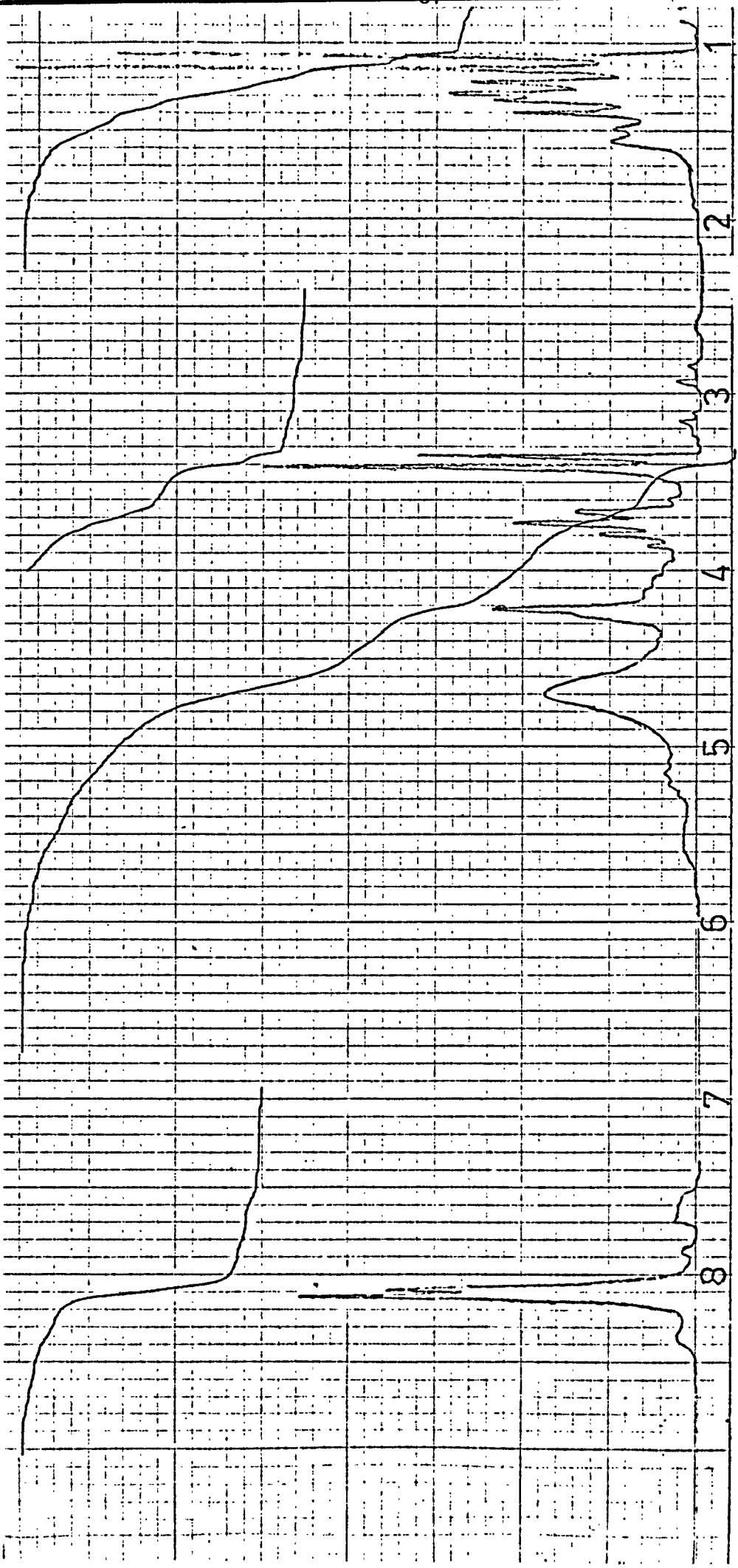


FIGURE 3.20 90 MHz NMR spectrum of P(TP)_n heated at 150°C for 0.5 hours

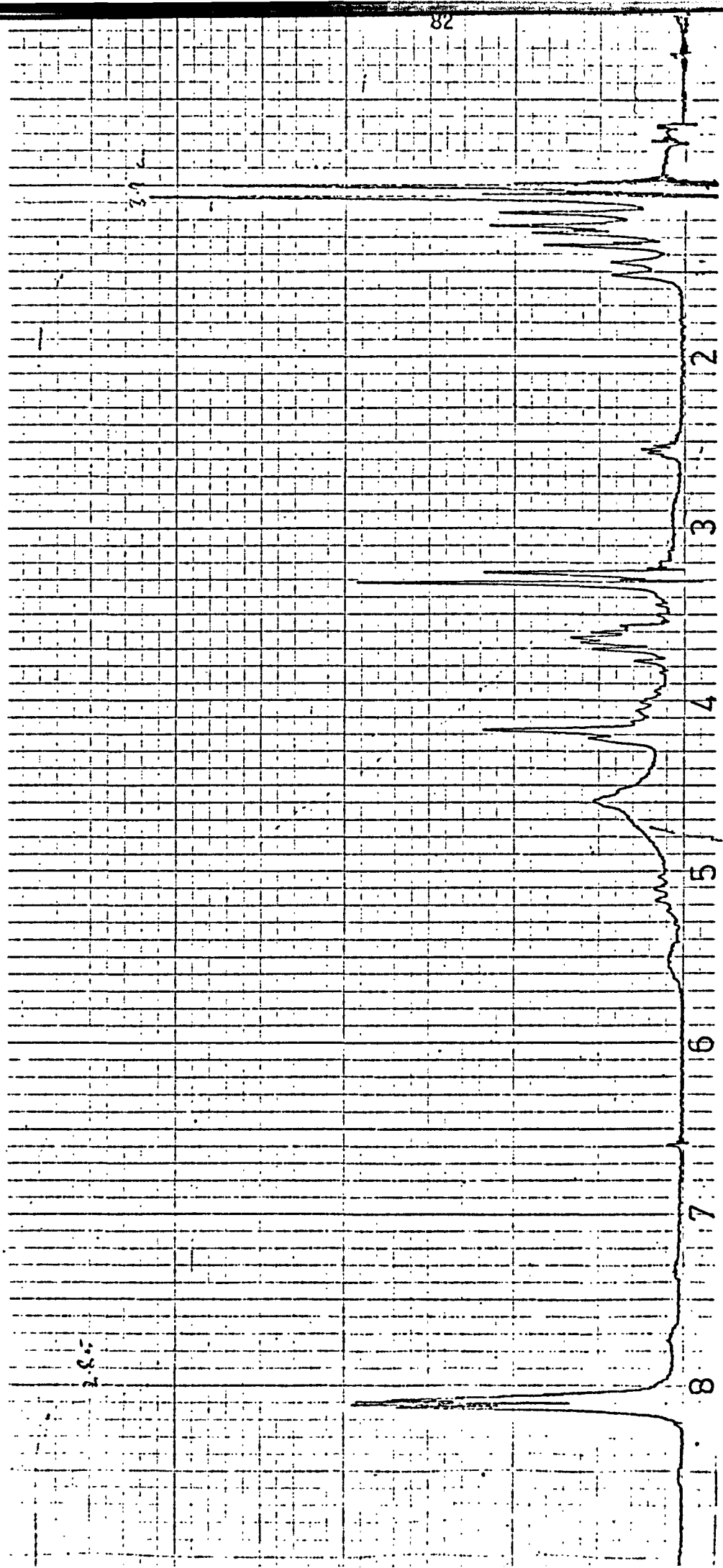


FIGURE 3.21 90 MHz NMR spectrum of P(TP)_n heated at 160°C for 5 hours

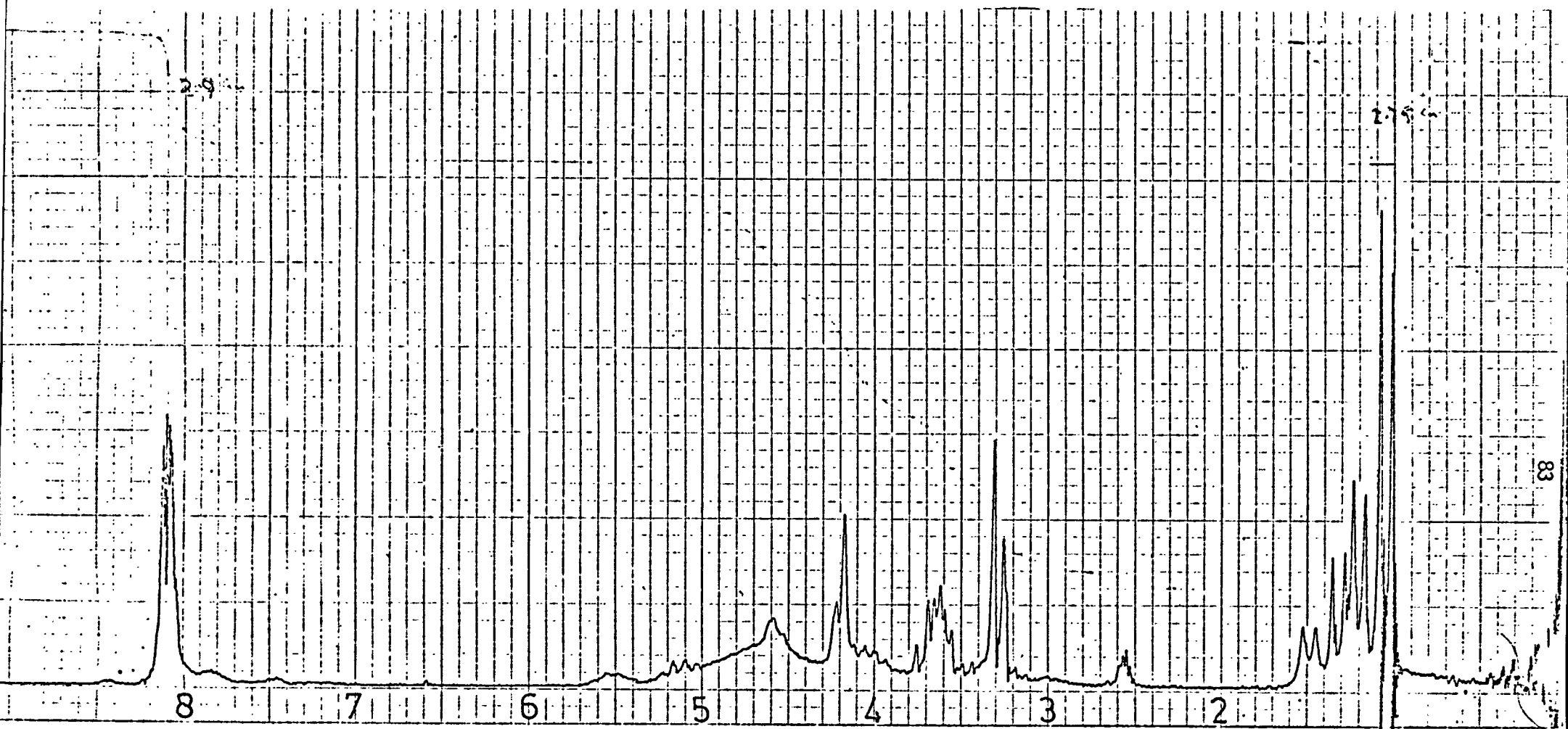


FIGURE 3.22 90 MHz NMR spectrum of $P(TP)_n$ heated at 170°C for 5 hours

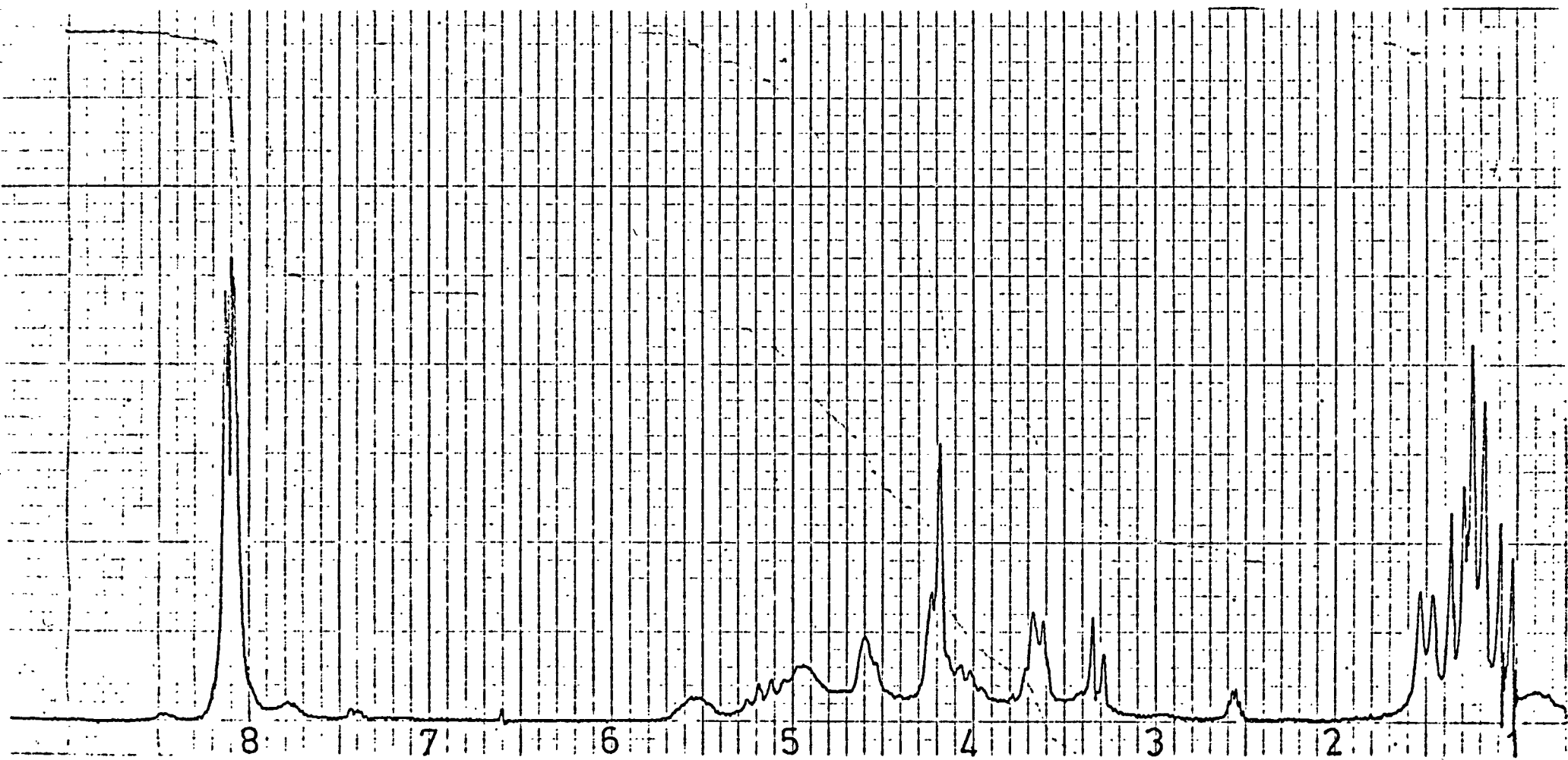


FIGURE 3.23 90 MHz NMR spectrum of P(TP)_n heated at 180°C for 5 hours

The same methods were used here to estimate the loss of propylene glycol and the primary/secondary ratio in the terminal propylene glycol molecules in the reaction products.

A gradual change was shown for $P(TP)_n$ in the loss of propylene glycol units and a decrease in the free propylene glycol which was present in the original $P(TP)_n$ prepolymer. However, quantitative analysis of the reaction products for both systems using GPC and 90 MHz NMR are shown in Table 3.4. The molecular weight determination and the degree of isomerization of the PTP_1 original isomer to a product of mixed isomers were recorded.

Estimation of Molecular Weights using GPC and NMR

To determine the molecular weight from GPC chromatograms, the areas of different peaks were divided by the number of carbonyl groups present in the species to which the peak was assigned, i.e. the PTP_1 peak area was divided by 2 and $P(TP)_3$ by 6 etc. to give the oligomer concentration, see Section 2.1.

The following tables (3.2 and 3.3) represent examples of average molecular weight calculations from GPC chromatograms:

TABLE 3.2

PTP_1 heated to 160°C for 5 hours (Figure 3.7)

No of Peak	Species	M.Wt.	Molar Concentration	Mole Fraction	Ni Mi
1	PTP_1	282	20.43	0.637	179.53
2	$P(TP)_2$	488	7.63	0.238	116.18
3	$P(TP)_3$	694	2.90	0.090	62.72
4	$P(TP)_4$	900	1.12	0.035	31.5

Average molecular weight = 389.93

TABLE 3.3

P(TP)_n heated to 160°C for 5 hours (Figure 3.12)

Peak No	Species	M.Wt.	Molar Concentration	Mole Fraction	Ni Mi
1	PTP	282	21.00	0.657	185.27
2	P(TP) ₂	488	6.78	0.212	103.46
3	P(TP) ₃	694	2.85	0.089	61.77
4	P(TP) ₄	900	1.00	0.031	28.18
5	P(TP) ₅	1106	0.31	0.01	11.06

Average molecular weight = 389.74

Molecular weights determined from NMR depended on the relationship of the number of phenyl protons to the number of methyl protons as assessed by the integrated trace values, i.e.

$$\frac{4n}{3(n+1)} = \frac{\text{ratio of phenyl protons}}{\text{ratio of methyl protons}}$$

where n is the number of -PT- repeating units in the prepolymer chain, i.e. in PTPTPTP n is equal to three. In this case n = 3, therefore the average molecular weight should be:

$$1 \times 282 + (3-1) \times 206$$

where 282 is the molecular weight of PTP and 206 is the molecular weight of a -PT- unit.

TABLE 3.4
Characterization data for prepolymers

Sample	Temperature	Av. Mol.Wt		Mean	Deviation %	Loss of P %	% of Primary Isomer
		GPC	NMR				
PTP ₁	150°C	370	341	355.5	4.1	10	44
PTP ₁	160°C	390	352	371	5.1	12	43
PTP ₁	170°C	411	368	389.5	5.3	13	41
PTP ₁	180°C	-	457	-	-	23	44
P(TP) _n	150°C	380	339	359.5	5.7	10	33
P(TP) _n	160°C	390	354	372	4.8	15	34
P(TP) _n	170°C	409	376	392.5	4.2	20	35
P(TP) _n	180°C	420	385	402.5	4.3	20	35

Time Dependence

In order to find out whether the change taking place was instantaneous or time dependent, two temperatures were examined, 150° and 180°C to represent the range of temperatures used. At 150°C for one hour the GPC chromatogram showed two peaks indicating the presence of PTP₁ and P(TP)₂ at elution volumes 120 and 104 ml, see Figure 3.24.

At 180°C for one hour the change was greater than that at 150°C. Three distinct peaks were shown in the chromatogram indicating the presence of species up to P(TP)₃, see Figure 3.25. When PTP₁ was heated for 3 hours at 180°C, the chromatogram obtained implied the presence of oligomers up to P(TP)₅, see Figure 3.26. These experiments showed that the polycondensation is temperature and time dependent, but when PTP₁ was heated to 150°C for half an hour the NMR spectrum of the product showed that ester interchange took place. The spectrum showed a ratio for primary/secondary propylene glycol ends similar to those obtained for samples heated for 5 hours, see Figure 3.27.

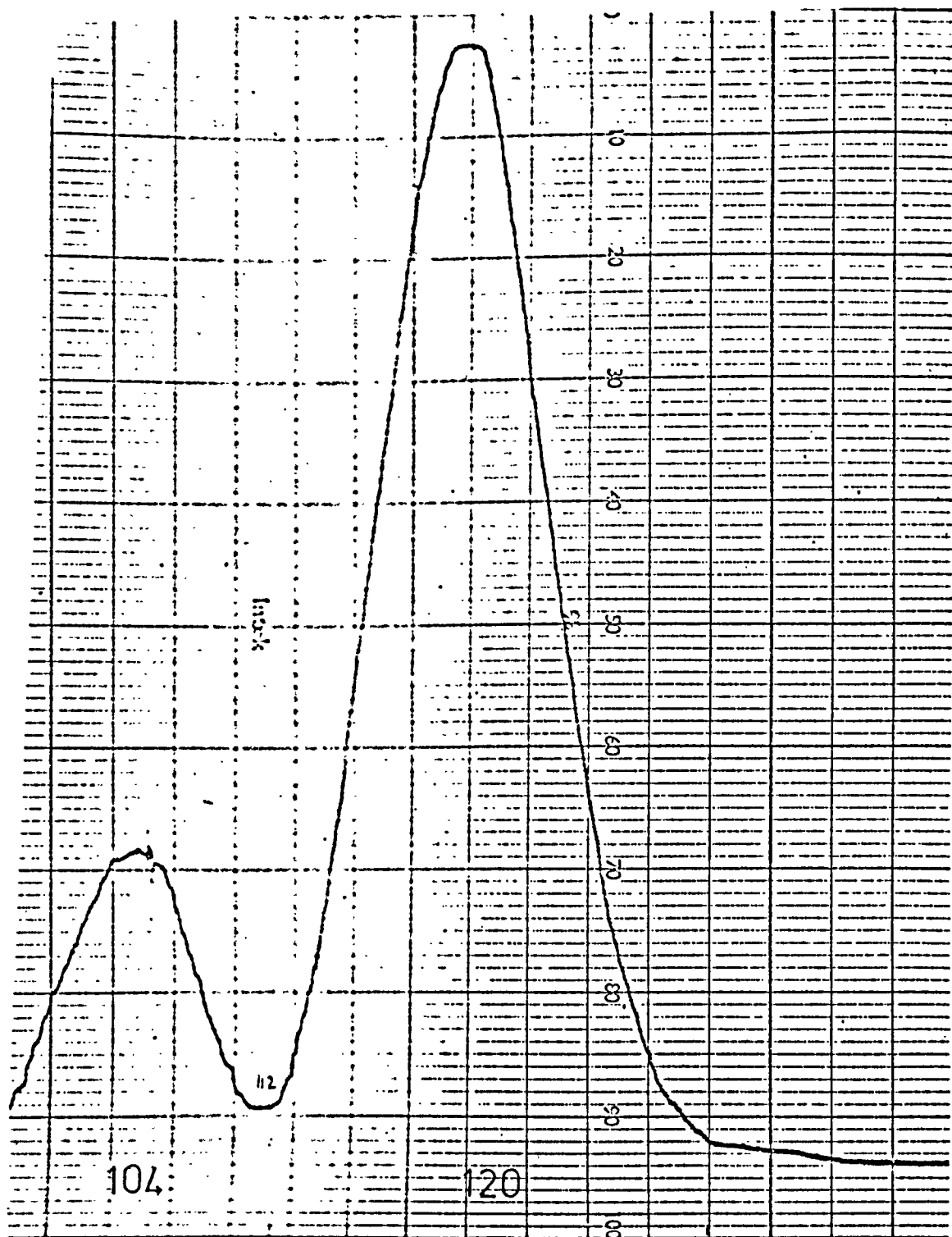


FIGURE 3.24 GPC Chromatogram of the product of PTP_7 heated at 150°C for one hour

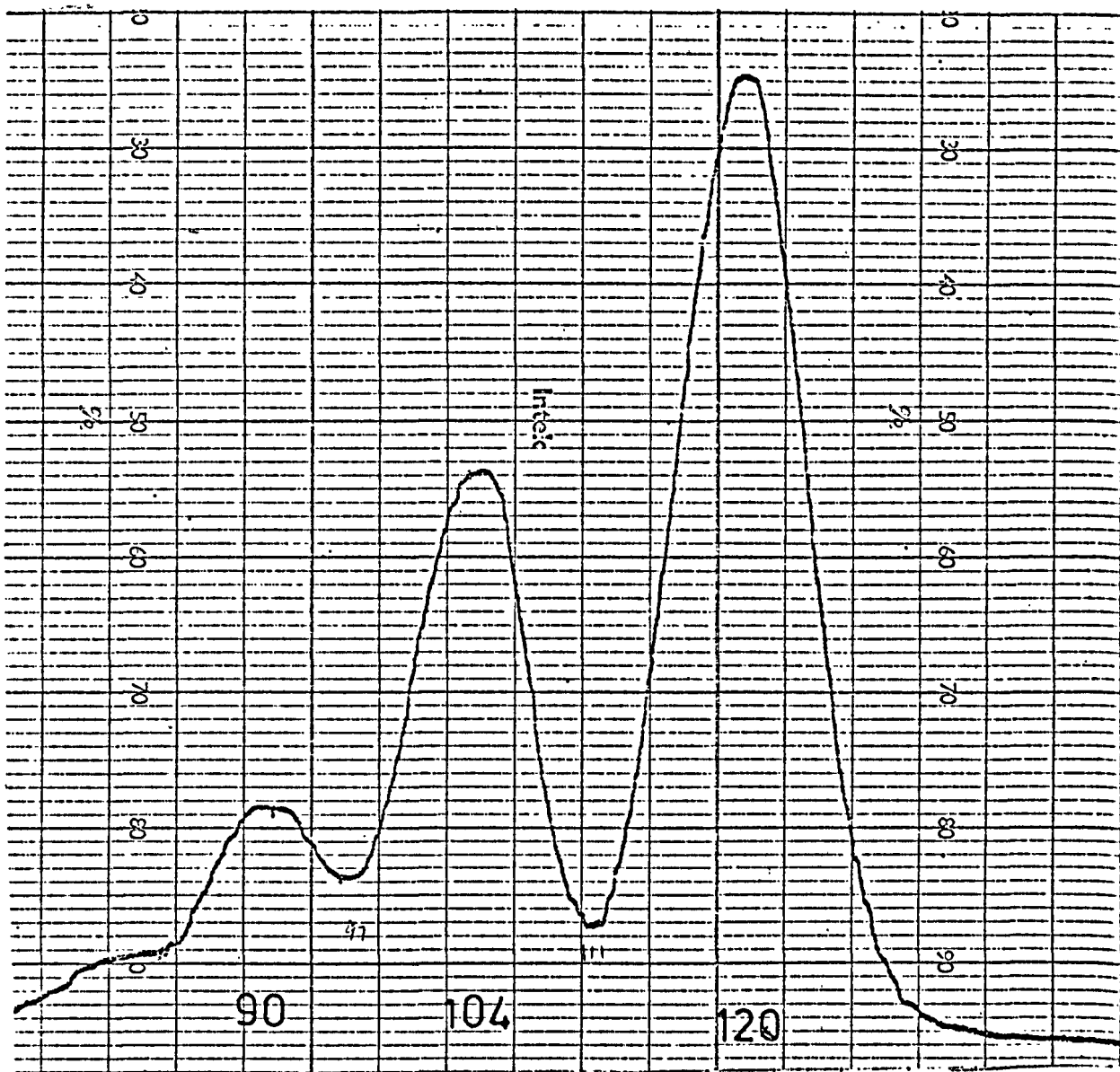


FIGURE 3.25 GPC Chromatogram of PTP₁ heated at 180°C for one hour

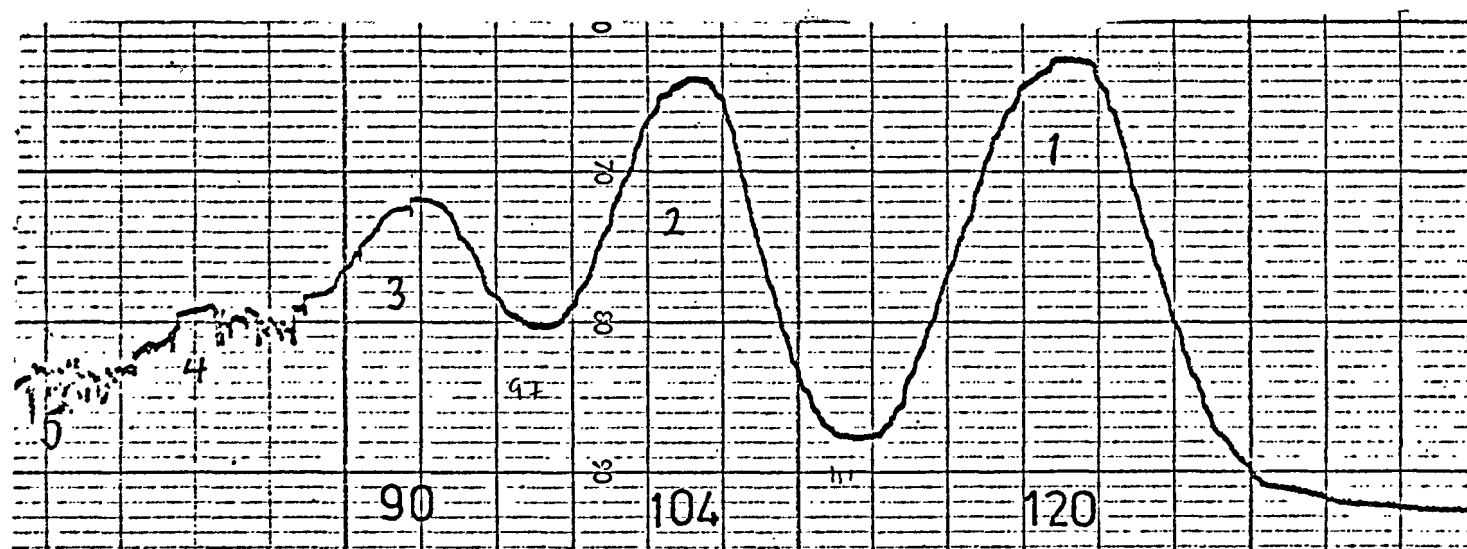
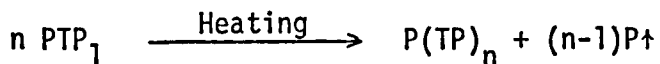


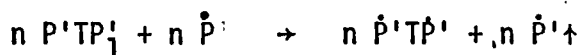
FIGURE 3.26 GPC Chromatogram of the product of PTP₁ heated at 180°C for 3 hours

Suppression of Polycondensation

The chemical effect of heating PTP_1 can be represented as follows:

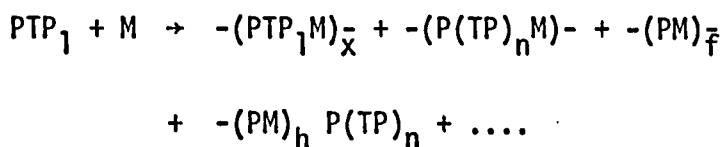


This was clearly shown by the moderate changes of $P(TP)_n$ on heating as compared to the changes which happened for PTP_1 , due to the effect of free propylene glycol present in $P(TP)_n$. As further confirmation, free propylene glycol was deliberately added to PTP_1 to compensate for the loss of propylene glycol. The mixture was heated to 150°C for 5 hours. On varying the molar ratio of the mixture of PTP_1 and propylene glycol, it was found that the product of the mixture 1 PTP_1 :1.25 PG (molar ratio) gave a single peak in the GPC chromatogram, see Figure 3.28. The molar ratio of 1 PTP_1 :1 PG gave a single peak with a small side peak, see Figure 3.29. The NMR spectrum in Figure 3.30 confirmed that PTP_1 was not changed to $P(TP)_n$ in the 1:1.25 molar ratio, but the primary isomer was partly changed to the secondary isomer (34%). The effect of polycondensation suppression can be represented as follows:



where P' is a propylene glycol unit in PTP_1 and P' is a free propylene glycol molecule.

Although the originally isolated isomer of PTP_1 isomerizes on heating, even if it was not reacted with any other species, the presence of propylene glycol suppresses further polycondensation of PTP_1 in the heating experiments. It could be suggested that on heating PTP_1 alone with maleic anhydride (MA), instead of forming an alternating copolymer the product could be portrayed as follows:



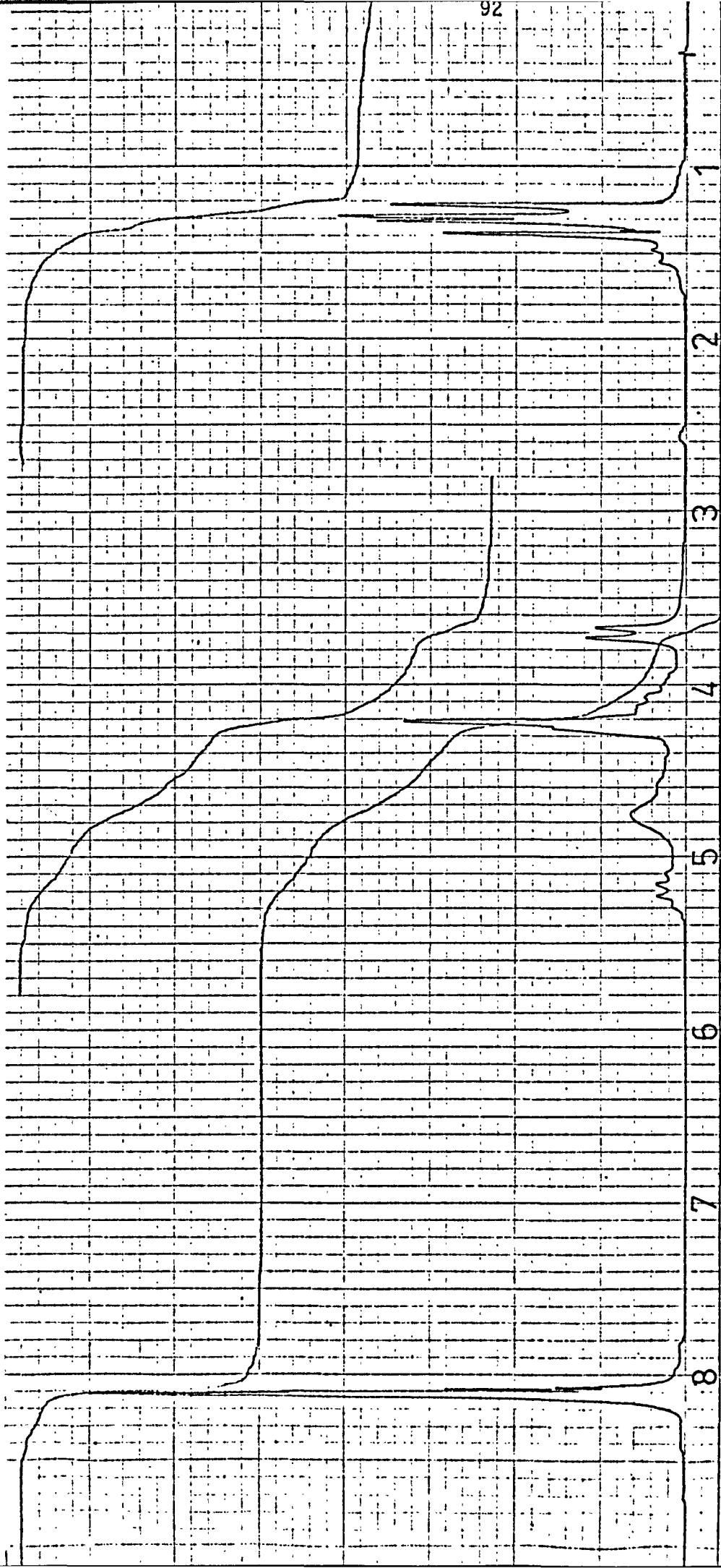


FIGURE 3.27 90 MHz NMR spectrum of PTP₁ heated at 150°C for 30 minutes

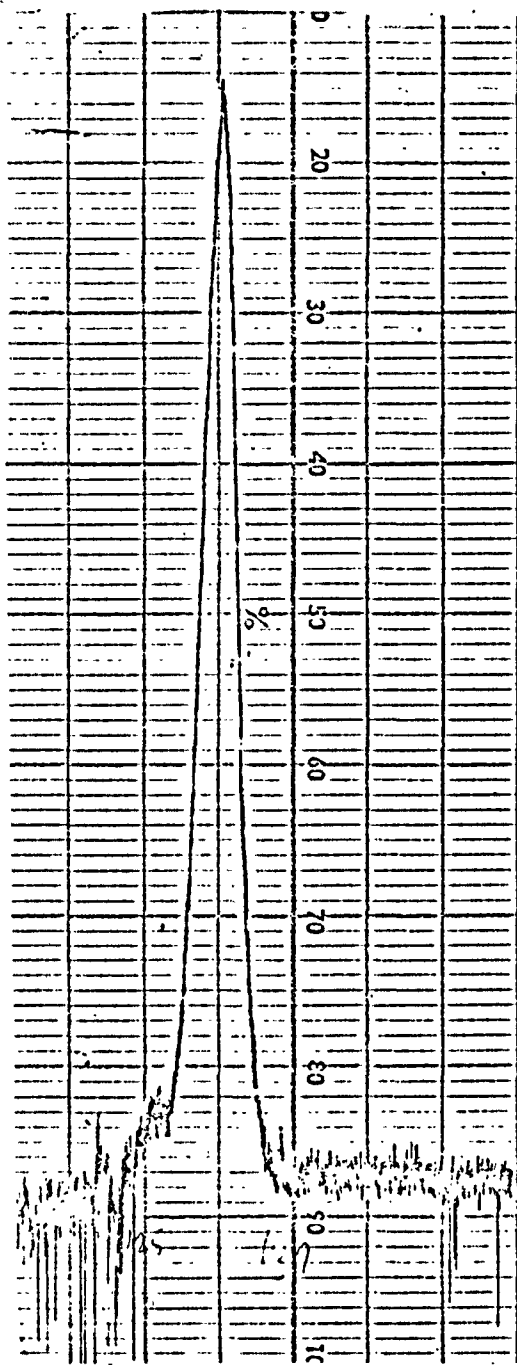


FIGURE 3.28 GPC Chromatogram of
(1 PTP₁:1.25 PG)
heated at 150°C for
5 hours

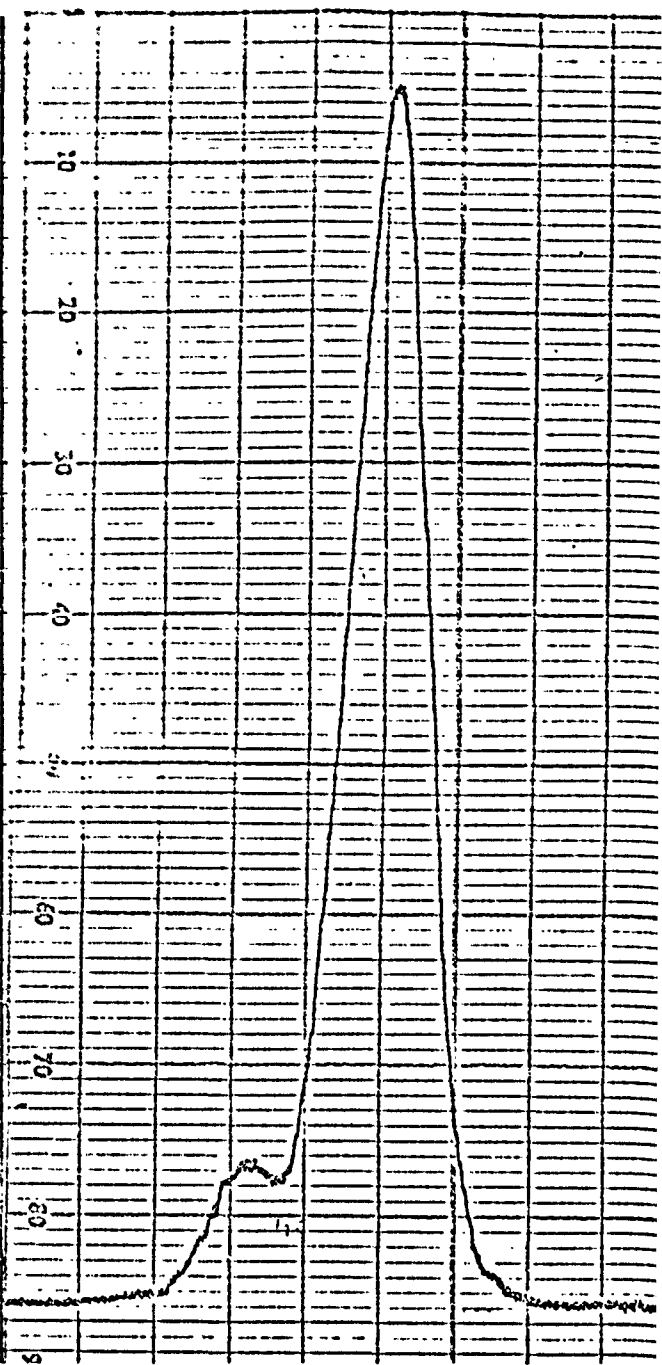


FIGURE 3.29 GPC Chromatogram of
(1 PTP₁:1 PG)
heated at 150°C for
5 hours

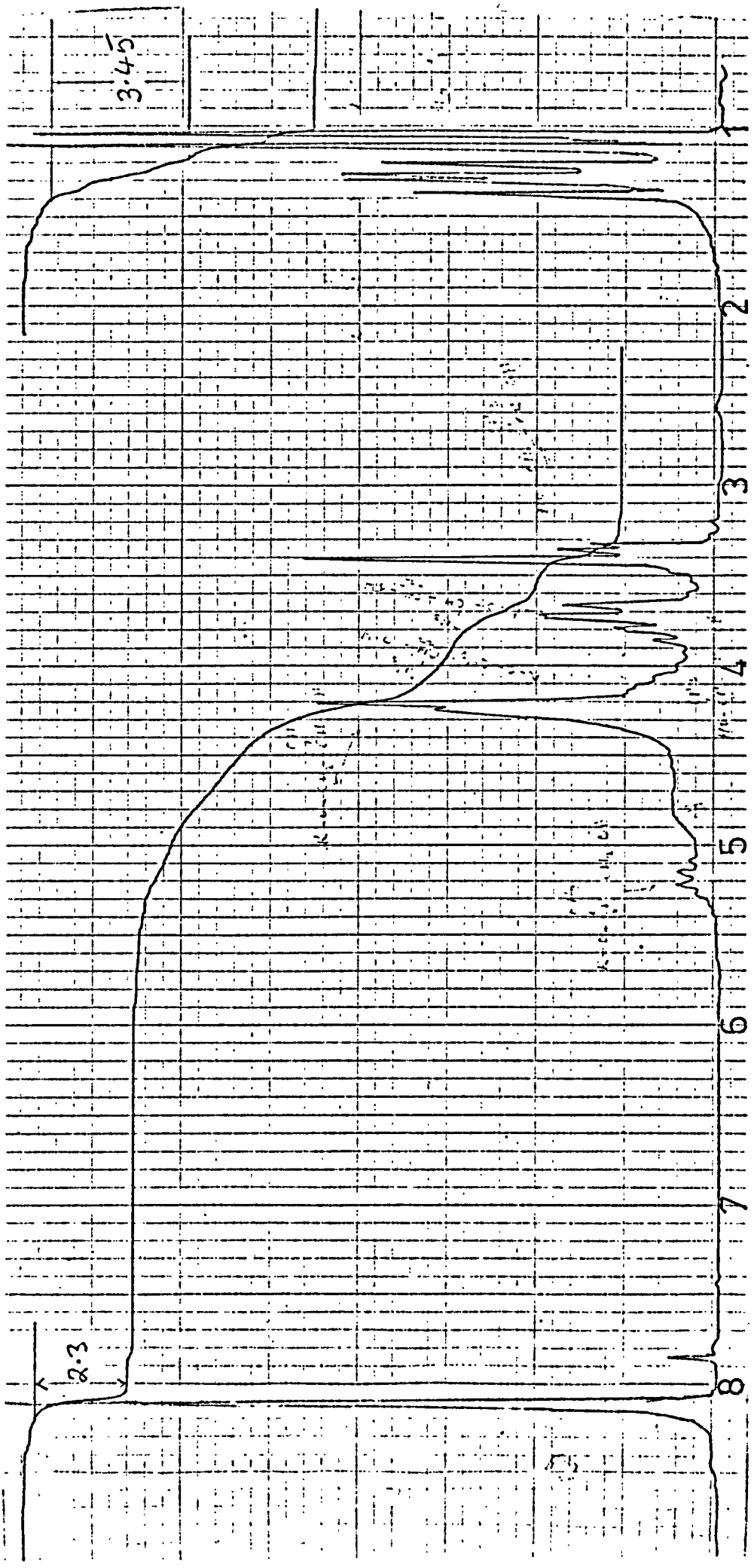


FIGURE 3.30 90 MHz NMR spectrum of (1 PTP₁:1.25 PG) heated at 150°C for 5 hours

3.3 Polycondensation Reactions of Bis (Hydroxy Propyl) Isophthalate

These reactions were intended to provide a comparison of the effect of temperature on prepolymers based on isophthalic acid and those based on terephthalic acid.

Preparation of PIP₁

The same apparatus used for the preparation of PTP₁ was used here (Figure 3.3). PIP₁ was prepared through different routes. Basic and acidic catalysis (pyridine, sulphuric acid) were used for direct esterification of isophthalic acid with an excess of propylene glycol (10:1) at 180°C under nitrogen with continuous stirring for 10 hours. Another method used was the esterification of isophthaloyl chloride with an excess of propylene glycol (8:1) using pyridine as an acid-acceptor under nitrogen at 55°C with continuous stirring for 15 hours. Direct esterification of the acid was also employed using tetrabutyl titanate as a catalyst.

Purification and Characterization of the Product

The reaction mixture was poured into chloroform and washed with water thrice. The water layer was again washed with chloroform and the chloroform layers were added together. The solution of the product in chloroform was washed 3 times with saturated sodium bicarbonate solution. The product solution was then washed with water twice to remove the sodium salt. From the wet solution of product in chloroform the chloroform and water were distilled leaving behind a yellowish brown solution. The product was then dried in a vacuum oven at 70°C for 10 hours. The final product was a light brown viscous oil which showed no transition above 0°C on DTA analysis.

When a solution of the product in chloroform was eluted through the GPC column it produced only one peak at elution volume 112 ml. (Figure 3.31) suggesting a single component. Then a mixture of samples from the product and PTP₁ was eluted through the column. The result was still one peak at elution volume 112 ml (Figure 3.32) which confirmed that the product consisted of one component with a GPC peak which is superimposable with the peak obtained for PTP₁ i.e. of the same retention volume.

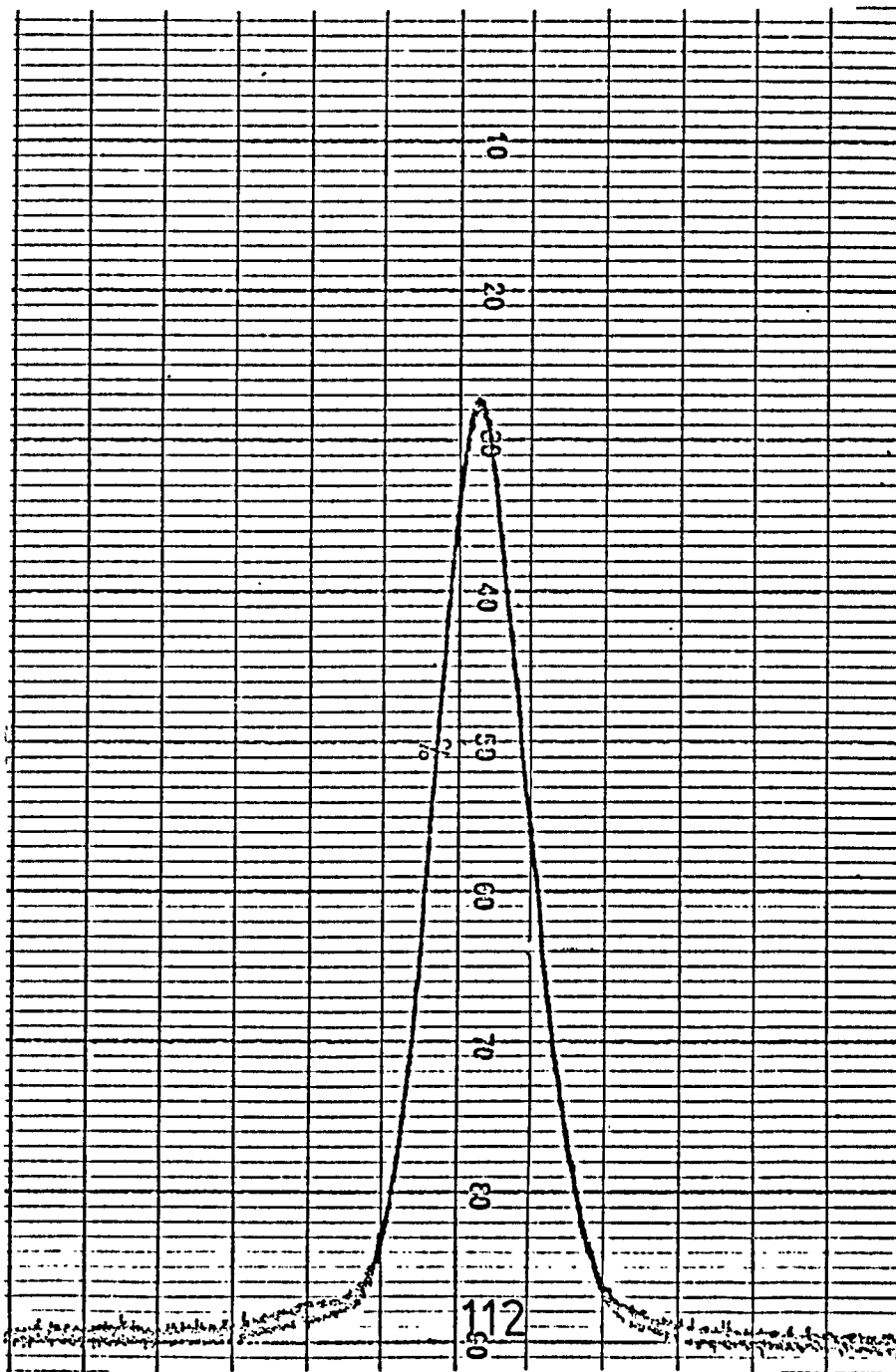


FIGURE 3.31 GPC Chromatogram for PIP₁

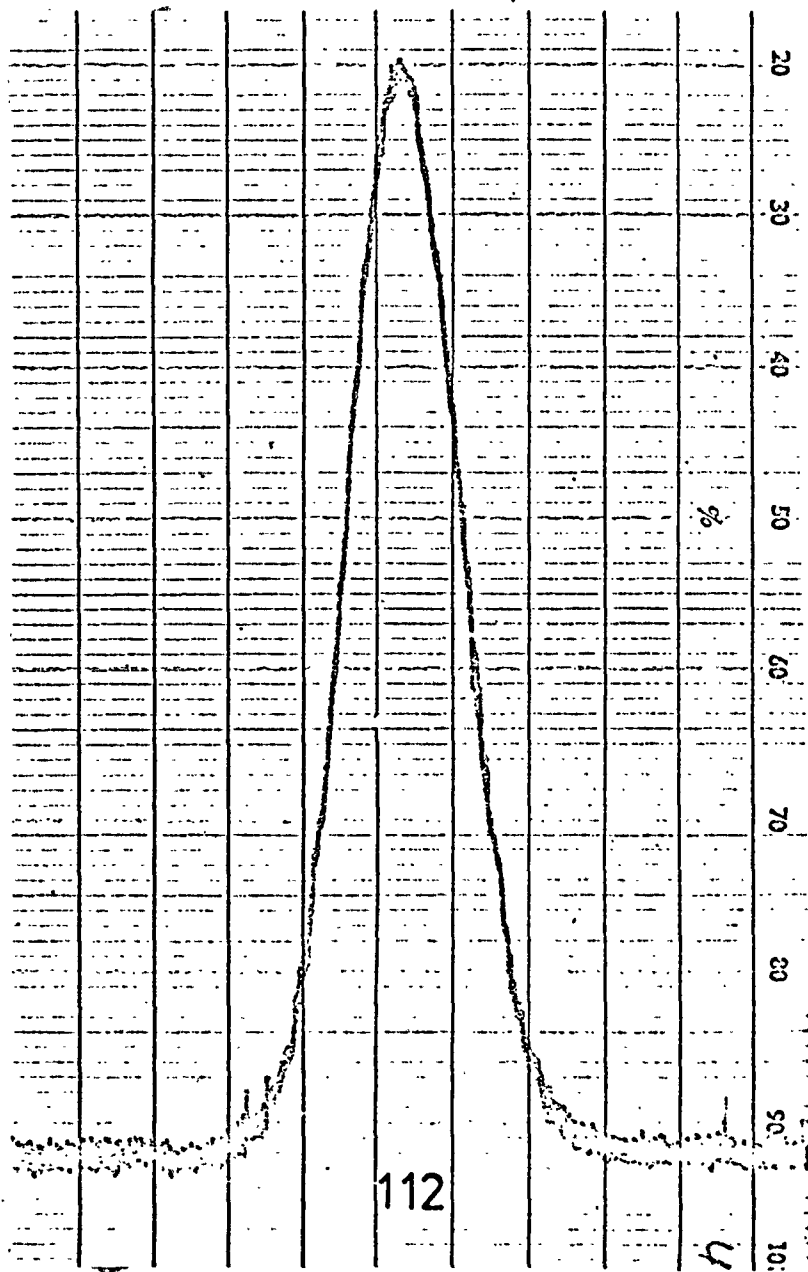
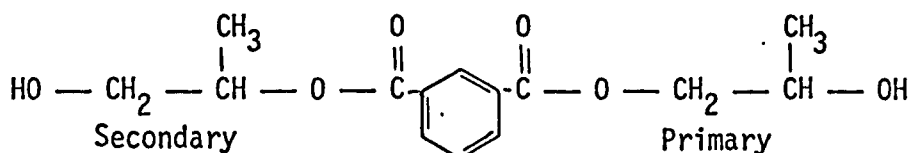


FIGURE 3.32 GPC Chromatogram of $PIP_1 + PTP_1$

The NMR spectrum obtained for the product (Figure 3.33) confirmed that the product consisted of a single component with the absorptions of the following structure, at approximately the same chemical shifts observed for PTP₁



Bis (hydroxy propyl) isophthalate

The product was consisted of a mixture of isomers in which the primary isomer ratio to the secondary isomer was 4:1 (80% primary ends of propylene glycol reacted).

Heating Experiments of PIP₁

The same apparatus for PTP₁ heating experiments was used here. A small amount of PIP₁ (2.0g) was placed in the reaction vessel and heated in an oil bath under nitrogen at different temperatures (150°C, 160°C, 170°C and 180°C) for 5 hours. Samples of the products were analysed by GPC and NMR .

PIP₁ exhibited less polycondensation at lower temperatures than PTP₁. At 150°C and 160°C the GPC chromatograms for PIP₁ (Figures 3.34, 3.35) showed little change. At 150°C the highest oligomers formed in the PIP₁ systems were P(IP)₂ at elution volume 102 ml while in the PTP₁ system oligomers P(TP)₃ and P(TP)₄ were produced (see Figure 3.5). At 160°C an additional small side peak, indicating the presence of P(IP)₄, occurring at elution volume 85 ml was shown for PIP₁, while PTP₁ produced four distinct peaks and a side peak for P(TP)₅, see Figure 3.36. Although PIP₁ resisted polycondensation in rates comparable to PTP₁ systems at 150°C and 160°, at 170°C and 180°C, PIP₁ polycondensation proceeded at much higher rates than at lower temperatures. At 170°C the chromatogram of the product, Figure 3.36, showed a considerable increase in the number of peaks at low elution volumes: 85, 80, 74, 69 and 65 ml. This higher reactivity was even more apparent at 180°C where the product contained a substantial quantity of high oligomers. The formation of these high oligomers can be seen from the number of peaks appearing at low elution volumes i.e. 85, 80, 74, 69, 65, 60, 57 and 54 ml in Figure 3.37.



FIGURE 3.33 90 MHz NMR spectrum of PIP₁

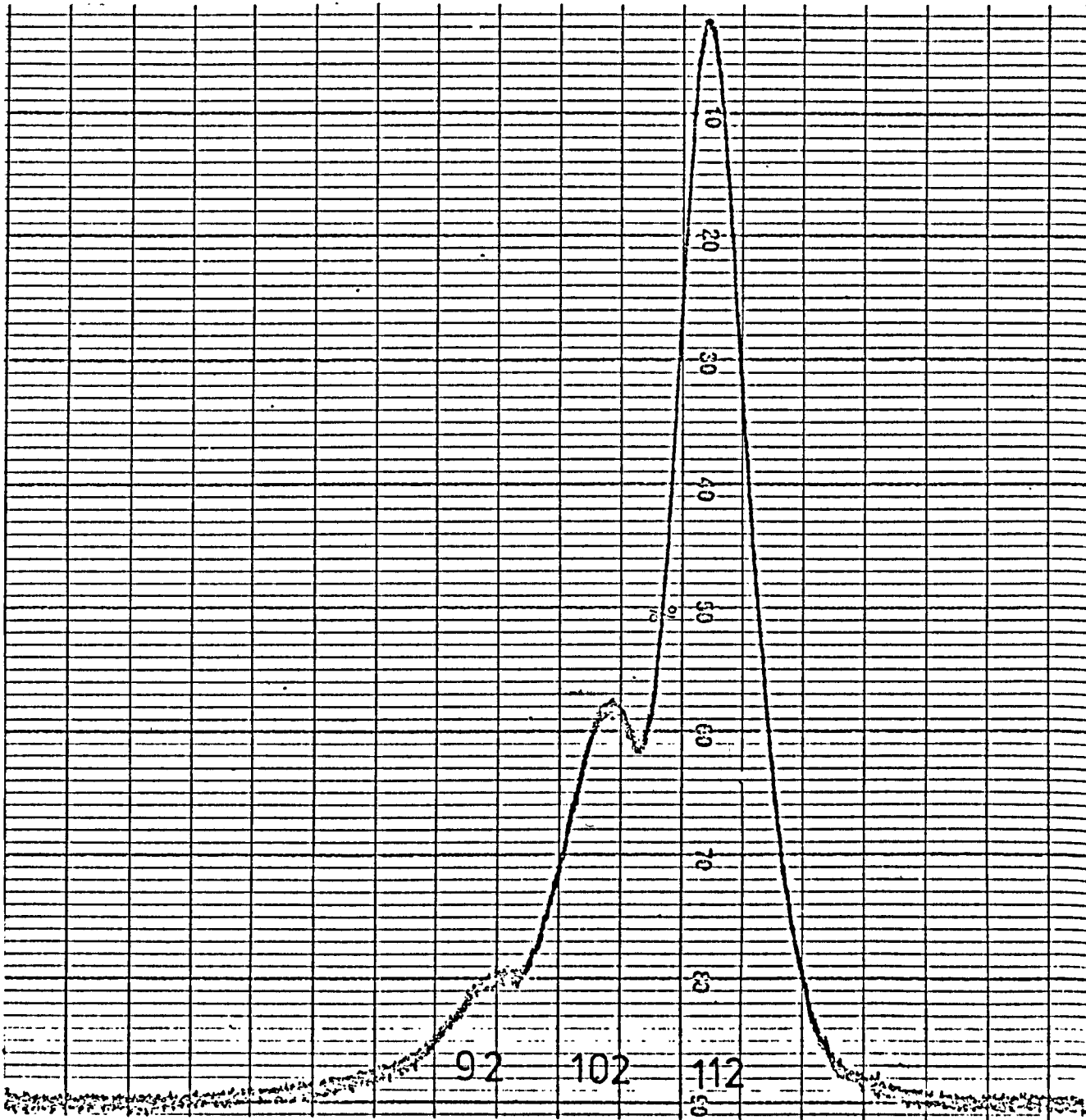


FIGURE 3.34 GPC Chromatogram of PIP_1 heated at 150°C for 5 hours

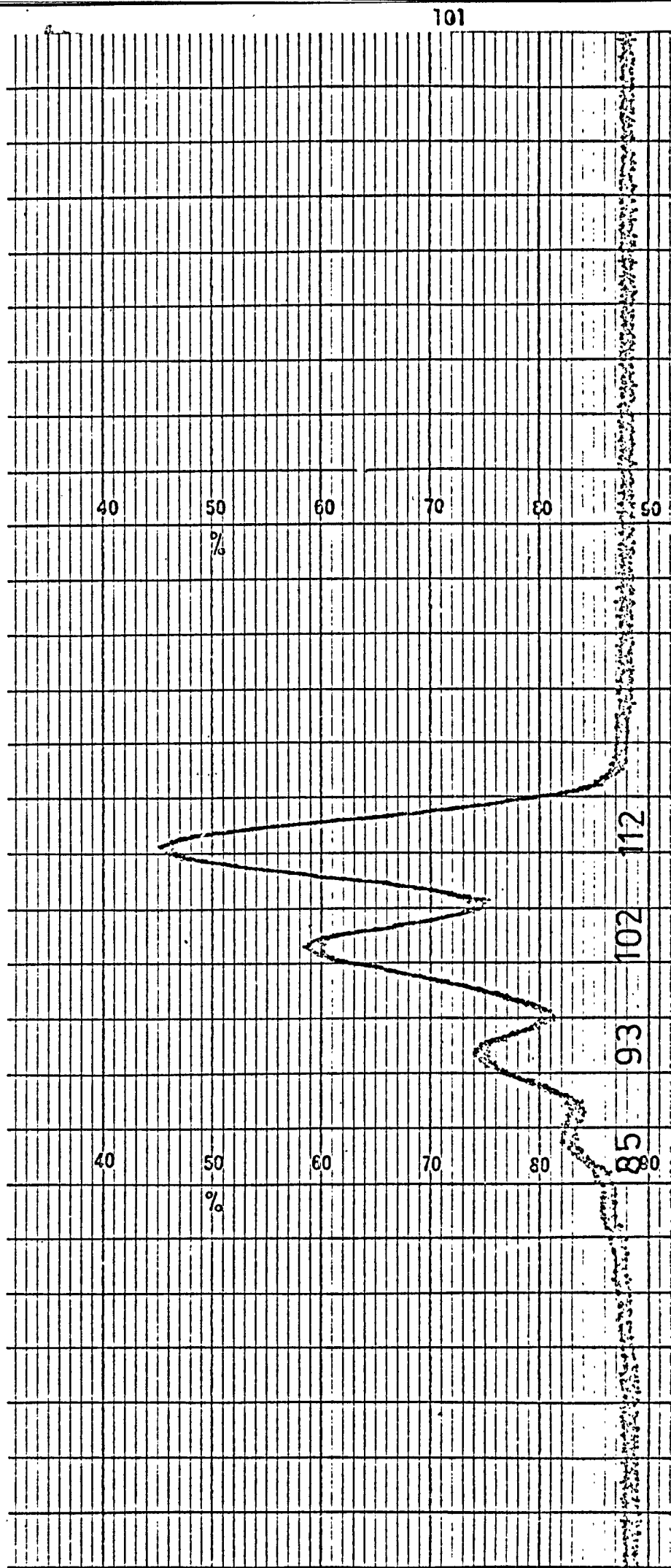


FIGURE 3.35 GPC Chromatogram of PIP₁ heated at 160°C for 5 hours

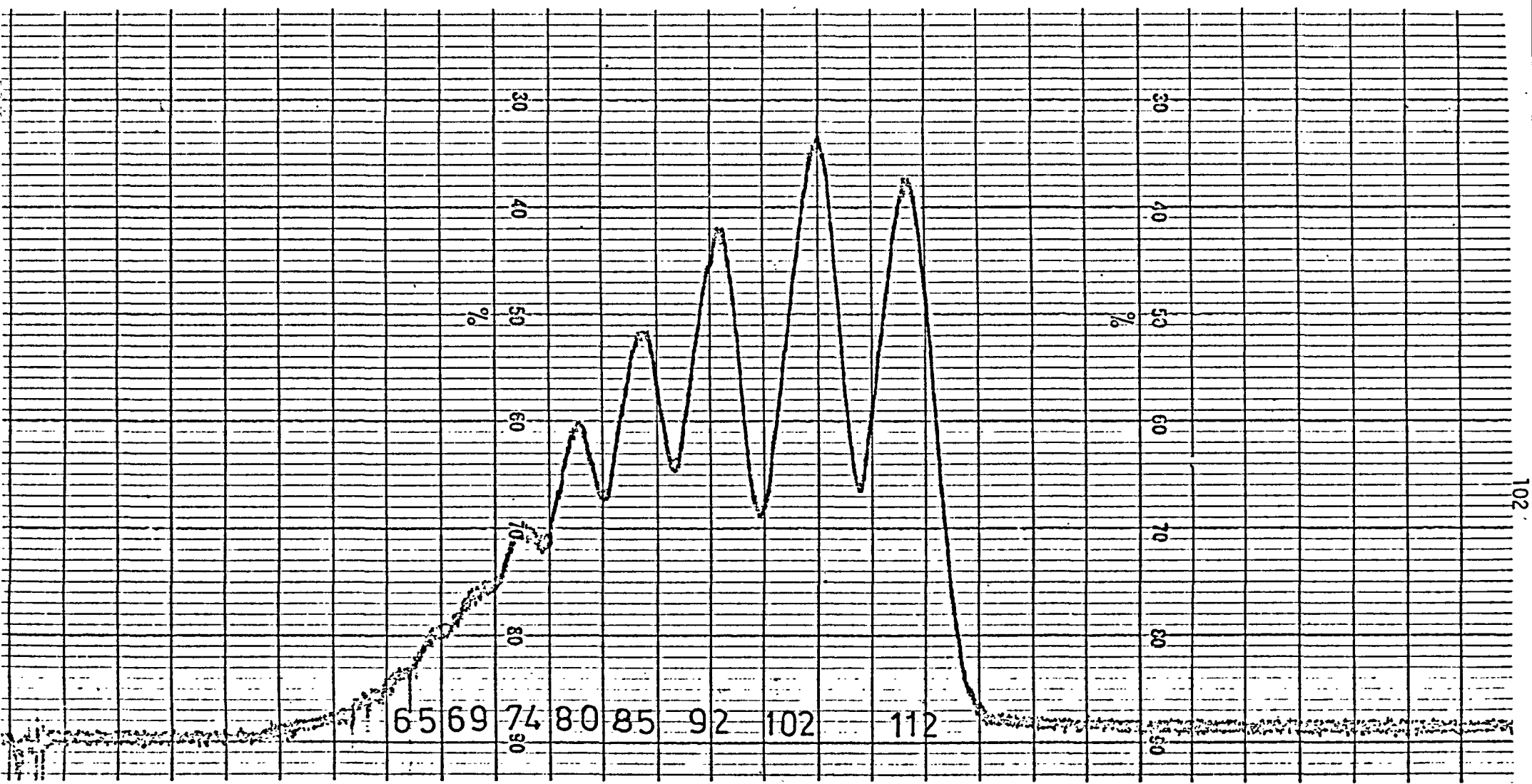


FIGURE 3.36 GPC Chromatogram of PIP₁ heated at 170°C for 5 hours

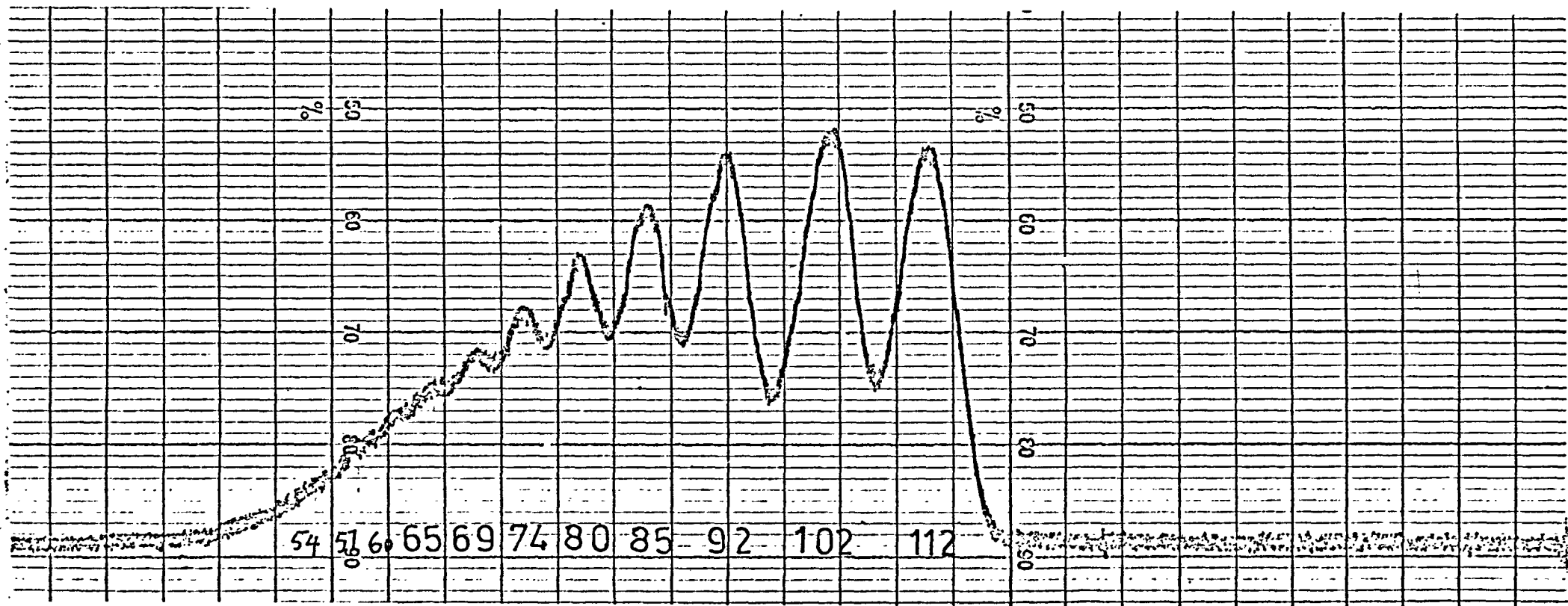


FIGURE 3.37 GPC Chromatogram of PIP₁ heated at 180°C for 5 hours

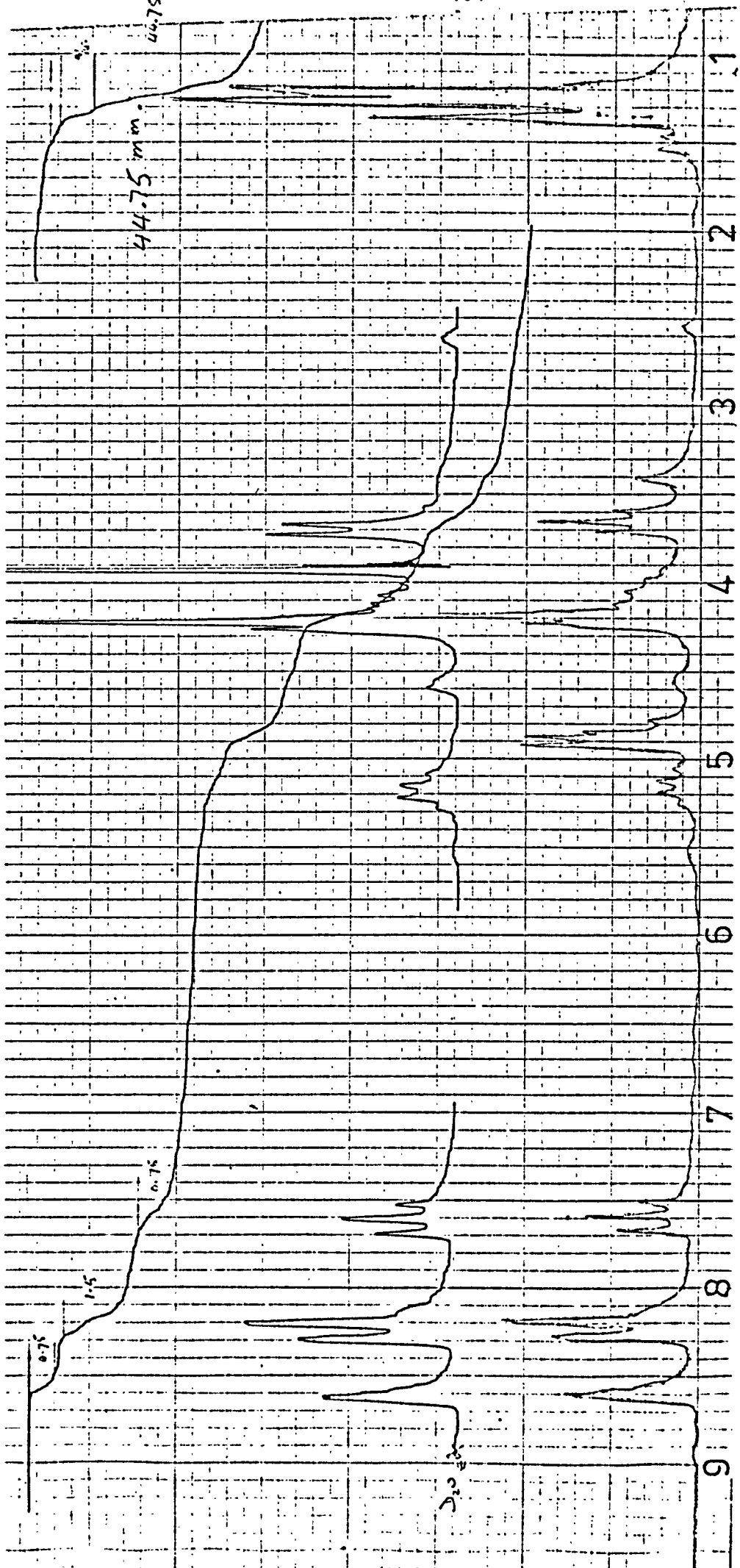


FIGURE 3.38 90 MHz NMR spectrum of PIP₁ heated at 150°C for 5 hours

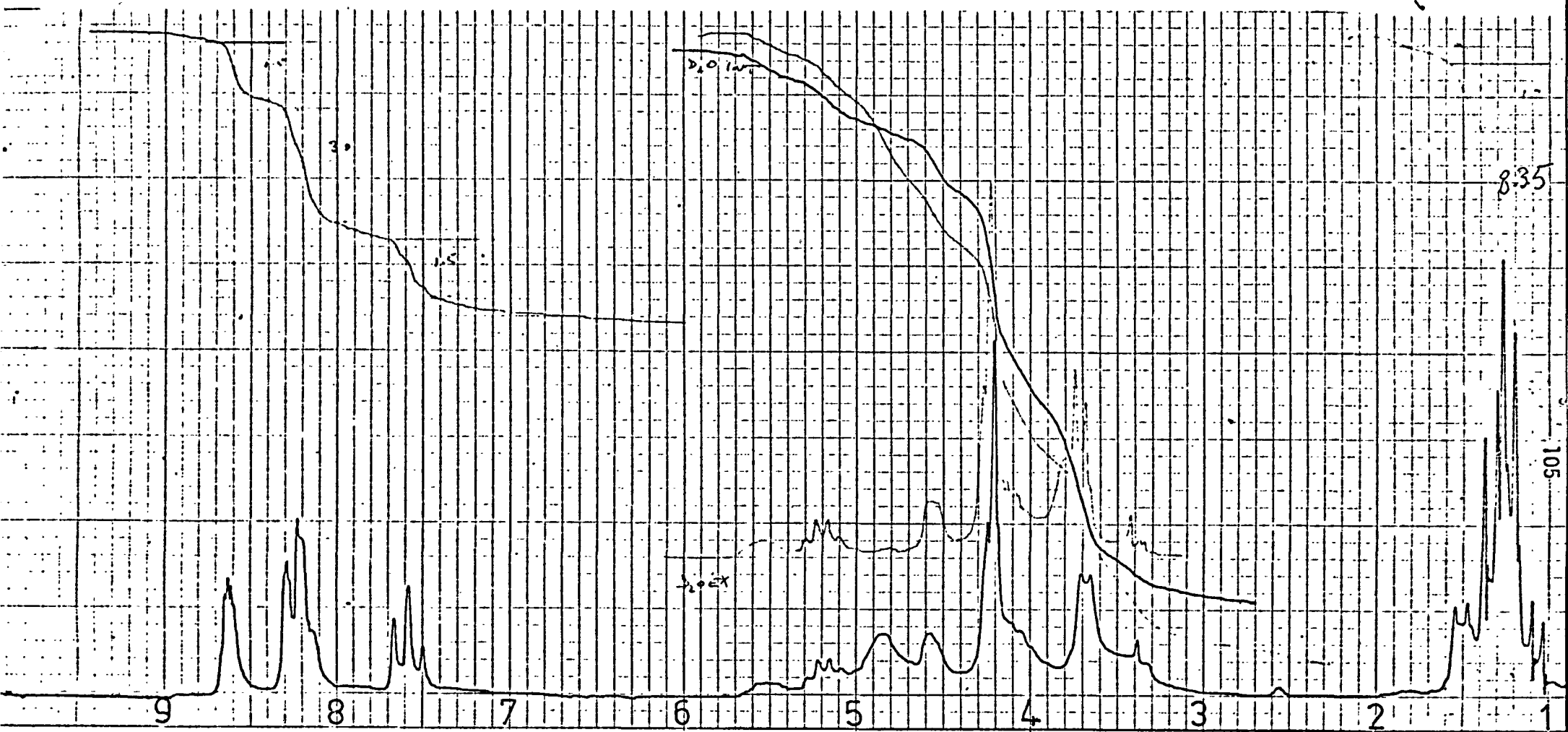


FIGURE 3.39 90 MHz NMR spectrum of PIP, heated at 160°C for 5 hours

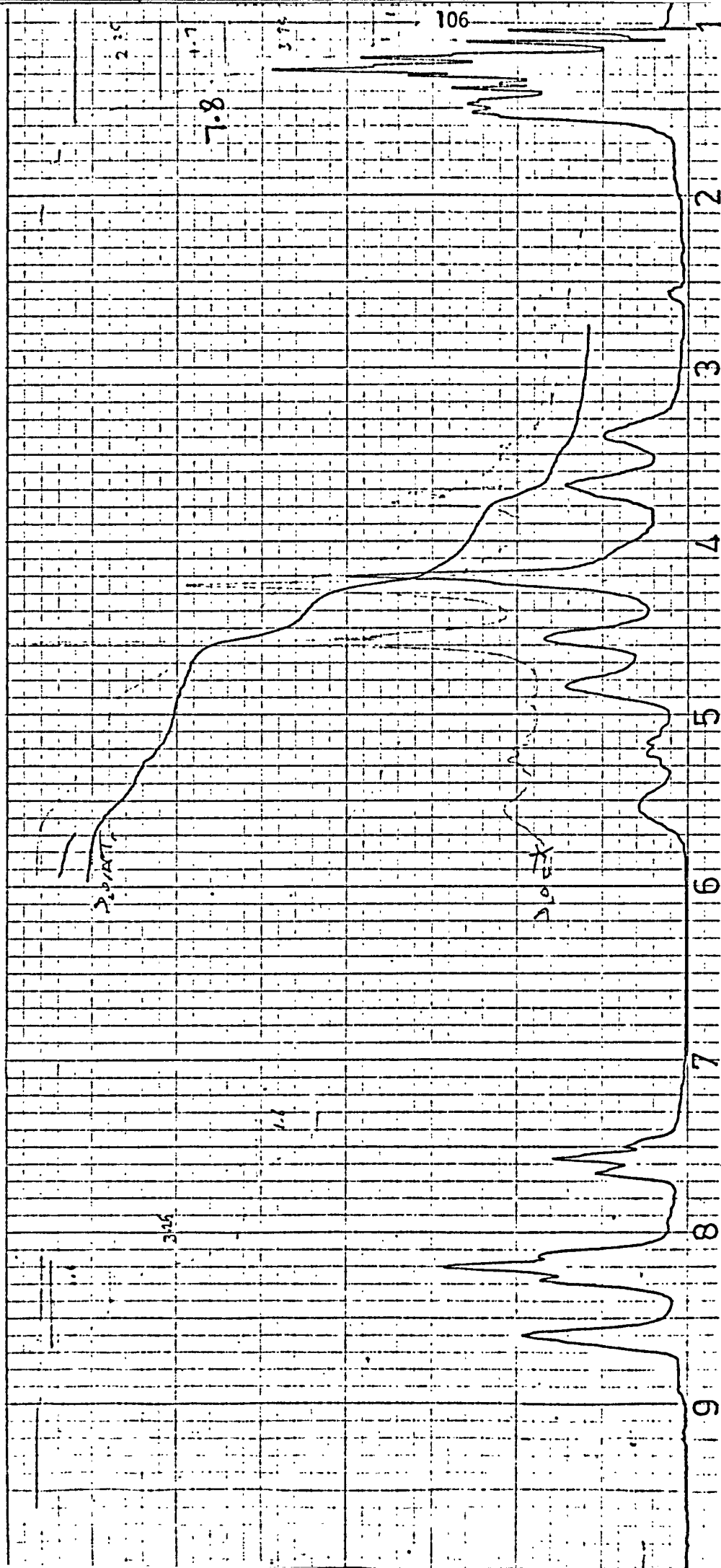


FIGURE 3.40 90 MHz NMR spectrum of PIP₁ heated at 170°C for 5 hours

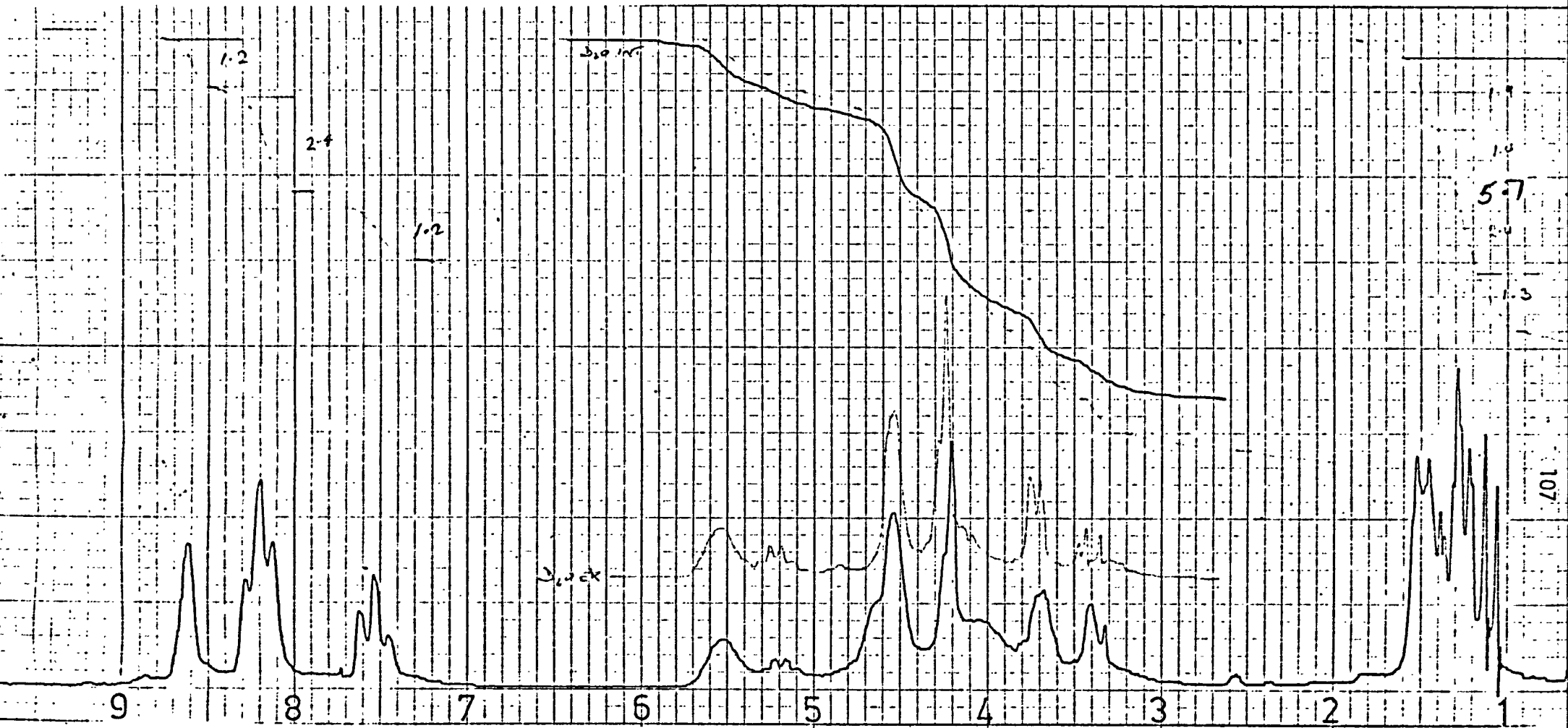


FIGURE 3.41 90 MHz NMR spectrum of PIP₁ heated at 180°C for 5 hours

It could be noticed that at higher temperatures PIP_1 displayed greater tendency to polycondensation than PTP_1 . At 170°C PIP_1 showed a greater increase in the number and ratio of higher oligomers showing up to $P(IP)_8$, as shown in Figure 3.36, while PTP_1 showed lower number and ratio of higher homologues ($P(TP)_5$) at the same temperature, see Figure 3.7. At 180°C both prepolymers showed a noticeable increase in the number and ratio of higher oligomers. PIP_1 produced higher oligomers up to $P(IP)_9$ and $P(IP)_{10}$ as shown in Figure 3.37.

90 MHz NMR spectra, Figures 3.38-3.41, obtained for the products of PIP_1 heating experiments showed very good agreement with GPC in estimating the molecular weights of products as shown in Table 3.5. These spectra, in Figures 3.38-3.41, reflected a difference in the isomerization behaviour of the two prepolymers (i.e. PIP_1 and PTP_1). The ratio of primary to secondary isomers in PIP_1 systems decreased as a function of temperature seemingly towards equal values of primary and secondary isomers. This was not the case for PTP_1 which reached approximately the same ratio for primary and secondary isomers for all temperatures, as shown in Table 3.4.

The same procedures were followed for the determination of molecular weight by GPC and NMR, and for the estimation of primary to secondary ratio of the isomers of prepolymer. The results obtained for PIP_1 systems are shown in Table 3.5.

TABLE 3.5

Characterization data for PIP_1 systems

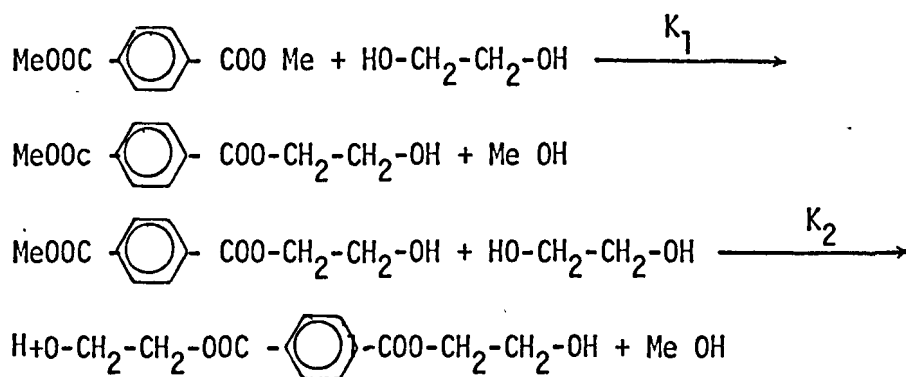
Sample	Temperature	Av. Mol. Wt		Mean	Deviation %	Loss of P	% of Primary Isomers
		GPC	NMR				
PIP_1	150°C	326	314	320	1.9	6.8	78.6%
PIP_1	160°C	365	338	351.5	3.8	10	74.4%
PIP_1	170°C	520	465	492.5	5.6	23.5	70.3%
PIP_1	180°C	575	522	548.5	4.8	29.4	64.71%

The sudden changes in molecular weight at 170°C and the loss of propylene glycol, illustrate the higher rates of polycondensation reactions at this temperature. The same behaviour can be noticed more clearly at the reaction temperature 180°C. However the decrease in the % of primary isomers did not seem to be affected by the rate of polycondensation. The same independence of this isomerization from polycondensation was found for PTP₁ systems.

3.4 General Discussion

Very few reviews seem to have been published about the ester-interchange reactions involved in the preparation of unsaturated polyester resins based on poly (propylene) terephthalate or poly (propylene) isophthalate. However the chemistry of polymers such as polyethylene terephthalate has been widely discussed in literature.

Polyethylene terephthalate has been prepared by ester-interchange (alcoholysis) of dimethyl terephthalate with ethylene glycol. The reaction proceeds stepwise:



If the methanol produced is removed from the reaction mixture high molecular weight polymers are obtained. In the absence of catalyst, Peebles and Wagner⁽¹¹⁰⁾ reported that at 175°C, $K_1 = 7.1 \times 10^{-5}$ and $K_2 = 23 \times 10^{-5}$ l/mole sec. From these results it is clear that the hydroxyl end group concentration is of importance in these ester-interchange reactions, which could explain the fast polycondensation achieved at a relatively low temperature i.e. 150°C in the polycondensation of PTP₁. However, it was reported by Challa⁽⁶⁰⁾ that if polyethylene terephthalate (PET) was prepared from bis (2-hydroxy ethyl) terephthalate as starting material, the rate decreases in the later stages of the reaction which could be caused by the decrease in the contents of ethylene glycol as it was distilled off the reaction mixture.

The ester interchange and polycondensation are also affected by the saturated acid used in the preparation of prepolymer. In the studies on the ester interchange reactions of dimethyl esters of dicarboxylic acids with ethylene glycol, Giehl et al⁽¹¹¹⁾ and Sumoto et al⁽¹¹²⁾ reported the rate of alcoholysis to decrease in the order:

dimethyl terephthalate > dimethyl sebacate > dimethyl
isophthalate > dimethyl phthalate.

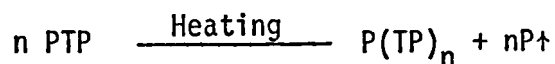
Again here, these results gave the same order of reactivity for the dicarboxylic acid based prepolymers (PTP₁ and PIP₁) in the ester interchange reactions described in this Chapter at 150°C and 160°C. However, the two prepolymers (PTP₁ and PIP₁) showed higher reactivity at 170°C and 180°C especially PIP₁.

In addition to the concentration of hydroxyl end groups and the type of the saturated acid of the prepolymer in the PTP₁ and PIP₁ systems, the fast ester interchange and the subsequent polycondensation seem to be brought about by the labile nature of propylene glycol. The dependence of polyesterification on the type of glycol was studied by Vancso-Szmercsanyi et al⁽¹¹³⁾ using saturated dibasic acids and ethylene, butylene, and hexamethylene glycols. They found that the rate constants of the forward reaction and values of equilibrium constants increase considerably with the growth of the chain length of the glycol; at the same time the rate constant of hydrolysis decreases. Using dimethyl terephthalate, Giehl et al⁽¹¹⁴⁾ reported that there were very small differences in the rates of alcoholysis with alcohols such as ethylene glycol, 1,3-butane diol, 1,4-butane diol, benzoyl alcohol or octyl alcohol.

One of the interesting points about the heating reactions with PTP₁ and PIP₁ was the big change in the polycondensation rate of these prepolymers at 180°C. This implied greater reactivity and higher rate constants at this temperature. This observation was also noticed for other systems in the work of Vancso-Szmercsanyi et al⁽¹¹⁵⁾ who examined the effect of temperature on the equilibrium reaction of adipic acid

and ethylene glycol at various temperatures (140°C - 180°C). They reported that the equilibrium constant was practically independent of temperature, but at 180°C a sharp increase in the rate constants of the forward and reverse reactions was noticed, as well as the difference between the two rates.

The production of high oligomers on heating PTP₁, just like (PET) systems, can be brought about by distilling the resulting glycol by-product from the reaction vessel:



However in the PIP₁ experiments products the NMR spectra, on the contrary to PTP₁, show absorptions indicating the presence of free propylene glycol. These absorptions increase their intensity with the increase in temperature.

CHAPTER 4

AN INVESTIGATION OF MALEIC ANHYDRIDE POLYMERIZATION
WITH TEREPHTHALIC AND ISOPHTHALIC BASED PREPOLYMERS4.1 Introduction

Following the investigation of the ester-interchange and polycondensation reactions in the heating experiments with (PTP₁) and (PIP₁), it was of interest to see the effect of these reactions on the polymerization of these prepolymers with maleic anhydride (MA).

It is well known that these polymerization reactions with maleic anhydride (MA) are highly exothermic and that a number of secondary reactions may occur, as described in Chapter 1. Therefore, it was intended to curb these reactions to simple situations in which the reaction products would essentially be of low molecular weights and could easily be analysed and detected. This was attempted by performing these reactions, under nitrogen, for only a short period of time (30 minutes) and at a constant low temperature (150°C). This temperature was sufficiently high to melt all the prepolymer (PTP₁, M.P = 141°C), in which (MA) dissolves. The findings reached from these reactions were then used to interpret the data obtained from other polymerization reactions which were carried out for longer periods of time (5 hours). Similar polymerization reactions were carried out, under nitrogen, for 30 minutes but at a higher temperature (180°C) so as to see the effect of temperature on these systems.

4.2 Apparatus and Method

The apparatus used here was the same as that used for the heating experiments with PTP₁ and PIP₁ (Figure 3.4). The reactions of PTP₁ and PIP₁ with (MA) at 150°C was carried out at the same time in the same oil bath under the same conditions. 1.41g of PTP₁ (or PIP₁) was charged into the flask, together with 0.49g of MA (1:1 molar ratio). The flask was flushed with nitrogen and left under nitrogen throughout the reaction time. The flask was immersed in an oil bath already heated to the required temperature (150°C) with a temperature control of $\pm 2^\circ\text{C}$. The reaction mixture formed a clear brown solution and reached the

required temperature in about 3 minutes. The mixture was left to stand for 30 minutes to give the product (viscous material) which was analysed by GPC and NMR. The same experiments were repeated for PTP₁ and PIP₁ with (MA) at 180°C.

4.3 Qualitative GPC Analysis of Polymerization Products at 150°C

The two products of the polymerization reactions of PTP₁ and PIP₁ with maleic anhydride at 150°C were analysed by GPC with a twin-column arrangement (Figure 2.3).

Solutions of samples (0.02g) in chloroform (3 ml) were applied to the GPC two-column arrangement. The infra red detector was pre-set at the maximum carbonyl absorption region determined previously by experiment. The flow rate was in the range of 12-15 ml/hr. The highest molecular weight component started to emerge from the column after 12 hours. The chromatogram obtained for these products can be seen in Figure 4.1 and Figure 4.2. The sequence of the increase in molar mass for the peak components of these chromatograms followed the order: $a < b < c < d < e < f$ and $g < h < i < j < k < l$ for Figure 4.1 and Figure 4.2 respectively.

As it was already proved in Chapter 3 that PTP₁ and PIP₁ were eluted at the same elution volume from the column, it was further assumed that the elution volume of the same species in the products resulting from the reaction of PTP₁ and PIP₁ with maleic anhydride will have the same elution volume. According to this assumption three main differences can be observed from the relative areas of the peaks in these two chromatograms. From the relative areas of the peaks d, e and f and j, k and l after normalising the chromatograms in Figures 4.1 and 4.2 respectively, it could be suggested that PIP₁/(MA) produced larger quantities of higher molecular weight species appearing at elution volumes up to 204 ml in the two chromatograms. In the chromatogram obtained for PIP₁/(MA), which is shown in Figure 4.1, peaks d, e and f have relatively larger areas than peaks j, k and l in Figure 4.2 after normalisation. The other two differences lie in the components in the low molecular weight region which appear at elution volumes higher than 204 ml in both chromatograms (Figures 4.1 and 4.2). The lowest molar mass component in PTP₁/(MA), peak (a) at elution volume 230 ml, has larger relative GPC area after normalisation than the

corresponding component in PIP/(MA), peak (G) at elution volume 234 ml. Also in Figure 4.1 the peak containing the next higher molecular weight component, peak (b) at elution volume 204 ml, is more than twice larger than the area of the first peak in the same figure (a) and also far larger than the other peaks at lower elution volumes. If peak (b) in Figure 4.1 after normalisation is compared to the corresponding peak in Figure 4.2, peak 'h' at elution volume 224 ml, it was found that peak 'h' was also more than twice as large in GPC area as the first peak (G) in the same chromatogram. But peak 'h' is different from peak 'b' in that it appears closer in elution volume to the peak of higher elution volume, peak 'G', the first peak. Another difference is that peak 'h' in Figure 4.2 is followed and partly overlapped by another considerable peak, peak (i) at elution volume 209 ml, while peak 'b' in Figure 4.1 is followed by much smaller peaks with elution volumes below 204 ml.

Comparative GPC Analysis of Polymerization Products at 150°C

The analytical traces shown in Figures 4.1 and 4.2 were obtained at different times and not at exactly the same eluant flow rate in the GPC system. So, more GPC experiments were performed to see whether the peaks at the highest elution volumes in the two chromatograms are of the same molar mass and also to examine the reality of the apparent difference in the elution volume of peak (b) and peak (h).

To a sample from the product of PTP₁/(MA) a small quantity of PTP₁ was added and the mixture was applied to the GPC column. Similarly, a small quantity of PIP₁ was added to a sample taken from the product of PIP/(MA) and applied to the GPC system. The mixture of PTP₁ and PTP₁/(MA) produced the chromatogram shown in Figure 4.3. When this chromatogram is compared to Figure 4.1, it can clearly be shown that peak (a) in Figure 4.1 was enhanced by the addition of PTP₁ in Figure 4.3.

The chromatogram obtained for the mixture of PIP₁ and PIP₁/(MA) is shown in Figure 4.4, which also showed that the component in peak 'G' in Figure 4.2 was enhanced by the addition of PIP₁. Therefore peaks (a) and (G) in both systems were representing components of the same molar mass which is equal to the molar mass of PTP₁/PIP₁.

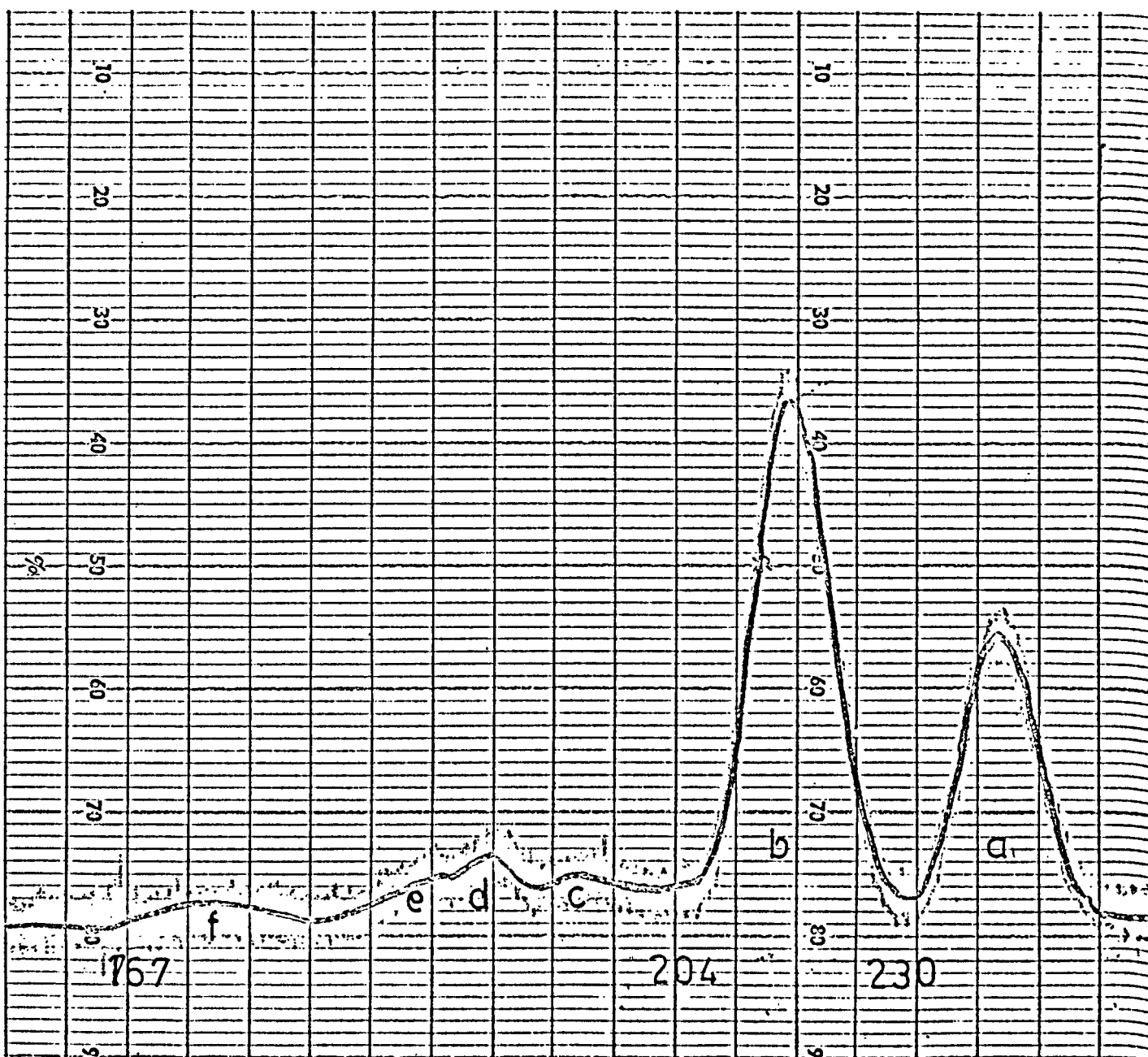


FIGURE 4.1 GPC Chromatogram of (1 PTP₁:1M)/150°C, 30 mins

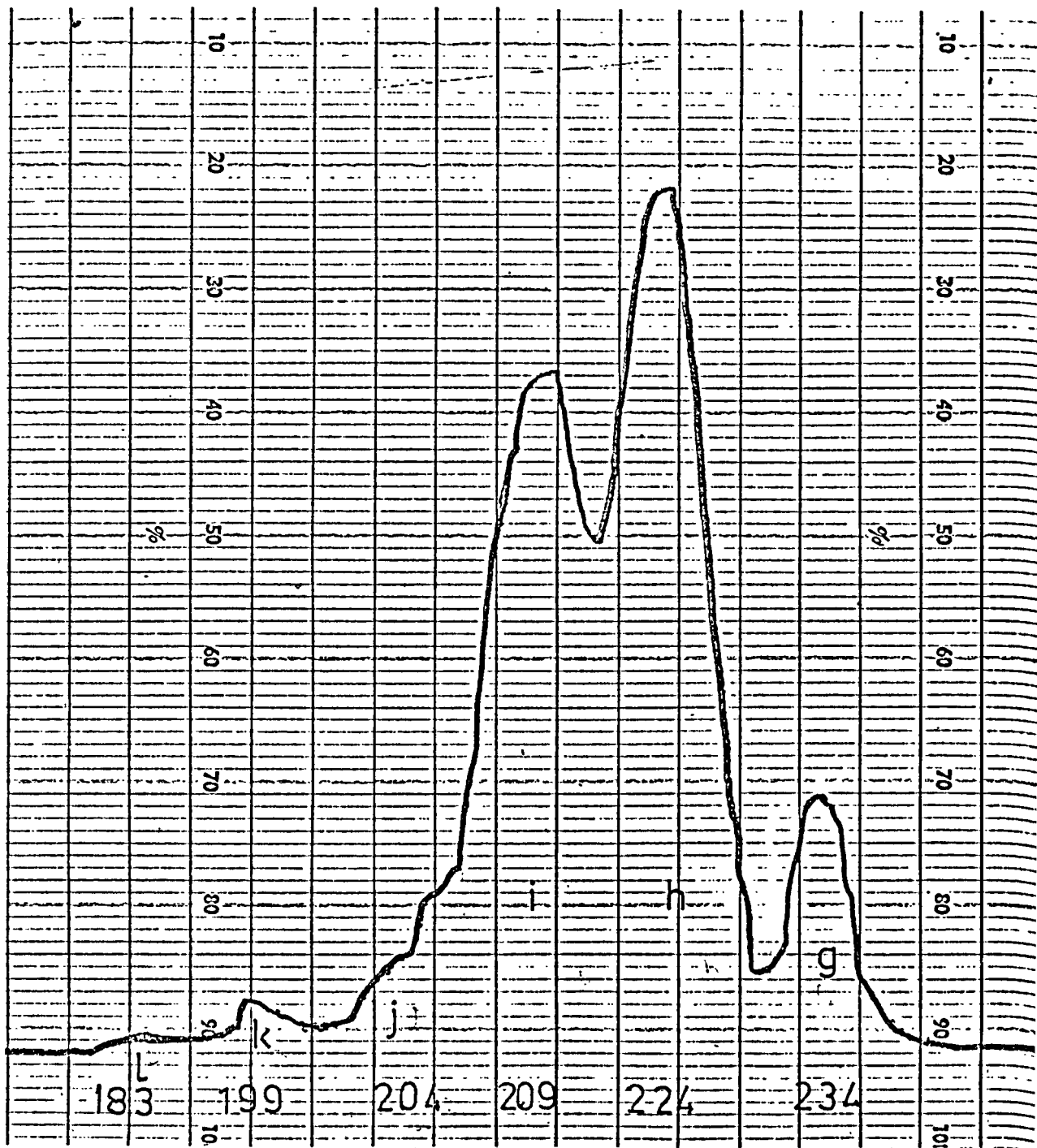


FIGURE 4.2 GPC Chromatogram of (1 PIP₁:1 M)/150°C, 30 minutes

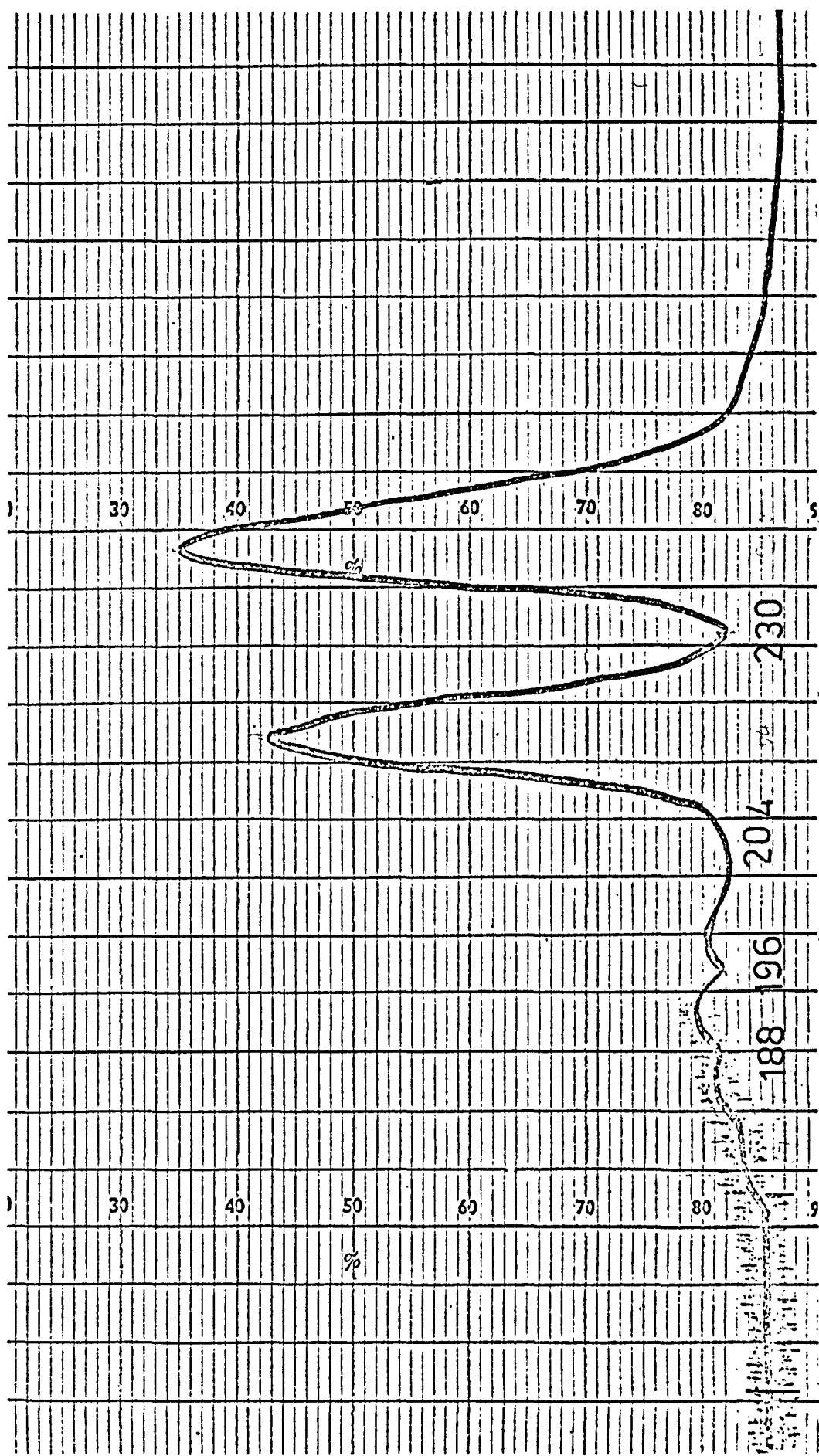


FIGURE 4.3 GPC Chromatogram of (1 PTP₁:1 M)/150°C, 30 mins + PTP₁

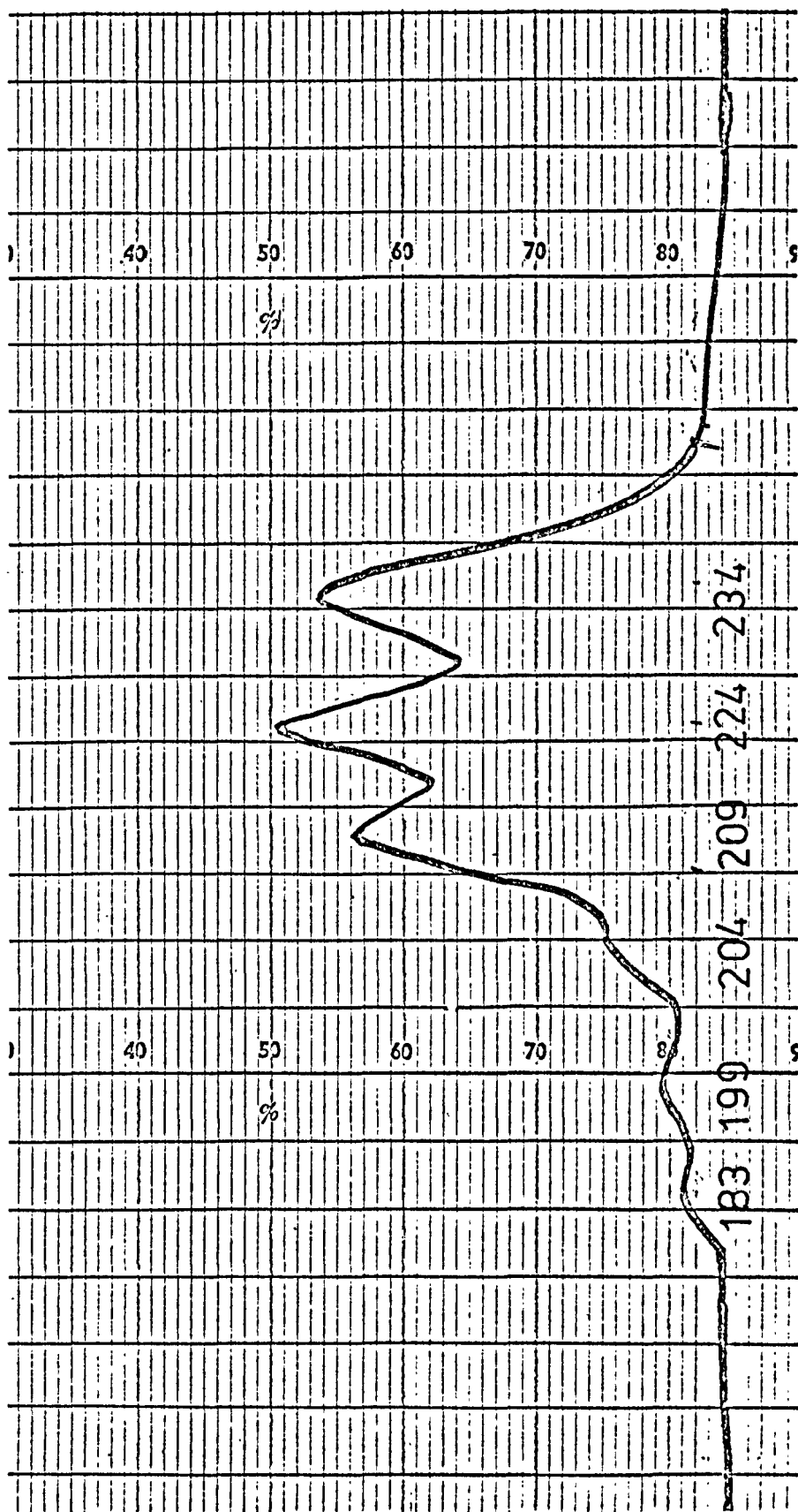


FIGURE 4.4 GPC Chromatogram of (1 PIP:1M)/150°C, 30 min + PIP₁

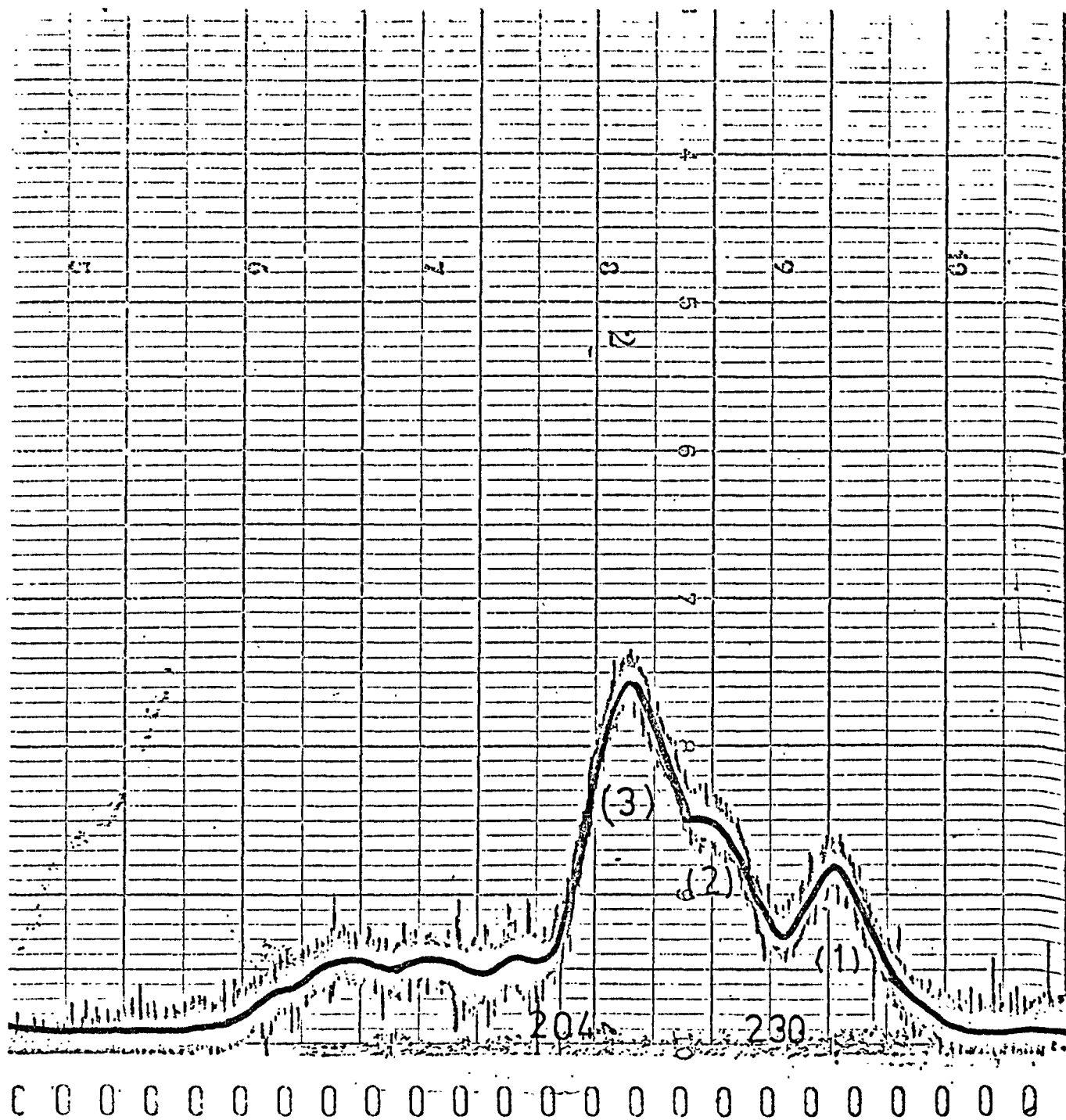
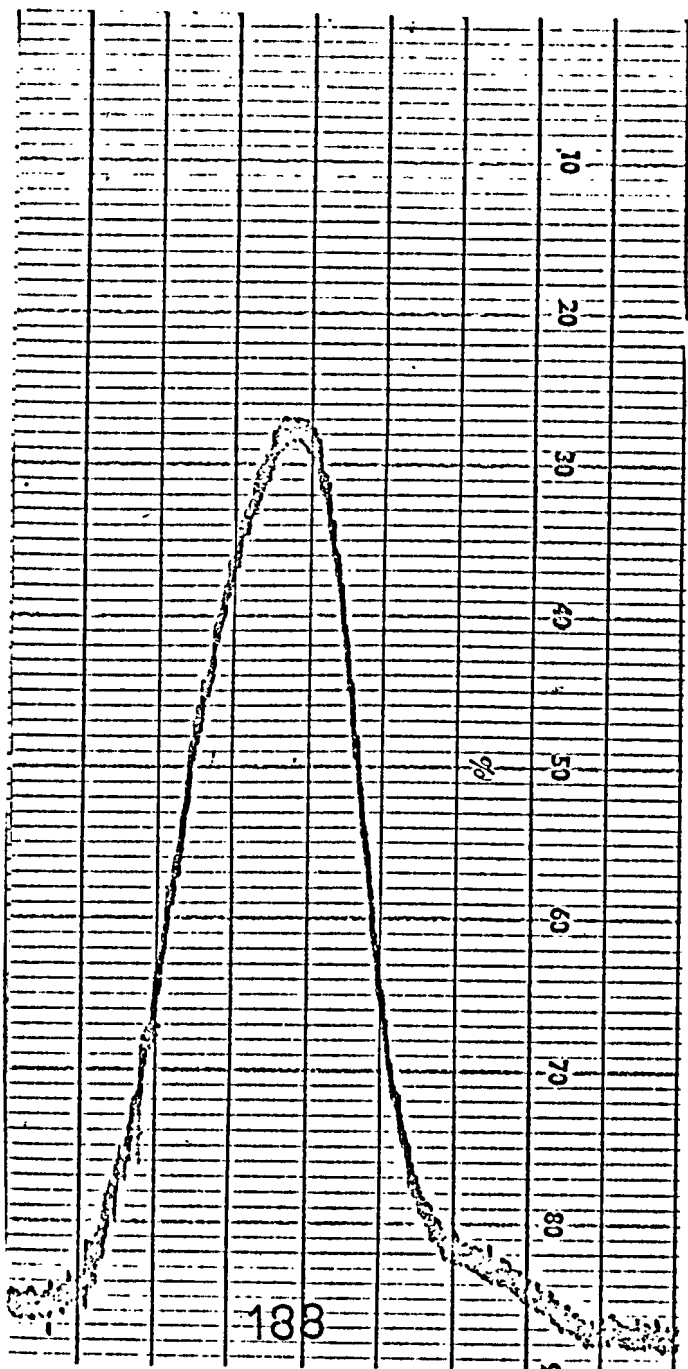
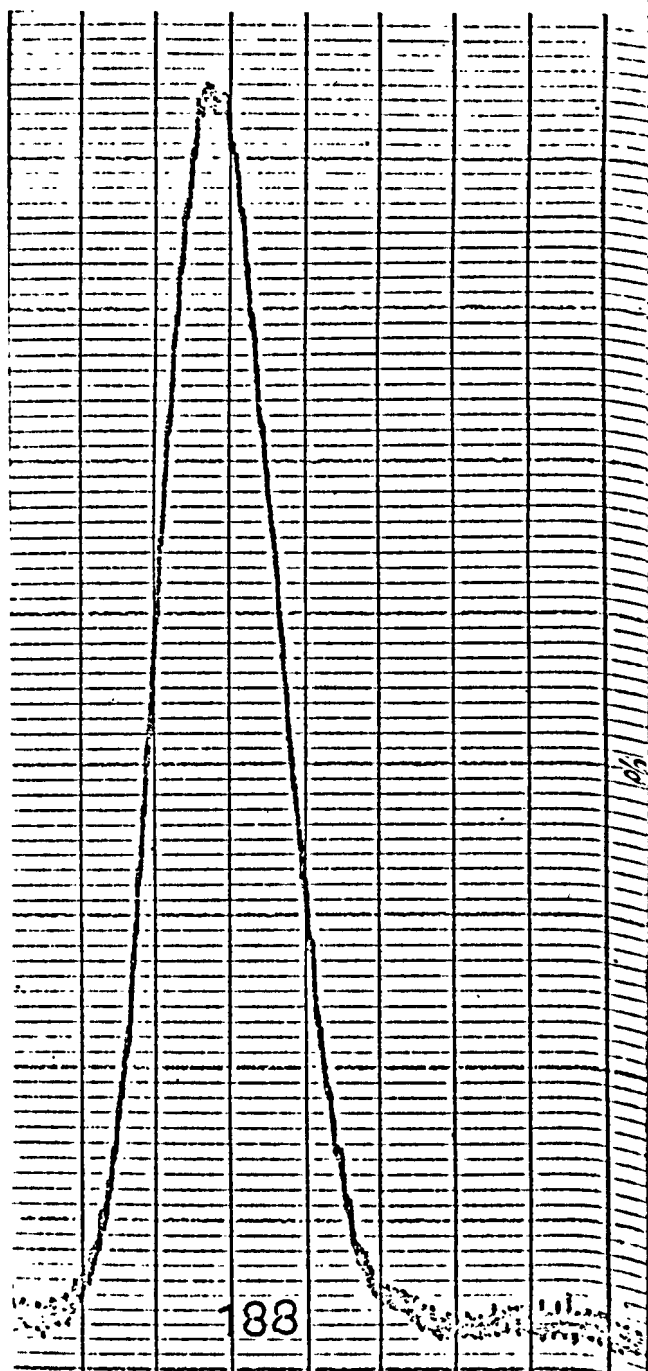


FIGURE 4.5 GPC Chromatogram of (1 PTP₁:1 M)/150°C, 30 mins + (1PIP₁:1M 150°C, 30 mins

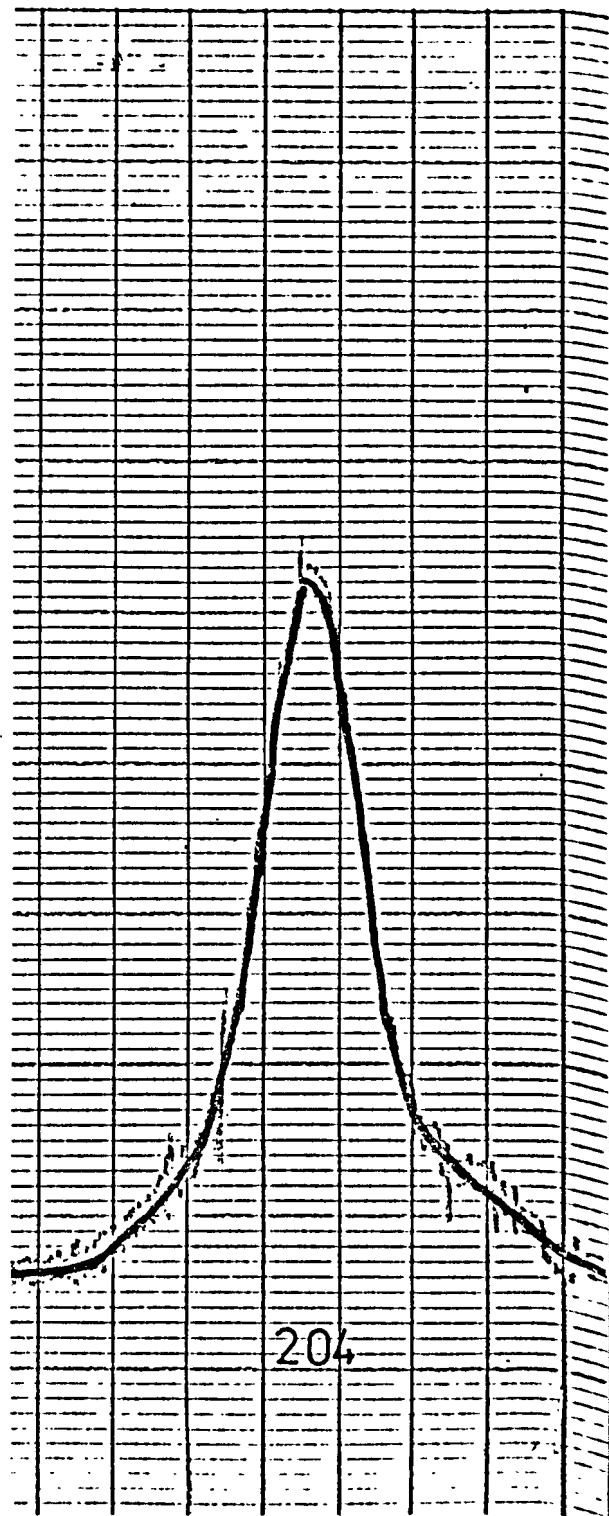
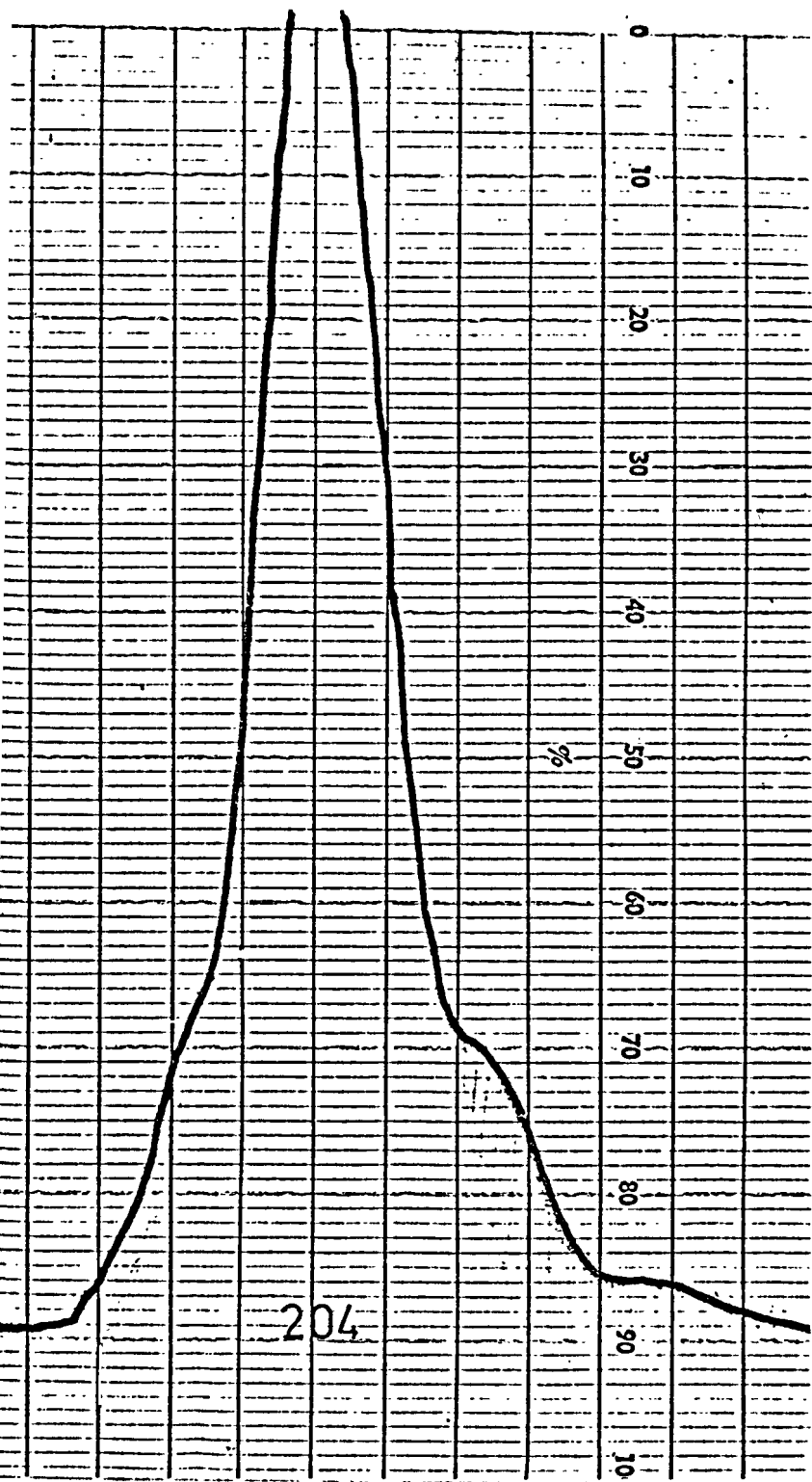


Peak 'd' PTP₁/M 150°C
2nd fractionation



Peak 'd' PTP₁/H 150°C
Final form

FIGURE 4.6



Peak 'J' PIP₁/M 150°C
2nd Fractionation

Peak 'J' PIP₁/M 150°C
Final Form

FIGURE 4.7

In the other GPC experiment, performed to examine the differences in elution volume of peaks (b) and (h), small quantities from the products of PTP_1/MA and PIP_1/MA reactions were mixed and the resulting sample was applied to the GPC system. The chromatogram obtained is shown in Figure 4.5. When this is compared to Figures 4.1 and 4.2, it can be noticed that the higher elution volume region, above 204 ml, was more enhanced which means a concentration of the large peaks from both systems in this region. Peak (1), the peak of lowest molecular weight, highest elution volume, in Figure 4.5, was proved by the previous experiments to be the result of peak (a) in Figure 4.1 and peak (G) in Figure 4.2. The next peaks in Figure 4.5, peak (2) and peak (3) were taken to correspond to peak 'h' and (i) in Figure 4.2. But peak (3) in Figure 4.5 was much larger than peak (2) whilst the corresponding peak in Figure 4.2, peak (i) was smaller than peak 'h'. It could be then suggested that peak (3) in Figure 4.5 was the result of peak 'b' in Figure 4.1 and peak (i) in Figure 4.2. This result confirmed the suggestion that peak (b) in Figure 4.1 was due to a higher molecular weight component than the component in peak 'h' in Figure 4.2 and it came at a lower elution volume. Therefore the difference observed earlier in their elution volumes is real.

4.4 Quantitative GPC Analysis of Polymerization Products at 150°C

Samples from the products of polymerization reactions of PTP_1/MA and PIP_1/MA at 150°C were fractionated by a preparative two-column GPC system. As the flow rate was relatively slow (~ 10 ml/hr) the fractionation process of each sample took about 24 hours. Sufficient quantities of samples (0.10g) were dissolved in chloroform (1.0 ml) and applied to the first GPC column. It was noticed that a slight increase in the volume of solvent reduced the viscosity of the sample and improved the resolution obtained. This is provided that enough time was allowed for injection ports and the top part of the column to be washed with small volumes of solvent (0.3 ml), i.e. the flow of the eluant was not resumed unless the sample was a few centimetres down the column. When the fractions were eluted from the second column through the infra red cell, the solvent containing these fractions ran through a short length of PTFE tubing into sample tubes. These sample tubes were

placed as near as possible to the infra red cell to avoid contamination by subsequent fractions. The eluant obtained at each GPC peak was collected separately. The solvent (chloroform) was then evaporated at reduced pressure at low temperature (40-50°C). The residue was dissolved again and applied to the GPC system. As an example, the procedure for fraction 'j' in the analytical separation in Figure 4.2 will be considered. A preparative fractionation was performed and the fraction corresponding to 'j' was collected and refractionated. An analytical GPC trace for this fraction at this stage is shown in Figure 4.7. The chromatograms obtained at this stage usually showed a contamination with higher and lower molecular weight components. The process was repeated till a single peak was obtained for each fraction. Examples of peaks obtained for fractions 'j' and 'd' are cited in the Figures 4.6 and 4.7.

4.5 NMR Analysis of Fractions

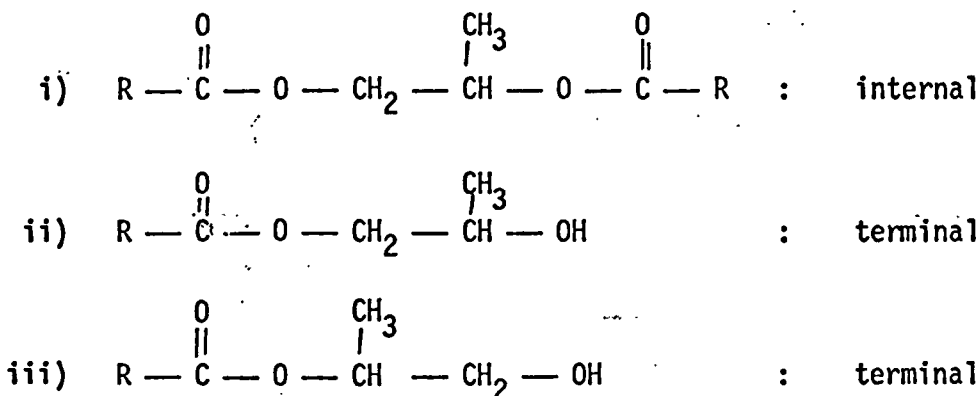
NMR spectra were recorded for the fractions obtained from the preparative, GPC fractionation. Fourier Transform 300 MHz NMR spectrometer was used in these investigations. A full spectrum was obtained and then the spectrum was subdivided into three regions and separate magnified spectra were obtained for the different regions with better resolution. Integrated traces at different intensities were also obtained to facilitate the measurements of integrals which were later used with GPC for the results of quantitative analysis.

Data from these spectra were used to assign fractional components to each GPC peak. Other information such as the degree of maleate/fumarate conversion and the ratio of secondary linked to primary linked terminal propylene glycol molecules, was obtained. The parameters used to assign fractional components to GPC peaks, shown in Tables 4.1, 4.2 and 4.3 and Tables 4.4, 4.5 and 4.6 were as follows.

The data in column one in Tables 4.1 and 4.4 depend on the numerical ratios of the type of molecules present in the fractional component. This was determined by measuring the integrated traces for the phenyl protons (7.3 - 8.6 ppm), the unsaturated acid protons (6.35 ppm,

6.8 ppm) and propylene glycol protons in the form of methyl (1.18-1.47 ppm) or (methylene + methine) protons (3.7 - 5.5 ppm). Then each value obtained was divided by the number of protons present in each group to give the numerical ratio of molecules for each type. It could be mentioned here that the ratio of maleate to fumarate species can also be calculated from their integrals as the maleates absorb at ~ 6.3 ppm and the fumarates absorb at ~ 6.8 ppm.

Propylene glycol molecules in terminal positions were compared (as percentage values) to those placed internally, i.e. incorporated between acids (2nd column tables 4.1 and 4.4). 'p' can be present in one of these environments:

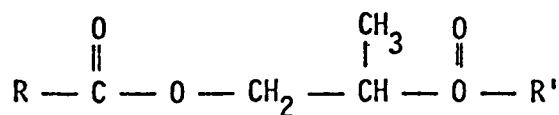


where R is a saturated or unsaturated acid, the absorptions in δ values for these structures are:

	(i)	(ii)	(iii)
methyl protons	(i) 1.3 - 1.53	(ii) 1.18 - 1.25	(iii) 1.3 - 1.36
methylene protons	(i) 4.18 - 4.57	(ii) 4.05 - 4.15	(iii) 3.7 - 3.84
methine protons	(i) 5.2 - 5.58	(ii) 4.0	(iii) 5.0 - 5.2

As the methylene groups chemical shifts are well separated in the field they are therefore the ideal choice for the comparison between different types of molecules in components of reasonably low molecular weights. This comparison will show the environments of propylene glycol (P) in the molecule and whether it is (P) terminal or internal.

The methine protons in internal propylene glycol molecules exhibit different absorptions according to the type of acids attached to both ends of the propylene glycol molecule (see column 3, tables 4.3 and 4.6). If we consider the following structure:



when:

R = T(or I), R' = T(or I), methine absorptions = 5.5-5.58 ppm

R = T(or I), R' = M " " = 5.35-5.5 ppm

R = M , R' = M " " = 5.2-5.35 ppm

The integrated trace obtained for the methine protons at each chemical shift in the same spectrum can then be measured and compared to each other. Therefore the ratio of different segments (-MPM-, -TPM-, -TPT) could be determined for the different fractions.

The above mentioned parameters gave a good description of the components present under each fraction by giving the numerical ratio of the types of molecules present, a quantitative description of the environment of (P), whether terminal or internal, in primary or secondary isomer form, and finally the distribution of saturated and unsaturated acid components in the molecules. However, the comparisons, based on integral measurements, were confined to the same spectrum in each case to attain the maximum accuracy of results.

Assignments of Fractional Components

Fraction (a) and (G):

Fractions under peak (a) and (G) in Figures 4.1 and 4.2 were proved to be eluted at the same elution volume as PTP₁ and PIP₁ respectively. In each case their fractional component gave an NMR spectrum which displayed the presence of the prepolymer, i.e. giving peaks at the same chemical shifts of the prepolymers.

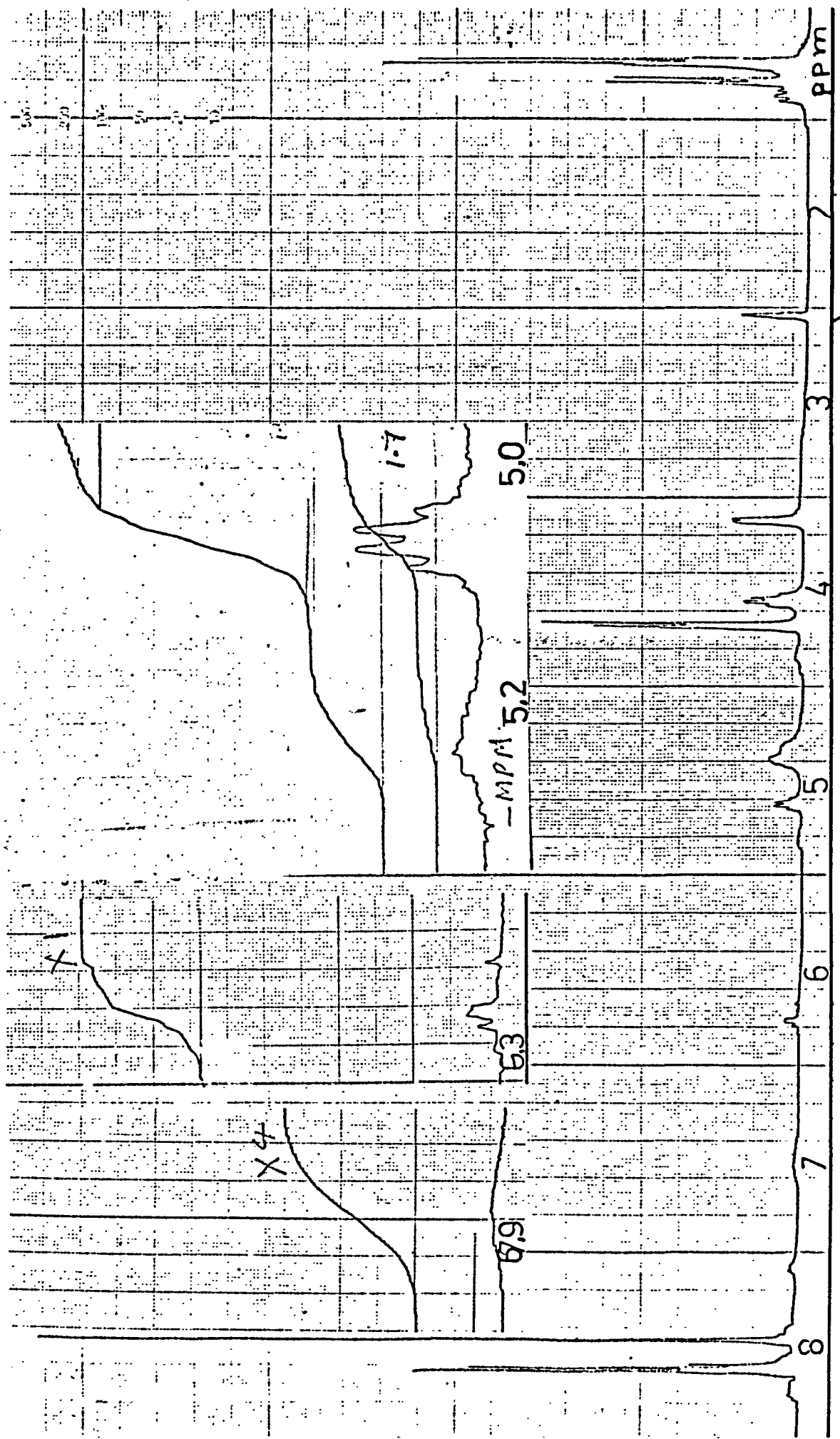


FIGURE 4.8 300 MHz NMR Spectrum of peak (a) in Figure 4.7.

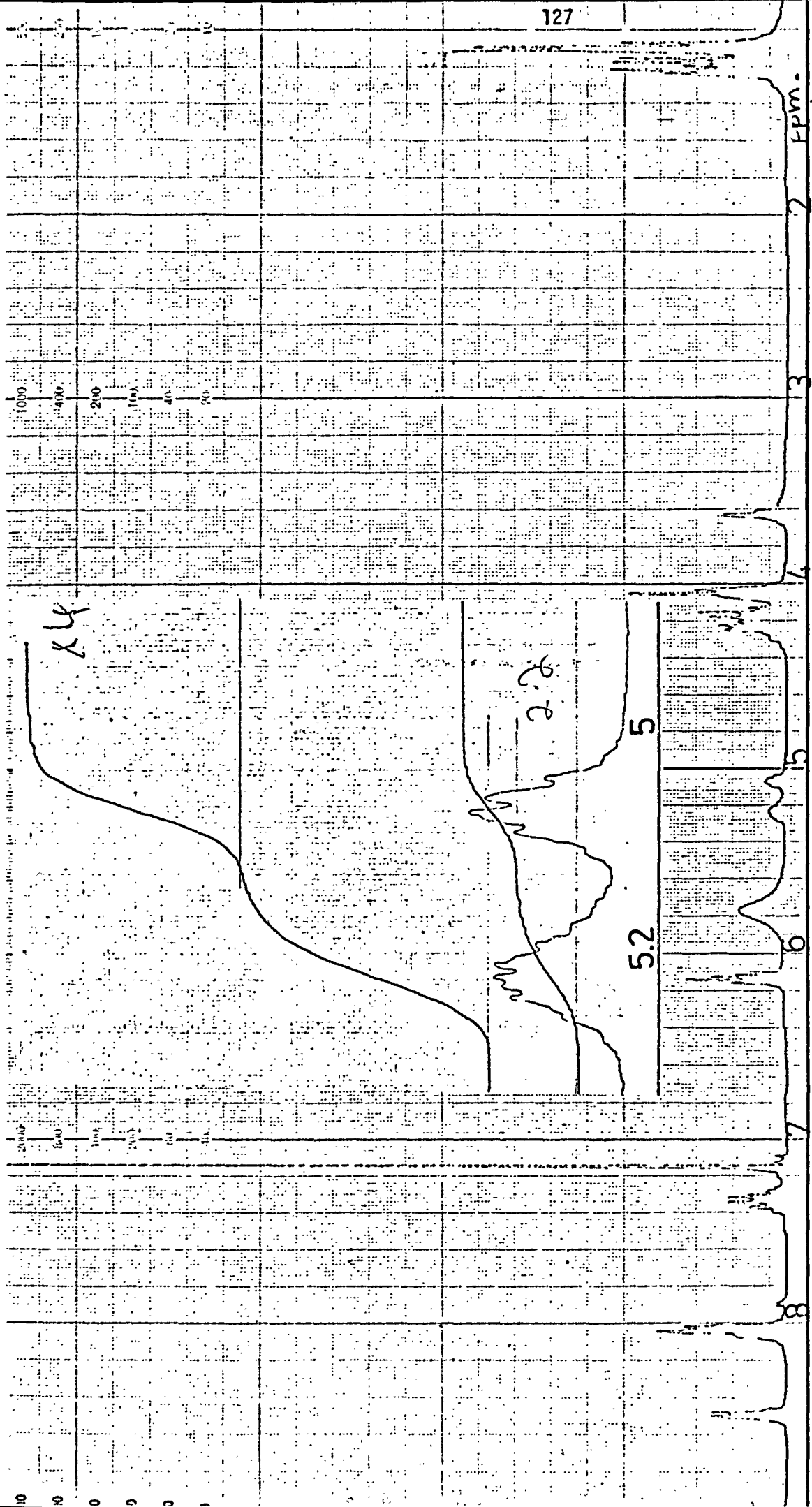


FIGURE 4.9 300 MHz NMR Spectrum of peak 'G' in Figure 4.12

In Figure 4.8 there are two peaks at 1.15 ppm and 1.25 ppm for the primary and secondary methyl protons in PTP_1 ; two peaks at 3.7 ppm and 4.2 ppm for the secondary and primary methylene protons in PTP_1 ; two peaks at 4.05 ppm and 5.05 ppm for the primary and secondary methine protons in PTP_1 and the normal aromatic absorption for PTP_1 at 8.1 ppm. But together with this they showed other interesting features: the presence of unsaturated acid components mainly at 6.3 ppm, methine absorptions at 5.2-5.3 ppm corresponding to an -MPM- segment, a broad peak at 4.4-4.5 ppm for methylene absorptions in an internal (P) molecule; and a multiplet at 1.4-1.5 ppm, a characteristic of methyl protons in an internal (P) molecule.

In Figure 4.9 the absorptions due to the prepolymer are also noticed within approximately the same chemical shifts for PTP_1 except the phenyl protons which occupy the region between 7-9 ppm in the spectrum. Also, together with these absorptions additional peaks are present; the absorption at 6.3 ppm for maleate species, the peak at 5.2-5.35 ppm for the methine protons in -MPM- type environments, the multiplet at 4.2-4.4 ppm for internal (P) methylene protons and a similar multiplet at 1.3 ppm for the methyl protons of an internal (P) molecule.

In Figure 4.8 and Figure 4.9 parts of the extended spectra, for the unsaturated component protons and the methine protons, are included. However, because there are no absorptions corresponding to -TPT- (5.5 δ) or -TPM- segments (5.4 δ), the observations above suggested the presence of a prepolymer and another component constituted of (P) and (M) containing segments of the -MPM- type. The following procedure was followed to assign the suitable structures:

Ratio of integrals:	for (G)	(1 in table 4.4)
M/F	I	P
3.2	9.2	16.2
for PTP_1 -	9.2	13.8

We are then left with 3.2 (M/F) and 2.4 (P) which is the correct ratio for MPM.

Similarly for (a) (1 in table 4.1)

M/F	T	P
3.8	8	14.85
for PTP ₁ -	8	12

there remains 3.8 M/F and 2.85 (P) which is also the correct ratio for MPM. Therefore these components were assumed to be PTP₁ + MPM and PIP₁ + MPM for fraction (a) and (G) respectively. In fraction 'a' the ratio of PTP₁ to MPM was calculated in the following way:

$$\text{Numerical ratio for 'T'} = \frac{8}{4} = 2 = \frac{\text{integral value}}{\text{No of protons in phenyl terephthalate ring}}$$

2 units of 'T' will produce 2 PTP molecules

$$\text{Numerical ratio for (M/F)} = \frac{3.8}{2} = 1.9$$

1.9 units of (M/F) will give $\frac{1.9}{2} = \underline{0.95}$ MPM molecules

Therefore the ratio of PTP₁:MPM in fraction 'a' is 2:0.95

Similarly in fraction (G) the ratio of PIP₁ to MPM was calculated in the following way:

$$\text{The numerical ratio for (I)} = \frac{9.4}{4} = 2.35$$

2.35 units of (I) will give 2.35 PIP₁ molecules

$$\begin{aligned} \text{Numerical ratio for (M/F)} &= \frac{3.2}{2} = \frac{\text{integral value}}{\text{No of protons in unsat.}} \\ &= 1.6 \end{aligned}$$

1.6 units of (M/F) will give 0.8 MPM molecules

Therefore the ratio of PIP₁:MPM in fraction 'G' is 3:1.

These ratios obtained for the fractional components of fractions (a) and (G) also satisfy the ratios of terminal/internal (P) molecules as shown in Tables 4.1 and 4.4.

TABLE 4.1

Fractionation data for PTP/M/150°C, 30 minutes

No	Experimental Values from spectra			Terminal (P)	Between Acids P	Assigned Fractional Component	Calculated Ratios of species			Calculated Values		Primary / Secondary ratio of term.(P) from spectra	
	M/F	T	P				M/F	T	P	Terminal (P)	Internal (P)	Primary	Secondary
1	3.8	8	14.85	89	11	PTP 2 MPM 0.95	1.90	2	4.95	82.6	17.4	69	31
2	7.6	16	18	25	75	TPMPTP MPTPM	2	2	3	20	80	68	32
3	6.45	11.5	17.1	43	57	(PTPM) ₂ P 4 M(PTPM) ₂ 1	1.1	0.8	1.9	33	67	69	31
4	4.6	8	14.7	7	93	(PTPM) ₂ PM	5	4	10	20	80	-	-
5	6.15	8	12.6	15	85	PM(PTPM) ₃	3	2	4	14	86	-	-
6	6.9	6.8	13.4	26	74	PM(PTPM) ₃ PMP	2	1	2.6	22	78	-	-

TABLE 4.2

Calculation of Ratio of Species from GPC Areas and Assigned Structures in PTP/M, 150°C

Fraction Number	Fractional Component	% of whole sample	GPC Area	Real Area	Areas due to		Calc. from (T) P
					M	T	
1	PTP MPM	43.1	0.486	0.183	0.0891	0.0938	0.2321
2	TPMPTP MPTPM	46.1	1.175	0.1958	0.0997	0.0997	0.1496
3	(PTPM) ₂ P	4.2	0.144	0.018	0.0104	0.0076	0.0179
4	(PTPM) ₂ PM	3.9	0.165	0.0165	0.0093	0.0072	0.0180
5	PM(PTPM) ₃	2.3	0.135	0.0096	0.0053	0.0038	0.0079
6	PM(PTPM) ₃ PMP	0.4	0.033	0.0018	0.0012	0.0006	0.0015
					0.2140	0.2127	0.2136
					106%	100%	104%

TABLE 4.3

Estimation of segments ratios and m/f transformations in PTP/M/150°C, 30 minutes

Structure	Calculated Value of (P)	Calculated			Experimental Spectral Values			% of f/m		Real GPC Area due to	
		-MPM-	-MPT-	-TPT-	-MPM-	-MPT-	-TPT-	f	m	f	m
PTP MPM	0.2321	0.0464	-	-	100%	-	-	18	82	0.0149	0.0661
TPMPTP MPTPM	0.1496	-	0.0997	-	-	100%	-	-	100	-	0.0668
(PTPM) ₂ P	0.0179	-	0.0132	-	0.0016	0.0111	0.0007	12	88	0.0011	0.0079
(PTPM) ₂ PM	0.0180	0.0035	0.0106	-	0.0087	0.0104	0.0018	18	82	0.0016	0.0031
PM(PTPM) ₃	0.0079	-	0.0068	-	0.004	0.0069	0.0009	27	73	0.0011	0.0015
PM(PTPM) ₃ PMP	0.0015	-	0.0004	-	0.0011	-	0.007	0.0087	0.0007	-	-

Totals:

0.0474 0.1313

25.2% 25.2%

73.5% 1.7%

Sum of fractions values:

27.7% 72.3%

11% 89%

Whole sample values:

22.2 77.8%

TABLE 4.4

Fractionation data for (1 PIP₁:1M)/150°C, 30 minutes

No	Experimental Values					Assigned Fractional Component	Calculated Component Ratios			Calculated Values		Primary / Secondary ratio of terminal P	
	Spectra Values			Terminal P	Internal P		M/F	I	P	Terminal (P)	Internal (P)	Primary	Secondary
1	3.2	9.4	16.2	80.4	12	PIP 3 MPM 1	1	1.5	3.5	85	15	72	28
2	7	11.5	16.9	47.6	52.4	PIPM 10 PMPM 1	1	1	2	50	50	48	52
3	8	8.05	15.6	32.7	67.3	PMPIM 7 PIPMPM 1	2	1	2.6	33	67	64	35
4	6.4	11	14.8	35	65	P(IP) ₂ MP 2 MPIPMPM 1	1	1	2	36	64	67	33
5	4.7	9.8	13.4	30	70	(PIPM) ₂	1	1	2	25	75	67	33
6	7.4	7.8	12.4	32	68	PMP(PIPM) ₂ PM	2	1	3	17	83	-	-

TABLE 4.5

Calculation of Ratios of Species from GPC Areas and Assigned Structures in PIP/M, / 150°C

No	Fractional Component	% of the whole sample	GPC Area	Real Area	Ratios of areas due to acids		
					I	M	P
1	PIP 3 MPM 1	19.4	0.107	0.0428	0.0257	0.0171	0.0600
2	PIPM 10 PMPM 1	48.47	0.475	0.1188	0.0594	0.0594	0.1188
3	PMPIM 7 PIPMPM 1	26.93	0.396	0.066	0.0221	0.0446	0.0572
4	P(IP) ₂ MP 2 MPIPMPM 1	4.1	5.047	0.0059	0.0030	0.0030	0.0060
5	(PIPM) ₂	1.31	0.026	0.0033	0.0017	0.0017	0.0034
6	PM(PIPM) ₂ PM	1.41	0.035	0.0035	0.0012	0.0023	0.0026
					0.1130	0.1275	2 x 0.1240

100%

112%

109%

TABLE 4.6

Estimation of segments ratios and m/f conversions from PIP/M, 150°C, 30 minutes

Structure	Calculated Value of (P)	Calculated			Experimental Spectral Values			% of f/m		Areas of GPC due to f & m	
		-MPM-	-MPT-	-TPT-	-MPM-	-MPT-	-TPT-	f	m	f	m
PIP MPM	0.0600	0.0086	-	-	0.0086	-	-	-	100	-	0.0158
PIPM MPMP	0.1188	0.0054	0.054	-	0.0112	0.0467	0.0025	13	87	0.0077	0.0517
PMPiPM 7 PIPM 1	0.0572	0.0037	0.0553	-	0.0024	0.0416	-	11	89	0.0048	0.0392
P(IP) ₂ MP 2 MPIPM 1	0.0060	0.0004	0.0018	0.0009	0.0005	0.0023	0.0008	42	58	0.0012	0.0017
(PIPM) ₂	0.0034	-	0.0015	-	0.0004	0.0034	0.0004	27	73	0.0004	0.0012
PM(PIPM) ₂ PM	0.0026	0.0004	0.0017	-	0.0007	0.0028	0.0007	-	100	-	0.0021

Sum of fractions values 17.7% 81.3% 1%

Values of the whole sample 17.3% 76% 67% 18% 78% 4% 11% 89%

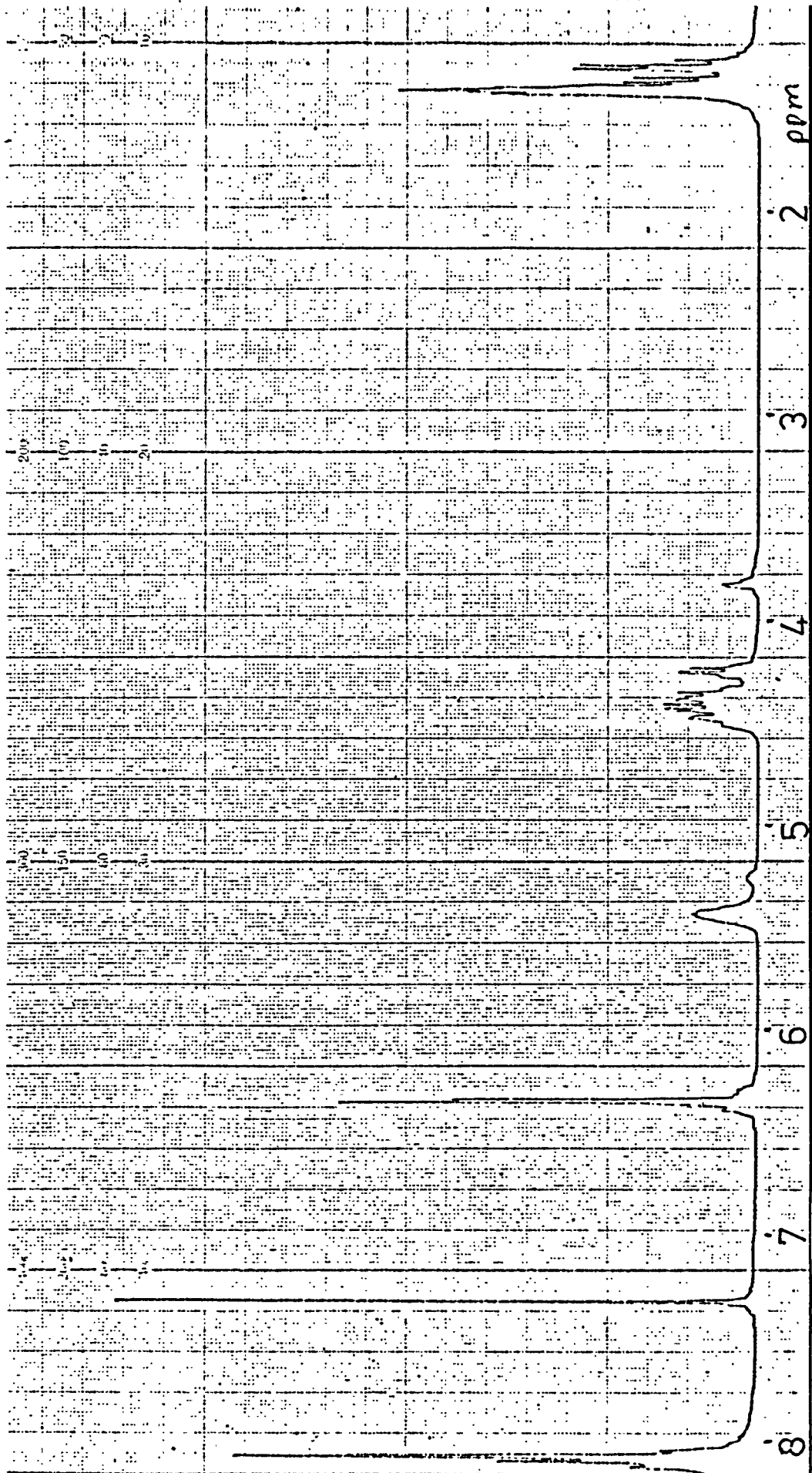


FIGURE 4.10 300 MHz NMR Spectrum of peak (b) in Figure 4.1.

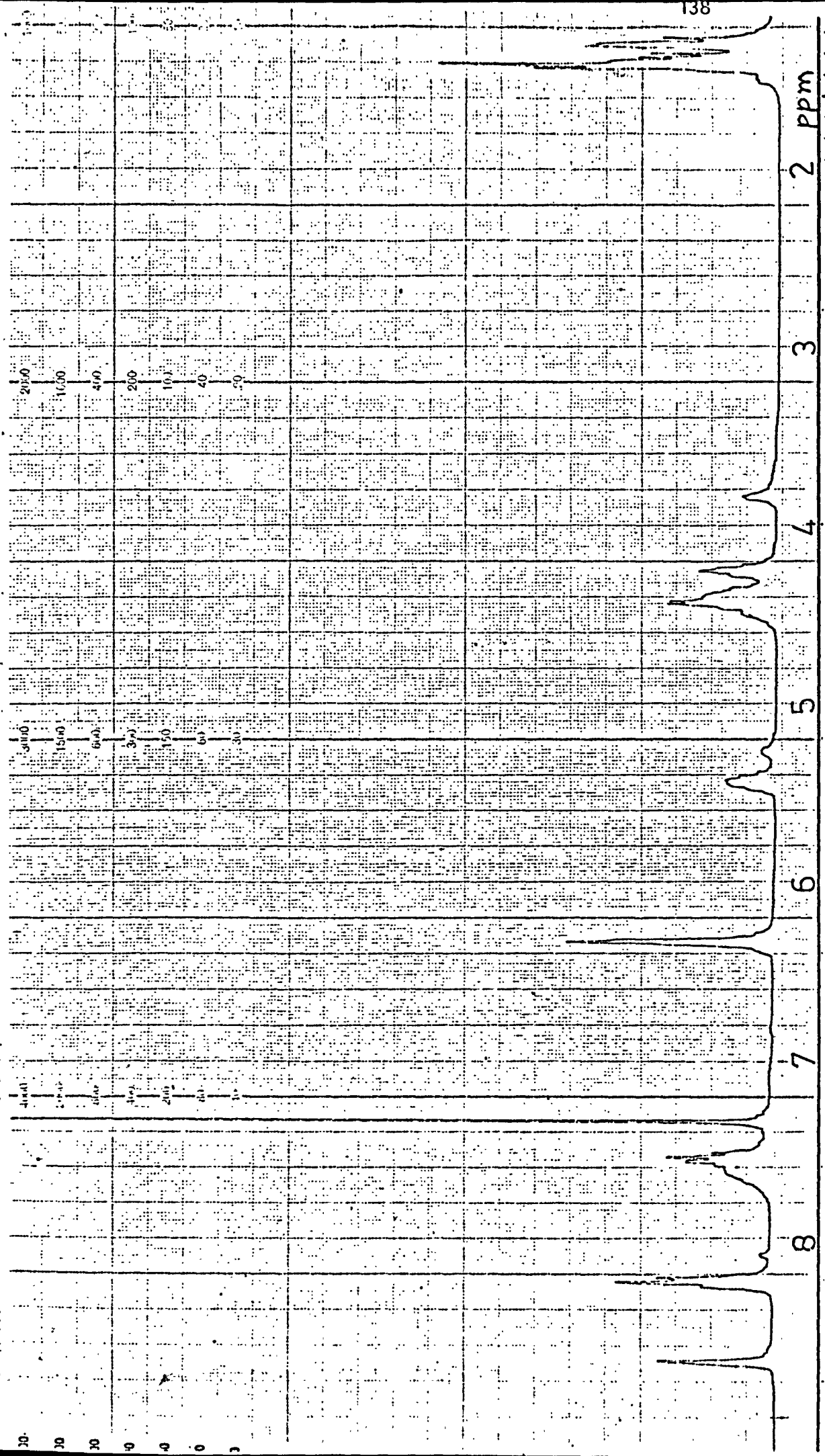


FIGURE 4.11 300 MHz NMR Spectrum of Peak (h) in Figure 4.2

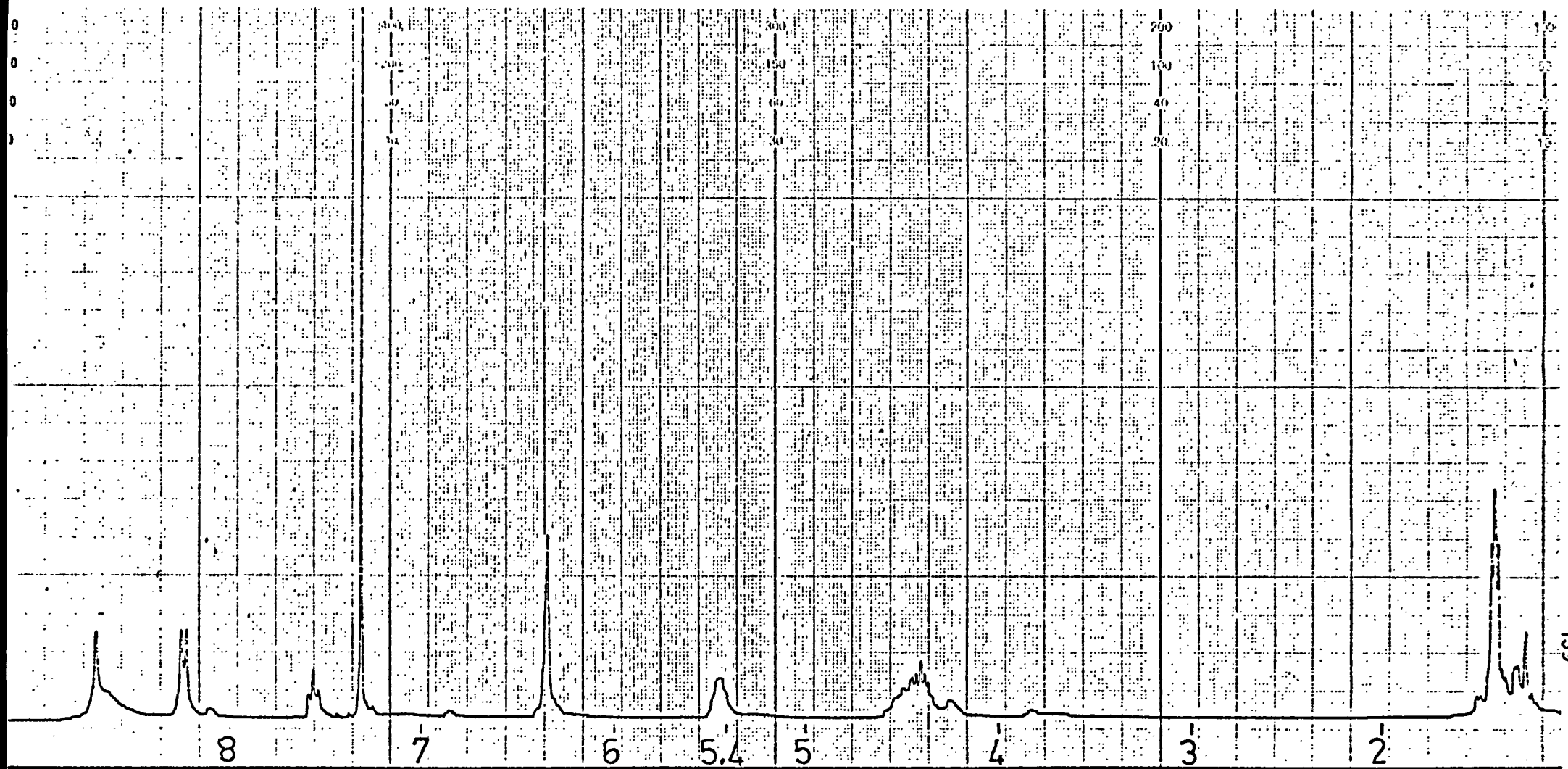


FIGURE 4.12 300 MHz NMR Spectrum of peak (i) in Figure 4.2

	M/F	I	P	Terminal P	Internal P
(h)	1	1	2	48%	52%
(i)	2	3	1	33%	67%

The type of segments indicated by methine absorptions were:

(h)	(-IPM-)	+	contamination with (-MPM-)
(i)	(-IPM-)	+	contamination with (-MPM-)

The structures assigned were:

(h) PIPM and (i) PMPIP

However to make up for the presence of minor traces of (-MPM-) segments in (h), $(PM)_2$ was assigned in very small quantities. (10 PIPM: 1 $(PM)_2$). It could be said here that this small quantity is close to experimental error. Also small quantity (12.5%) of PIPMPM was found appropriate for (i). The same procedure was followed for the assignment of fractional components for all the other fractions. However, the examples cited above cover all the important peaks in Figures 4.1 and 4.2, and they represent 89.2% of the products for PTP_1/M and 94.8% of the products of PIP/M .

4.6 Verification of the Assignments of Peak (a) and (G) by Thin Layer Chromatography (TLC)

A thin layer chromatography experiment was performed to verify the presence of two components in fraction (a) and (G) in Figures 4.1 and 4.2. Four samples (dissolved in chloroform) were prepared, a sample from fraction (a), a sample from fraction (G) and a mixture of PTP_1 isomers and a mixture of PIP_1 isomers. The four samples were applied to thin layer chromatography plates and introduced to a TLC tank containing a solvent consisting of 100 parts chloroform and 8 parts methanol. The plates were left to stand for about 45 minutes and then removed, dried, and photographed under U.V. light (Figure 4.13).

Fraction (a)

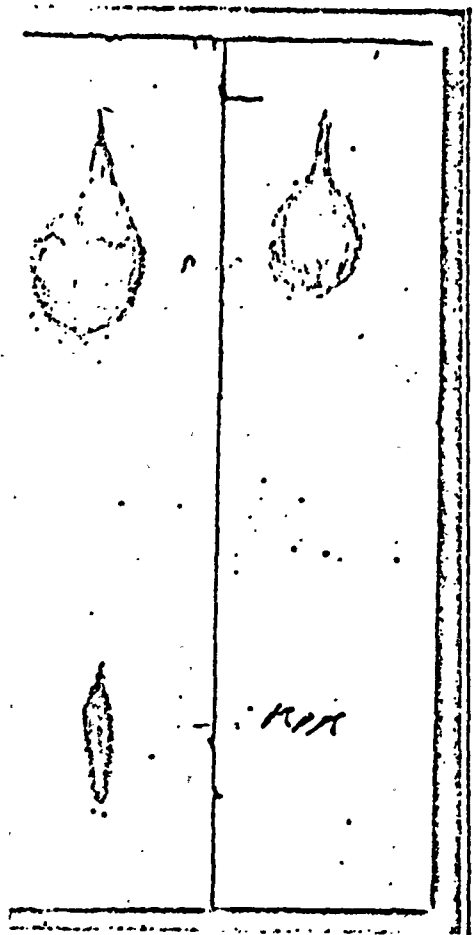
PTP

Fraction (G)

PIP

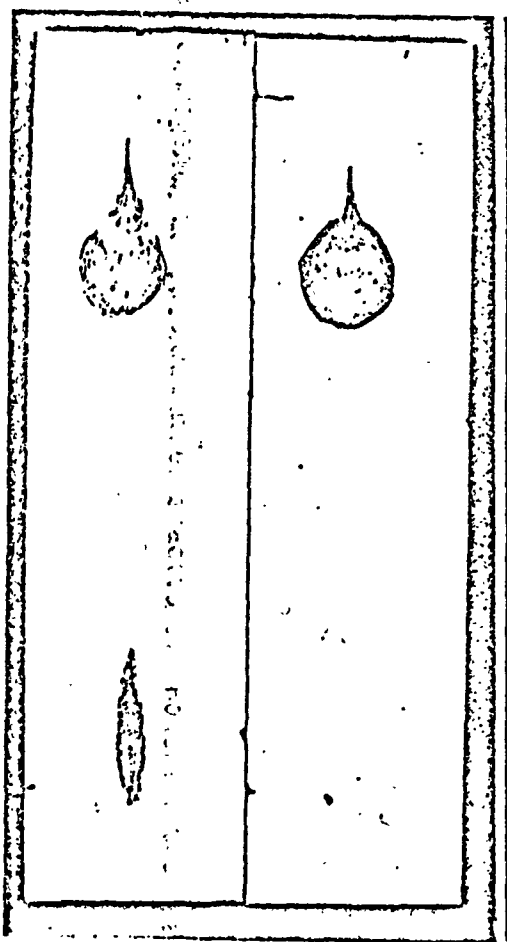
Synthesised mpm+PTP

Synthesised MPM



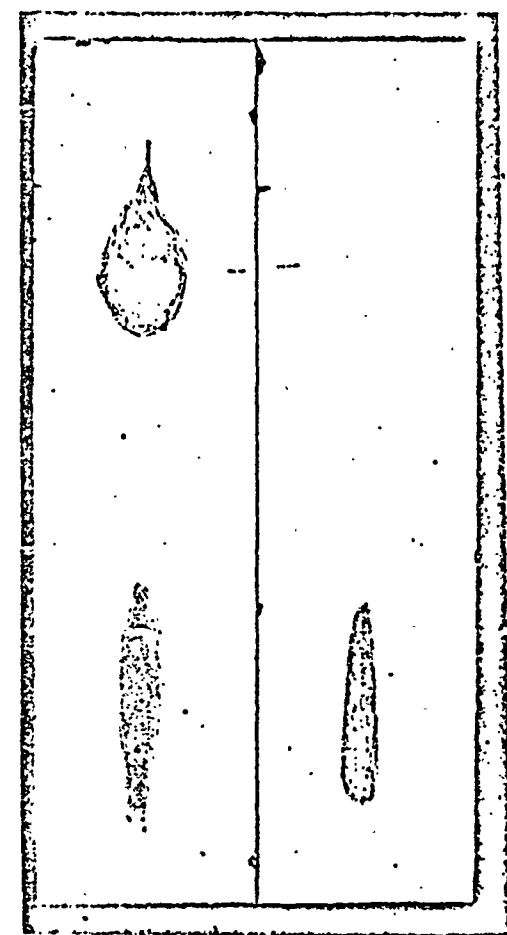
I

II



III

IV



V

VI

FIGURE 4.13 TLC of Fractions Containing MPM and/or PTP₇ and PIP₇

Plates II and IV contained PTP₁ and PIP₁ respectively while plate I contained sample (a) and plate III contained sample (G). Plates containing only the prepolymers showed spots nearer to the solvent level at the top, whilst plates containing sample (a) and sample (G) showed an additional spot at the bottom of the plate just above the level of the sample application region. This confirmed that the samples from fraction (a) were composed of the prepolymers and an additional compound in each case.

Further TLC Identification of the Additional Compounds:

As further identification of the additional compound, propylene glycol was reacted with maleic anhydride at 150°C for 30 minutes and analysed by GPC. To the product obtained a small quantity of PTP₁ was added and also applied to the GPC system. The two chromatograms obtained (Figures 4.14 and 4.15) showed that PTP₁ enhanced the peak of the largest area in the chromatogram of the pure sample. This peak was then fractionated and applied to thin layer chromatography. It gave the same spot observed for the additional compound present in fraction (a) and (G), see plates V and VI, Figure 4.13.

NMR Analysis of the Additional Compound

A further fractionation was carried out to collect the component under the peak in Figure 4.14 which gave the same spot in the TLC test for the additional compound in fractions (a) and (G) in Figures 4.1 and 4.2. The sample obtained was analysed by 90 MHz NMR to give the spectrum in Figure 4.16. The numerical ratios obtained from the integrals of the methyl protons and the protons attached to the maleic/fumaric unsaturation gave the ratio of 1P:1.89 M/F. This was considered to be in good agreement with the ratios of MPM.

This experiment confirmed that the additional spot on the TLC plates containing fractions (a) and (G) was MPM. It also showed that in the reaction of (M) with (P) at 150°C, MPM was the major product. This could be attributed to the slow reactivity of maleic or fumaric acid ends once they are formed compared to other reactions taking place and involving ring opening reactions of maleic anhydride.

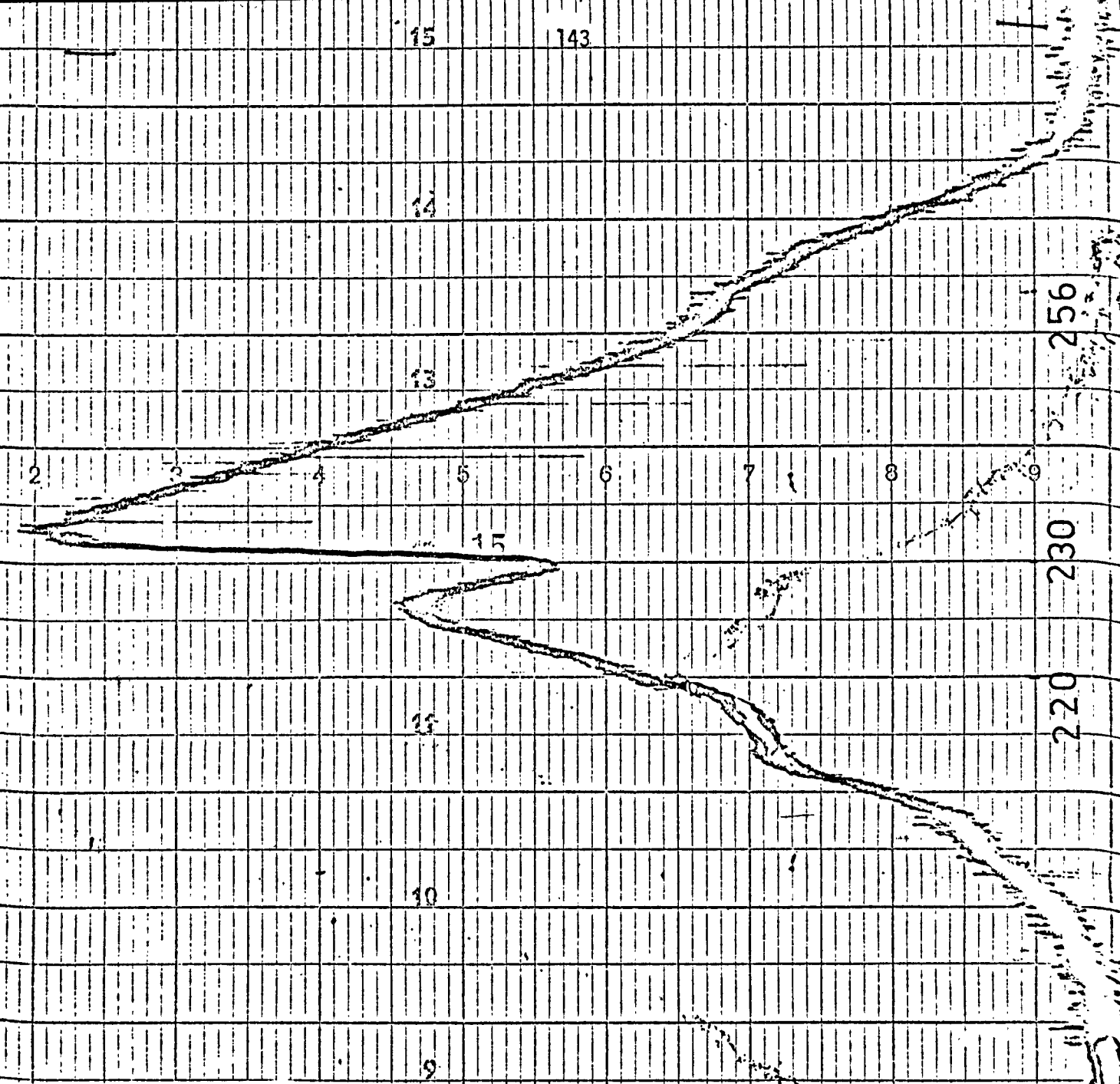


FIGURE 4.14
GPC Chromatogram of (1 PG:1M)/
150°C, 30 mins

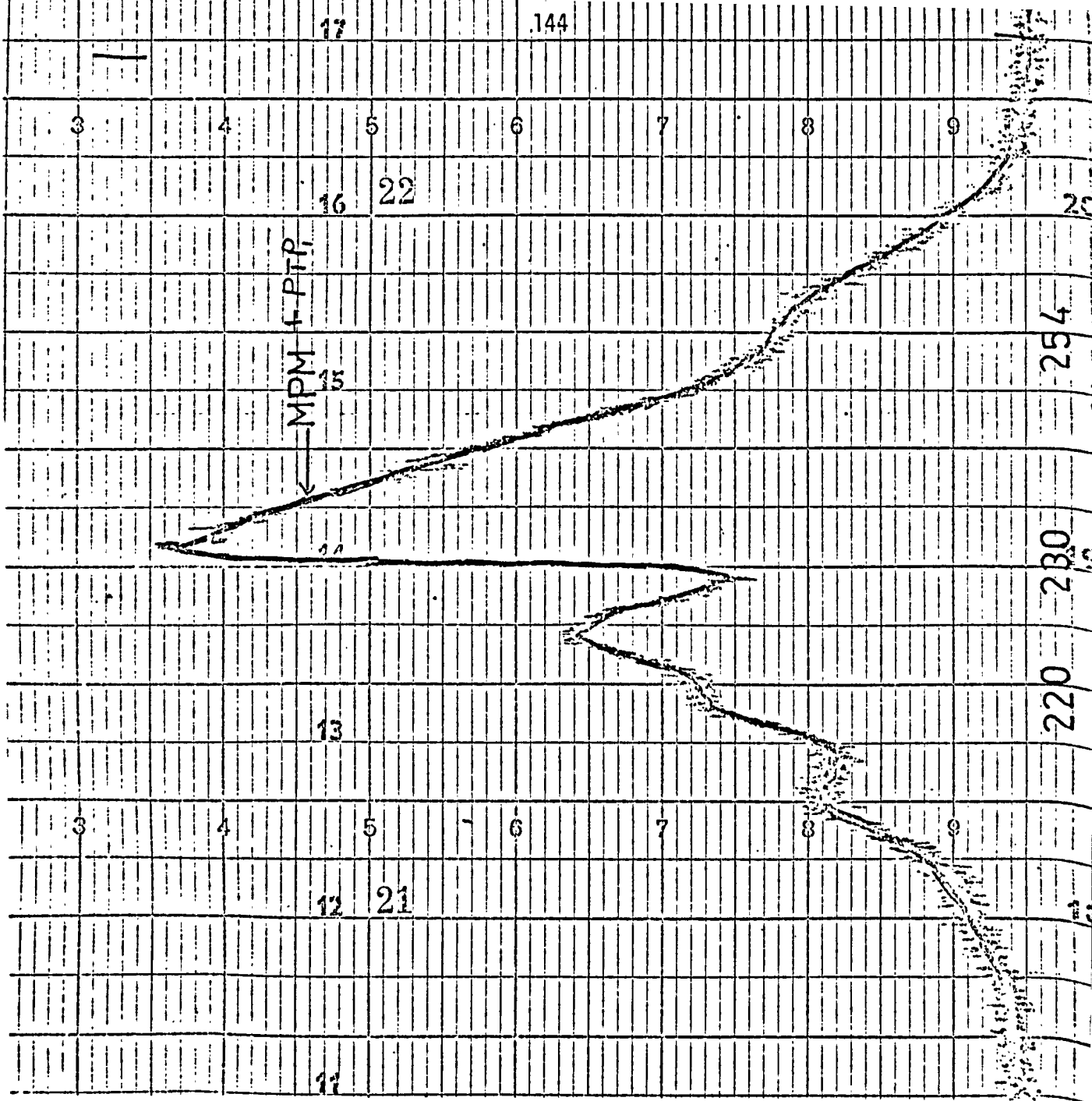


FIGURE 4.15
 GPC Chromatogram of (1PG:1M)/
 150°C, 30 mins + PTP

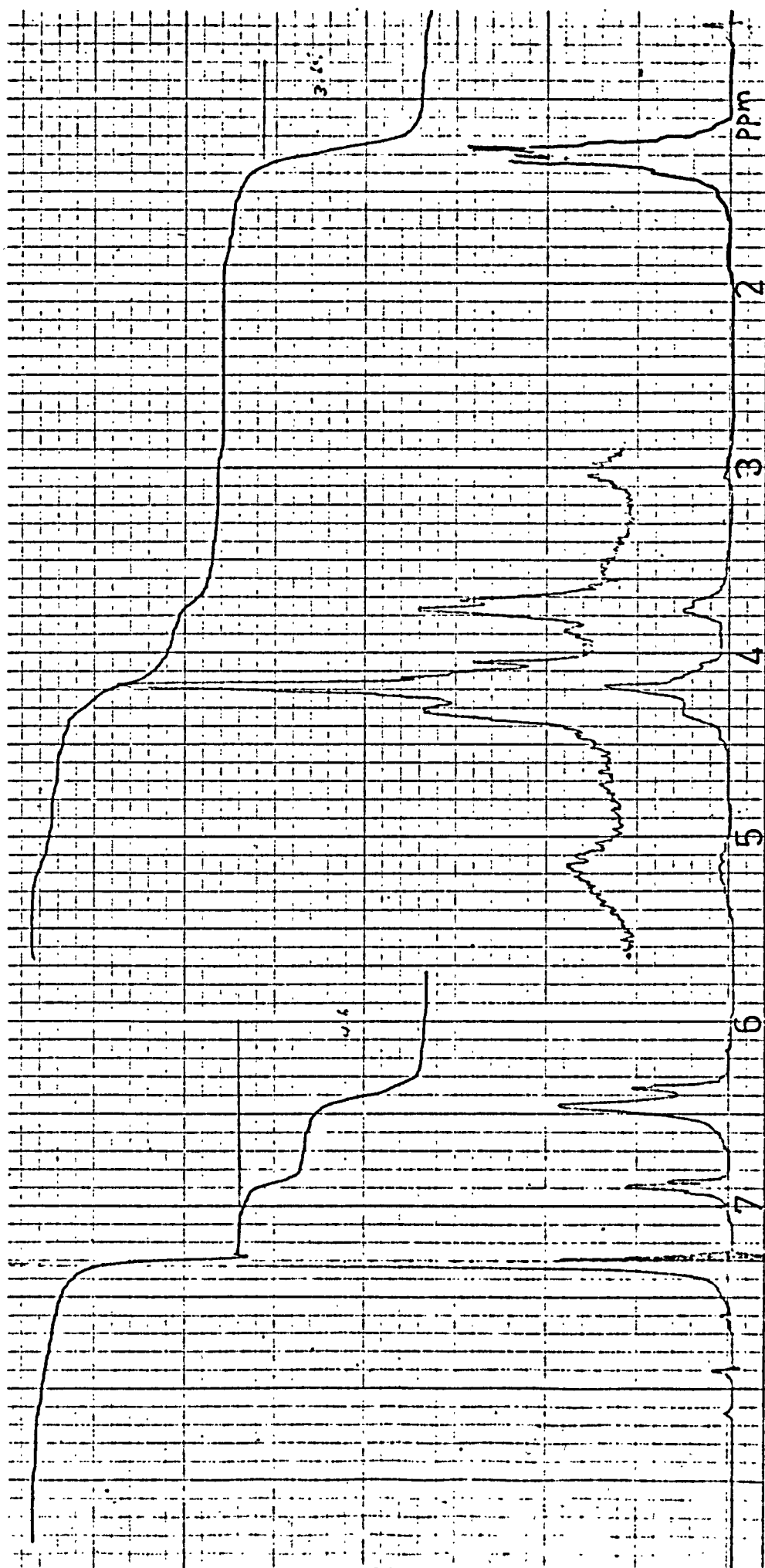


FIGURE 4.16 90 MHz NMR Spectrum of MPM Fraction from (1 PG:IM)/150°C, 30 mins

4.7 GPC Evidence of Fractions Assignments

After proposing the assignments to the fractions the areas under the GPC peaks were converted to real areas by:

$$\frac{\text{GPC area}}{\text{number of carbonyl groups}} = \text{real area}$$

so that these real areas are proportional to the molar quantities of different components in the whole sample.

For the fractions shown in Tables 4.2 and 4.5 the \log_{10} values of molecular weights of fractions were plotted against elution volume. The graphs obtained showed a linear relationship in both cases (Figures 4.17 and 4.18). This serves as further evidence that the assignments proposed are reasonable.

4.8 Comparison of Fractions Data with Whole Sample Data

The data obtained for all the fractions in each sample are shown in Tables 4.1-4.6. In these tables the molar ratio of the monomer molecules in each fraction were estimated from the GPC peaks areas of the assigned fractional components. Also the type of chain segments present in these fractions were estimated from their NMR spectra as well as the maleic/fumaric transformations. When the data obtained for these fractions were summed and compared to the values obtained for the whole sample, before fractionation, the two values were found to be in good agreement. The total ratio of the number of monomer molecules determined for all the fractions in each sample were very close to the molar ratios of the starting materials. The amounts calculated from Table 4.2 gave the following values for PTP₁/MA:

104% of P

100% of T

106% of M

and those determined for PIP₁/MA from Table 4.5 gave:

104% for P

100% of T and

112% of M

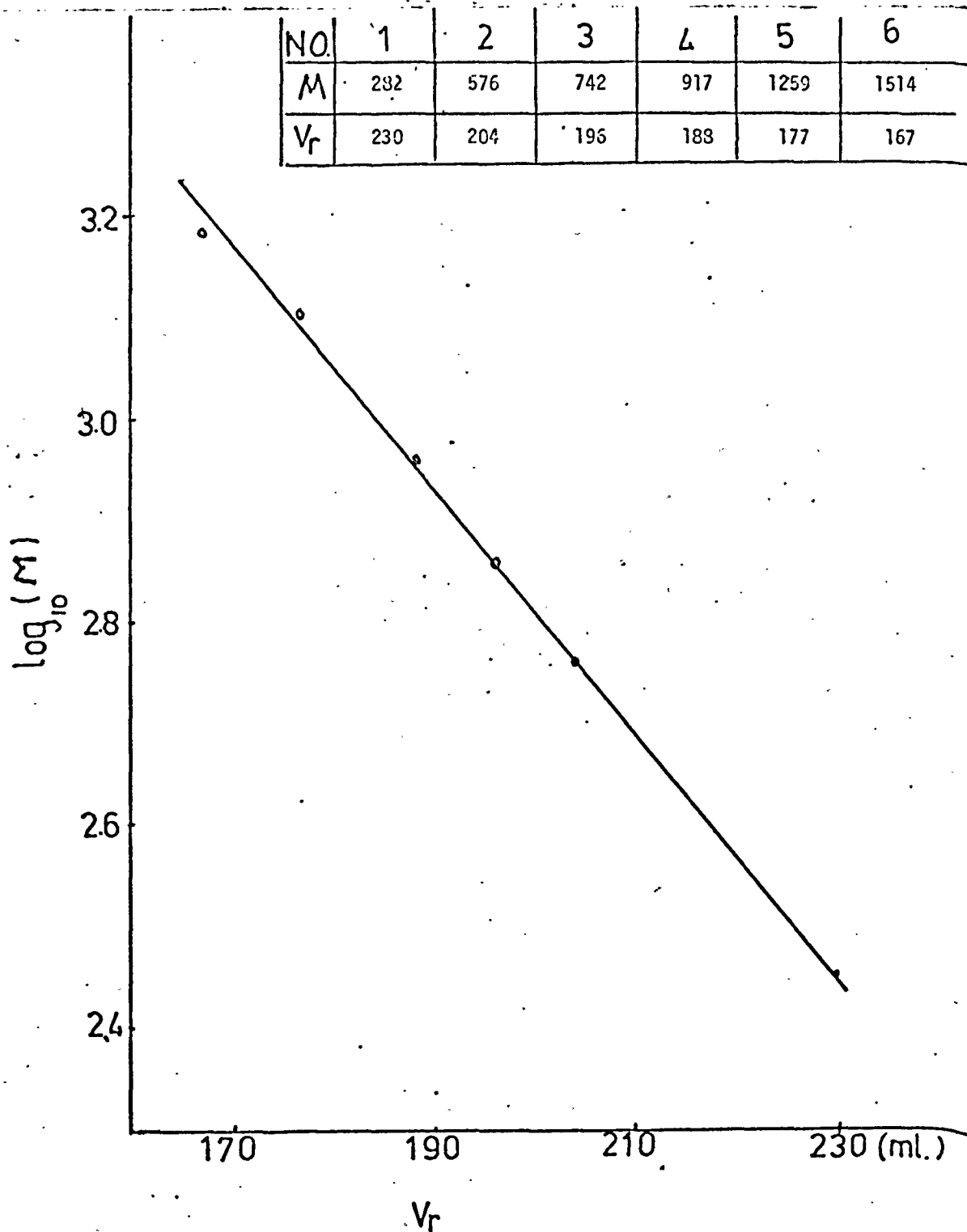


FIGURE 4.17 $\log_{10}(M)$ versus V_r for (PTP₁/M)/150°C, 30 minutes

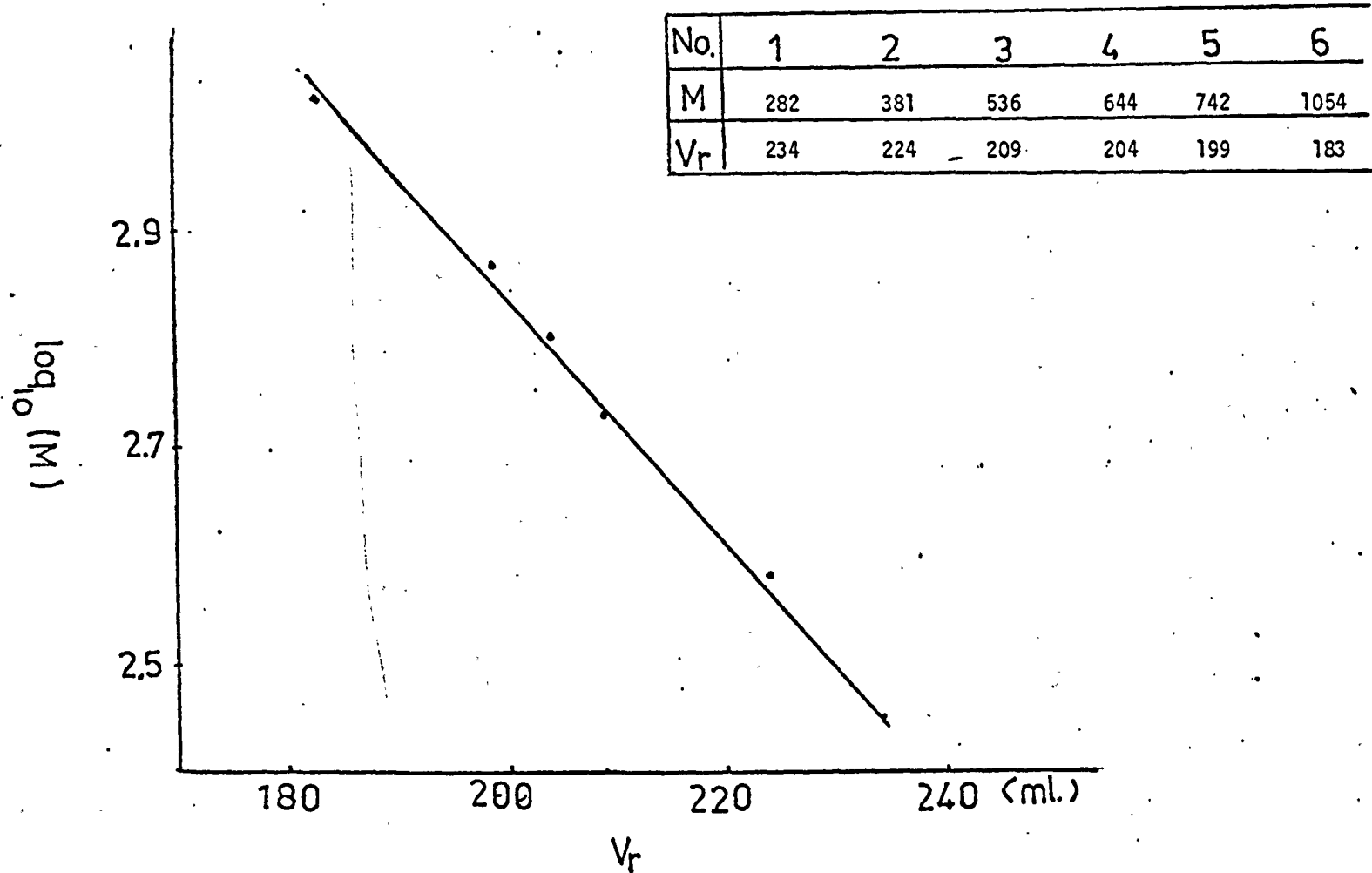


FIGURE 4.18 $\log_{10}(M)$ versus V_r for $(PIP_1/M)/150^\circ\text{C}$, 30 minutes

The different environments shown in the spectra for propylene glycol molecules within the polymer chain indicated the ratios of the different types of segments (sequences) within different fractions. When these were summed they gave results which were not far from the values obtained for the whole samples for the two reaction products:

For PTP₁/MA (Table 4.3):

	<u>Whole Sample Values</u>	<u>Total Values for Fractions</u>
-MPM-	22.2%	26.3%
-MPT-	77.8%	73.7%
-TPT-	-	-

For PIP₁/MA (Table 4.6):

	<u>Whole Sample Values</u>	<u>Total Values for Fractions</u>
-MPM-	17.3%	17.7%
-MPI-	76%	81.3%
-IPI-	6.7%	1%

The slight difference here could be attributed to the presence of too small quantities of P(IP)_n oligomers shown in Table 4.12, which were not accounted for in the assignments.

The ratios of maleic/fumaric transformation for the whole samples were found to be about 3% which was lower than values of about 10% obtained for the total of the fractions for both reaction products. However, no loss of double bonds was encountered in these short time reactions (30 minutes) carried out at a low temperature (150°C).

4.9 Polymerization Reactions of Prepolymers with Maleic Anhydride at 180°C

These reactions were carried out in the same way as the reactions carried out at 150°C for 30 minutes. The only difference was in the temperature used, which was 180°C. Analytical GPC chromatograms for the products of these reactions are shown in Figures 4.19 and 4.20.

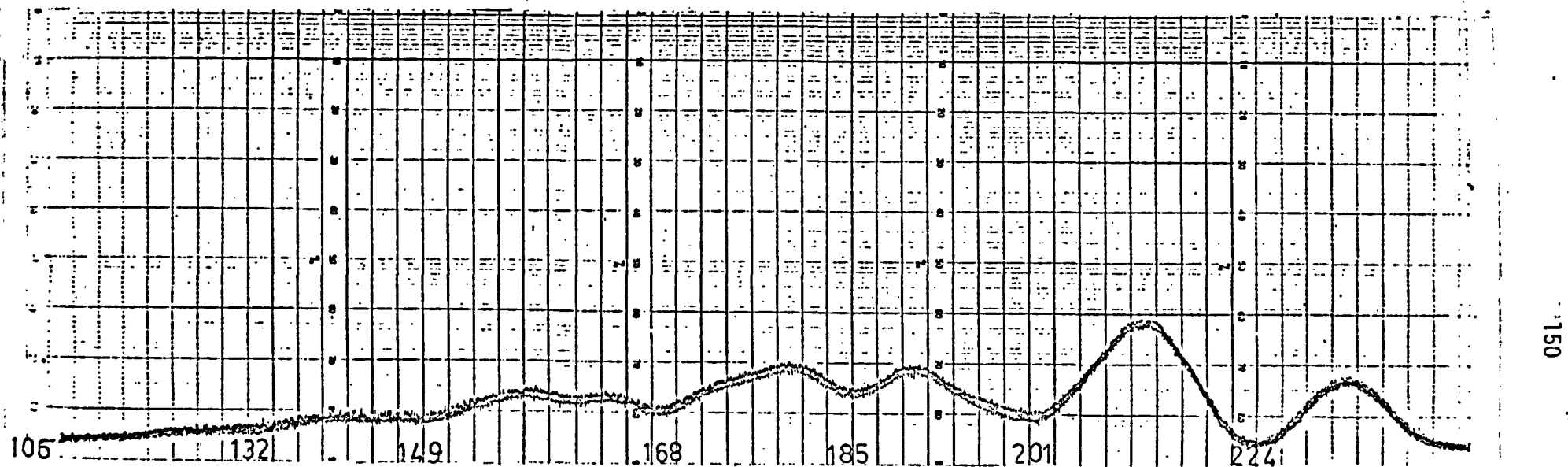


FIGURE 4.19 GPC Chromatogram of (PTP₁/M) 180°C / 30 mins

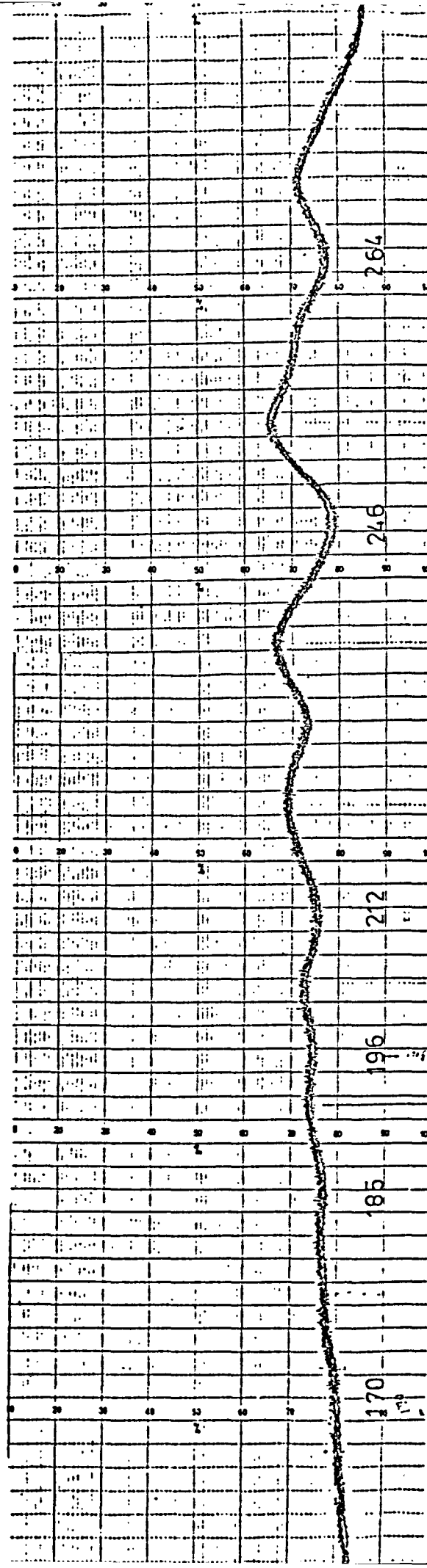
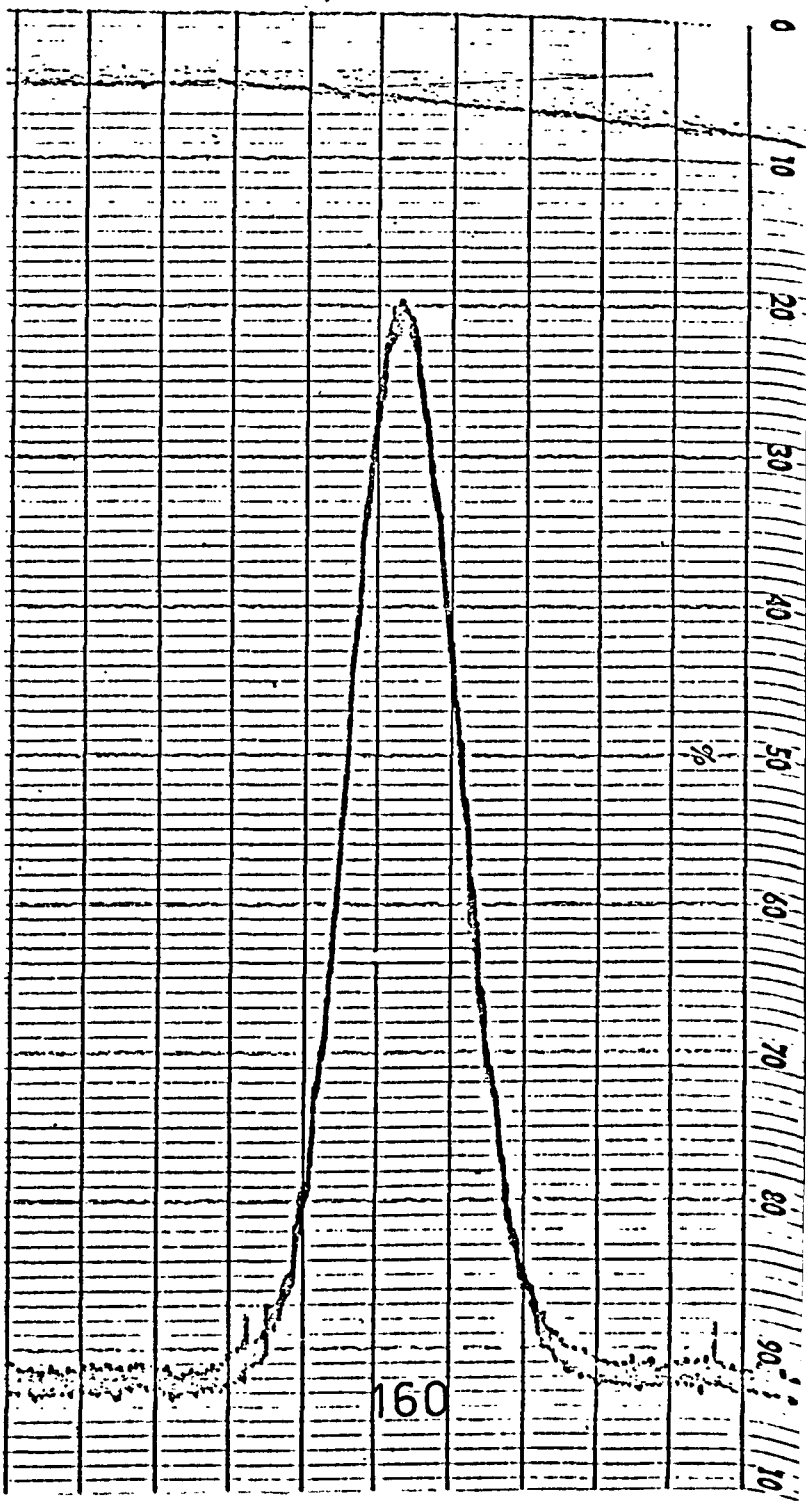
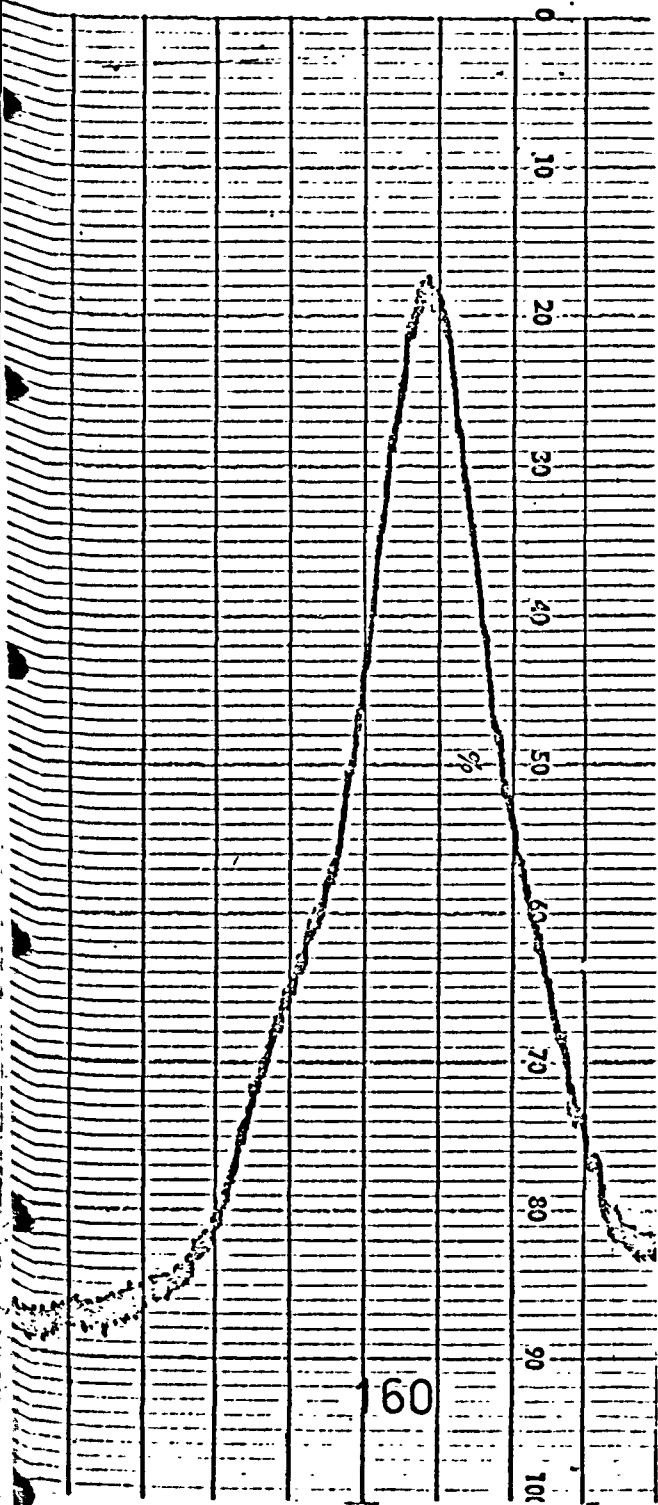


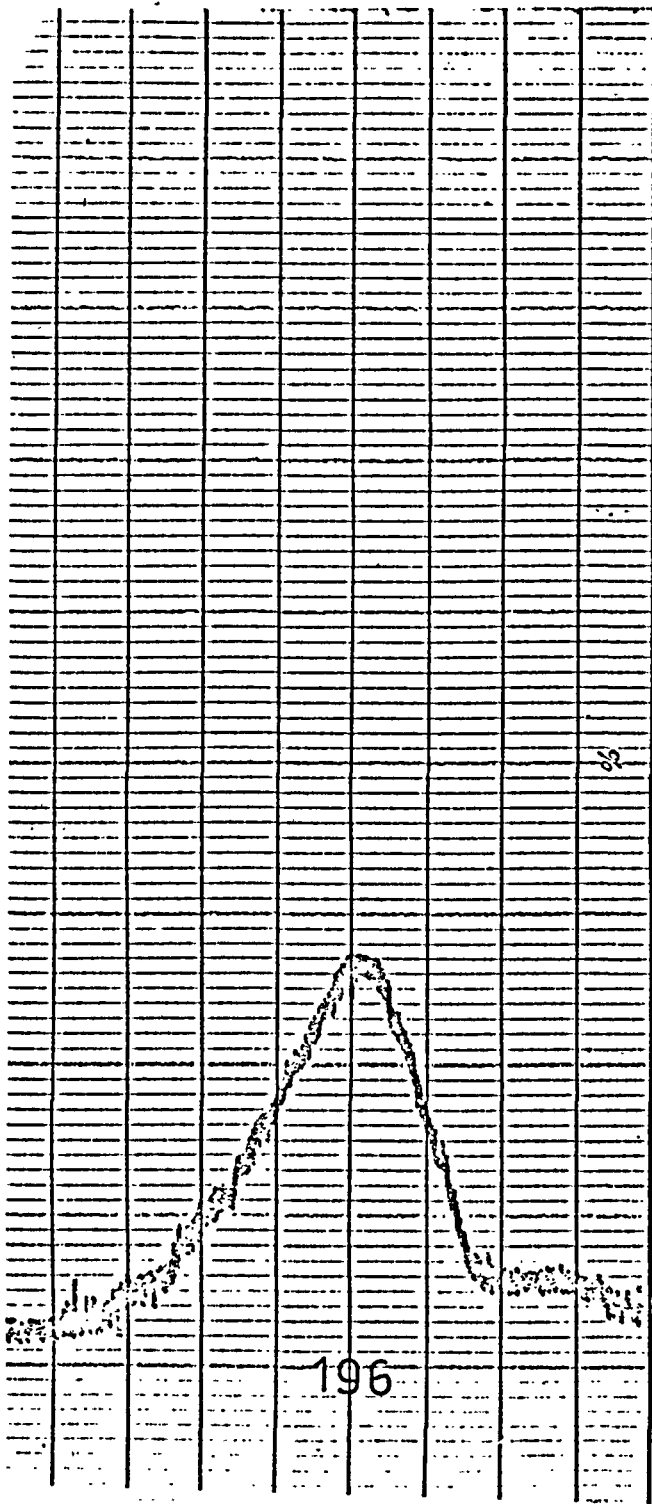
FIGURE 4.20 GPC Chromatogram of PIP/M 180°C / 30 mins



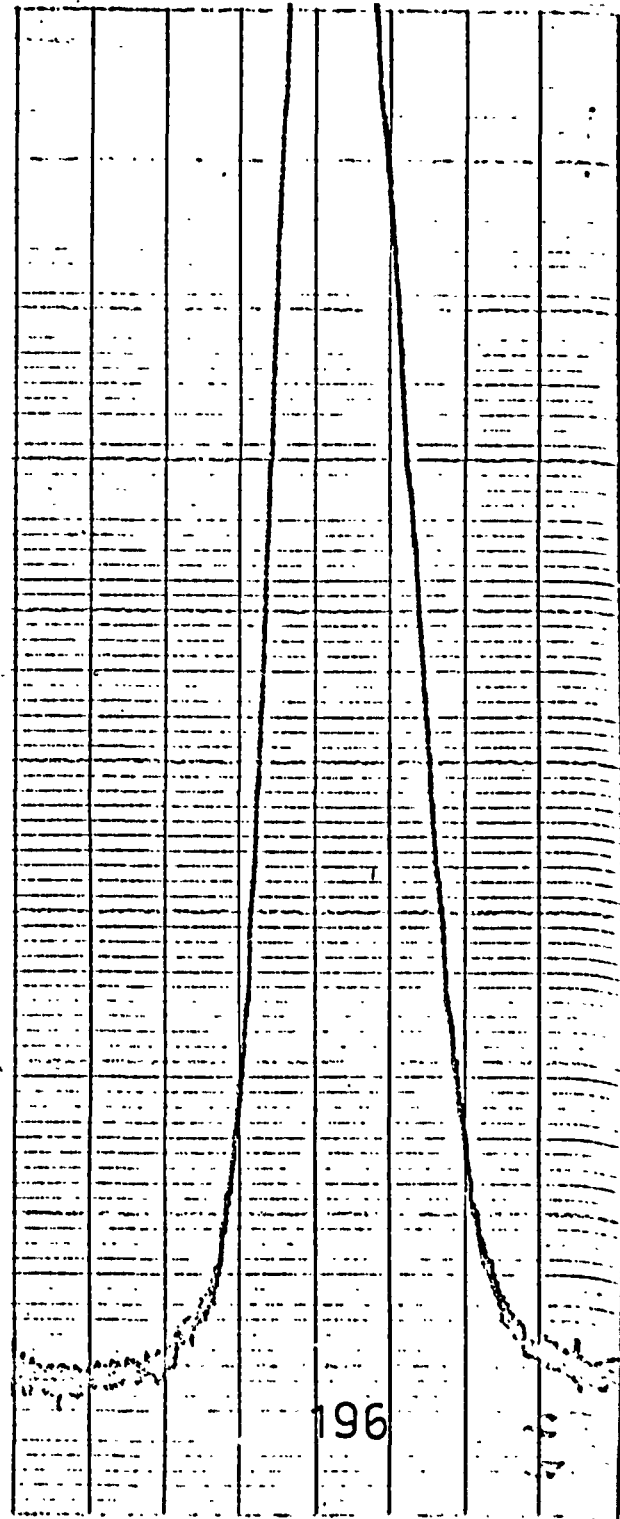
Peak '5' PTP₁/M 180°C
2nd fractionation

Peak '5' PTP/M 180°C
Final form

FIGURE 4.21



Peak '5' PIP/M 180°C
2nd fractionation



Peak '5' PIP/M 180°C
Final form

FIGURE 4.22

TABLE 4.7

Fractionation data for PTP/M, 180°C

No	Experimental Values					P Between Acids	Assigned Fractional Component	Calculated Ratios of Species			Calculated Values		Primary/Secondary ratios of terminal (P) from spectra	
	Spectra Values (cm)			Term- inal P	M			P	T	Inter- nal (P)	Termi- nal (P)	Primary	Secondary	
	M/F	I	P											
1	3.05	2	3.21	53.4	46.6	PTPM PMPM	1 1	3	2	1	50	50	44	56
2	1.0	6.55	11.2	65	35	PTPTP PTPMP	1 1	1	6	3	33	67	56	44
3	4.25	7.4	10.9	46	54	PTPMPT (PM) ₃ P	2 1	3.5	6	3	61	39	67	33
4	2.4	4.85	6.9	28	72	(PTPM) ₂		1	2	1	75	25	65	35
5	3.0	4.85	7.9	26	74	M(PTPM) ₂ P		3	5	2	80	20	-	-
6	5.8	10.5	15.7	21	79	(PTPM) ₂ PMP (PTPM) ₃	1 1	6	10	5	75	25	-	-
7	5.8	10.3	17.9	27	73	(PTPM) ₃ P M(PTPM) ₃	7 1	6	12	5	73	27	-	-
8	5.5	6.85	13	-	100	MPM(PTPM) ₃		3	4.5	2	100	-		

TABLE 4.8

Calculation of Ratios of Species from GPC Areas and Assigned Structures in PTP/M, 180°C

No	Fractional Component	% of the whole sample	GPC Area	Real Area	Areas due to		Value of P (balanced with _p T)
					T	M	
1	PTPM 1 PMPM 1	17	0.226	0.0565	0.0141	0.0424	0.0283
2	PTPT 1 PTPMP 1	37.6	0.499	0.1248	0.0936	0.0312	0.1871
3	PTPMP 2 (PM) ₃ P 1	16.1	0.321	0.0535	0.0229	0.0306	0.0536
4	(PTPM) ₂	14.4	0.382	0.0478	0.0239	0.0239	0.0478
5	M(PTPM) ₂ P	3.8	0.126	0.0126	0.0050	0.0076	0.0126
6	(PTPM) ₂ PMP 1 (PTPM) ₃ 1	6.4	0.211	0.0211	0.0084	0.0127	0.6200
7	M(PTPM) ₃ 1 (PTPM) ₃ P 7	3.5	0.138	0.0115	0.0058	0.0058	0.0116
8	MPM(PTPM) ₃	1.3	0.062	0.0044	0.0016	0.0028	0.0032

Total:	0.1753	0.1570	0.1822
% of original feed:	100%	90%	104%

TABLE 4.9

Estimation of segments ratios and m/f conversions in PTP/M, 180°C

Structure	Calculated Value of (P)	Calculated Values			Experimental Values			f/m Ratios		Areas of GPC due to f & m		
		-MPM-	-MPI-	-IPI-	-MPM-	-MPI-	-IPI-	f	m	f	m	
PTPM PMPM	1 1	0.0283	0.0071	0.0071	-	0.0071	0.0071	-	29	71	0.0126	0.0299
PTPTP PTPMP	1 1	0.1871	-	0.0312	0.0312	-	0.0259	0.0365	100	-	0.0312	-
PTPMPT (PM) ₃ P	2 1	0.0536	0.0083	0.0247	-	0.006	0.0252	0.0022	23	77	0.0070	0.0235
(PTPM) ₂		0.0478	-	0.0359	-	-	0.034	0.002	42	58	0.010	0.0139
M(PTPM) ₂ P		0.0126	-	0.01	-	0.0008	0.0088	0.0005	25	75	0.0021	0.0057
(PTPM) ₂ PMP (PTPM) ₃	1 1	0.0200	0.0024	0.0119	-	0.0019	0.0126	0.0015	36	64	0.0038	0.0068
M(PTPM) ₃ P (PTPM) ₃	1 7	0.0110	-	0.0097	-	0.0011	0.0077	0.0009	27	73	0.0016	0.0042
MPM(PTPM) ₃		0.0032	0.0005	0.0027	-	0.004	0.0057	0.0008	45	55	0.0013	0.0015
Sum of fractions values:			0.0183	0.1332	0.0312	16.1%	62%	21.3%			0.0696	0.0856
Whole sample values:			10%	72.9%	17.1%						44.8%	55.2%
			69	75	18.1							

TABLE 4.10

Fractionation data for (1 PIP/M)/180°C, 30 minutes

No	Experimental Values					Assigned Fractional Components	Calculated Ratio of Species			Calculated Values		Primary/Secondary ratios of terminal (P) from spectra		
	M/F	I	P	Terminal P	(Internal)		M/F	I	P	Terminal P	Internal P	Primary	Secondary	
1	2.4	8.5	15	7.36	26.4	PIPIP PIPMP	1 2	1	2	4.5	67	33	78	22
2	11.1	11	15.7	55	45	MPIPMP PMPPIP	1 1	2	1	3	43	57	72	28
3	4.4	11	10.8	10	90	(IP) ₃ MPM (IP) ₂ MPIP	3 1	2	3	4	-	100	-	-
4	9	11.4	16.5	34.5	65.6	(PIPM) ₂ PMP		3	2	6	34	66	67	33
5	6	12.35	19.8	9	91	(PIPM) ₃ PM		3	3	6	14.3	85.7	-	-
6	6.2	11.7	18.9	21.6	79.4	(PIPM) ₄ P		1	1	2	22.2	77.8	-	-
7	4.7	9.9	15.3	33.9	96.1 100	I(PIPM) ₄ PM		5	5	9	-	100	-	-

TABLE 4.11

Calculation of Ratios of Species from GPC Areas and Assigned Structures in (PIP/M)/180°C

No.	Fractional Component	% of the whole sample	GPC Area	Real Area	Areas due to I & M		Values Calculated from I
					I	M	
1	PIPIP 1 PIPMP 2	28.6	0.404	0.101	0.0673	0.0337	0.1514
2	MPIPMP 1 PMPMPIP 1	32	0.677	0.113	0.0373	0.0746	0.1119
3	(IP) ₃ MPM 3 (IP) ₂ ^M PIPMP 1	14.2	0.502	0.0502	0.0301	0.0201	0.0401
4	(PIPM) ₂ PMP	11.6	0.496	0.0408	0.0163	0.0245	0.0489
5	(PIPM) ₃ PM	6.2	0.262	0.0218	0.0109	0.0109	0.0218
6	(PIPM) ₄ P	4.6	0.263	0.0164	0.0082	0.0082	0.0164
7	I(PIPM) ₄ PM	2.7	0.171	0.0095	0.0048	0.0048	0.0086
			TOTAL:		0.1749	0.1768	0.3995% =0.19975

Percentage of the original feed = 100% 101%
in reaction mixture

114%

TABLE 4.12

Evaluation of Segment Ratios and M/F Conversions in PIP/M 180°C

Structure	Calculated (P) Internal	Calculated Values			Spectra Values			f/m Ratios .6		Areas of GPC due to f & m	
		-MPM-	-PPI-	-IPI-	-MPM-	-MPI-	-IPI-	f	m	f	m
PIPIP 1 PIPMP 2	(0.0505)	-	0.0337	0.0168	-	0.035	0.0152	29.2	70.8	0.0098	0.0239
MPIPMP 1 PMPMP 1	(0.0646)	0.0129	0.0517	-	0.0139	0.0442	0.0065	70	30	0.0522	0.0224
(IP) ₃ MPM 3 MPIPMP 1	(0.0400)	0.0075	0.015	0.0175	0.0034	0.0181	0.0185	50	50	0.0100	0.0100
(PIPM) ₂ PMP	(0.0326)	0.0064	0.02616	-	0.0067	0.0271	-	33	67	0.0090	0.0182
(PIPM) ₃ PM	(0.04160)	0.0070	0.0346	-	0.0027	0.0108	0.0018	48.3	51.7	0.0060	0.0065
(PIPM) ₄ P	(0.0128)	-	0.0128	-	0.0018	0.0095	0.0015	54.8	45.2	0.0045	0.0038
I(PIPM) ₄ PM	(0.0086)	0.0010	0.0067	0.0010	0.0018	0.0057	0.0011	42.6	57.4	0.0020	0.0028
TOTALS:	(0.2507)	0.0348	0.18066	0.0353	0.0303	0.1514	0.0446			0.0935	0.0876
% for summation of fractions =		13.9%	72%	14.1%	13.4%	66.8%	19.8%			51.6%	48.4%
Values for whole sample =		11.1%	75.3%	13.6%							

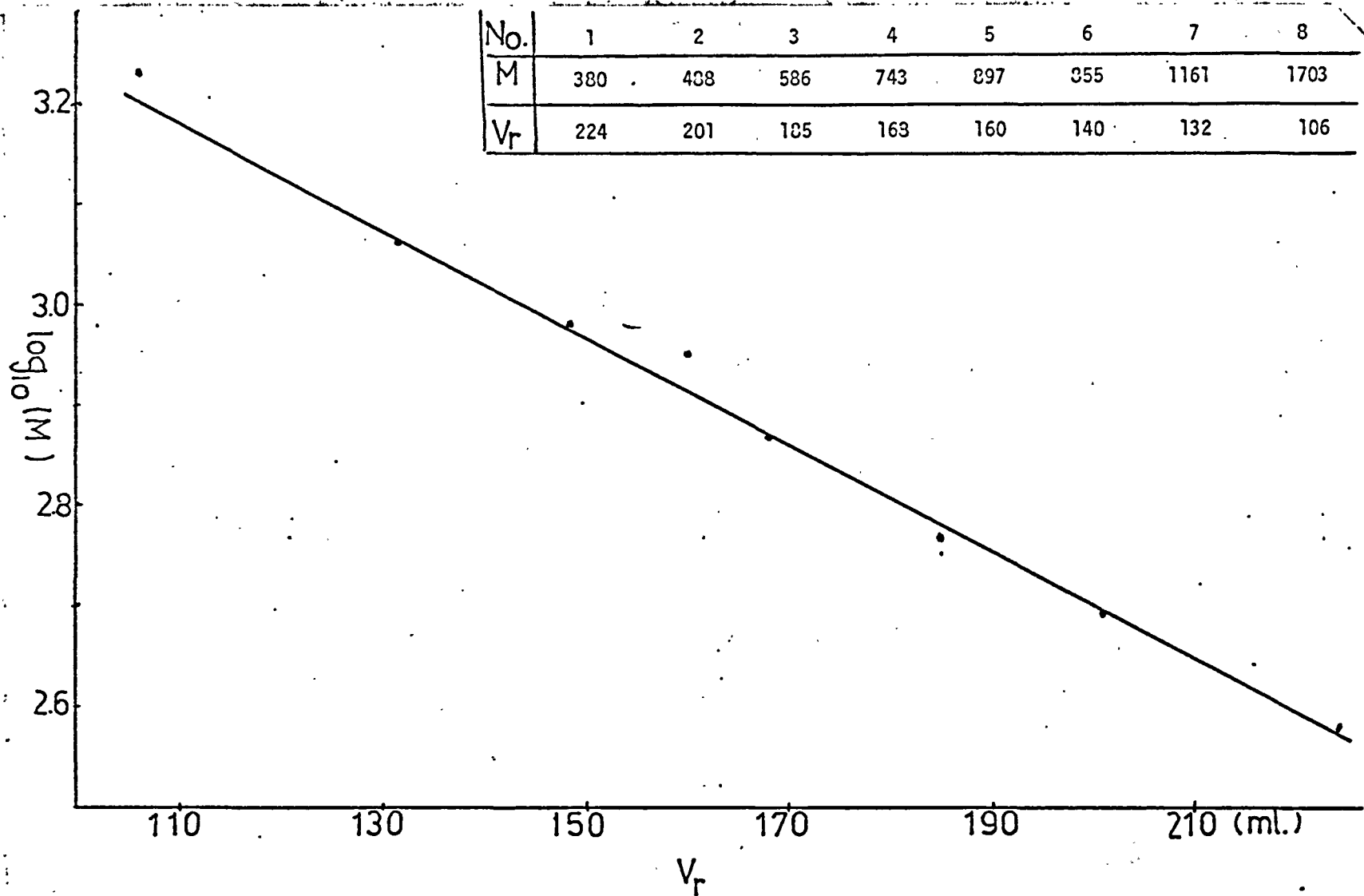


FIGURE 4.23 $\log_{10} (M)$ versus V_r for (PTP_1/M) , 180°C , 30 minutes

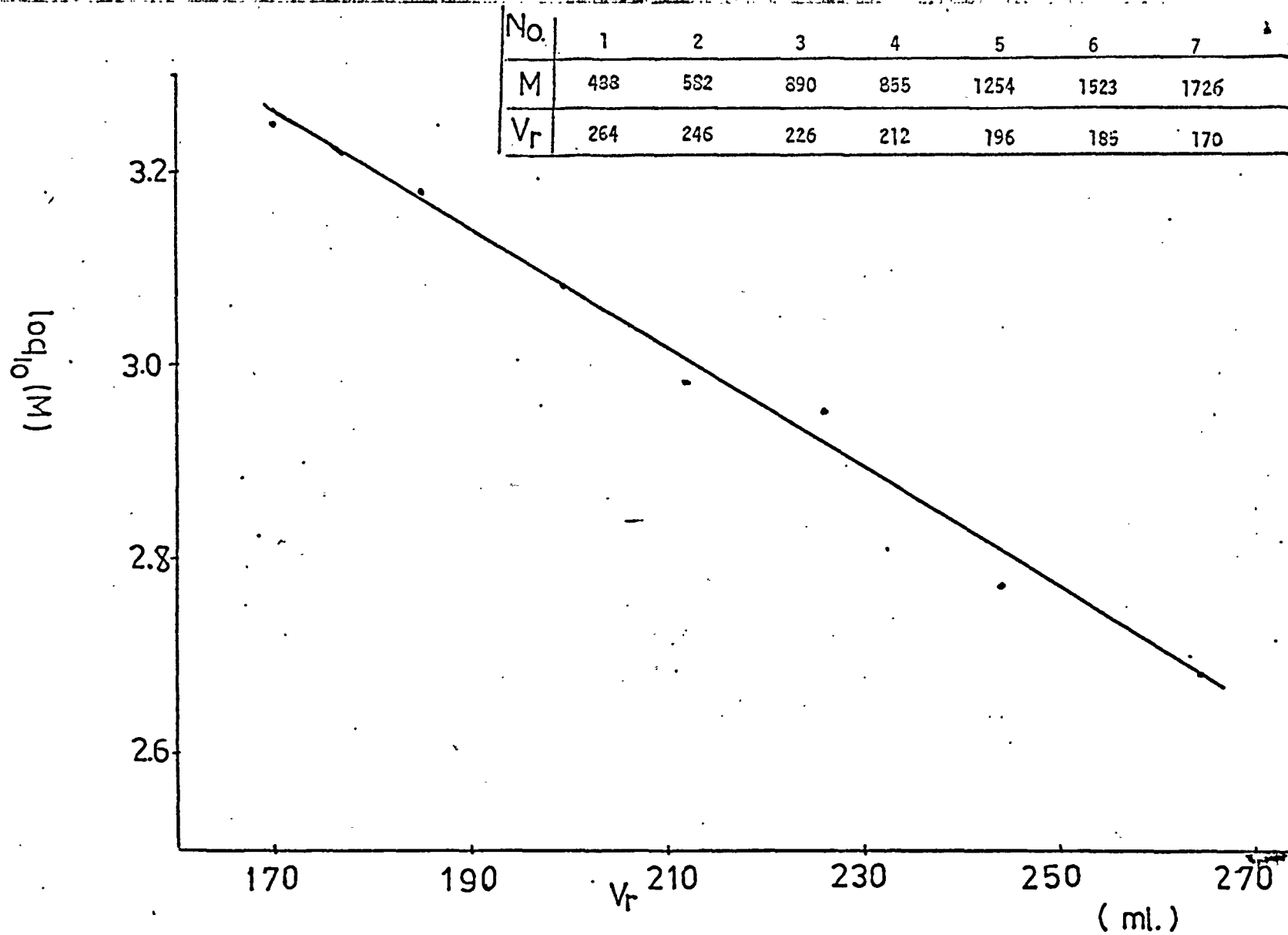


FIGURE 4.24 $\log_{10}(M)$ versus V_r for $(PIP_1/M)/180^\circ\text{C}$, 30 minutes

The products of these reactions were analysed in the same way following the same procedures. The preparative GPC fractionation was performed to give a single peak for each component, examples of which are shown in Figure 4.21 and Figure 4.22. Similar methods for obtaining the data from NMR spectra were followed and these data are shown in Tables 4.7, 4.8 and 4.9, and Tables 4.10, 4.11 and 4.12 and the graphs of \log_{10} molecular weights versus elution volumes are shown in Figures 4.23 and 4.24.

The values obtained for the ratios of monomer molecules for all the fractions were:

For PTP₁/MA: 104% of (P) and 90% of (M) and 100% of (T)

For PIP₁/MA: 114% of (P) and 101% of (M) and 100% of (I)

The values obtained for the types of segments in molecules were as follows:

For PTP₁/MA

	<u>Whole Sample Values</u>	<u>Total Values for Fractions</u>
-MPM-	6.9%	10%
-MPT-	75%	72.9%
-TPT-	18.1%	17.1%

For PIP/MA

	<u>Whole Sample Values</u>	<u>Total Values for Fractions</u>
-MPM-	8.6%	13.6%
-MPT-	75.3%	70.8%
-TPT-	13.6%	15.6%

All these comparisons lend support to the validity of assignments proposed for the fractional components. However, the values for the ratios of M/F transformations showed higher rates for the total values of fractions than the values determined for the whole sample.

For PIP₁/MA:

	F	M
Whole sample values:	45%	55%
Fractions values:	52%	48%

For PTP₁/MA:

Whole sample values:	28%	72%
Fractions values:	45%	55%

4.10 Discussion of Results

Reaction Mechanisms at 150°C

At 150°C the reaction between PTP₁ and maleic anhydride is faster than the reaction of PIP₁ with maleic anhydride. This is manifested in the higher percentage of higher molecular weight components determined for PTP₁/MA (10.8% compared to 6.82%). It is worthwhile to refer here to the heating experiment with the prepolymers (Chapter 3) in which at 150°C PTP₁ has shown a greater tendency for ester interchange and polycondensation, i.e. the propylene glycol molecules are more labile in PTP₁ than in PIP₁ at 150°. However, when bis(2 hydroxypropyl) terephthalate was heated on its own for half an hour at 150°C it gave a ratio of 70:30 of secondary linked to primary linked propylene glycol molecules in the prepolymer. This was found to be the same ratio of the terminal propylene glycol molecules in fractional component No 1 (PTP₁ + MPM). This greater ability of propylene glycol molecules to dissociate from PTP₁ provides the free propylene glycol molecules for reaction with maleic anhydride to form MPM species. The formation of MPM resulted in the consumption of about 40% of the total amount of maleic anhydride in the reaction mixture in PTP₁/MA systems. From Table 4.2: (M) consumed in the formation of MPM

$$= \frac{0.0891}{0.2140} \times 100 = 41.6\%$$

It is clear that this amount of MPM has involved about 10% of the total propylene glycol molecules in the reaction mixture. This amount of (P) has been made up for by the formation of terephthalate ended molecules

seen in the second fraction in Tables 4.1 and 4.2 (peak 'b' in Figure 4.1). The shortage of (P) in this fraction amounted to about 11.7% of the total propylene glycol molecules present in the reaction mixture:

$$\text{Shortage of (P) in fraction (b)} = \left(\frac{0.1496}{3 \times 2} / 0.2136\right) \times 100 = 11.7\%$$

The quick formation of saturated acid ended species through the dissociation of the saturated acid from its diester was reported by Fontana⁽⁶³⁾ in his work on the polycondensation of polyethylene terephthalate. He also reported that a free glycol molecule was found more than twice as reactive as the half esterified glycol molecule. However, an important observation in these reactions was that half ester molecules of maleic or terephthalic or isophthalic acids were not detected to exist on their own, but with the exception of the first components (PTP₁ (or PIP₁) + MPM) they were present in other fractions as parts of fractional components. This observation could explain why Higgins⁽³⁹⁾ was not able to isolate (PM) species which he assumed to be present in his fractionation products.

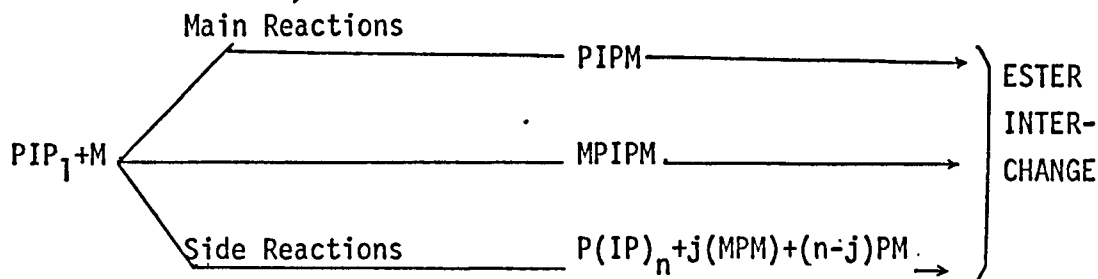
The extent of ester-interchange is lower in PIP₁ which exhibited a slower reaction with maleic anhydride. Although MPM structures were also formed, in PIP₁ reactions with maleic anhydride, they only consumed 13% of the total amount of maleic anhydride in the reaction mixture and had removed about 3% of the propylene glycol molecules from PIP₁.

From Table 4.4:

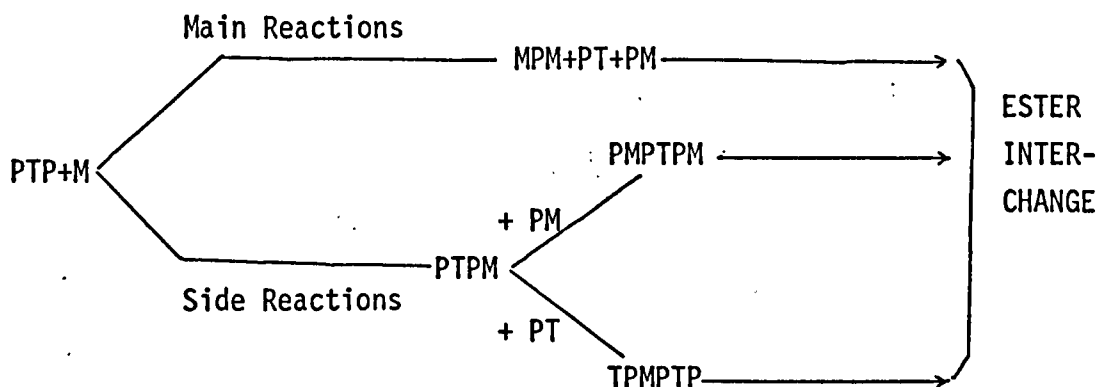
Amount of (M) consumed in MPM formation

$$= \frac{0.0171}{0.1271} \times 100 = \underline{13.4\%}$$

It could be said that the reaction between (P) and (MA) to form MPM is much more important in PTP₁ systems than in PIP₁ systems. The slow rate of dissociation of (P) from PIP₁ enabled the reaction of PIP₁ with MA, to form PIPM, to proceed to a considerable extent, forming more than 40% of the whole reaction product. This slow reaction can be portrayed in the following mechanism:



In the reaction of PTP_1 with M the structure $PTPM$ was not detected. It could be suggested that this was either due to the formation of very small quantities of $PTPM$ at a time, together with the formation of MPM as the main product of the reaction; then the $PTPM$ formed was removed as it was formed by the ester-interchange reactions. Or it could be suggested that MPM and other species constituted from (M and P) were the first products of the reaction between PTP_1 and MA , and all the other products were the result of later ester-interchange reactions between these products and monomers present in the reaction mixture. However, the overall picture of the assigned structures makes one more inclined to assume the formation of $PTPM$ as a direct product of the reaction of PTP_1 and MA . It could be suggested that a possible mechanism for the reaction of PTP_1 and maleic anhydride could be as follows:



GPC evidence for the importance of (MPM) formation in PTP_1/MA Systems

A series of polymerization reactions were carried out at $150^\circ C$ for 30 minutes and 60 minutes using different molar ratios. The molar ratios used were: 1 PTP_1 : 1 MA , $\frac{1}{2}$ PTP_1 : MA : $\frac{1}{2}$ PG and 1 PTP_1 : 1 MA : 1 PG . "PG" is used to denote propylene glycol.

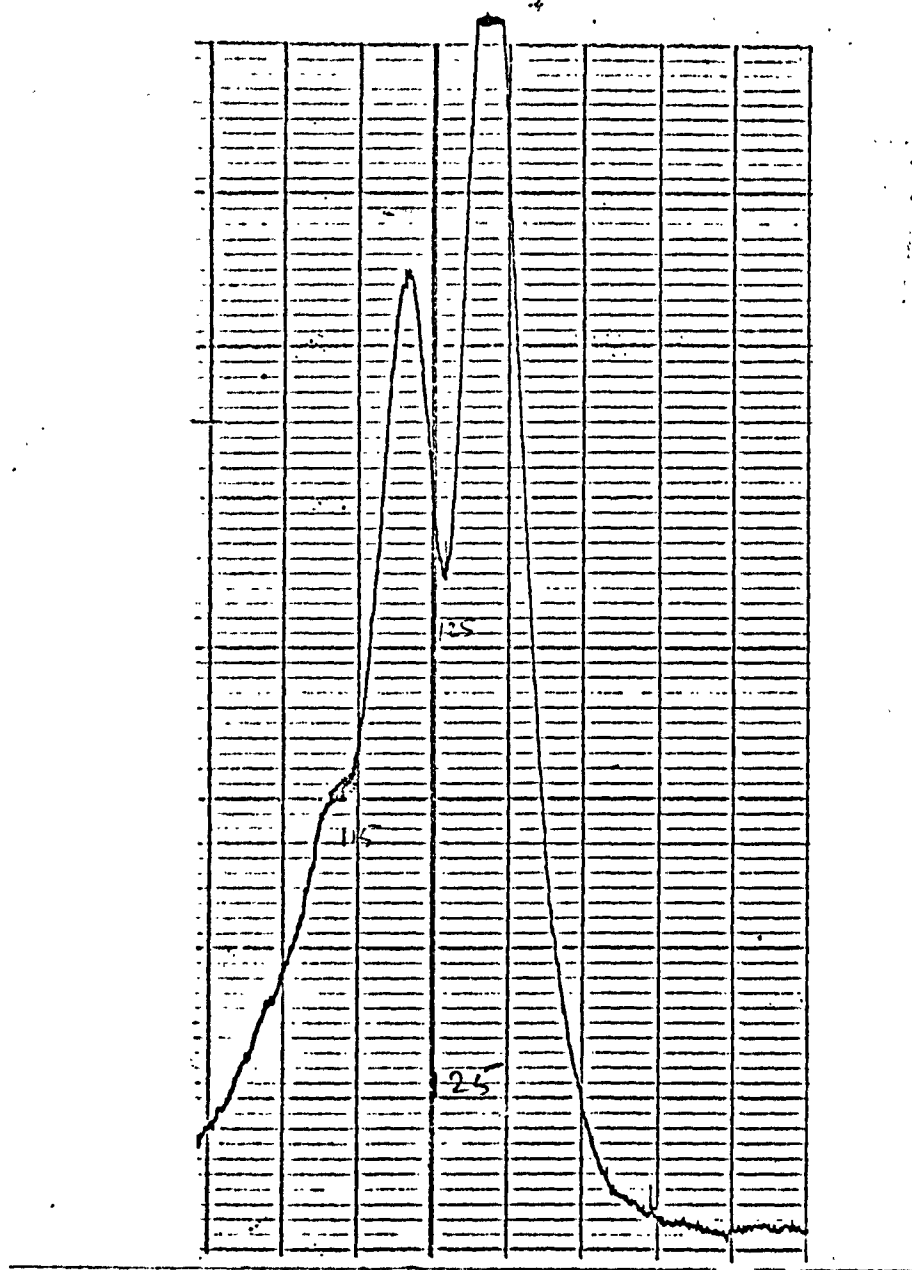


FIGURE 4.25 GPC Chromatogram of ($\frac{1}{2}$ PG; $\frac{1}{2}$ PTP; 1M) 150°C/30 mins

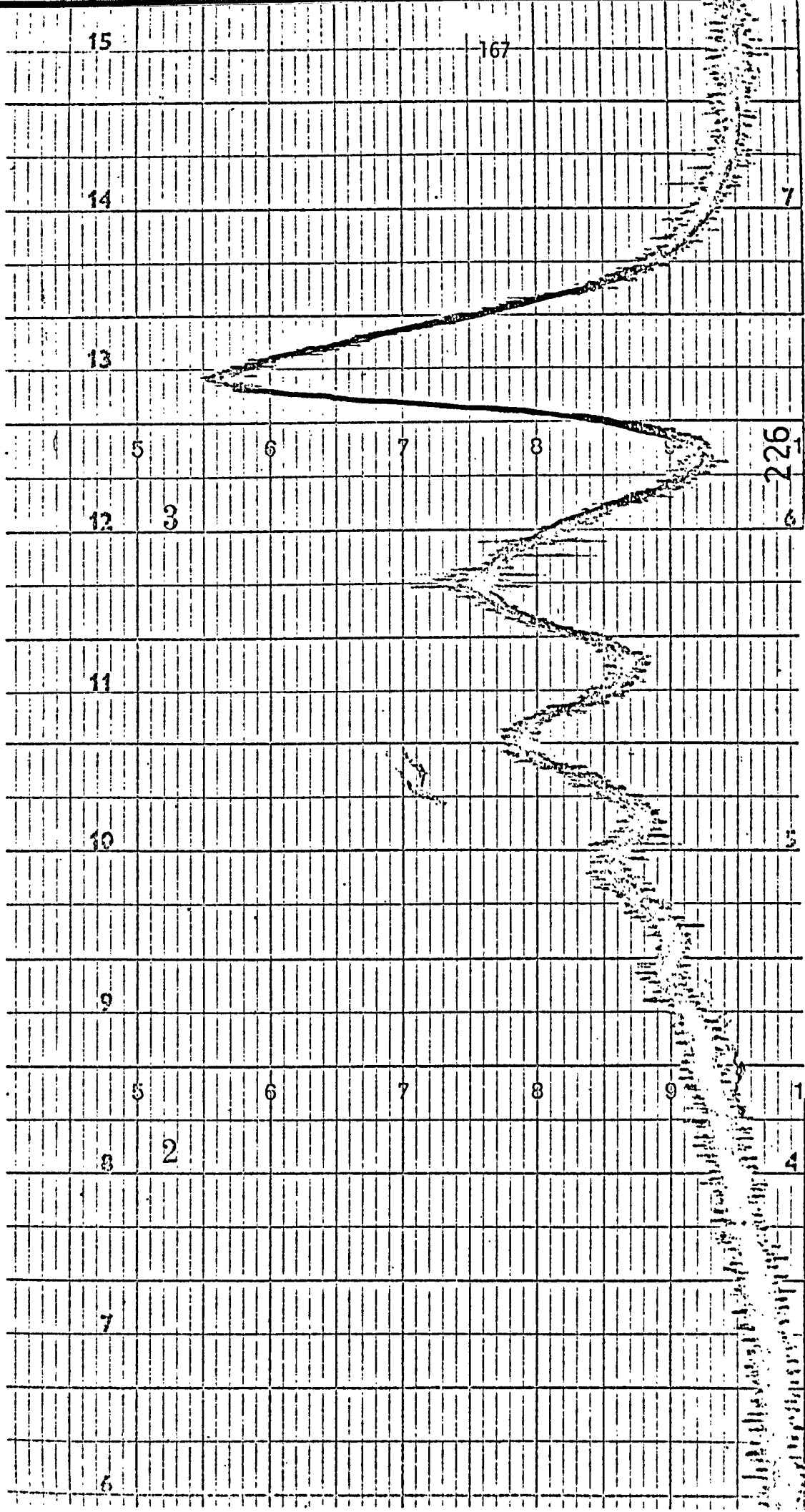


FIGURE 4.26 GPC Chromatogram of (1 PG: 1M: 1 PTP)/150°C, 30 mins

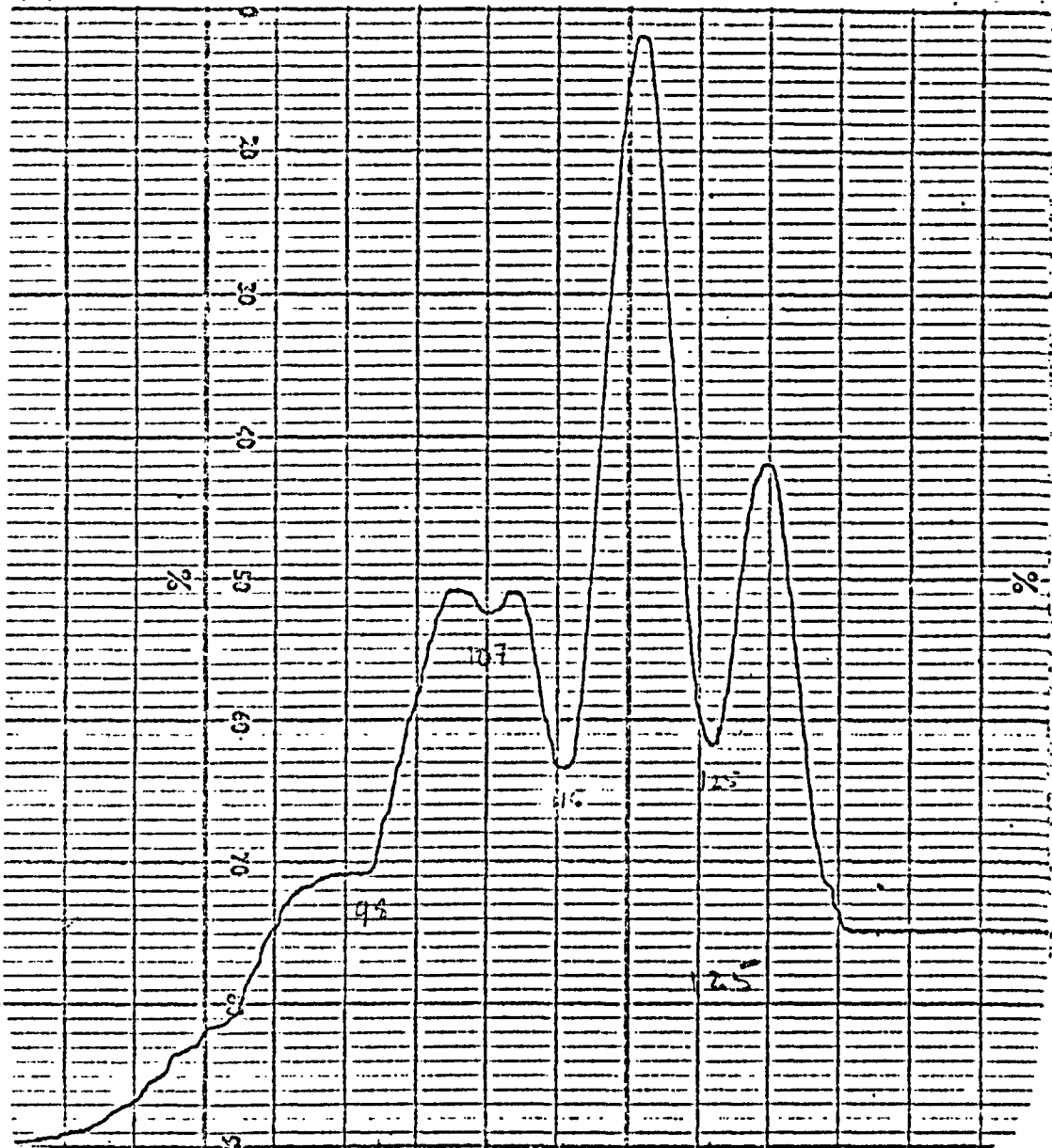


FIGURE 4.27 GPC Chromatogram of (1 PTP₁:1M)/150°C, 1 hour

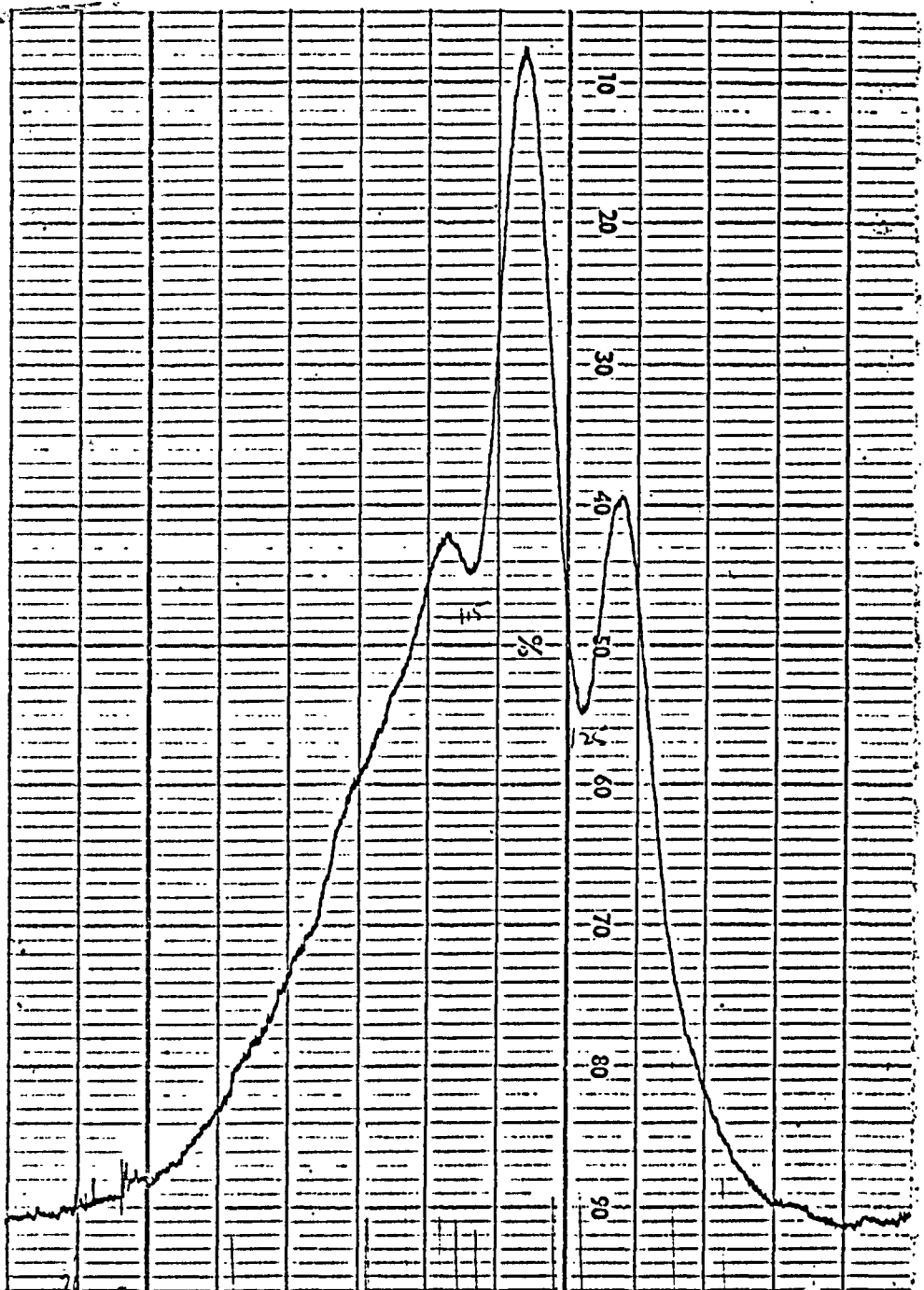


FIGURE 4.28 GPC Chromatogram of ($\frac{1}{2}$ PG: $\frac{1}{2}$ PTP: 1M) 150°C, 1 hour

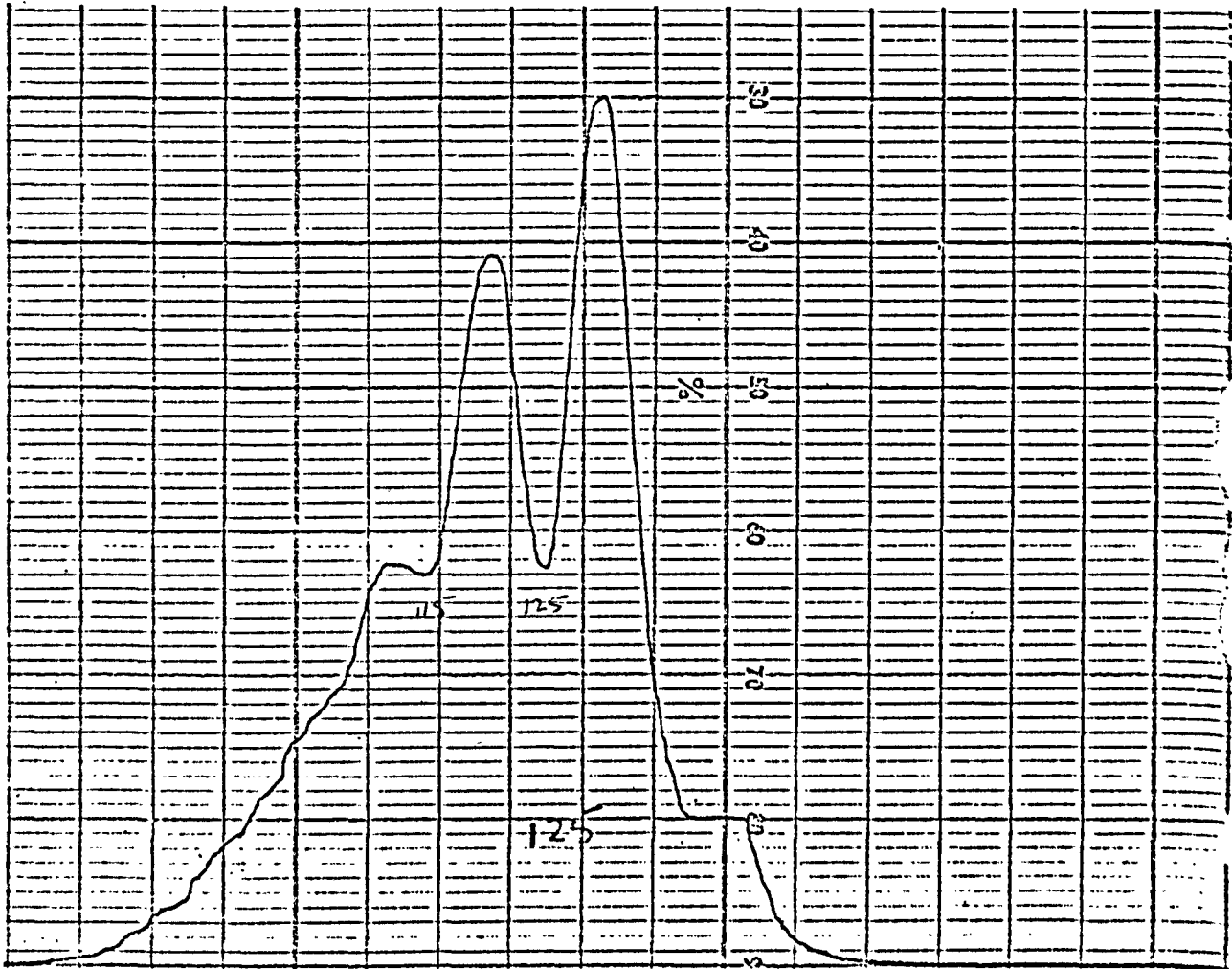


FIGURE 4.29 GPC Chromatogram of (1 PG: 1 PTP: 1M)/150°C, 1 hour

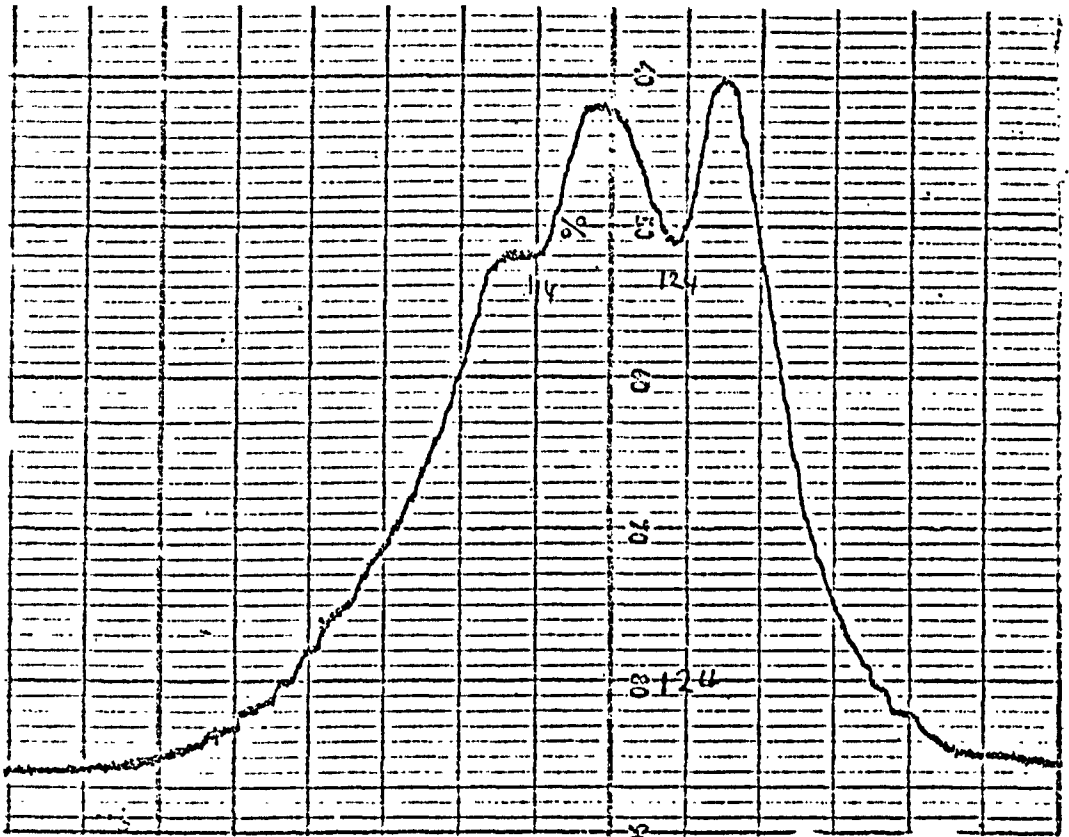
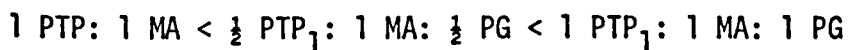


FIGURE 4.30 GPC Chromatogram of (1 PG: 1M)/150°C, 1 hour.

GPC chromatograms were obtained for each product, Figures 4.1, 4.14 and 4.25-4.30. In all these chromatograms the peak corresponding to the lowest molecular weight could be attributed to $PTP_1 + MPM$, depending on the mechanism proposed earlier. It could be observed that from the chromatograms that all those reactions which were performed for 30 minutes, did not proceed to form high molecular weight species and almost 90% of the reaction products were confined to the first three peaks.

In Figure 4.1 (1 PTP:1 MA) the first peak (a) is smaller than the second peak (b). The first peak (a) was proved to contain MPM (Section 4.5) but its relative size is smaller than the corresponding peaks in Figures 4.26 and 4.27. In Figure 4.26 ($\frac{1}{2}$ PTP: 1 MA: $\frac{1}{2}$ PG) the first peak (of lowest molecular weight) is larger than the second peak. The size of this peak was enhanced by the presence of free propylene glycol which formed MPM from the reaction with maleic anhydride. In Figure 4.27 the similar peak (of lowest molecular weight) was more enhanced and due to the presence of higher molar ratio of propylene glycol (1 PTP: 1 MA: 1 PG), the reaction between (PG) and (MA) went further to form higher molecular weight species which could be seen in Figure 4.27.

The size of the first peak (lowest molecular weight), in all the reactions carried out for 30 minutes, could directly be related to the amount of free propylene glycol present in the reaction mixture, and it followed the sequence:



This showed the predominance of MPM at this stage. When the reaction proceeded to 60 minutes the decrease in the first peak was comparable to the decrease of this peak in the chromatograms obtained for the reaction of propylene glycol with maleic anhydride (1:1 molar ratio) see Figures 4.14 and 4.30).

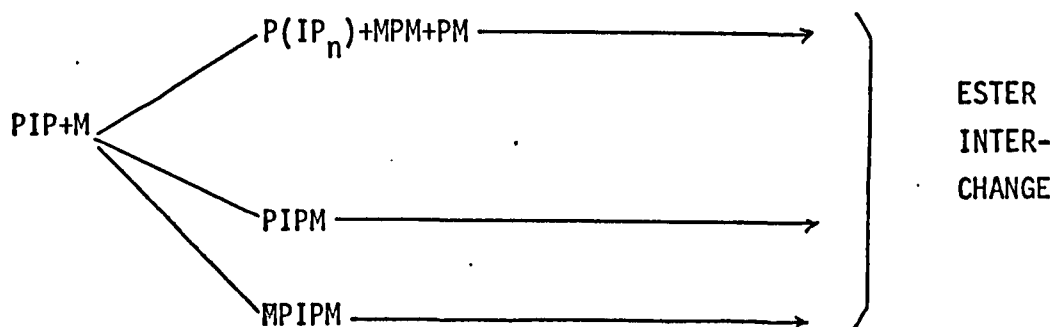
Reaction mechanisms at 180°C

At 180°C, the high temperature appeared to have activated the prepolymers, so that their direct reaction with maleic anhydride proceeded at much higher rates than was permitted at 150°C. The high

temperature also encouraged self condensation of the prepolymers which resulted in higher ratios for (-IPI-) and (-TPT-) segments. However, the presence of PT and PM as well as MPM was not detected, suggesting that these structures are not stable at 180°C.

As expected from the polycondensation reactions at 180°C, the order of reactivity at 180°C was reversed (Section 3.3). PIP₁ exhibited greater reactivity with maleic anhydride which resulted in higher molecular weight components, i.e. greater tendency for ester interchange. This greater reactivity was also manifested in the higher rate of self-condensation. Although the total contents of oligomers formed was almost the same in both systems, it could be noticed that P(IP)_n oligomers where n = 3 or 2 were present in four fractional components while in PTP₁ systems the only component containing P(TP)_n was in the form of P(TP)₂ (see Tables 4.7 and 4.10). In both systems the ester-interchange reactions showed their effect in producing saturated acid ended molecules (6.5% of T and 6.4% of I were half esterified). In spite of the fact that under these reaction conditions the production of PTPM and PIPM could be expected to be predominant, it could be suggested that the ester-interchange reactions were responsible for the transformation of all PIPM to PIPMP and other species and most of the PTPM to other species leaving behind a quantity of PTPM involving only 9% of all the maleic acid present in the reaction mixture.

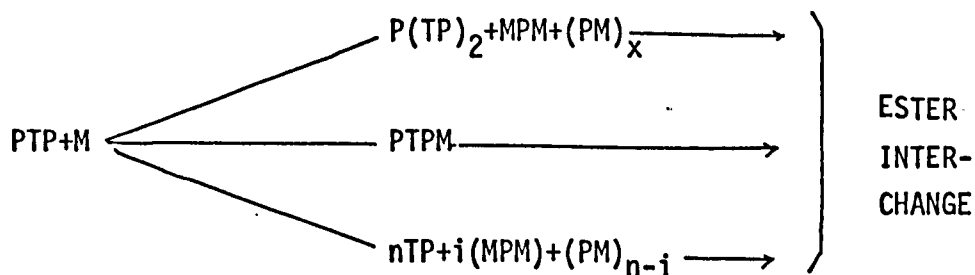
However the following reaction mechanism could be outlined for PIP₁/MA at 180°C:



An important feature of this mechanism is that the saturated acid ended molecules were all in the form of $(IP)_n$. About 36% of all isophthalic acid present in the reaction mixture was in the form of $P(IP)_n$ or $(IP)_n$. 17% of isophthalic acid molecules were in the form of the trimer $P(IP)_3$ which were all changed to $(IP)_3$. 19% of all isophthalic acid were present in the form of the dimer $P(IP)_2$ of which $\sim 3\%$ changed to $(IP)_2$ while about 16% remained as they were $P(IP)_2$. These observations lead to the assumption that MPM and $(PM)_x$ were formed by a side reaction after the oligomerization took place. However the three routes for the reaction mechanism suggested above for PIP/M at 180°C seem to be of importance.

In PTP_1/MA at 180°C the dimer $P(TP)_2$ was stable, a characteristic also noticed for $P(IP)_2$ in PIP/M systems at 180°C . But the saturated acid ended molecules in PTP/M at 180°C contained (TP) fragments and none of $(TP)_2$ or any higher homologue. Following the above observations it could be noticed that the reaction mechanism for PTP/M is different from that of PIP/MA at 180°C .

In Tables 4.7 and 4.8 some of the MPM and $(PM)_x$ species could be assumed to be formed as a result of (P) dissociation from PTP_1 in the process of the dimer formation. It could also be suggested that some of these species (MPM and $(PM)_x$) were formed via an independent route similar to that noticed in PTP_1/MA reaction at 150°C . The presence of proposed structure $(PTPMPT)$ in fraction (3) Table 4.7 supports this suggestion. Thus the reaction mechanism suggested for PTP_1/MA at 180°C could be:



Another interesting point in all these reactions at 150°C as well as at 180°C is that the isomerization of terminal propylene glycol molecules is almost unaffected by the reaction with maleic anhydride. When the prepolymers were heated alone for 30 minutes at the corresponding temperature the ratio of primary-linked to secondary-linked terminal propylene glycols was as follows: PTP₁ at 150°C 70:30; at 180°C 69:31; PIP₁ at 150°C 88:22; at 180°C 76:24. These values are very near to the values noticed for the reacted prepolymer which might suggest that ester-interchange in the prepolymer systems was faster than the polymerization reaction. However, more interesting are the exceptions from these generalizations mainly component (1) in PTP/MA at 180°C and component (2) in PIP/MA at 150°C (see Tables 4.7 and 4.4). Both were assigned similar structures PTPM + PMPM and PIPM + PMPM, and both show a low percentage of primary-linked terminal propylene glycol molecules, 44% and 48% respectively while the general ratios in other fractions show ~ 64% for PTP₁/M systems and ~ 67% for PIP/M systems. It could be suggested that the reactions forming these molecules started after the isomerization of the terminal (P) molecules took place and then the reaction preferred primary-linked propylene glycol molecules causing a depression in its ratio in the resulting molecules and moreover resisting its restoration to the expected ratio for the two isomers. Then the following ester-interchange reactions produced other molecules from these molecules and restored the normal ratio for primary-secondary terminal (P) molecules.

Maleic/fumaric isomerization

The maleic/fumaric transformations were rather low at 150°C. In both cases only about 10% of the maleic molecules were transformed to fumaric molecules. From the results displayed in Tables 4.3 and 4.6, some important observations can be mentioned:

The smaller molecules did not seem to have great influence on the transformation of maleic species to fumaric species. However, as seen in the fractions 1 and 2 in the Tables 4.3 and 4.6, the higher ester-interchange rate in PTP₁ seems to have caused relatively greater influence on the isomerization of MPM to F containing species.

Longer molecules in these reactions displayed a better effect in the way of transforming maleic to fumaric species. The fact that

no pattern of M/F transformation was noticed in these molecules might support the inference that the transformation could also be dependent on the molecule history of ester-interchange to some extent.

At 180°C the rate of transformation of maleic to fumaric species was much increased in both systems, see Tables 4.9 and 4.12. This confirmed the well known fact that the maleic/fumaric transformation is temperature dependent. However the difficulty in seeing a dependence of this conversion on the molecular weight size or any other structural factor might be attributed to the predominance of ester-interchange reactions prompted in these systems by the labile propylene glycol molecules. It was noticed that at both temperatures PTPM and MPM have low conversion ratios. They could be assumed to be the first products of the reaction of maleic anhydride and PTP₁ or the dissociated (P) from the prepolymer. This assumption could be supported by their size and the fact that PTPM contained lower ratios of primary propylene glycol ends (see reaction mechanism at 180°C). It could also be of interest to mention that component 2 in PTP/MA at 180°C (PTPMP) gave 100% maleic/fumaric conversion (Table 4.9) and also fraction 2 in PIP/MA at 180°C (MPIPMP + (PM)₂ PIP) led to 70% maleic/fumaric conversion (Table 4.12). These were the highest ratios of maleic/fumaric isomerization in all the fractions, although structures like (PTPM)₂ and (PIPM)₄^P led to 40% and 50% conversion ratios respectively. Depending on the observation that structures like PTPM and MPM gave very low conversion ratios and that the highest conversions were observed in structures composed of a mixture of the prepolymer, unsaturated acid and propylene glycol dissociated from the prepolymer: it could be assumed, in support to previous observations, that the ester-interchange involving these labile propylene glycol molecules was responsible for these high conversions.

Effect of propylene glycol on the isomerization of diethyl maleate

An experiment was performed to see the effect of free propylene glycol on the isomerization of maleic species in diethyl maleate.

A small amount of diethyl maleate (DEM) in one reaction vessel and an equimolar mixture of diethyl maleate (DEM) and propylene glycol (PG)

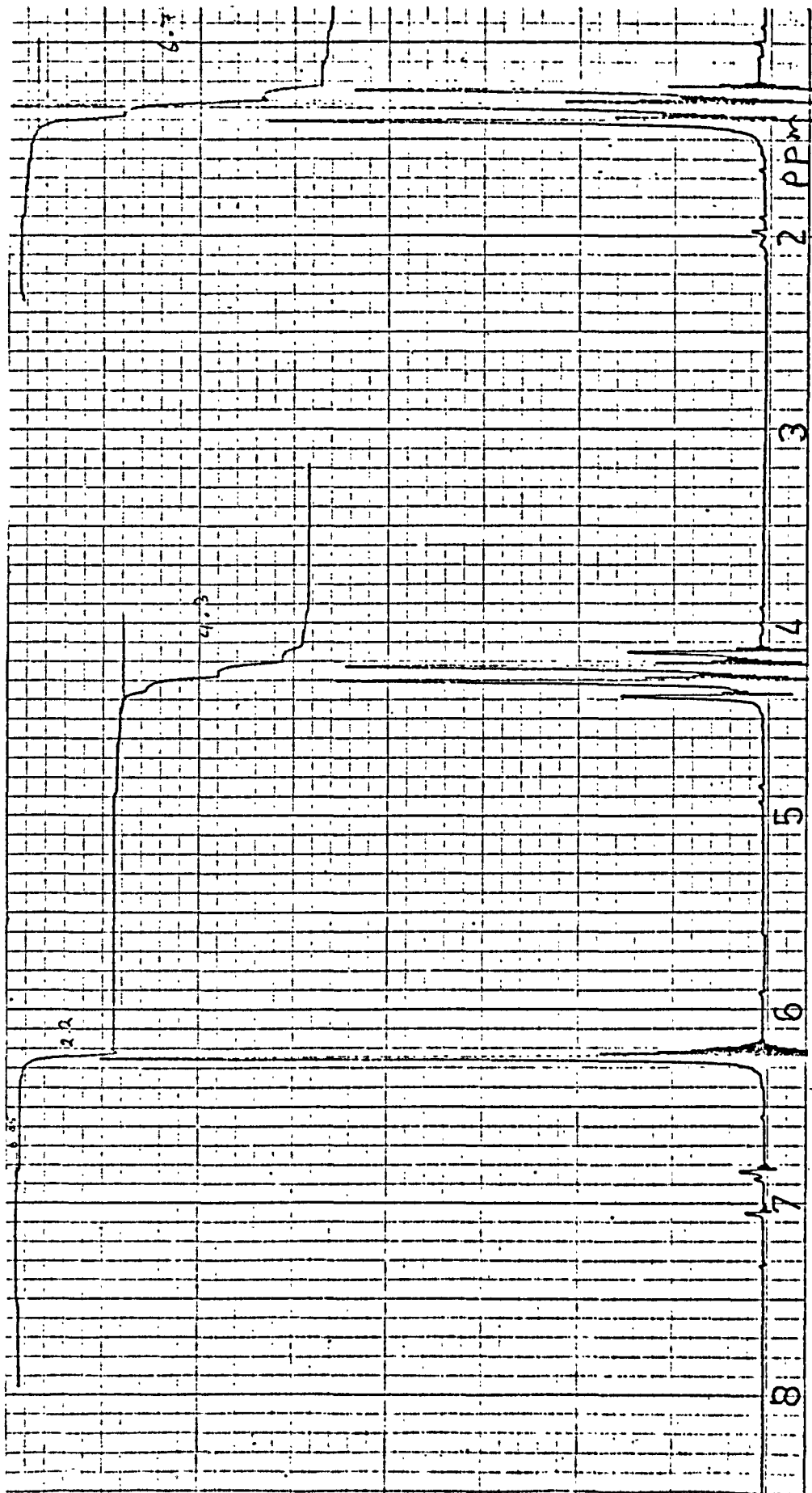


FIGURE 4.31 90 MHz NMR Spectrum of DEM/150°C, one hour

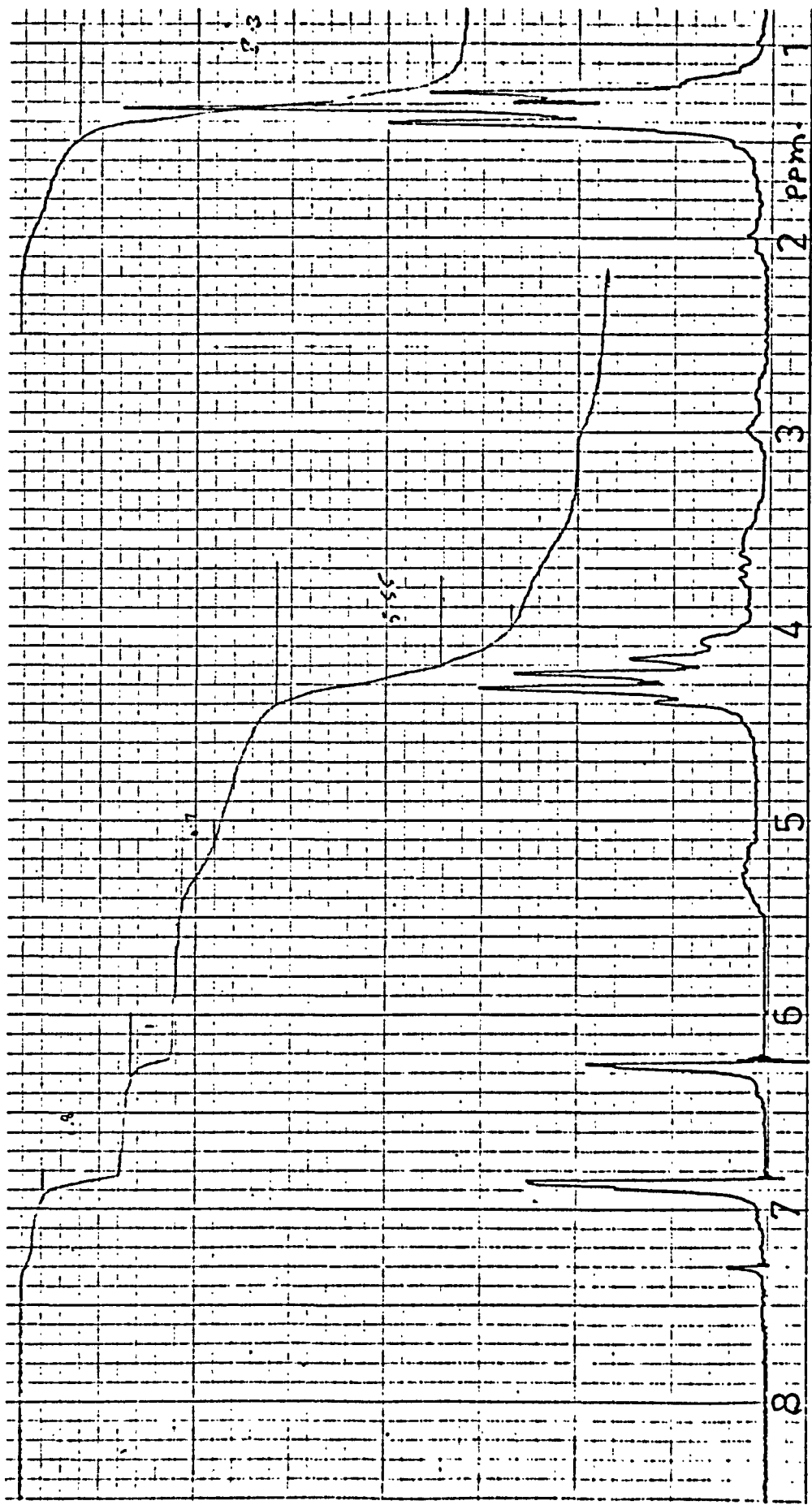


FIGURE 4.32 90 MHz NMR Spectrum of (1 PG)/150°C, 1 hour

in another reaction vessel were heated at 150°C for one hour, under nitrogen. The two products were examined by 90 MHz NMR spectrometer, spectra are shown in Figures 4.31 and 4.32. The results showed that when diethyl-maleate was heated on its own for one hour 98% of the maleic species remained unchanged.

On the other hand, in the spectrum of the products of the equimolar ratio of (DEM) and (PG) heated for one hour, 64% of the maleic molecules were changed to fumaric molecules in spite of the fact that only about 30% of the propylene glycol was actually attached to the maleic acid molecules in the final product. This could serve as further evidence for the importance of ester-interchange reactions in the M/F isomerization.

CHAPTER 5

SOME POLYMERIZATION REACTIONS OF PREPOLYMERS
WITH MALEIC ANHYDRIDE AND FUMARIC ACID

5.1 Bis (2-hydroxy propyl) terephthalate (PTP₁) Polymerizations
with Maleic Anhydride and Fumaric Acid

5.1.1 PTP₁/Maleic Anhydride Systems

The experiments described in this section were performed at 150°C under nitrogen for 5 hours. The reactants were: propylene glycol (PG), bis (2-hydroxypropyl) terephthalate (PTP₁), maleic anhydride (M), in small quantities, i.e. the molar ratio 1 PTP₁:1M was 0.005 mole to 0.005 mole. Hydroquinone was used as an inhibitor and the temperature was 150°C ± 2°C for the first 30 minutes, and then it remained constant. The apparatus was the same as that used for the polycondensation reactions described in Chapter 3. The experiments performed can be categorised according to the following molar ratios shown in Table 5.1:

TABLE 5.1
Molar ratios used in PTP₁/M systems

Experiment	PG	:	M	:	PTP ₁
A	0	:	1	:	1
B	$\frac{1}{2}$:	1	:	$\frac{1}{2}$
C	1	:	1	:	1
D	2	:	1	:	1
E	1	:	1	:	0

These experiments were also conducted for one hour at the same temperature, (150°C), see Chapter 4.

Qualitative GPC Analysis

The GPC technique used was the same as that described for the polycondensation reactions in Chapter 3, in which the carbonyl

absorbance at $1715-1720\text{ cm}^{-1}$ was monitored by an IR spectrophotometer. Samples from the products of the experiments listed in Table 5.1 were fed to a single GPC column and the chromatograms in Figures 5.1-5.4 were obtained. It could be observed from Figure 5.1 that the products portrayed in the close pattern of overlapping peaks in this chromatogram were formed of species which exhibited a gradual increase in molecular weight as we go from high to low elution volumes. The chromatogram in Figure 5.1 showed that an increasing amount of the reaction product of (PTP_1) and (M) was constituted of long polymer molecules which were eluted at low elution volumes (84-41 ml). The sharp rise at the start of the peak at elution volume 41 ml suggests that a substantial amount of the product was totally excluded in the GPC separation process. However, the presence of low molecular weight species can also be detected at high elution volumes (109-126 ml), the last of which was of very low height and came at the elution volume 126 ml, an elution volume very near to the generally noticed (V_r) value for PTP_1 in one column GPC systems. In Figure 5.2, which displays the chromatogram of the product of experiment (B), all the species produced in the reaction were within the effective separation range of the GPC system. The low molecular weight region is more enhanced and most of the product is concentrated in the elution volume range between 80-128 ml. If Figures 5.1 and 5.2 are compared, we find that Figure 5.1 which was obtained for the reaction product of experiment A (1 PTP_1 :1M) showed greater enhancement of the high molecular weight region than Figure 5.2 for the molar ratio $\frac{1}{2}$ PTP_1 :1M: $\frac{1}{2}$ PG. This can be explained in terms of the observations made earlier in Chapter 4; that the contribution of (PG) in experiment (B) was much greater than PTP_1 . In the first stages of the reaction (PG) reacted predominantly with (M) producing low molecular weight species while PTP_1 was mainly incorporated in the later ester-interchange reactions. On the other hand, the reaction of (M) in experiment (A) which involved more PTP_1 , in spite of the dissociation of (P) from PTP_1 as observed earlier, produced more of the higher molecular weight species due to the higher molecular weight of PTP_1 (282) compared to PG (76).

The chromatogram obtained for the product of experiment (C) is shown in Figure 5.3. It could be noticed that the reaction produced mainly low molecular weight species which were eluted at high elution

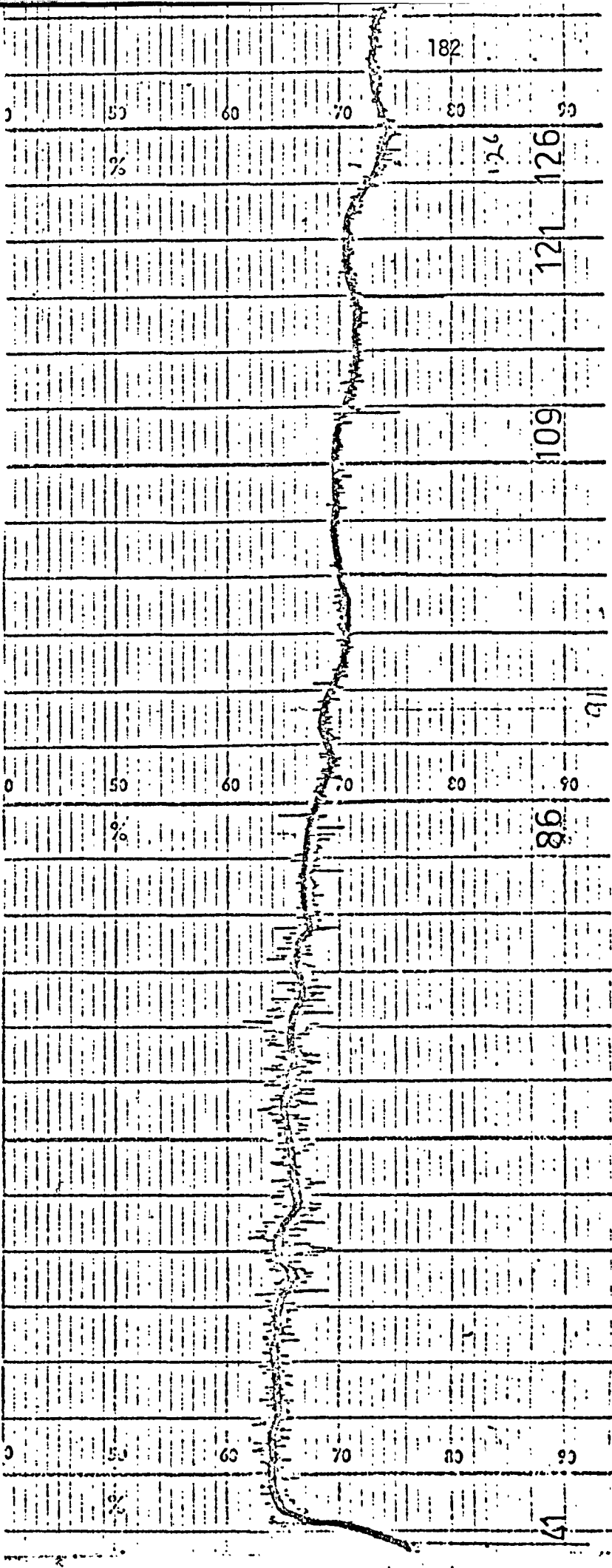


FIGURE 5.1 GPC Chromatogram of (1 P.T.P.₁: 1M)/150°C, 5 hours

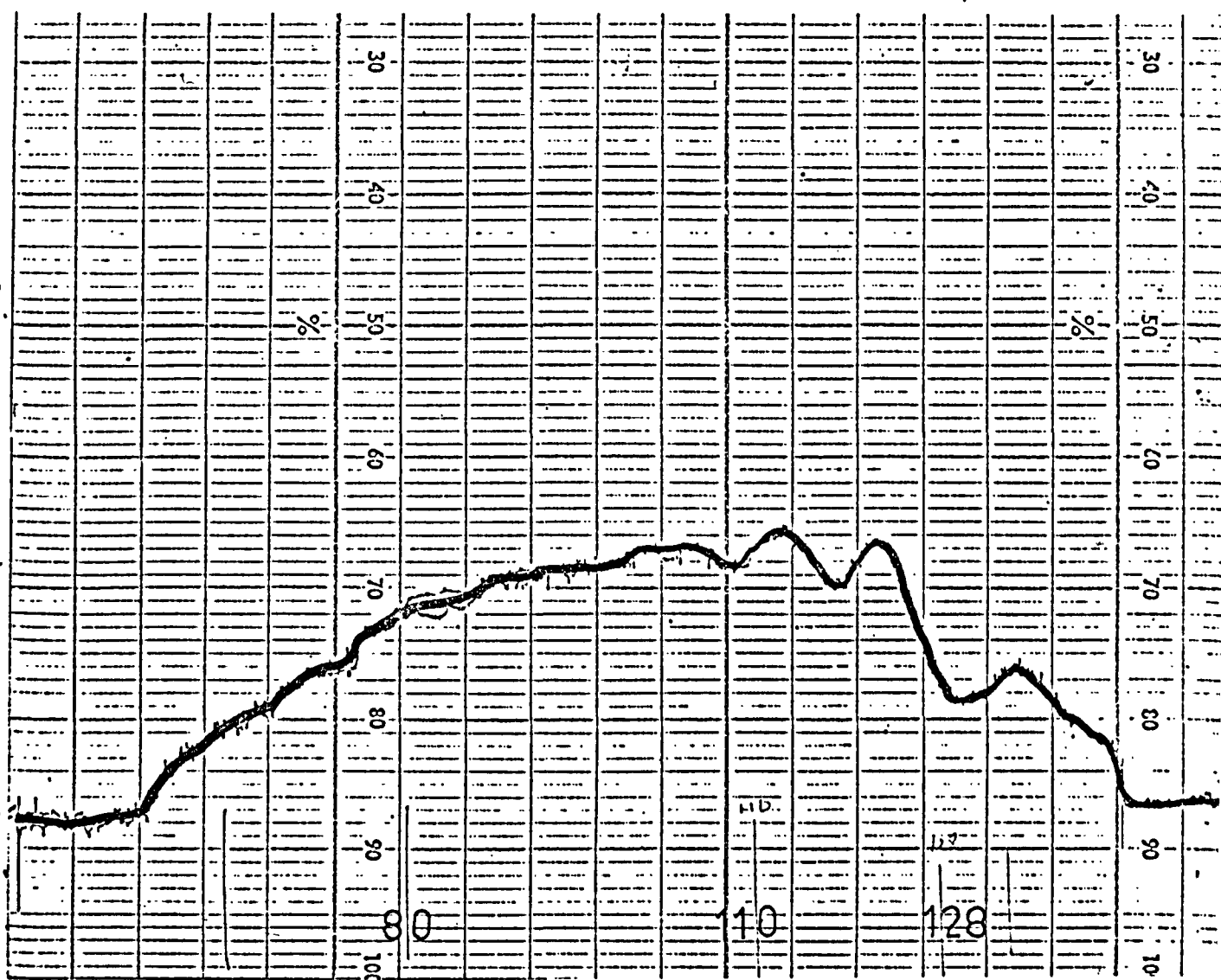


FIGURE 5.2 GPC Chromatogram of the product of ($\frac{1}{2}$ PG; $\frac{1}{2}$ PTP₁; 1M)/150°C, 5 hours

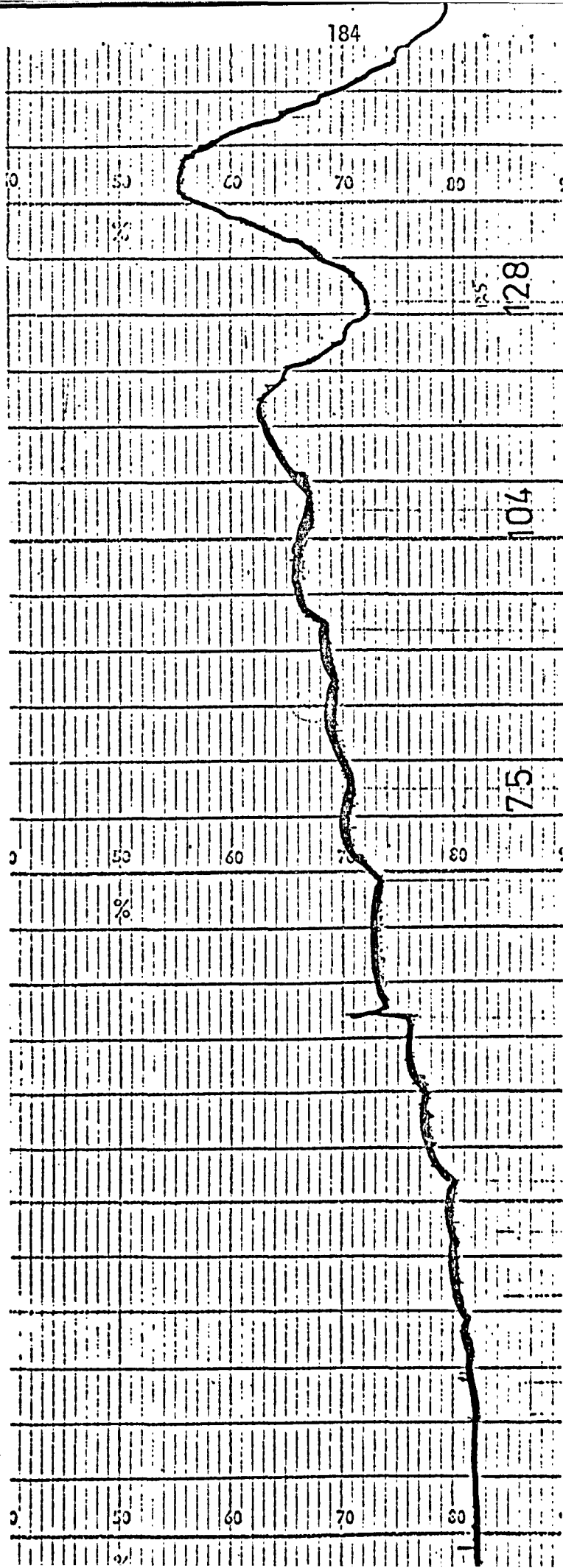


FIGURE 5.3 GPC Chromatogram of (1 PG: 1 PTP₁: 1M)/150°C, 5 hours

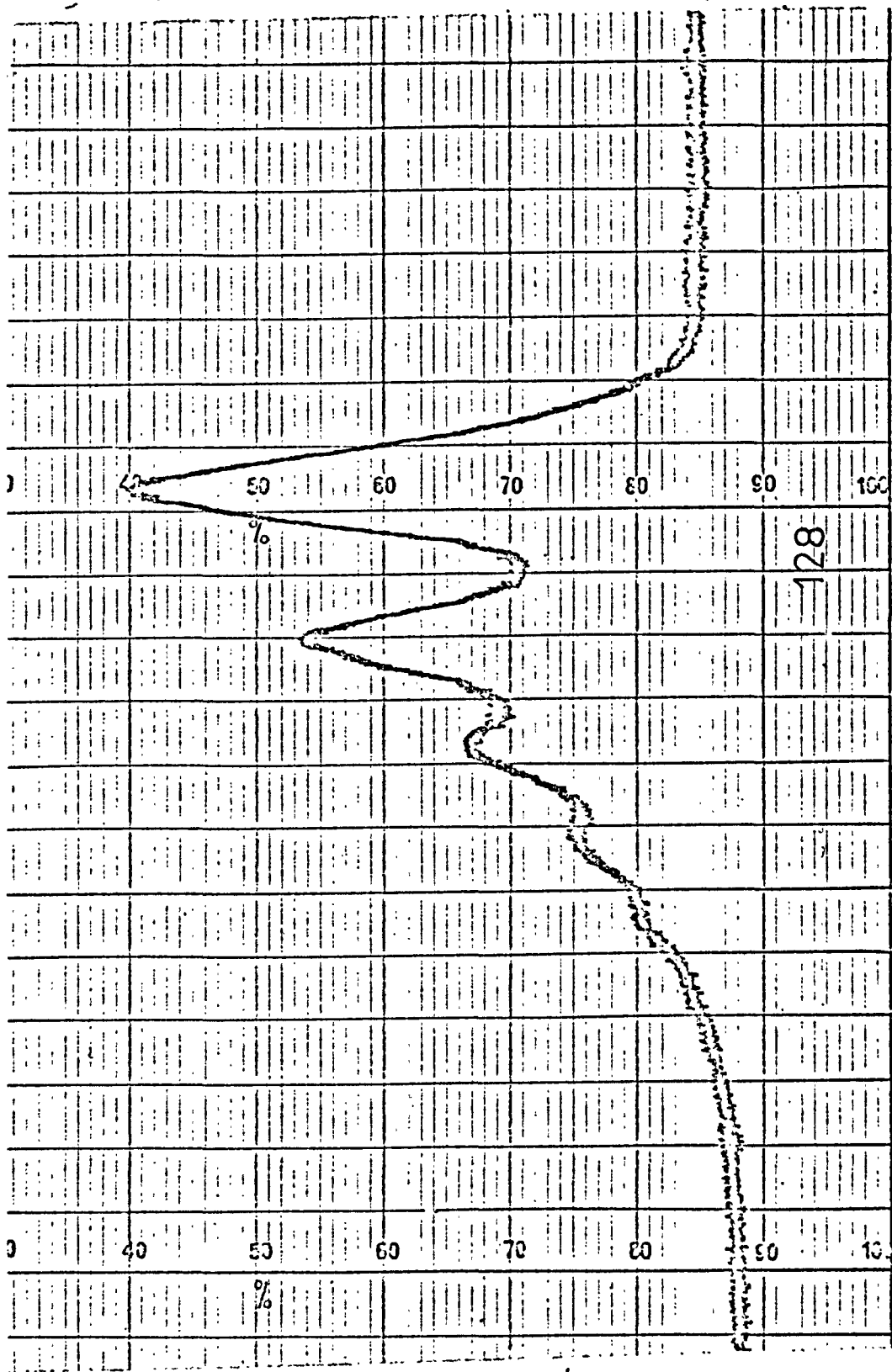


FIGURE 5.4 GPC Chromatogram of (2 PG: 1 PTP₁: 1M)/150°C 5 hours

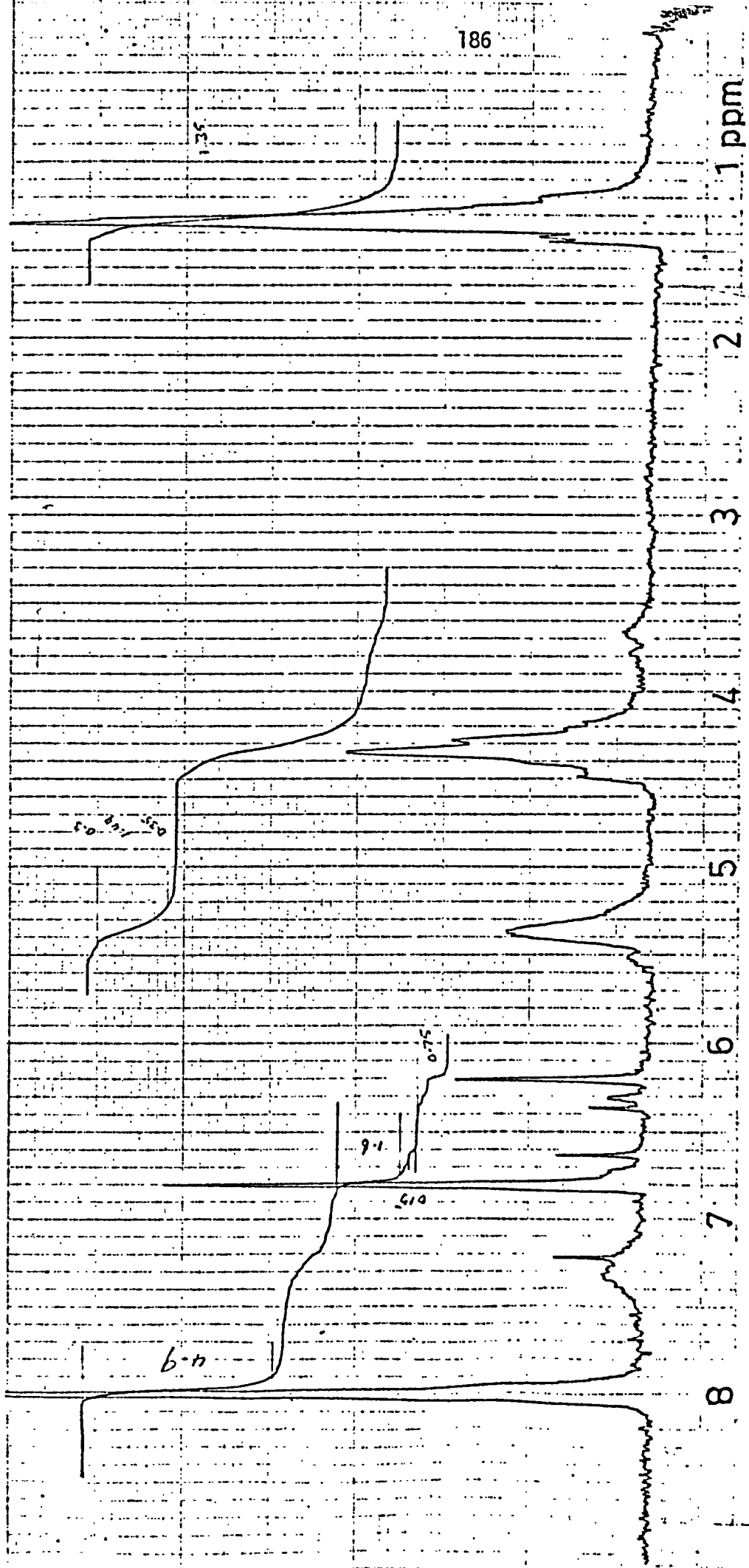


FIGURE 5.5 220 MHz NMR Spectrum of (1 PTP)₁M/150°C, 5 hours

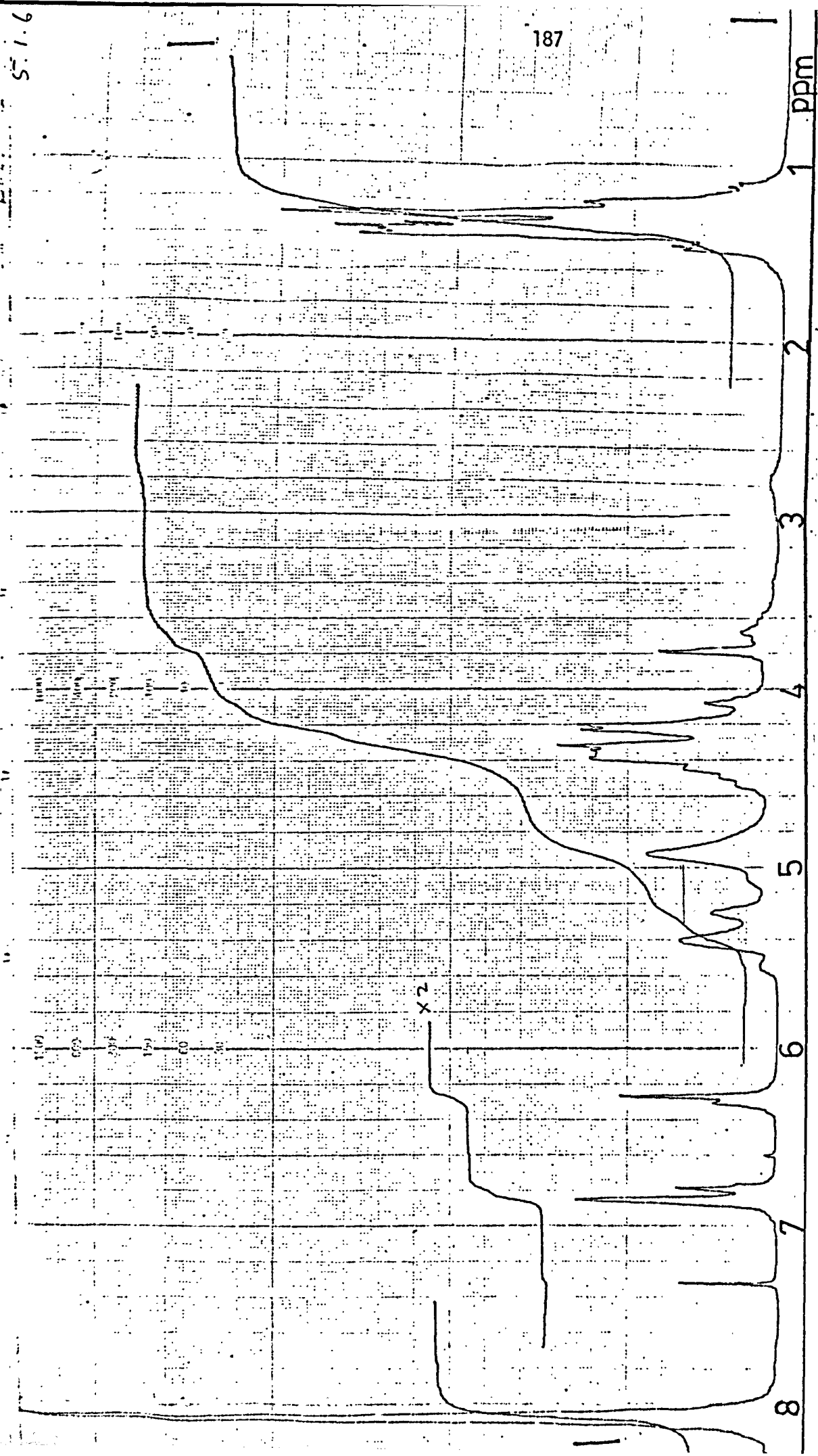
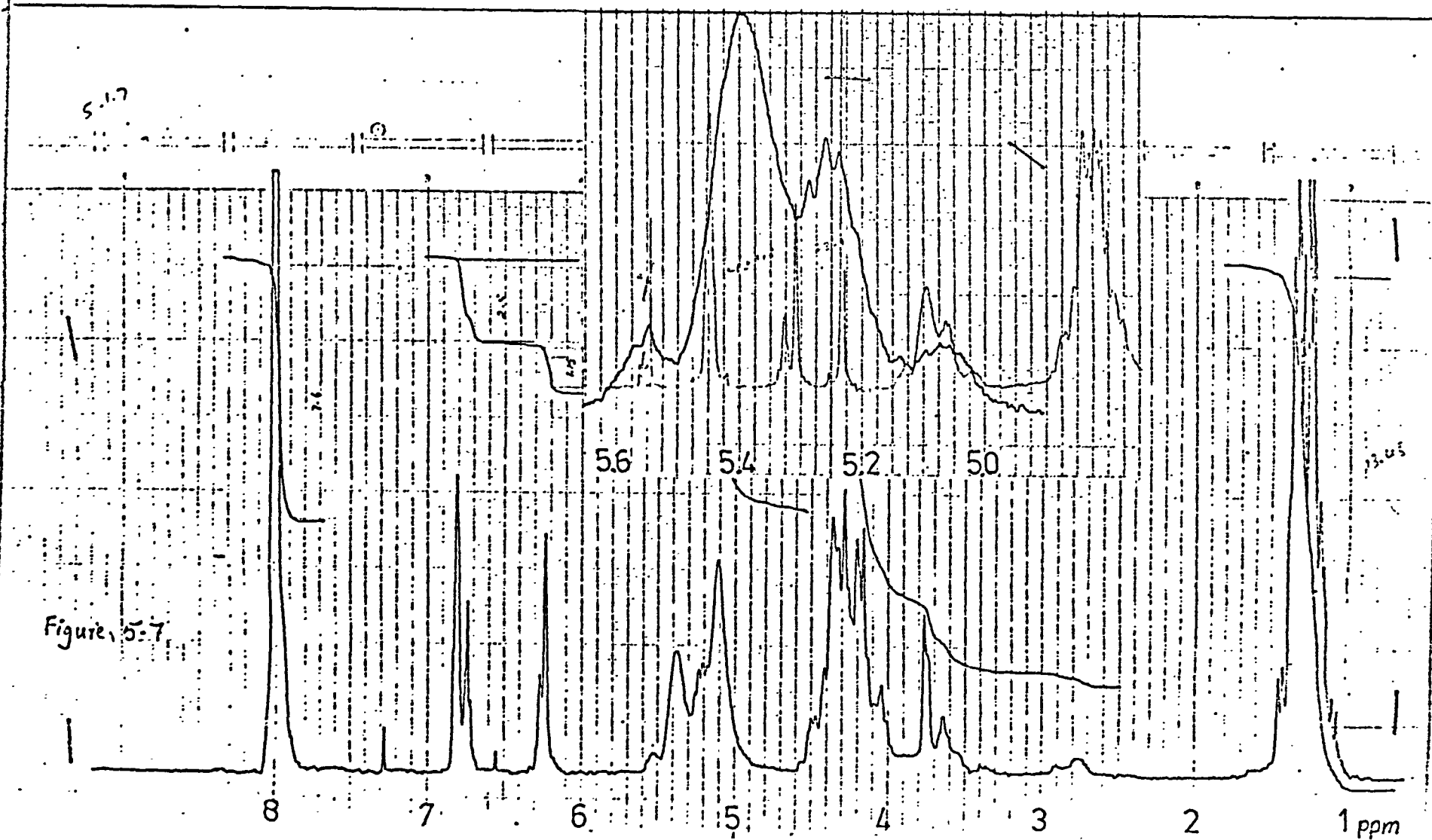


FIGURE 5.6 220 MHz NMR Spectrum of ($\frac{1}{2}$ PG: $\frac{1}{2}$ PTP₁: 1M)/150°C, 5 hours

FIGURE 5.7 220 MHz NMR Spectrum of (1 PG: 1 PTP₁: 1M)/150°C, 5 hours



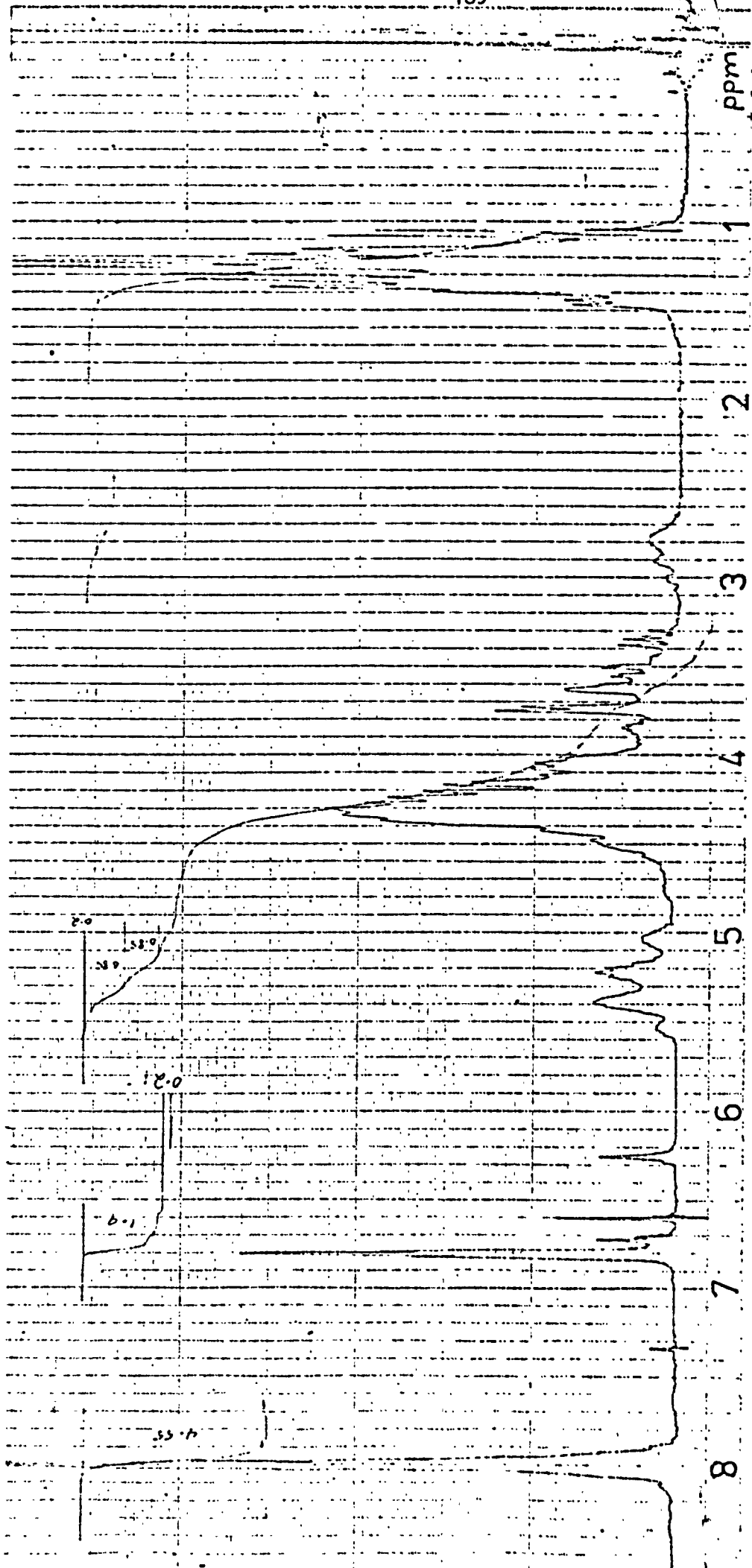


FIGURE 5.8 220 MHz NMR Spectrum of (2 PG: 1 PTP)₁M/150°C, 5 hours

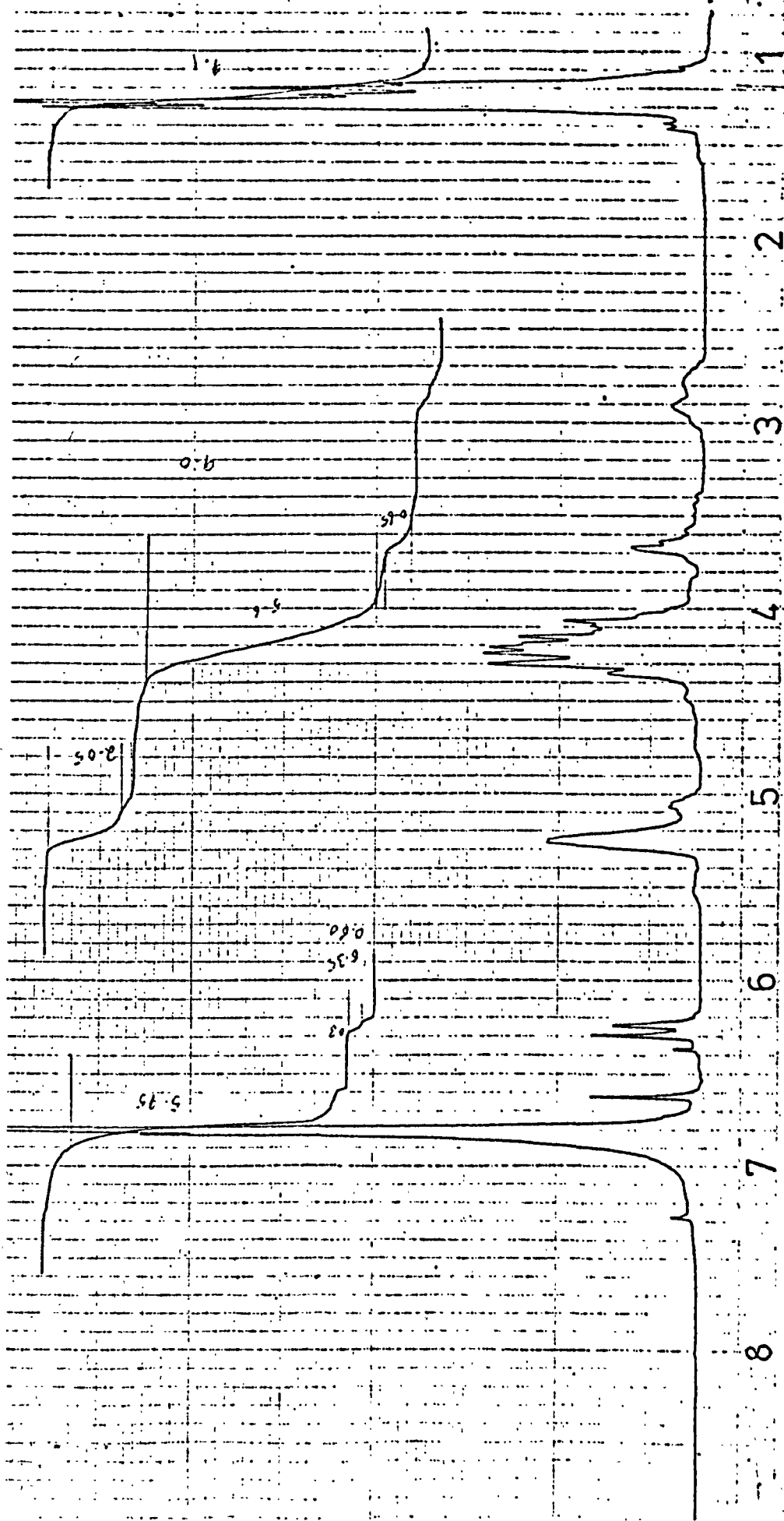


FIGURE 5.9 220 MHz NMR Spectrum of (1 PG: 1M)/150°C, 5 hours

volumes 75-128 ml. The non-stoichiometric nature of the reaction mixture was the obvious reason for the low molecular weight products. However, the lowest molecular weight peak at elution volume 128 ml is much larger than the other peaks. This confirms that the propylene glycol reaction with maleic anhydride was faster than the reaction of maleic anhydride with PTP₁. The chromatogram for the product of experiment (D), shown in Figure 5.4, adds more support to the suggestion that the role of (PG) in these reactions is greater than PTP₁. In Figure 5.4 the peak of lowest molecular weight, elution volume 128 ml, was much more enhanced.

NMR Analysis

Samples from the products of these experiments were dissolved in CDCl₃ and analysed by a 220 MHz NMR spectrometer, see Figures 5.5 - 5.9. The spectrum shown in Figure 5.5 for the product of experiment (A) showed absorptions at chemical shifts which suggested that most of the PTP₁ has reacted. In the methyl region (1.3 - 1.5 ppm), the methyl absorptions of the primary and secondary terminal propylene glycol molecules are represented by small shoulders in the region 1.1 - 1.25 ppm. The large peak in the area (1.3 - 1.4 ppm) represents overlapping methyl absorptions in -TPM- and -MPM- environments. Another small peak was shown at 1.5 ppm representing methyl protons in -TPT- environment. The methylene protons in this spectrum also showed only a little peak at 3.6 - 3.7 ppm for the secondary terminal propylene glycol molecule and a smaller shoulder at 4.15 ppm for the primary terminal propylene glycol molecule whilst the methine protons of these molecules showed peaks which are unidentifiable from the base line noise of the spectrum.

However, an interesting feature is that the maleate and fumarate regions showed a number of peaks indicating different environments for both types of molecules. The spectrum drawn for the product of experiment (B) is shown in Figure 5.6. This spectrum showed similar absorptions to the spectrum in Figure 5.5 (for experiment A.), but it is different in that the absorptions of the terminal propylene glycol protons are shown more clearly in this spectrum, e.g. the methyl protons around 1.2 ppm and methylene protons at 3.7 ppm and 4.15-4.2 ppm,

Figure 5.6 also showed the presence of small traces of free propylene glycol, methyl protons at 1.1 ppm and methylene protons at 3.8 ppm. In addition to these observations, the peaks in the methyl and methylene absorption regions are more resolved which means that the sample was constituted of lower molecular weight species. These observations are in agreement with the GPC results for this product.

In Figure 5.7 the spectrum for experiment (C) showed more enhancement of the peaks resulting from the presence of PTP₁ and free propylene glycol. However, because of the overlap of the peak resulting from OH protons on the methine absorption peaks, the absorption of OH groups was shifted in an extended spectrum obtained for this region using CHCl₂COOH instead of the generally used solvent in this work CDCl₃. The resulting peaks in the region 5.0 - 5.6 ppm are displayed in the same figure (5.7). The spectrum obtained for experiment (D) in Figure 5.8 showed even greater enhancement of the intensity of absorptions at the chemical shifts corresponding to PTP₁ and free propylene glycol than the spectrum shown in Figure 5.7 and higher resolution was also obtained. These observations are also in good agreement with the GPC results as they indicate the presence of low molecular weight species. Figure 5.9, which displays the spectrum of experiment (E), shows the presence of two peaks at the methine absorption region, one at 5.0 - 5.1 ppm which is the chemical shift for the methine protons of the secondary isomer of a terminal propylene glycol molecule, and another at 5.2 - 5.3 ppm a peak assigned in Chapter 2 for the -MPM- chemical environment. Table 5.2 provides a summary of the results showing estimates of double bond losses using the phenyl protons as an internal reference. Also the degree of isomerization of maleate to fumarate is reported in the form of $\frac{f}{f+m}\%$.

TABLE 5.2

Loss of unsaturation and m/f conversion in PTP/M systems

EXPT	Molar Ratios			Temp °C	Loss of Unsaturation		$\frac{f}{f+m}$ %	
	PG	M	PTP ₁		1 Hour	5 Hours	1 Hour	5 Hours
A	0	1	1	150	-	-	9.5	65
B	$\frac{1}{2}$	1	$\frac{1}{2}$	"	2.5	2.3	22.5	67
C	1	1	1	"	3	4	35.6	70
D	2	1	1	"	5.8	7.7	50.9	90
E	1	1	0	"	10.5	18	67.8	95

From Table 5.2 the following conclusions can be made:

- i) no loss of double bonds was noticed in the reaction of PTP₁ with maleic anhydride
- ii) the other values reported for the losses in unsaturation are low and it is clear that these losses were kept at a minimum level by the presence of an inert atmosphere, addition of free radical inhibitor, and keeping the reaction temperature controlled at 150°C. However, losses in unsaturation were introduced into the system by the addition of propylene glycol and they increased with the increase of the propylene glycol molar ratio.
- iii) the isomerization of maleic species to fumarate species was greatly enhanced by the presence of propylene glycol in the reaction mixture and it reached the maximum value in a formulation containing only PG and M. The maleate/fumarate conversion was clearly shown to be a gradual process starting with low degrees of conversion in the early stages of the reaction and increasing with time.

To investigate the structures of polymer molecules formed in these reactions, Table 5.3 shows an estimation of the percentages of the types of links (segments) formed in the course of these reactions.

These were determined from a relative comparison of the integrated traces for the three methine absorptions within the same spectrum. However, the values obtained from integrals were compared to the values obtained from measuring the areas under the peaks in the extended spectra obtained for each product and were found to be in good agreement. In experiment (C) the values shown in Table 5.3 were obtained by measuring the areas under the peaks of the extended spectrum for the methine region, see Figure 5.7.

TABLE 5.3

Ratios of Segments in the product of PTP_1/M at $150^\circ C$

	Molar Ratios			% of segments after 1 hr			% of segments after 5 hr		
	PG	M	PTP_1	-MPM-	-TPM-	-TPT-	-MPM-	-TPM-	-TPT-
A	0	1	1	21	76.6	2.4	16.4	69.6	14
B	$\frac{1}{2}$	1	$\frac{1}{2}$	41	59	-	33.6	61.7	4.7
C	1	1	1	30.6	64.4	5	32.3	59.3	8.4
D	2	1	1	65.4	29.8	4.8	46	46	8

The values tabulated for experiment A confirm the same phenomenon observed for the distribution of segments in the earlier fractionation experiments in Chapter 4. The presence of high percentages of -MPM- type of segments in experiment A support the suggestion that propylene glycol units were depleted from PTP_1 by the reaction with maleic anhydride. The high values for -MPM- in the other experiments with different molar ratios could be expected to be due to the greater reactivity of propylene glycol with maleic anhydride compared to PTP_1 . Although the presence of an equimolar quantity of free propylene glycol with PTP_1 was shown to suppress its polycondensation, the ester-interchange reactions occurring in these systems produced appreciable quantities of -TPT- type segments in reaction mixtures containing free propylene glycol.

5.1.2 PTP_1 /Fumaric Acid Systems

A number of experiments of PTP_1 polymerizations with fumaric acid were performed using the same molar ratios as the PTP_1/M systems described in Section 5.1.1. All reactions here were carried out under

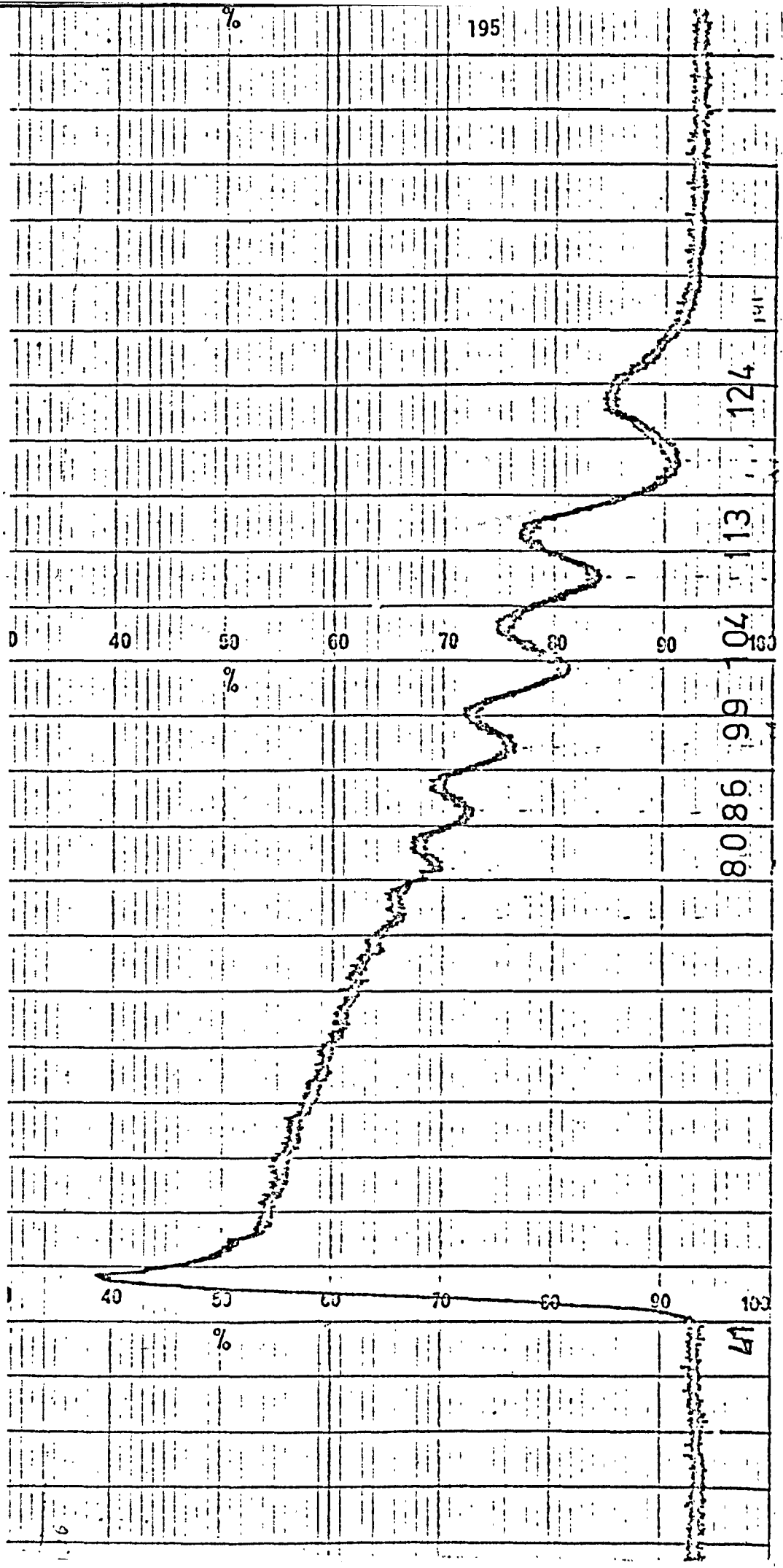


FIGURE 5.10 GPC Chromatogram of (1 PTP₇: 1F)/180°C, 5 hours

5.11

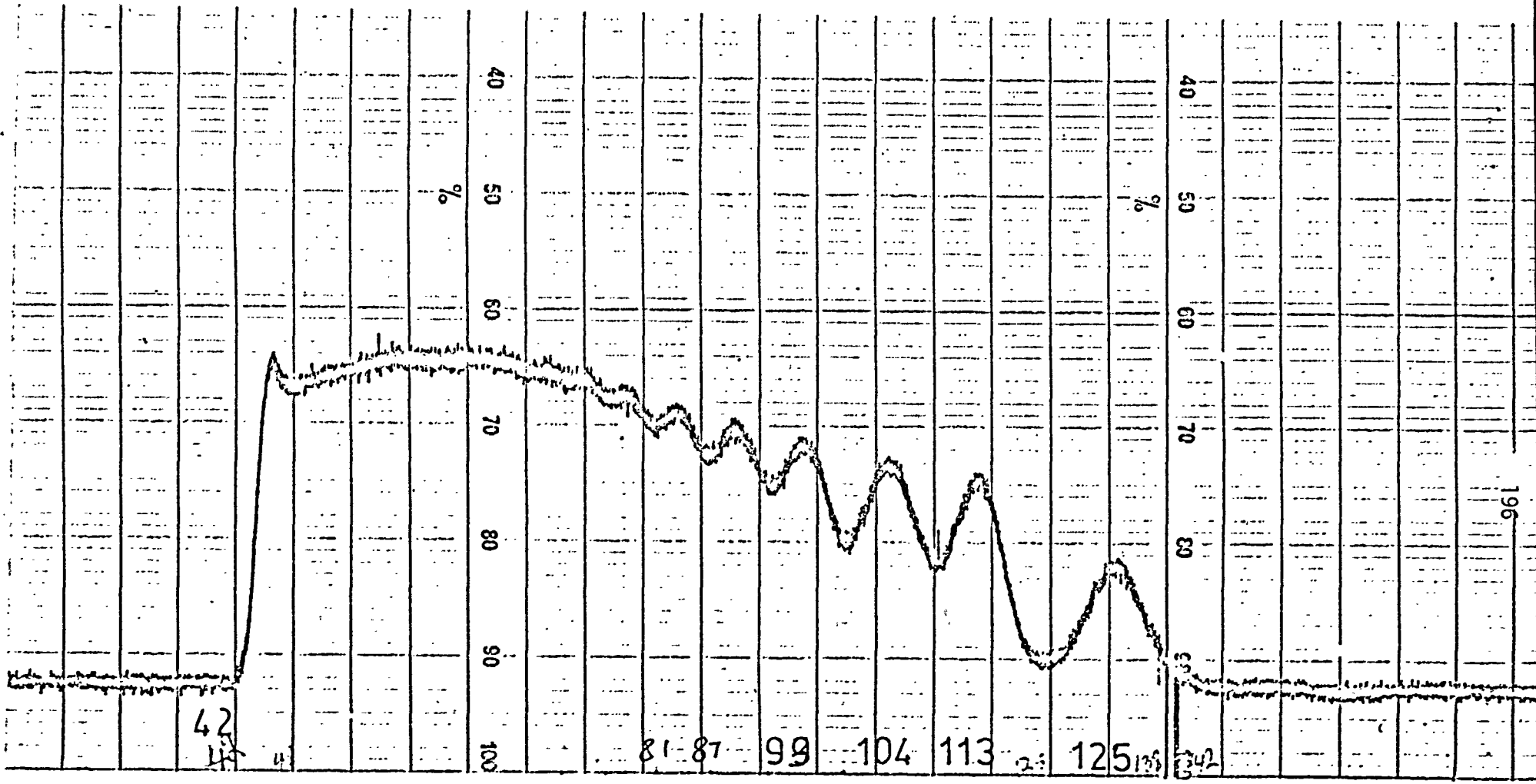


FIGURE 5.11

GPC Chromatogram of ($\frac{1}{2}$ PG: $\frac{1}{2}$ PTP: 1F)/180°C, 5 hours

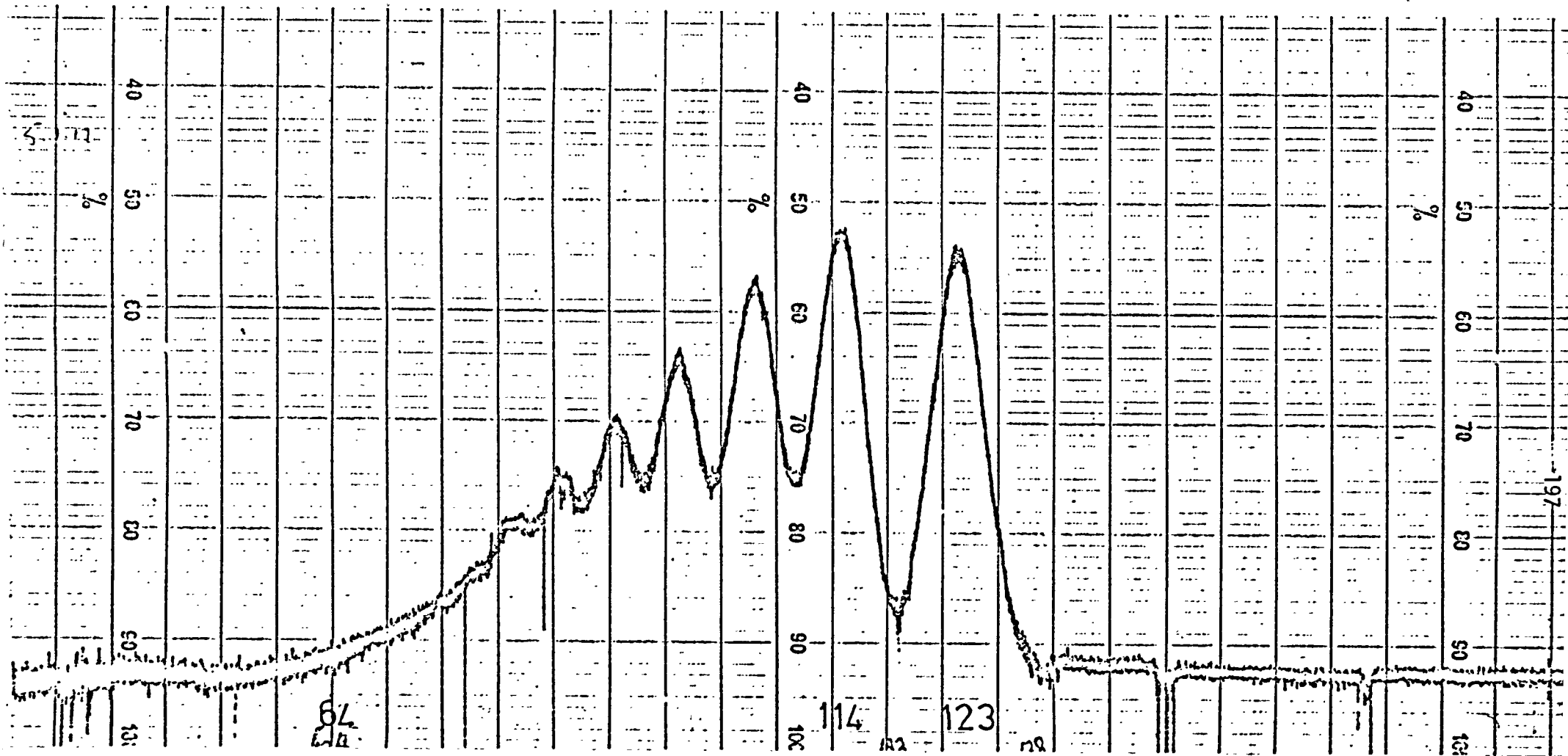


FIGURE 5.12 GPC Chromatogram of (1 PG: 1 PTP₁: 1F)/180°C, 5 hours

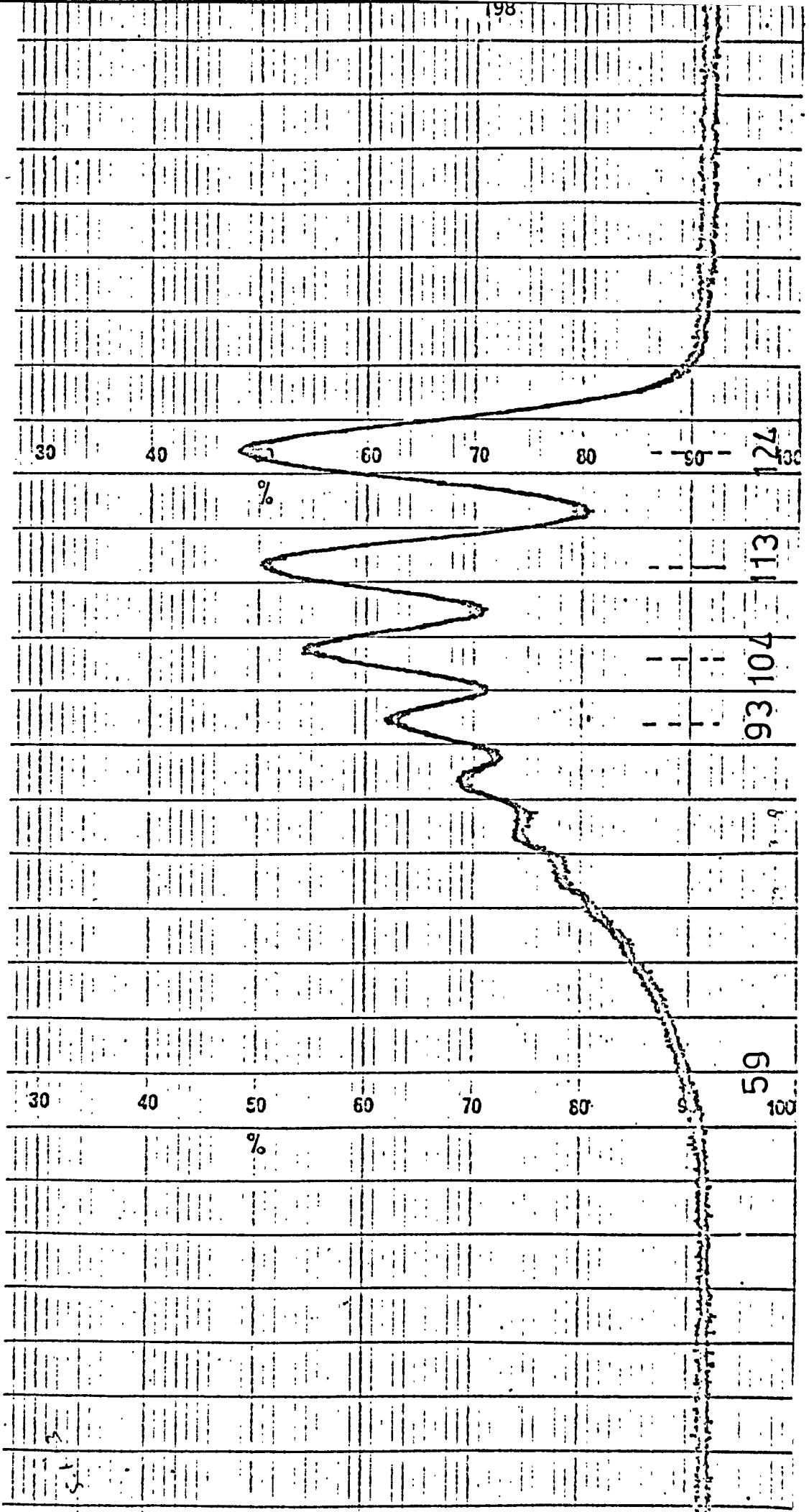


FIGURE 5.13 GPC Chromatogram of (2 PG: 1 PTP: 1F)/ 180°C, 5 hours

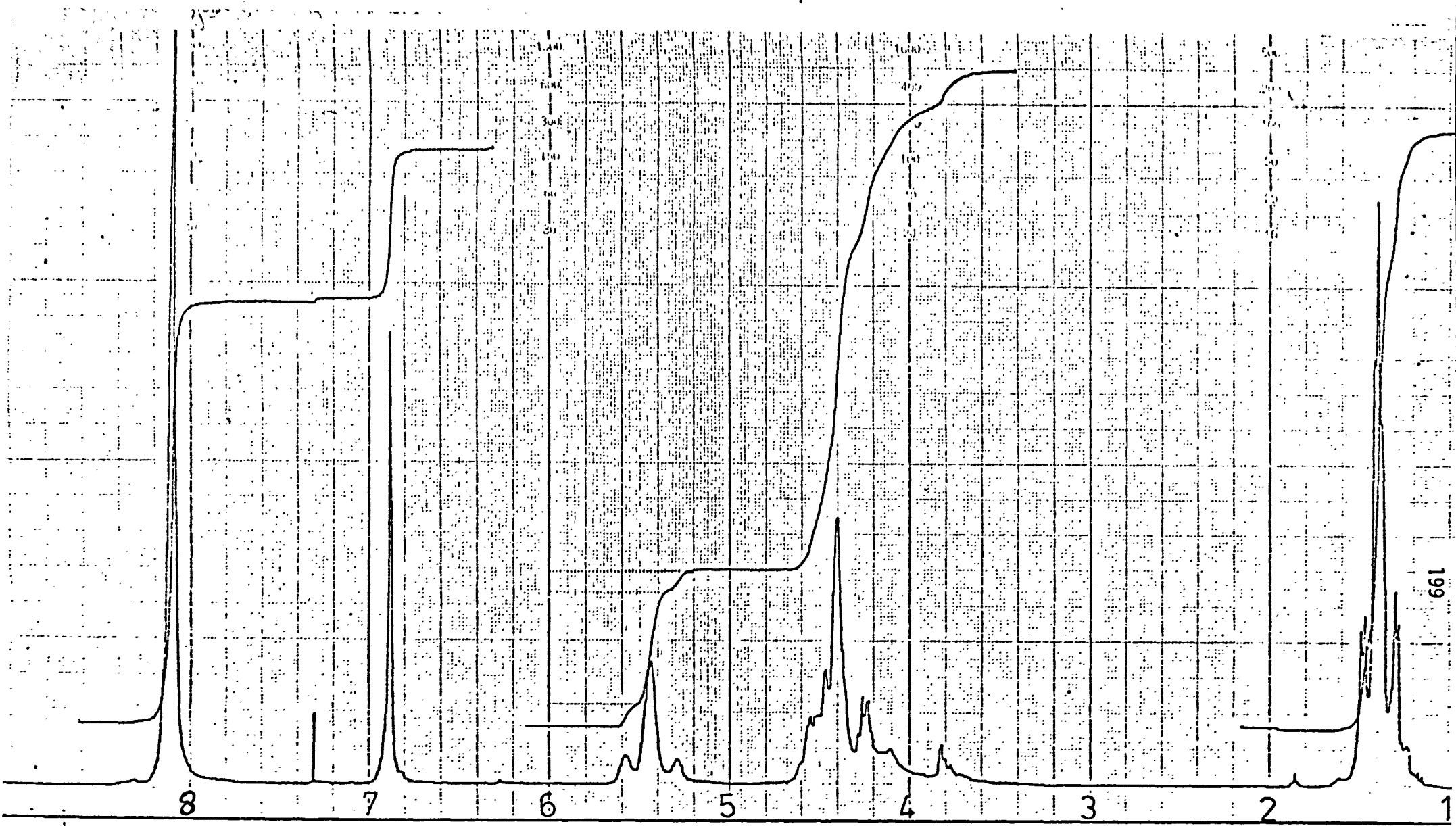


FIGURE 5.14 300 MHz NMR Spectrum of (1 PTP, : 1F)/180°C. 5 hours

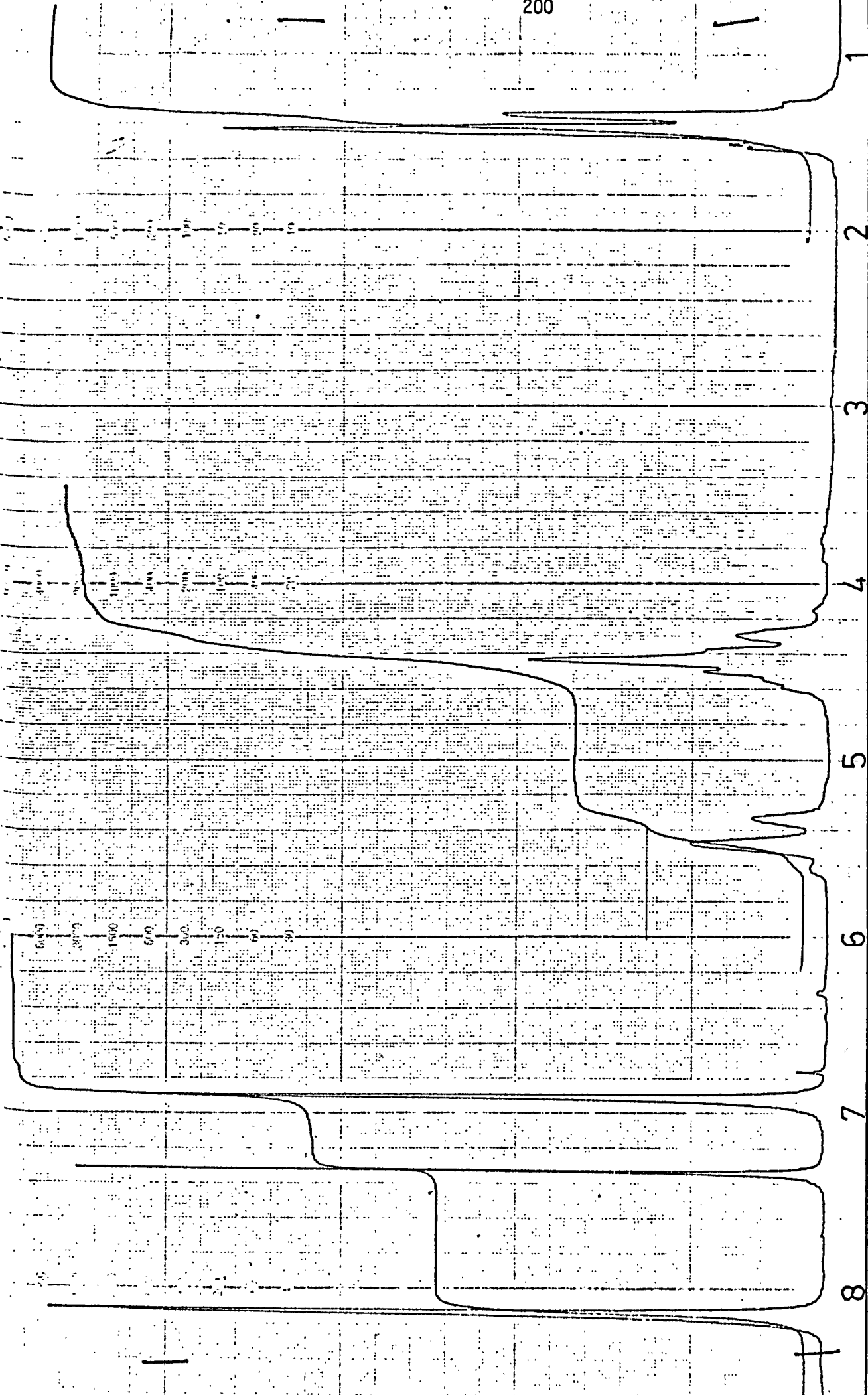


FIGURE 5.15 300 MHz NMR Spectrum of (1 PG; 1 PTP: 1F)/180°C, 5 hours

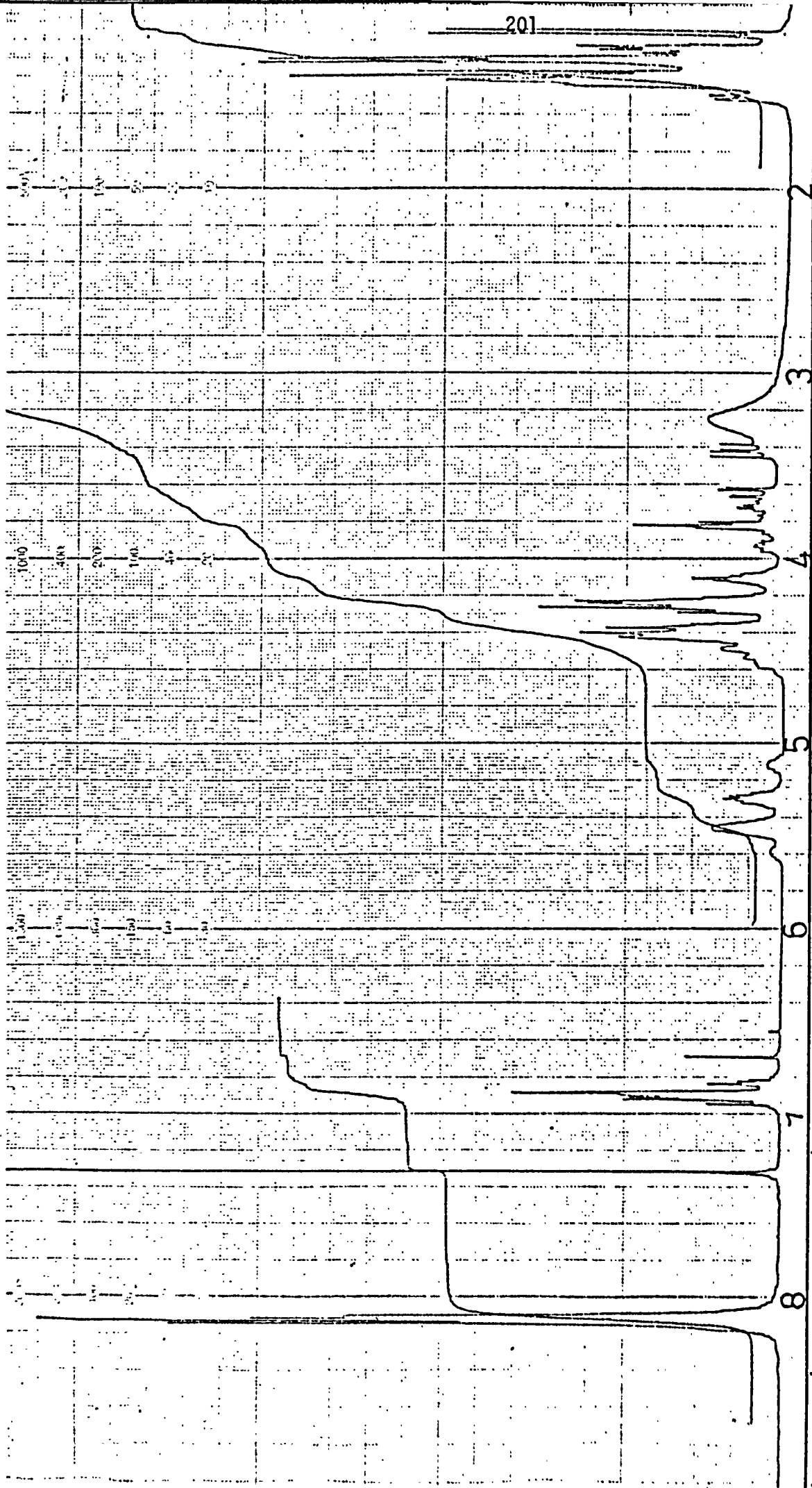


FIGURE 5.16 300 MHz NMR Spectrum of (1 PG: 1 PTP₁: 1F)/180°C, 5 hours

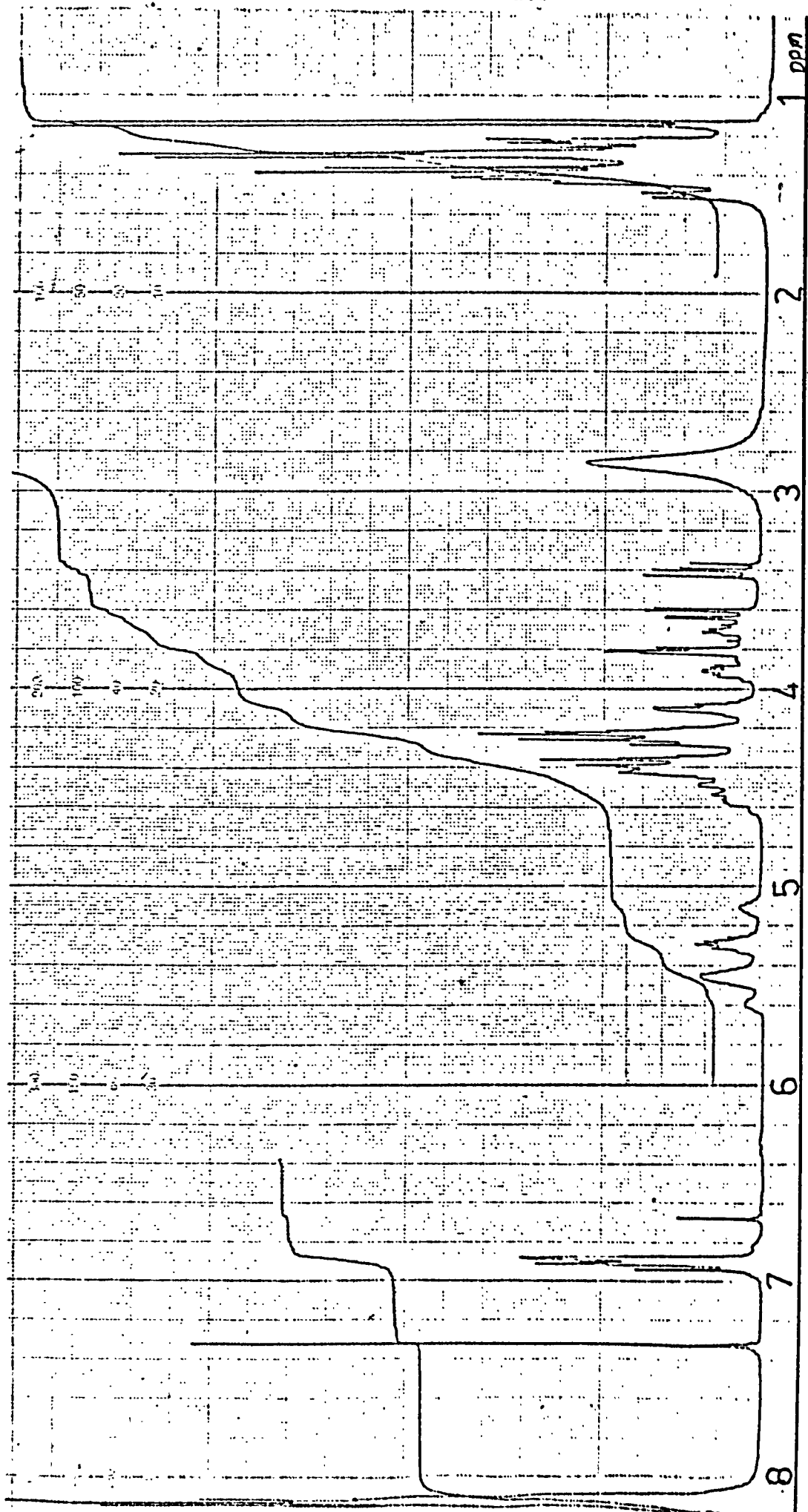


FIGURE 5.17 300 MHz NMR Spectrum of (2 PG: 1 PTP: 1F)/180°C, 5 hours

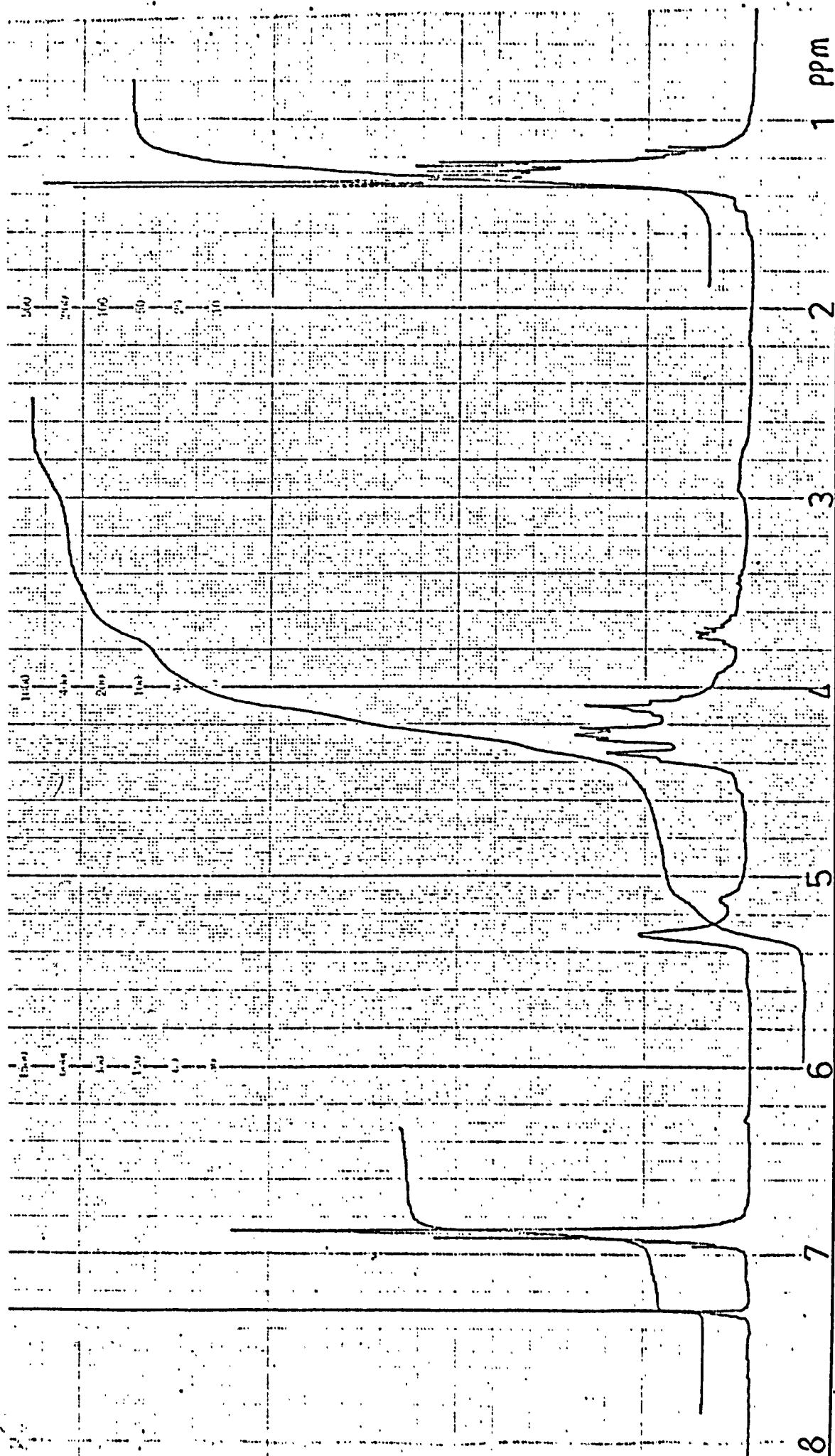


FIGURE 5.18 300 MHz NMR Spectrum of (1 PG: 1F)/180°C, 5 hours

nitrogen atmosphere for 5 hours at 180°C as fumaric acid does not dissolve completely in PTP₁ below this temperature. Hydroquinone was used as a free radical inhibitor.

Qualitative GPC Analysis of Products

The results obtained from a qualitative GPC analysis are displayed in Figures 5.10 - 5.13. The chromatogram obtained for the product of the molar ratio (1 PTP₁:1F) is shown in Figure 5.10. The chromatogram showed that a substantial amount of the product was totally excluded from the gel. This could be noticed in the sharp rise of the peak appearing at elution volume 41 ml and in the height of the peak. A number of peaks appeared at the high elution volume region (80 - 124 ml), indicating that the product also contained low molecular weight species. Figure 5.11 shows the GPC chromatogram of the product of the molar ratio (½ PTP₁:1F:½P). This chromatogram exhibited the phenomenon noticed in Figure 5.10 and Figure 5.1, that part of the product was beyond the effective separation range of the GPC system (elution volume 42 ml). However the excluded part was less in this chromatogram and the chromatogram showed a higher ratio of low molecular weight components (elution volumes 80 - 125 ml). Figures 5.12 and 5.13 indicate that the products were constituted of low molecular weight species. These GPC results confirm the proposals previously made about the importance of the reaction of propylene glycol with maleic anhydride. They also generally show the same pattern exhibited by PTP₁/M systems in the distribution of molecular weights of products for each molar ratio. 1 PTP₁:1F produced the biggest proportion of high molecular weight molecules followed by the molar ratio ½ PTP₁:1F; ½ PG. It is clear, from the chromatograms obtained for PTP₁/F systems, that the fumarate systems produced higher molecular weights than the maleate systems. This could be attributed to the higher temperature (180°C) at which the fumarate reactions were performed.

NMR Analysis

The NMR spectra of the samples taken from the products of the PTP₁/F systems are shown in Figures 5.14-5.18. The spectrum in Figure 5.14

is obtained for the molar ratio (1 PTP :F). As for the spectrum in Figure 5.5, this spectrum did not display well defined peaks for PTP₁ suggesting that most of (PTP₁) had reacted with (F). In the same way it shows a peak at 1.5 ppm for the methyl protons in -TPT- environment and methine absorptions at 5.3 ppm, 5.4-5.5 ppm and 5.5-5.6 ppm. Corresponding to -FPF-, -FPT-, and -TPT- segments respectively. No peak was noticed at 6.3 ppm except a very small rise on the base line at 6.3 ppm which could be due to an impurity in the fumaric acid. The spectrum in Figure 5.15 displayed the same tiny peaks which were also noticed in Figure 5.6, the corresponding molar ratio in PTP/M systems, which indicate the presence of small traces of PTP₁ and free propylene glycol. Figures 5.16 and 5.17 are typical examples of low molecular weight spectra in which all the peaks are well resolved and they show the same absorptions described in Section 5.1.1 for PTP₁ and free propylene glycol together with the polymer products of these two reactions, (PTP₁:1 PG: 1F) and (1 PTP₁:2 PG: 1F) respectively. The fumarate absorptions showed a number of peaks in Figures 5.16 and 5.17 which were the result of the different chemical environments in which they existed.

Generally, these spectra indicate no isomerization of fumarate to maleate. The comparison of the integrals for aromatic protons to those of the unsaturated components did not show any considerable loss of double bonds in these systems.

The ratios of the type of segments formed are estimated from a direct comparison of the integrals of the methine protons absorptions in each spectrum. The spectrum drawn for the reaction of propylene glycol with fumaric acid in Figure 5.18, showed the same peaks observed in spectrum 5.9 (1 PG: 1M) for the methine absorptions. These are the secondary terminal propylene glycol methine protons at 5.1 - 5.2 ppm and the -MPM-methine protons at 5.3 ppm.

The types of segments formed are listed in Table 5.4.

TABLE 5.4

Distribution of segments in the products of PG/PTP₁/F systems

	Molar Ratios			% of segments formed		
	PG	F	PTP	-FPF-	-FPT-	-TPT-
F	0	1	1	13.6	71.6	14.8
G	$\frac{1}{2}$	1	$\frac{1}{2}$	40	48.9	11.1
H	1	1	1	30.2	62.8	7
I	2	1	1	35.2	57.4	7.4

When Table 5.4 is compared with Table 5.3 (table for PTP/M systems) the data in Table 5.4 suggested a similarity in the reaction mechanisms of PTP₁ with M and F. However, with the exception of experiment (G), Table 5.4 showed a slight decrease in the ratio of -FPF- as compared to the ratio of -MPM- in the PTP₁/M experiments. This could either suggest a slower reaction between the fumaric acid and propylene glycol, or it could be the result of further ester-interchange reactions, which mixed the initial products more thoroughly and hence increased the -FPT- ratio due to the high temperature at which PTP₁/F experiments were carried out. It may be of interest to notice that the ratios of -TPT- segments were approximately the same in both systems for similar molar ratios except in experiment (B) Table 5.3 and (G) Table 5.4. The results shown for experiment (G) suggest that the structures containing -FPF- segments are less reactive than those containing -MPM- segments. This could be the reason for the approximately equal distribution of -FPF- and -FPT- together with a relatively high ratio for -TPT- segments.

5.2 P(TP)_n Polymerizations with Maleic Anhydride and Fumaric Acid

Three molar ratios were chosen to compare the Impolex T400B P(TP)_n systems, i.e. P(TP)_n/M and P(TP)_n/F, to those of PTP₁. These were (1 P(TP)_n: 1 M/F), ($\frac{1}{2}$ P(TP)_n:1 M/F; $\frac{1}{2}$ PG), and (1 P(TP)_n:1 M/F; 2 PG). The original Impolex T400B prepolymer is a mixture of P(TP)_n and free propylene glycol. This was due to the fact that the prepoly-

mer was initially prepared by ICI under high temperature and pressure. The vigorous reaction conditions as well as the subsequent water distillation step involved in the process led to the loss of a certain amount of propylene glycol. In order to compensate for the losses an additional amount of propylene glycol was added. The amount of the free propylene glycol in the prepolymer was determined from 90 MHz NMR spectra. The results obtained were in good agreement with the values reported by Kyriacos for the amount of free propylene glycol in this prepolymer (8.6% by weight). In the molar ratios where free propylene glycol was included in the reaction mixture, further propylene glycol was added to the amount of free propylene glycol present in the original prepolymer in order to reach the required ratio. In the case of the molar ratio of $(1 \text{ P(TP)}_n : 1 \text{ M/F})$ a product of heating PTP_1 for 5 hours at 150°C (molecular weight 355.5) was used for the P(TP)_n prepolymer (molecular weight 359.5). No further propylene glycol was added in this case.

The reaction conditions for $\text{P(TP)}_n/\text{M}$ and $\text{P(TP)}_n/\text{F}$ systems were the same as those used for PTP_1/M and PTP_1/F respectively. The products of both systems were analysed by single column GPC and 300 MHz NMR spectrometer, see Figures 5.19-5.30.

GPC Analysis

In Figure 5.19 the chromatogram obtained for the molar ratio $1 \text{ P(TP)}_n : 1 \text{ M}$ showed a higher rate of conversion to high molecular weight products (at elution volumes 42-66 ml) together with the presence of smaller proportions of much lower molecular weight species appearing at higher elution volumes e.g. 123 ml. There is a clear difference between the molecular weight distribution shown in this chromatogram (Figure 5.19) and that shown for $1 \text{ PTP}_1 : 1 \text{ M}$ in Figure 5.1, which displayed a succession of increasing molecular weight products. It could be suggested that the difference was because of the presence of higher molecular weight homologues in P(TP)_n which could form relatively high molecular weight molecules in the first reactions with maleic anhydride. This was manifested in the elution of most of the product under a large GPC peak at the end of the high molecular weight region beyond the exclusion limit at (V_r) 42 ml). The chromatogram obtained for the

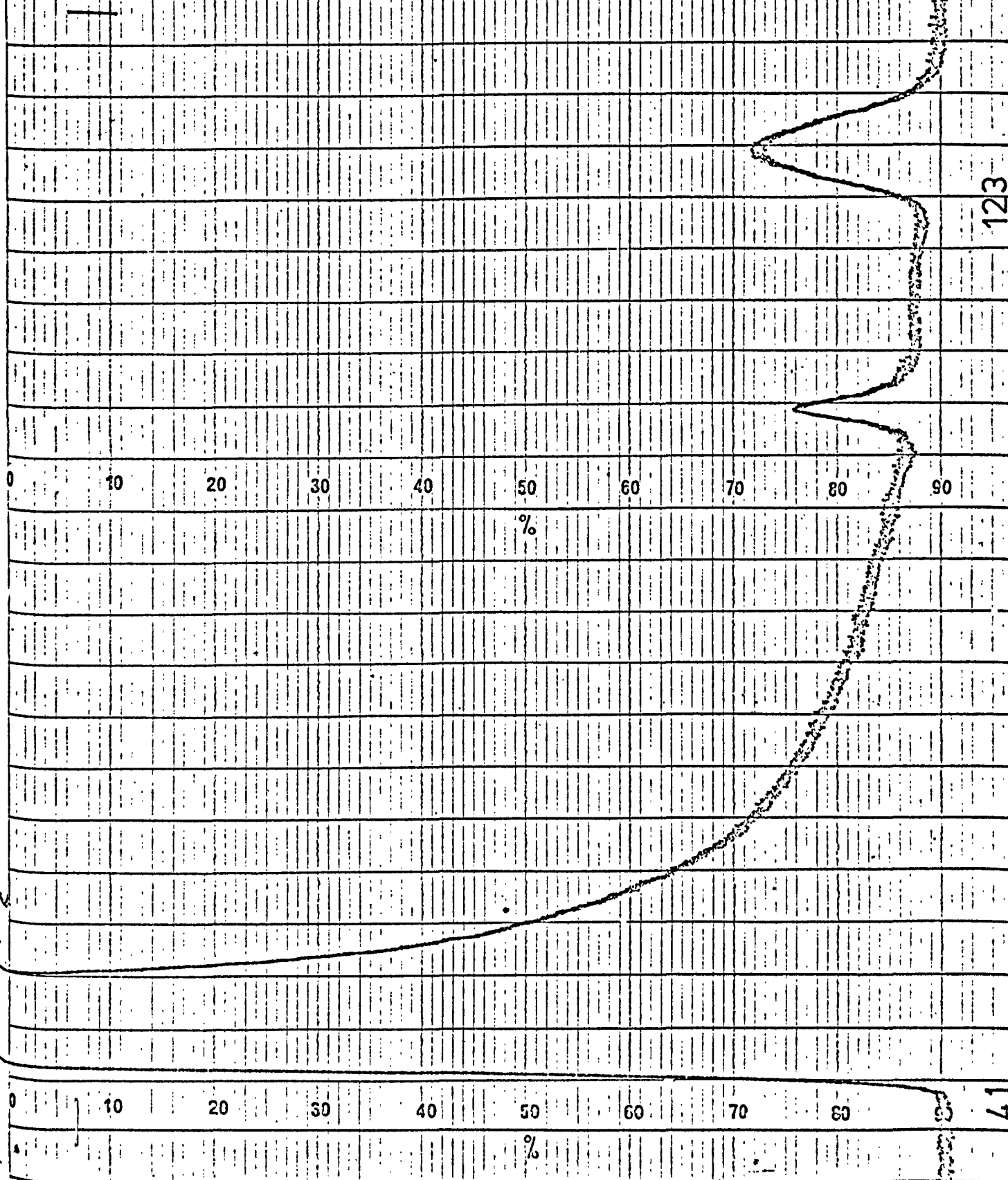


FIGURE 5.19
GPC Chromatogram of
(IP(IP)_n: 1M)/1500C
5 hours

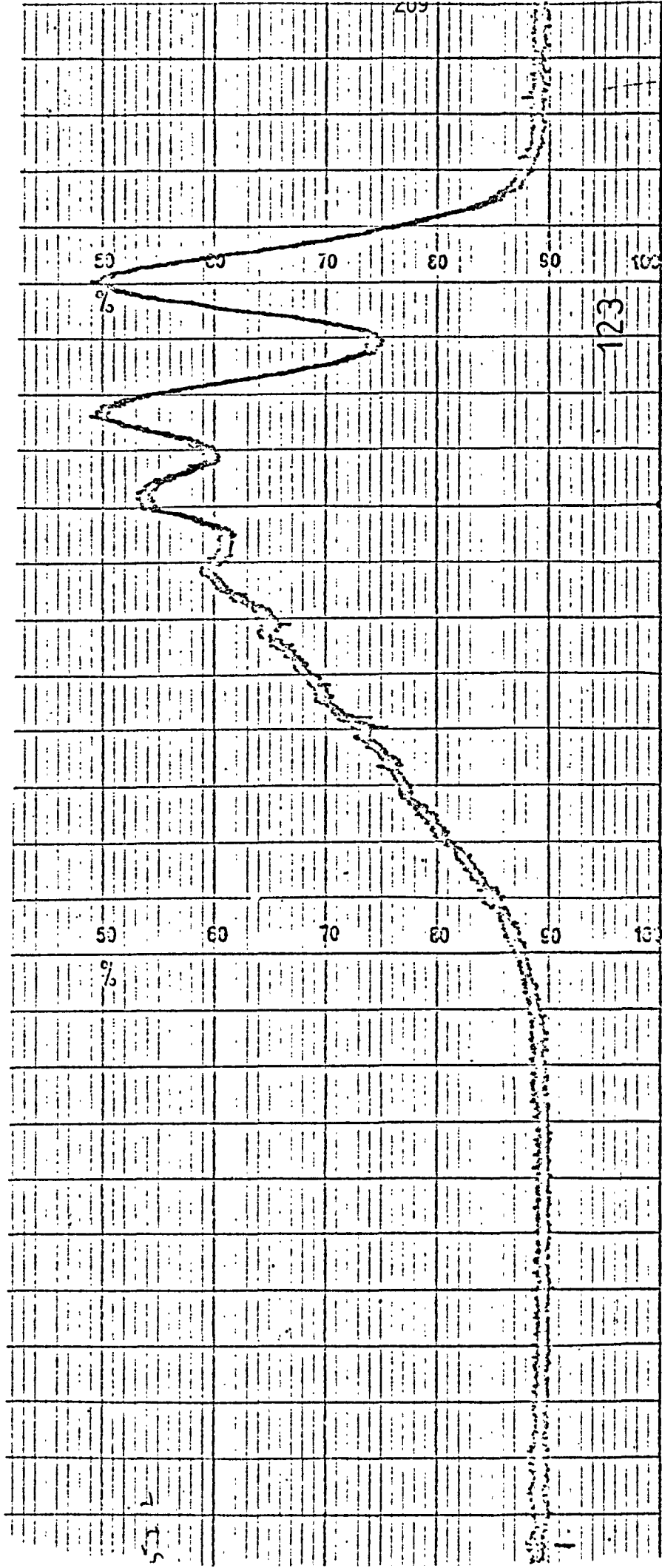


FIGURE 5.20 GPC Chromatogram of (1/2 PG: 1/2 P(TP)_n: 1M)/150°C, 5 hours

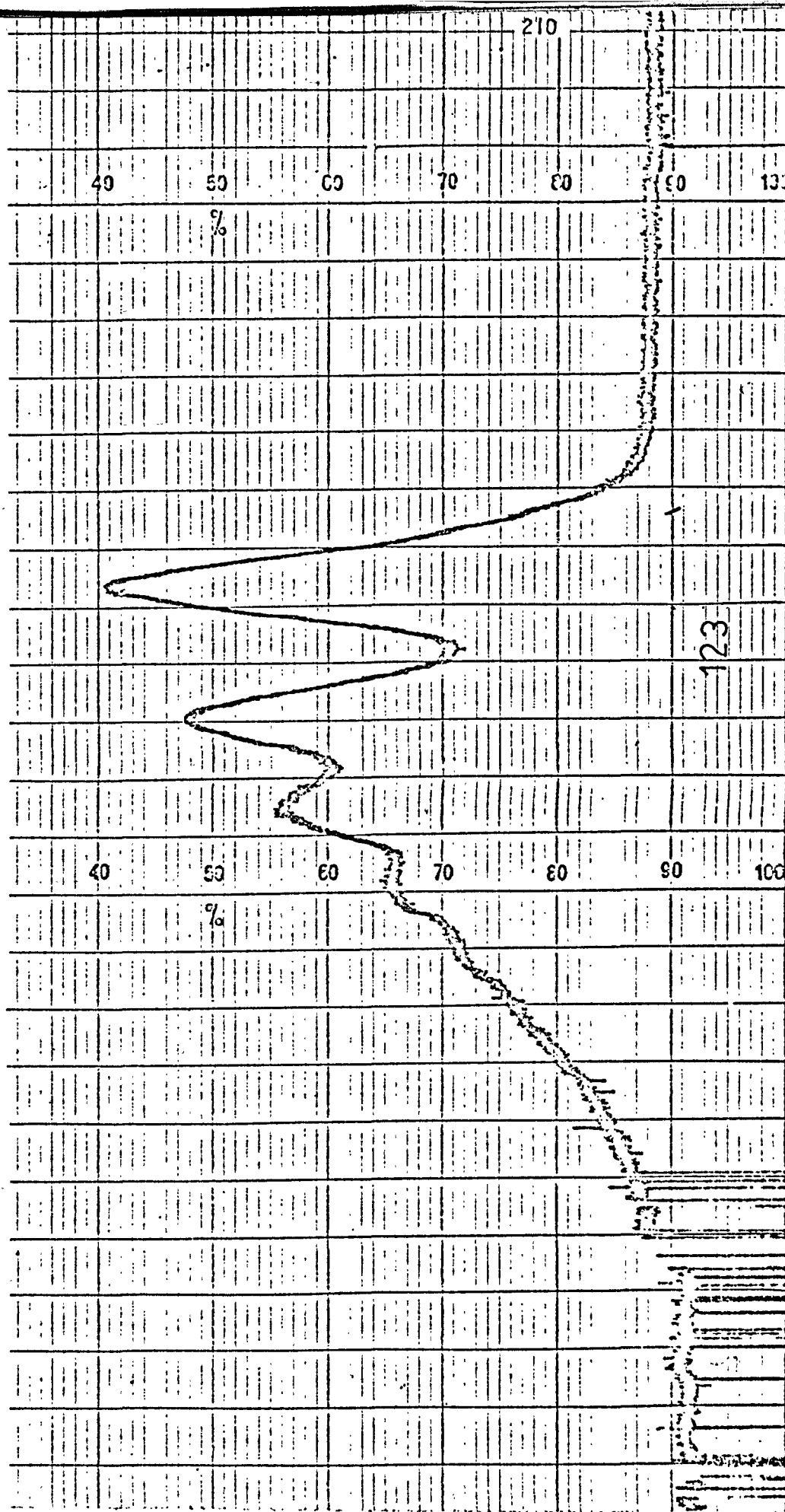


FIGURE 5.21 GPC Chromatogram of (2 PG: 1 P(TP)_n: 1M)/150°C, 5 hours

5.2.3

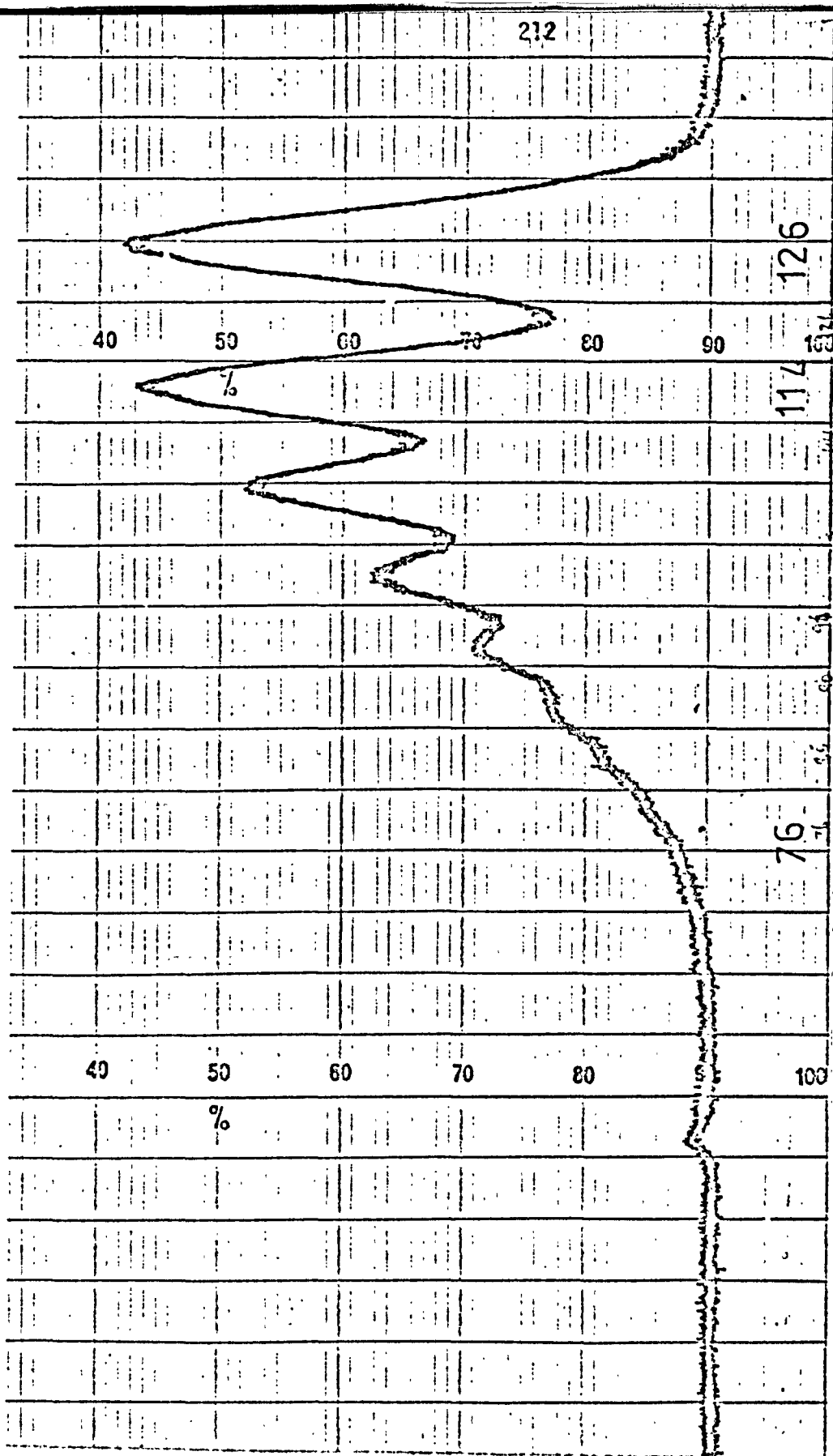


FIGURE 5.23 GPC Chromatogram of (1/2 PG: 1/2 P(TP)_n): 1F/180°C, 5 hours

5-2.5

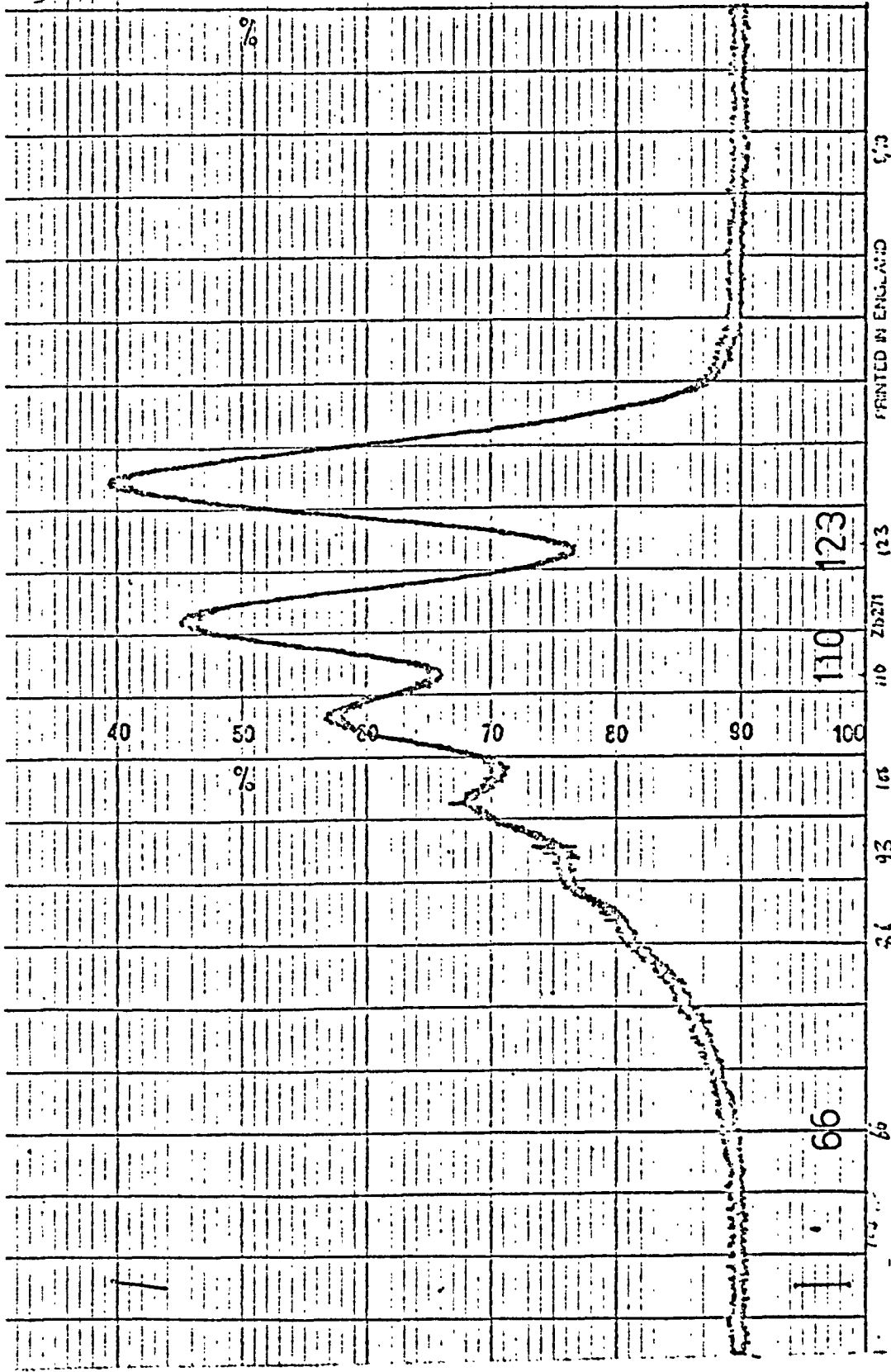


FIGURE 5.24 GPC Chromatogram of (2 PG: 1 P(TP)_n: 1F)/180°C, 5 hours

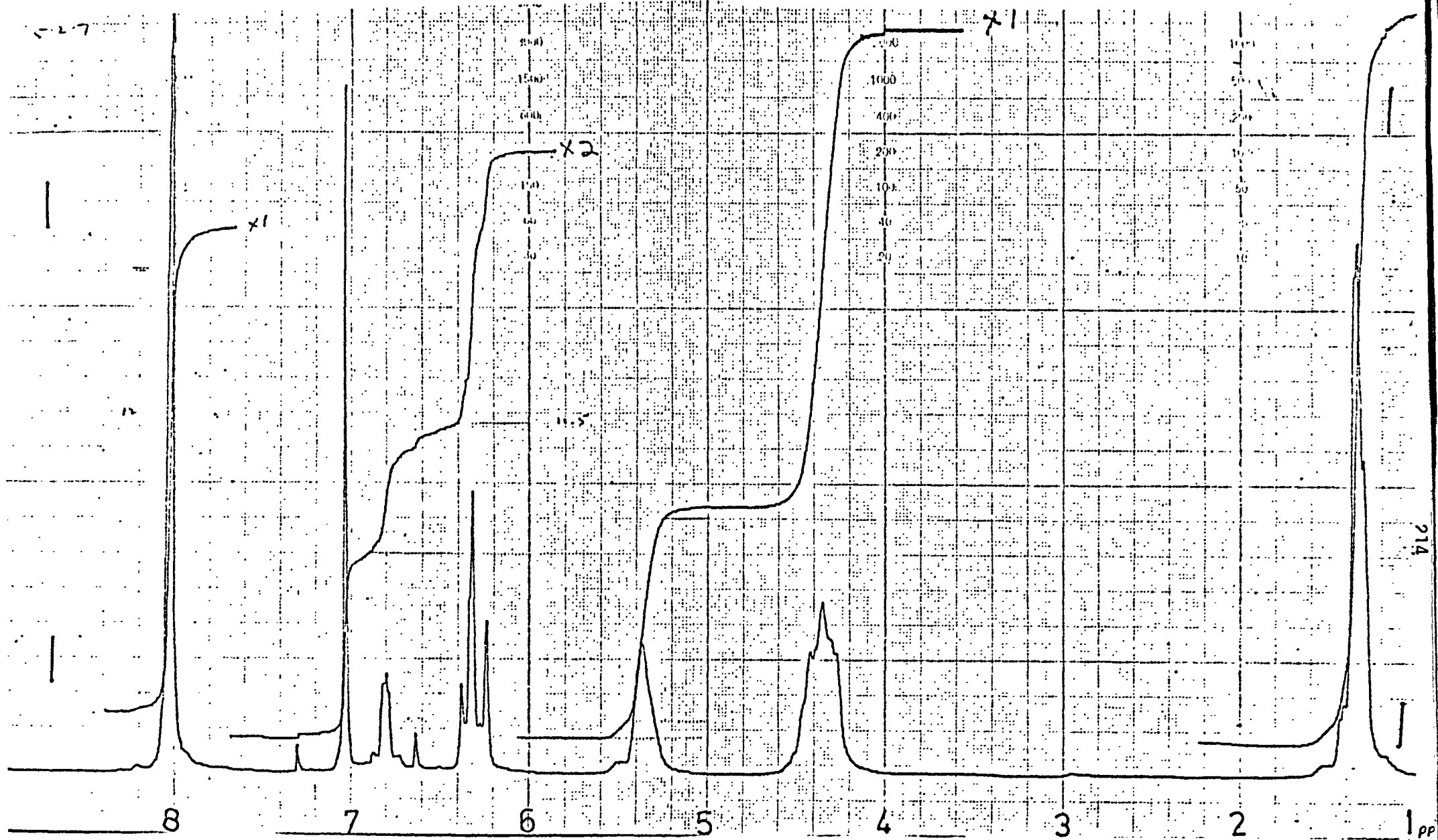


FIGURE 5.25 300 MHz NMR Spectrum of (1 P(TP)_n: 1M)/150°C, 5 hours

experiment corresponding to (G), in Table 5.4, which appears in Figure 5.20, shows a greater concentration of low molecular weight species and a considerable enhancement of the last peak appearing at elution volume 123ml. It could be mentioned that the sizes of molecules produced in this reaction were much smaller than those obtained in experiment (F). This might suggest a greater difference in reactivity between $P(TP)_n$ and (P) in the reaction with maleic anhydride. Figure 5.21 which shows the chromatogram of the experiment corresponding to (H), Table 5.4, is a further illustration for the production of low molecular weight species in experiments containing free propylene glycol in the $P(TP)_n/M$ systems. Although $P(TP)_n$ produced higher molecular weights in the reaction with (M) than PTP_1 this conclusion could be reversed when the other molar ratios are considered.

In the molar ratio ($\frac{1}{2} P(TP)_n$: 1M; $\frac{1}{2}$ PG), Figure 5.20, a greater portion of the product was eluted at the lower molecular weight region if compared to that shown for the similar molar ratio in PTP_1/M systems in Figure 5.2. The same observation could be noticed from Figures 5.21 and 5.4 showing the chromatogram for the product of experiment (D). This could be taken as an indication that $P(TP)_n$ was less reactive than PTP_1 in formulations containing free propylene glycol.

The chromatograms drawn for $1P(TP)_n:1F$ in Figure 5.22 and $1PTP_1:1F$ in Figure 5.10 gave the same difference in the molecular weight distribution described for the similar molar ratios with maleic anhydride. The other molar ratios (Figures 5.23 and 5.24) also displayed the same differences mentioned for the systems containing maleic anhydride and propylene glycol. They also exhibited the same drop in molecular weight when moving from $1P(TP)_n:1F$ to the other molar ratios. However $P(TP)_n$ seemed to produce higher molecular weight species with (F) at 180°C than with (M) at 150°C as noticed for PTP_1 .

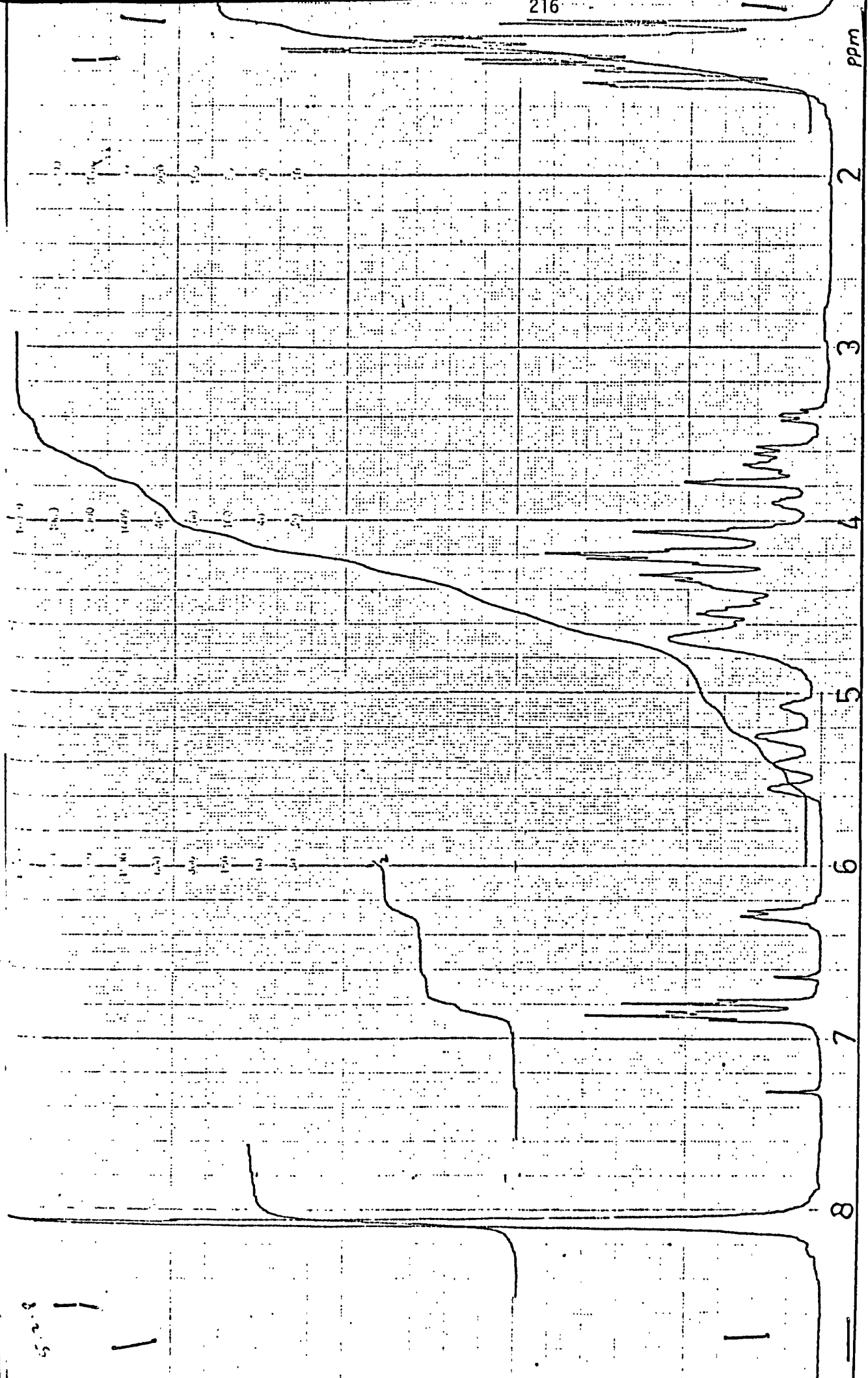


FIGURE 5.26 300 MHz NMR Spectrum of $\frac{1}{2}$ PG: $\frac{1}{2}$ P(TP)_n: 1M/150°C. 5 hours

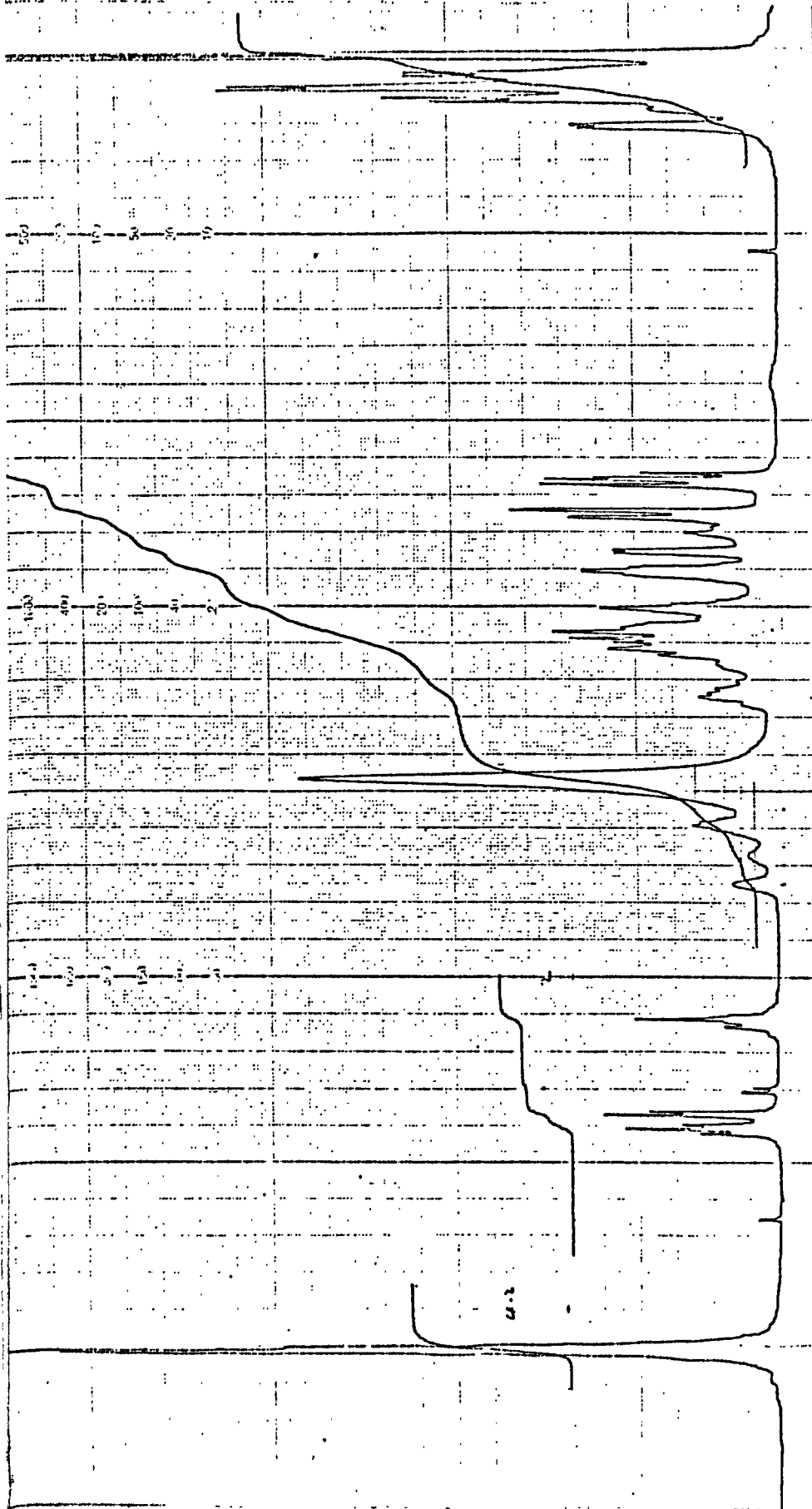


Figure 5.27 300 MHz NMR spectrum of (2PG: 1P(TP)_n: 1M)

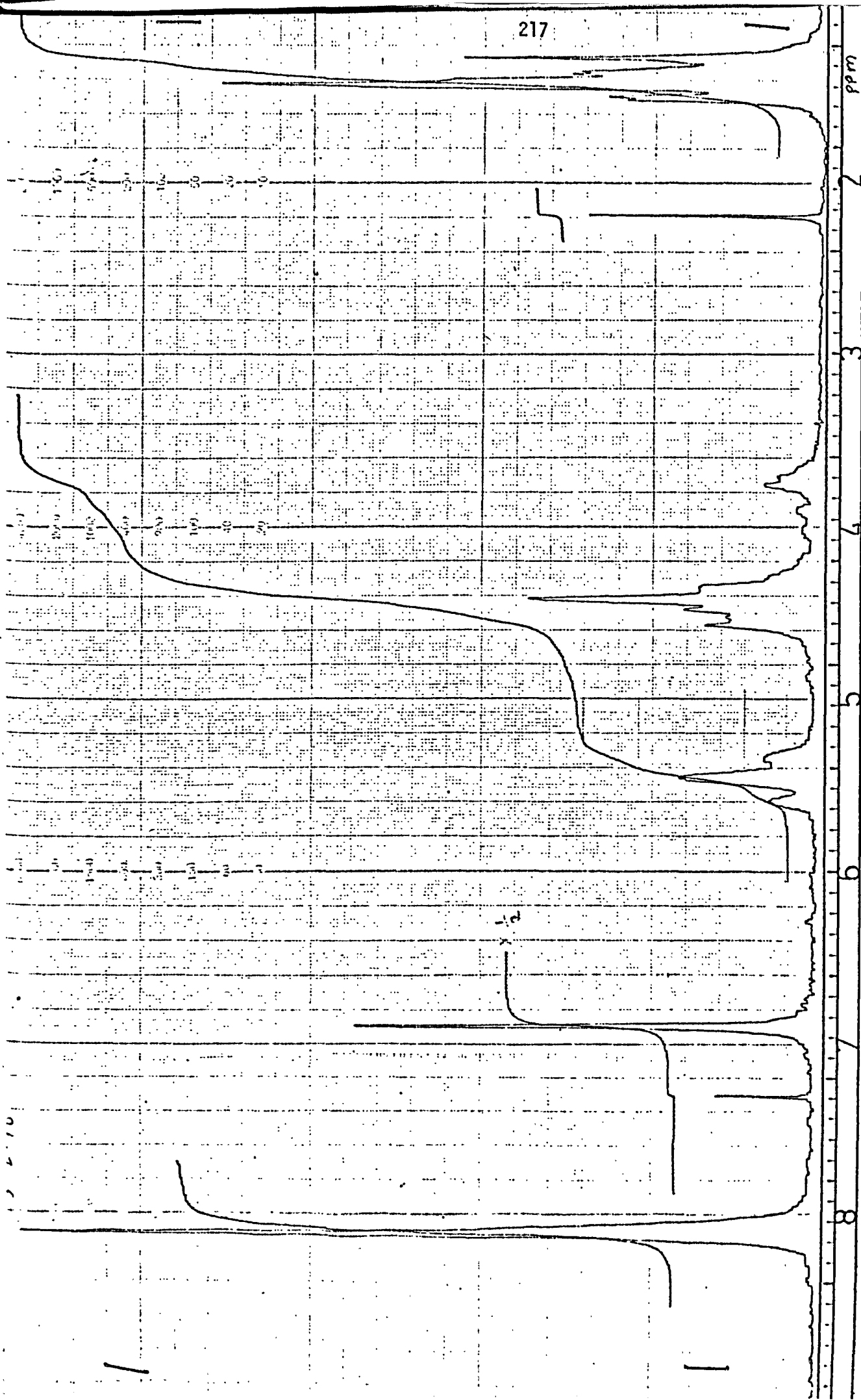


FIGURE 5.28 300 MHz NMR Spectrum of (IP(TP))_n : 1F/180°C, 5 hours

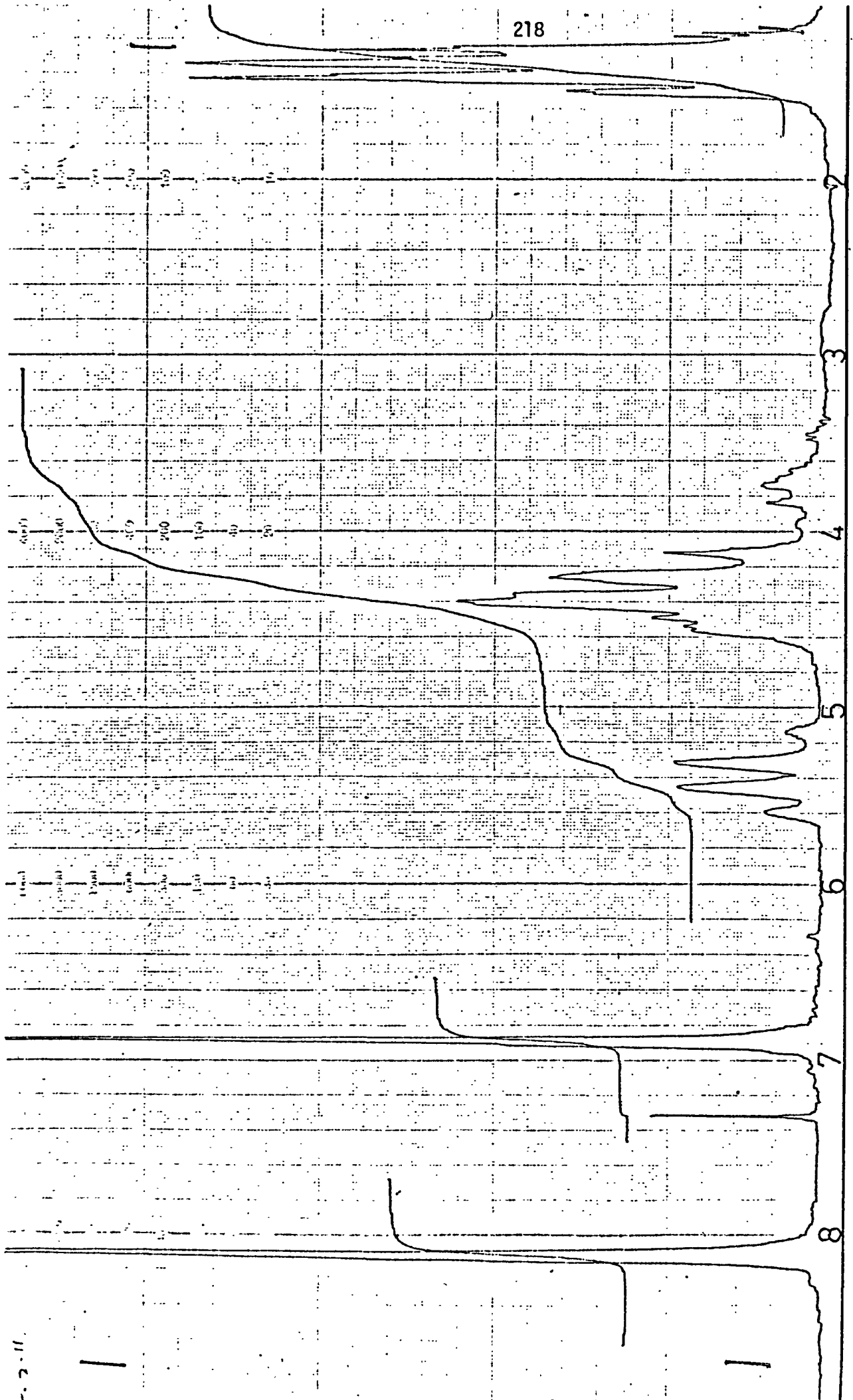


FIGURE 5.29 300 MHz NMR Spectrum of (1PG : 1/2P(TP))_n 1F/180°C, 5 hours

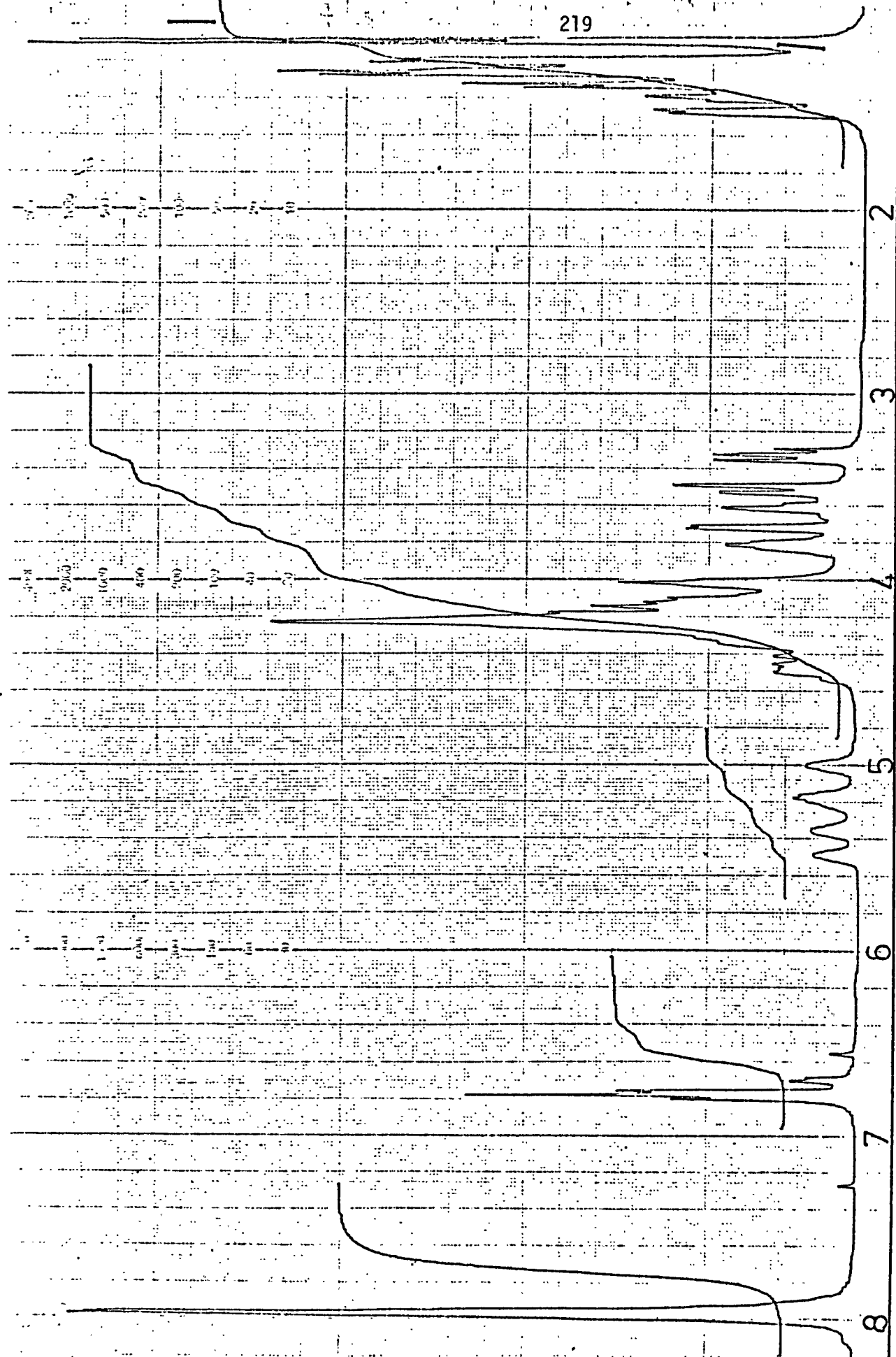


FIGURE 5.30 300 MHz NMR Spectrum of (2PG : 1P(IP)_n)_n : 1F/180°C, 5 hours

NMR Analysis

The spectra obtained from a 300 MHz NMR spectrometer for $P(TP)_n/M$ systems are shown in Figures 5.25-5.27. The results calculated from these spectra are shown in Table 5.5. The spectrum obtained for the molar ratio (1 $P(TP)_n$:1M) is shown in Figure 5.25. The peaks representing the absorptions of protons in the propylene glycol ends in PTP_1 are not easily distinguishable from the base line in this spectrum. The peaks for methyl protons appear at 1.3-1.4 ppm with a small side peak at 1.5 ppm. The absorptions due to methylene protons did not show any peak at 3.7 ppm for the secondary terminal propylene glycol molecules in PTP_1 or at 4.15 ppm for its primary isomer, but they gave a large overlapped peak at 4.25-4.5 ppm. The absorptions exhibited in the methine region were at 5.4 ppm and 5.5 ppm. All these observations suggest that the product is composed mainly of high molecular weight species and the chemical shifts at which the peaks appear, especially in the methine region, are characteristic of the (-TPM-) segment environment. It could also be noticed from the spectrum that the peaks at the maleate and fumarate chemical shifts (6.3 ppm and 6.8 ppm respectively) suggest a greater proportion of maleates.

The spectrum of the product of the molar ratio ($\frac{1}{2} P(TP)_n$: $\frac{1}{2} PG$:1M) is shown in Figure 5.26. This spectrum is different from the previous spectrum (in Figure 5.25) in the appearance of more peaks representing the proton groups of PTP_1 and free propylene glycol. This is clearly shown in the methyl region absorptions at (1.1-1.3 ppm), the methylene region (absorptions in the range 3.4 ppm to 4.2 ppm) and the methine region (absorptions in the range 5.0 - 5.15 ppm). Another difference is that the chemical shifts of the absorption of methine protons are characteristic of the segment types (-MPM-) at 5.2-5.3 ppm, (-MPT-) at 5.4 ppm, and (-TPT-) at 5.5-5.58 ppm. It could also be shown that the peak for methyl protons at 1.5 ppm is much larger than the corresponding one in Figure 5.25. The spectrum of the molar ratio (2 PG: 1 $P(TP)_n$:1M), in Figure 5.27, shows the same characteristics of the spectrum of Figure 5.26, but it is different in that the methine protons absorptions showed greater enhancement of the (-MPM-)

type of segment and a decrease in the (-MPT-) type. Figures 5.26 and 5.27 are essentially spectra of low molecular weight species. However, the main differences between the spectra of $P(TP)_n/F$ systems, in Figures 5.27-5.29, and $P(TP)_n/M$ systems can best be shown in the absorption region of methine protons (5.0-5.6 ppm). The presence of a peak at 5.3 ppm in Figure 5.28 indicates the presence of the (-FPF-) type of segments in the product of (1 $P(TP)_n$:1F) molar ratio, which is missing in the corresponding molar ratio in the $P(TP)_n/M$ reaction product. Another difference in this region could be seen for the relatively larger peak representing (-FPF-) segments in the ($\frac{1}{2}$ $P(TP)_n$: $\frac{1}{2}$ PG:1F) molar ratio (Figure 5.29) than the corresponding peak for the same molar ratio in the maleic system. The products of these systems showed very little losses in double bonds which are very close to the experimental error. However the maleate/fumarate conversion rates in $P(TP)_n/M$ systems were of lower values than those reached in PTP_1/M experiments especially in the 1:1 molar ratio of the prepolymer and maleic anhydride. The types of segments formed estimated from the spectra, Figures 5.25-5.30, are also listed in Table 5.5.

TABLE 5.5
NMR data for $P(TP)_n$ reactions with (M) and (F)

Molar ratios			System	% of Segments			F:M %		Loss of double bonds %
PG	M/F	$P(TP)_n$		-FPF- -MPM-	-FPT- -MPT-	-TPT-	F	M	
0	1	1	M	-	92	8	33	67	4
$\frac{1}{2}$	1	$\frac{1}{2}$	M	34	30	36	74	26	-
2	1	1	M	47	30	23	70	30	4.4
0	1	1	F	26	52	21	100	-	-
$\frac{1}{2}$	1	$\frac{1}{2}$	F	36.0	24.0	35	100	-	-
2	1	1	F	44	38	18	100	-	-

The molar ratio 1 P(TP)_n:1M produced a polymer constituted mainly from structures containing -TPM- segments which could be attributed to the type of prepolymer which experienced an ester-interchange and polycondensation reaction before its polymerization with maleic anhydride. This might suggest the reaction mixture favoured a direct reaction between maleic anhydride and the higher homologues in P(TP)_n. It is also of interest to notice that in the molar ratios containing free propylene glycol the fractions of -TPM- segments were considerably lower than those produced by PTP₁ systems. But the values estimated in all the PTP₁ and P(TP)_n systems for -MPM- segments was very close in each particular molar ratio. This may lead to the assumption that the reaction of (M) with (P) was dominant and was not affected by the type of the prepolymer in question.

5.3 PIP₁ Polymerization with Maleic Anhydride and Fumaric Acid

Three molar ratios were chosen for the reaction of PIP₁ with maleic anhydride. These were: 1 PIP₁:1M, ½ PIP₁:1M:½ PG, and 1 PIP₁:1M:2 PG. These reactions were carried out under the same conditions described before for the prepolymer/maleic anhydride systems. The products of these reactions were analysed by a single GPC column and 300 MHz NMR spectrometer.

GPC Analysis

The GPC results are shown in Figures 5.31-5.33. The chromatogram obtained for the molar ratio 1 PIP₁:1M shown in Figure 5.31 indicated that the reaction produced mainly low molecular weight molecules. This is illustrated by the presence of the considerable peaks at elution volumes 112 ml, 121 ml and the peak starting at elution volume 128 ml. However, it could also be noticed that the broad peak starting at elution volume 56 ml showed a short height of a steep rise which indicated that a small amount of the product sample was totally excluded i.e. of high molecular weight. Figure 5.32 displays the GPC chromatogram of the product of the molar ratio (½ PG:½ PIP₁:1M). The chromatogram shows that all the sample components were within the separation

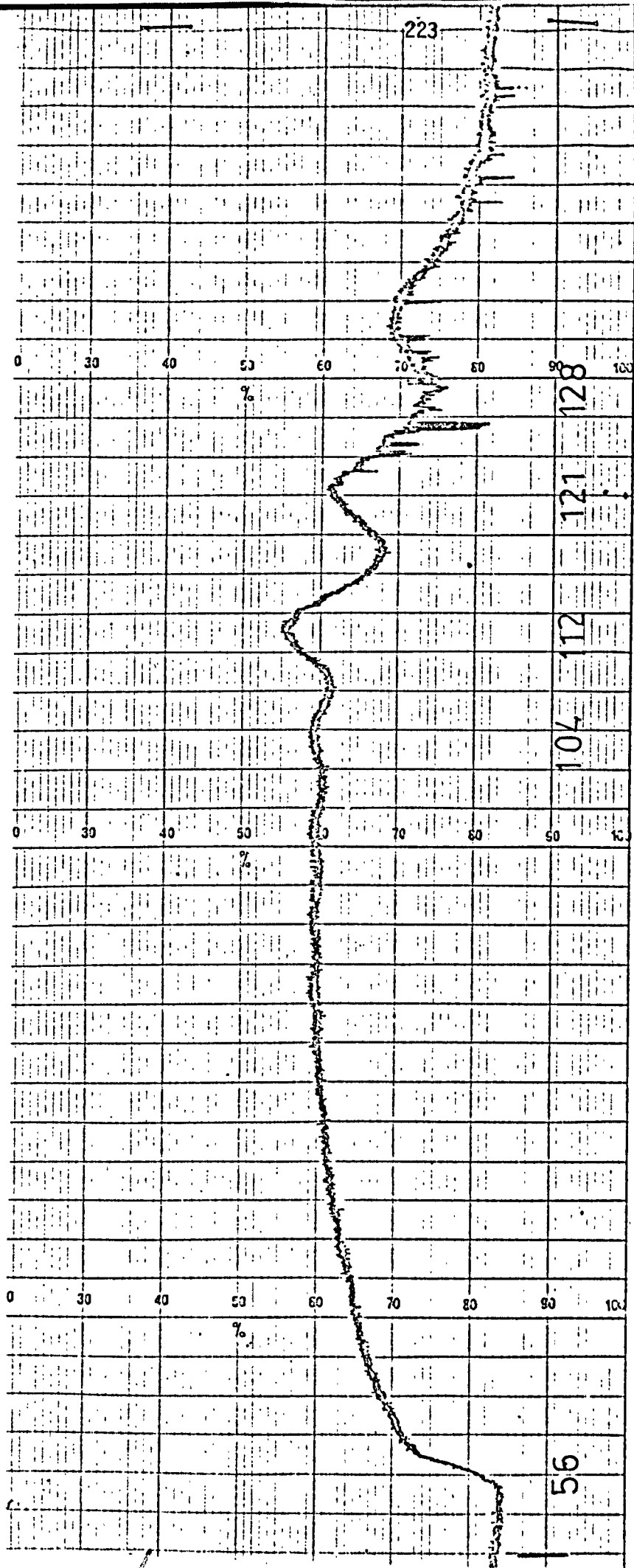


FIGURE 5.31 GPC Chromatogram of (1 PIP₁ : 1M)/150°C 5 hours

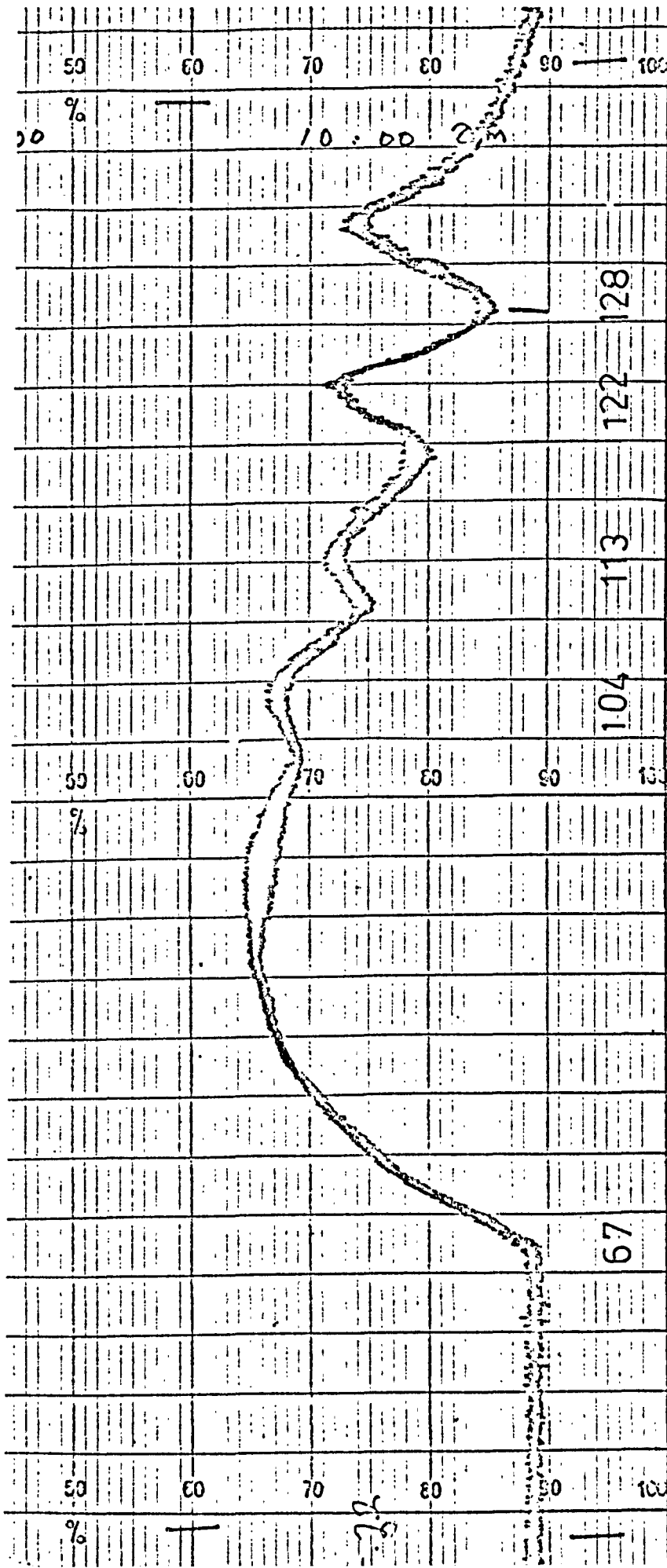


FIGURE 5.32 GPC Chromatogram of (1/2)PG : (1/2)PIP₁ : 1M/150°C, 5 hours

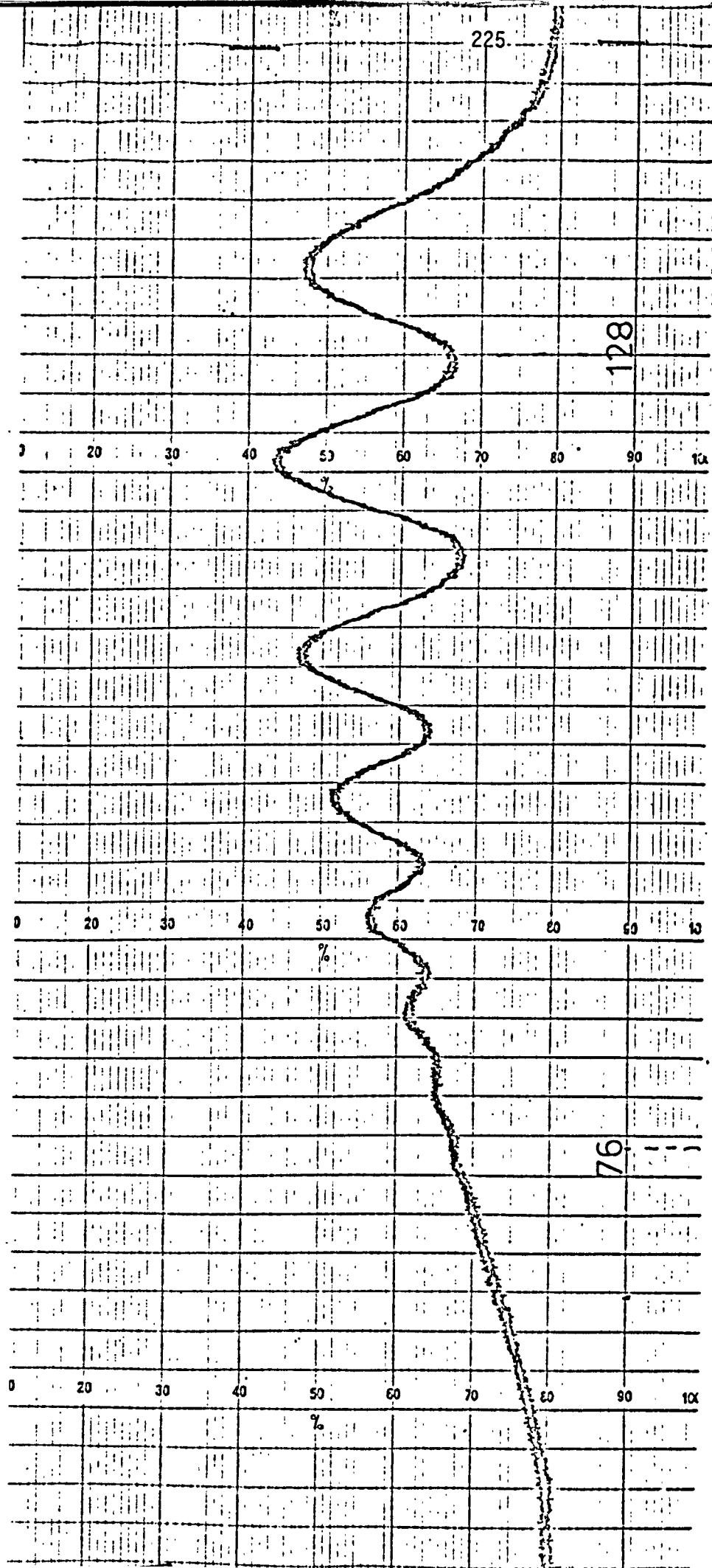


FIGURE 5.33 GPC Chromatogram (2PG : 1 PIP. : 1M)/150°C, 5 hours

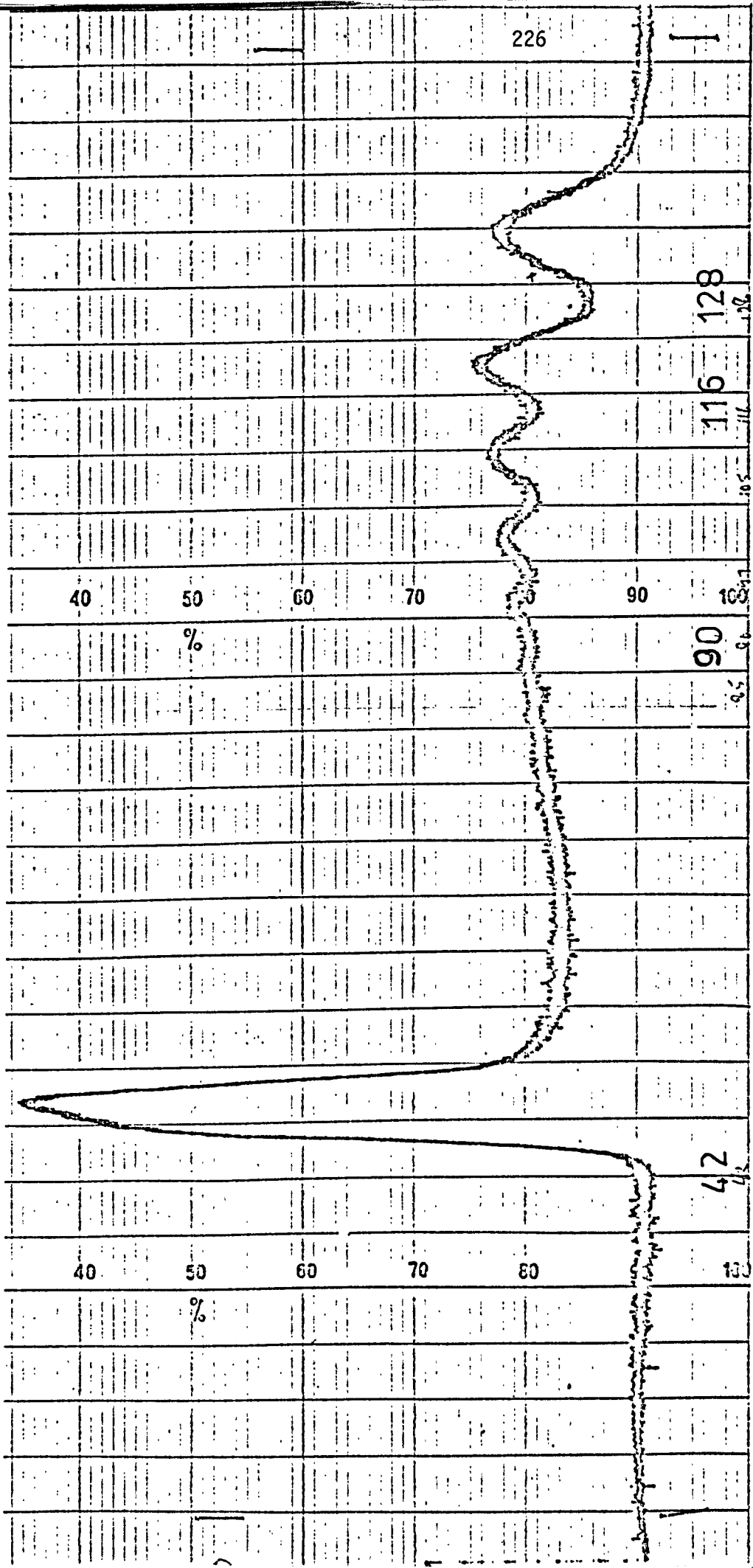


FIGURE 5.34 GPC Chromatogram (1 PIP : 1F)/180°C, 5 hours

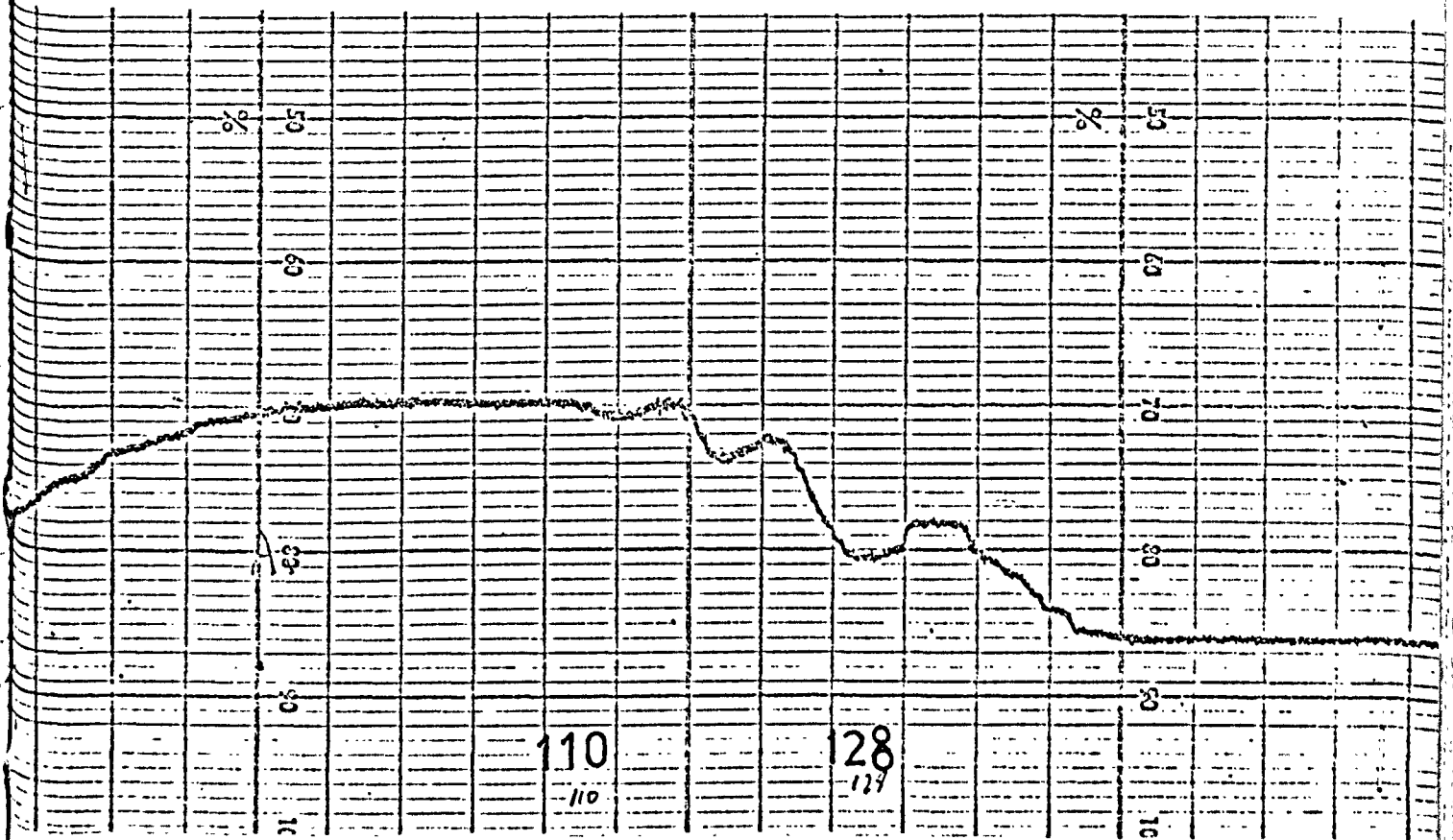


FIGURE 5.35 GPC Chromatogram of ($\frac{1}{2}$ PG: $\frac{1}{2}$ PIP: 1F)/180°C, 5 hours

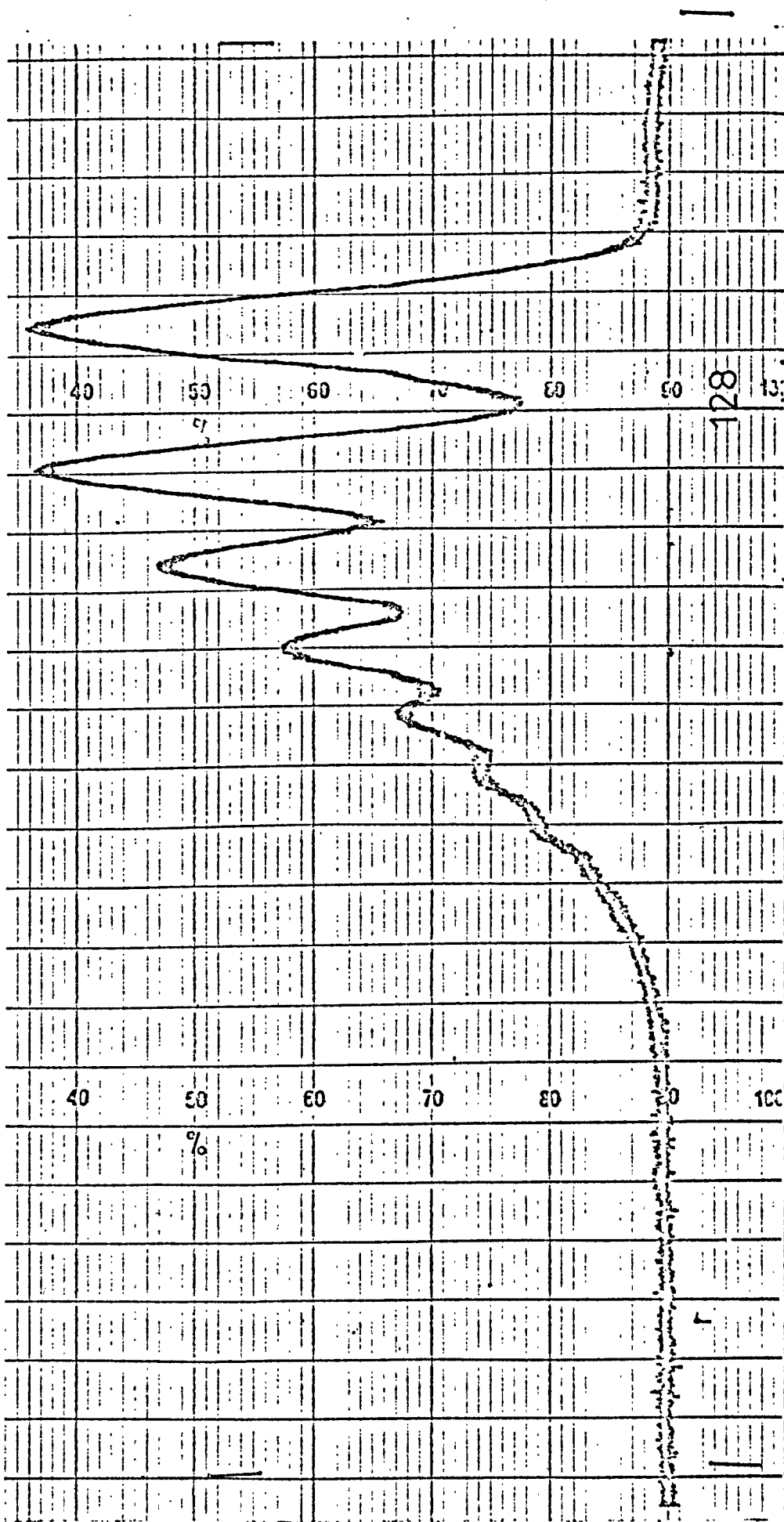


FIGURE 5.36 GPC Chromatogram of (2 PG: 1 PIP: 1F)/180°C, 5 hours

range of the GPC system. Most of the product came under the peaks which occur at the high elution volumes in the chromatogram, i.e. 104 ml, 113 ml, 122 ml and the last peak at 128 ml. Those peaks, appearing at elution volumes 104-128 ml, are more enhanced in Figure 5.31 than in Figure 5.30. The molar ratio (2 PG: 1 PIP: 1M) produced mainly low molecular weight products as demonstrated by the chromatogram in Figure 5.33 giving all the peaks at high elution volumes. A comparison between Figure 5.31 and Figure 5.1, the product of similar molar ratios in the PTP_1/M system, reflects the lower reactivity of PIP_1 prepolymers at $150^\circ C$, which was also observed earlier in Chapter 4. The fact that PTP_1 produced higher molecular weight species was not only shown in the 1 PTP_1 :1M molar ratio, but was also clearly demonstrated in the chromatograms of other molar ratios shown in Figures 5.32 and 5.33 for PIP_1/M systems and Figures 5.2 and 5.4 for PTP_1/M systems.

In PIP_1/F experiments the same molar ratios as PIP_1/M were used. The GPC results produced under the same conditions are shown in Figures 5.34-5.36. The chromatogram obtained for the product of the (1:1) molar ratio of PIP_1 and fumaric acid is shown in Figure 5.34. A great part of the product was totally excluded in the GPC separation as shown by the sharp rise at the beginning of the high peak at the elution volume 42 ml. In spite of this, 5 peaks can clearly be seen in the high elution volume region 90-128 ml. This shows the presence of low molecular weight components in the reaction products. The chromatogram in Figure 5.34, for the molar ratio ($\frac{1}{2}$ PIP_1 : $\frac{1}{2}$ PG:1F), suggests that the product of this reaction produced molecules of lower molecular weight which were all within the separation range of the GPC. The GPC result obtained for the last molar ratio (2 PG: 1 PIP_1 :1F) showed even lower molecular weights for the products of this reaction, i.e. all peaks were eluted at high elution volumes. These chromatograms showed that these systems are similar to PTP_1/F and $P(TP)_n/F$ systems in producing species of higher molecular weights than those formed by the maleic anhydride systems. This could be attributed to the higher temperature at which these experiments were performed. In comparison with PTP_1/F systems, PIP_1 was similar to $P(TP)_n$ in giving products of higher molecular weights with the fumaric acid, in the (1:1) molar ratio with fumaric acid, than PTP_1 . The same similarity was

noticed in forming products of lower molecular weights than PTP₁ in the other molar ratios. See Figures 5.35 and 5.36. It was mentioned before that P(TP)_n produced high molecular weight species with fumaric acid because of the nature of the prepolymer, being in the P(TP)_n form. The production of high molecular weight species in the reaction of PIP₁ with fumaric acid could be explained in terms of the greater reactivity exhibited by PIP₁ at 180°C, which was also observed in the fractionation experiments described in Chapter 4.

NMR Results for Short Time Products

The NMR analysis of the products of molar ratio 1 PIP₁:1M was compared to 1 PTP₁:1M in a series of other reactions carried out, under the same conditions described for the PIP/M systems, for short periods of time. From the NMR spectra, which are not shown in this text, the results were obtained using the same procedure described in Section 5.1 and followed throughout this chapter. These results can be seen in Table 5.6.

TABLE 5.6

NMR data for short time reactions of PIP/M and PTP/M

System	Time min.	Temper- ature °C	% of Segments			$\frac{f}{f+m}$ %
			-MPM-	-T/IPM-	-IPI- -TPT-	
PIP/M	30	150	17.3	76	6.7	3
"	60	150	18.8	74.6	6.6	10
"	90	150	19.8	73.6	6.6	20
"	90	180	15	71	14	51
PTP/M	30	150	22.2	77.8	0	2
"	60	150	21.1	76.3	2.6	13
"	90	150	20.5	75.7	3.8	24
"	90	180	13	73	14	43

Two conclusions can be drawn from Table 5.6. (1) PIP₁ appears to show lesser reactivity with M as compared with PTP₁ at 150°C. This is shown in the lower percentage of both -MPM- and -IPM- segments and the presence

of -IPI- segments in bigger quantities. At 180°C there is no significant difference between the two systems as far as the segments distribution. (2) The maleate/fumarate isomerization was at about the same rate at 150°C in the two systems, but a few per cent increase was shown in PIP₁/M systems at 180°C.

NMR Analysis

The NMR spectra for the experiments carried out for 5 hours, in the 3 molar ratios described before, are shown in Figures 5.37-5.42. The spectrum, in Figure 5.36, was drawn for the (1 PIP₁:1M) product. It shows the presence of three different environments as illustrated by the chemical shifts of the peaks in the methine region (5.2 ppm, 5.35-5.4 ppm, and 5.5 ppm). The phenyl protons are represented by three peaks at 7.5 ppm, 8.15 ppm, and 8.6 ppm. If this spectrum is compared to the spectrum obtained for the product of the molar ratio ($\frac{1}{2}$ PIP: $\frac{1}{2}$ PG:1M), in Figure 5.37, two differences can be noticed. The first one is the presence of absorptions representing free propylene glycol and PIP₁, i.e. absorptions at 1.1-1.15 ppm for methyl protons and absorptions at 3.5-4.1 ppm for methylene protons. The second difference is shown in the very small peak representing the maleate components at 6.3 ppm. The spectrum in Figure 5.38 (molar ratio 2 PG:1 PIP:1M) share the same characteristics of the spectrum obtained for the ($\frac{1}{2}$ PIP: $\frac{1}{2}$ PG:1M) molar ratio.

The spectra obtained for the PIP₁/F systems are shown in Figures 5.40, 5.41 and 5.42 for the products of the molar ratios (1 PIP:1F), ($\frac{1}{2}$ PIP: $\frac{1}{2}$ PG:1F), and (2 PG:1 PIP:1F) respectively. They generally show the same features described for the spectra of the corresponding molar ratio products in PIP₁/M systems except that the unsaturated component here is in the fumarate form absorbing at 6.8 ppm. No loss of double bonds was encountered in these experiments. The maleate/fumarate transformation was rather low in 1 PIP₁:1M molar ratio, but it was exceptionally high when propylene glycol was present in the reaction mixture, see Table 5.7.

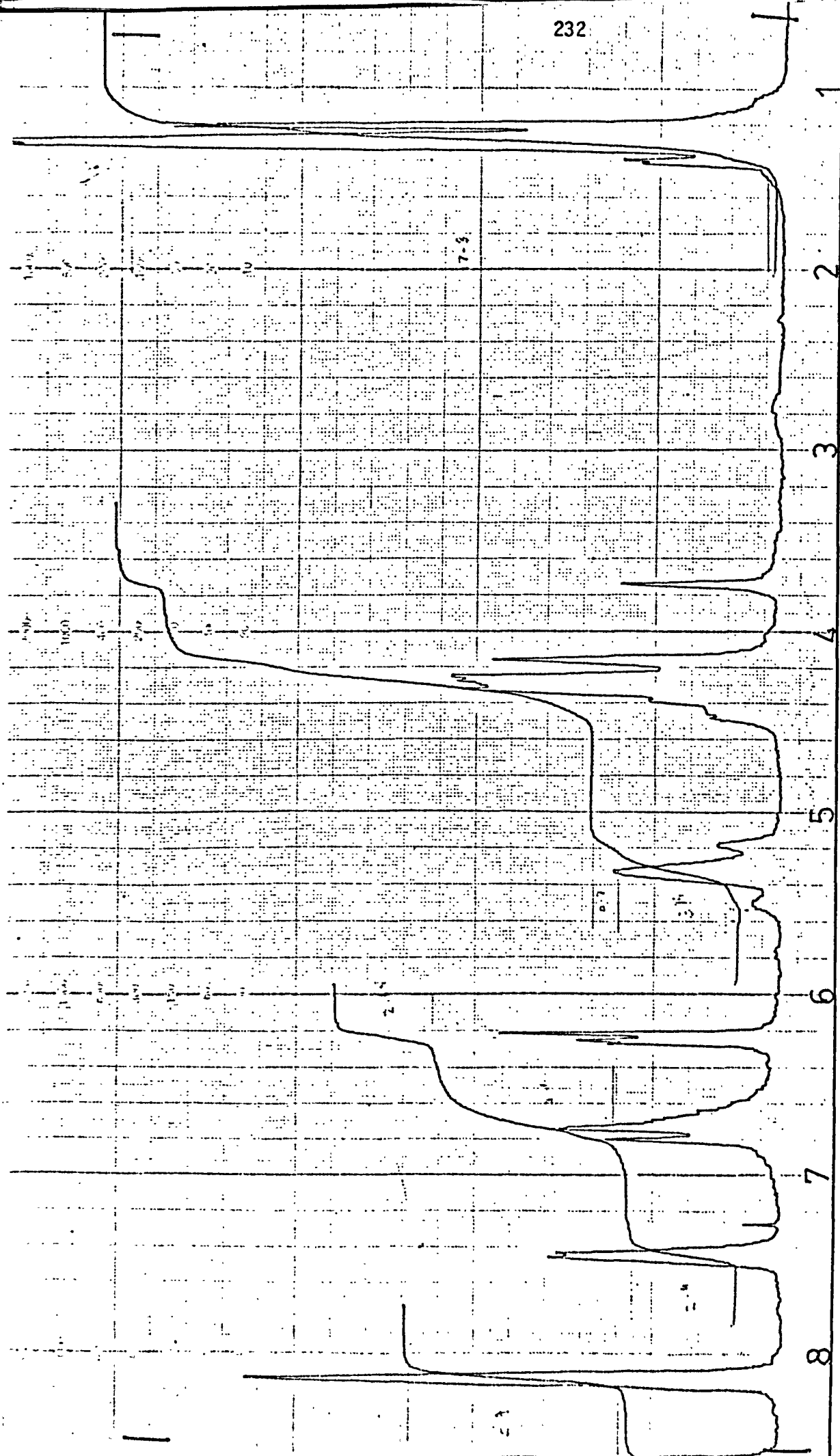


FIGURE 5.37 300 MHz NMR Spectrum of (1 PIP: 1M)/150°C, 5 hours

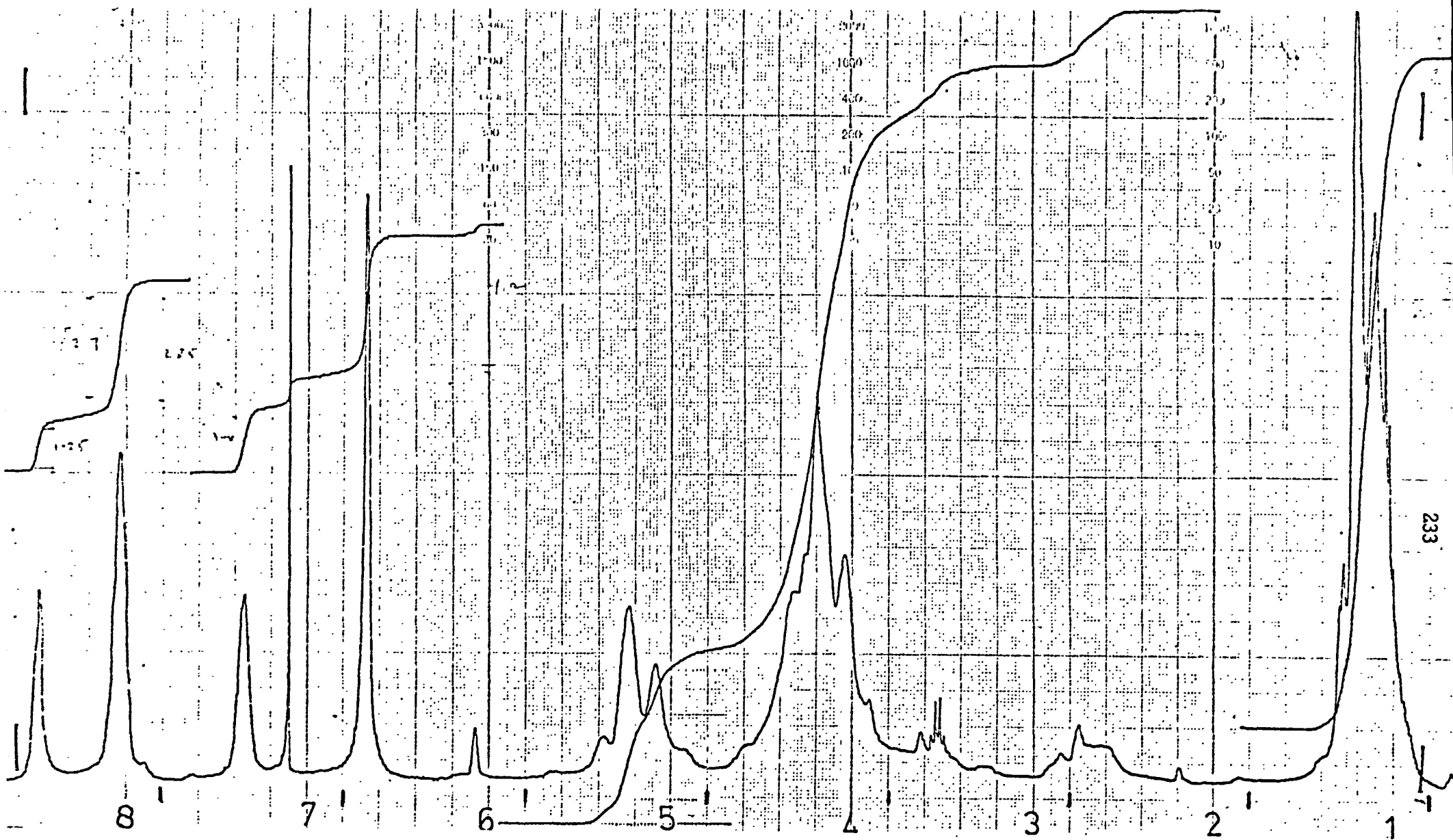


FIGURE 5.38 300 MHz NMR Spectrum of ($\frac{1}{2}$ PG: $\frac{1}{2}$ PIP: 1M)/150°C, 5 hours

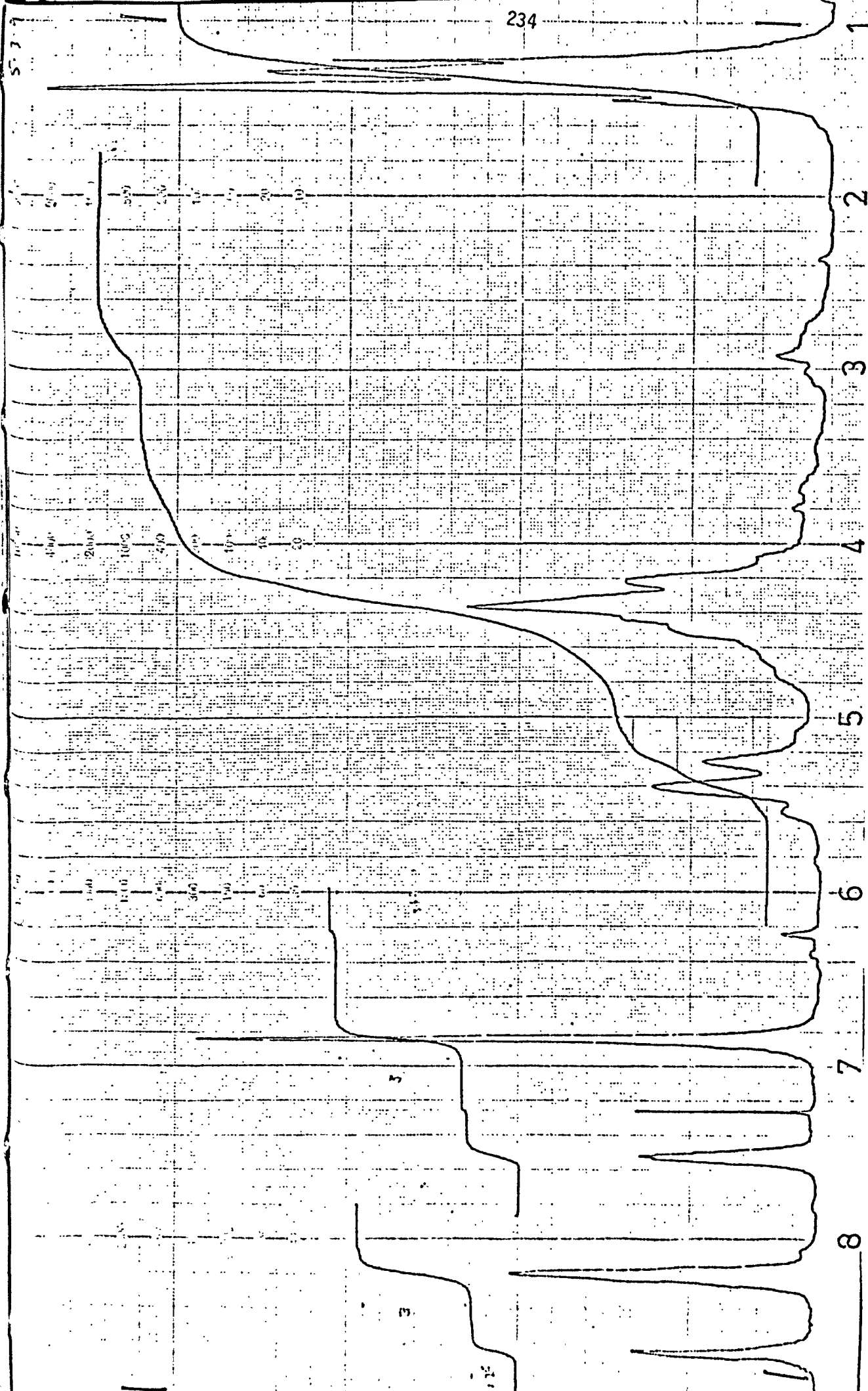


FIGURE 5.39 300 MHz NMR Spectrum of (2 PG: 1 P(IP)₁: 1M)/150°C, 5 hours
 FIGURE 5.40 300 MHz NMR spectrum of (1P)₁: 1P/100°C, 5 hours

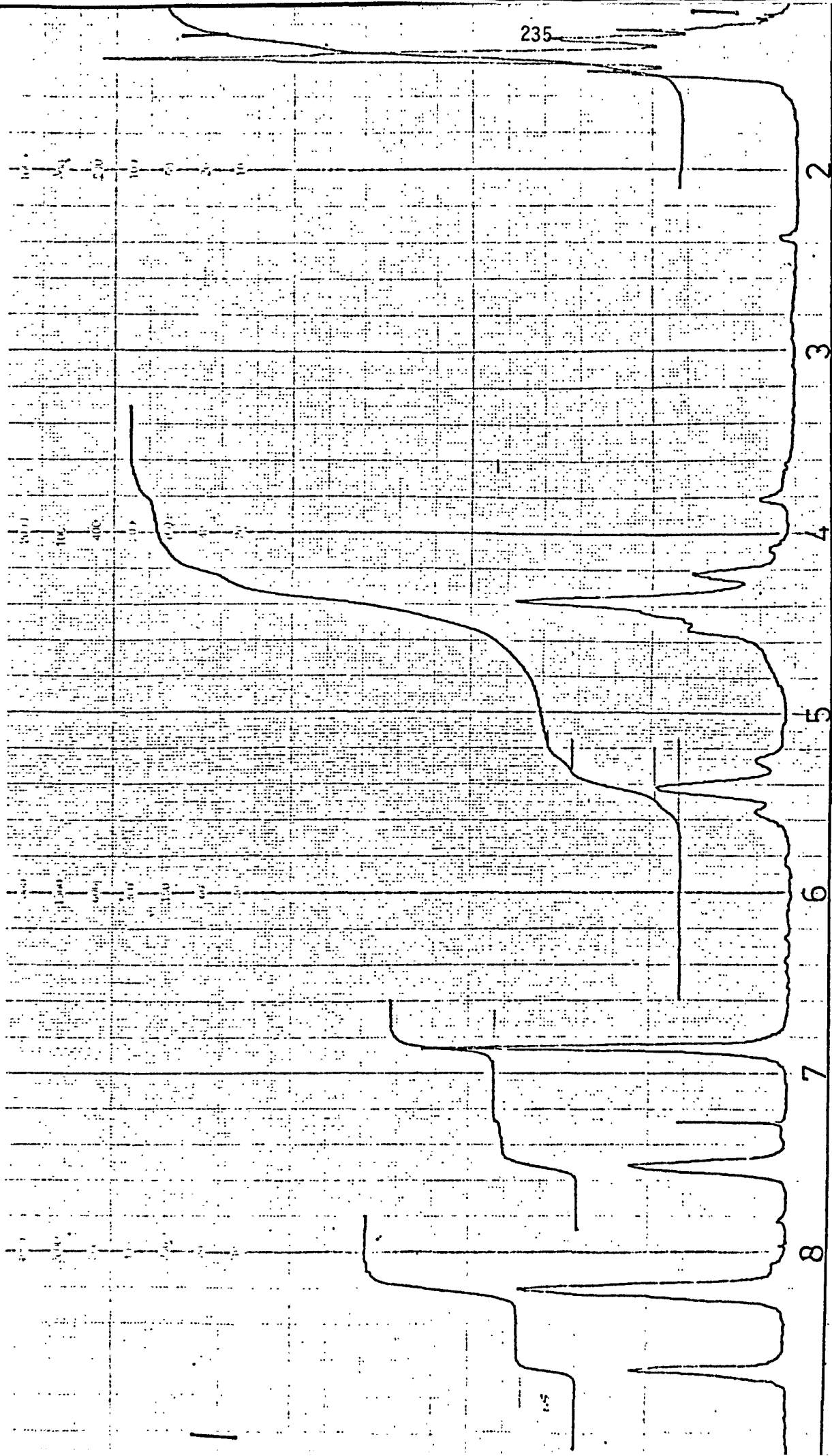


FIGURE 5.40 300 MHz NMR Spectrum of (PIP₁: 1F)/180°C, 5 hours

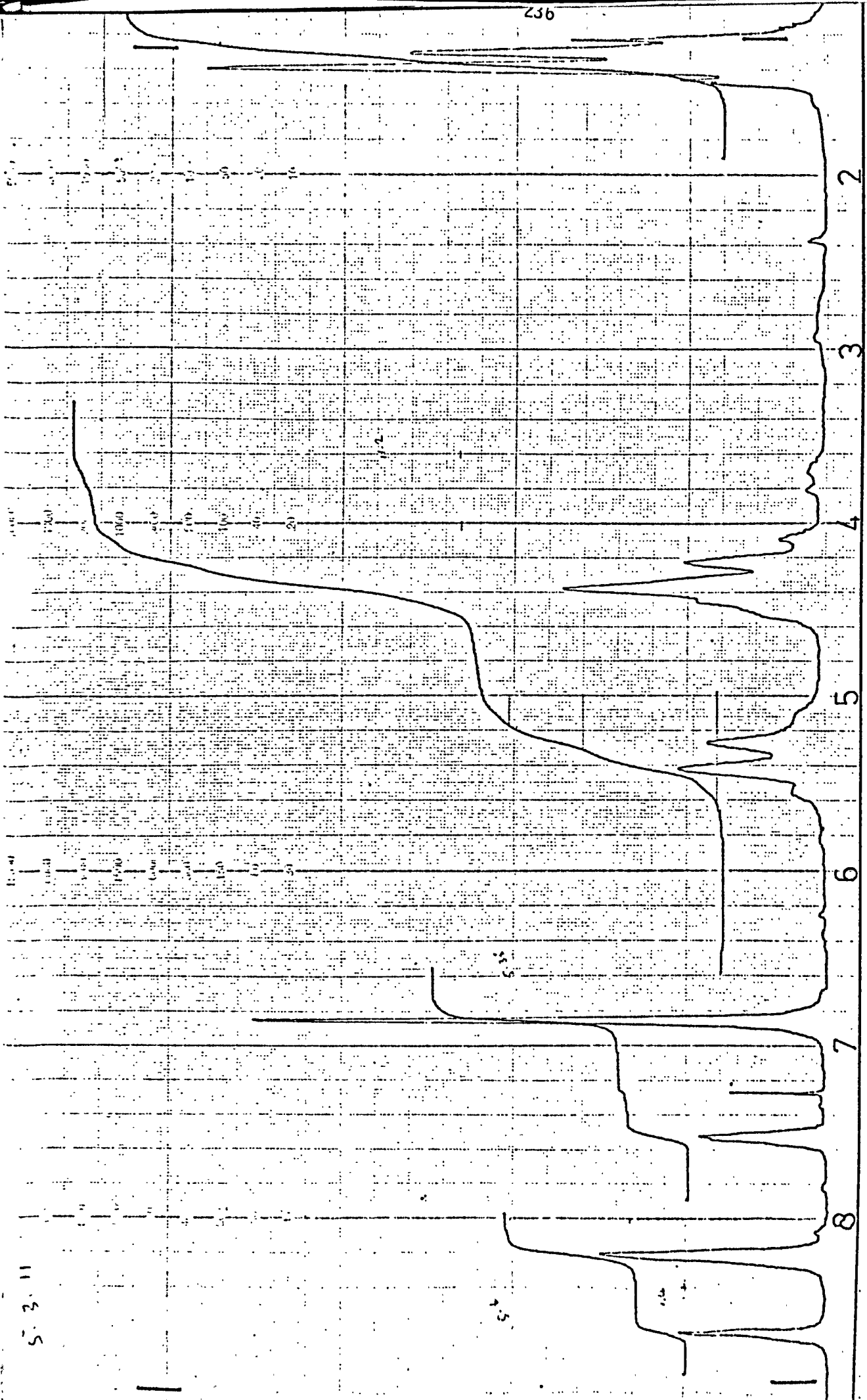


FIGURE 5.41 300 MHz NMR Spectrum of (1 PG; 1 PIP; 1F)/180°C, 5 hours

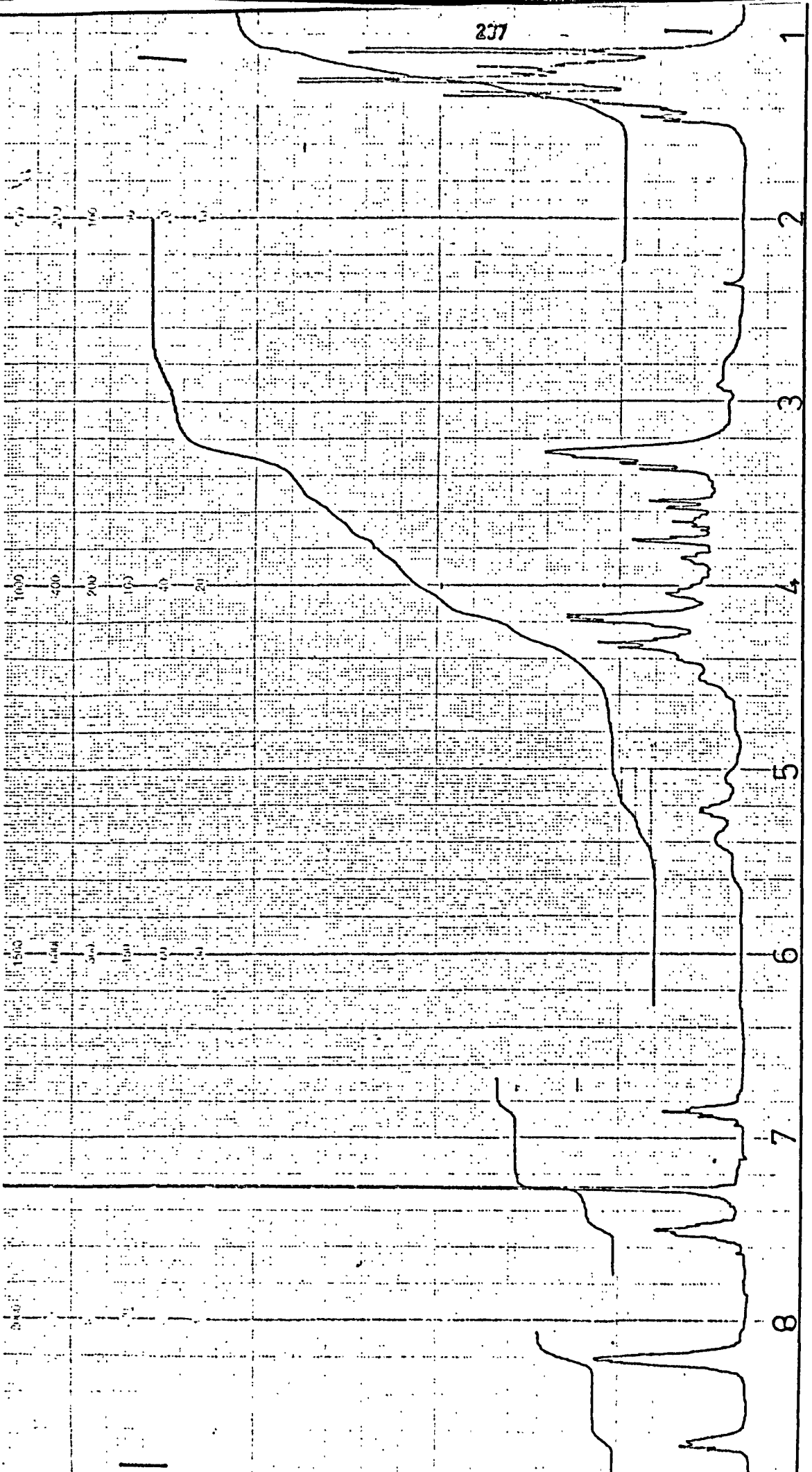


FIGURE 5.42 300 MHz NMR Spectrum of (2 PG: 1 PIP.: 1F)/IRDOF (5) hours

TABLE 5.7

Sequence distributions and M/F conversions in PIP systems.

System	Molar ratios			% of Segments			$\frac{f}{F+m}$ %
	PG	M/F	PIP	-FPF- -MPM-	-IPM/F-	-IPI-	
M	0	1	1	17	73	10	55
M	$\frac{1}{2}$	1	$\frac{1}{2}$	29	54	15	90
M	2	1	1	32	58	10	95
F	0	1	1	17	64	19	100
F	$\frac{1}{2}$	1	$\frac{1}{2}$	35	53	12	100
F	2	1	1	42	47	11	100

It is clear from Table 5.7 that the types of segments formed were generally not far different in the products of fumaric acid and maleic anhydride with PIP₁. However PIP/M systems produced slightly higher (-IPM-) ratios while PIP/F segments showed an increase in the (-FPF-) ratios.

5.4 General Discussion

In the systems containing propylene glycol the products of the reaction of the unsaturated acid components (both maleic anhydride and fumaric acid) with PIP₁ and PTP₁ showed a greater tendency to form an alternating terpolymer, than P(TP)_n (Impolex) systems. This is illustrated by the greater ratios of (-IPM- and -TPM-) segments and the lower (-IPI- and -TPT-) segments ratios which represent the degree of polycondensation within the prepolymer. For P(TP)_n systems the (1:1) molar ratio with maleic anhydride (MA) showed a greater tendency to produce an alternating terpolymer with (MA) with about 8% of the product in the P(TP)_n term, than when propylene glycol was added. It could be of importance to remember that P(TP)_n was already heated at 150°C (the same temperature as its reaction with (MA), for 5 hours). Therefore, one may suggest, for 1:1 molar ratios, that this tendency can be explained in terms of the reluctance of P(TP)_n to dissociate

free propylene glycol molecules, at 150°C, together with the quick ring opening reaction of the maleic anhydride with the terminal hydroxyl end groups. Then the ester-interchange reactions which took place later led to the homogeneous incorporation of the reactants in the system. This could also well mean that a lot of terephthalate ended molecules were produced. The production of terephthalate ended molecules in polycondensation reactions was suggested by the work of Fontana⁽⁶³⁾, Challa⁽⁶⁰⁾ and Griehl^(111,114) among other workers. It was also suggested by the results discussed in Chapter 4.

In the molar ratios containing free propylene glycol, PIP₁/M systems produced higher ratios of (-IPI-) segments than the corresponding molar ratios in PTP₁/M systems. This could be taken, in support to the observations made in Chapter 4, as a sign of the slower reactivity of PIP₁ with (M) as compared to the reactivity of PTP₁ with (M) at 150°C.

Considering the type of the initial products in these systems discussed in Chapter 4, it could be suggested here that the transesterification reaction between different chains, after the initial polycondensation reactions, seem to happen at lower temperatures in these systems. Challa⁽⁶⁰⁾ used a temperature range of 223-254°C for the polycondensation reaction of polyethylene terephthalate and he reported that the redistribution reactions (transesterification) proceed considerably faster than polycondensation reactions at temperatures such as 280°C. Nevertheless, the general distribution of segments in the products of all the PTP₁ and PIP₁ reactions with the unsaturated component showed an important role of the reaction of the unsaturated acid with (P), whether deliberately added or dissociated from the prepolymer. This is not unusual for the role of alcohols in the reaction with polymer molecules. The ester-interchange of high polymer molecules was investigated in the early work of Takigawa⁽¹¹⁵⁾ and Sakurada⁽¹¹⁶⁾ et al. They found that the methanolysis⁽¹¹⁵⁾ of polyvinyl acetate in methanol was catalysed by sodium methoxide and sodium hydroxide. However, in a 40:60 methanol-water mixture the rates of simultaneous alcoholysis and hydrolysis were related as 5.2:1, which show the ease with which alcoholysis can occur.

CHAPTER 6

GENERAL CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The work described in this thesis was performed in order to clarify a number of points in the reactions involved in the preparation of unsaturated polyester alkyds by the two-stage process.

The earlier work of Kyriacos⁽²¹⁾ made it clear that Impolex T400B prepolymer produced by ICI was not only in the form of PTP_1 but also contained higher oligomers ($P(TP)_n$). This was attributed to the preparation conditions (high temperature and pressure) of the Impolex prepolymers. A model compound constituted solely of (PTP_1) was prepared to prove this point. A similar compound was used later by Higgins⁽³⁹⁾ in the preparation of unsaturated polyesters with maleic anhydride. Higgins⁽³⁹⁾ did not consider that (PTP_1) might change its original structure in these reactions. In this thesis different systems were compared and the molecular weight distribution and structures of the products were detected. The effect of temperature on these reactions, as well as the effect of added propylene glycol, were studied. From the results shown in this work it was shown that vigorous reaction conditions were not necessary for the formation of high oligomers ($P(TP)_n$). The PTP_1 showed very fast ester-interchange reactions at low temperatures i.e. 150°C . It also formed a considerable amount of higher oligomers when heated at temperatures above its melting point, i.e. in the range $150-180^\circ\text{C}$. The polycondensation was temperature dependent and showed a sharp increase in its rate at 180°C . The Impolex T400B ($P(TP)_n$) also gave higher oligomers on heating but the change was more gradual and less overall. This polycondensation was found to be suppressed by the presence of free propylene glycol. For example in reactions of propylene glycol with PTP_1 the polycondensation was completely suppressed for molar ratios slightly greater than (1:1).

When PTP_1 was compared with PIP_1 , the latter showed less tendency for polycondensation at low temperatures; 150°C and 160°C , but the polycondensation was much higher at 170°C and 180°C . The results obtained for both systems suggest that the ester-interchange reactions were not completely dependent on the polycondensation reactions. This could be shown by the difference in the results obtained for the increase in the molecular weight of the products and the primary/secondary ratio

of terminal propylene glycol molecules at different temperatures (see Chapter 3).

These results show the importance of ester-interchange reactions and the important role of propylene glycol in these reactions. This conclusion was supported by the fractionation experiments described in Chapter 4. The presence of (MPM) in the low molecular weight fraction of the products of PTP₁ and PIP₁ reactions with maleic anhydride, in the absence of propylene glycol, amounts to the same conclusion. It could also be added here that in the reaction with maleic anhydride, PTP₁ dissociated more (P) than PIP₁ at 150°C, which is in good agreement with the difference reported in polycondensation between the two prepolymers at 150°C in Chapter 3. However, at 180°C, both prepolymers assumed higher reactivity. From these results, it could be concluded that it is very difficult to produce an alternating copolymer with regular spacing of double bonds along the polymer chain by the two-stage process. Therefore, instead of having only (PTPM)_n species, -(PM)_n and -(P(TP)_n)- can also be found in the reaction product, which will lead to an irregular placing of double bonds along the polymer chains and different concentrations of crosslinks at different regions in the same product in the curing step. This conclusion was positively proved by the results, discussed in Chapter 4, of the type of segments distribution in the polymerization products of PTP₁ and PIP₁ with maleic anhydride in the (1:1) molar ratios. The results obtained for these experiments showed higher ratios of (-TPM-) and (-IPM-) types of segments than in the molar ratios containing free propylene glycol. The presence of propylene glycol led to the production of low molecular weight products in the stoichiometric formulations and in all cases to low ratios of (-TPM-) and (-IPM-) segments.

The polymerization experiments described in this work were run at low temperatures and the losses of double bonds encountered were very small. Some losses were noticed in formulations containing only propylene glycol and maleic anhydride.

The rates of maleate/fumarate transformations were found to be temperature dependent and to some extent depend on the type of saturated acid incorporated in the prepolymer i.e. PIP₁ systems showed higher maleate/fumarate conversions at high temperatures (180°C) than PTP₁ systems. However, the main factor, found to affect the maleate/fumarate conversions was the presence of free propylene glycol in the reaction

mixture. This may be due to its faster ester-interchange reaction rates. The fact that propylene glycol increases the conversion rate of maleate to fumarate was apparent from the high rates of conversion in reactions containing free propylene glycol and the low rates of conversion in the $P(TP)_n$ reactions with maleic anhydride. This could further be supported by the results of the reaction of propylene glycol with diethyl maleate, described in Chapter 4, which was carried out at 150°C for one hour. The NMR analysis showed that 60% of the maleate molecules were converted to fumarate while only 30% of the total propylene glycol molecules were incorporated in the final product.

From these results several suggestions for further work can be formulated. The experiments discussed in this thesis were carried out within the temperature range of 150°C - 180°C . Although these experiments were quite useful in elucidating the basic reactions involved in these systems, it will be useful to investigate similar reactions at higher temperatures (220°C) as most of the commercial grades of unsaturated polyesters are prepared at temperatures above 200°C .

In spite of the fast ester-interchange observed for these systems in this work, it could be of value to prepare cured unsaturated polyesters based on PTP_1 and $P(TP)_n$ to see the effect of thermal treatment history and the distribution of segments on the physical properties of the final products.

Finally to complete the investigations started in the research programme, a similar investigation can be made on $P(IP)_n/M$ systems, and the work could be extended to involve phthalic anhydride/propylene glycol/maleic anhydride one-stage systems which were not considered in this work.

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