

## Anionic polymerisation of methyl methacrylate

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A THESIS ENTITLED  
ANIONIC POLYMERISATION  
OF  
METHYL METHACRYLATE

PRESENTED BY

SENA YADDEHIGE

IN PART FULFILMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

OF THE

UNIVERSITY OF NEW SOUTH WALES

SEPTEMBER 1980



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### DECLARATION

It is hereby declared that the work submitted in this thesis was investigated at the Department of Polymer Science, University of New South Wales, Kensington, Australia during the period between 1 March 1976 and 1 January 1979 and contains no materials previously submitted for a degree and contains no materials previously written by another person except where due reference is made in the text.



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## ABSTRACT

The literature concerned with the anionic polymerisation has been surveyed with emphasis upon that of methyl methacrylate. The mechanism, side reactions and stereochemistry of the process, along with variations of the reaction under different temperature, solvent and counterion conditions have been reported.

The relative importance of different reactive species, namely free ion and ion pairs and their effect on the molecular weight distribution of the resulting polymers have been investigated. A comparative study of the influence of counterion on the kinetics of propagation and termination reactions, and stereospecificity has been made using one technique under otherwise similar conditions. Using high vacuum techniques and all pyrex greaseless systems, the polymerisations were carried out in sealed glass reactors. Six initiator systems with  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  as counterions have been employed. Gel permeation chromatography was used as a mechanistic and kinetic tool to obtain the relevant information. Additional information on the nature of reactive species was obtained using high resolution NMR spectroscopy.

The polymerisation technique employed was capable of producing very narrow distribution polymers with polydispersity index less than 1.1. The double initiation method produced polymer with slightly narrower distribution than by single initiation. The kinetics of monomer addition to the ion pair was found to be simple first order at 195 K.



The rate constants for this reaction were determined to be 11, 84 and 310 dm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> for Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> counterions respectively. No appreciable termination or chain transfer reactions were found at this temperature and the original monomer concentration and the fractional conversion both showed a simple linear relationship with the number average degree of polymerisation. When di-functional  $\alpha$ -methyl styrene was used as the initiator with Na<sup>+</sup> and K<sup>+</sup> as counterions, the molecular weights obtained were less than the theoretically expected.

At 250 K, and above, in the presence of excess monomer the polymethyl methacryl anion reacts with the monomer ester function at a significant rate. The termination rate constant for this reaction, for the ion pair with Na<sup>+</sup> as counterion were found to be 0.26 dm<sup>3</sup> mol<sup>-1</sup> sec<sup>-1</sup> at 220 K, while 1.67 dm<sup>3</sup> mol<sup>-1</sup> sec<sup>-1</sup> at 255 K. The activation energy calculated from the linear Arrhenius plot was 24.63 K cal mol<sup>-1</sup> and frequency factor had a value of 5.22. Due to broader molecular weight distributions, it was difficult to obtain a systematic relationship for the ion pair with K<sup>+</sup> counterion. The rate constant for intramolecular termination of PMMA<sup>-</sup> Li<sup>+</sup> ion pairs at 250 K was found to be  $> 10^{-3}$  sec<sup>-1</sup> while that for PMMA<sup>-</sup> K<sup>+</sup> was  $2 \times 10^{-5}$  sec<sup>-1</sup>. For PMMA<sup>-</sup> Na<sup>+</sup> it was  $2.5 \times 10^{-5}$  sec<sup>-1</sup>.

The polymers prepared with Li<sup>+</sup> as the counterion showed a complete absence of isotactic triads. The triad sequence distribution of polymers prepared with Li<sup>+</sup> and K<sup>+</sup> as counterions indicated a Markovian behaviour while that with

$\text{Na}^+$  counterion approached Bernoullian process. The original monomer concentration or the nature of the carbanion, irrespective of whether monofunctional or di-functional had no appreciable effect on the steric triad distribution while higher temperatures showed a detectable tendency towards an increased isotacticity. The probability of isotactic addition increased in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ .

The polymerisation of methyl methacrylate in tetrahydrofuran initiated with organo-alkali initiators can be said to proceed by simple anionic mechanism. The increase in reactivity of the ion pair with the increase in size of the counterion showed that the active species were not specifically solvated by tetrahydrofuran molecules but preferentially internally solvated by the adjacent ester groups of the same chain. The major reactive species in this polymerisation system can be referred to the internally solvated special form of contact ion pair.

The most important termination reaction in the polymethyl methacrylate/tetrahydrofuran system polymerised by ion pairs is the reaction with the monomer ester function.

The stereo-regulation of the poly methyl methacrylate under these conditions can be broadly considered as a Markovian process.



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## Chapter 1

### Introduction and Historical Review

#### 1.1 Anionic polymerisation

The potential of anionic polymerisation for the design of various types of polymers (1 - 7) has created considerable interest during the last decade. The salient feature of this process is the consecutive addition of monomer through a reactive carbanion until either the reactivity of the species or the supply of monomer diminishes. However, it is the sustained reactivity in the absence of terminating agents that brought the use of the term "living polymers" for such systems. It has been demonstrated that by this technique, virtually monodisperse polymers with a poisson distribution of molecular weights can be produced (8) as well as star shaped polymers (1), (2), comb shaped polymers (3), block polymers (4), (5), or polymers with variety of single or bifunctional groups at the chain end (6), (7). Hence polymers can be made to specifications by anionic polymerisation.

Historically, anionic polymerisation processes had been used, without being recognised for the production of resins and gums, polybutadiene (9), polyisoprenes (10) and polystyrene (11) by reacting the respective monomer with metallic sodium. Even though some workers persisted that the reactive species in this type of reaction was a radical, it was Staudinger (12) who recognised the anionic character. Ziegler's work (13) on styrene and butadiene, too, had been

misinterpreted (14 - 16) for a long time due to the lack of knowledge of the dimerisation of radical ions to form dianions. Finally, it was Walling et al (17) who conclusively showed the true carbanionic nature of alkali metal initiation. The long observed coloured complexes of alkali metals and hydrocarbons (18) were known to initiate polymerisations. The reactive species responsible for this reaction too was also interpreted as a radical ion (19, 20) until Szwarc showed that (20-b) the electron transfer processes producing radical ions is only the first step of the polymerisation reaction and that it rapidly dimerises to form stable dicarbanion which is the true propagating species.

The first to differentiate between rates of initiation and propagation of an "anionic" polymerisation system was Abkin and Medvedev (21). Their work on butadiene was followed by Sanderson et al (22) who proposed a mechanism for anionic polymerisation of styrene in liquid ammonia. But it was Higginson and Wooding (23) who with their extensive work on kinetics demonstrated the true anion  $\text{NH}_2^-$  as the initiating species while bringing to notice the concept of ion pairs and free ions in an elementary manner.

Even though Dostal et al (24) produced a kinetic scheme without termination and Ziegler's mechanism of the butadiene polymerisation did not involve any termination, a living polymer system was not envisaged until Flory (25) discussed it. Studying a system of ethylene oxide in

an aprotic solvent, he showed the effects of a terminationless process. However, it was only after Szwarc rediscovered true living polymer systems thirteen years later, in a study of vinyl monomers, that the rapid development and use of living polymer systems began. Soon, other bases such as alkyl alkali compounds and Grignard reagents were found to initiate polymerisation reactions and propagate through only one end in contrast to two-ended propagation from electron transfer processes.

The use of alkyl lithium has been well documented (26) especially in hydrocarbon solvents. The early studies of anionic polymerisation carried out in liquid ammonia was complicated by extensive chain transfer reactions to solvent (22, 23) and lead to the use of aprotic media like hydrocarbons and ethers, where it was negligible or absent. In both types of solvents, initiation was always rapid. The overall rate of polymerisation and polymer configuration was dependent on the nature of the carbanion as well as the polarity of the reaction medium. However, acceptable explanations for such differences were obtained only as a result of extensive kinetic work carried out on styrene polymerisation (30, 33, 64).

Allen et al (27) found that the kinetics of anionic polymerisation of styrene in dioxane with sodium naphthalene was first order as expected in a terminationless process. Pseudo-first order constants were observed for living end concentrations and this was attributed to the presence of only one reactive species; presumably the ion pair.



However, in tetrahydrofuran (THF), the reaction was more complex (28) and the rate increased with dilution. After eliminating the possibility of association of living ends by viscosity measurements, it was postulated that ionic dissociation was taking place, producing a small but important fraction of free ions. Worsford and Bywater experimentally determined the dissociation constant of polystyryl sodium (29) and Bhattacharyya et al (30) and Schulz et al (33) in independent studies found that the bimolecular propagation rate constant was proportional to the reciprocal of the living end concentration. The linear relationship of this clearly indicated that free ions and ion pairs both participated in the propagation process, the equilibrium being undisturbed by the propagation reaction:



where  $K_D$  is the dissociation constant.

On this basis, the following simplified rate equation, in good agreement with experimental results, was obtained:

$$K_p = K_{(+)} + K_{(-)}(K_D)^{\frac{1}{2}} [I]^{\frac{1}{2}}$$

where  $K_p$  = Overall rate of propagation

$K_{(+)}$  = Rate constant of ion pairs

$K_{(-)}$  = Rate constant of the free ion

$[I]$  = Living end concentration

Even though the exact values varied slightly, the values of  $K_{(-)}$  obtained by various workers clearly indicated that the nature of the solvent (31, 32) or the counterion (33), (34) had no significant effect on it and the value is

approximately  $65,000 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  at 298 K.

However, when the free ion was suppressed by the addition of excess sodium tetraphenyl boride ( $\text{Naph}_4\text{B}$ ), the propagation rate constant dropped by more than 3 orders of magnitude to  $80 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  in THF(45). This was comparable to  $3,600 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  in dimethoxyethane, a better solvating medium, and  $3.4 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  in a poor solvating medium (dioxane). This indicated that the solvent polarity was controlling the propagation rate of ion pairs.

A similarly large solvent dependence was shown by poly( $\alpha$ -methylstyrene)(64). This has now been explained as due to the presence of two types of ion pairs, viz contact and solvent separated, in equilibrium with each other. The latter species, the more reactive pair, is believed to be predominant in better solvents with higher donicities and responsible for higher rates.

The ionic radius of the counterion seems to be a major factor in the solvent interaction process. According to spectroscopic measurements  $\text{C}_8^+$  salt exists only as contact ion pairs, even at 200 K when all other alkali metal salts exist as solvent separated ion pairs to a large extent (35). However, this has recently been questioned by Schulz et al (81) according to whom there could be some solvated ion pairs. His deductions were based on thermodynamic considerations. Even though no simple relationship could be found for the dependence of  $K_p(+)$  on the counterion and solvent, the order of reactivity in polar solvents was  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{C}_8^+$  while the reverse was true for

nonpolar media (35).

The temperature dependence of  $K_{p(\pm)}$  supports the idea of two ion pairs. In tetrahydrofuran, the polystyryl  $\text{Na}^+$  ion pair showed an increase in the rate constant from 80 to  $270 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  when cooled from 298 K to 213 K. Curved Arrhenius plots observed by Schulz for a number of solvating media (36) in the temperature range of 173 - 353 K give further support to this concept and could be represented by the following expression:

$$K_{p(\pm)} = K_{p(\pm)_C} + K_{p(\pm)_S} \left( \frac{K}{1 + K} \right)$$

where  $K_{p(\pm)_C}$  = Rate constant for contact ion pair

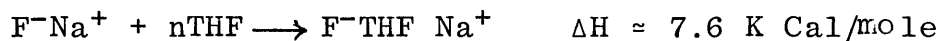
$K_{p(\pm)_S}$  = Rate constant for solvated ion pair

$K$  = Equilibrium constant for two ion pairs.

The rate constant of solvent separated ion pairs was calculated to be  $20,000 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  at 298 K. The negative activation energy observed could be explained as due to the exothermic solvation of contact ion pairs, in agreement with the assumption that at low temperatures in loose or solvated ion pairs, the solvation shell of counterion is complete. Accordingly, the higher reactivity of the latter ion pair could be explained as due to the reduced interaction by the counterion.

The concept of ion pairs had been originally used in the justification and explanation of organic reaction mechanisms and kinetics (37) (38). Utilising electrostatic as well as thermodynamic approaches, it was established that the molecules of different polarities could generate different

entities depending on the nature of the surrounding (39 - 44). Factors such as the dipole moment, dielectric constant and donicity of the solvent, all affect the extent of each entity available. Direct physical evidence for two kinds of ion pairs was produced by Hogen - Esch and Smid (35). In the absorption spectrum of fluorenyl sodium, bands at 355 nm and 373 nm were reversible and temperature dependent. The band at 373 nm appearing at low temperature (243 K) suggests that it is the solvated pair.



The ion pair equilibrium is strongly affected by the change in temperature, type of cation and the nature of the solvating medium. (The latter factor has been questioned by some authors who still accept the existence of solvated ion pairs (41).) Hogen-Esch and Smid demonstrated, spectroscopically, the solvent effect, by addition of a small amount of powerful solvating agent (dimethyl sulfoxide; donicity No 29.8, dielectric constant 45.0) to a fluorenyl lithium solution in dioxane (dielectric constant 2.21) when the absorption band shifted completely to the higher wave length. Extensive electron spin resonance (47)(48), nuclear magnetic resonance (139) and ultraviolet (46) spectroscopic studies have strongly supported this concept. Recently Hendricks et al (138) reconfirmed the validity of Hirota's observations (47) on the solvent effect and Cation effect on the ion pair equilibrium by studying the hyperfine splitting constants and sign reversal for all Group 1-A naphthalene compounds.



## 1.2 Reactions of Methyl Methacrylate

In contrast to styrene, the anionic polymerisation of methyl methacrylate is very complex. The polymerisation conditions greatly influence the nature of products as well as the configuration of the resulting polymer. Fox and coworkers found (49) that polymers formed in hydrocarbon (nonpolar) solvents favoured an isotactic product while polar etherial solvents favoured a syndiotactic product. The presence of the ester group seemed to be responsible for these effects either as a result of the attack on carbonyl group of the monomer or some interactions with the cation, monomer and solvent or all. Thus the nature of the cation, temperature and monomer concentration would be expected to affect the final product and its molecular weight distribution. In an effort to examine this complex process, some of the significant work is summarised below.

Following Wenger's work (50) using sodium naphthalene and butyl lithium as initiator at 195 K, which showed that the propagating species were reactive long after the polymerisation was complete, Schreiber found that at higher temperatures termination reactions were significant (51). Graham's work on the same system (52) verified that reactive ends were not rapidly self-terminating at low temperatures (198 K), but at 243 K this was considerable with at least one mode of termination producing methoxide. It is unlikely that the methoxide initiated new chains as was suggested in this particular case, even though in certain other systems it has been observed (53)(55). Owens et

al (54) found that the reaction of phenyl-magnesium bromide with acrylates and methacrylates gave three ketones as by-products, one of which is a cyclic keto ester corresponding to three monomer units. When polymerised in toluene at 273 K, a similar product with an approximate molecular weight of 346 was obtained as a major fraction, which was identified as the cyclic- $\beta$ -keto ester from infra-red evidence.(56). There was no 1.2 addition of Grignard reagent to monomer but the molecular weight distribution was very broad with  $M_V^-/M_n^- > 20$ . The principal mode of termination suggested to explain these results was intramolecular cyclisation. The reaction scheme is given in Figure 1.

With a complex catalyst system, diethyl aluminium diphenylamide Murahashi et al (57) reported the formation of  $\beta$ -keto ester similar to the above when equimolar mixture of MMA and catalyst in toluene was reacted at 223 K.

Allen and Bateup recently showed that the continued classification of the polymerisation of methyl methacrylate by Grignard reagent as a true anionic reaction may be erroneous (58, 59). In a systematic study of reactions of varying alkyl magnesium compounds and corresponding Grignard reagents with methyl methacrylate in tetrahydrofuran/toluene solutions, they found that the reaction kinetics were different from that of the conventional anionic polymerisation. Polymerisation reactions were slower at higher THF concentrations, and the characteristic oxygen sensitive ultraviolet absorption bands of propagating

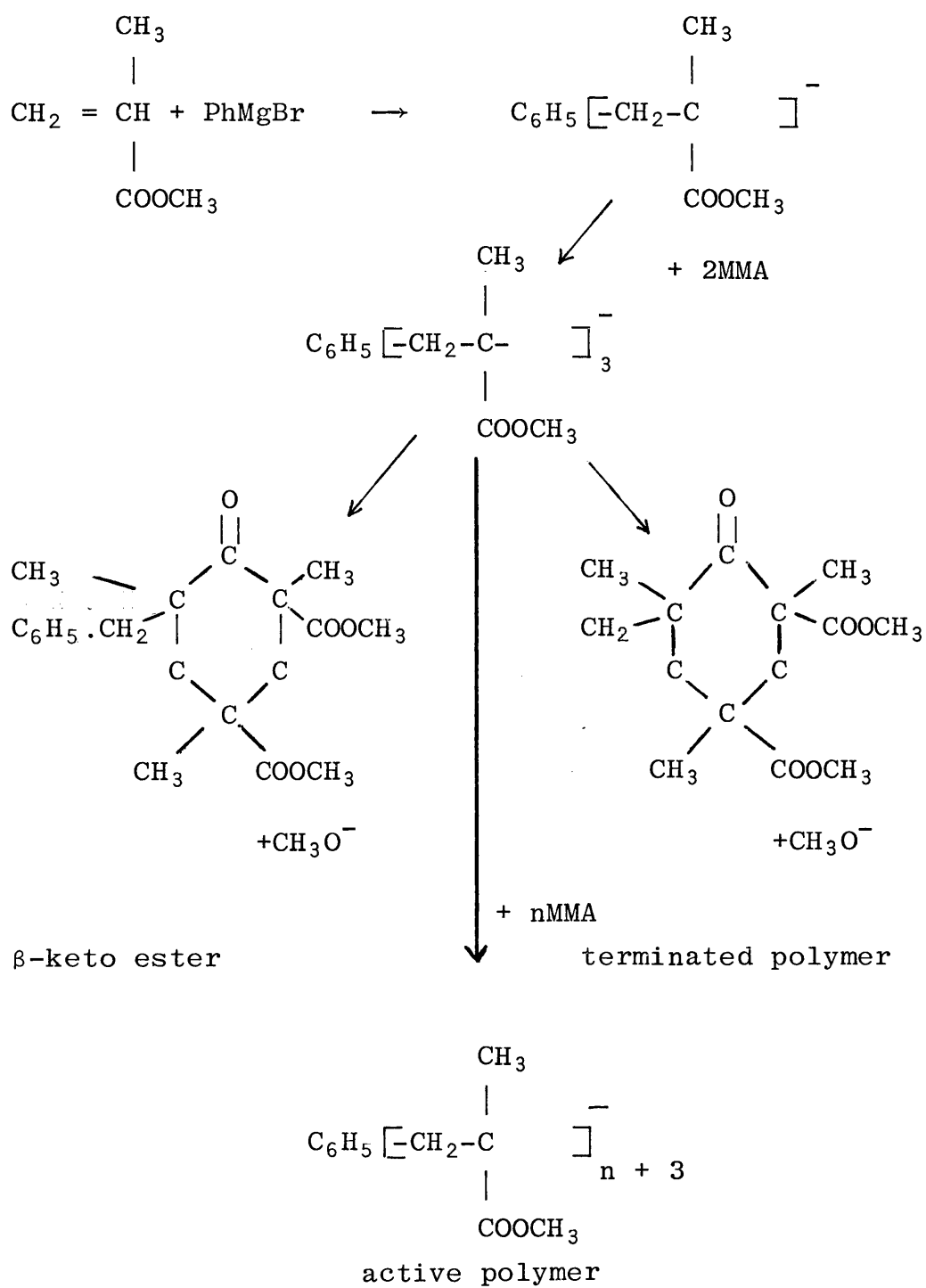


Figure 1.1

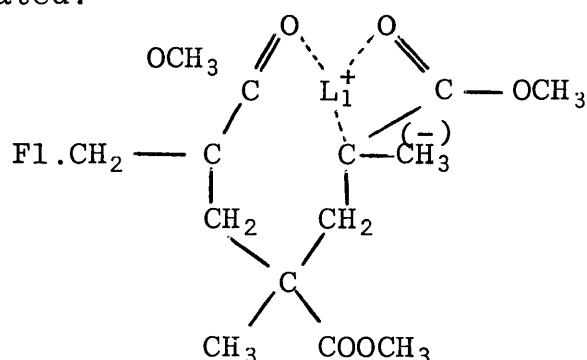
carbanions at 290 nm and 330 nm were absent. In most cases during initial stages, yellow-green colour was observed as in the reaction with triethyl aluminium (60)(61). The results were attributed to the formation of a monomer-initiator complex which rearranged to form nonpropagating side products or proceeded to form high polymer through a monomer-propagating end complex, (58). Side products were probably formed as a result of nucleophilic attack on the carbonyl group of the monomer (61)(62).

At 223 K n-butyl magnesium bromide and n-dibutyl magnesium gave similar results with MMA with respect to kinetics and products. However with s-dibutyl magnesium and t-dibutyl magnesium entirely different molecular weight distributions and steric sequences from those with corresponding Grignard reagents were obtained. Even though no systematic relationship could be obtained for the latter, they showed that in the former case whether initiated by n-butyl magnesium bromide or n-dibutyl magnesium, the same propagating species were involved and two major polymer products, methanol soluble and methanol insoluble were formed at two distinct, independent, multistate sites. The presence of magnesium halides did not have any significant effect on the propagation reaction but the possibility of the participation of magnesium methoxide on the propagating site could not be excluded. The proposed co-ordination insertion reactions mechanism was similar to the cationic polymerisation of propene (63)(63-b) and the polymerisation of alkenes by trialkyl aluminium (62).



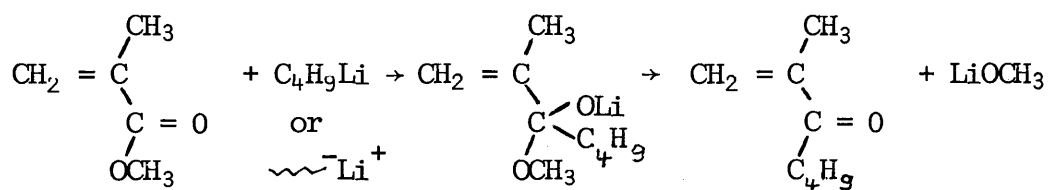
Even though the evidence for the non-ionic nature of the polymerisation reactions with organomagnesium compounds was extensive, the chemical nature of active centres have not been identified. Even with this limitation, this work is of significant importance to an understanding of the reactions of organo-magnesium compounds as well as anionic polymerisation by covalently bonded organo-metallic initiators.

Glusker studied the polymerisation of MMA with fluorenyl lithium as initiator at low temperatures, 195 K and 213 K. in toluene with varying amounts of ether (65)(66)(67). The addition of monomer was by 1.4 addition and the polymers obtained showed a bimodal distribution with 90% of the polymer having a molecular weight less than 2000. However, with tritium labelled acetic acid and  $C^{14}$  carbon dioxide, he showed that at least 80% of the chains were active to the end of the polymerisation. To explain this, he proposed that most of the chains were reversibly cyclised or pseudoterminated.



(Pseudoterminated reversibly cyclised trimer)

Wiles and Bywater studied the polymerisation of MMA by n-butyl lithium in toluene at 243 K. (68)(69). Their results had a resemblance to that of Glusker with fluorenyl lithium, but they suggested that the observed formation of methoxide was due to carbonyl attack by the reactive ends on the monomer (70). The increased production of methanol with conversion was attributed to this.



Korotkov et al (71) also suggested that the inactive products formed in a similar system was due to this reaction. Kawabata and Tsuruta (72) found extensive carbonyl attack by n-butyl lithium, both in hexane and THF, at 200 K. Butane was detected in both cases, though not at higher temperatures, but no cyclic ester was reported. However, with 1.1 diphenylhexyl lithium as initiator, in contrast to butyl lithium, no methanol was observed during the first stages of the reaction (73). At 190 K, a constant fraction of methanol was produced, showing a temperature dependence as above. This has been explained as due to the low activation energy for the reaction of this reagent with monomer carbonyl group. However, the resonance and steric effects (74) may play an important role in this reaction.

With potassium as counterion in THF, no carbonyl addition product was obtained (73). Itarumita et al (75) observed that with sodium as counterion at 195 K in THF, no carbonyl attack takes place in the propagation reaction, even though

at room temperature, it was extensive both in the initiation and propagation steps, with conversion being stoichiometric with respect to the initial initiator concentration.

With cesium as counterion, Löhr and Schulz (76) confirmed that no side reactions occur and the addition occurs by simple 1,4 addition.

### 1.3 Kinetics of Anionic Polymerisation of Methyl Methacrylate

Glusker carried out the first major kinetic study on the polymerisation of MMA by using fluorenyl lithium as initiator in the solvent media of toluene/diethyl ether and toluene/tetrahydrofuran (65-67). Initiation was rapid by 1.4 addition across the acrylic double bond and after the rapid consumption of three monomer units, first order monomer consumption up to high conversion was observed. In the toluene/diethyl ether (7-20%) system, at low temperatures the kinetic was first order in initiator and independent of ether concentration, while in toluene/tetrahydrofuran the order was 0.5. There was no appreciable termination but the amount of low molecular weight polymer formed was high. They accounted for this result by assuming that a cyclic  $\beta$ -keto ester (55-57) was formed from the pseudo-terminated trimer and further suggesting that the probability of pseudo-termination decreases after 8-10 monomer units have been added and would be a function of the configuration of last three units. The proposed mechanism was complex and their proposition that a polymer of 8-10 monomer units forms a helical conformation and was responsible for the change in reactivity, could not be justified since the way in which initial conditions selectively affect the equilibrium of the pseudo-termination process could not be explained.

Using n-butyl lithium as initiator, Wiles and Bywater (68) found that the kinetics was too complex to fit into a simple scheme. At 243 K, in toluene, at low initiator concentrations the initial rapid rate of monomer consumption was followed by a slow rate. After about 25% of the monomer was consumed,

the rate increased again showing an approximate first order dependence but the initiator loss was up to 60%. On the basis of formation of methanol from  $\text{LiOCH}_3$ , they concluded that the major side reaction was carbonyl attack. However, with diphenylhexyl lithium, the kinetics was less complex and the propagation rate was first order up to high conversions, both in monomer and initiator concentrations at temperatures from 193 K - 273 K, even in pure toluene (77). The resulting polymers had a single broad molecular weight distribution in contrast to bimodal distribution in the case of n-butyl lithium. They proposed that the bimodal distribution was caused by the presence of lithium methoxide, which complexed with some active chains to produce an active chain with a different characteristic rate from that of the uncomplexed one and that they do not interchange rapidly.

L'Abbe et al (78) found the polymerisation kinetics to be simpler with the complex initiator - n-butyl lithium diphenyl zinc, than with n-butyl lithium. At 213 K in toluene/THF solution, the reaction was first order with no apparent termination, but the initiator efficiency was constant at 34%. They obtained the rate expression:

$$R_p = k.f. [I]_0 [M]$$

where  $R_p$  = Overall rate of propagation

$f$  = Initiator efficiency

$[I]_0$  = Initial initiator concentration

$[M]$  = Monomer concentration

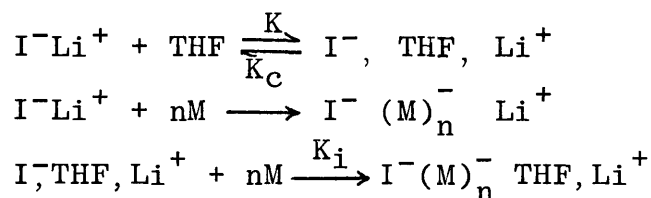
However, the overall rate constant  $k$  was a complex function showing a linear dependence on tetrahydrofuran



concentration:

$$k = k_1 + k_1^1 [\text{THF}]$$

Rate coefficients were interpreted in terms of two propagating species in equilibrium with each other, equivalent to contact and solvent separated ion pairs.



where  $K_c$  and  $K_i$  are the respective bimolecular rate constants of propagation for contact and solvated ion pairs. Allen et al investigated the same system with the disodium salt of  $\alpha$ -Methyl styrene tetramer as initiator (79). At low THF concentrations 0.5 - 2.0 M and below 278 K, the kinetics was simple, showing first order monomer consumption up to high conversions, with negligible termination.

$$-\frac{d}{dt} \ln [\text{MMA}] = K_p [\text{---}^-\text{Na}^+]$$

The term  $K_p$  was expressed as a complex rate coefficient to account for low Arrhenius parameters. Similar to the observation by L'Abbe (78),  $K_p$  was found to be proportional to the THF concentration and this was attributed to the solvent participation in the equilibrium process of contact and solvated ion pairs. In subsequent work, Allen, Chaplin and Jordan (80) found the rate of polymerisation to be strongly dependent on the mode of initiation. The rate of propagation after single step initiation was more than a thousand times greater than that after double step initiation. Assuming that the difference was due to slow relaxation of reactive pair in nonequilibrium excess, they

calculated propagation coefficients for two ion pairs, assigning a value  $> 25 \text{ m}^{-1} \text{ sec}^{-1}$  for the solvated ion pair. The relaxation mechanism they proposed for two types of ion pairs (or reactive species) could be a plausible explanation for observed results, yet it is difficult to envisage such comparatively large relaxation times at low temperatures. However, it is possible that the results were complicated by the effect of free polymethyl methacrylate anion, which was known to be present in appreciable though minute quantities (81),(82). It is difficult to understand the exact reason for not observing any effect on addition of sodium tetraphenyl boride but this could be due to spectroscopic technique used as detector. On the other hand, the observed reduction in the concentration of reactive species after the addition of the first aliquot of monomer cannot be assigned to termination reactions by impurities and monomer, or to relaxation of excess reactive species. However, it is noteworthy that the structure of the macroanion proposed for the cyclic form as an alternative ion pair, with the ester group of the penultimate unit in the first shell of the cation with additional THF molecules, was similar to the structure of the propagating species later proposed by Schulz et al (87).

The fact that the polymerisation of methyl methacrylate by Grignard reagent cannot be possibly considered as truly anionic anymore (58, 59) makes it necessary to consider the kinetic work by Allen and Bateup. They observed that in toluene/tetrahydrofuran solution within the THF

concentration 0.5 - 2.9 M at 223 K up to a conversion of 25%:

$$D_{p_n}^- = c \cdot \frac{\alpha}{[I]_0}$$

where  $D_{p_n}^-$  = Degree of polymerisation

c = constant

The important feature here was that  $D_{p_n}^-$  was independent of the monomer concentration, while proportional to the fractional conversion,  $\alpha$ .

At fixed THF concentrations up to a conversion of  $\alpha \leq 0.4$ , the following simplified rate equation was obeyed.

$$R_o = k [I]_0 [M]_0$$

However, in clear contrast to true anionic polymerisation, the rate decreased with increasing tetrahydrofuran concentration. By considering the enthalpy of polymerisation, they found that the pre-steady state exothermicity could be attributed to a reaction step, probably the complex formation. They proposed that the polymerisation reaction (both initiation and propagation) proceeded through an equilibrium process of complex formation between the monomer and reacting ends. This view was supported by the absence of spectroscopic evidence for ionic species.

Itarumita et al (75) showed that in pure tetrahydrofuran at 195 K, the side reactions were virtually absent.

Kinetics was simple and showed first order monomer addition. However, at 208 K, one third of the initiator, sodium  $\alpha$ -methylstyrene dianion was consumed by carbonyl attack on monomer during the initiation step while propagation was undisturbed. At room temperatures, when

initiated with sodium naphthalene, the reaction ceased within a second, producing methanol in stoichiometric proportions. From these results, they deduced that the propagating species in the  $\text{PMMA}^-\text{Na}^+/\text{THF}$  system was a contact ion pair and assigned a value  $100 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$  for the rate constant. It is difficult to assess the validity of the kinetic results, owing to the fact that they ignored the participation of free ions, which would be expected to have an effect in this system, as observed by Löhr (81), who reported that the overall propagation constant in the presence of excess sodium tetraphenyl boride was almost one third its value without it. Furthermore, the value of dissociation constant used is rather ambiguous and the interaction of the free cation with the solvent was disregarded in calculating interionic distances.

Löhr and Schulz (76)(81) conducting a comparative kinetic study on the effect of counterion on the anionic polymerisation of methyl methacrylate using  $\alpha$ -methylstyryl sodium and  $\alpha$ -methylstyryl cesium, found that at 195 K, no detectable termination occurs and the kinetics was first order, satisfying the following integrated rate equation.

$$\ln \frac{[\text{M}]_0}{[\text{M}]_t} = K_p^- [\text{I}] t$$

where  $K_p^-$  = Overall rate constant of propagation

$[\text{I}]$  = Initiator concentration

$[\text{M}]_0, [\text{M}]_t$  = Original and final monomer concentration at time  $t$

To account for the observed increase in  $K_p^-$  with decreasing initiator concentration and the independence in the presence of excess free sodium ion, the overall rate constant was expressed as a complex function of component rate coefficients (33), similar to polystyryl ion pairs:

$$K_p^- = K_{p(\pm)}^- + K_{p(-)} \left[ \frac{K_D}{[I]} \right]^{\frac{1}{2}}$$

where  $K_{p(\pm)}^-$  = Overall rate constant of propagation by ion pairs

$K_{p(-)}$  = Rate constant of free ions

$K_D$  = Overall dissociation constant

From a linear plot according to this expression and using a  $K_D$  value one order of magnitude higher than that reported elsewhere (82), they obtained the following values:

$$K_{p(-)} = 4.5 \approx 4.8 \times 10^{-4} \text{ dm}^3 \text{ m}^{-1} \text{ sec}^{-1}$$

$$K_{p(\pm)} \quad (\text{pMMA}^-\text{Na}^+) = 60 \text{ dm}^3 \text{ m}^{-1} \text{ sec}^{-1}, E_a = 2.3 \text{ Kc m}^{-1}$$

$$K_{p(\pm)} \quad (\text{pMMA}^-\text{Cs}^+) = 80 \text{ dm}^3 \text{ m}^{-1} \text{ sec}^{-1}, E_a = 4.5 \text{ Kc m}^{-1}$$

One important feature observed in this study was that in clear contrast to polystyryl ion pairs where the ratio of  $K_{p(\pm)}$  values for  $\text{Ps}^-\text{Na}^+ : \text{Ps}^-\text{Cs}^+$  in THF was 400:1,  $\text{PMMA}^-\text{Na}^+$  and  $\text{PMMA}^-\text{Cs}^+$  ion pairs both had a similar value. Assuming that sodium ion is generally highly solvated in THF at low temperatures with respect to cesium ion which is very poorly solvated, producing more reactive thermodynamically distinct solvent separated ion pairs (81), they proposed that the dissociation of polymethylmethacryl sodium ion pairs was not accompanied by any appreciable gain in

solvation energy as a result of sodium ion being already solvated by the ester group of the active end unit of the chain. Even though this explanation is plausible, the activation energy calculated seems to be too low to be described by only one type of ion pair. Also, if the  $\text{PMMA}^-\text{Na}^+$  dissociates appreciably as shown by the calculated  $K_D$  values, some solvated ion pairs (ion pairs separated by THF) are to be expected, unless the ester group has a higher solvating power than tetrahydrofuran. However, if the observed values are independent of experimental conditions and techniques, at least it is apparent that in tetrahydrofuran the counterion effect in  $\text{PMMA}^-\text{M}^+$  ( $\text{M}^+$  = Metallic ion) was overridden by a factor originating from the ester group of MMA.

Later Schulz and Warzelhan (83) showed that bifunctional chains would undergo intra-molecular association by ring formation. It was suggested that the bimodal distribution observed at low conversions was due to two propagating species, one being the associated species, having lower propagation rate, while the other, unassociated one has the higher rate. The structure of the cyclised polymer chain was not given. However, if this is equivalent to that of triple ion formation as reported by Bhattacharyya (30) (84), such a model cannot be justified in the presence of excess free counterion. Moreover, the rate of such an ion would be much higher than that of the ion pair, as opposed to the observed results. (84).

On reinvestigation of the kinetics of anionic polymerisation of MMA by ion pairs using monofunctioned initiator, with  $\text{Na}^+$  as the counterion in a stirred reactor (85), Hocker and Warzelhan found (89) that within the temperature range of 173 K - 223 K, the propagation kinetics obeyed the same first order relationship as earlier. For a system where the free ion was suppressed, the integrated rate equation was given as:

$$\ln \frac{[M]_0}{[M]_t} = K_{(\pm)}^- [I] t$$

where  $K_{(\pm)}^-$  is the overall rate constant of ion pairs.

The number average degree of polymerisation,  $\text{Dp}_n^-$  was linearly dependent on conversion  $\alpha$ .

$$\text{Dp}_n^- = \alpha \frac{[M]_0}{[I]}$$

The rate constants were unaffected by dilution and the Arrhenius parameters calculated from the linear plot from the expression

$$\log_e K_{(\pm)} = 2.303 A - \frac{E_a}{RT}$$

where,  $A = 7.0$ ,  $E_a = 4.4 \text{ K cal/mole}$ . The value of the activation energy,  $E_a$ , obtained was twice the value calculated by Löhr, but does not depend on the assigned value of the dissociation constant of the ion pair. It is not clear whether this difference was due to the improved technique or the use of monofunctional initiators or both. The polymers produced at low temperature, 173 K, had a very narrow molecular weight distribution which broadened with increase in temperature. When fluorenyl sodium was used as the initiator, even at low temperatures, a very

broad molecular weight distribution polymer was obtained, with in particular a long low molecular weight tail. The rate of initiation was slower than that of the propagation. To avoid the chain transfer reactions due to proton abstraction, 9-methyl fluorenyl sodium was used but the rate of initiation was found to be  $1.0 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ . Their explanation of broad molecular weight distribution in terms of transfer reactions only, seem to be rather inadequate, especially when 9-methyl fluorenyl lithium at low temperature was used. The claim that initiator ends were present even after the complete conversion could not be justified unambiguously by spectroscopic (absorption) observations alone.

Kraft, Muller et al repeated the comparative study of  $\text{PMMA-Na}^+$  and  $\text{PMMA-Cs}^+$  using monofunctional initiators in a flow tube and the stirred reactor (86). Combining these results, they found that up to 263 K,  $\text{PMMA-Cs}^+$  ion pair obeyed the first order kinetics, while for  $\text{PMMA-Na}^+$  it was only up to 248 K.

The important observation they made was that Arrhenius plots for both ion pairs,  $\text{PMMA-Na}^+$  and  $\text{PMMA-Cs}^+$  were linear and identical.  $E_a = 4.9, 4.7 \text{ K cal/mole}$   
 $A = 7.7, 7.4$  for cesium and sodium ion pairs respectively. From this, they postulated that only one type of ion pair exists in this system, ie an ion pair with the counter ion solvated intramolecularly by penultimate and anti-penultimate ester groups of the polymer, similar to that suggested by Muller et al (87) and earlier by Fowells (88) for the  $\text{Li}^+$  ion. This model appears to explain most



of the observed data, but its merits have to be measured against the results of similar polymerisation processes in solvents with different donicities. Low donicity solvent media would not be expected to affect the results appreciably while a solvent with high donicity with respect to ester group and tetrahydrofuran should seriously affect the kinetics as well as the sequential distribution of placement of monomer units in the polymerisation by two ion pairs.

Löhr et al investigated the kinetics of termination reactions of polymethylmethacrylate ion pairs in pure THF, using cumyl cesium as the initiator (90). They found that as the reaction temperature was increased from 198 K to 268 K, deactivation of chain ends increased, broadening the molecular weight distribution and finally the polymerisation ceased before reaching complete conversion. By fractionation of the resulting polymers, the integral mass distribution curves were obtained and hence the fractions of chains deactivated.

From the expressions:

$$D_{p\max} = -\left(\frac{1}{K}\right) \ln(1 - \alpha a)$$

$$K = \frac{K_t(\pm)}{K_p(\pm)}$$

where  $D_{p\max}$  = maximum degree of polymerisation of the deactivated chains

$\alpha a$  = the mole fraction of deactivated chains

$K_t(\pm)$  = rate constant of termination

$K_p(\pm)$  = overall rate constant of propagation

$K_{t(\pm)}$  could be calculated, given the value for  $K_{p(\pm)}$ . From linear Arrhenius plots of  $K_{t(\pm)}$  and  $K$ , activation energies for termination and propagation were found to be 11 K cal/mole and 4 K cal/mole respectively, with a value of 11 for the frequency factor. Even though these values are reasonable, it is difficult to assess their validity due to the following considerations. The methanol soluble low molecular weight product, which had been reported as a major fraction of prematurely terminated polymers (56) (57)(65)(69), seems to have been neglected. The relatively adiabatic change up to 10° C during the polymerisation process could lead to an over-estimation of the effect of termination reactions. The basic assumption that the only termination process operating was that with the monomer is too restrictive. This was reflected in the recent work of Warzelhan et al (89). If the termination by monomer is the only process involved, a plot of  $[I]_t V_s \propto$  for the following expression (91) would be linear.

$$[I]_t = [I]_0 - \frac{K_{t(\pm)} \cdot \alpha [M]_0}{K_{t(\pm)} + K_{p(\pm)}}$$

where  $[I]_t$  = Final concentration of living ends  
 $[I]_0$  = Original concentration of living ends  
 $[M]_0$  = Original concentration of monomer

However, it was observed (89) that with monofunctional  $Na^+$   $\alpha$ -methyl styrene ion pairs, the above plot curved sharply downwards both at 222 K and 230 K, indicating more than one termination process. Higher degrees of internal non-uniformity observed could also be explained on this basis.

Warzelhan et al (89) studied the decay of polymethyl methacrylate living ends with time at a temperature range of 200 K - 230 K. Considering only intramolecular termination by backbiting on the anti-penultimate ester group of the same polymer chain, they found that the decay process obeyed the following first order law:

$$\log_e \frac{[I]_0}{[I]_t} = K_t \cdot t$$

The values obtained from linear Arrhenius plots of  $K_t$  were of the same order as that obtained by Löhr even though the reaction considered was the neglected one. However, this result could not exclude the possibility of termination by monomer or slow intermolecular termination with another polymer chain.

#### 1.4 Stereospecificity and Mechanism of Anionic Polymerisation of Methyl Methacrylate

It has been known for sometime that the polarity of the solvent medium plays an important part in the stereo regulation of the product during the anionic polymerisation of MMA (92). Hydrocarbon or nonpolar media favour isotactic addition while polar media favour syndiotactic addition. Mixed solvents are known to produce intermediate sequences. Various mechanisms have been proposed to explain these differences (57) (93-101) (109) but recent workers seem to favour the theory of intramolecular solvation of the counter ion by ester groups of last three monomer units, which to varying degrees (87)(96) influence the direction of monomer approach. Yet, none of them have been able to fully account for all observed facts with respect to molecular weight distribution, kinetics and tactic sequences.

The tacticity studies carried out by Allen and Bateup (59) with Grignard initiation system, even though the mechanism seems to be non-anionic, would be useful to an understanding of the stereospecificity of the anionic polymerisation of MMA. They found that when initiated with organo-magnesium compounds, the stereo sequence of PMMA was strongly dependent on the structure of the alkyl group, similar to the observation by Watanabe (137). However, the replacement of  $n\text{-BuMgBr}$  by  $n\text{-Bu}_2\text{Mg}$  or the presence of excess  $\text{MgBr}$  had no effect, while  $s\text{-butyl}$  and  $t\text{-butyl}$  compounds showed entirely different products from that by corresponding Grignard reagents. Polymers produced by  $t\text{-BuMgBr}$  were highly isotactic while

that by n-BuMgBr was predominantly syndiotactic. In both cases, the distribution of triads was non-Bernoullian. Polymers produced by s-butyl compounds had an intermediate character. Furthermore, in the case of n-BuMgBr initiated polymers, methanol soluble fractions had a different triad distribution from that of the methanol insoluble fractions, still both being non-Bernoullian, suggesting that the steric control of the addition of a monomer unit to complete a diad was not independent of the configuration of the previous unit. Considering the stereo block nature of the main polymer, they suggested that the steric distribution was governed by first order Markovian statistics, even though the solvent and temperature effects were also consistent with the Coleman and Fox two-state mechanism (97)(98). The model proposed for the active end group was different from Bovey's model in that the monomer was already co-ordinated to the counterion. At low THF concentrations, they proposed that the penultimate ester group occupied one co-ordination site on the magnesium, while at higher THF concentrations, it was a molecule of THF. The former was expected to favour isotactic placement while the latter a syndiotactic one. Even though the effort to replace the solvent THF in the co-ordination site by glyme failed, due to precipitation of the initiator, using a better solvent compatible with the system, one would expect that even low concentrations would have a pronounced effect on the tacticity. The proposed octahedral state for magnesium would be more appropriate for a co-ordinated insertion mechanism, but this would allow the increased influence of solvent molecules

on the reactivity and stereospecificity.

Fowells et al (88) studied the mechanism of anionic propagation by using stereospecifically  $\beta$ -deuterated MMA initiated with fluorenyl sodium and fluorenyl cesium in a range of THF concentrations at 195 K. Changes in monomer and initiator concentrations had no significant effect on the tacticity. With lithium as counterion, in the near absence of THF, polymers were predominantly isotactic but approached Bernoullian model, while in pure THF it was mainly syndiotactic. In mixed solvents, distribution was still predominantly isotactic though slightly less than in pure toluene, but the mechanism of addition of monomer was different.

The observed tacticity differences were explained based on a model with three propagating species, viz "naked" contact ion pair, peripherally or specifically solvated ion pair and solvent separated ion pair, mainly forming a chelate structure with the counterion. Even though this failed to account for bimodal distribution of polymers, they showed that tacticity differences were slight in two fractions. It is interesting to note that Warzelhan and Schulz reported recently (83) that with  $\text{Na}^+$  as counterion, low molecular product had a much higher isotacticity (i : s = 29 : 28) in contrast to high molecular weight fraction (i : s = 5 : 62) when polymerisation was carried out in THF at the same temperature.

Using n-BuLi at 195 K, Amerik et al (100) showed that the effect of monomer concentration on the tactic placement

in polymers prepared in toluene was important, even though not significant when prepared in THF. The sequence distribution in THF could be described by the Bernoullian model where as in toluene it was not applicable. He explained the penultimate effects were due to the existence of two active site complexes in toluene, intramolecular and intermolecular (with monomer) while none exists in THF. This obviously failed to account for the predominant syndiotacticity in THF.

Warzelhan et al recently reported (89) that in anionic polymerisation of MMA initiated by monofunctional ion pairs with  $\text{Na}^+$  as counterion, the syndiotactic triads increased with decrease in reaction temperature while the heterotactic triads decreased. The tacticity was independent of monomer concentration and the conversion. The multi-state mechanism of Coleman-Fox model as well as Markovian mechanism for the influence of the configuration of the chain end were both not applicable. However, with  $\text{Cs}^+$  as counterion under the same conditions, the Coleman-Fox model was still not applicable but steric distribution favoured Markovian statistics (85)(86). They explained the two different behaviours of two ion pairs in terms of two cyclic complexes in equilibrium, one solvated by penultimate ester group favouring the latter while the other was solvated by the anti-penultimate ester group of the polymer chain, relative amounts of each being possibly dependent on the size of the cation and the different levels of external solvation by THF.

### 1.5 Gel Permeation Chromatography and Molecular Weight Distribution

The gel permeation chromatography (GPC) is the newest analytical tool used for the characterisation of polymers, both in research and industry, (125). Basically, this is a fractionation process according to size where large molecules elute first and the small molecules last. The exact separation mechanism is not clearly understood, but the currently acceptable model still with shortcomings, seems to be that by Cassasa(123) (124) that the number of molecular conformations which are allowed in free solution but forbidden in a pore of a given size is determined by the r.m.s. end to end distance of the polymer coil in free solution. However, the peak separation is dominated by this steric exclusion according to the pore size of the beads of the cross-linked polystyrene gel, while restricted diffusion (107) and separation due to flow (117) are also believed to be operating simultaneously(106)(108)(116). The relative concentration of the species eluting at any given instant is continuously measured by one or more methods, such as differential refractive index, ultraviolet absorption or, recently introduced, LASER scattering, and recorded as a continuous curve. Even though this chromatogram does not give the Molecular Weight Distribution (MWD) directly, ultra modern equipment with built-in microcomputer and laser scattering units, could readily give the molecular weight values, provided that the columns are packed with high efficiency packing materials (120) and proper experimental conditions are maintained.



In general, the chromatogram is the representation of the retention volume ( $V_R$ ) distribution of the polymer sample, which has to be converted to the MWD through a calibration curve given by the equation:

$$M = C_1 \cdot \exp(C_2 V_R)$$

where  $M$  = Molecular weight

$C_1$  and  $C_2$  = Constants

However, the peak value of the retention volume  $V_R$  is a function of molecular structure, as well as the molecular weight. Even though this necessitates the construction of a calibration curve for every polymer type, due to practical problems of obtaining narrow standards, adapted practice is to construct a curve for well characterised polystyrene (primary calibration curve) and transforms it for use in other polymers (115). Various methods have been proposed for this (95)(104)(105)(118) but the widely used is the one based on the hydrodynamic volume of the polymer to establish a universal calibration curve (95) (120). It is assumed that, at a given elution volume, all polymers have the same hydrodynamic volume,  $[\eta]M$  values, where  $[\eta]$  and  $M$  are the intrinsic viscosity and the molecular weight of the polymer respectively.

$$\log [\eta]_1 M_1 = \log [\eta]_2 M_2$$

Intrinsic viscosity and the molecular weight are related by the Mark-Houwink viscosity equation.

$$[\eta] = KM^a$$

where  $K$  and  $a$  are Mark-Houwink constants.

These parameters are inter-related by the equation:

$$\log M_2 = \left[ \frac{1 + a_1}{1 + a_2} \right] \log M_1 + \left[ \frac{1}{1 + a_2} \right] \log \frac{K_1}{K_2}$$

where subscripts refer to polymer 1 (polystyrene) and polymer 2.

Using readily available standards of polystyrene and finding Mark-Houwink constants for the polymer under consideration by appropriate means (105)(120) molecular weights could be calculated and universal calibration curve constructed. In the absence of specific interactions, for linear and randomly coiled polymers, this calibration method is well applicable (119). However, according to Dawkins et al (104) at high molecular weight levels excluded volume effect could introduce appreciable variations from the calculation based on hydrodynamic volume alone (104). Chaplin overcame this difficulty to a satisfactory level by applying the Dawkin's correction method to the Universal Calibration equation (121).

The MWD of a polymer is usually derived in one of two ways. First one is by solving differential equations for the concentration of each species as a function of time, based on an assumed mechanisms of polymerisation. Second is the statistical approach by determining the probability of finding each species as a function of the extent of reaction. By elaborate mathematical treatments, theoretical distribution functions for polymers under all possible conditions and conceivable mechanisms have been obtained (41)(122).

Two general methods are used for actually determining the distribution of molecular weights in a polymer; by determination of various averages of the distribution and by fractionation. With the recent developments in calibration techniques in GPC, it could combine the best of both methods and satisfactory distribution curves could be obtained. Comparative study of theoretical and experimental distribution curves could reveal the applicability of a mechanism. Other than in mechanistic studies, within recent times GPC has been looked upon as a kinetic tool too. It is known that the proper estimation of the concentration of living ends at the onset of polymerisation is always masked by the terminations due to impurities which are hard to avoid. However, if the mechanism of propagation is not interfered by termination or transfer reactions, the mean kinetic chain length is given by the number average degree of polymerisation. Chaplin used this method to calculate the concentration of living ends, as an additional method (80). For difunctional initiators:

$$[\text{PMMA}^- \text{Na}^+] = \frac{2\alpha [\text{MMA}]_0}{D_{p_n}^-}$$

According to Schulz et al (86), for narrow distribution polymers, the  $D_{p_n}^-$  could be replaced with  $D_{p_n}$  corresponding to peak value of the GPC elution volume curve.

For monofunctional initiators:

$$I = \frac{\alpha [\text{M}]_0}{D_{p_n}^-} = \frac{\alpha [\text{M}]_0}{D_{p_{\max}}}$$

In evaluating  $K_p$ , they eliminated the effect of the termination reactions by taking the initial slope of the first order plot and by calculating  $D_{p_n}^-$  from the GPC eluogram using the "stripes method" (86). However, with reliable calibration methods, (112, 120), even broad molecular weight distributions could be used to obtain reliable values for  $M_n^-$  and hence the initiator concentration, provided that the number of chains remained constant.

Unlike the  $M_n^-$ , MWD is greatly affected by the disturbances in the polymerisation reaction, even if the number of chains remained constant. The relative breadth and symmetry of the curve is a measure of these processes. In an undisturbed system, all the molecules are theoretically identical in size and  $M_w^- = M_n^-$ , making  $M_w^-/M_n^- = 1$ . Thus it is customary to measure the uniformity of a polymer sample by the ratio  $M_w^-/M_n^-$ . The closer its value to unity, the more uniform will be the molecules with respect to size. However, the mathematical treatment of a terminationless process gives the distribution known as Poisson distribution, where  $M_w^-/M_n^- \approx 1.01$ . Schulz recommended a slightly different version for the polymer uniformity given by U (dishomogeneity factor). (133)

$$U = \frac{M_w^-}{M_n^-} - 1$$

where monodisperse polymers would have U values close to zero, while Zimm prefers the relative dispersion factor based on z-average molecular weight (41). The simplest and widely used way of expression of the dispersity of a polymer is the first one. Even though it is difficult to

differentiate between a dispersity of 1.01 and 1.05 (41), the comparative study of polymers with respect to  $M_n^-$  and actual distribution curve along with the dispersity ratio could be used to obtain valuable information on the kinetics and mechanism.

## 1.6 Scope of this Work

Unlike the anionic polymerisation of styrene, the most widely investigated simple nonpolar vinyl monomer, where distinct sets of kinetic and thermodynamic parameters concerning all active species viz, free anions, solvent separated ion pairs and contact ion pairs, are known, the anionic polymerisation of methyl methacrylate has been found to be complex. Probably because of the differential polarity of the ester group and the conformations it can assume, various association and termination processes have been reported to occur, the extent of which are dependent on factors such as the solvent polarity, the nature of the counterion and the temperature. The termination product (methoxide ion) may also have an important effect on the active species. Studies on the effect of monomer concentration with Grignard reagents have lead to the observation that this type of polymerisation is not anionic. Despite much work having been reported on the mechanism of anionic polymerisation of MMA, no comparative study of the nature of the counterion and temperature under the same set of conditions and by one particular technique has been reported. Furthermore, the data obtained from spectrophotometric and conductometric measurements have been ambiguous. With recent developments in column characteristics and calibration techniques in gel permeation chromatography, molecular weight distributions were expected to provide direct information pertaining to the nature of the active species and the processes involved. This study was carried out aimed at

obtaining such relevant information, using gel permeation chromatography as the mechanistic and kinetic tool.

## Chapter 2

### Experimental Techniques

#### 2.1 High Vacuum System and Reaction Vessels

The fact that the growing end of the initiators and that all the anions in an anionic polymerisation system are extremely reactive and are most readily deactivated by impurities like moisture, carbon dioxide, oxygen etc, necessitates the use of techniques capable of "absolute" exclusion, and meticulously clean conditions. Even though absolute purity is not possible, the use of high vacuum technique and special cleansing procedures enables a satisfactory level of purity and cleanliness to be attained. When it is required to deal with very dilute concentrations such as  $10^{-7}$  moles, the importance of this is self-evident.

In the high vacuum system, all greased conventional ground glass connections were avoided and high vacuum glass stopcocks were used only where they were essential and were restricted to the vacuum generating section only. The standard mercury diffusion pump with a 2 stage mechanical pump coupled to one piece welded vacuum system with appropriate liquid  $N_2$  traps was capable of providing a vacuum of  $10^{-5} - 10^{-6}$   $\mu$  ( $1\mu = 10^{-3}$  mm of Hg) (Figure 2.1) On line solvent reservoirs and reactor units were all separated by teflon seals in Villier's metal stopcocks connected by fused glass-metal joints.

The reagents used in the experiments, ie initiator solution, "cleaning solution", monomer solution, terminating agent



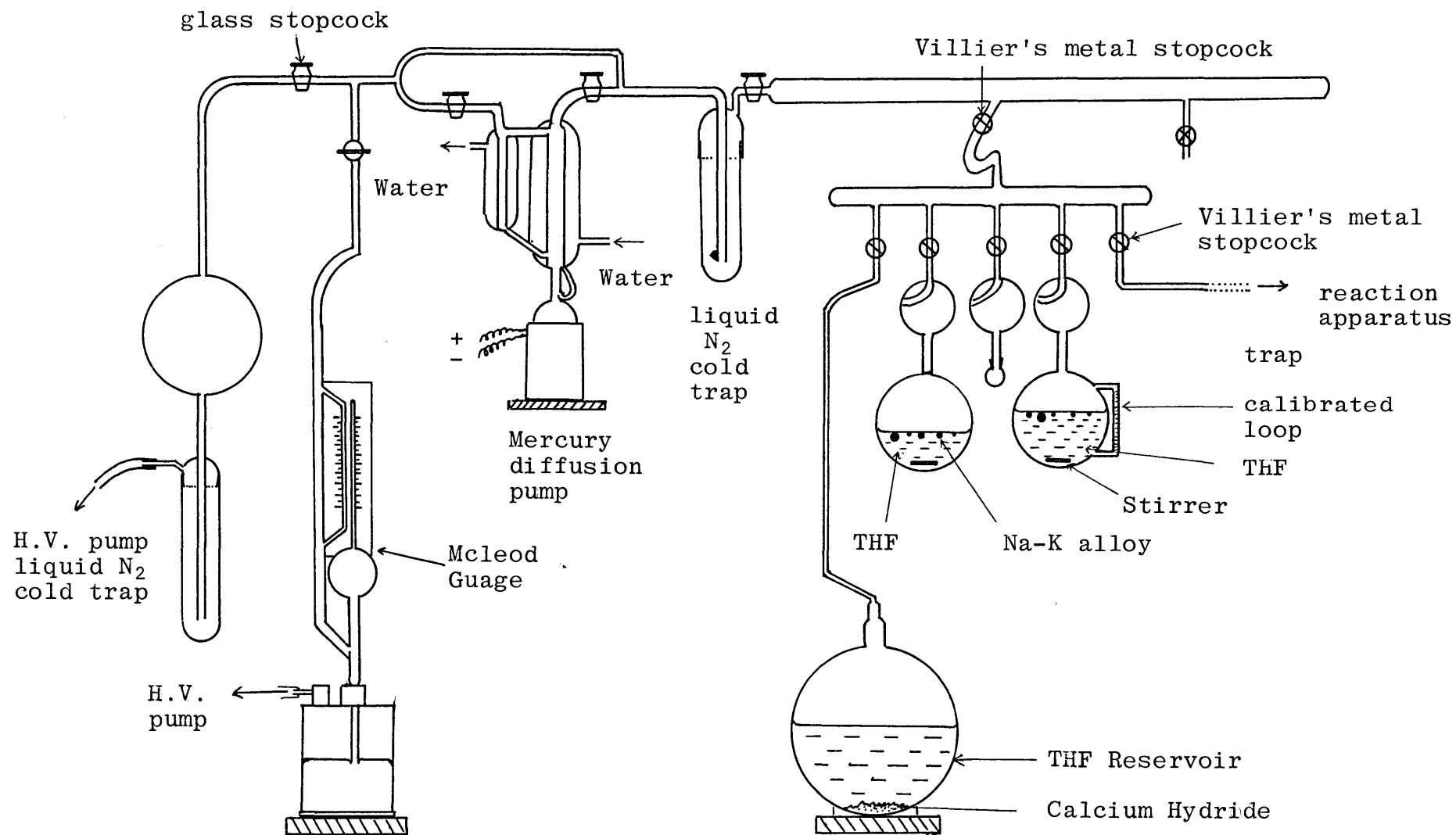


Fig 2.1 - High Vacuum system and the solvent unit

and other reagents used in the preparatory work, were all kept in evacuated ampoules equipped with a magnetic breakseal and fused to the apparatus.

The apparatus was fused to the vacuum line and was thoroughly flamed under vacuum and after distilling the required amount of Tetrahydrofuran (THF) purified as detailed in 2.2.1, the vessel was sealed off. During this period, it was necessary to keep the methyl methacrylate (MMA) solution and initiator at sub-zero temperatures to avoid undesirable side reactions. This was achieved by keeping them enveloped in dry ice. It is an experimental detail but an important one, that before the flaming procedure, the ampoules be brought to room temperature under very high vacuum to remove traces of moisture trapped in the break seal joint. This was essential in experiments carried without a separate purging step.

THF was kept frozen with liquid  $N_2$  while sealing off the apparatus at  $10^{-4}$  -  $10^{-5}$   $\mu$  range. The final cleaning of the reaction vessel was done by crushing the break seal of cleansing solution or initiator solution and washing the inside wall, followed by washing with pure solvent.

## 2.2 Purification of Reagents

### 2.2.1 Tetrahydrofuran (THF)

THF was refluxed with potassium for 24 hours and fractionated through 1 m column. After a second reflux over potassium and fractional distillation, it was stored over  $\text{CaH}_2$  under vacuum, connected to the vacuum line by greaseless Villier's stopcock. The final step of purification was achieved by distilling the THF under vacuum on to distilled Na/K alloy (20% Na : 80% K, melting point 263 K) and stirring magnetically until the strong blue colour appeared. Whenever required, THF was distilled directly from this  $\text{K}^+$  solution. Amounts being distilled were measured against a calibrated vertical loop on the side of the flask.

The usual practice of adding a little benzophenone, naphthalene, anthracene, or any other aromatic hydrocarbon to produce colourful organo-metallic solution, was completely avoided because of the possible contamination of the reaction system that inevitably would ensue.

### 2.2.2 Toluene

Toluene was refluxed with sodium for 24 hours and fractionated on to  $\text{CaH}_2$ . After degassing three times by repeated freezing, evacuating and thawing, it was stored under vacuum and directly distilled into the apparatus whenever required.

### 2.2.3 Methyl Methacrylate (MMA)

Koch-Light Laboratories MMA obtained fresh, was washed three times with 10% sodium hydroxide solution, to remove

the stabiliser, followed by washing with distilled water till washings were neutral to litmus. The separated MMA was stirred well with excess of anhydrous  $\text{MgSO}_4$  and left for 2 days. Further drying was done by distilling the MMA on to fresh  $\text{CaH}_2$  in an atmosphere of  $\text{N}_2$ , the first and last 20% of the distillate being discarded. The slurry of MMA and  $\text{CaH}_2$  was stirred magnetically for 24 hours under vacuum when the evolution of  $\text{H}_2$  ceased. After degassing three times by repeated freezing, evacuating and thawing, the monomer was distilled again on to fresh  $\text{CaH}_2$ . This was finally stored at 250 K under vacuum for two weeks.

Final purification was effected just before incorporating into ampoules as a 20% solution in THF. This was usually done by distilling the MMA from  $\text{CaH}_2$  slurry onto Na mirror or Na/K alloy and allowing it to stand for 12 hours in darkness, after which the final distillation was carried out (Fig 2. 2). Ampoules were stored at 250 K.

#### 2.2.4 $\alpha$ -Methyl styrene

$\alpha$ -Methyl styrene supplied by Koch-Light Laboratories stabilised with 2,4 dimethyl tert. butylphenol was used. The method of purification was essentially the same as that described for MMA. The purified monomer was stored under vacuum at 250 K.

#### 2.2.5 Fluorene

Obtained from Aldrich Chemical Co, fluorene was recrystallised 4 times; 3 times from methanol and once from hexane and was dried under vacuum.

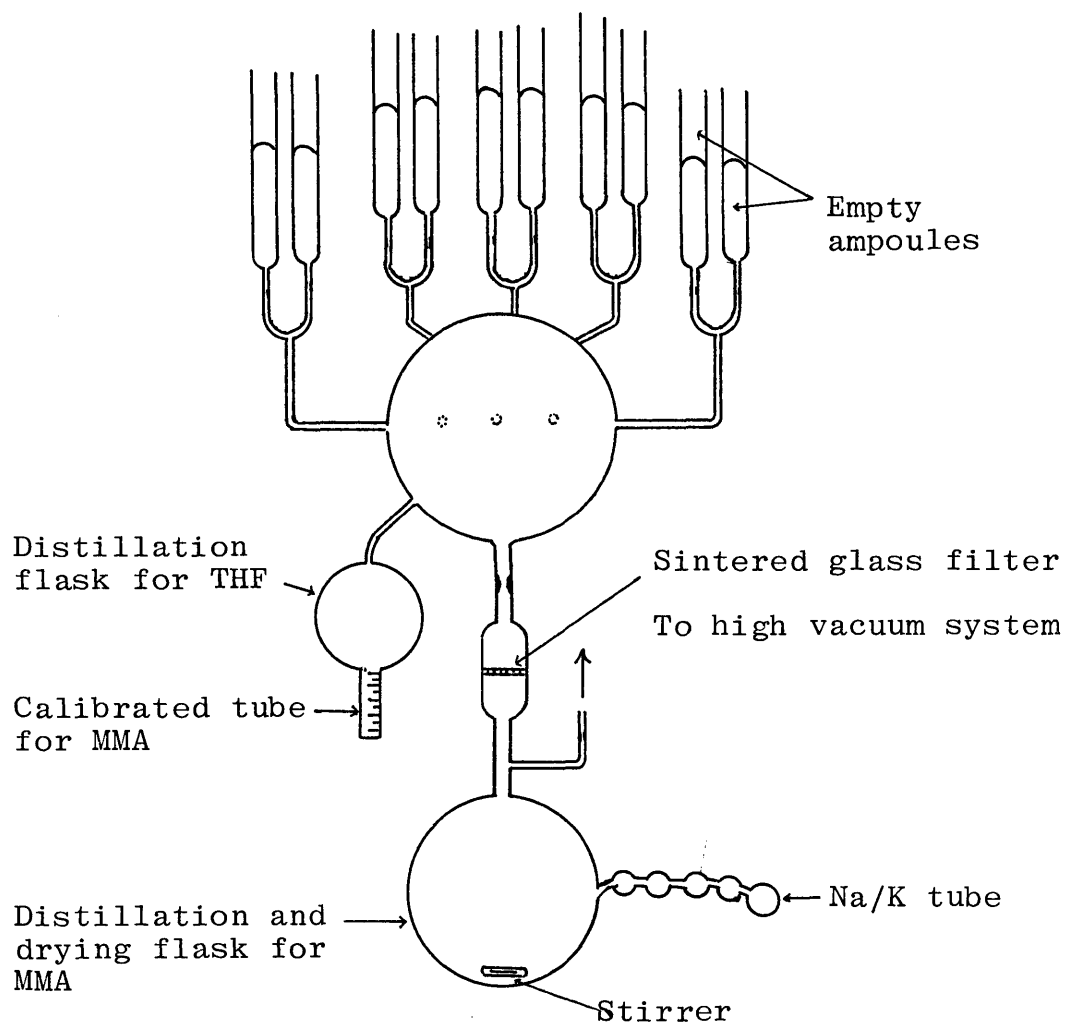


Fig 2.2 - The apparatus used for the preparation of monomer solution

#### 2.2.6 Methyl iodide

This was left overnight with Na wire and distilled twice to obtain a clear, colourless liquid and stored in darkness.

#### 2.2.7 Naphthalene

Naphthalene was purified by recrystallisation and sublimation.

#### 2.2.8 n-Butyl Lithium

Ventron-Alfa products, USA n-Butyl lithium, supplied as a 19.9 wt% in hexane was filtered through sintered glass under vacuum in a specially made apparatus to obtain a pale yellow clear liquid. (Fig 2.3). This was incorporated into evacuated ampoules and stored at 260 K in darkness.

#### 2.2.9 Sodium tetraphenylboride ( $\text{NaBPh}_4$ )

$\text{NaBPh}_4$  acquired from BDH chemicals was recrystallised from aqueous acetone - 3 parts of acetone by 1 part of water and dried in vacuo for 48 hours.

#### 2.2.10 Potassium Tetraphenyl Boride

Purified sodium salt was used as the starting material. A dilute aqueous solution of sodium tetraphenyl boride was treated with an equivalent amount of potassium chloride in solution. The precipitated salt was filtered, washed and recrystallised from aqueous acetone.

#### 2.2.11 Lithium Tetraphenyl Boride

A concentrated solution of lithium chloride was added in slight excess to a concentrated solution of the purified sodium salt. The precipitated NaCl was removed by centrifugation and the lithium salt recovered by evaporation. By dissolving in ethylene dichloride, excess lithium

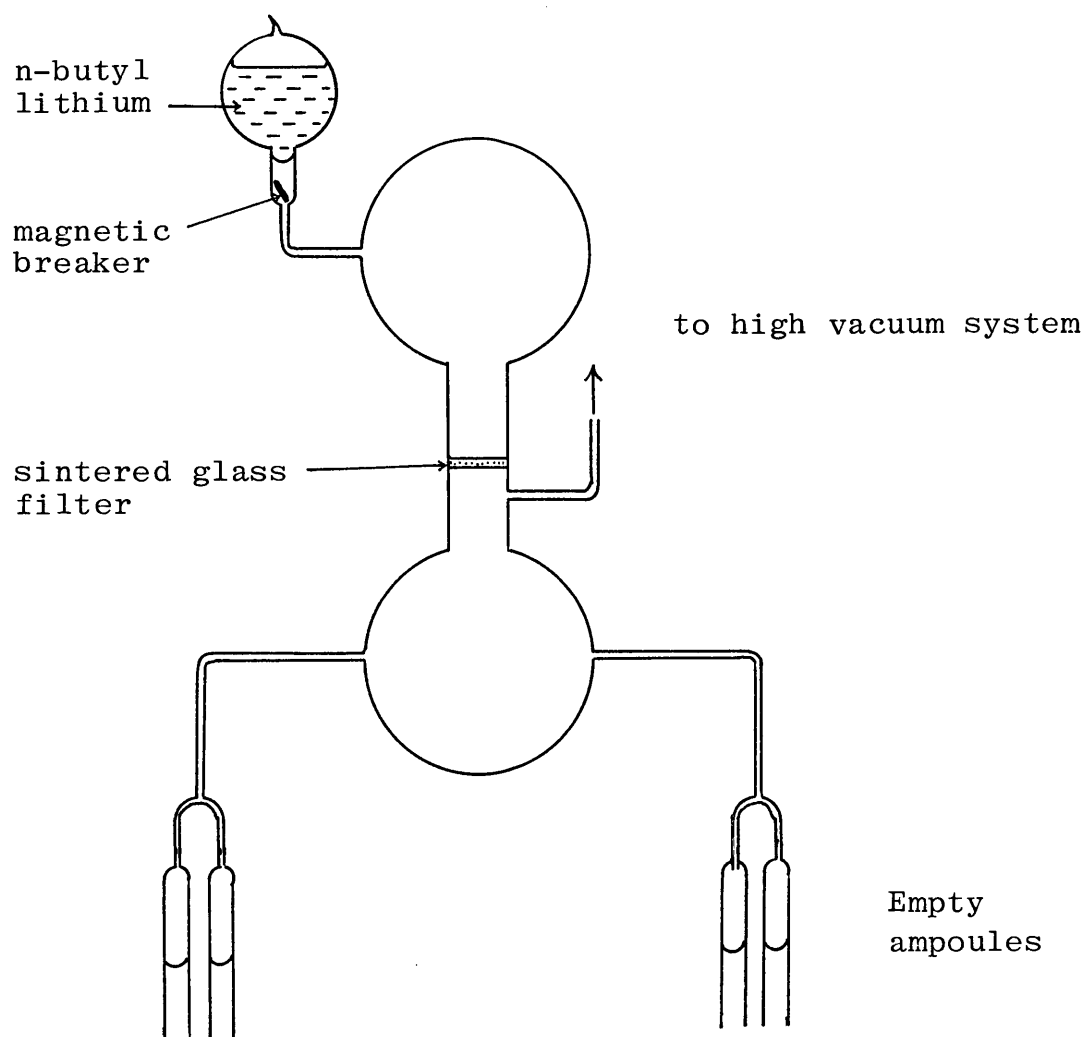


Fig 2.3 - The apparatus for the purification  
of n-butyl lithium solution

chloride was filtered off, and  $\text{LiBPh}_4$  was precipitated by addition of cyclohexane. This was filtered and dried in vacuo.

#### 2.2.12 Sodium and Potassium

The central portion of metal sticks was obtained by trimming and was twice distilled under vacuum. Special distillation tube with a number of constrictions and two lobes was designed and additional care was taken to exclude paraffin contamination. (Fig 2.4)



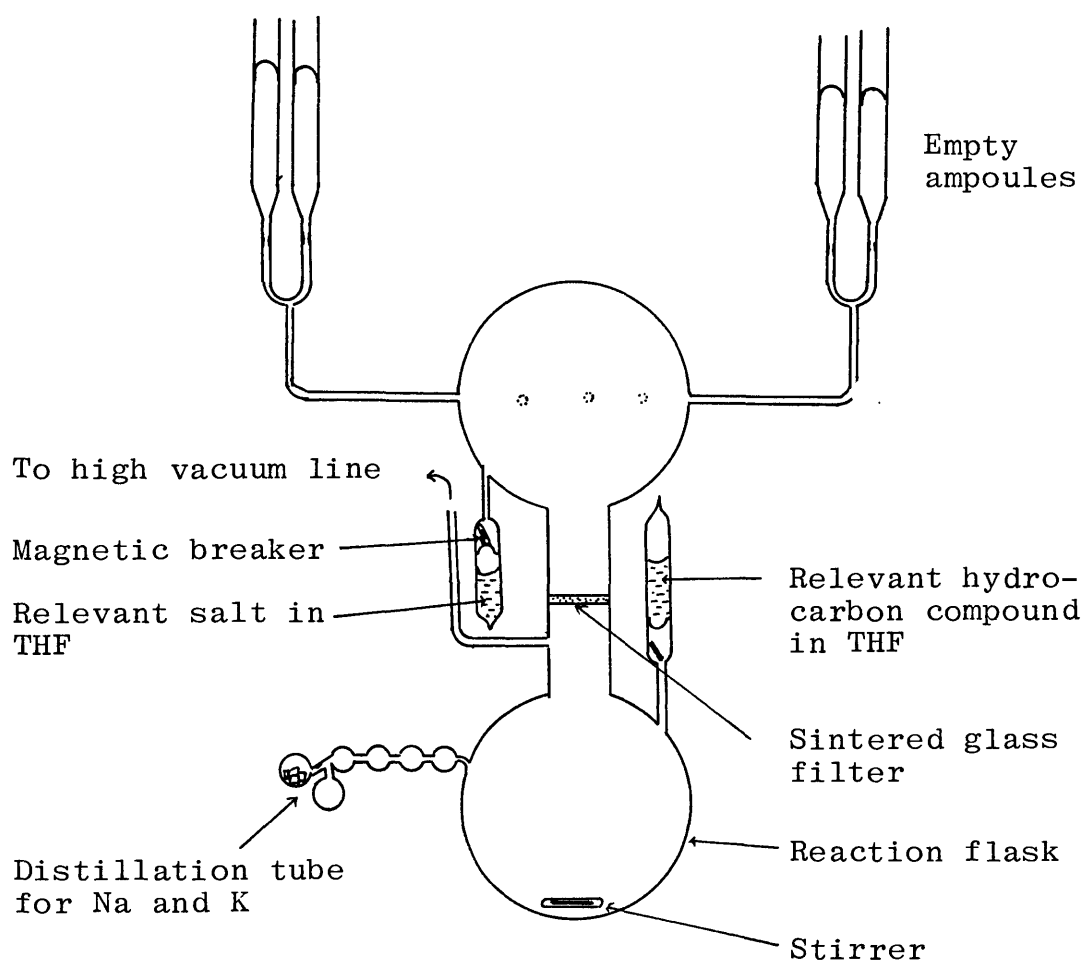
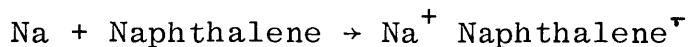


Fig 2.4 - The apparatus for the preparation of initiator solutions

- (i) Sodium naphthalene
- (ii) Sodium  $\alpha$ -methyl styrene
- (iii) Fluorenyl sodium
- (iv) Potassium  $\alpha$ -methyl styrene
- (v) Fluorenyl potassium

## 2.3 Preparation of Initiator Solutions

### 2.3.1 Naphthyl Sodium (Sodium Naphthalenide)



1	1 mole	1 mole
mole		

Reagents were purified as detailed in the previous section. The all-pyrex apparatus used was baked in a glass annealing oven overnight.

0.1 g of naphthalene placed in an ampoule was dissolved in 5 ml of tetrahydrofuran, distilled directly on to it under vacuum and the ampoule was sealed off. Similarly, 0.3 g of Sodium tetraphenyl boride was incorporated into an ampoule. They were fused to the apparatus which in turn was fused to the vacuum line. Making sure that all joints were leak-proof by a high voltage leak detector, the side tube was cut, 1.0 g of sodium was introduced and refused. The whole unit was flamed thoroughly while being evacuated (Fig 2.4).

Establishing a steady vacuum of less than  $10^{-4}$   $\mu$  of Hg, sodium in globe one was distilled through globe two and four constrictions, finally making a continuous mirror. The sodium tube was then sealed off. 60 ml of THF was distilled directly from the strong blue  $\text{K}^+$  solution on to the sodium mirror and the apparatus was sealed off, at liquid  $\text{N}_2$  temperature. After thawing, naphthalene solution was run into THF by crushing the breakseal while rapidly stirring magnetically. The appearance of the characteristic green colour was instantaneous and deepened with time. The

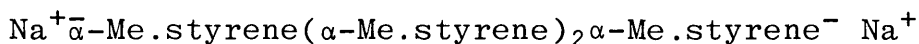
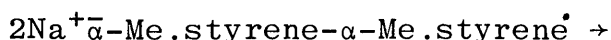
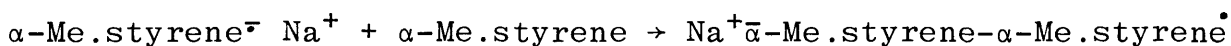
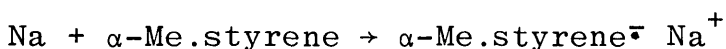
reaction was allowed to proceed for 6 hours at room temperature. Pyrex glass encapsulated magnets were used as breakers and stirrers. By inverting the apparatus, the solution was filtered through sintered glass to remove excess sodium.

Five ampoules were filled to the predetermined levels by tilting the apparatus and were sealed off. The sodium tetraphenyl boride solution was run into the rest of the solution and remaining ampoules were sealed off with required amounts. Strength of the initiator solution was determined by acid titration. The ampoules were stored at 250 K until used in polymerisations.

### 2.3.2 $\alpha$ -Methylstyryl Sodium

#### Preparation of concentrated tetramer

This was prepared by a method similar to that by Szwarc (111).



An apparatus similar to that given in Fig 2.4 was used.

$\alpha$ -methylstyrene was distilled once more on to  $\text{CaH}_2$  and after 4 hours of constant stirring under vacuum, 3.0 ml of it was incorporated into an ampoule. By following the method described in the previous preparation, dark red coloured anion was readily obtained. Reaction was carried out for 4 hours at room temperature with a steady rate of stirring, at the end of which the solution was filtered through

sintered glass and the tetramer was incorporated into capsules. The concentration of the tetramer solution was determined by opening a capsule in 50 ml of distilled water and titrating against 0.1 N HCl.

#### Preparation of Initiator Solution

Using the apparatus in Fig 2.5, the concentrated tetramer of  $0.0943 \text{ M/dm}^3$  was made into a dilute solution of  $0.9259 \times 10^{-2} \text{ M/dm}^3$  by dilution of 10 ml of tetramer with 72 ml of THF. All respective ampoules, including that of 0.35 g of sodium tetraphenyl boride, and an extra capsule of concentrated tetramer for "cleaning" were fused to the "octopus" with 16 ampoules. Following the usual technique starting from flaming under vacuum, THF was distilled and the apparatus was sealed off at  $10^{-5} \mu \text{ Hg}$ . The tetramer capsule in Section B was used for final cleaning of the apparatus and the THF. Leaving for 1 hour to react with any undesirable substances, the solution was transferred to flask B. Followed by washing with pure solvent and transferring to flask B, THF was redistilled to flask A and was sealed off at liquid  $\text{N}_2$  temperature.

After opening the initiator and salt ampoules, the apparatus was inverted a few times and the solution was well-mixed. Sealing of ampoules with required amounts was done carefully at room temperature in the shortest possible time to minimise changes in concentrations. It was possible to seal off an ampoule in 5 - 8 seconds. Sealing at room temperature was preferred over any effort to cool ampoules, because of the error introduced by the change in

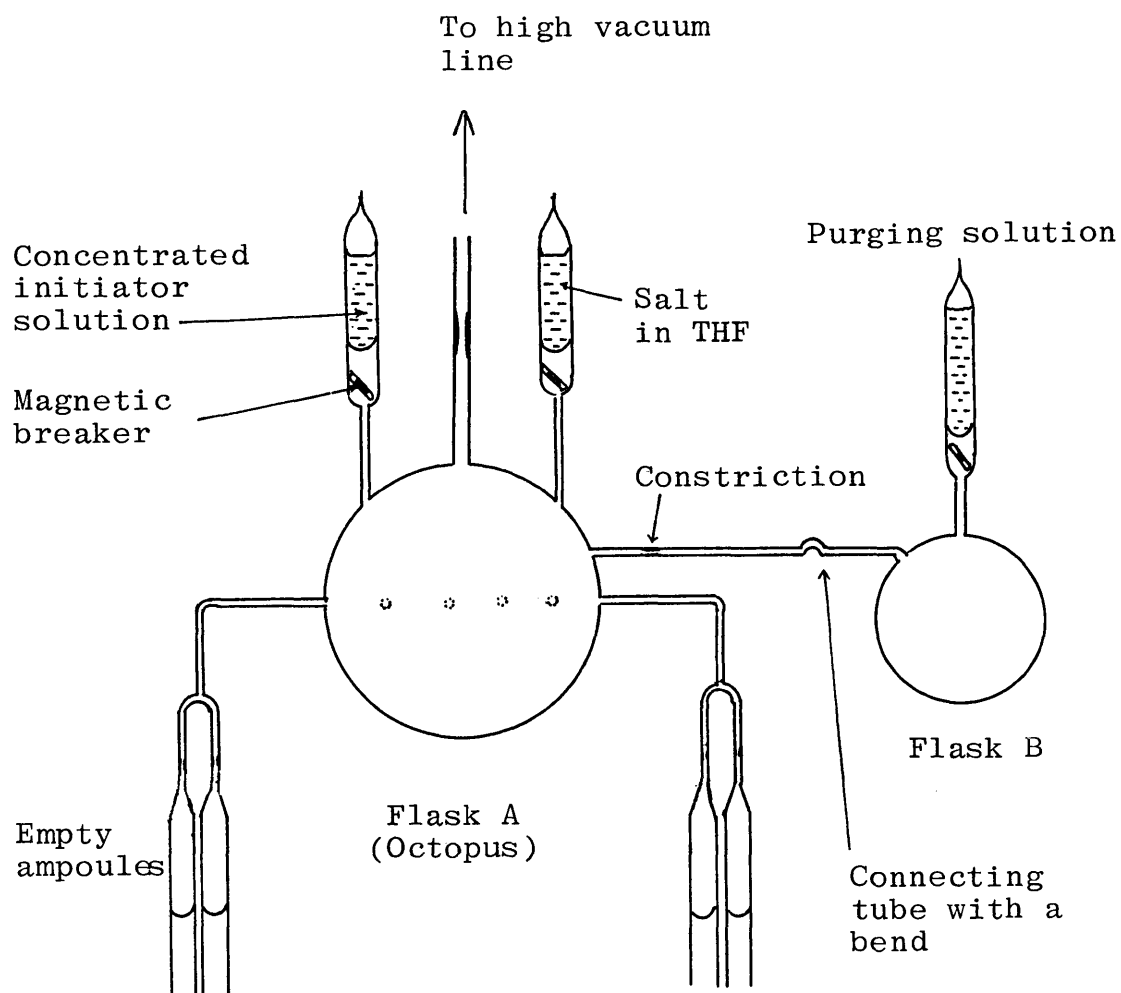


Fig. 2.5 - The apparatus for the dilution of  
initiator and incorporating into  
ampoules

concentration, which would be very considerable. The ampoules were stored at 250 K immediately.

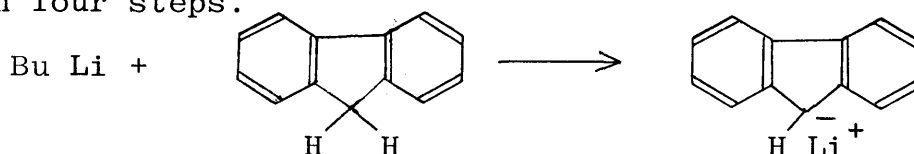
### 2.3.3 $\alpha$ -Methylstyryl Potassium

3.0 ml of  $\alpha$ -methylstyrene was reacted with 1.0 gram of Potassium in THF, following the same method and using a similar apparatus. (Fig 2.4 and 5) The dull red colour of  $\alpha$ -methylstyryl potassium developed immediately.

The concentrated solution of the tetramer obtained was 0.2118 M. 2.01 ml of this was diluted with 48.0 ml of THF to make a final solution of  $8.5 \times 10^{-3}$  M/dm<sup>-3</sup>. After separating some ampoules, 0.72 g of well dried potassium tetraphenyl boride in THF was added, but most of it remained undissolved making it necessary to dispense into capsules as a suspension. The ampoules were stored at 250 K until further use.

### 2.3.4 Fluorenyl Lithium

Fluorenyl lithium was prepared by a method similar to that by Evans and Rees (126-8) by direct reaction of fluorene with n-Butyl lithium in toluene. This was done in four steps.



- (i) Purification and encapsulation of n-Bu Li (Fig 2.3)
- (ii) Replacement of solvent medium n-hexane with toluene (Fig 2. 6) and reacting with fluorene (Fig2.6b)
- (iii) Separation of Fl.Li. crystals and drying and dissolution in THF

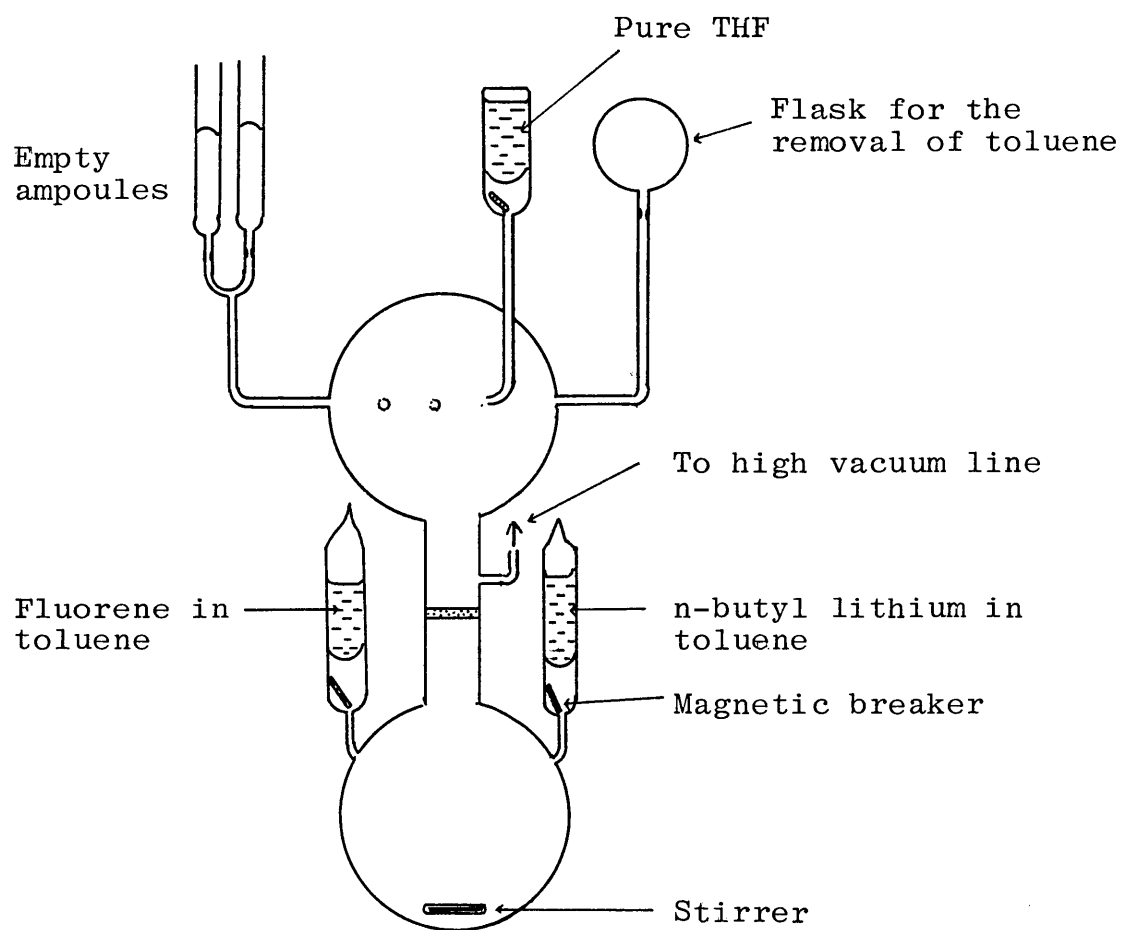


Fig 2.6.b - The apparatus used for the preparation of fluorenyl lithium

(iv) Preparation of initiator solution of required strength.

The n-Bu-Li was encapsulated as described earlier. This was fused on to another vacuum apparatus and hexane was replaced with pure toluene by distilling off hexane and opening the ampoule of toluene to give a n-Bu Li concentration of  $3.16 \text{ M dm}^{-3}$ . Ampoules with 10.0 ml of this solution, 3.2 g of fluorene in 40 ml of toluene and 38 ml of THF were all fused to the apparatus (Fig 2.6). Following the usual flaming and other vacuum procedures, the apparatus was sealed off at  $10^{-5} \mu \text{ Hg}$ . The fluorene and n-Bu Li were run in by crushing the breakseals and, with constant stirring, the reaction was carried out for 3 days, at room temperature. Pale yellow liquid, which turned orange, gradually started separating out light yellow crystals. At the end, the Fl-Li crystals were filtered off by inverting the apparatus and were washed with pure toluene by condensing it on the inside wall. The crystals were vacuum dried and frozen toluene was sealed off, at liquid  $\text{N}_2$  temperature. On entering THF the colour of the crystals turned deep orange and readily dissolved to give a dark red solution of  $0.4848 \text{ M dm}^{-3}$ . The ampoules of this, 8.0 ml and 2.3 ml respectively, were connected to the apparatus (Fig 2.5), and following the same technique as in the earlier preparation, 18 ampoules of diluted initiator solution of strength  $0.0153 \text{ M dm}^{-3}$  and light orange colour were separated off. Salt was not incorporated into the bulk solution. The ampoules were stored at 250 K in darkness.



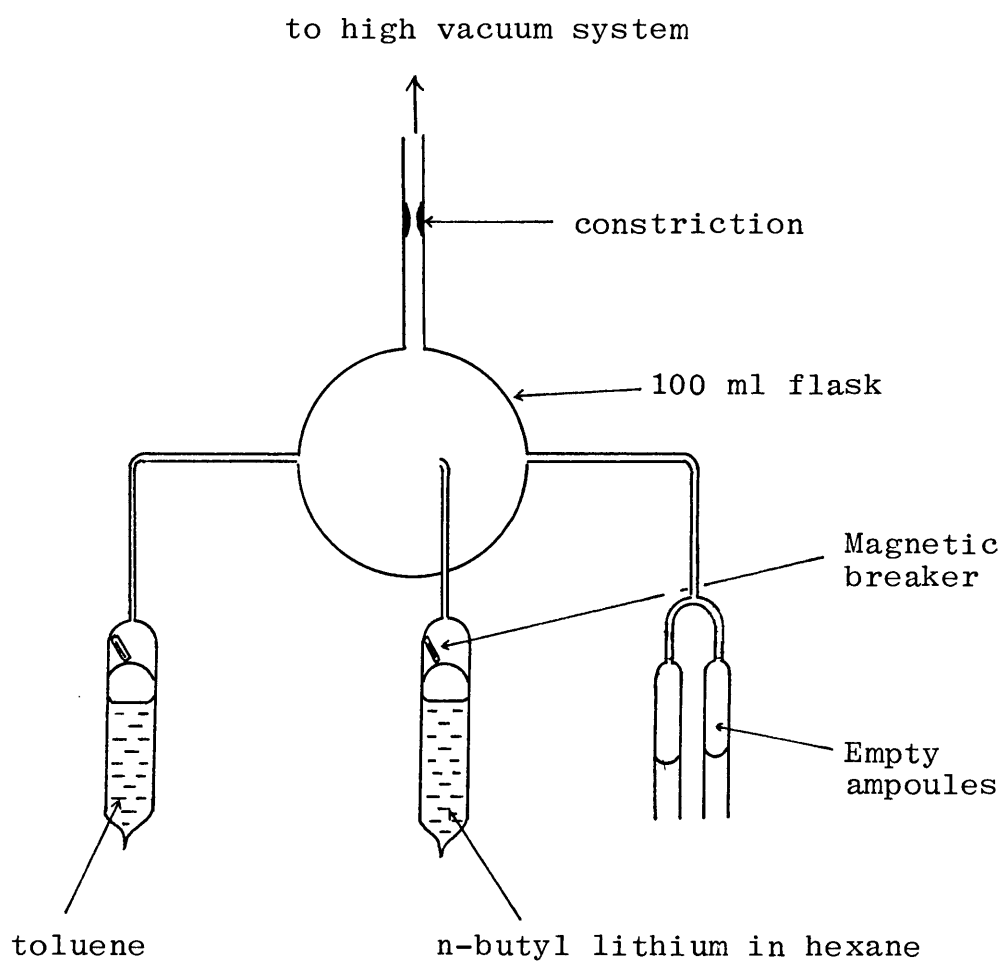


Fig 2.6 - The apparatus for the replacement of solvent  
hexane with toluene in n-butyl lithium  
solution

### 2.3.5 Fluorenyl Sodium

This was prepared by a method similar to that for the preparation of Naphthyl sodium, by direct metalation, using identical equipment (Fig 2. 4).(127)

1.11 g of purified fluorene was reacted with the Na mirror at room temperature for 24 hours with constant stirring. The reaction was extremely slow compared with the former and the colour developed gradually from colourless through pale yellow to orange.

The concentrated F1 Na obtained had a concentration  $0.0685 \text{ M dm}^{-3}$ . 12.0 ml of this solution was made to 100 ml of  $7 \times 10^{-3} \text{ M dm}^{-3}$  by diluting with THF. After sealing off 4 ampoules, 0.22 g of NaBPh<sub>4</sub> in 4 ml of THF was added and the rest of the ampoules were sealed off. The ampoules with clear yellow solution were stored at 250 K.

### 2.3.6 Fluorenyl Potassium

The fluorenyl potassium was prepared following exactly the same method as above for F1 Na. 1.082 g of fluorene was reacted with the potassium mirror in THF. The reaction was very rapid, unlike with Na, giving a deep orange colour. After 24 hours, the solution was brownish red. 5.0 ml of this was diluted with 92.0 ml of THF to obtain a final concentration of  $3.1481 \times 10^{-3} \text{ M dm}^{-3}$ . Five ampoules were separated without salt and 0.102 g of potassium tetraphenyl boride was added to the rest of the solution. Most of the salt remained insoluble. With some effort, the salt was kept as a suspension and was incorporated into ampoules. They were stored at 250 K.

## 2.4 Polymerisation Procedure

The apparatus used is shown in Fig 2.8. Basically this is a 250 ml pyrex round-bottomed flask with a drawn neck of 14 mm and three or four 10 mm inlet tubes, three-quarters of the way up the flask, equipped with a magnetic stirrer. In comparative studies for the determination of the fraction of termination before polymerisation due to impurities, a separate section with a flask and an inlet tube horizontally connected by a tube with a half-loop was used. All pyrex apparatus was washed with distilled water and baked in a glass annealing oven at a maximum of 600° C overnight.

After a steady vacuum of  $10^{-4}$  -  $10^{-5}$   $\mu$  was achieved, the required ampoules, viz methanol, initiator and one or two MMA ampoules depending on the mode of initiation, were fused to the reaction vessel incorporating magnetic breakers for breakseals, in that order. The order of fusing the ampoules to the reaction vessel is important for minimising the exposure of MMA and initiator to light and ambient temperatures. They were kept at sub-zero temperatures while being fused. Finally the apparatus was fused to the vacuum line and was thoroughly flamed. Throughout the procedure, the ampoules were kept enclosed in dry ice and covered until the polymerisation was effected, except for a short time which was necessary to evacuate the trapped moisture. The calculated amount of THF was distilled directly from the blue solution of THF/Na/K which had been intact for more than 7 days. With the help of a scaled, precalibrated side tube, it was possible

to distil off a required amount within an accuracy of  $\pm 2$  mls. The THF was frozen at liquid  $N_2$  temperature and at a vacuum of  $10^{-4}$  -  $10^{-5}$   $\mu$  and the reactor was sealed off from the vacuum line. On thawing, the breakseal of the initiator capsule was crushed by magnetic breaker and the whole unit was washed with the solution by tilting. Initiator adhering to the inside surface was washed down with pure solvent by cooling the outside with cottonwool pads dipped in liquid  $N_2$ .

Where an additional ampoule of initiator was used for "cleaning", the whole solution and washings were transferred to the flask B (Fig 2.8) and pure solvent was distilled back. The flask B was sealed off and the real initiator was introduced by crushing the breakseal. Keeping the reactor in the tall, thermally insulated low temperature dry ice/acetone bath, the temperature was brought to the required level, while stirring continuously (Fig 2.7). Depending on the mode of initiation, polymerisation was done in two ways, viz

- (1) Single initiation method
- (2) Double initiation method

(1) Single Initiation Method

To the rapidly and constantly stirred initiator solution at 196 K, the MMA solution which had been kept at the same temperature was introduced at once by crushing the breakseal. After the required length of time throughout which the temperature and rate of stirring was kept constant, methanol was added, terminating the living ends.

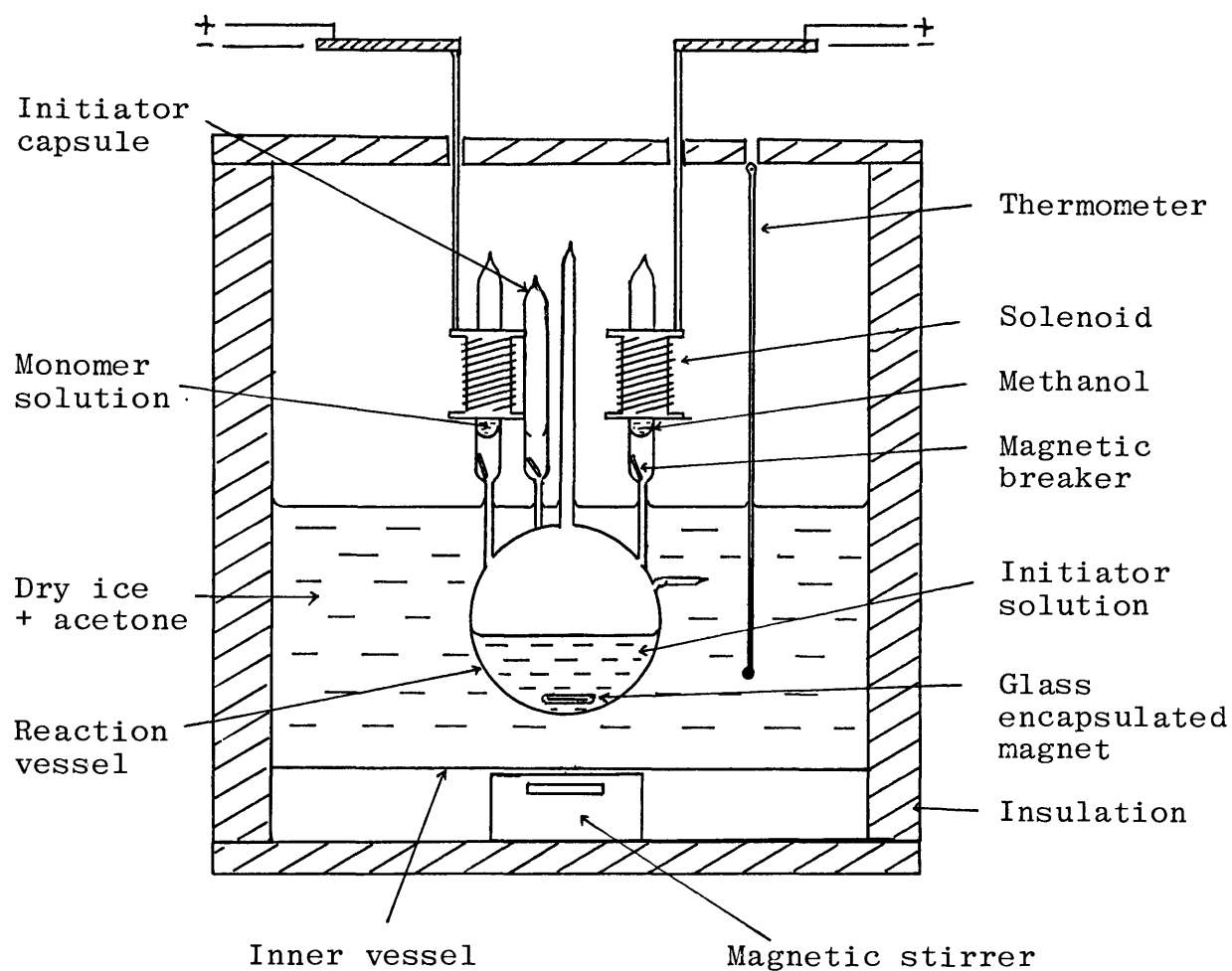


Fig 2.7 - The apparatus used for the kinetic studies  
of anionic polymerisation of Methylmethacrylate

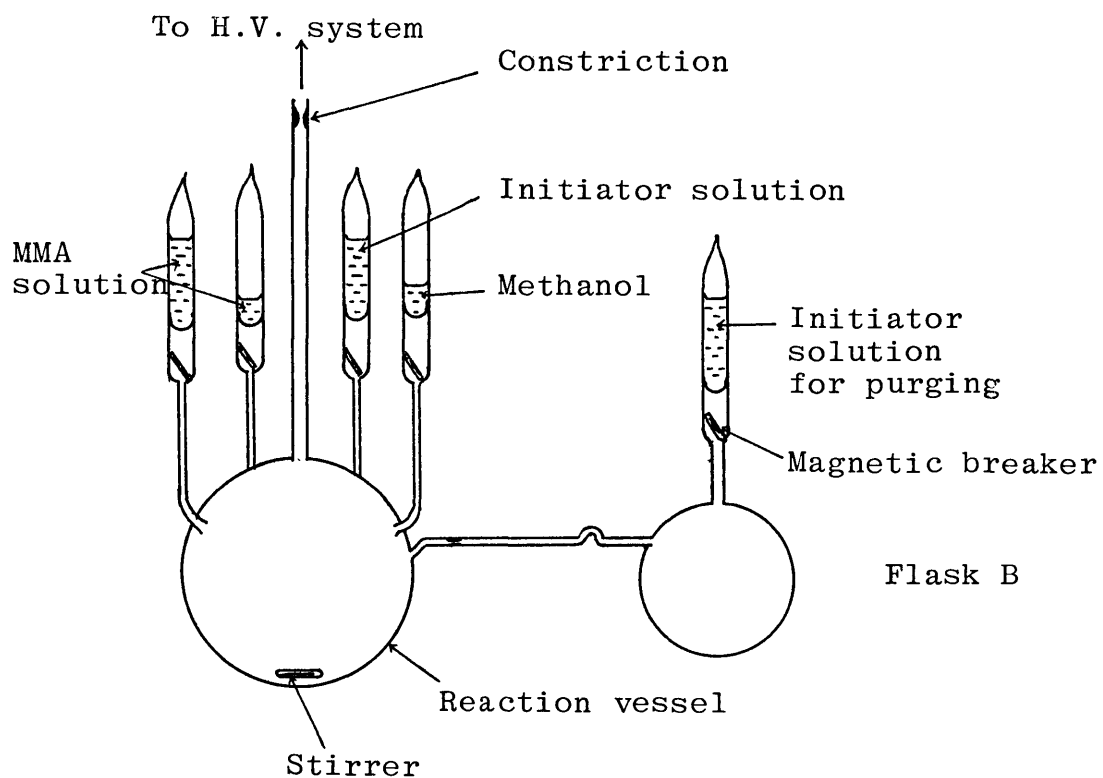


Fig. 2.8 - The apparatus used for the anionic polymerisation of methylmethacrylate by double initiation

The apparatus was opened to the atmosphere at room temperature. The volume of polymer solution and that of each ampoule was measured accurately, the latter with a 10 ml burette. The polymer was separated by vacuum evaporation and was dried in vacuo at 315 K for 24 hours and weighed.

The accurate measurement of volumes of the initiator and monomer solutions is important. The original concentrations of the monomer and initiator in the reaction mixture are calculated from their volumes in the respective ampoules. Accurate measurement of concentrations is necessary for the calculation of expected molecular weights as well as for kinetic studies. Since the dilution factor is normally about 10, even a small error in measurement is magnified by the same factor. To overcome this, the ampoules were placed in a fixed vertical position and the menisci were marked at room temperature. After the polymerisation, they were separated and filled with acetone to the same level in the same position from a 10 ml microburette and the volume was read.

## (2) Double Initiation Method

In this method, instead of adding all the monomer to the initiator solution at once, approximately 8 - 10% was added at first. This was kept in a separate ampoule and after breaking the seal, allowed to react for 5 minutes, at the initiation temperature (Fig 2. 8). While keeping the temperature at the desired level, the bulk of the monomer was added to this solution and the polymerisation

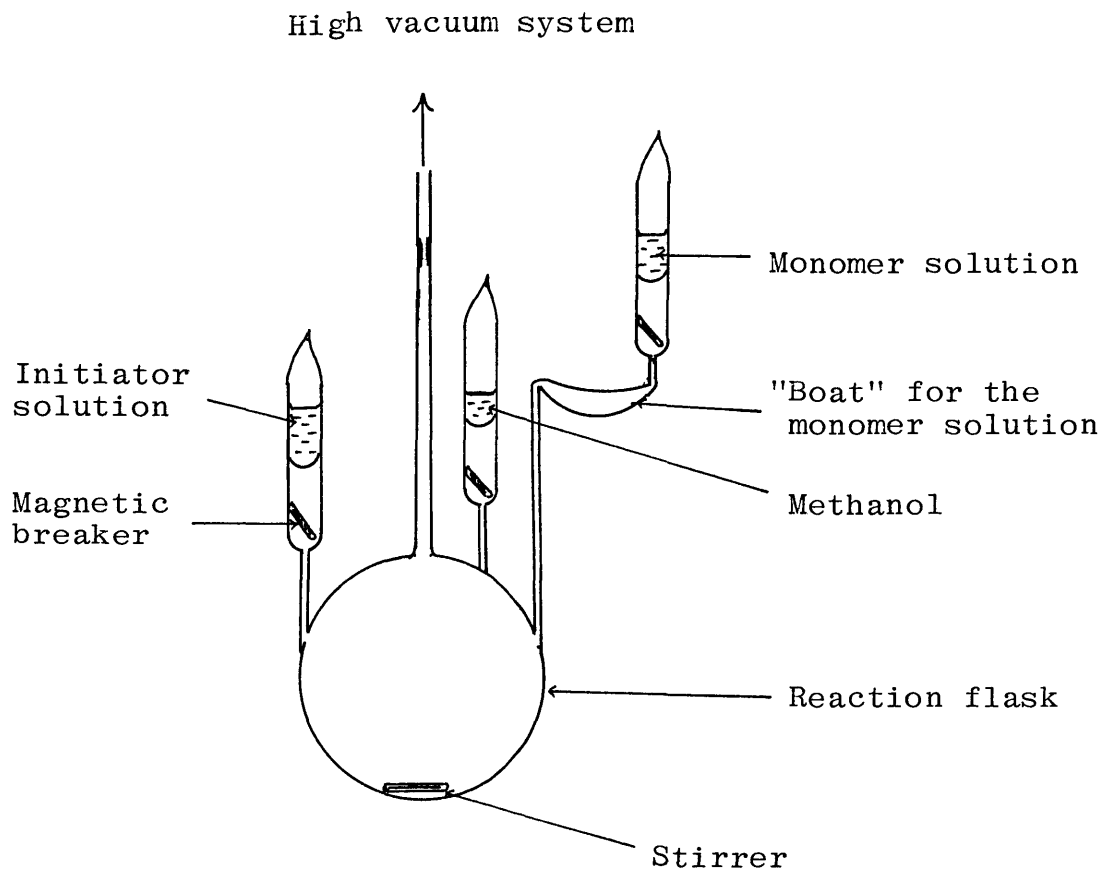


Fig 2.9 - The apparatus used for the anionic polymerisation  
of methyl methacrylate by continuous addition of  
monomer



was carried out for 30 minutes. The termination, separation of polymer and measurement of quantities were carried out as above.

(3) Slow continuous addition of monomer

In the third method, instead of adding the bulk of the monomer solution after initiation, it was added slowly and continuously (Fig 2.9). The initiation was carried out as in the double initiation method, by adding approximately 8-10% of the monomer solution to the initiator solution kept at the desired temperature. This was achieved firstly by freezing the monomer capsule before opening and allowing the monomer solution to collect in the "boat" as it thawed and then tilting the apparatus slightly without disturbing the stirring. The careful design of the apparatus as well as freezing of the monomer solution were both necessary to facilitate convenient transfer of the monomer and to stop forceful suction of it at the moment of opening on to the initiator solution at 195 K.

After reacting for 5 minutes, the rest of the monomer was added slowly at a rate of approximately 0.5 ml/minute. The termination, separation of polymer and measurement of quantities were carried out as above.

## 2.5 Kinetic Studies

All initiator and monomer solutions used in kinetic studies were freshly prepared, and for every set of experiments, reagents from the same single batch were used.

In an effort to avoid all premature terminations caused by external factors, the batch method was used instead of conventional continuous one, where samples from reacting mixtures are drawn at specific time intervals. Thus for every predetermined interval or time from 0.5 - 360 secs, a separate polymerisation step was carried out. The initiator and monomer concentrations were kept constant within practically possible limits.

Experiments were performed in stirred glass reactors under vacuum (Fig 2.7). This is essentially similar to the normal polymerisation reaction vessel described earlier, and was equipped with a glass encapsulated stirrer magnet. The monomer and methanol ampoules were made with the same dimensions, incorporating magnetic breakers of equivalent weight and dimensions. They were fused to the reactor with tubes of exactly the same size, maintaining the breakseals at the same level.

The ampoules were centrally placed in powerful solenoids of equal field strength, made into aluminium housing. When activated, these could instantly throw the magnetic breakers against fragile breakseals, simultaneously switching on or off the timer accordingly. The complete system was housed in a thermally insulated box with a facility for dry ice/acetone bath, immersion heaters, and was fitted

with a powerful magnetic stirrer at the bottom.

The purification and cleaning procedure detailed elsewhere was strictly adhered to. The monomer kept at 195 K was added to rapidly stirred initiator solution in pure THF kept at the same temperature by activating the solenoid and hence the timer. After the required length of time, methanol was added by the same method and the time was recorded. By making the reactor assembly as detailed earlier, the rate of entry of reagents was kept equal.

The conversion and rate of reaction were measured gravimetrically by evaporating the polymer solution to dryness. The polymer was finally dried under vacuum at 315 K until constant weight was achieved.

Each sample was characterised with respect to molecular weights and molecular weight distribution by gel permeation chromatography.

## 2.6 Termination Studies

The study of termination reactions of polymethylmethacrylate anion was carried out in two sets of experiments. In the first set, single ended initiator fluorenyl sodium in concentrations of approximately  $3 \times 10^{-3} \text{ M dm}^{-3}$  in THF was used with  $10^{-3} \text{ M dm}^{-3}$  sodium tetraphenyl boride. The apparatus used was similar to that described under the polymerisation techniques (Fig 2.8). A separate cleansing step with an ampoule of fluorenyl sodium was carried out just before every reaction.

To the rapidly stirred solution of fluorenyl sodium at 200 K, the small ampoule of monomer was crushed open. This was approximately 10% of the total monomer concentration. After 5 minutes, the temperature of the bath was rapidly increased to 220 K with the help of two 2000 W heating elements and the bulk of the monomer was added. After 30 minutes, the reaction was terminated with methanol and the polymer was isolated as usual. Following exactly the same procedure, other reactions were carried out at 245 K and 256 K.

In the second set of experiments, different initiator systems with a variety of anions and cations were used, viz, naphthyl sodium,  $\alpha$ -methyl styryl potassium, fluorenyl sodium and fluorenyl lithium. In this, the monomer was added to initiator at 200 K and after reacting for 30 minutes at the same constant temperature, it was stored at 253 K for 12 hours. The second polymerisation was effected in the same system by lowering the temperature to

200 K and introducing an equal amount of monomer by crushing the breakseal. After 30 minutes, methanol was added to terminate the reaction and the polymer was recovered as above. One control experiment was carried out without the addition of a second monomer aliquot but terminating at the end of 12 hours at 253 K.

The polymers were characterised with respect to molecular weight and molecular weight distribution by gel permeation chromatography.

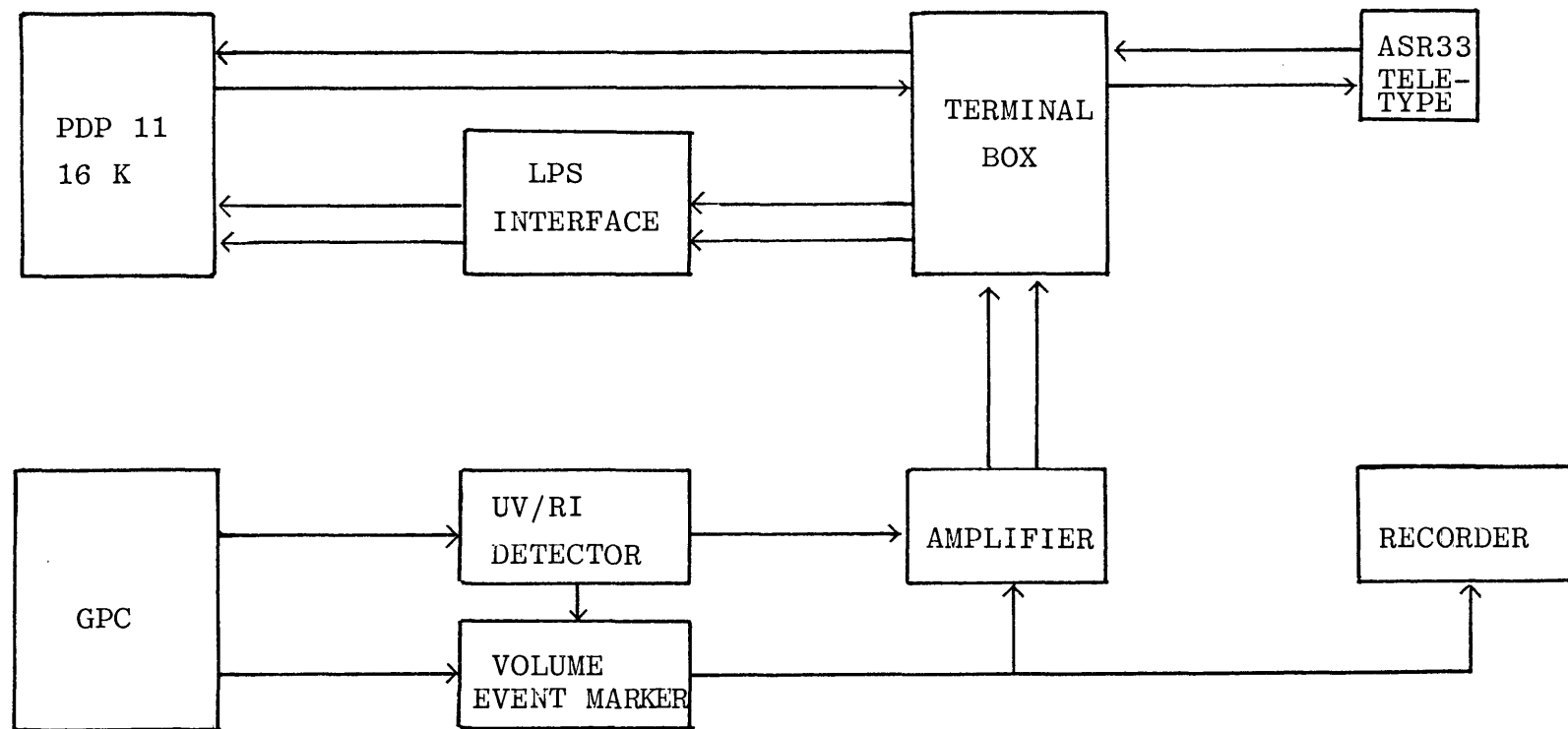


Fig 2.10 Schematic diagram of GPC and Computer Units

## 2.7 Polymer characterisation and analysis

(Measurement of MWD and molecular weight averages)

### 2.7.1 Gel permeation chromatography (GPC)

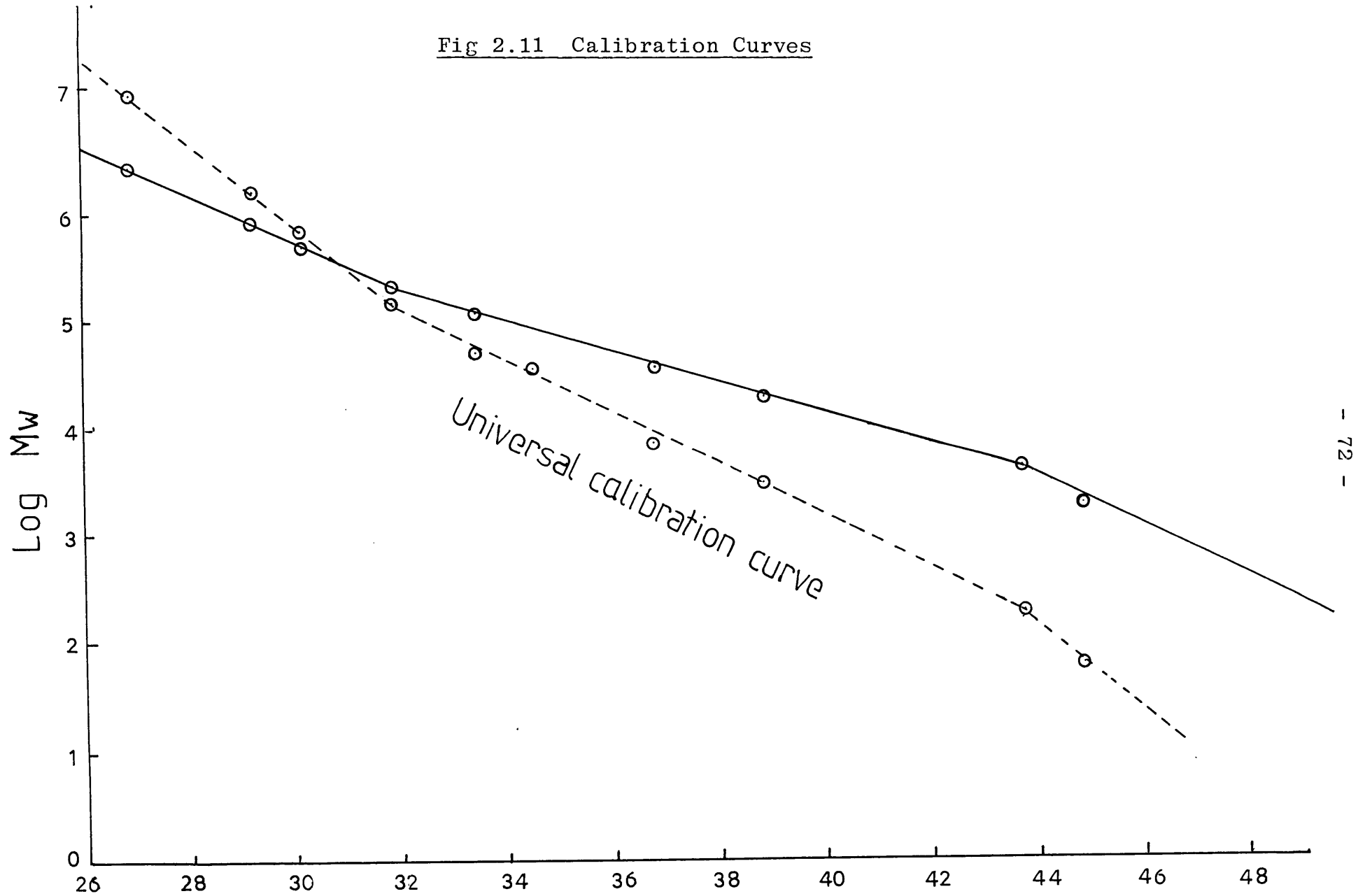
The most important tool used for the characterisation of polymers was GPC. The GPC chromatograms were obtained as instrument recordings and  $M_n^-$ ,  $M_w^-$ ,  $M_v^-$  and dispersity index were calculated from these following a method developed by Chaplin (112) (113).

The GPC unit was constructed from individual Waters Associates modules namely 6000 A precision pump U6K injector and R-400 differential refractometer coupled to a series of 5 columns also made by Waters Associates. The columns contained  $\mu$ -styragel packing with nominal exclusion limits of  $10^5$ ,  $10^4$ ,  $10^3$ , 500 and 100 Å<sup>0</sup>. These were housed in a thermally insulated box and the complete unit was operated in an air conditioned, thermostatted room. The solvent volume was monitored using a volume-event marker which caused a 10 mV signal spike at 5 ml intervals, to be superimposed upon the output voltage of the detector. The detector voltage (0 - 100 mV) was amplified 10 times before feeding into the recording unit of the computer system via a LPS-11 laboratory peripheral system (Fig 2.10).

The computer had been preprogrammed to commence recording at the initiation of a schmidt trigger. The chromatograms were recorded in a magnetic tape. By recording 10 elution volume units on either side of the peak eluting at 2 ml/minute it was possible to store 5 chromatograms per cassette.

The solvent THF used was distilled from CaH<sub>2</sub> and potassium

Fig 2.11 Calibration Curves





metal in turn and filtered through 0.45  $\mu\text{m}$  filter before use. BHT antioxidant was added to give 25 ppm and the solvent was kept under a dry  $\text{N}_2$  blanket in the instrument reservoir. It was necessary to use fresh solvent every second day even with the above precautions in order to obtain consistent and accurate results. Polymer concentrations of approximately 0.2% w/v were employed. The dissolution of polymers was allowed for 24 hours and the polymer solution was filtered three times through 0.45  $\mu\text{m}$  micropore filter before injecting into the unit. General sample size injected was varied from 100-400  $\mu\text{l}$ .

### Calibration

The generally accepted basis of hydrodynamic volume of polymer chains in solution was used to establish the universal calibration curve (105) (Fig 2.11) and the correction method of Dawkins (104) which includes a term for the excluded volume of polymer chains was applied to the universal calibration equation.

In this method, it was required to make GPC and viscosity measurements for a series of broad MWD polymers of PMMA and polystyrene and to construct the calibration curve from it. The well-characterised polydisperse PMMA standards supplied by Scientific Products, New York and Rohm and Hass (Aus) Ltd were used to calculate the Mark Houwink parameters  $k$  and  $a$ , over the range of molecular weights under study, ie 600 - 200,000. Initially the Mark Houwink constant  $a$  was calculated from intrinsic viscosity data and this was combined with GPC data and osmometric data to

measure the Mark Houwink constant  $k$ . When the Mark Houwink constants are known, the molecular weight of the sample  $M_2$  at any given elution volume can be easily calculated from the following equation:

$$M_2 = \left[ \frac{k_1}{k_2} \right] \frac{1}{a + 1} M_1 \left[ \frac{a_1 + 1}{a_2 + 1} \right]$$

where  $M_1$  is the molecular weight of the standard and subscripts 1 and 2 refer to the standard and the polymer respectively.

#### Calculation of molecular weight averages

The molecular weight averages were calculated according to the following expression.

If the normalised function for MWD,  $W(M)$ , of a polymer sample is given by;

$$\int_0^{\infty} W(M) dM = 1$$

then, the  $k^{\text{th}}$  molecular weight average,  $M_K^-$  is given by the following expression:

$$M_K^- = \frac{\int_0^{\infty} W(M) M^{k-1} dM}{\int_0^{\infty} W(M) M^{k-2} dM}$$

where  $k = 1, 2, 3$  corresponds to the number average, weight average and Z average molecular weights respectively. The values of the integrals are found by numerical integration techniques such as Simpsons Rule. This method was suitable for narrow distribution polymers as well as broad distribution ones for obtaining accurate values of molecular weight averages.

The sequence of operations in a typical calculation of molecular weight averages of a polymer sample is as follows:

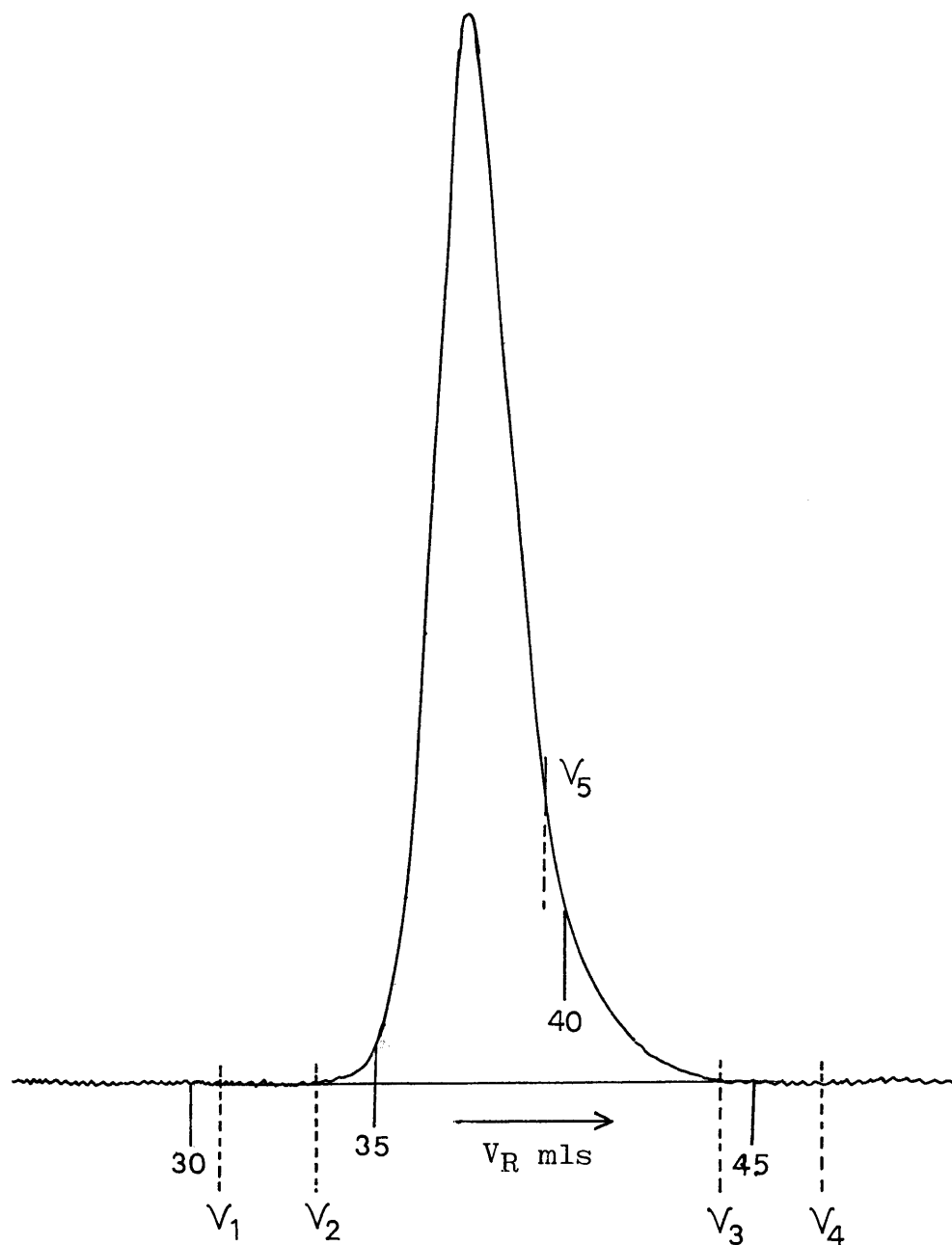


Fig 2.12 Typical gel permeation chromatogram  
Column packing:  $\mu$  styragel, Solvent : THF, Flow rate  
2.0 ml/min  
Detector : Differential refractometer (8 x)  
V = Retention volume

After initiating the programme (Appendix II), the sampling rate and the total number of data points required are entered. The latter is necessary to define the area of a peak, so that baseline fluctuations can be excluded and economical use of the tape can be made. The volumes  $V_1$ ,  $V_2$ ,  $V_3$ ,  $V_4$  and  $V_5$  (Fig 2.12) which can be read directly from the chromatogram are also entered.

The data from the cassette are then put into the main memory of the computer and calculation initiated between  $V_2$  and  $V_3$ . The baseline under the peak is calculated by plotting linear line through  $V_1$  to  $V_2$  and  $V_3$  to  $V_4$ , and then extending between  $V_2$  and  $V_3$ . This is subtracted from the apparent peak height values to obtain absolute peak heights. Using these values, the equation of  $M_{\bar{k}}$  was solved for  $k$  values from 1 to 3.

### 2.7.2 Visometry

Measurements were made with ubbelohde-type viscometers fitted with an electronic timing system at 298 K. Data at five concentrations up to 1 g/dl in THF were extrapolated linearly by Huggins and Kraemer method to a common intercept to find an accurate value for intrinsic viscosity ( $\eta$ ).

### 2.8 Tacticity Measurements

The high resolution nuclear magnetic resonance instrument was used to establish the sequence of monomer configurations along the polymer chains. NMR spectra were obtained on a Varian HA 100 spectrometer at 100 MHz. Polymers were reprecipitated in methanol, dried well in vacuo and dissolved in deuterated chloroform to make approximately 12% w/v solution. Tetramethyl silane was used as the internal standard. The structure was determined from relative areas under peaks due to methyl resonances. These are reported as percentage triads of isotactic, syndiotactic and heterotactic configurations following the Bovey's method (110). In an effort to obtain optimum resolution, some samples had been run at 330 K. Sweep time of 150 sec was normally used.

## CHAPTER 3 : RESULTS AND DISCUSSION

### Section 1 : The propagation of anionic polymerisation of Methyl methacrylate

#### 3.1.1 Propagation by PMMA<sup>-</sup>Li<sup>+</sup> ion pairs

##### 3.1.1.1 Kinetics

The kinetics of anionic polymerisation of MMA was investigated using fluorenyl lithium as the initiator. The initiation is known to be instantaneous (67). The narrow MWD polymers obtained and the observed linear relationship of fractional conversion versus number average molecular weight (Figure 3.2) show that no new chains are formed during the propagation. Hence the rate of initiation was assumed to be much faster than that of propagation. The conversion of the monomer was measured at different reaction times and the time versus conversion curve plotted according to the following integrated rate equation.

$$\ln \frac{[M]_0}{[M]_t} = k_{p(\pm)} [I] t \quad (1)$$

where  $[M]_0$  = initial monomer concentration in moles dm<sup>-3</sup>

$[M]_t$  = final monomer concentration at time t

$k_{p(\pm)}$  = rate constant of propagation for ion pairs  
in dm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup>

t = time in seconds

$[I]$  = concentration of living ends in moles dm<sup>-3</sup>

If the fractional conversion is x, expression (1) can be written as:

$$\ln \left[ \frac{[M]_0}{[M]_0 - x[M]_0} \right] = k_{p(\pm)} [I] t \quad (2)$$

$$\therefore \ln \left( \frac{1}{1-x} \right) = k_{p(\pm)} [I] t \quad (3)$$

The plot of  $\ln \left( \frac{1}{1-x} \right)$  vs time is given in Figure 3.1. The straight line plot shows that the concentration of reactive species does not change appreciably with the increasing conversion and the propagation reaction is first order with respect to consumption of monomer.

From the slope of the integrated rate plot the rate constant of propagation can be calculated if the actual concentration of initiator taking part in the polymerisation reaction is known.

Although throughout the polymerisation procedure, strict high vacuum techniques are adhered to, some termination of initiator cannot be avoided. The fraction of termination of initiator due to impurities in the reaction apparatus as well as the monomer solution could generally vary from 5% - 35% or more, when the amount of initiator used is between  $6 \times 10^{-5}$  to  $12 \times 10^{-5}$  moles. Hence the original concentration of the initiator may not be valid and the real concentration of initiator taking part in the reaction is calculated from the observed molecular weights of resultant polymers.

Table 3.1

Experimental data for the determination of rate constant of propagation by ion pairs,  $k_{p(\pm)}$  for  $\text{PMMA-Li}^+$  at 195 K in THF

Initiator - Fluorenyl lithium

$[\text{Li(Ph)}_4\text{B}] \quad 1 \times 10^{-3} \text{ m/dm}^3$

Expt No	$[\text{M}]_0$ moles $\text{dm}^{-3}$	$[\text{I}]_0 \times 10^4$ moles $\text{dm}^{-3}$	Fractional Conversion	Time sec	$\overline{M}_n$ GPC	Chromato gram
A-1	0.09	8.8	0.02	1.5	< 1000*	Fig 3.4
A-2	0.08	8.8	0.03	3.2	< 1000*	
A-3	0.08	8.4	0.065	10	$\approx 800^*$	
A-4	0.08	8.6	0.22	30	2200	
A-6	0.09	8.5	0.40	60	4540	

\*Molecular weights could not be calculated by GPC measurements, due to interference of the polymer peak over  $V_R > 50$  range.



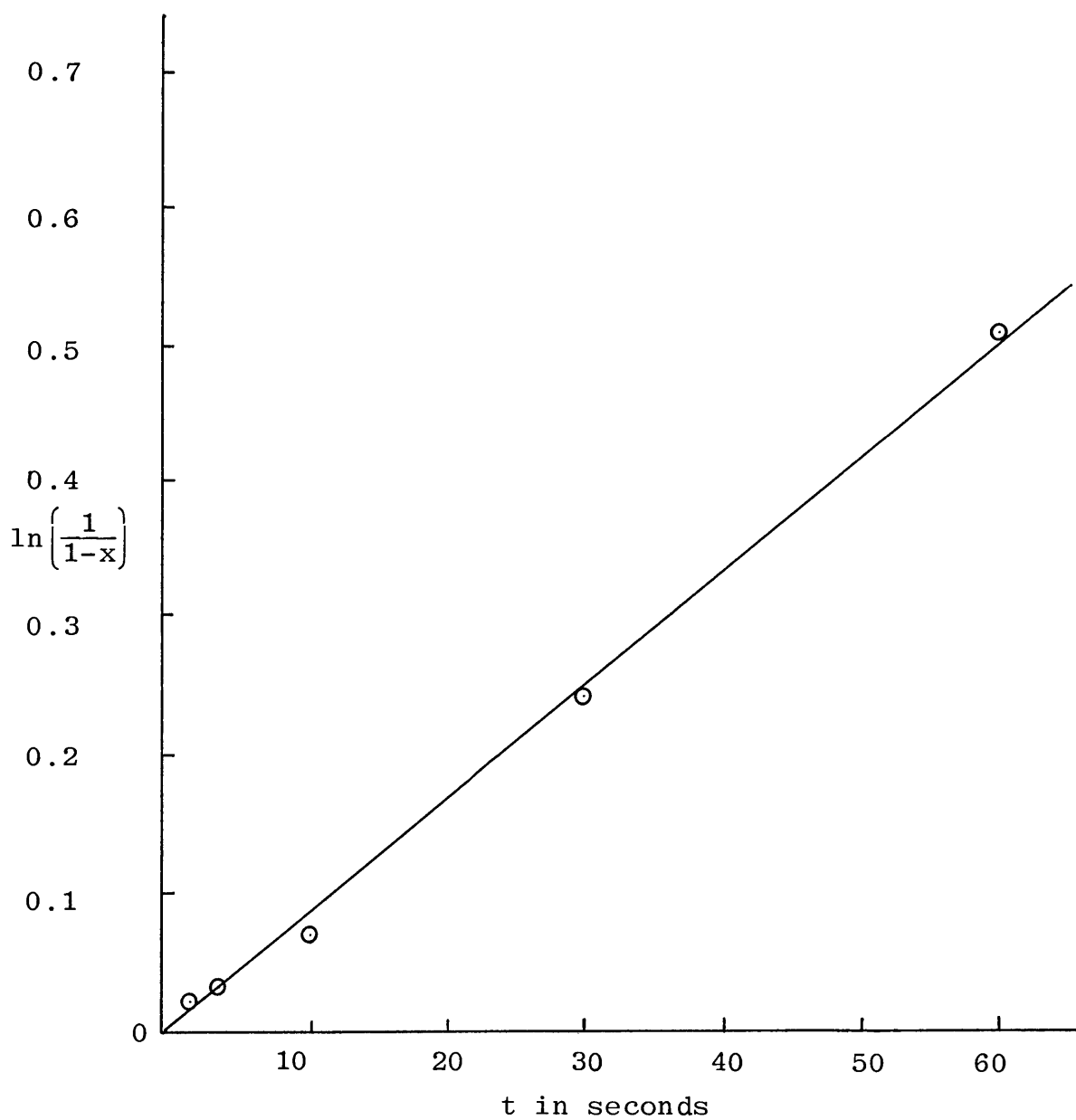


Figure 3.1 First order plot of conversion vs time for the polymerisation of methyl methacrylate in tetrahydrofuran with  $\text{Li}^+$  as counterion

Initiator - fluorenyl lithium

$[\text{I}]_0 \approx 8.8 \times 10^{-4} \text{ M/dm}^3$

Experimental data as given in Table 3.1

Table 3.2 The dependence of the number average degree of polymerisation on the fractional conversion.

Initiator = Fluorenyl lithium

$$[M]_0 = 0.08 \text{ M/dm}^3$$

$$[I]_0 = 8.8 \times 10^{-4} \text{ M/dm}^3$$

Expt No	Fractional Conversion $x_p$	$D_{pn}^-$ GPC
A-3	0.065	$\approx 8$
A-4	0.22	22
A-6	0.40	45.4
A-7	1.0	110

Table 3.3 The dependence of the polydispersity index on the fractional conversion for PMMA

Initiator = Fluorenyl lithium

$$[M]_0 = 0.08 \text{ M/dm}^3$$

$$[I]_0 = 8.8 \times 10^{-4} \text{ M/dm}^3$$

Expt No	Fractional Conversion	PDI	Chromatogram
A-3	0.065	$\approx 1.14$	Fig 3.4
A-4	0.22	1.14	Fig 3.5
A-6	0.40	1.16	Fig 3.6
A-8	0.84	1.09	Fig 3.7
A-7	1.00	1.07	Fig 3.10

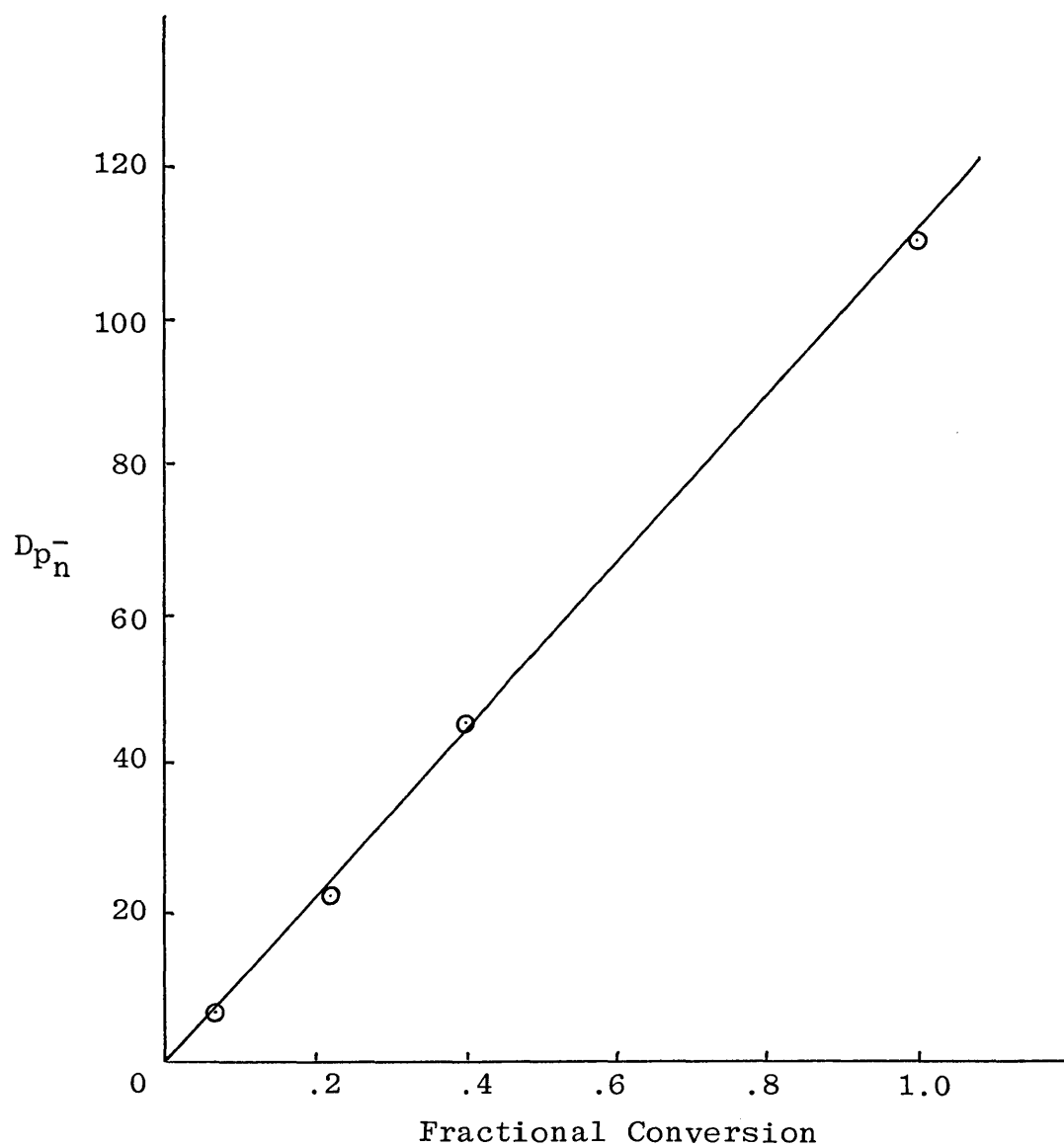


Figure 3.2 Dependence of the number average degree of polymerisation on the fractional conversion for the polymerisation of methyl methacrylate in THF.

Initiator = Fluorenyl lithium

Experimental data as in Table 3.2

For a monofunctional initiator in a terminationless process, the degree of polymerisation (number average)  $D_{pn}^-$  is related to the concentration of monomer  $[M]_0$  and the initiator  $[I]_0$  by the following expression:

$$D_{pn}^- = \frac{x_p \cdot [M]_0}{[I]_0} \quad (4)$$

where  $x_p$  = fractional conversion

$$\text{Hence } [I]_0 = \frac{x_p \cdot [M]_0}{D_{pn}^-}$$

Since the molecular weight distributions of resultant polymers are narrow, the above expression was used for the determination of the concentration of the initiator.

From the linear plot of  $D_{pn}^-$  vs  $x_p$  (Figure 3.2), by linear regression:

$$\text{slope} = \frac{55.7673}{.5028} = 110.9134$$

$$\text{From equation (4) slope} = \frac{[M]_0}{[I]}$$

$$\text{Since } [M]_0 = 0.085 \text{ moles dm}^{-3}$$

$$[I] = \frac{0.085}{110.9134} \text{ moles dm}^{-3}$$

Now, determining the slope of the integrated rate plot (Figure 3.1)  $k_{p(\pm)}$  can be simply calculated as follows:

$$\text{By linear regression: slope} = \frac{20.4}{2420.05}$$

$$\text{From equation (3) the slope} = k_{p(\pm)}[I]$$

$$\begin{aligned}\therefore k_{p(\pm)} &= \frac{20.4}{2420.05} \times \frac{110.9134}{.085} \\ &= 10.9994\end{aligned}$$

$$\therefore k_{p(\pm)} = 11.0 \text{ dm}^3\text{mol}^{-1} \text{ sec}^{-1}$$

The dependence of the number average degree of polymerisation on the conversion is given in Figure 3.2. The straight line plot shows that the degree of polymerisation increases linearly with conversion satisfying expression (4). This is evidence for the absence of chain transfer reactions that could effectively reduce the chain length. The relationship between the number average molecular weight and monomer concentration is also linear. (Figure 3.3 Table 3.4.) A three fold increase of monomer concentration ( $0.09 \text{ M dm}^{-3}$  to  $0.26 \text{ M dm}^{-3}$ ) results in only a little broadening of the molecular weight distribution being observed.

In general, the MWD of polymer samples is very narrow. In fact some samples produced at 195 K in THF show dispersity index values  $\approx 1.07$  or non-uniformity values  $< 0.1$  (Figure 3.10), with the number average molecular weight being equal to the theoretically expected from  $[M]_0/[I]_0$  ratio. However, it is interesting to note that at conversions less than 40%, the MWD is relatively broader. (Table 3.3) As the conversion increases, it becomes narrower and above 85% conversion dispersity of the polymer approaches 1.1 or less. The distribution of polymers at low conversions less than 10% cannot be obtained accurately, because of low molecular weights.

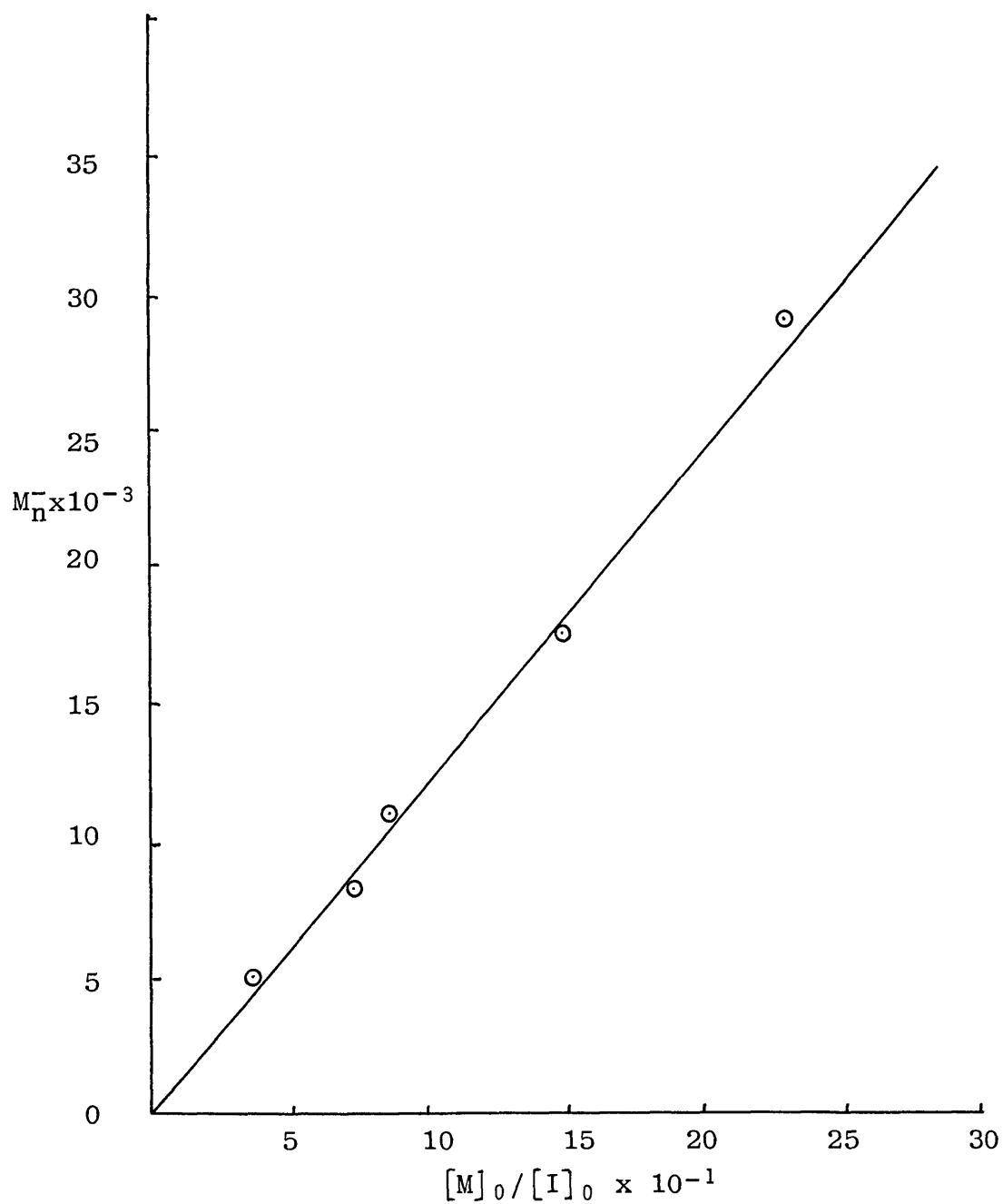


Figure 3.3 The dependence of number average molecular weight on the monomer concentration for the anionic polymerisation of MMA by ion pairs, in THF.

Initiator = fluorenyl lithium

Experimental data as in Table 3.4

Eluting at 2.0 ml/minute, these oligomers have retention volumes greater than 45 mls. It was observed that, beyond 50 mls all other low molecular weight species begin to elute, making it difficult to obtain an isolated peak, for the polymers eluting at this range. In addition another disturbance originating from stabilised THF also contributed to this difficulty. However, the comparison of breadth of the peaks wherever possible shows that low conversion products have a slightly broader distribution (Fig 3.4 - 3.10).

Table 3.4 The dependence of number average molecular weight on the monomer concentration

Initiator = fluorenyl lithium

Expt No	$[M]_0$ moles $\text{dm}^{-3}$	$[I]_0 \times 10^3$ moles $\text{dm}^{-3}$	$[M]_0 / [I]_0$	$M_n$ calculated	$M_n$ GPC
A-9	0.086	2.33	37	3712	5146
A-10	0.095	1.12	76	7675	8130
A-11	0.095	1.14	83	8340	11130
A-12	0.163	1.07	152	15251	17630
A-13	0.26	1.14	228	22834	29100

When the overall reaction is considered, the number average degree of polymerisation is well described by the simple  $[M]_0 / [I]_0$  ratio at all initiator levels. It shows that the concentration of reactive species does not change during the reaction. This observation, along with the very narrow molecular weight distributions, shows the lack of any associated species, is clear contrast to that observed for  $\text{Li}^+$  counterion in non-polar media (26), as well as the absence of any detectable chain transfer reactions, in this system.

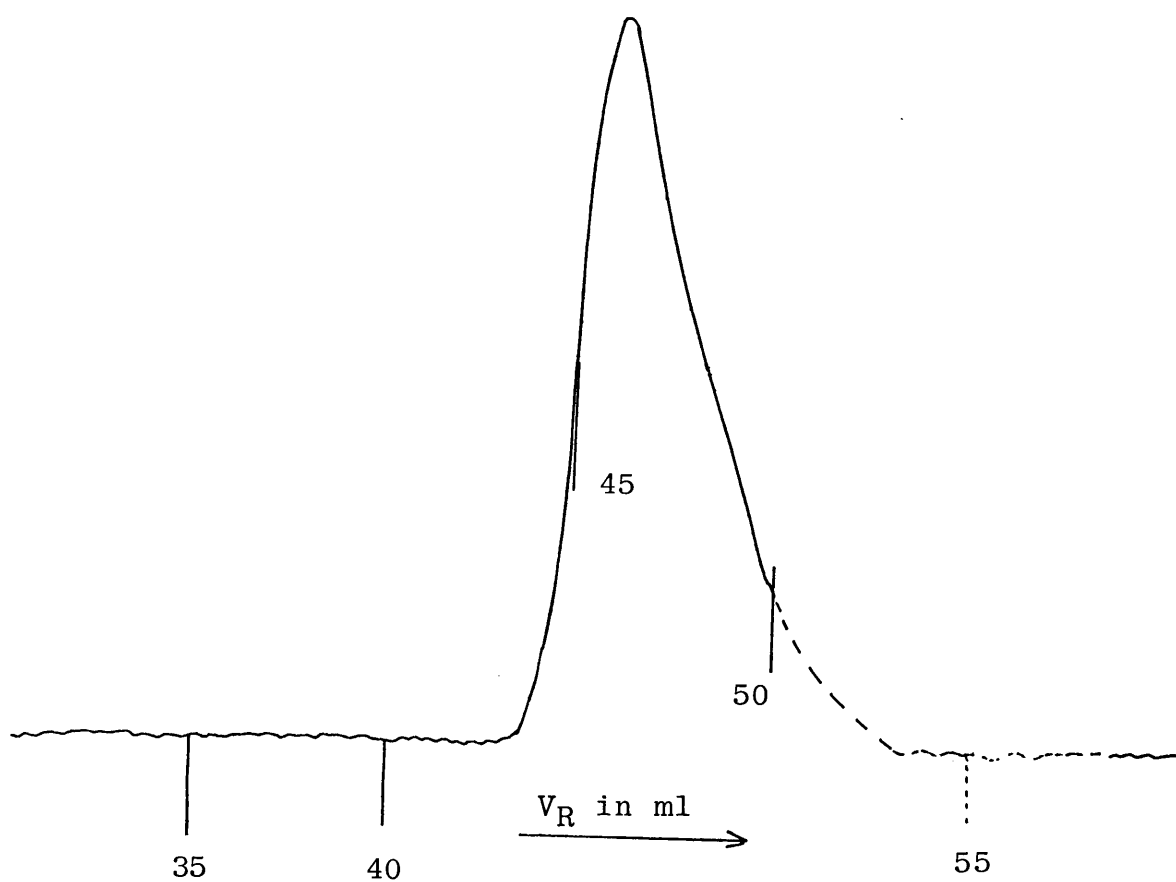


Figure 3.4 GPC chromatogram of polymethyl methacrylate  
at fractional conversion 0.065  
Reaction conditions in Table 3.3



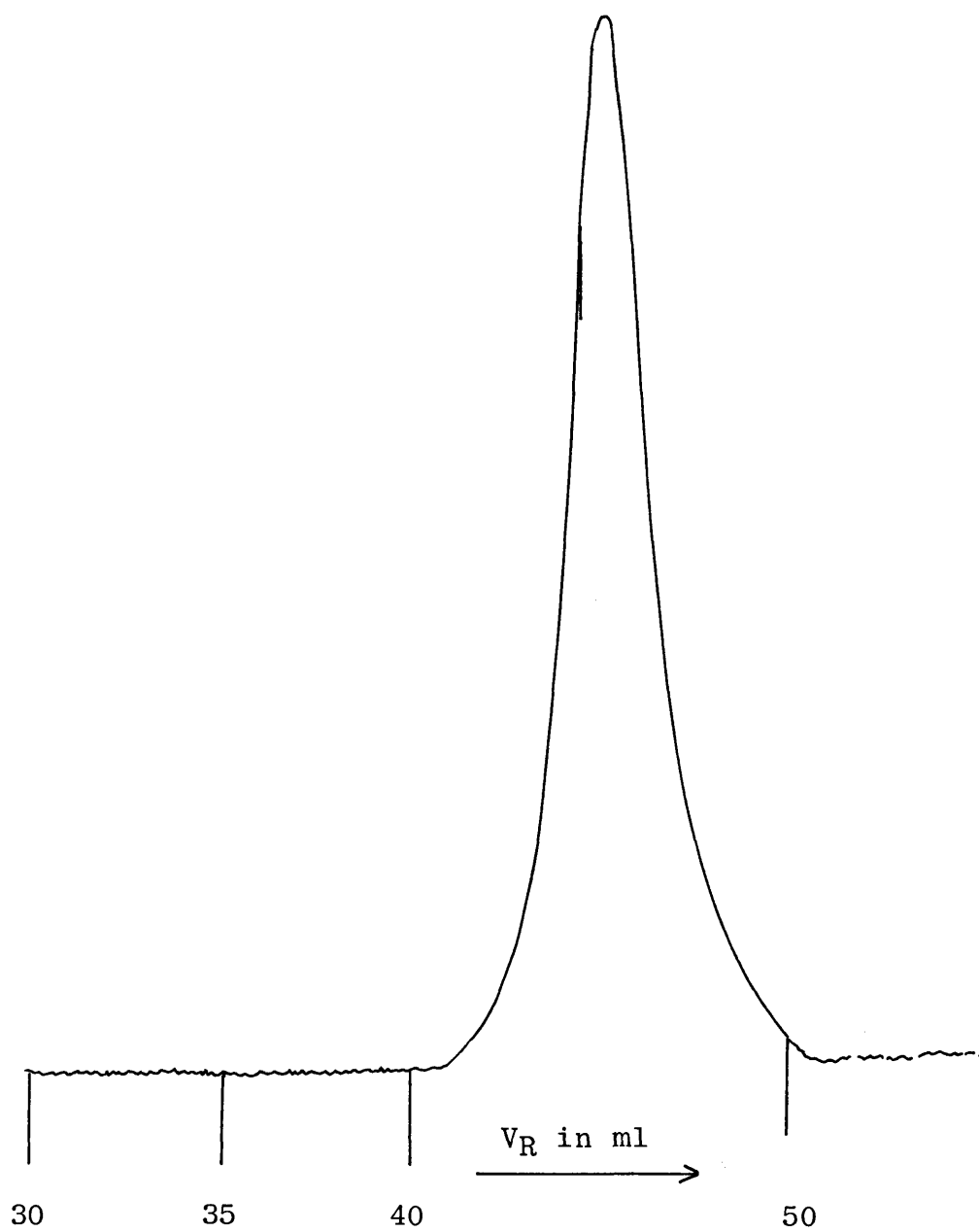


Figure 3.5 GPC chromatogram of polymethyl methacrylate  
at fractional conversion 0.22

Reaction conditions in Table 3.3

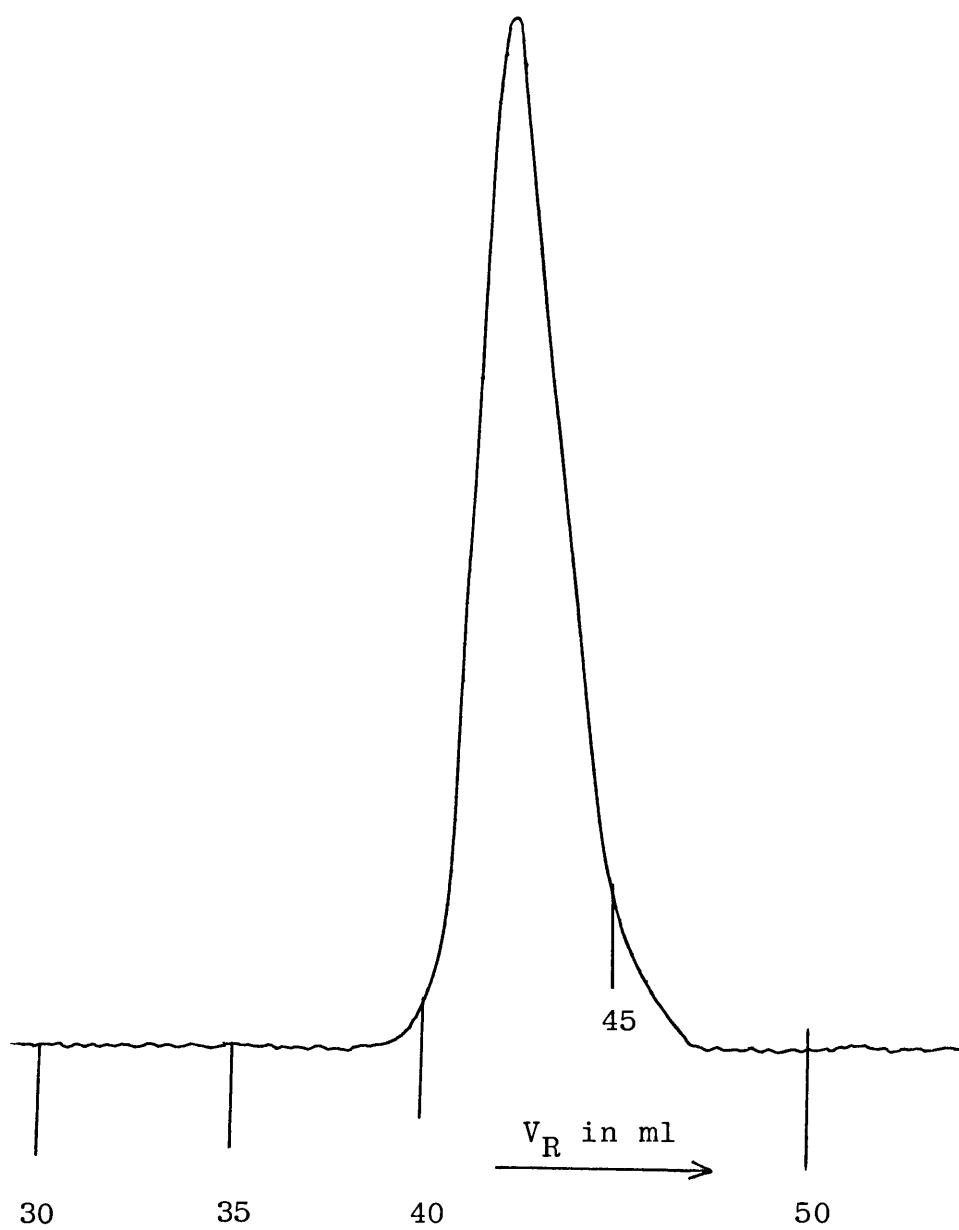


Figure 3.6 GPC chromatogram of PMMA at fractional conversion of 0.4

Reaction conditions in Table 3.3

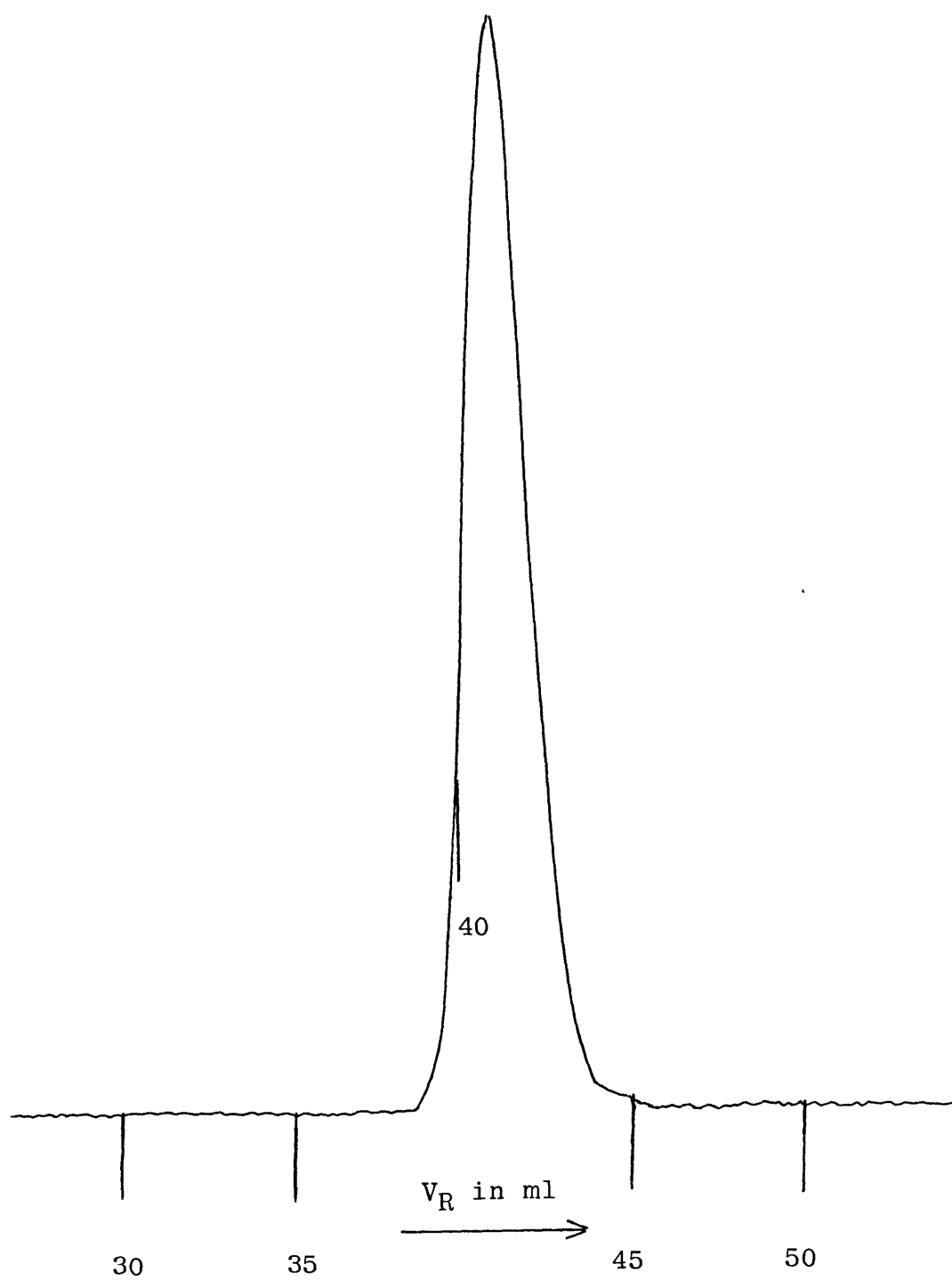


Figure 3.7 GPC chromatogram of PMMA at fractional conversion 0.84

Reaction conditions in Table 3.3

Table 3.5 The effect of monomer concentration on the molecular weight distribution of PMMA. Initiator - fluorenyl lithium T = 195 K

Expt No	$[M]_0$ M/dm <sup>3</sup>	$[M]_0 / [I]_0$	$M_n^-$ GPC	PDI	Remarks
A-10	0.095	76	8130	1.11	One aliquot of monomer
A-12a	0.166	161	16438	1.16	Two aliquots of monomer at an interval of 200 seconds
A-12b	0.163	152	17600	1.17	Two aliquots of monomer together
A-13	0.261	229	39100	1.15	Three aliquots of monomer together

Table 3.6 The effect of addition of salt on the molecular weight distribution of PMMA. Initiator - fluorenyl lithium T = 195 K

Expt No	$[M]_0$ M/dm <sup>3</sup>	$[I]_0 \times 10^3$ M/dm <sup>3</sup>	$M_n^-$ calculated	$M_n^-$ GPC	PDI	Remarks
A-14	0.095	1.14	8355	11133	1.07	With salt (Li(Ph) <sub>4</sub> B) = $1.5 \times 10^{-3}$ M/dm <sup>3</sup>
A-15	0.095	1.24	7675	8130	1.11	No salt

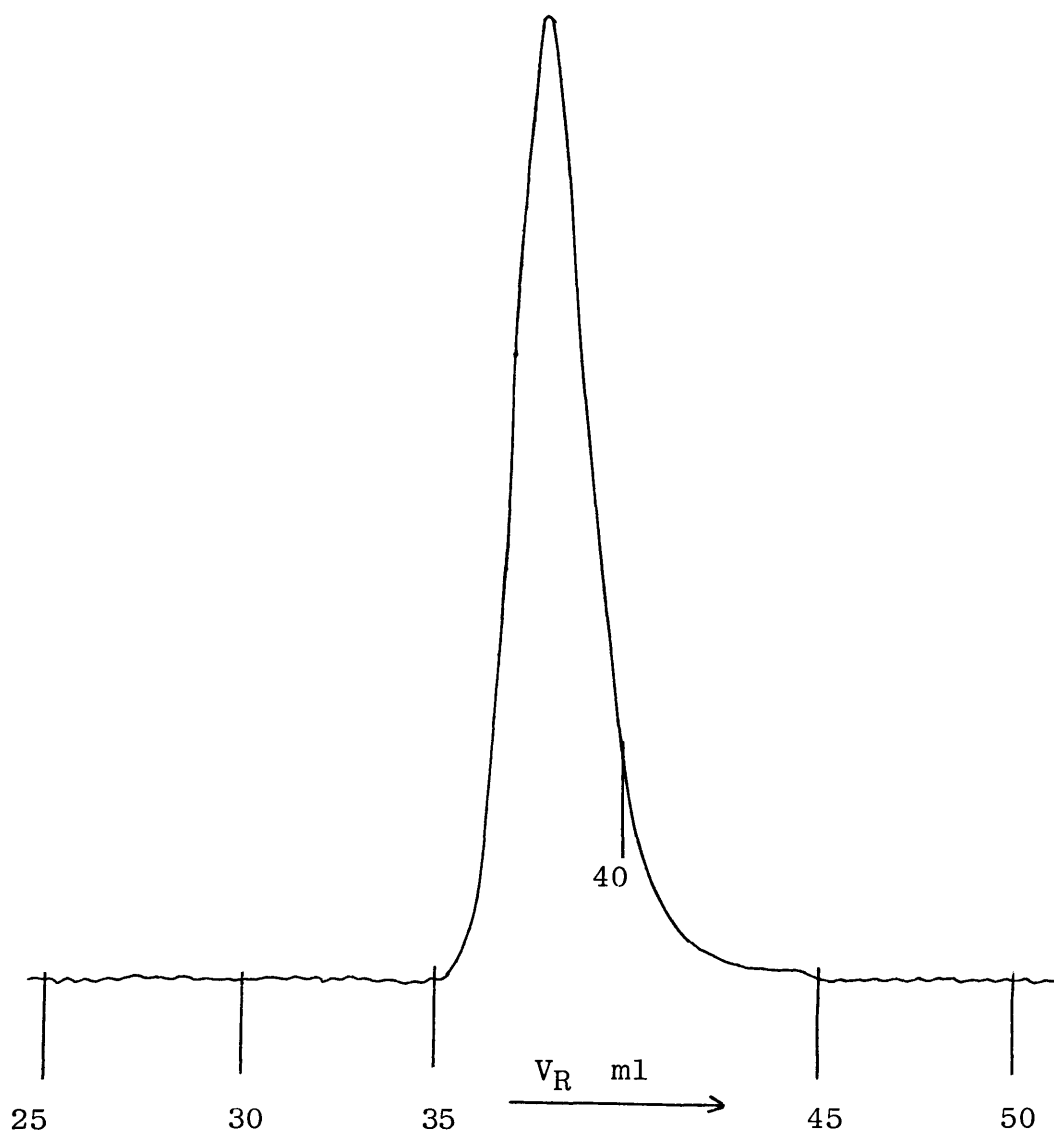


Figure 3.8 GPC chromatogram of PMMA prepared by the addition of two equal aliquots of monomer together.

Initiator = fluorenyl lithium

$$[I]_0 = 1.06 \times 10^{-3} \text{ M/dm}^3 \quad [M]_0 = 0.163 \text{ M/dm}^3$$

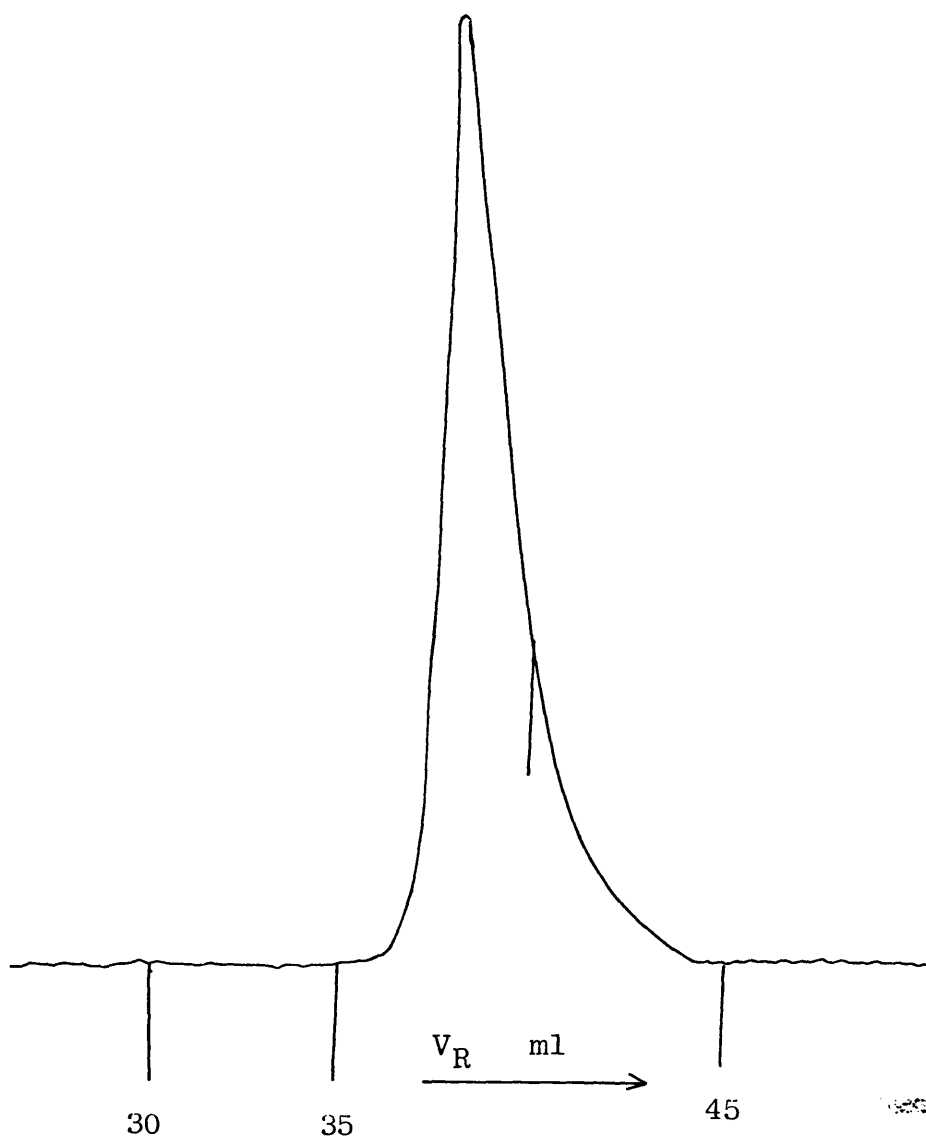


Figure 3.9 GPC chromatogram of PMMA prepared by the addition of two equal aliquots of monomer at an interval of 200 seconds.

Initiator = fluorenyl lithium  $[I]_0 = 1.03 \times 10^{-3} \text{ M/dm}^3$

#### 3.1.1.2 The effect of original monomer concentration of the MWD

The concentration of monomer seems to have some effect on the MWD of the resultant polymer. Apparently at lower monomer concentrations, a narrower MWD is obtained (Table 3.5). When the monomer was added in two equal aliquots, the second aliquot being added 200 seconds after the first, the observed MWD was narrower than when it was added together. The chromatogram of the resultant polymers are given in Figures 3.8 and 3.9. At higher monomer levels, they show a low molecular weight tailing, which is absent in polymers prepared with low monomer concentrations.

Although the difference is not very conspicuous, this indicates a certain disturbance at the initial phase of the propagation reaction, when higher monomer concentrations are used. One or more of the following factors may have contributed to its occurrence. Primarily, as suggested by Szwarc (41) slow reacting impurities, that may have been associated with the monomer solution and left unpurged at the onset of polymerisation, could lead to a slow deactivation of some living chains. The chain transfer to monomer is also a possibility. Although such a reaction in an anionic system under the conditions of this experiment is not expected, it could explain the initial broadening of MWD.

Having a low rate of propagation, the ion pairs may also possibly undergo a intermolecular termination reaction with the monomer, in the presence of excess monomer. This reaction will be discussed in the Section 2. The momentary

increase in temperature due to heat of polymerisation may contribute towards the higher activation energy that is considered to be necessary for such a reaction. The formation of monomer-active species complex similar to that reported by Allen (59) is another possibility, but highly unlikely in this case, since the number average degree of polymerisation has a linear relationship with the monomer concentration.

Because of experimental limitations, it is difficult to isolate one factor as being mainly responsible for the observed broadening of MWD. However, the possibility that most of the processes mentioned above operate to different levels, imparting the cumulative effect on the MWD, cannot be discarded.



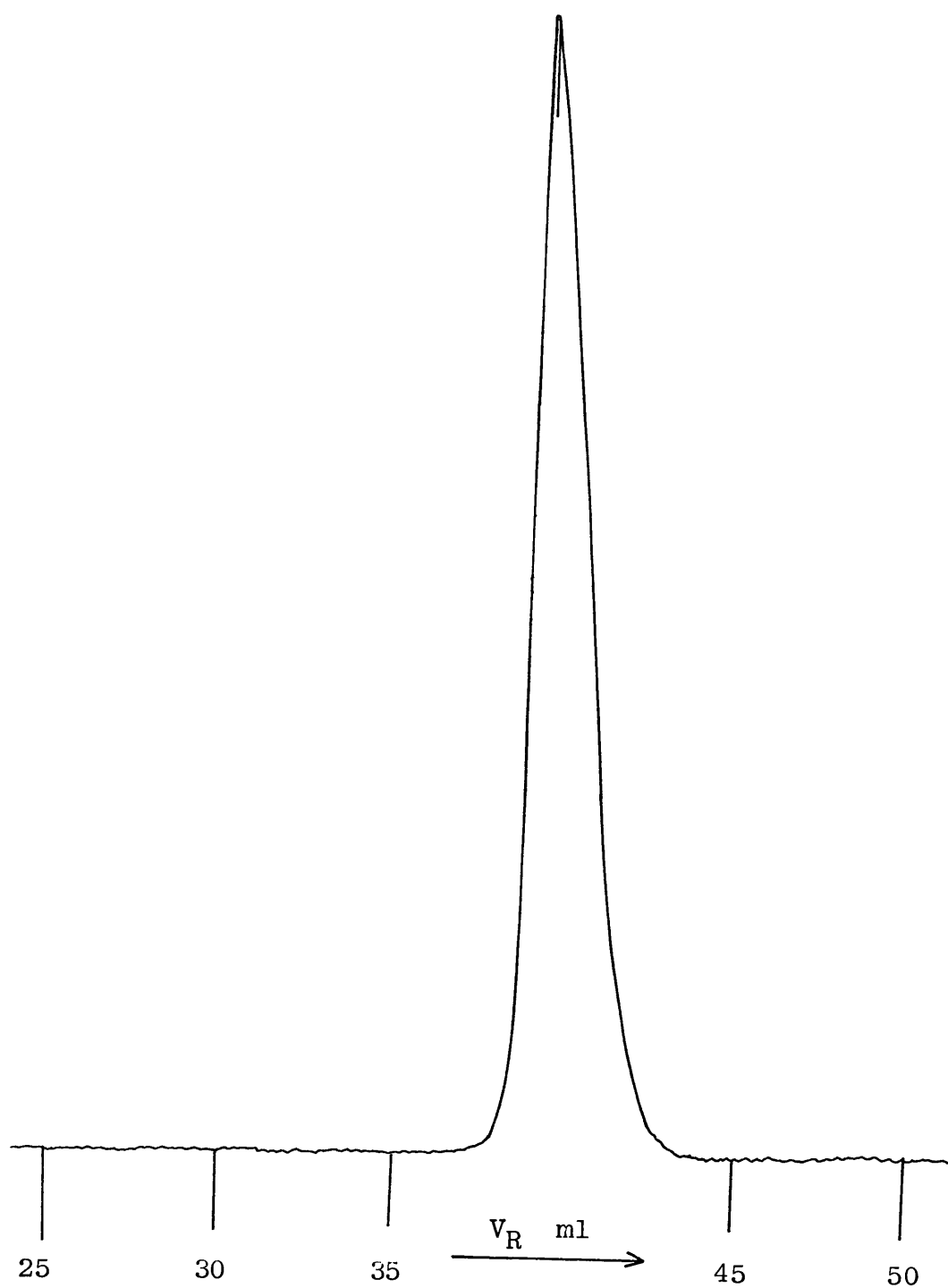


Figure 3.10 GPC chromatogram of PMMA prepared in the presence of  $\text{Li}(\text{Ph})_4\text{B}$

Reaction conditions in Table 3.6

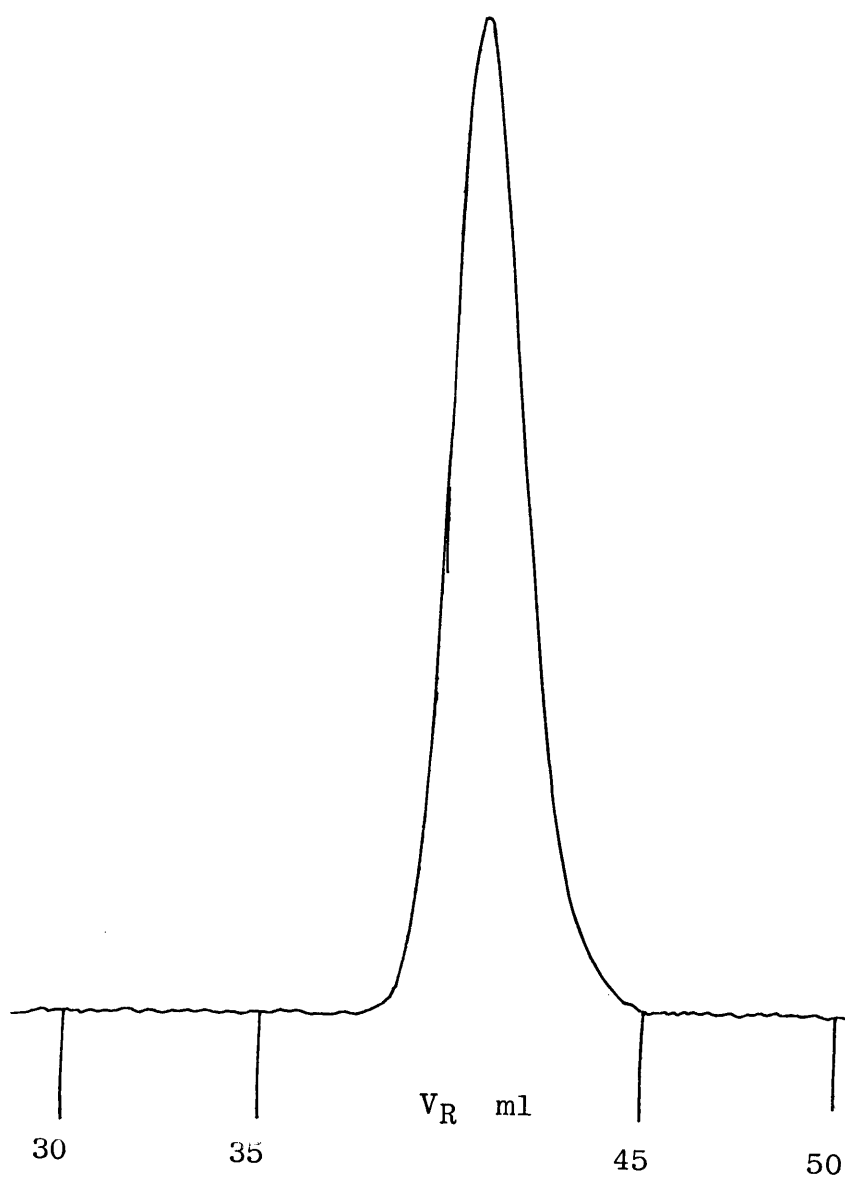


Figure 3.11 GPC chromatogram of PMMA prepared in the absence of salt  $\text{Li(Ph)}_4\text{B}$

Initiator - fluorenyl lithium (Table 3.6)

3.1.1.3 The effect of addition of salt  $\text{Li(Ph)}_4\text{B}$  on the MWD and kinetics of methyl methacrylate

The results of the comparative study of the effect of salt,  $\text{Li(Ph)}_4\text{B}$  on the propagation reaction of MMA is given in the Table 3.6. The dispersity index of the polymer produced in the absence of salt (Figure 3.11) is higher than that of the polymer produced in the presence (Figure 3.10). Given the known higher reactivity of the free ion, one would have expected to find a different result. Hogen-Esch (35) reported that at 195 K, the dissociation constant of fluorenyl lithium in THF is  $2 \times 10^{-5} \text{ M dm}^{-3}$  and at this temperature all fluorenyl lithium ion pairs are solvent separated. The addition of well soluble common cation salt  $\text{Li(Ph)}_4\text{B}$  therefore suppresses the formation of free ions so that in the initiator solution there is only one type of ion pair. Although the rate of reaction is slow, the process is practically terminationless and the fact that only one type of reactive species is operating, could possibly have been the reason for the observed narrow MWD. However, the possibility that excess  $\text{Li}^+$  or some complex or another impurity originating from  $\text{Li(Ph)}_4\text{B}$  could have accelerated the propagation reaction cannot be excluded. This follows from the unusual observation that, when the solvent and the complete apparatus was purged with a separate fluorenyl lithium capsule prior to the polymerisation reaction, the conversion obtained at the end of 30 minutes reaction time is significantly lower than the quantitative conversion. In a comparable study, it was found that the unpurged

systems showed quantitative conversion while in the control experiment with the purged system, it was only 84%. It is difficult to explain this behaviour except as a catalytic effect, but the limits of experimental errors due to gravimetric procedures cannot be discarded.

Even though no definite mechanism can be proposed for such an effect, it may be pointed out that Bywater observed a similar occurrence in which purged conditions lead to a lowering of the rate of initiation with several monomers (26).

The MWD of two polymers produced in the presence and absence of salt can also be used to obtain qualitative information on the nature of reactive species. If the concentration of free  $\text{MMA}^-$  carbanions is comparable to that of fluorenyl, the polymerisation is expected to be almost instantaneous, considering that the reported value for the rate of propagation by free  $\text{MMA}^-$  ion is  $48000 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ . With a 1% fraction of free ions, the conversion would have been complete within 10 seconds. However, the observed conversion under these conditions on repeated experiments is less than 8%. Hence there is no evidence in this system at least, for the presence of highly reactive free ions in any detectable concentration even in the absence of a common ion salt at 200 K. This may indicate the absence of any solvent participation in the dissociation of ion pairs of  $\text{PMMA}^- \text{ Li}^+$  and also the lack of any specific solvation of the counterion of the ion pair by THF.

However, another alternative explanation for the case of the free ion may be that, because of the greater reactivity,

it undergoes chain transfer to monomer or polymer.

Although such a reaction is rare in anionic systems, it could explain the observed broadening of the MWD in the absence of salt.

### 3.1.2 Propagation of anionic polymerisation of methyl methacrylate by PMMA<sup>-</sup>Na<sup>+</sup> ion pairs

#### 3.1.2.1 Kinetics

The kinetics of anionic polymerisation of methyl methacrylate by ion pairs with Na<sup>+</sup> as counterion was investigated using sodium  $\alpha$ -methyl styrene tetramer as the initiator at 195 K. The dissociation of ion pairs into free ions was suppressed by the addition of excess sodium tetraphenyl boron.

Results of the kinetic investigations are given in Table 3.7 and the time versus conversion curve plotted according to equation (3) is given in Figure 3.12. Initiation is instantaneous. The termination of reactive ends is not significant during propagation and the propagation reaction can be described as first order with respect to monomer. From this plot, which is a straight line, the rate constant of propagation for PMMA<sup>-</sup> Na<sup>+</sup> ion pairs is calculated as follows.

By linear regression:

$$\text{the slope} = \frac{19.1322}{263.8} = .725$$

The concentration of initiator was found to be

$$[I] = 8.58 \times 10^{-4} \text{ moles dm}^{-3}$$

From equation (3), the slope =  $k_p(\pm)[I]$

$$\begin{aligned} \therefore k_p(\pm) &= \frac{19.1322}{263.8} \times \frac{1}{8.58 \times 10^{-4}} \\ &= 84.5284 \end{aligned}$$

$$\therefore k_p(\pm) = 84.5 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

This value is in good agreement with that obtained by L  hr and Schulz (81). However, recently Warzelham et al

reported much higher values for rate constant of propagation by ion pairs for a range of temperatures using mono-functional sodium  $\alpha$ -methyl styrene. It is apparent that these values differ by a factor of two.

The dependence of number average molecular weight ( $M_n^-$ ) on fractional conversion is given in the Figure 3.13. Although a certain amount of scattering of points is observed, the linear relationship is clearly seen. The dependence of  $M_n^-$  on the concentration of monomer is also linear (Fig 3.25) which indicates that there is no detectable formation of monomer-active species complexes as seen in systems initiated with Grignard's reagent (59). It follows therefore that the polymerisation can be said to be simple anionic.

Table 3.7 Experimental data for the determination of rate constant of propagation by ion pairs  $k_{p(\pm)}$  for  $\text{PMMA}^- \text{Na}^+$  at 195 K in THF. Initiator = sodium  $\alpha$ -methyl styrene tetramer.  $[\text{Na}(\text{Ph})_4\text{B}] = 1.25 \times 10^{-3} \text{ moles dm}^{-3}$

Expt No	$[\text{M}]_0$ moles $\text{dm}^{-3}$	$[\text{I}]_0 \times 10^3$ moles $\text{dm}^{-3}$	Fractional Conversion	Time Seconds	$M_n^-$ GPC
B-1	0.235	1.10	0.06	0.5	$\approx 2000^*$
B-2	0.240	1.08	0.24	3.0	8960
B-3	0.240	1.11	0.48	10.0	15900
B-4	0.245	1.10	0.63	15.0	16225
B-5	0.24	1.09	0.79	20.0	21031
B-6	0.247	1.12	1.0	130.0	26600

\*Molecular weight cannot be measured accurately by GPC measurements due to interference of the polymer peak over  $V_R > 50$  range.

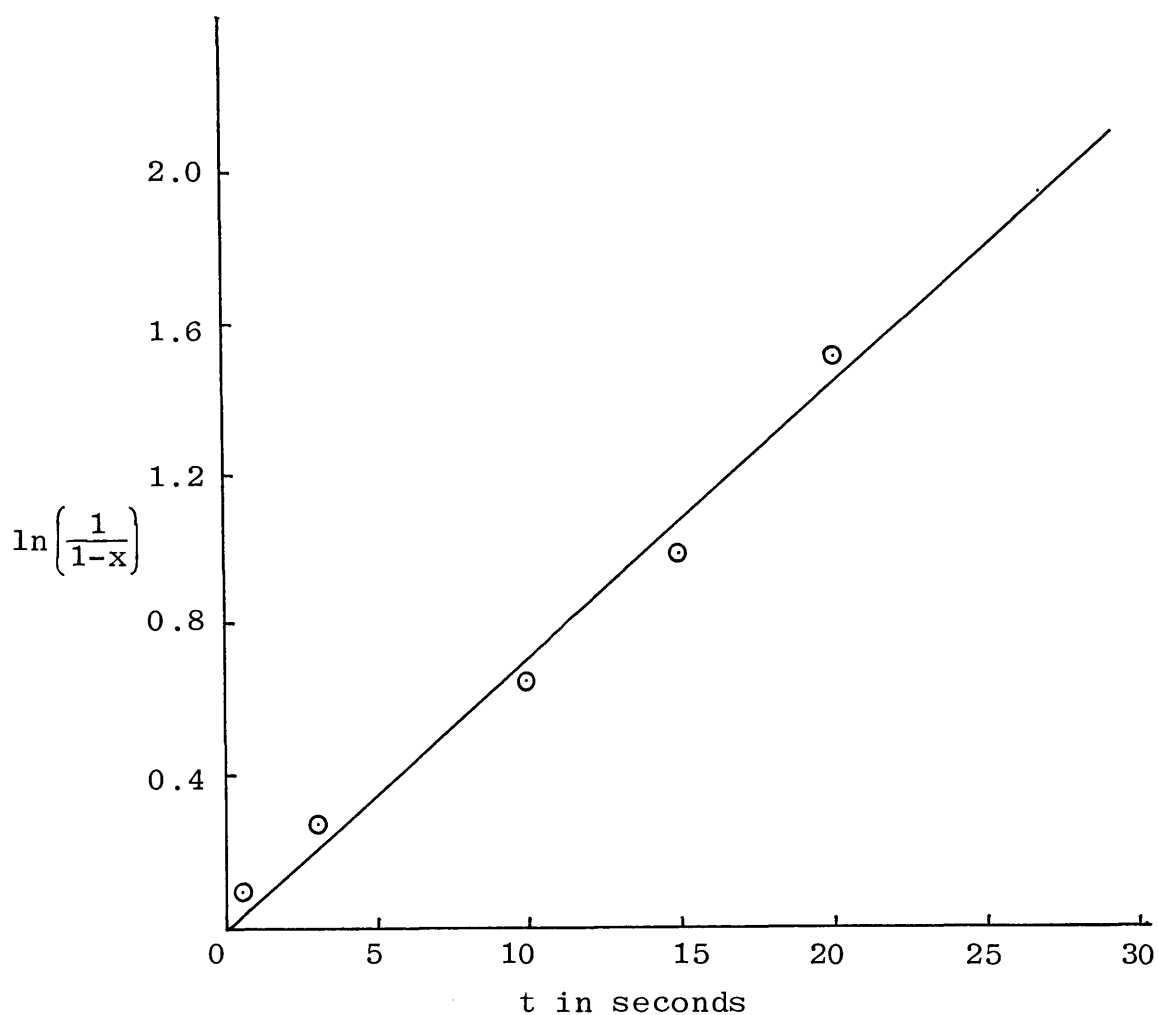


Figure 3.12 First order plot of conversion vs time for the polymerisation of methyl methacrylate in tetrahydrofuran by ion pairs with  $\text{Na}^+$  as counterion.

Initiator - Sodium  $\alpha$ -methyl styrene tetramer

$$[\text{I}] = 1.1 \times 10^{-3} \text{ M dm}^{-3}$$

$$[\text{Na(Ph)}_4\text{B}] = 1.25 \times 10^{-3} \text{ M dm}^{-3}$$

Temp = 195 K

Experimental data as in Table 3.7



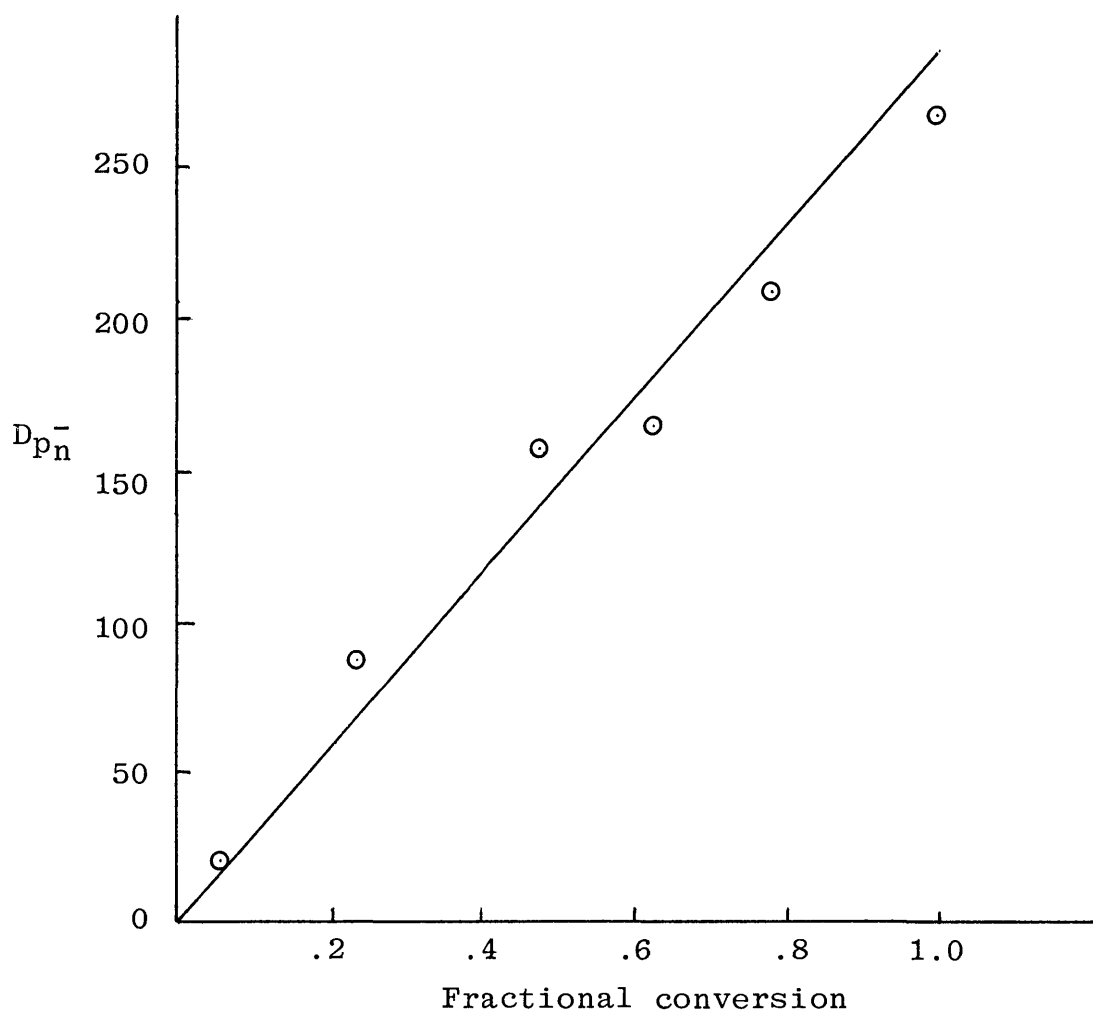


Figure 3.13 Dependence of the number average degree of polymerisation on the fractional conversion for the polymerisation of methyl methacrylate in THF  
Initiator = sodium  $\alpha$ -methyl styrene  
Experimental data as in Table 3

However, the results show that the number average molecular weight,  $M_n^-$ , as determined by GPC is always less than the theoretical value calculated from simple ratio of initial concentrations of initiator and monomer. This, of course, is not a case of deactivation of initiator. Any reduction of the effective concentration of initiator would cause a corresponding increase in the molecular weight rather than a decrease. Extensive chain transfer reaction to monomer may lead to lower molecular weights by increasing the number of polymer chains, but that would also result in a much broader MWD than observed. In the expression, which is used for the calculation of theoretically expected  $M_n^-$ ,

$$D_{p_n}^- = \frac{M_n^-}{100.12} = \frac{2[M]_0}{[I]_0}$$

$[M]_0$  and  $[I]_0$  can be determined to a level of satisfactory accuracy. Hence the only possible variable in the expression is the factor 2, which represents the number of carbanions per molecular of sodium  $\alpha$ -methyl styrene initiator. With fluorenyl sodium as the initiator, the observed molecular weights from GPC are only slightly higher than the theoretically expected, which can be readily explained as due to the initial loss of initiator caused by impurities present in the system at the onset of polymerisation. Since the method of determination of initial concentration of initiator is the same, it is apparent the deviation is related to the factor 2. It is difficult to explain how such an effect could arise. Although the mechanism of formation of  $\alpha$ -methyl styrene tetramer (111) cannot be questioned on the basis of these experimental observations

alone, it is possible that the monofunctional species is the major reactive species. An explanation in terms of chain transfer to monomer cannot be considered to be significant since at very low initiator concentrations, higher molecular weights than theoretically expected have been observed.

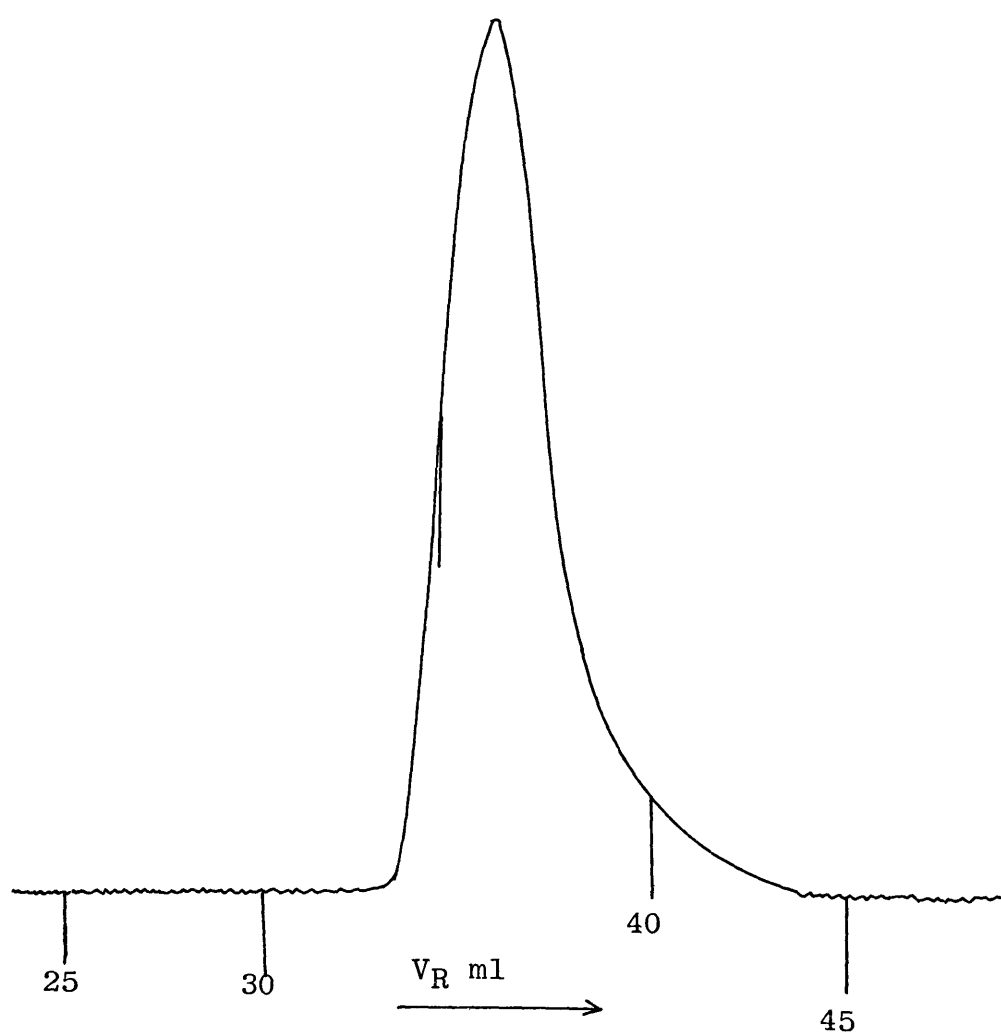


Fig 3.14 GPC chromatogram of PMMA prepared by single initiation at 195 K

Initiator - sodium naphthalene ( $\text{Na}(\text{Ph})_4\text{B}$ ) =  $1.2 \times 10^{-3} \text{ M dm}^{-3}$   
 $[\text{M}]_0 = 0.131$        $[\text{I}]_0 = 0.96 \times 10^{-3} \text{ M dm}^{-3}$

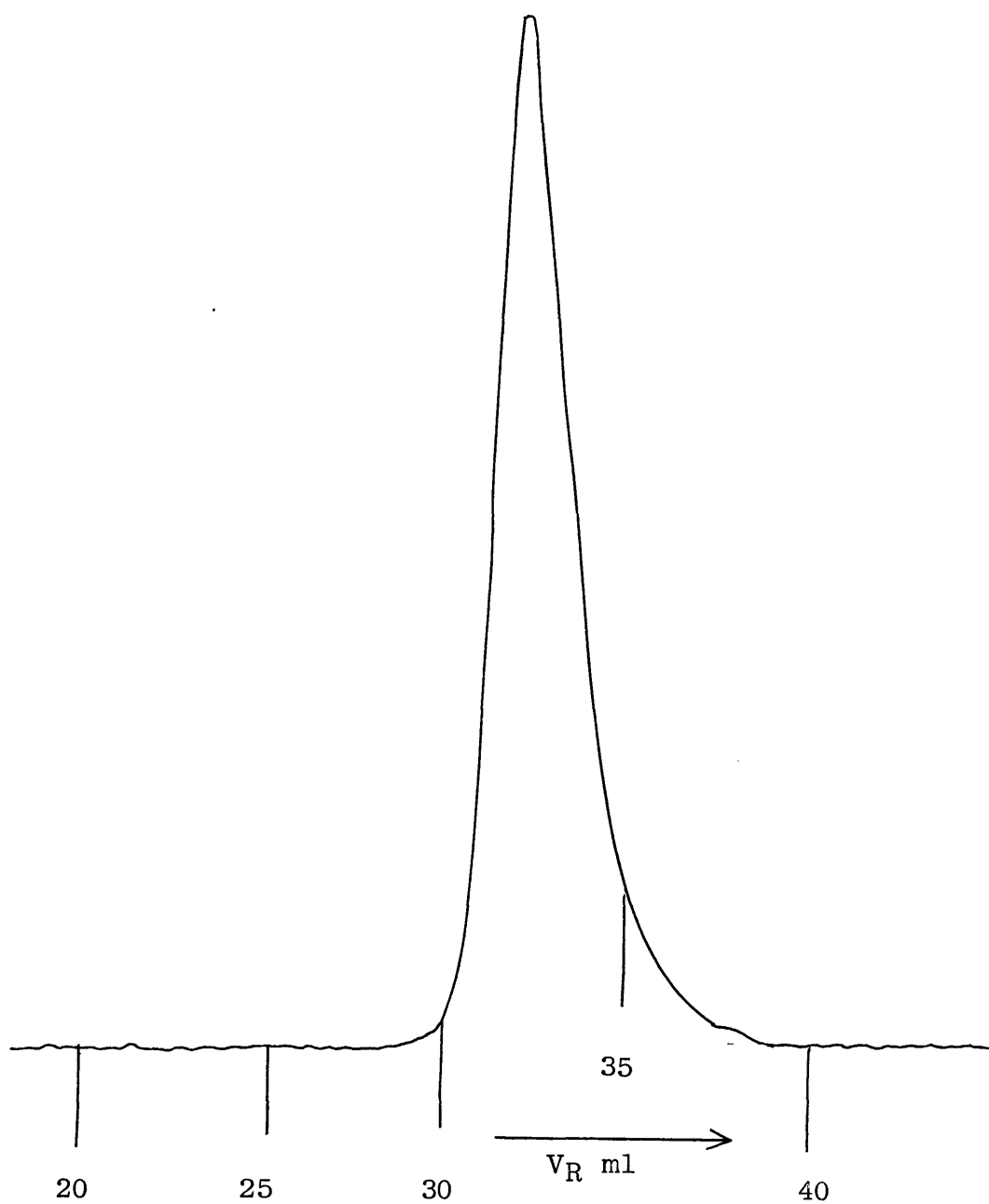


Figure 3.15 GPC chromatogram of PMMA prepared by double initiation at 195 K.

Initiator - sodium naphthalene ( $\text{Na(Ph)}_4\text{B}$ ) =  $1.2 \times 10^{-3} \text{ M dm}^{-3}$

$[\text{M}]_0 = 0.15 \text{ M dm}^{-3}$        $[\text{I}]_0 = 0.98 \times 10^{-3} \text{ M dm}^{-3}$

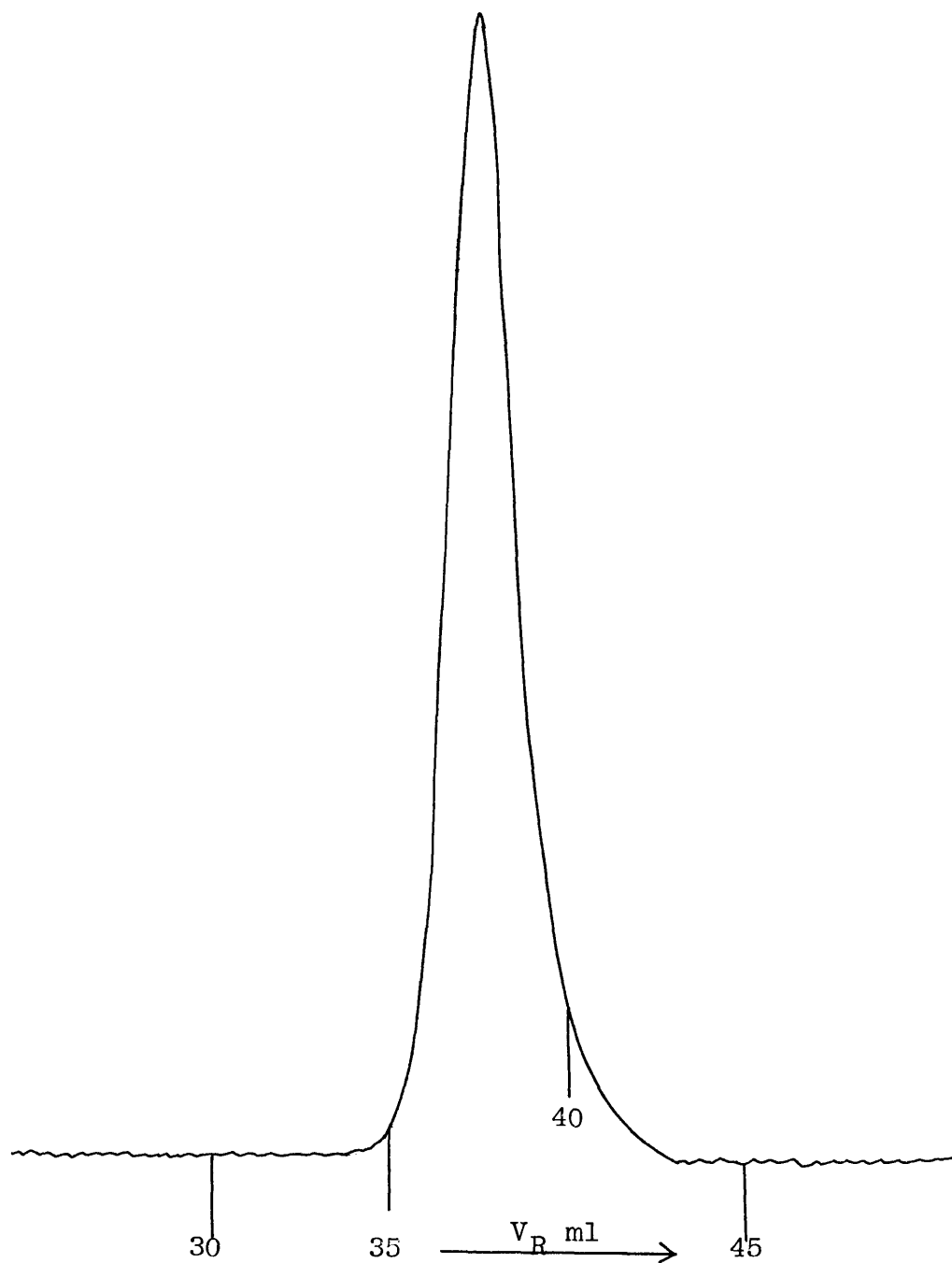


Figure 3.16 GPC chromatogram of PMMA prepared by slow continuous addition of monomer.

Initiator - sodium naphthalene  $[\text{Na}(\text{Ph})_4\text{B}] = 1.2 \times 10^{-3} \text{ M dm}^{-3}$

$[\text{M}]_0 = 0.14 \text{ M dm}^{-3}$      $[\text{I}]_0 = 1.1 \times 10^{-3} \text{ M dm}^{-3}$

### 3.1.2.2 The mode of addition of monomer

Three modes of monomer additions were employed under otherwise identical polymerisation conditions, using sodium naphthalene and sodium  $\alpha$ -methylstyrene tetramer as initiator:

- (i) single addition of monomer ("single initiation");
- (ii) double addition of monomer ("double initiation");
- (iii) slow continuous addition of monomer.

Typical gel permeation chromatograms of polymers prepared by these three techniques are given in Figures 3.14 - 3.16. When polymerisations were carried out at 195 K, the slow continuous addition of monomer produced a slightly narrower MWD than that by double addition.. The MWD of polymers produced by the single addition of monomer was detectably broader than those by double addition. However, the differences are not very conspicuous and generally all polymers can be regarded as having narrow MWD's.

It has been noticed in all polymers prepared by the above techniques, there is a certain amount of disturbance during the initial phase of propagation reaction, as indicated by the small low molecular weight tailing present. Any specific broadening of MWD due to the different modes of addition of monomer is overlapped by this effect. However, the examination of chromatograms provides some qualitative information. The presence of a low molecular weight tail in the polymer prepared by slow continuous addition technique indicates that there is some side reactions occurring even in the absence of excess monomer. This probably may be due

to side products that may have been produced during the initiation(56)(77). The chain transfer reactions cannot be significant in this case, since the effect is restricted only to the initial phase of polymerisation reaction.

Two factors may have contributed to the slightly increased broadening of the MWD of polymers prepared by single addition. Firstly, the presence of excess monomer at the initiation stage may have lead to a relatively higher extent of side reactions. (The main side reaction referred here is that of the initiator with the monomer ester function producing methoxide.) The inefficient mixing could also lead to some broadening (41). Since the initiation is instantaneous and the rate of propagation is fast, a better distribution of monomer molecules would lead to an even growth of living chains as the case may be in the slow continuous addition of monomer.

The effect of different modes of addition of monomer on the MWD is more prominent at temperatures 250 K and above. The polydispersity index of polymers prepared by single initiation is significantly broader than in those prepared by double initiation. This can be attributed to the increased carbonyl attack by initiator on the monomer ester function at higher temperatures (75).



Table 3.8 Effect of initiation temperature on the MWD

Initiator - Sodium naphthalene

$$[\text{Na}(\text{Ph})_4\text{B}] = 1 \times 10^{-3} \text{ moles dm}^{-3}$$

Mode of initiation = double initiation

Expt No	$[\text{M}]_0$ moles $\text{dm}^{-3}$	$[\text{I}]_0 \times 10^3$ moles $\text{dm}^{-3}$	$\overline{M}_n$ GPC	Fractional Conversion	PDI	Initiation Temp K	Propagation Temp K
C-1	0.122	0.83	53370	1.0	1.2	195	195
C-2	0.120	0.91	30260	0.60	1.8	233	233
C-3	0.110	0.81	$\approx 12000$	0.30	2.64	253	253
C-4	0.150	0.95	55000	0.77	1.6	195	233
C-5	0.120	0.94	14800	0.5	1.85	195	253
C-6	0.170	1.3	6350	0.18	2.10	195	263

Table 3.9 The dependence of fractional conversion on the temperature

Initiator - Sodium naphthalene

$$[\text{M}]_0 = 0.16 \text{ M dm}^{-3}$$

$$[\text{I}]_0 = 1 \times 10^{-3} \text{ M dm}^{-3}$$

$$[\text{Na}(\text{Ph})_4\text{B}] = 1.2 \times 10^{-3} \text{ M dm}^{-3}$$

Expt No	Temp K	Percentage Conversion	$\log \alpha$	$\frac{10^3}{T}$
C-6b	268	15	1.18	3.73
C-5	253	58	1.76	3.95
C-4	235	77	1.89	4.26
C-7	195	100	2.0	5.13

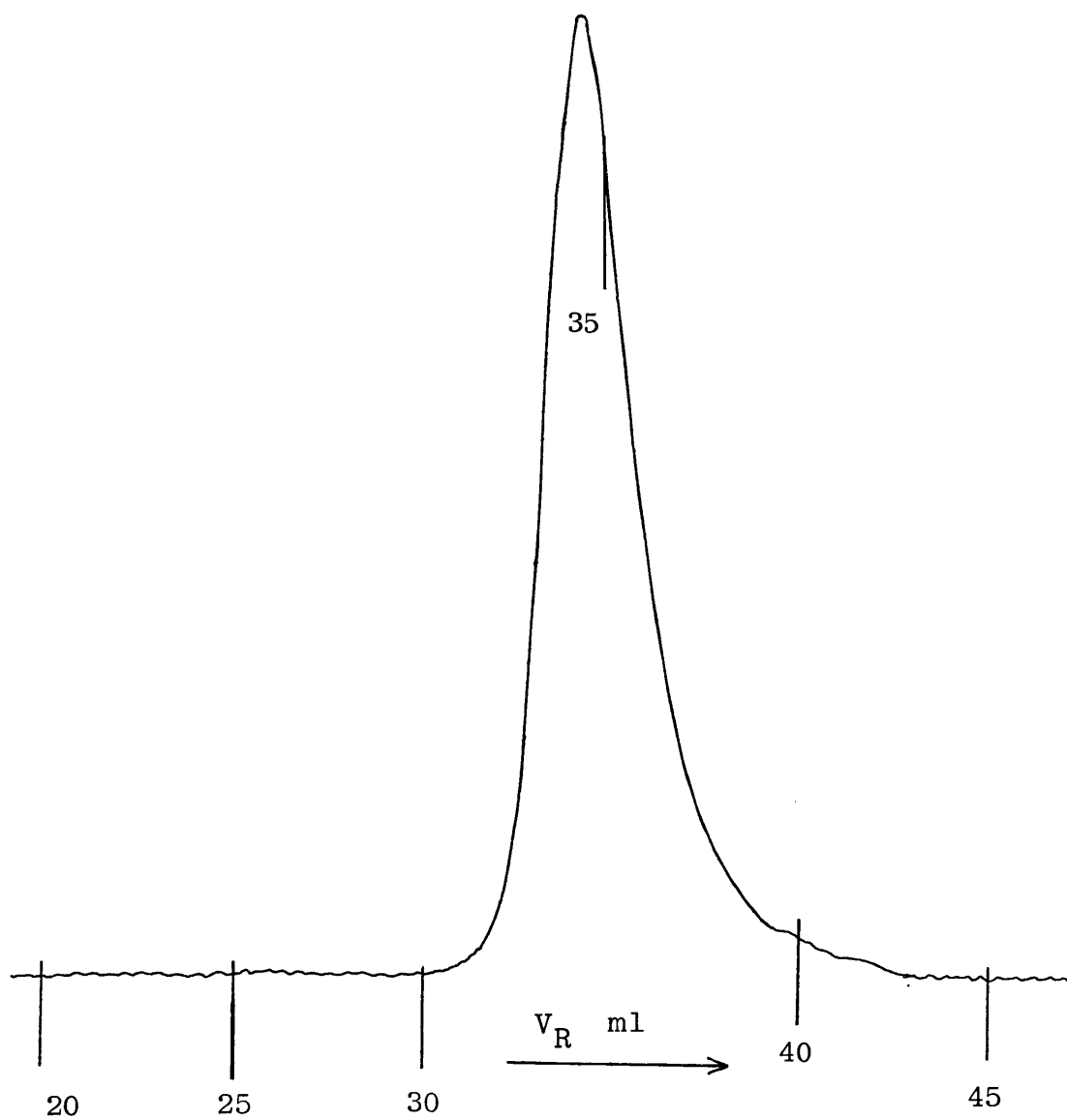


Figure 3.17 GPC chromatogram of PMMA produced at 200 K  
double initiation

$$[I]_0 = 0.83 \times 10^{-3} \text{ M/dm}^3 \quad [M]_0 = 0.122 \text{ M/dm}^3$$

$$[\text{Na(Ph)}_4\text{B}] = 1.2 \times 10^{-3} \text{ M/dm}^3$$

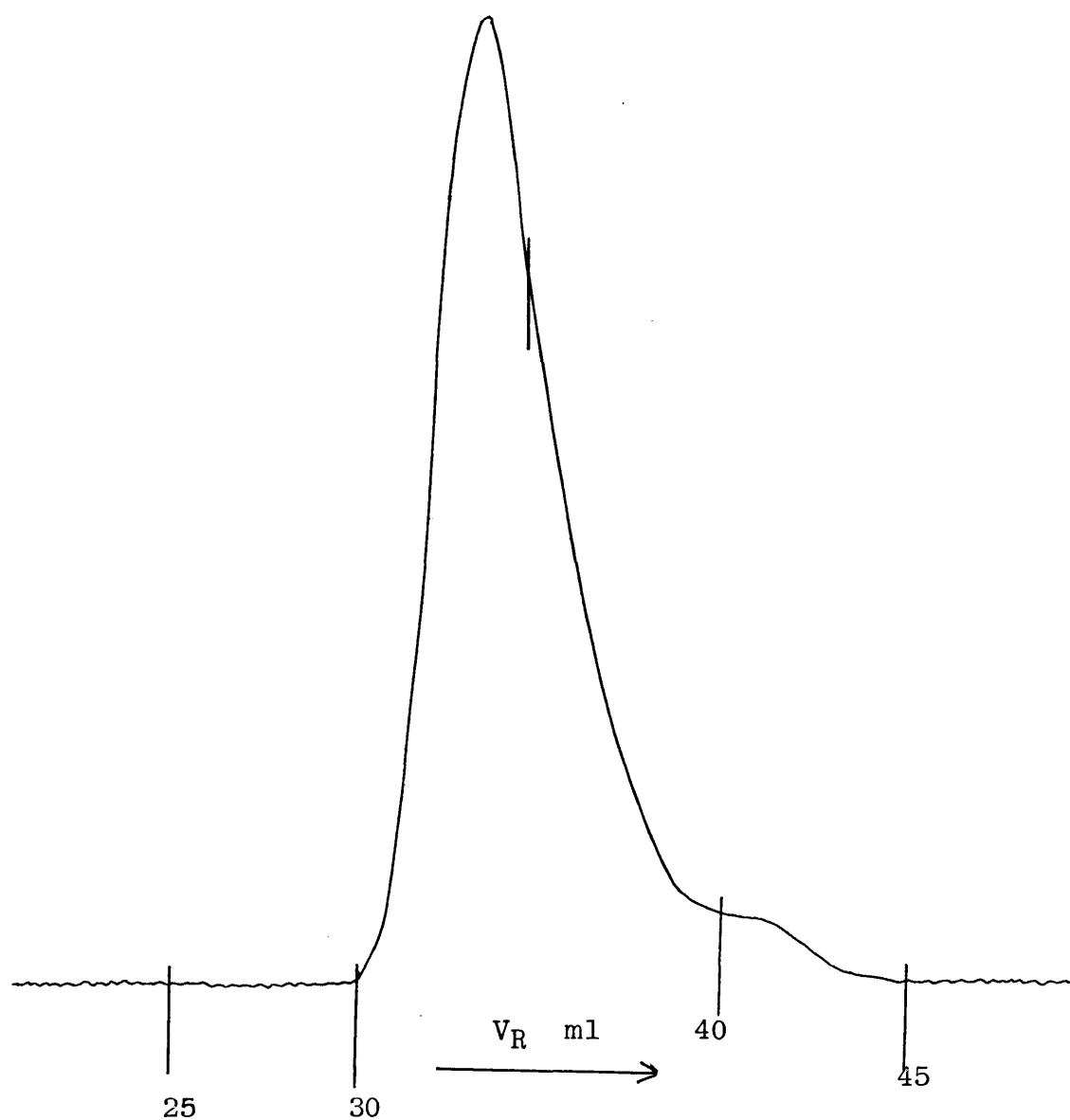


Figure 3.18 GPC chromatogram of PMMA produced at 230 K.

Double initiation. Initiator - sodium naphthalene

$$[I]_0 = 0.91 \times 10^{-3} \text{ moles/dm}^3 \quad [M]_0 = 0.12 \text{ moles/dm}^3$$

$$[\text{Na(Ph)}_4\text{B}] = 1.2 \times 10^{-3} \text{ M/dm}^3$$

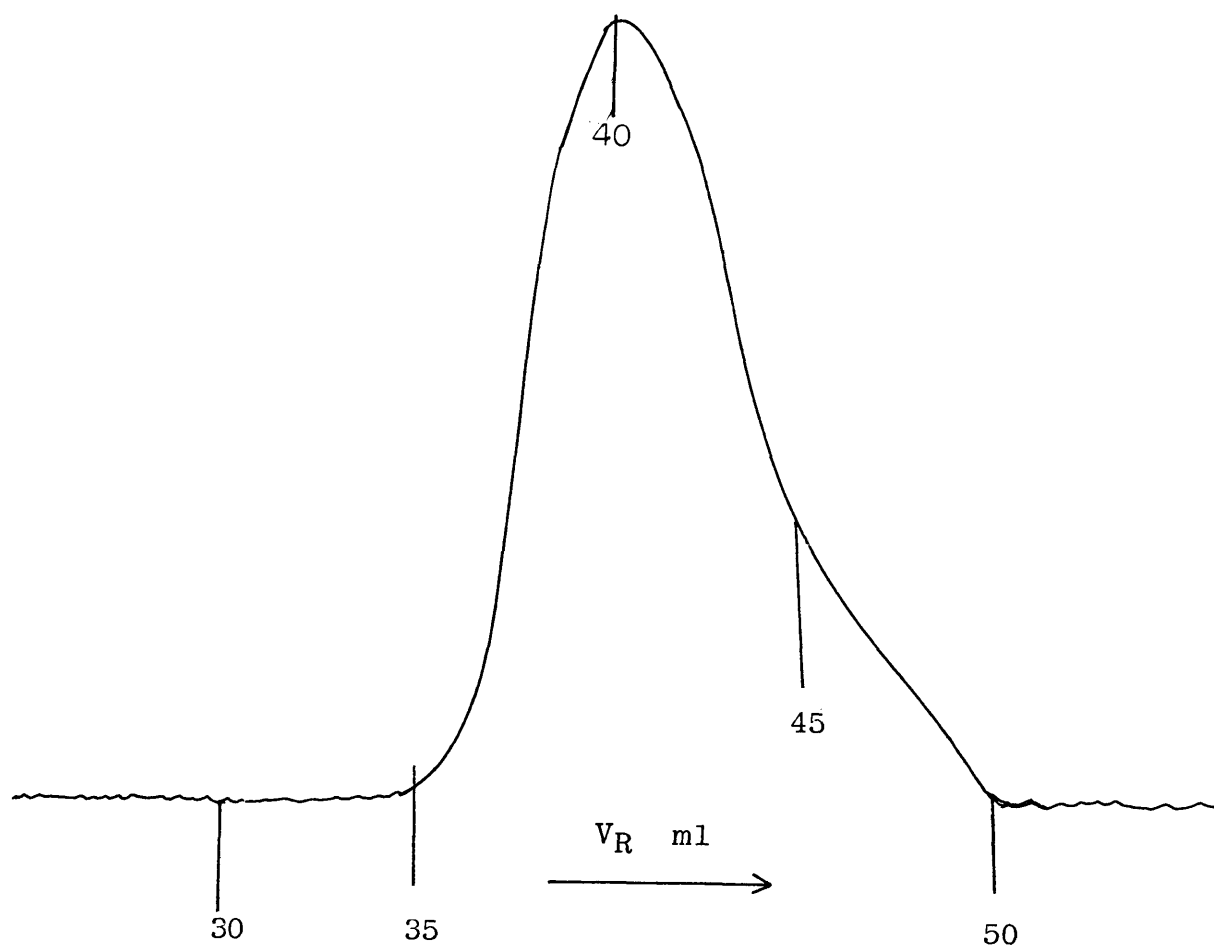


Fig 3.19 GPC chromatogram of PMMA prepared by double initiation at 253 K. Initiator - sodium naphthalene

$$[M]_0 = 0.11 \text{ M/dm}^3 \quad [I]_0 = 0.81 \times 10^{-3} \text{ M/dm}^3$$

$$[\text{Na(Ph)}_4\text{B}] = 1.1 \times 10^{-3} \text{ M/dm}^3$$

### 3.1.2.3 The effect of initiation temperature on the MWD

Using sodium naphthalene as initiator, polymerisations were carried out at 195 K, 233 K and 253 K, in THF in the presence of excess  $\text{Na(Ph)}_4\text{B}$ . The respective chromatograms are given in Figs. 3.17, 3.18 and 3.19 and the experimental data in Table 3.8. When the initiation and propagation both are carried out at 195 K, the MWD of the resultant polymer is narrow. Hence the side reactions do not seem to play an effective role in the initiation step at this temperature. But when the initiation is carried out at elevated temperatures such as 253 K and 233 K, the effect is clearly seen in the much broadened MWD (Figure 3.18 and 3.19) and reduced conversion (Table 3.8).

At 233 K, the colour of the final solution remains yellow and only 60% conversion is observed. The polymer has a broad MWD and the low molecular weight part of the curve indicates considerable termination of reactive ends during the early phase of reactions. At 253 K, the conversion is less and the colour of the solution becomes deep yellow. It is apparent that the yellow colour is associated with the termination of reactive ends but no definite mechanism could be given. However, it appears that some complex with initiator molecules incorporating naphthyl group, is formed in a side reaction at higher temperatures. The MWD of the resultant polymer is extremely broad and has a tailing on both low molecular and high molecular weight sides. When the initiation is effected at 195 K and propagation is carried out at elevated temperatures, the conversion improves and the MWD becomes relatively narrow. (Table 3.8)

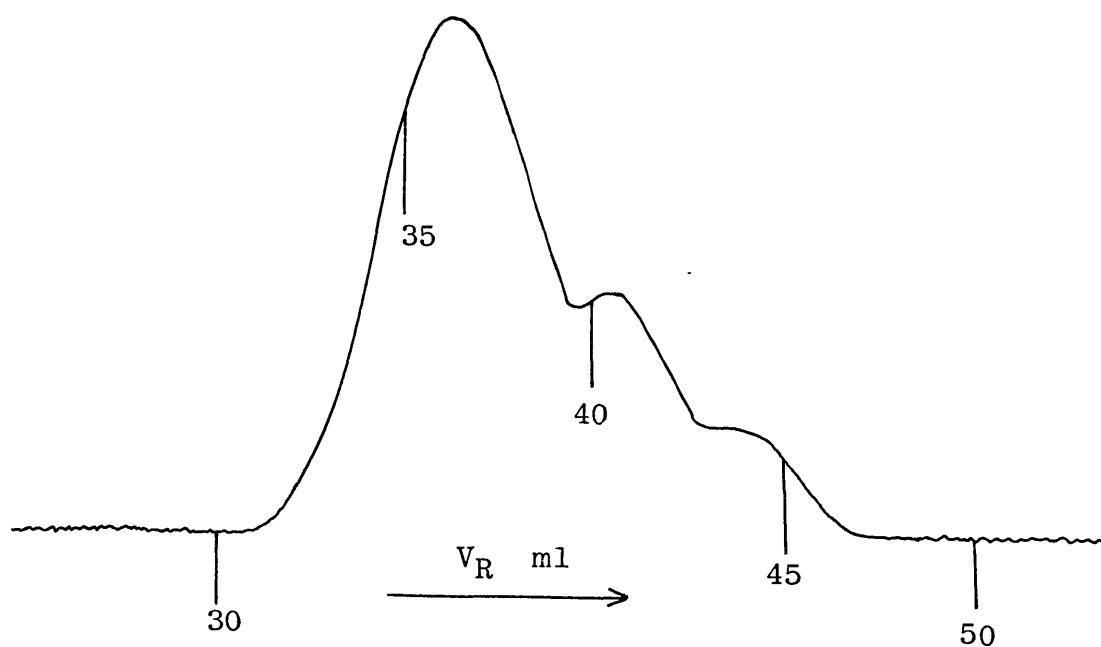


Fig 3.20 GPC chromatogram of PMMA prepared by double initiation. Initiation at 195 K. Propagation at 253 K.

$$[M]_0 = 0.12 \text{ M/dm}^3 \quad [I]_0 = 0.94 \times 10^{-3} \text{ M/dm}^3$$

$$[\text{Na(Ph)}_4\text{B}] = 1.1 \times 10^{-3} \text{ M/dm}^3 \quad \text{Initiator - sodium naphthalene}$$

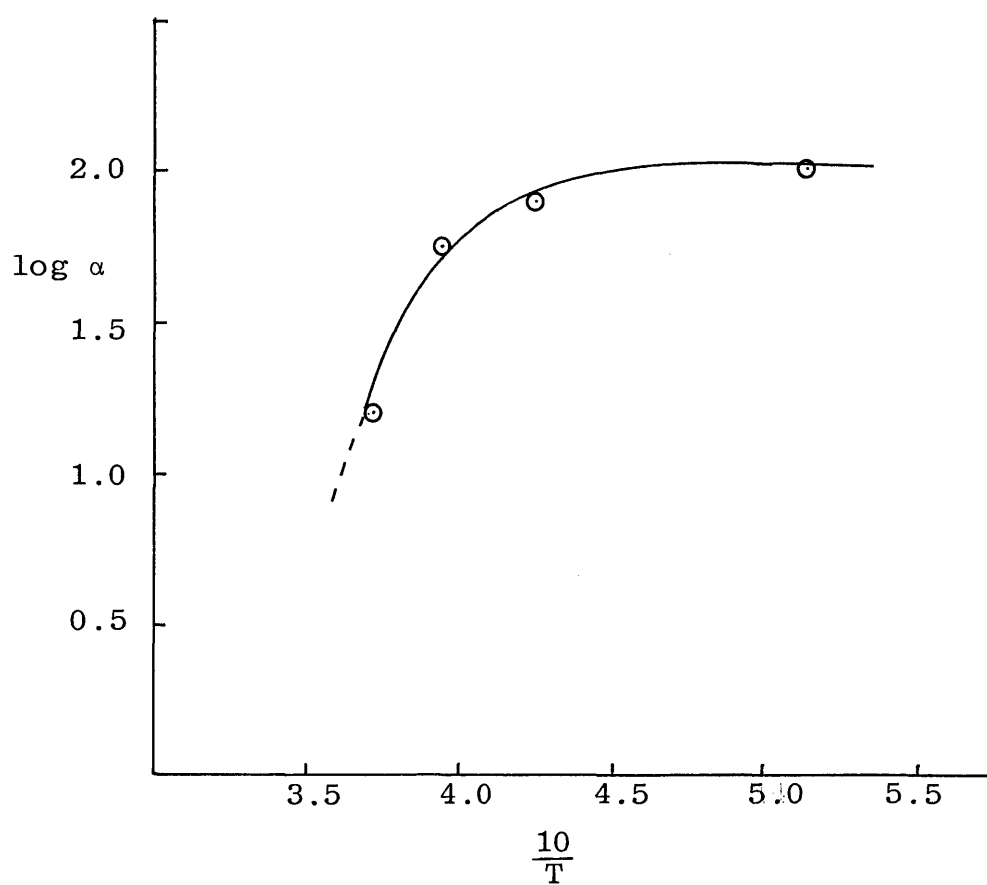


Fig 3.21 Conversion vs temperature for the anionic polymerisation of MMA by ion pairs with  $\text{Na}^+$  as counterion.

Initiator : sodium naphthalene

$$[\text{M}]_0 = 0.16 \text{ M dm}^{-3}$$

$$[\text{I}]_0 = 1 \times 10^{-3} \text{ M dm}^{-3}$$

$$[\text{Na}(\text{Ph})_4\text{B}] = 1.2 \times 10^{-3} \text{ M dm}^{-3}$$

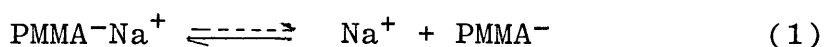
Figure 3.20 is a polymer prepared at 253 K after initiating at 195 K. In spite of 50% conversion observed and the extensive termination occurred, the polymer shows three distinct peaks indicating three major groups of polymer chains. This is significantly different from the polymer initiated at 253 K, in that the termination has occurred only during the propagation stage. These results suggest that the carbonyl attack on the monomer ester group, by the initiator, is not appreciable at 195 K but most significant at temperatures over 230 K. (Figure 3.21). This may be considered as further evidence for the reaction of initiator with the monomer ester function at a comparable rate to that of acrylic double bond at higher temperatures.



3.1.2.4 The effect of addition of common ion salt Na(Ph)<sub>4</sub>B on the MWD of PMMA

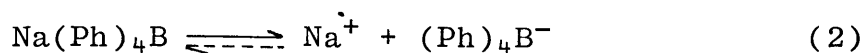
The comparative study of polymerisations of methyl methacrylate in the presence and absence of common cation salt sodium tetraphenyl boron was carried out at 195 K in THF using two types of initiators, viz fluorenyl sodium and naphthyl sodium. The former grows monofunctionally while the latter grows bifunctionally unless partially deactivated.

Table 3.10 shows the results of this study. It is apparent that the MWD of the polymer is broadened by the addition of salt with both types of initiator. Although this broadening is not very large, it is consistent. The explanation for this change may be found in the reactive species present in each polymerisation system. PMMA<sup>-</sup>Na<sup>+</sup> ion pair has an appreciable dissociation constant  $K_D = 3.5 \times 10^{-9} \text{ M/dm}^3$  (81) at 195 K in THF.



Hence in the polymerisation system, in the absence of salt, free ions and ion pairs both exist. Furthermore in the bifunctional polymer chains, some free ions could also associate with ion pair to form triple ions.

Sodium tetraphenyl boron having a very high dissociation constant under these conditions, is completely dissociated into respective ions



In the presence of excess of free Na<sup>+</sup> ions, the equilibrium

Table 3.10 The effect of addition of common ion salt on the MWD

Temp. - 195 K

Expt No	Initiator	$[M]_0$ moles $\text{dm}^{-3}$	$[I]_0 \times 10^3$ moles $\text{dm}^{-3}$	$M_n$ GPC	PDI	Remarks
C-7	Sod Naph	0.32	1.35	51000	1.21	Presence of salt
C-8	Sod Naph	0.34	1.35	49000	1.17	Absence of salt
D-8	Sod fluor	0.26	1.22	46000	1.28	Presence of salt
D-9	Sod fluor	0.27	1.23	36500	1.23	Absence of salt

of the dissociation process in the expression (1) is shifted to the left due to the common ion effect. This suppresses the formation of free ions and consequently any possibility of formation of triple ions. Thus the polymerisation in the presence of salt occurs mainly through ion pairs. The reactivity of free ions and triple ions is known to be several orders higher than that of ion pairs (48). Hence in the absence of salt, the polymerisation is complete before the termination reactions could occur to any appreciable level, making the MWD narrower than that of polymers produced by ion pairs alone.

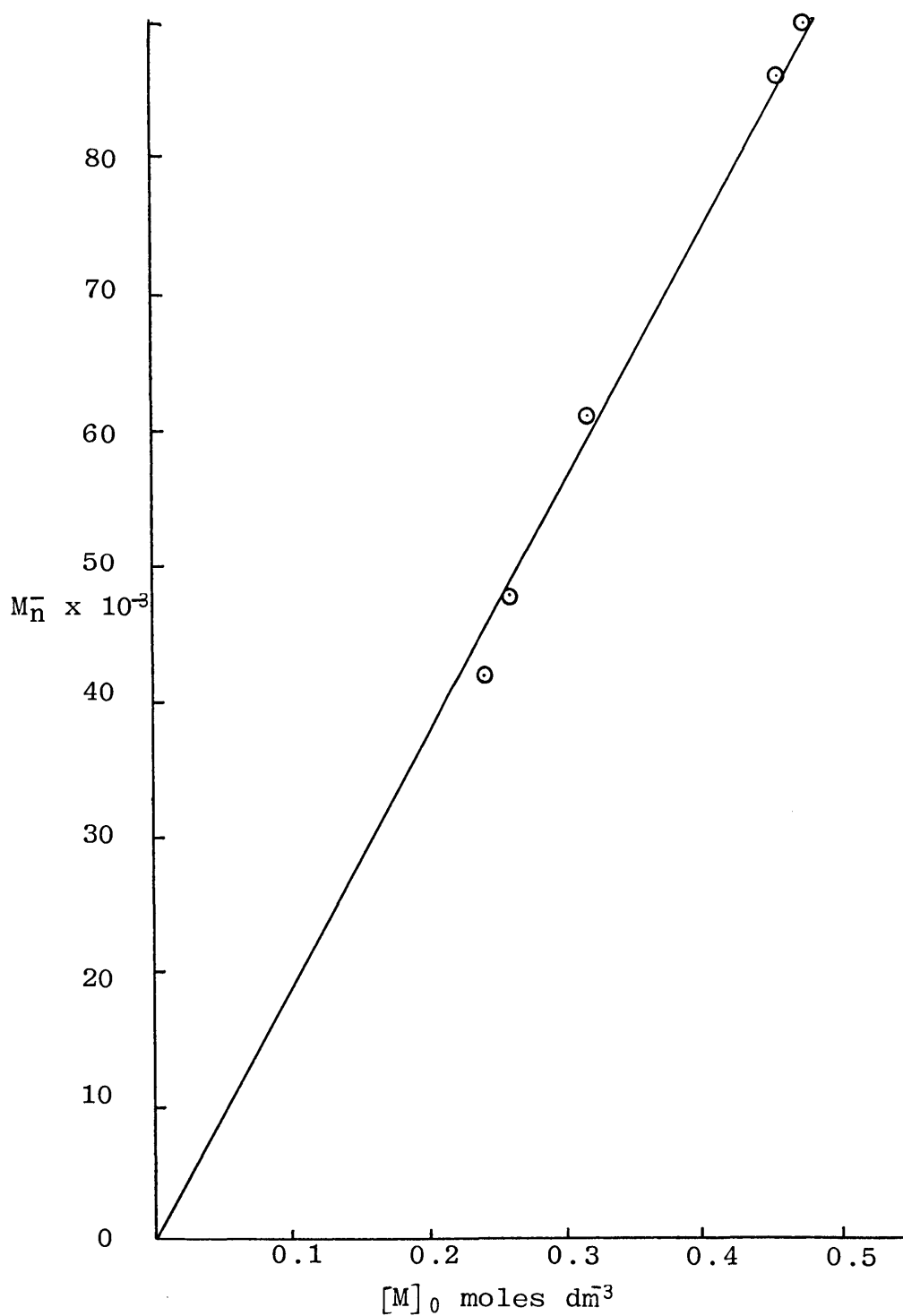
Table 3.11 The dependence of number average molecular weight on the concentration of monomer in the anionic polymerisation of MMA

Initiator - sodium naphthalene

$$[\text{Na(Ph)}_4\text{B}] = 1.1 \sim 2.2 \times 10^{-3} \text{ M/dm}^3$$

$$T = 195 \text{ K}$$

Expt No	$[\text{M}]_0$ moles/ $\text{dm}^{-3}$	$[\text{I}]_0 \times 10^3$ moles $\text{dm}^{-3}$	$[\text{M}]_0 / [\text{I}]_0$	$\overline{M}_n$ calc	$\overline{M}_n$ GPC	Remarks
C-8	0.251	0.989	254	50820	42885	
C-9	0.261	1.01	258	51745	47740	
C-7	0.320	1.02	314	62820	61000	
C-10	0.466	0.99	476	95265	85575	Gelation observed
C-11	0.476	0.97	497	99500	93300	Gelation observed
C-12	0.466	1.96	238	47608	44300	Gelation on the addition of second aliquot
C-13	0.262	2.04	128	25717	23450	
C-14	0.321	1.36	236	47262	49500	

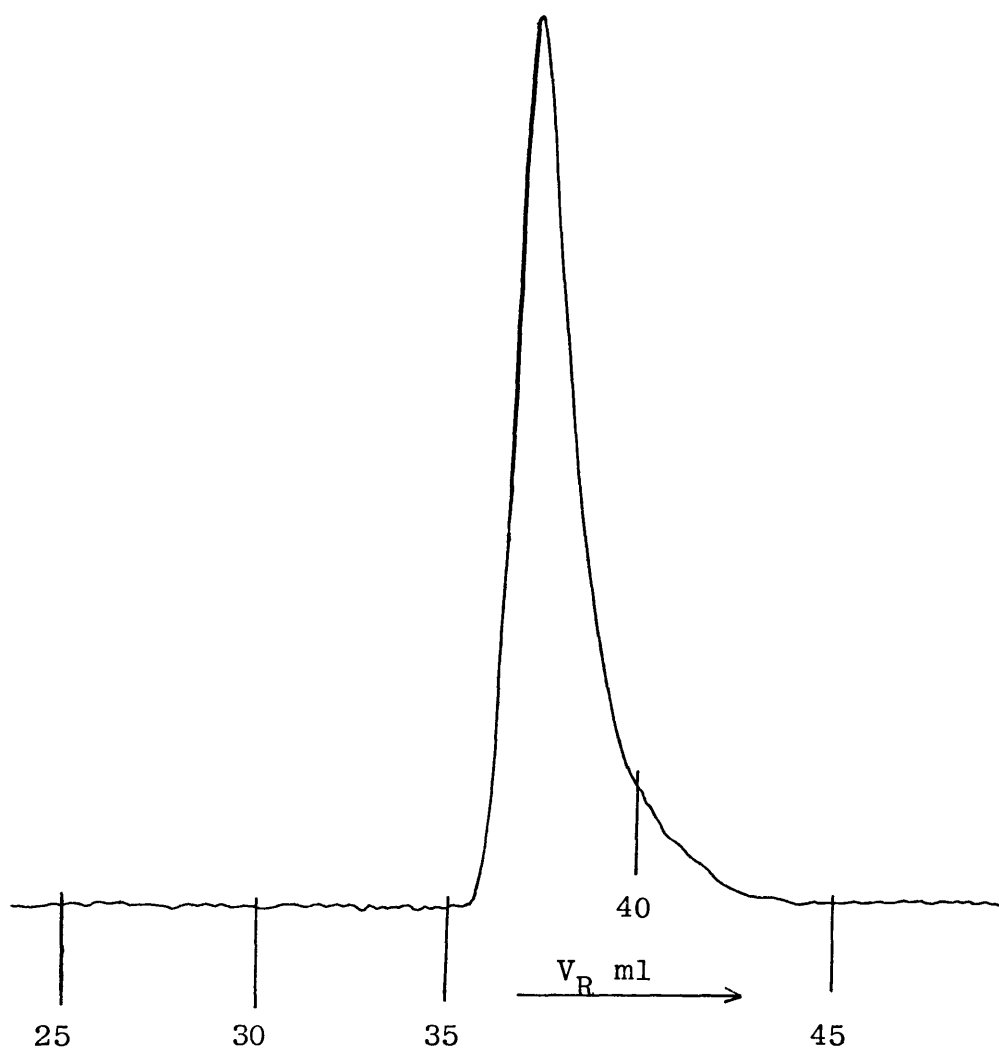


**Fig 3.22** Dependence of number average molecular weight on the monomer concentration for the anionic polymerisation of MMA.

Initiator - sodium naphthalene

$$[I]_0 = 0.99 \times 10^{-3} \text{ M dm}^{-3}$$

$$[\text{Na}(\text{Ph})_4\text{B}] = 1.2 \times 10^{-3} \text{ M dm}^{-3}$$



**Fig 3.23** GPC chromatogram of PMMA prepared by single initiation. Initiator - sodium  $\alpha$ -methyl styrene tetramer  
 $[I]_0 = 0.874 \times 10^{-3} \text{ M/dm}^3$      $[M]_0 = 0.171 \text{ M/dm}^3$   
 $[\text{Na(Ph)}_4\text{B}] = 1 \times 10^{-3} \text{ M/dm}^3$  .

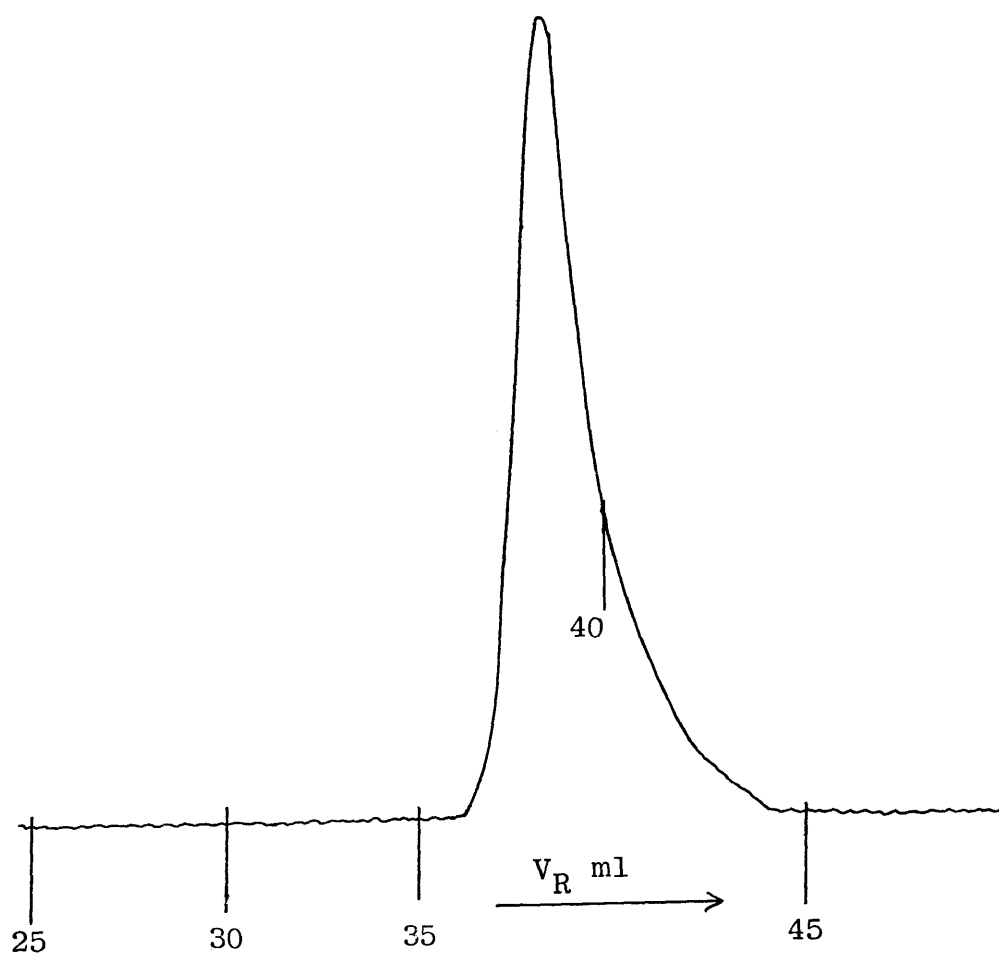


Fig 3.24 GPC chromatogram of PMMA prepared by double addition of monomer in two equal aliquots at an interval of 180 seconds

$$[I]_0 = 0.964 \times 10^{-3} \text{ M/dm}^3 \quad [M]_0 = 0.172 \text{ M/dm}^3$$

$$[\text{Na}(\text{Ph})_4\text{B}] = 1 \times 10^{-3} \text{ M/dm}^3$$

Initiator - sodium  $\alpha$ -methyl styrene tetramer

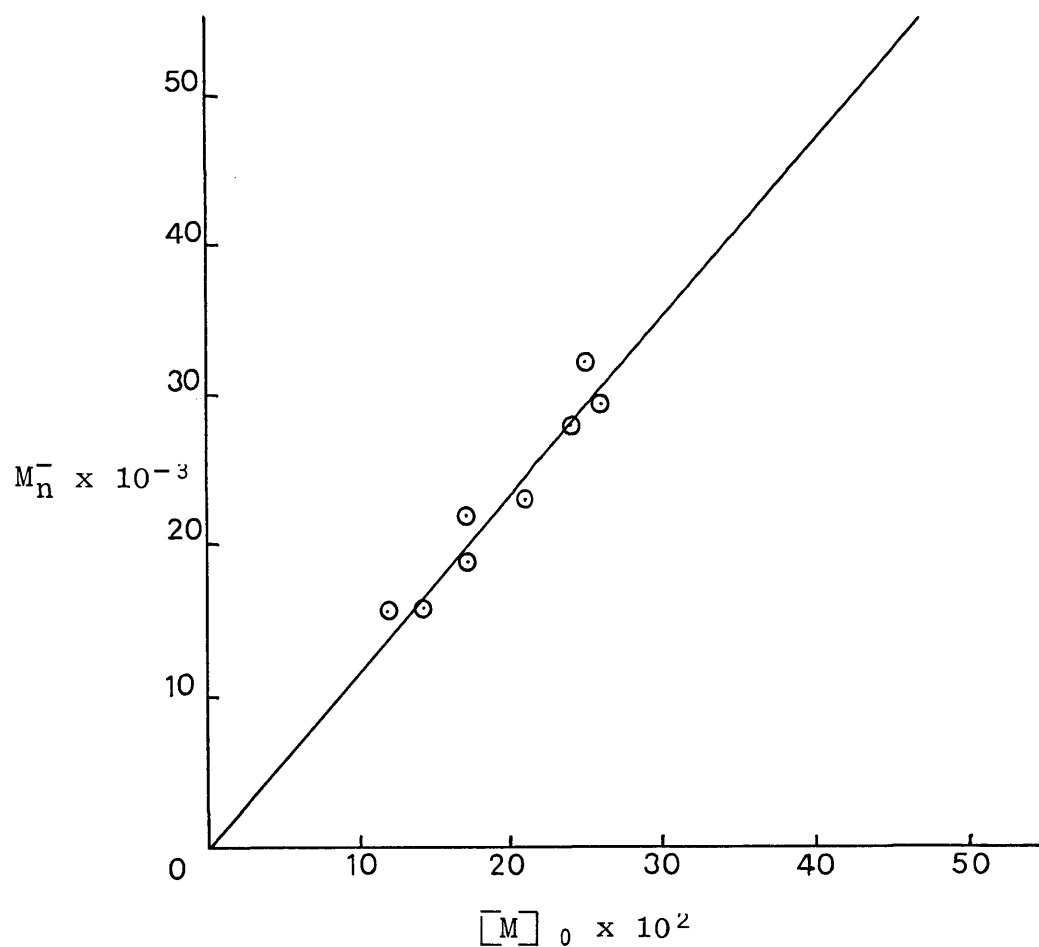


Fig 3.25 Dependence of number average molecular weight on the monomer concentration for polymerisation of methyl methacrylate by ion pairs in THF

Initiator - sodium  $\alpha$ -methyl styrene tetramer

Experimental data as in Table 3.13.

### 3.1.2.5 The effect of monomer concentration on $M_n^-$ and MWD

The dependence of  $M_n^-$  and MWD on the concentration of monomer was investigated with three initiators, viz sodium naphthalene, sodium  $\alpha$ -methyl styrene and sodium fluorine. All polymerisations were carried out in the presence of slight excess of sodium tetraphenyl boron, in pure THF at 195 K. Hence only ion pairs are believed to participate in the propagation of polymer chains.

With sodium naphthalene as initiator, a set of polymerisations were carried out at different  $[M]_0/[I]_0$  ratios by changing the monomer concentration while keeping initiator concentration approximately constant. In another set of experiments the same  $[M]_0/[I]_0$  ratio was maintained while increasing both  $[M]_0$  and  $[I]_0$ . The results are given in the Table 3.11. A plot of  $M_n^-$  vs  $[M]_0$  for the first set of experiments is given in Figure 3.22. From the linear plot it is apparent that the  $M_n^-$  increases proportionately with the increase in monomer concentration and under constant initiation conditions, it is a first order behaviour. Furthermore, the Table 3.11 shows that even under different initiator conditions up to  $2 \times 10^{-3}$  M/dm<sup>3</sup>, the theoretically expected molecular weights are still achieved, within experimental errors. It may be said that under the conditions of these experiments, the typical anionic mechanism is being observed and number average degree of polymerisation can be simply given by the ratio  $2[M]_0/[I]_0$ .



The increase in monomer concentration from 0.1 to 0.48 moles/dm<sup>3</sup> does not seem to have any significant effect on the MWD of the polymers. However, at monomer levels over 0.4 moles/dm<sup>3</sup>, the "gelation" of the living polymer solution was observed. (The terms "gel" and "gelation" here are being used only to indicate a temporary change of physical state of the polymer solution to a semi-solid state which resembles a gel in its inability to flow.) When the polymerisation was carried by two additions of equal aliquots of monomer, the "gelation" was observed on the addition of the second. This was observed at high concentration of initiator as well as at low concentrations. Increase in the temperature from 195 K to 273 K or termination by the addition of methanol, both reverse the process back to liquid state, but recooling to 195 K does not turn it back to "gel". It is difficult to attribute this observation to increase in viscosity of the polymer solution, since the immediate recooling of living polymer solution in the unopened reactor fails to turn it back to "gel" and also the drop in concentration of the solution due to addition of methanol is only 1.8 grams/dm<sup>3</sup>.

Apparently relatively higher concentrations of monomer and living ends are both required for this to occur, and may be thought of as a co-ordination network of monomer, living ends and THF. It is possible that low temperature and relatively high dielectric constant of solvent, as well as the structure of THF molecule help in the process. Although the occurrence of "gelation" does not seem to affect the MWD or the number of molecular weight detectably,

Table 3.12 The dependence of number average molecular weight on the concentration of monomer

Initiator - fluorenyl sodium

$$[\text{Na(Ph)}_4\text{B}] = 1.2 \times 10^{-3} \text{ M dm}^3$$

Expt No	$[M]_0$ moles $\text{dm}^{-3}$	$[I] \times 10^3$ moles $\text{dm}^{-3}$	$M_n^-$ calculated	$M_n^-$ GPC	PDI
D-1	0.253	0.9436	27100	35000	1.28
D-2	0.243	0.9134	26615	30000	1.30
D-3	0.273	1.032	26450	35600	1.25
D-4	0.381	0.9807	38800	40100	1.23
D-5	0.398	1.540	25800	26050	1.20
D-6	0.483	0.916	32870	49500	1.22
D17	0.489	1.877	26070	26650	1.35

Table 3.13 The dependence of number average molecular weight on the monomer concentration. Temperature 195-200 K  
Initiator - Sodium  $\alpha$  methyl styrene tetramer

Expt No	$[M]_0$ moles $\text{dm}^{-3}$	$[I] \times 10^3$ moles $\text{dm}^{-3}$	$M_n^-$ calculated	$M_n^-$ GPC	PDI
B-8	0.120	1.012	23743	15900	1.18
B-9	0.138	1.10	25121	16220	1.147
B-10	0.172	0.975	35324	19025	1.185
B-11	0.171	0.98	34940	22000	1.17
B-12	0.206	1.01	40841	23100	1.15
B-13	0.237	1.07	44352	28000	1.19
B-14	0.248	1.10	45145	32000	1.118

it may be an indication of a transient state similar to that reported by Allen for polymerisation of MMA with  $\text{Mg}^+$  as counterion (58). However, more plausible explanation may be that the counterions of the cyclic end of the active polymer chains are co-ordinated by weak electrostatic bonds to the negative centres of adjacent chain ends.

With fluorenyl sodium as the initiator also, the dependence of the number average molecular weight on the concentration of monomer is linear. The molecular weights obtained are generally close to theoretically expected values or are fractionally higher (Table 3.12). The latter result is readily explained if the loss of initiator due to the impurities is considered.

It was noticed that the polydispersity indices of the polymers prepared using fluorenyl sodium as initiator were consistently greater than those of the polymers prepared using sodium  $\alpha$ -methyl styrene tetramer as initiator. It is unlikely that the difference in the number of reactive ends per chain is responsible for this since that should have led to a reverse effect. This may be explained in terms of the uncertain chemical structure of fluorenyl sodium. Two isomeric species, which may be present in the initiating systems, could initiate at two different rates and possibly by two different mechanisms. Furthermore the slow rate of initiation of MMA by fluorenyl sodium in contrast to that by fluorenyl lithium may also be responsible for this broadening of MWD.

### 3.1.3 The anionic polymerisation of methyl methacrylate by ion pairs with $K^+$ as counterion.

#### 3.1.3.1 Kinetics

The kinetics of anionic polymerisation of methyl methacrylate by ion pairs with  $K^+$  as counterion was investigated with potassium  $\alpha$ -methyl styrene dimer as the initiator. As in the previous cases, the dissociation of ion pairs into free ions was suppressed by the addition of slight excess of potassium tetraphenyl boron.

The data of the kinetic studies are given in the Table 3.14. The time versus conversion curve was plotted according to equation (1), in a similar manner to those for ion pairs with  $Li^+$  and  $Na^+$  as counterions (Fig 3.26). The significant difference of this from the others is its much faster rate. Initiation is extremely rapid and within 10 seconds more than 90% conversion was observed. Termination reactions do not seem to be significant, since the first order monomer consumption is observed. From the linear integrated rate plot, the rate constant of propagation of  $PMMA^-K^+$  ion pairs is calculated.

By linear regression:

$$\text{The slope} = \frac{26.6854}{92.278} = 0.2892$$

The concentration of initiator was found to be

$$[I] = 7.8 \times 10^{-4} \text{ moles dm}^{-3}$$

From equation (3), the slope =  $K_{p(\pm)} [I]$

$$\therefore K_{p(\pm)} = \frac{26.6854}{92.278} \times \frac{1}{7.8 \times 10^{-4}}$$

$$k_p(\pm) = 370.75 \text{ dm}^3\text{mol}^{-1} \text{ sec}^{-1}$$

The dependence of number average molecular weight on the fractional conversion is approximately linear. However, there is a considerable variation and scattering of values compared to those calculated from an undisturbed polymerisation system, indicating a more complicated process than that observed for polymerisation with  $\text{Na}^+$   $\alpha$ -methyl styrene (Fig 3.33).

GPC chromatograms of the resultant polymers at different conversions offer a more detailed insight (Figs 3.27 to 3.31). As Fig 3.27 illustrates, at the lowest conversion of 17% at 0.6 seconds, bimodal distribution with fairly narrow individual peaks are obtained. The ratio of the molecular weights at the maxima of the peaks is approximately 1:5. With the increase in conversion, the peaks appear to merge (Fig 3.28) and at 92% conversion a narrow peak with very slight tailing is observed. However after that again a broadening of MWD appears to occur. At 30 seconds, a bimodal distribution with a high molecular weight approximately 400,000 is observed and broadening of MWD up to this region is observed in all polymerisations carried out up to 100% conversion (Table 3.15).

From the gel permeation chromatograms, it is apparent that two active species grow at different rates, the initially slower species becoming faster with increased conversion. The absence of low molecular tailing indicates the absence of termination reactions to any significant level. The appearance of high molecular area or peak with the

Table 3.14 Experimental data for the determination of rate constant of propagation by ion pairs,  $K_{p(\pm)}$  for PMMA-K<sup>+</sup> at 195 K in THF

Initiator - potassium  $\alpha$ -methyl styrene dimer

$[\text{K(Ph)}_4\text{B}] = 1.1 \quad 2.5 \times 10^{-3} \text{ moles/dm}^3$

Expt No	$[\text{M}]_0$ moles/ $\text{dm}^3$	$[\text{I}]_0 \times 10^3$ moles/ $\text{dm}^3$	fractional conversion	Time seconds	$M_n^-$ GPC
E-2	0.214	0.98	0.17	0.6	2800 and 14000 double peak
E-3	0.212	0.99	0.41	1.25	15200
E-4	0.220	0.98	0.72	4.0	31900
E-5	0.215	0.97	0.92	8.0	59500
E-6	0.215	1.01	0.97	12.0	54000

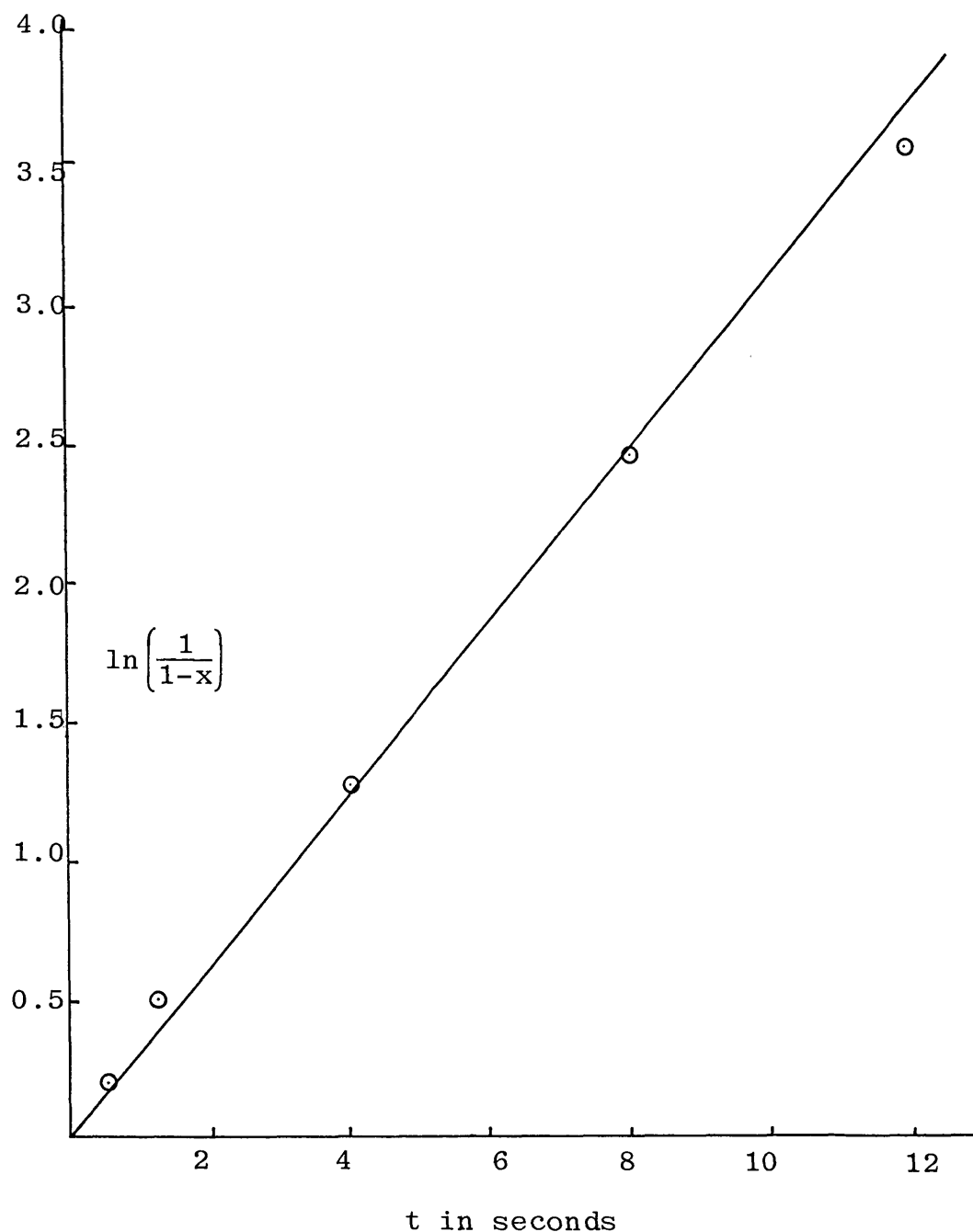


Fig 3.26 First order plot of conversion vs time for anionic polymerisation of methyl methacrylate in THF by ion pairs with  $K^+$  as counterion.

Initiator - potassium  $\alpha$ -methyl styrene dimer

$$[I] = 7.8 \times 10^{-4} \text{ moles dm}^{-3}$$

$$[K(Ph)_4B] = 1.1 \times 10^{-3} \text{ moles/dm}^3 \quad T = 195 \text{ K}$$

Experimental data as in Table 3.14

disappearance of low molecular weight peak also indicates that initially slower species overtake the initially faster ones towards the final phase of propagation. The manual peak resolution shows that the major polymer peak is always the lower molecular weight species and remains narrow while the spreading is in the high molecular weight fraction. Hence the broadness of MWD is a result of this high molecular weight fraction. The table 3.16 indicates that the MWD broadens with the decrease in  $[M]_0/[I]_0$  ratio. The highest PDI value close to 3 is observed for the lowest ratio, while at very high  $[M]_0/[I]_0$  ratio of 546 much narrower distribution is observed.



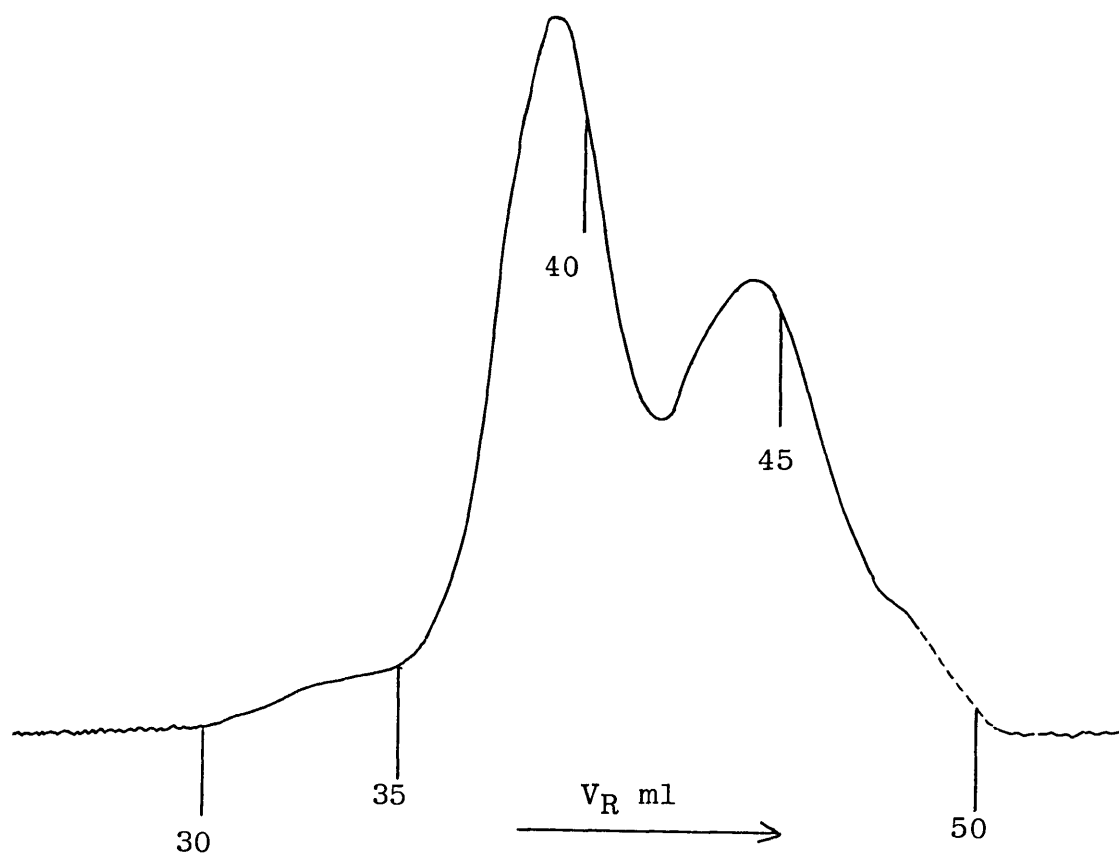


Fig 3.27 GPC chromatogram of PMMA at fractional conversion 0.17

Reaction conditions in Table 3.14

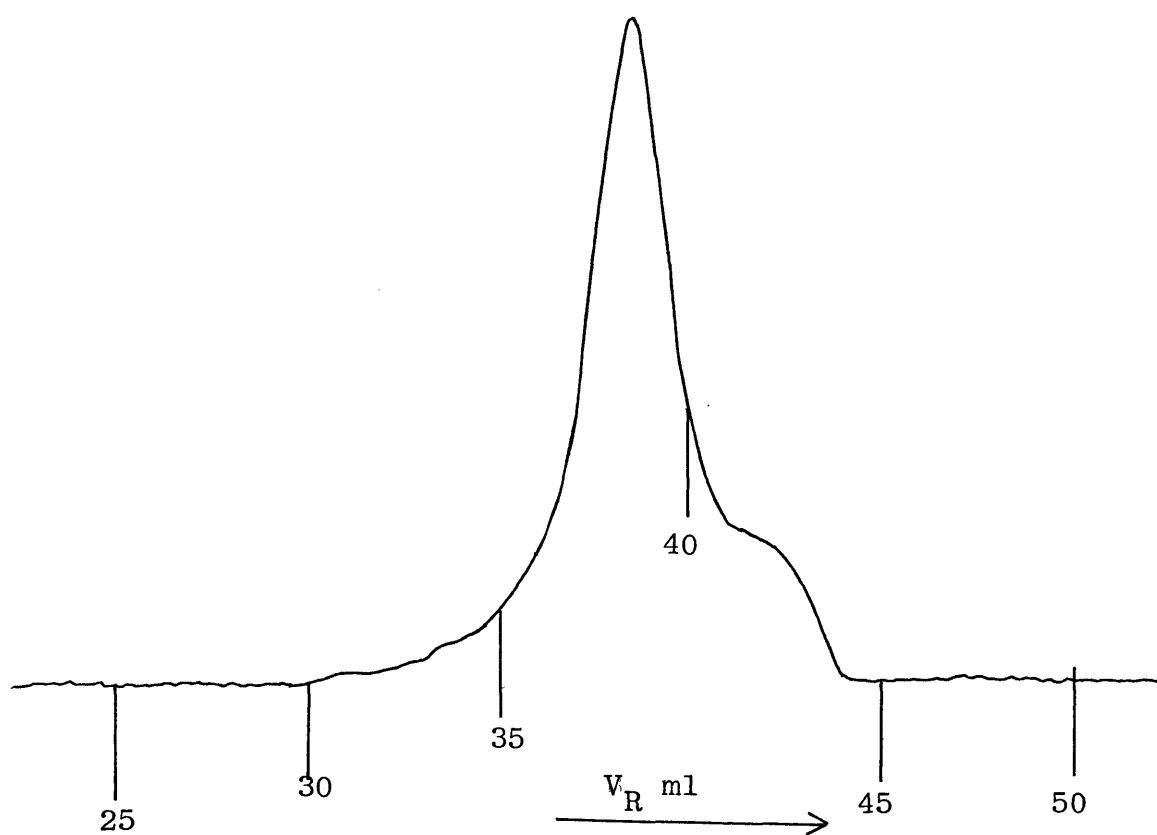


Fig 3.28 GPC chromatogram of PMMA at fractional conversion 0.41

Reaction conditions in Table 3.14

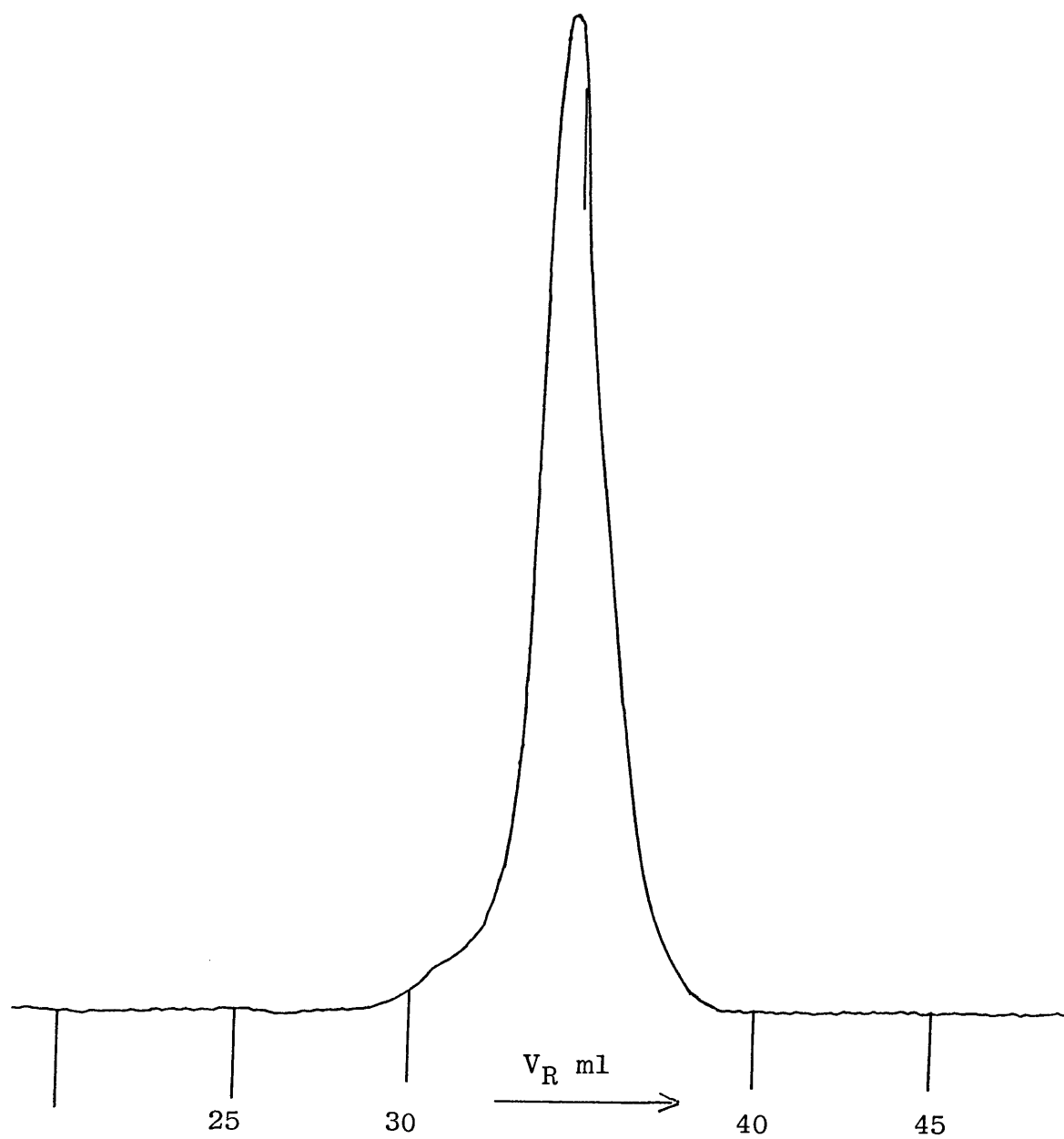


Fig 3.29 GPC chromatogram of PMMA at fractional conversion 0.9

Reaction conditions in Table 3.14

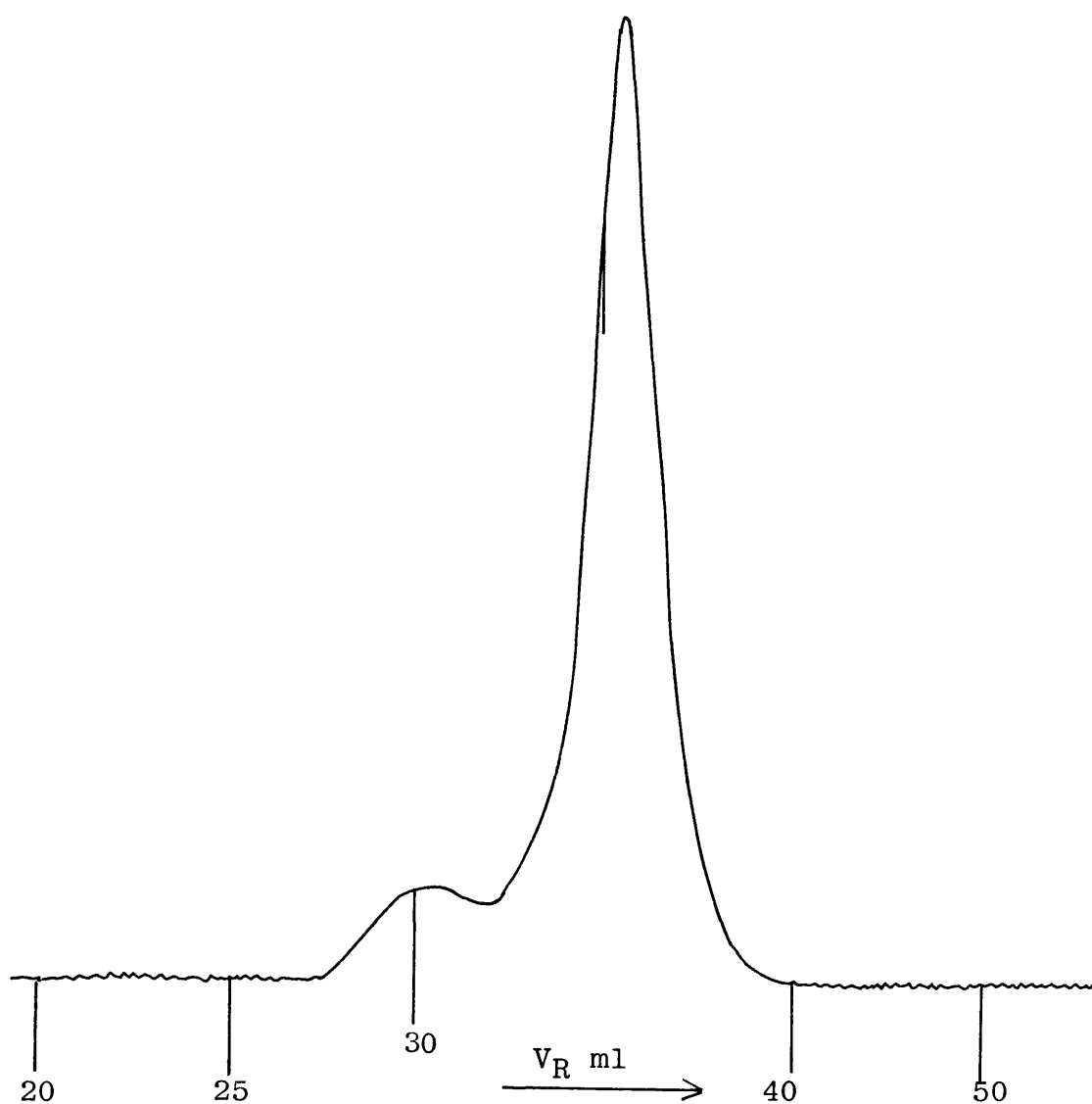


Fig 3.30 GPC chromatogram of PMMA at fractional conversion 0.97

Reaction conditions in Table 3.14

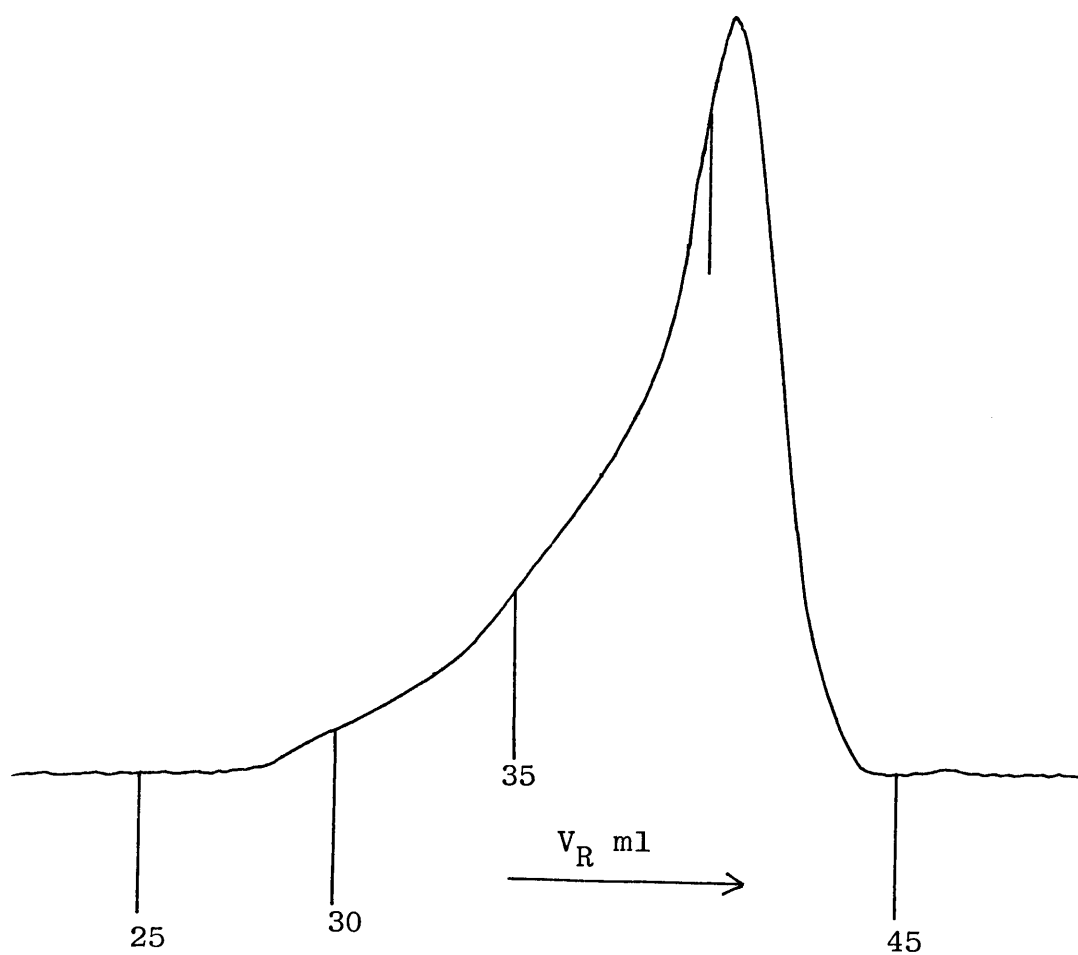


Fig 3.31 GPC chromatogram of PMMA at complete conversion

Reaction conditions in Table 3.14

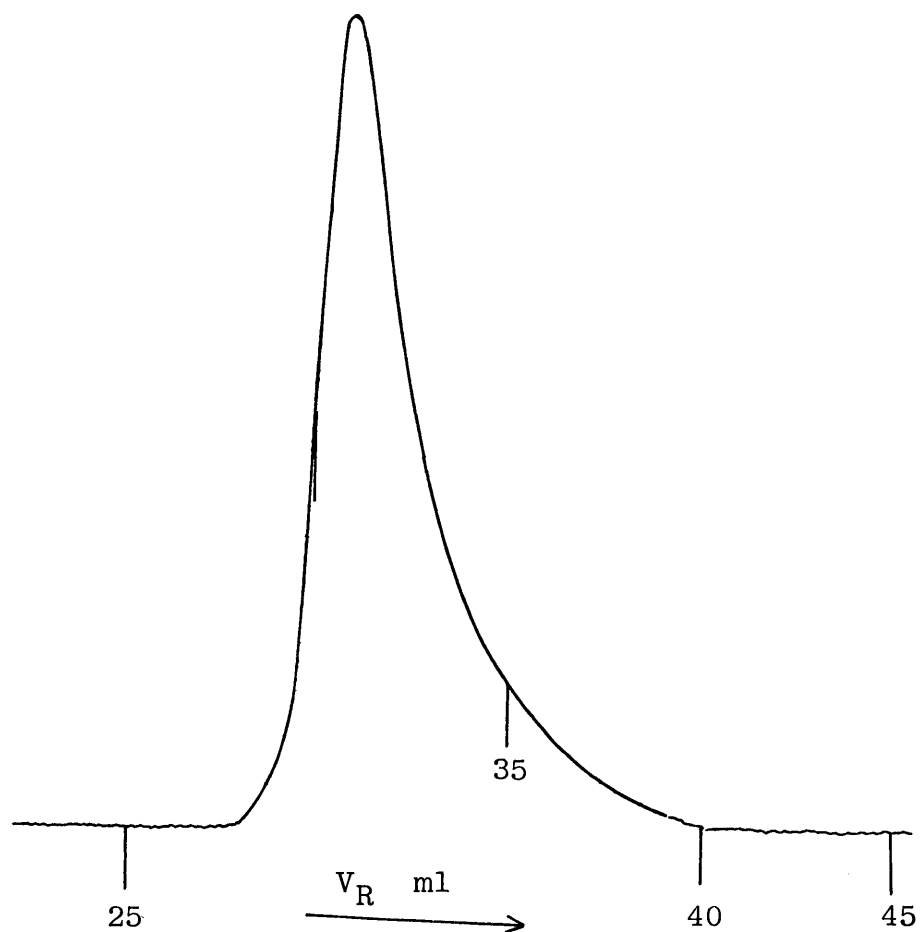


Fig 3.32 GPC chromatogram of PMMA produced at 200 K

Initiator - fluorenyl potassium

$$[M]_0 = 0.246 \text{ M/dm}^3 \quad [I]_0 = 3.78 \times 10^{-4} \text{ M/dm}^3$$

$$[K(\text{Ph})_4\text{B}] = 1 \times 10^{-3} \text{ M/dm}^3$$

Table 3.15 The dependence of  $M_n^-$  and MWD on the fractional conversion for the anionic polymerisation of methyl methacrylate by  $PMMA^-K^+$  ion pairs in THF

Initiator : potassium  $\alpha$ -methyl styrene dimer

T = 195 K

$[M]_0$  0.215 moles/dm<sup>3</sup>  $[I]_0 = 0.98 \times 10^{-3}$  moles/dm<sup>3</sup>

Expt No	Fractional conversion	$M_n^-$ GPC	PDI
E-2	0.17	2800, 13800	Bimodal
E-3	0.41	15000	1.62
E-4	0.72	31900	1.38
E-5	0.92	59600	1.21
E-6	0.97	54000	1.84
E-7	1.0	42358	2.06

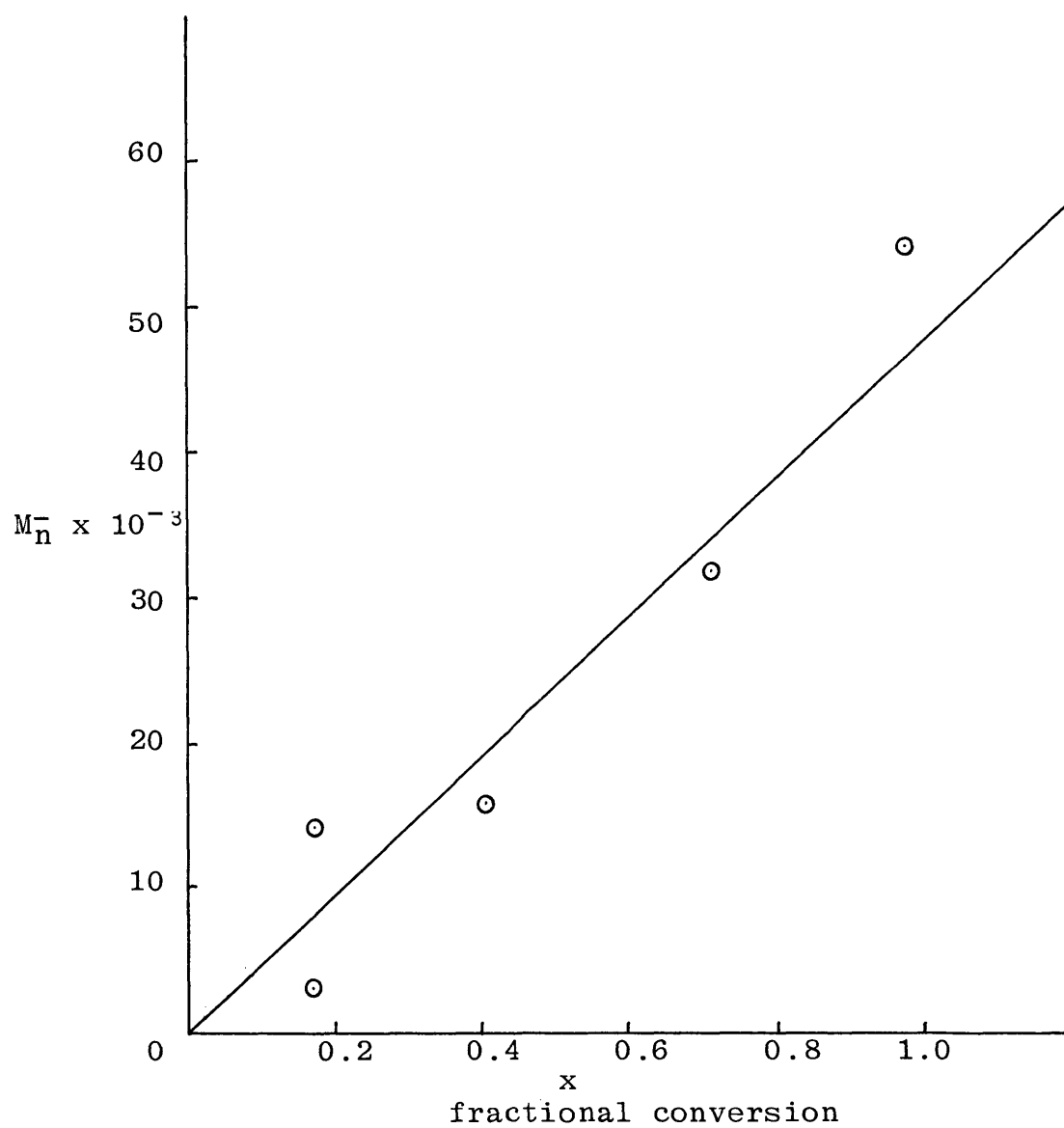


Fig 3.33 Dependence of number average molecular weight on the fractional conversion for anionic polymerisation of MMA by ion pairs with  $K^+$  as counterion



Table 3.16 Anionic polymerisation of methyl methacrylate  
by PMMA<sup>-</sup> K<sup>+</sup> ion pairs in THF at 195 K.

Initiator : potassium  $\alpha$ -methyl styrene dimer

Expt No	$[I]_0 \times 10^3$ moles /dm <sup>3</sup>	$[M]_0$ moles /dm <sup>3</sup>	$ M _0 /$ $ I _0$	$M_n^-$ calcu- lated	$M_n^-$ GPC	PDI
E-9	2.45	0.23	94	18798	14750	2.93
E-10	2.47	0.46	186	37291	22650	2.57
E-11	1.56	0.33	212	42358	26585	2.06
E-12	0.88	0.24	273	54610	32060	1.99
E-13	0.79	0.22	278	55763	33262	1.81
E-14	0.86	0.47	546	109433	152913	1.37

There are three ways by which these results could be looked at. Primarily, as a result of monofunctional (partially deactivated bifunctional species) and bifunctional species propagating at two rates. But this explanation does not appear to be acceptable since the ratio of molecular weights does not bear 1:2 ratio, which is expected if the same type of species is growing. Furthermore, no significant low molecular weight tailing is observed.

Secondly, an explanation in terms of non-interchanging contact and solvent separated ion pairs is also not favourable. The reason for this is that polymerisations of methyl methacrylate carried out under the same conditions with fluorenyl potassium (monofunctional) as the initiator (Fig. 3.32) show no indication of a high molecular peak or a spreading. In this polymer, a low molecular tail is significant which can be explained as due to uncertain chemical structure of the initiator and possibly to slow initiation.

The third is a modified version of the first model. If the high molecular fraction is assumed to be due to gradual increase in bifunctional species which had previously been in a less reactive form, the observed changes in MWD could be explained. A plausible mechanism for such a change is by intramolecular cyclisation of bifunctional species. The cyclised forms grow slower at first but once the chain lengths of approximately 80-100 units are attained, the ring form reverses to linear form and grows at a faster rate,

producing the high molecular weight fraction. The broadness of the high molecular fraction indicates that the reversal to the linear form is a gradual process and earliest formed reach the highest molecular weight values.

Since the concentration of monomer at this stage is very low, the increase in the number of linear bifunctional chains leads to a range of lengths of polymer chain and results in broadening the MWD. The relatively narrow MWD obtained for very low concentration of initiator is possibly a result of much lower number of cyclised bifunctional species present in the reaction medium.

### 3.1.3.2 The effect of addition of salt $K(Ph)_4B$

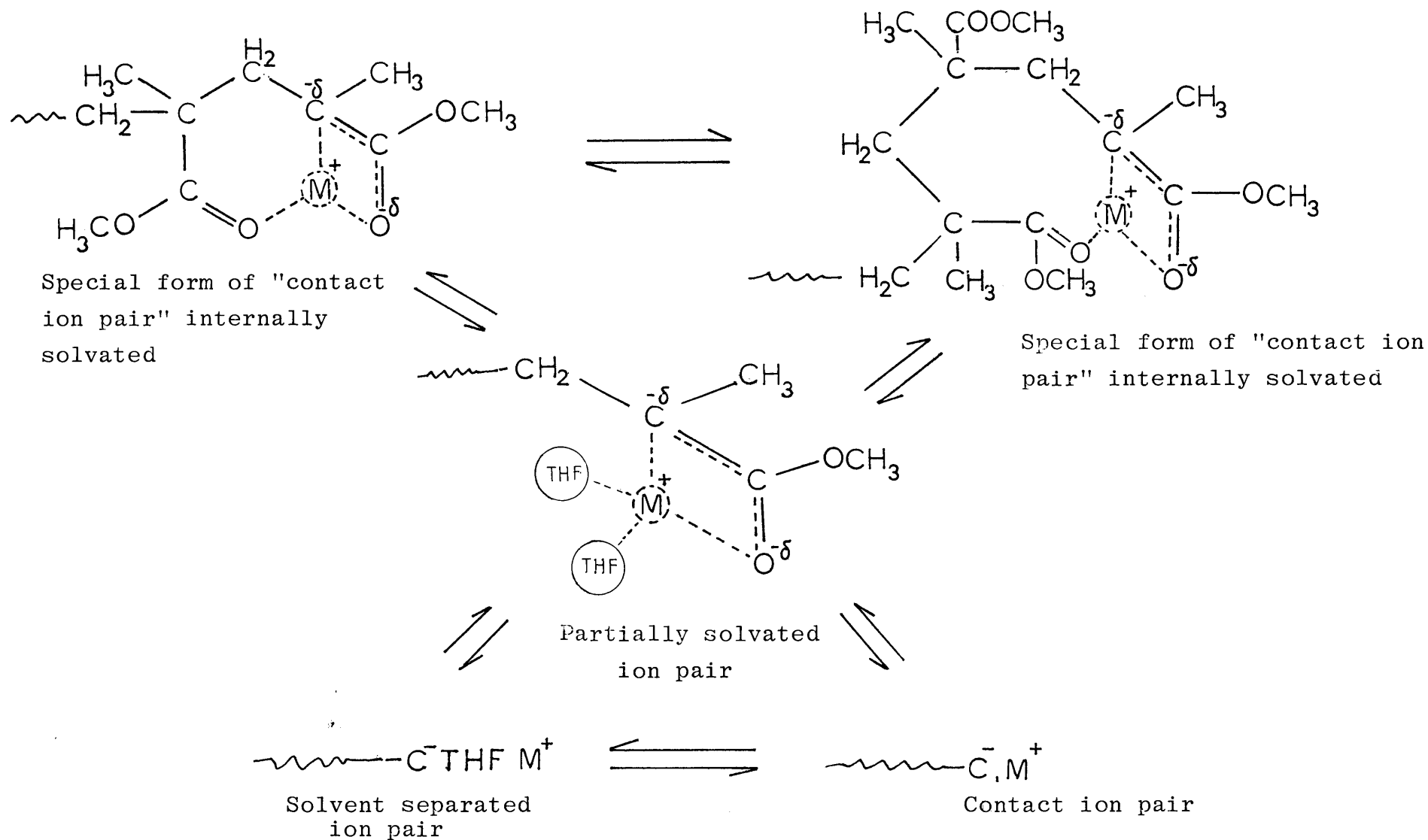
Table 3.17

Expt No	$ M _0$ moles/ $dm^3$	$ I _0 \times 10^3$ moles/ $dm^3$	PDI	Remarks
E-15	0.33	1.56	2.06	With salt
E-16	0.22	0.80	1.81	No salt

The effect of the presence of salt was investigated by carrying out polymerisations in THF at 195 K, in the presence and absence of potassium tetraphenyl borane, and comparing MWD's. From the table above, it is apparent that the polymer produced in the absence of salt has a narrower distribution than that produced in the presence. This is similar to that observed for  $Na^+$  counterion and can be simply explained as due to the presence of faster free ions, which helps to attain complete polymerisation before any appreciable termination. However, the unusually broad MWD observed even in the absence of salt indicates that the polymerisation is not as simple as that with  $Na^+$  and  $Li^+$  counterions. The termination reactions are not responsible for such broadening as apparent from the absence of low molecular tail (Fig 3.31) and low termination rate constants (Section 2). The greater broadening in the presence of salt excludes extensive chain transfer possibilities since highly reactive free ion should produce an opposite result. Thus it is apparent that the active species are undergoing some changes in reactivity in this system.

#### 3.1.4 Discussion

From the kinetics of propagation of anionic polymerisation of methyl methacrylate in THF, it is apparent that the rate constant of propagation for ion pairs decreases along the order  $K^+ > Na^+ > Li^+$ . The degree of polymerisation is a linear function of the monomer concentration, consumption of which can be described as a first order process. Any model proposed for the nature of propagating species or the mechanism of propagation has to account for the trend in the change of rate of propagation. In this context, it is appropriate to consider the kinetics of a non-polar vinyl monomer in polar and non-polar media. It is well reported that for the anionic polymerisation of styrene in THF by ion pairs with alkali metal counterions, the order of reactivity is  $Li^+ > Na^+ > K^+ > Cs^+$  (132), ie the order of reactivity decreases with the increasing size of the counterion. However, in dioxane which is a very poor solvent, reverse order of reactivity is observed (84). This can be explained in terms of higher solvating power of THF. In the transition state specific solvation of counterion by THF provides a considerable driving force for the propagation reaction. The  $Li^+$  counterion which becomes most solvated shows therefore the highest reactivity while  $Cs^+$  counterion with poor specific solvation is least reactive. In dioxane, there is no such solvation and the order of reactivity depends on the coulombic attraction between  $PMMA^-$  and alkali $^+$  ions. The tighter ion pair which has the highest interionic attraction is the slowest to react while the ion pair with least



**Figure 3.34** Active centres of PMMA in the anionic polymerisation

interaction becomes the fastest. Hence in this case  $\text{Cs}^+$  ion pair has the highest reactivity.

The fact that the reactivity of ion pairs in the anionic polymerisation of MMA in THF increases with the size of the counterion is in complete contrast to that observed for styrene under the same conditions but resembles the propagation in dioxane.

Following the same argument as above, it is apparent that the  $\text{PMMA}^- \text{Li}^+$  ion pair has higher interaction than  $\text{PMMA}^- \text{Na}^+$  which in turn has higher interaction than  $\text{PMMA}^- \text{K}^+$  ion pair. The simplest interpretation of this is that the counterions are not specifically solvated by THF, either in the initial or transition state. One possible explanation for this is that the last 2 or 3 ester groups of the polymer chain "solvate" the counterion in competition with THF. The counterion may be positioned in such a manner that the interaction with negative site is still maintained. A cyclic structure of the form in Figure 3.34 satisfies this model. The  $\text{Li}^+$  ion being very small could well fit into the cyclic structure closer to the carbanionic site imparting a greater interaction and lower reactivity. Consequently, the larger  $\text{K}^+$  counterion shows the least interaction. The steric hindrance may also play a part in this process. Sodium according to this model is intermediate in reactivity, which infact is the case. In all three cases, the two types of species ie contact and internally solvated contact pairs are in labile equilibrium. However, the partially solvated and

solvated ion pairs also may be in equilibrium, but the concentration of these species at any given instant would be minimal. The equilibrium concentration of any major type of ion pairs is determined by the nature of the counterion, temperature and the number of THF molecules which could be solvating externally.

According to this model, with  $\text{Li}^+$  as counterion, the formation of internally solvated contact ion pairs is the most favoured. If the participation of any other active species is negligible, this may explain the very narrow, almost poisson type distribution obtained for polymers prepared with  $\text{Li}^+$  as the counterion. As the size of the counterion increases, the equilibrium shifts slightly towards the other species and hence could lead to a relative broadening of MWD. This may possibly be a major factor responsible for the increase in broadening of MWD in the order  $\text{Li} < \text{Na} < \text{K}$ .



## Section 2

### 3.2 The termination mechanism in the anionic polymerisation of methyl methacrylate

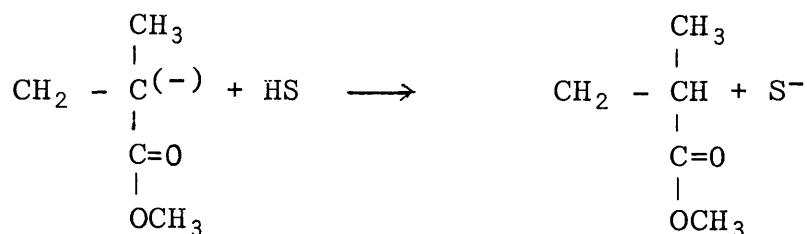
The importance of termination reactions involving the ester group, in the anionic polymerisation of methyl methacrylate has long been recognised (145). Although there is no direct evidence to establish which reactions are more important, it is generally understood that at higher temperatures and in non-solvating media, termination reactions play an increasingly important role (52)(56)(72). With the increased reliability of gel permeation chromatography as an important mechanistic tool, now it is possible to examine the proposed models and modify them, by examining molecular weight distributions (MWD) of polymers produced under different conditions of possible termination reactions.

In general, it is believed that in the anionic polymerisation of MMA, the anion could react possibly with one or more of the following present in the reaction mixture.

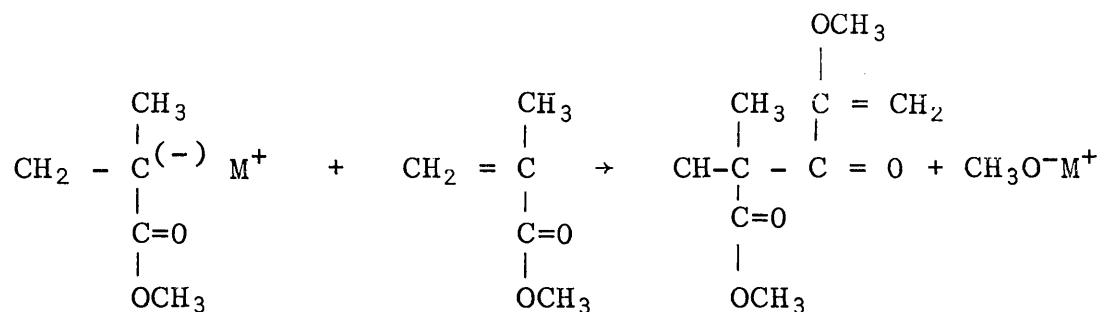
- (i) solvent,
- (ii) monomer ester function,
- (iii) another polymer chain, via ester group,
- (iv) ester groups of the same polymer chain.

These possibilities can be represented as follows:

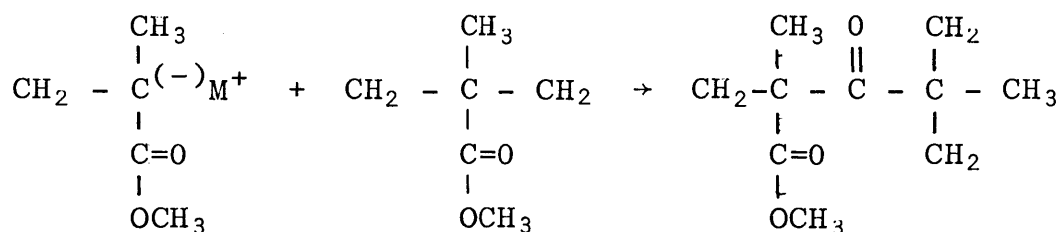
- (i) Reaction with the solvent:



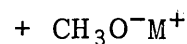
(ii) Reaction with monomer ester group:



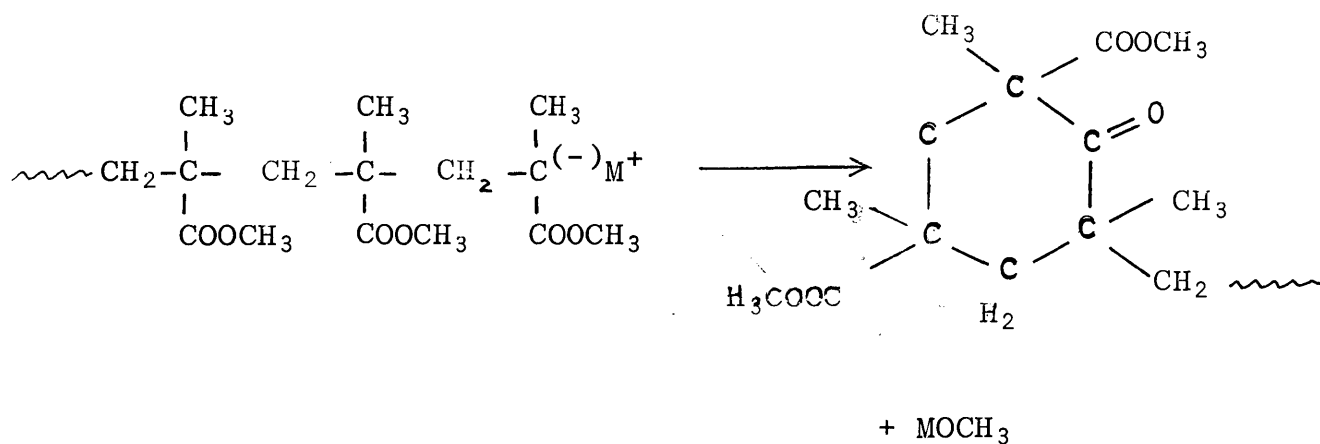
(iii) reaction with ester group of another polymer chain



Branched high m.wt polymer



(iv) Reaction with a ester group of the same polymer chain



In the presence of monomer, all the above reactions are possible even though to different extents, depending on the conditions. However, in the absence of monomer, only the first, third and fourth reactions could take place. The

expected effects of the above reactions on the MWD of the resultant polymers are tabulated in Table 3.18.

Table 3.18 Proposed termination reactions of the polymethyl methacrylate ion pairs and their effect on the MWD of the resultant polymer

Termination reaction of the anion	Effect on MWD	
	In the presence of Monomer	In the absence of Monomer
(i) with solvent	Broaden	Unchanged
(ii) with monomer	"	-
(iii) with another chain	"	Broaden
(iv) back-biting reaction	"	Unchanged

In all four types of termination reaction, the ultimate effect is the reduction of the number of reactive species. As a result, in the presence of monomer, all these processes would theoretically bring about a broadening of MWD since the dispersity of the polymer increases as the simultaneous propagation and termination proceed. In the absence of monomer however, any termination reaction with the solvent or the so-called back-biting reaction, which is the reaction of active site at the chain end with the penultimate or antipenultimate ester group of the same chain, does not affect the size of the molecule. Hence the MWD is not affected. The bimolecular reaction of polymer chains could lead to branched polymers of very high molecular weights.

### 3.2.1 Termination reactions in the absence of monomer

Considering the above possibilities, three types of experiment were planned.

#### Type A

1. Initiation at 200 K with little monomer
2. Propagation at the required temperature with the bulk of the monomer.
3. Termination with methanol after 30 minutes.

#### Type B

1. Initiation and propagation at 200 K
2. Storage at 250 K for 12 hours
3. Termination with methanol.

#### Type C

1. Initiation and propagation at 200 K
2. Storage at 250 K for 12 hours
3. Recool to 200 K
4. Second polymerisation and termination after 30 minutes.

Table 3.19

Termination reactions of polymethylmethacrylate ion pairs in THF.

$$[I] = 9.2 \times 10^{-4} \text{ M dm}^{-3}$$

$$[M] = 0.23 \text{ M dm}^{-3}$$

$$[Na(Ph)_4B] = 1.5 \times 10^{-3} \text{ M dm}^{-3}$$

Experiment Type	$M_n^-$ from GPC	PDI	Remarks
A	42500	1.19	Control at 200 K
B	32300	1.32	Complete conversion
C	40156	1.29	No polymerisation of the second batch of monomer. Complete conversion of the first.

Table 3.20 Termination reaction of polymethyl methacrylate ion pairs in THF. Initiator : Fluorenyl lithium

$$[I] = 8.4 \times 10^{-4} \text{ M dm}^{-3}$$

$$[M] = 0.25 \text{ M dm}^{-3}$$

$$[Na(Ph)_4B] = 1.5 \times 10^{-3} \text{ M dm}^{-3}$$

Experiment type	$M_n^-$ from GPC	PDI	Remarks
A	49300	1.15	Control reaction at 200 K.
B	25800	1.15	Coloured solution
C	(51000 ( (150000	1.20) ) 1.20)	Bimodal distribution Approximate calculation from GPC. Conversion complete with both monomers

Table 3.21 Termination reactions of polymethyl methacrylate ion pairs in THF. Initiator : Fluorenyl lithium

$$[I] = 1.2 \times 10^{-3} \text{ M dm}^{-3}$$

$$[M] = 0.20 \text{ M dm}^{-3}$$

$$[Li(Ph)_4B] = 1.5 \times 10^{-3} \text{ M dm}^{-3}$$

Experiment type	$M_n^-$ from GPC	PDI	Remarks
A	30135	1.15	Control at 200 K
B	32000	1.28	Complete conversion
C	80000	1.31	Complete conversion of the first batch of monomer, no polymerisation of the second.

Table 3.22 Termination reactions of polymethyl methacrylate ion pairs in THF Initiator : potassium  $\alpha$ -methyl styrene

$$[I] = 1.6 \times 10^{-3} \text{ M dm}^{-3}$$

$$[M] = 0.27 \text{ M dm}^{-3}$$

$$[K(Ph)_4B] = 2 \times 10^{-3} \text{ M dm}^{-3}$$

Experiment type	$M_n^-$ from GPC	PDI	Remarks
A	51400	1.12	Control at 200 K
B	-	-	-
C	(33500 (80000		Bimodal distribution Approximate calculation from GPC. Complete conversion of first batch of monomer, 50% conversion of the second batch.

Tables 3.19 - 3.22 show the results of the experiments carried out in the absence of monomer. As seen from the polydispersity values as well as GPC elution curves (Fig 3.35 - 3.39), irrespective of the type of anion, with all cations used there is considerable broadening of molecular weight distribution, when the living polymer solution was held at 250 K for 12 hours. This suggests that some reaction of the anions with polymer ester groups of difference chains has occurred. However, considering the original low concentration of the initiator, approx.  $10^{-4} \text{ M dm}^{-3}$  and the further low effective concentration of living ends available for such a reaction, it is reasonable to assume that the rate of termination by this mechanism is extremely slow. It is difficult to obtain accurate rate data because of the operation of intra-molecular termination processes simultaneously. Although

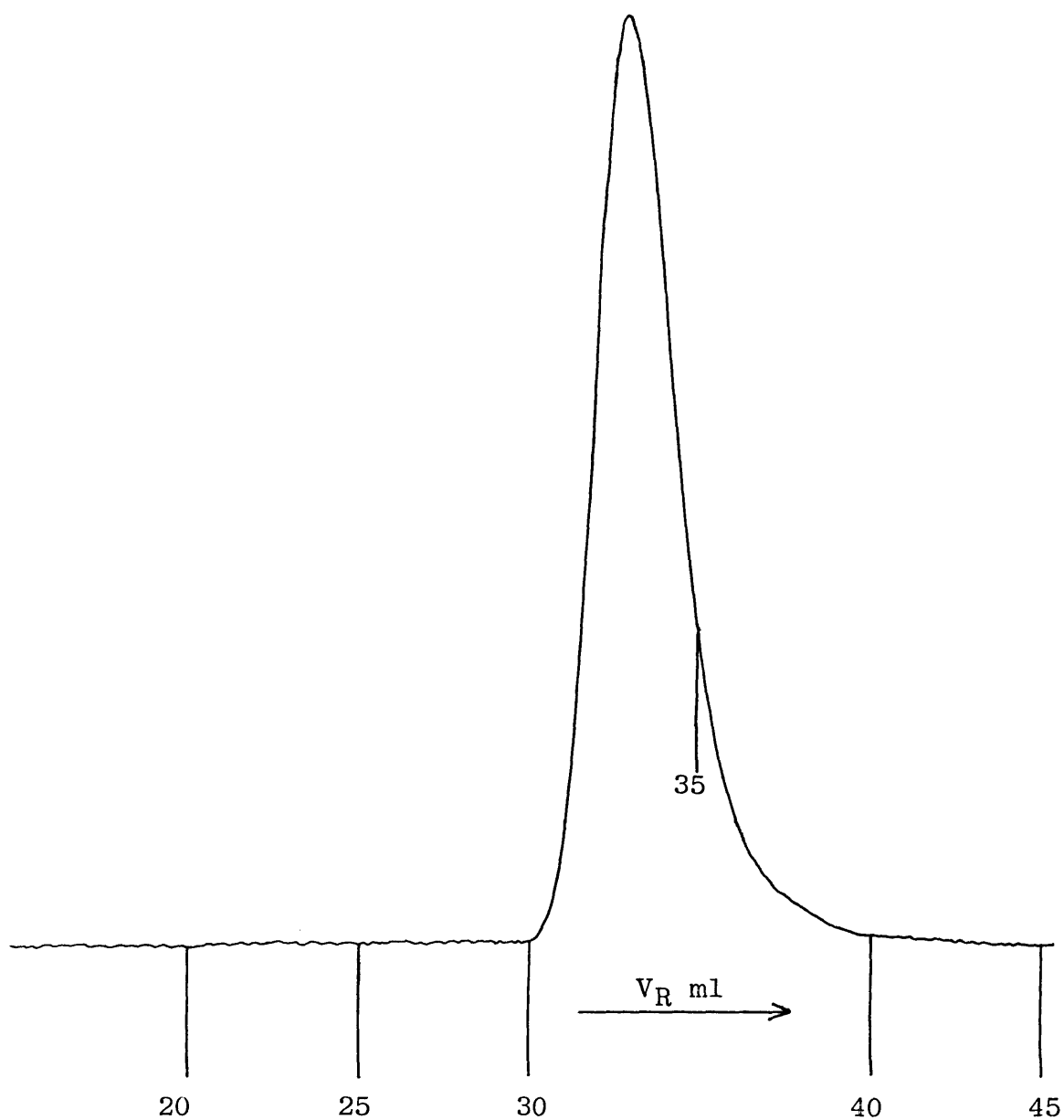


Figure 3.35 GPC chromatogram of PMMA prepared at 195 K living polymer solution held at 253 for 12 hours before the second polymerisation.  $[M]_0 = .2065, .1866 \text{ M/dm}^3$   
 $[I]_0 = 1.2 \times 10^{-3} \text{ M/dm}^3$   $(\text{Li(Ph)}_4\text{B})_2 = 1.3 \times 10^{-3} \text{ M/dm}^3$   
 Initiator = fluorenyl lithium

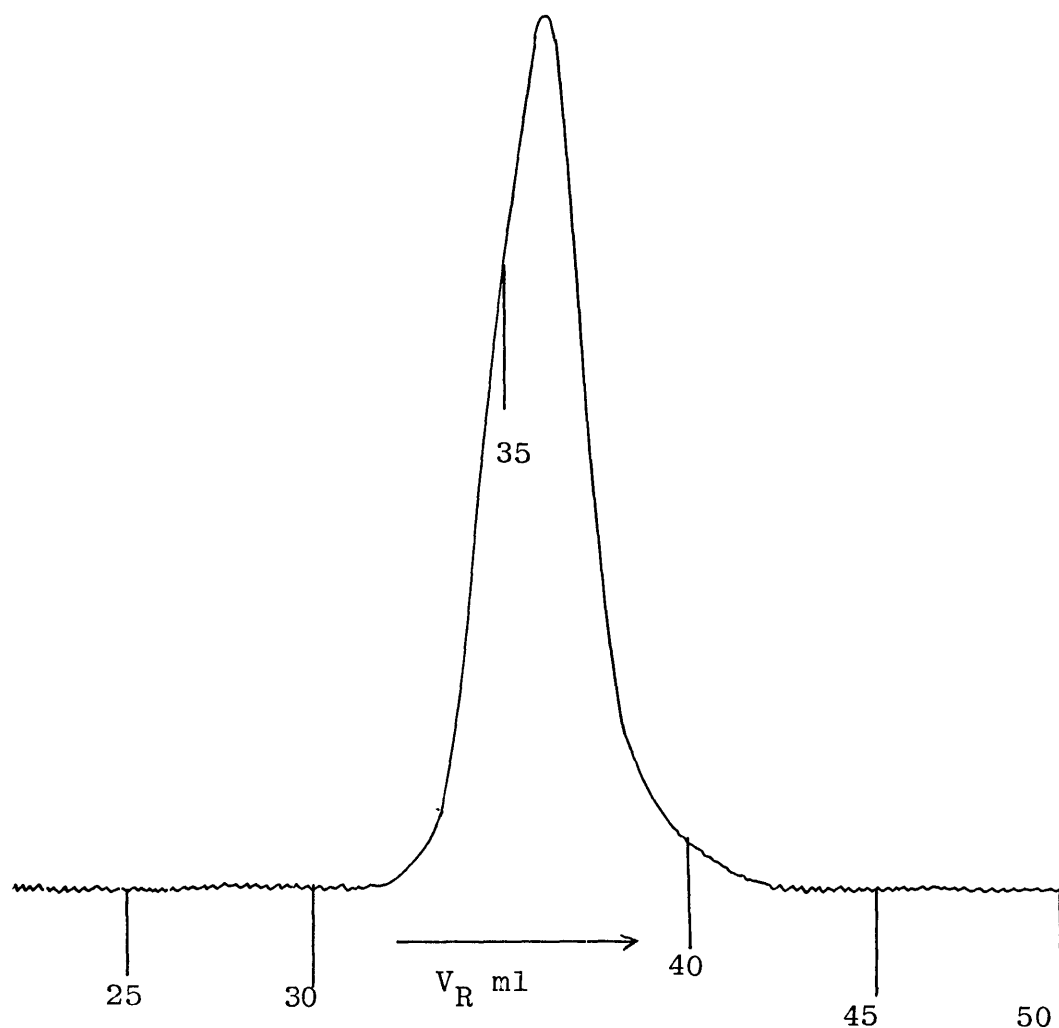


Fig 3.36 GPC chromatogram of PMMA prepared ay 195 K  
Living polymer solution was held at 253 for 12 hrs  
before the second polymerisation.

$$[M]_0 = 0.2362, 0.2082, [I]_0 = 0.9183 \times 10^{-3} \text{ M/dm}^3$$

$$[\text{Na(Ph)}_4\text{B}] = 1.1 \times 10^{-3} \text{ M/dm}^3$$

Initiator - sodium naphthalene



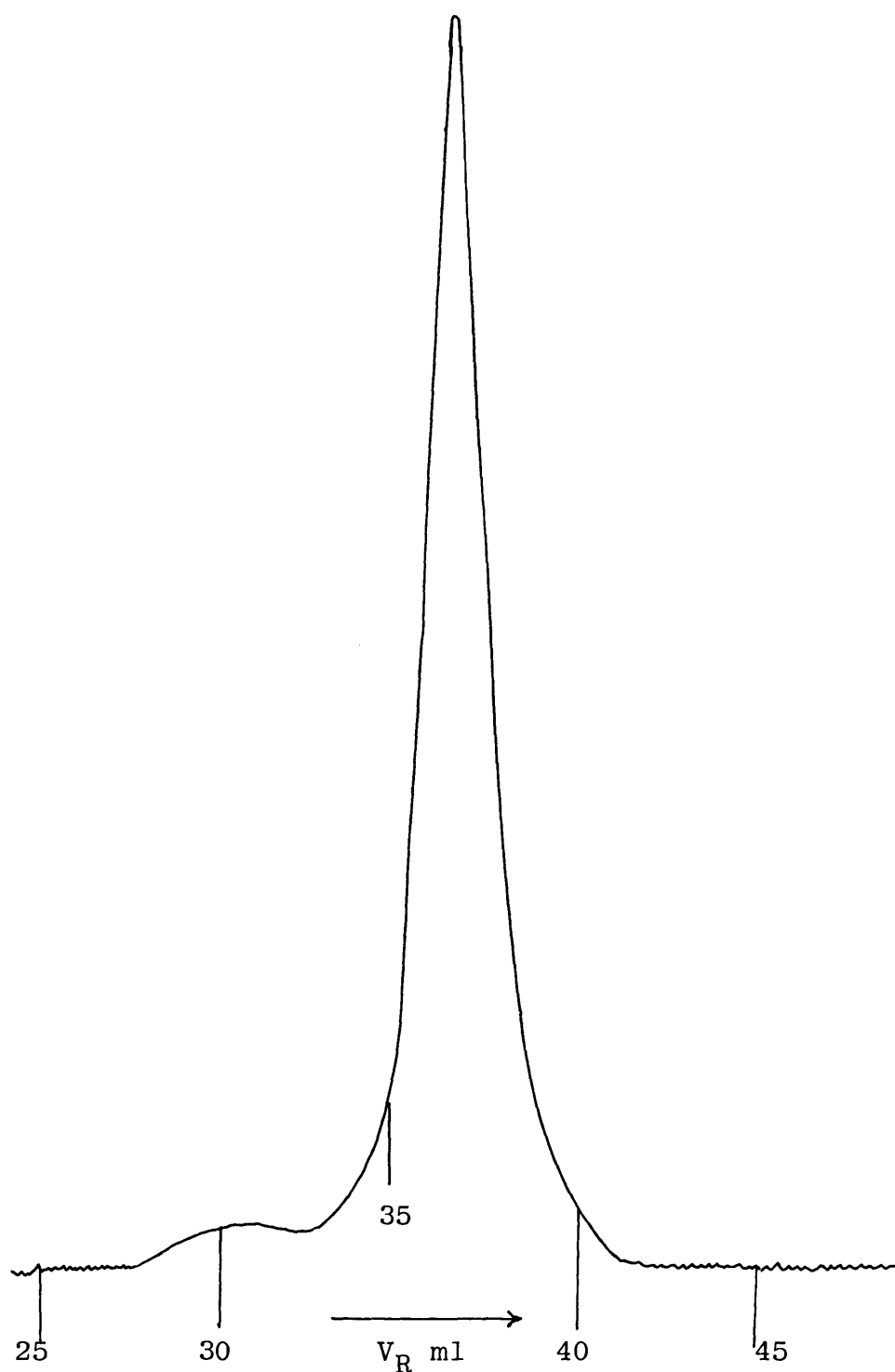


Fig 3.37 GPC chromatogram of PMMA prepared at 195 K

Living polymer solution held at 195 for 30 hours

$$[M]_0 = 0.2423 \text{ M/dm}^3 \quad [I]_0 = 0.8818 \times 10^{-3} \text{ M/dm}^3$$

$$[K(Ph)_4B] = 1.1 \times 10^{-3} \text{ M/dm}^3$$

Initiator - potassium  $\alpha$ -methyl styrene dimer

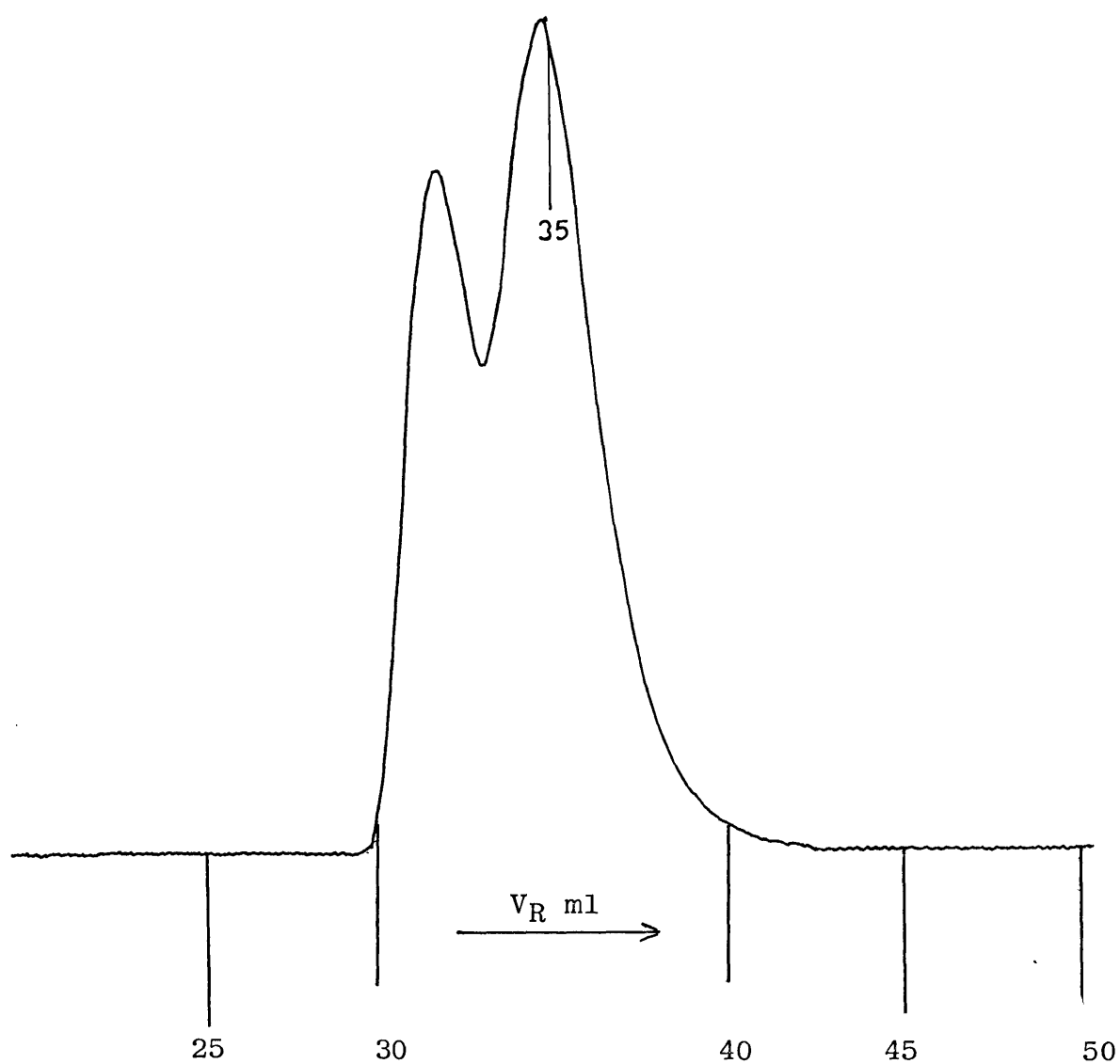
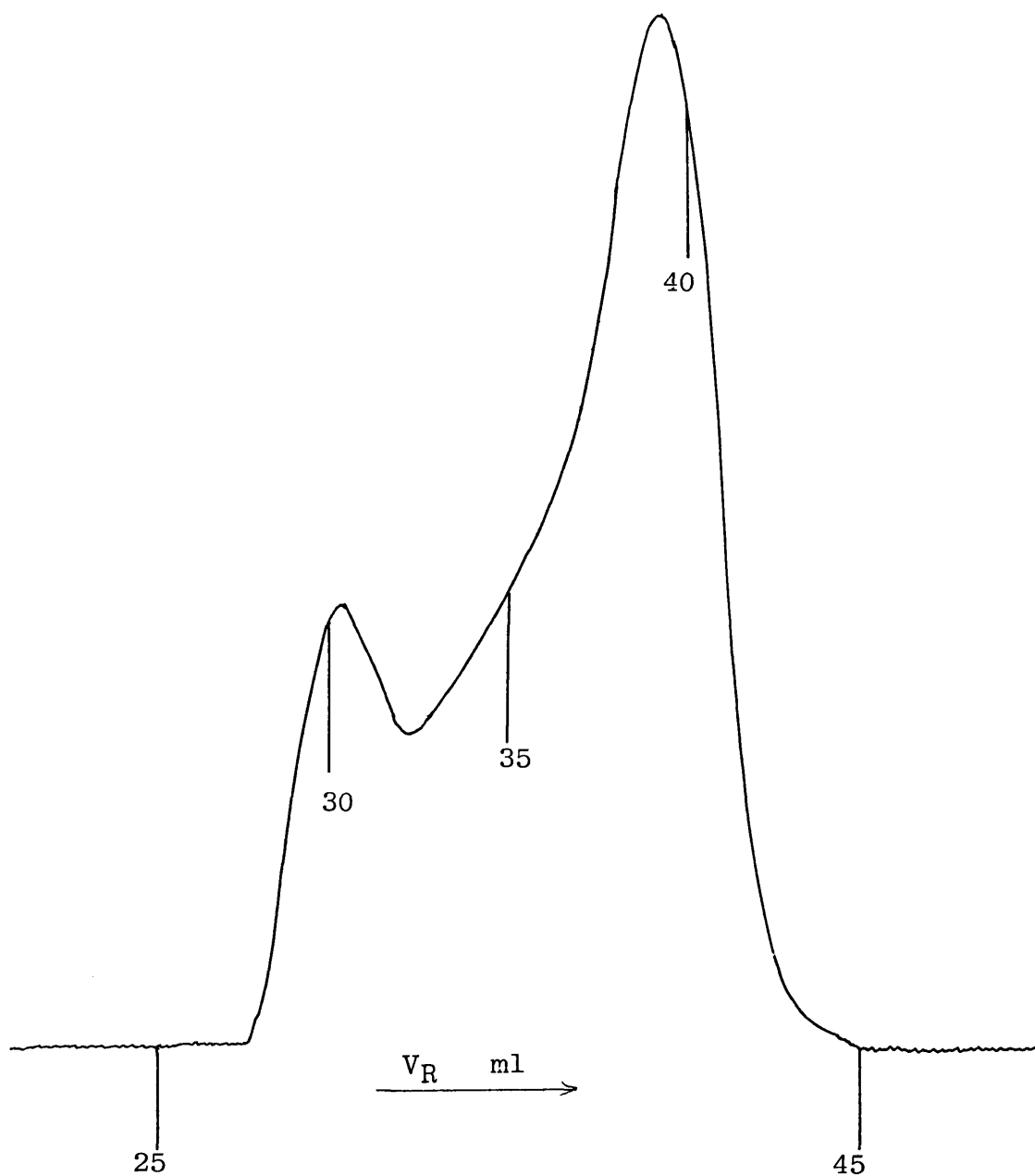


Figure 3.38 GPC chromatogram for PMMA prepared at 195 K  
Living polymer solution held at 253 K for 12 hours before  
the second polymerisation

$[M]_0 = 0.2593, 0.2310 \text{ M/dm}^3$   $[I] = 8.4 \times 10^{-4} \text{ M/dm}^3$

$[\text{Na(Ph)}_4\text{B}] = 1.1 \times 10^{-3} \text{ M/dm}^3$

Initiator - fluorenyl lithium



**Figure 3.39** GPC chromatogram of PMMA prepared at 195 K  
Living polymer solution held at 253K for 12 hours before  
the second polymerisation.

$[M]_0 = 0.2758, 0.2386 \text{ M/dm}^3$   $[I]_0 = 1.2053 \times 10^{-3} \text{ M/dm}^3$

$[K(Ph)_4B] = 1.5 \times 10^{-3} \text{ M/dm}^3$

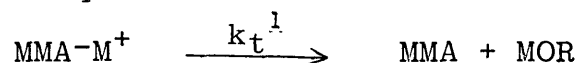
Initiator = potassium  $\alpha$ -methyl styrene

the MWD is not affected by such a process, the lifetime of reactive species is dependent on it. Examination of chromatograms of polymers from sodium naphthalene and fluorenyl lithium initiated polymerisation (Fig 3.36 and Fig 3.35) shows that termination is complete within 12 hours and no significant broadening was observed. With the evidence of these observations, it can be safely stated that the rate of interchain reaction is much slower than that by back-biting.

Further evidence for the occurrence of interchain reaction was obtained in a specific study carried out at 200 K with polymethyl methacrylate living polymer solution. Initiated with potassium  $\alpha$ -methyl styryl ion pairs, the polymer solution was held at 200 K for 32 hours. The chromatogram of the resulting polymer is given in Fig 3.37. This shows clearly a high molecular weight peak ( $> 200,000$ ) which is quite separate from the narrow peak of the main polymer, but less than 2% of the total polymer. However, it was generally noticed that there is a tendency to form broad bimodal distribution polymers when initiation is carried out with potassium  $\alpha$ -methyl styrene, thus it is difficult to discount the possibility of such an effect on this product.

The results shown in Table 3.19 - 3.22 also can be used to calculate the termination rate constant for  $\text{PMMA}^-\text{M}^+$  ion pairs for the self-termination reaction. From the given results, it appears that the termination occurs by a simple first order intramolecular process, which can be represented

by the equation:



where  $k_t^1$  is the termination rate constant for the intramolecular process.

As indicated earlier, the intermolecular processes also are operating simultaneously but the rates are considered to be extremely low compared to the intramolecular process at this temperature. Thus it can be disregarded for the sake of simplifying calculations. The calculation of rate constants can be carried out in two ways. If the monomer concentration is kept constant during the first and second polymerisations, the following expression will apply:

$$\ln \left[ \frac{\bar{M}_{n(2)}}{\bar{M}_{n(1)}} \right] = K_t^1 \cdot t$$

where  $\bar{M}_{n(1)}$  and  $\bar{M}_{n(2)}$  are the number average molecular weights of first and second polymer,  $k_t$ , the rate constant of termination and  $t$ , the time in seconds.

If accurate measurements of initiator concentrations were possible, the following expression could be used to calculate  $k_t^1$ , even if the monomer concentration changes.

$$\ln \frac{I_0}{I} = k_t^1 \cdot t$$

where  $I_0$  = Original concentration of the initiator for the first polymerisation

$I$  = Concentration of living polymer before the onset of second polymerisation

$K_t^1$  and  $t$  are as above.

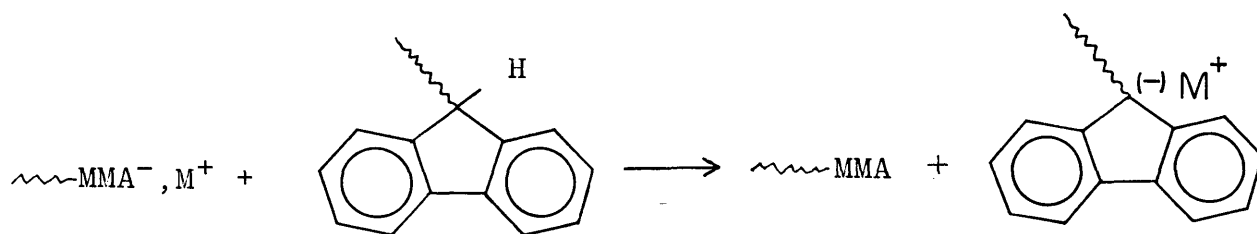
Calculated rate constants are given in Table 3.23.

Table 3.23 Rate constants of termination of PMMA ion pairs in THF, for intramolecular reaction

Initiator	$k_t^1(\pm) \text{ sec}^{-1}$	Temp K
Sodium Naphthalene	$>10^{-3}$	250
Fluorenyl sodium	$2.5 \times 10^{-5}$	250
Fluorenyl lithium	$>10^{-3}$	250
Pot. $\alpha$ -styrene	$2 \times 10^{-5}$	250

The higher rates observed for sodium naphthalene and fluorenyl lithium are reflected in the fact that none of them could initiate the second batch of monomer, and their GPC chromatograms are narrow bands in both cases. (Fig 3.35 and 3.36) The simplest explanation is that all living ends had been terminated before any appreciable broadening due to intermolecular reaction could occur.

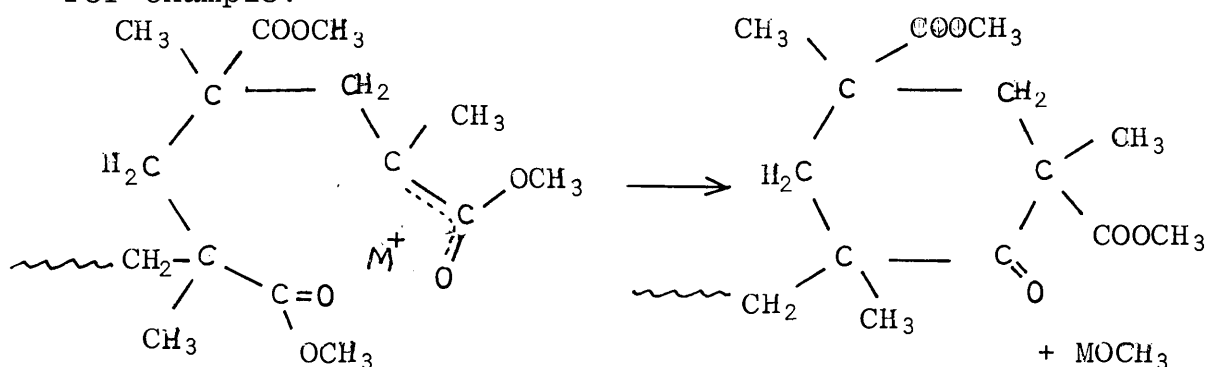
The hydrogen transfer from the solvent to anion is a theoretically possible reaction which could terminate reactive species without affecting the molecular weight distribution. The observed results do not allow such a possibility, at least under the conditions of this set of experiments. The initiator solutions which were prepared by methods described in the experimental section, in THF were still reactive after more than 8 months at 250 K and loss of reactivity was not very significant. With fluorenyl alkali metal initiators it has been suggested (135) that the living ends could be disturbed by a transfer reaction in which the proton in the 9-position of the fluorenyl group becomes incorporated at the end of the polymer chain.



According to this scheme, every polymer chain terminated would result in bifunctional chain, thus keeping the number of reactive ends constant. Although the type B results would not indicate a broadening of MWD even if this process is operating, type C results should show a broad and bimodal distribution of the second polymer. As seen in Table 3.21 with fluorenyl lithium, the second polymerisation did not occur suggesting the absence of such a reaction. Hence this process too could be discarded or disregarded for the systems under consideration.

Finally, in the absence of monomer and other processes referred above, the only acceptable explanation for termination seems to be the intramolecular reaction of living ends, the rates of which would be significantly high. The most favoured mechanism for such a reaction is the cyclisation, where the methoxy group of the penultimate or antipenultimate ester group is eliminated, giving rise to a cyclic ketone at the end of the polymer chain.

For example:



living end of polymer chain

dead end

Such a process can be considered in terms of the structures of possible reactive species. It is clear from the published literature that PMMA ion pairs show a greater degree of termination when polymerisations are carried out in non-polar solvents at higher temperatures, in contrast to the situation in polar solvents at lower temperatures (26) (56). This is indicative of the possibility that solvation could be a significant factor in termination reactions of this type. If it is assumed that the major reactive species, namely solvated and contact ion pairs are in dynamic equilibrium and the latter species could exist in forms in which penultimate, as well as anti-penultimate ester groups are co-ordinated with the carbanion and counterion, structures given in Figure 3.34 are possible.

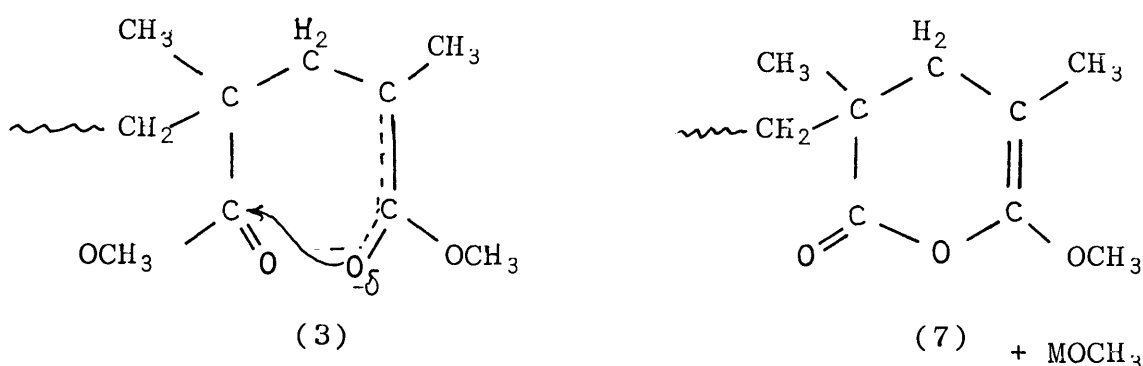
In this scheme, in the solvated ion pair, external solvation of the counterion is a competition between the THF molecules and ester groups of the penultimate and anti-penultimate units. The solvated form involving only THF is most likely to cause steric hindrance towards cyclisation, making it more difficult, whereas in the non-solvated or partially solvated form, it is comparatively unhindered.

According to this model, the anion with a lithium counterion could show the highest reactivity, while the lowest reactivity would be shown by a potassium counterion of the three systems studied. This trend is apparently due to the increase in size of the cation, where smaller lithium ion (ionic radius  $0.60\text{\AA}$ ) has a higher charge density, both



factors favouring the cyclisation mechanism. With the bigger potassium ion (ionic radius  $1.33^{\circ}\text{A}$ ), a lower effect would be observed. Sodium ion having an ionic radius of  $0.96^{\circ}\text{A}$  would be expected to have an intermediate effect. The evidence that with Cesium ion (ionic radius  $1.66^{\circ}\text{A}$ ) even at higher temperatures termination reactions are almost absent may be taken as supportive evidence for this model.

According to the foregoing schemes, structure 2 is the most favoured. However, it must be pointed out that nucleophilic attack by the oxygen anion on the carbonyl centre of the structure (3) could lead to the formation of a stable six membered ring (7), which would not be readily differentiated from structure (2) by assignment of IR maxima.



The observation that, according to quantum chemical calculations, in the free acrylate ion, more negative charge is localised around the oxygen atom than the  $\alpha$ -carbon atom (136) supports the above reaction scheme. Furthermore, a structure similar to that of (7) has been proposed by Volker (55) as a product of the anionic depolymerisation of PMMA trimers. Nucleophilic attack by the carbanion on the penultimate ester group leads to a four membered ring, which is not thermodynamically

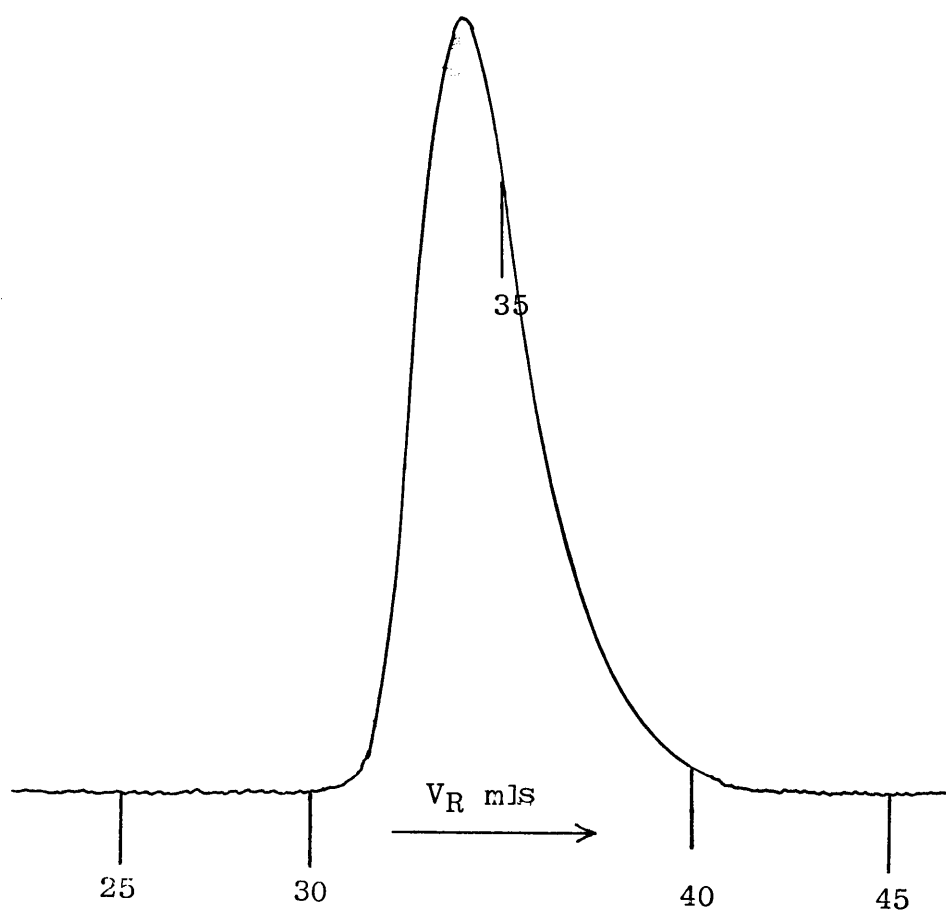


Fig 3.40 GPC chromatogram of PMMA prepared at 195 K in THF.

Initiator - fluorenyl sodium

$$[M]_0 = 0.2347 \text{ M/dm}^3 \quad [I]_0 = 3.2053 \times 10^{-4} \text{ M/dm}^3$$

$$[\text{Na(Ph)}_4\text{B}] = 1 \times 10^{-3} \text{ M/dm}^3$$

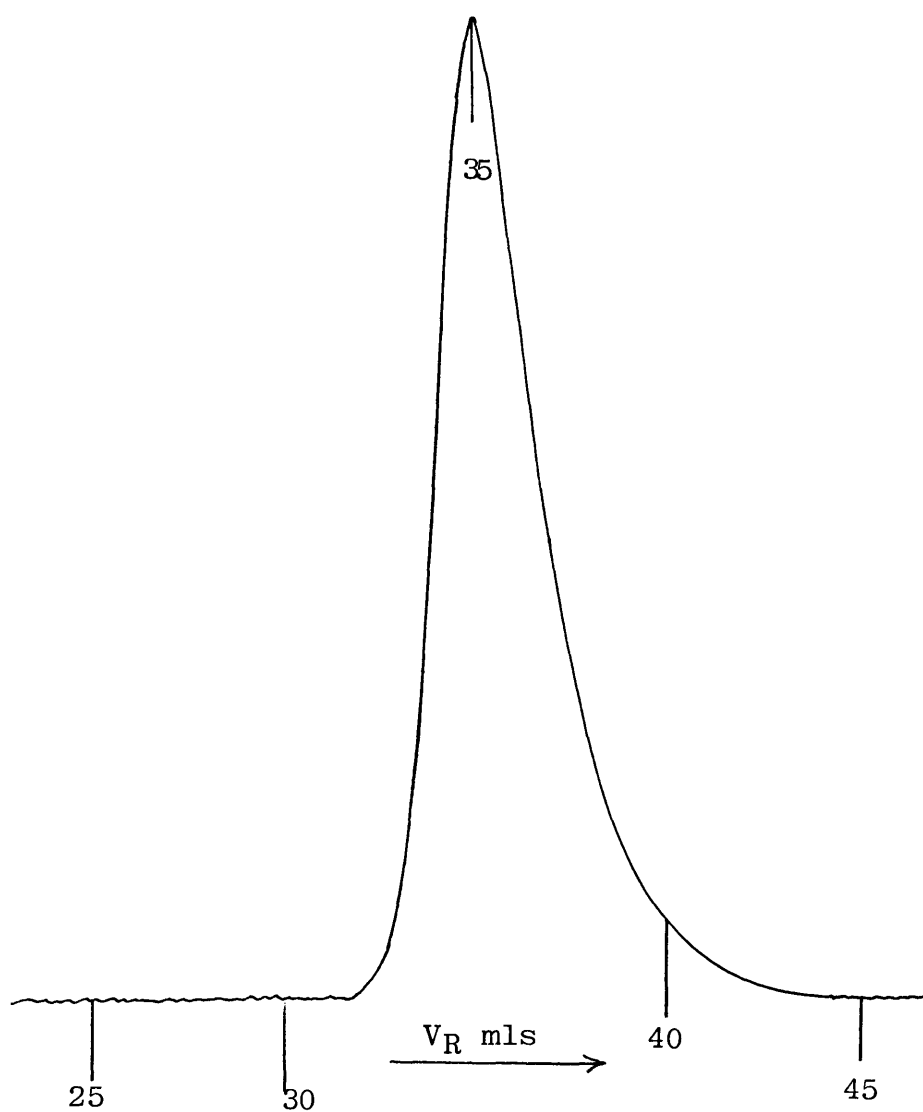


Figure 3.41 GPC chromatogram of PMMA prepared at 220 K  
Initiation 195 K.

$$[M]_0 = 0.2689 \text{ M/dm}^3 \quad [I]_0 = 3.6835 \times 10^{-4} \text{ M/dm}^3$$

$$[\text{Na(Ph)}_4\text{B}] = 1 \times 10^{-3} \text{ M/dm}^3$$

Initiator = fluorenyl sodium

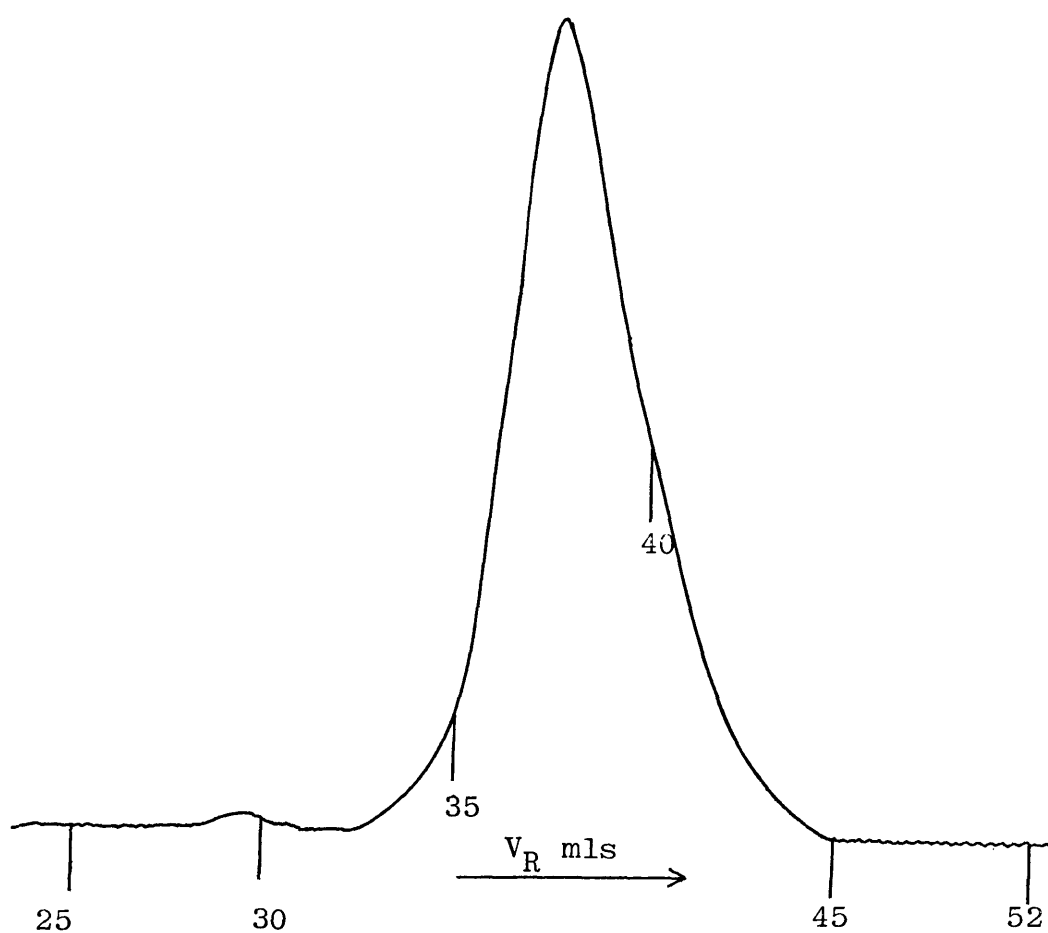


Figure 3.42 GPC chromatogram of PMMA prepared at 245 K

Initiation 195 K      Initiator - fluorenyl sodium

$$[M]_0 = 0.1673 \text{ M/dm}^3 \quad [I]_0 = 3.4891 \text{ M/dm}^3$$

$$[\text{Na(Ph)}_4\text{B}] = 1 \times 10^{-3} \text{ M/dm}^3$$

stable, hence not considered further.

### 3.2.2 Termination reactions in the presence of monomer

The study of termination reactions in the presence of monomer was carried out with monofunctional fluorenyl sodium and fluorenyl potassium initiators. The results of these experiments are given in Tables 3.24 and 3.25.

Table 3.24 Termination reactions of polymethyl methacryl sodium ion pairs in THF and MWD data for resultant polymers  
Initiator = fluorenyl sodium

$$[I]_0 = 3 \times 10^{-4} \text{ M dm}^{-3}$$

$$[M]_0 = 0.2 - 0.25 \text{ M dm}^{-3}$$

$$[Na(Ph)_4B] = 1 \times 10^{-3} \text{ M dm}^{-3}$$

Expt No	$M_n$ from GPC	PDI	$\alpha$	Temp K	Remarks
T1	60540	1.15	100	200	Colour remained
T2	40510	1.35	100	220	" "
T3	17746	1.42	70	245	Colour lost
T4	19007	1.47	42	256	Bimodal distribution

With fluorenyl sodium as initiator, the MWD s of the polymers produced show a slow but significant broadening as the temperature increased. From the percentage conversion values, it appears clear that at higher temperatures above 220 K, the termination reactions are prominent and conversion decreases with increase in temperature. The respective GPC elution curves are given in Figures 3.40 - 3.43. It is significant to note the gradual spreading of the high molecular end of the elution curves, while the peak itself is broadened. Finally at 256 K, a bimodal distribution is observed.

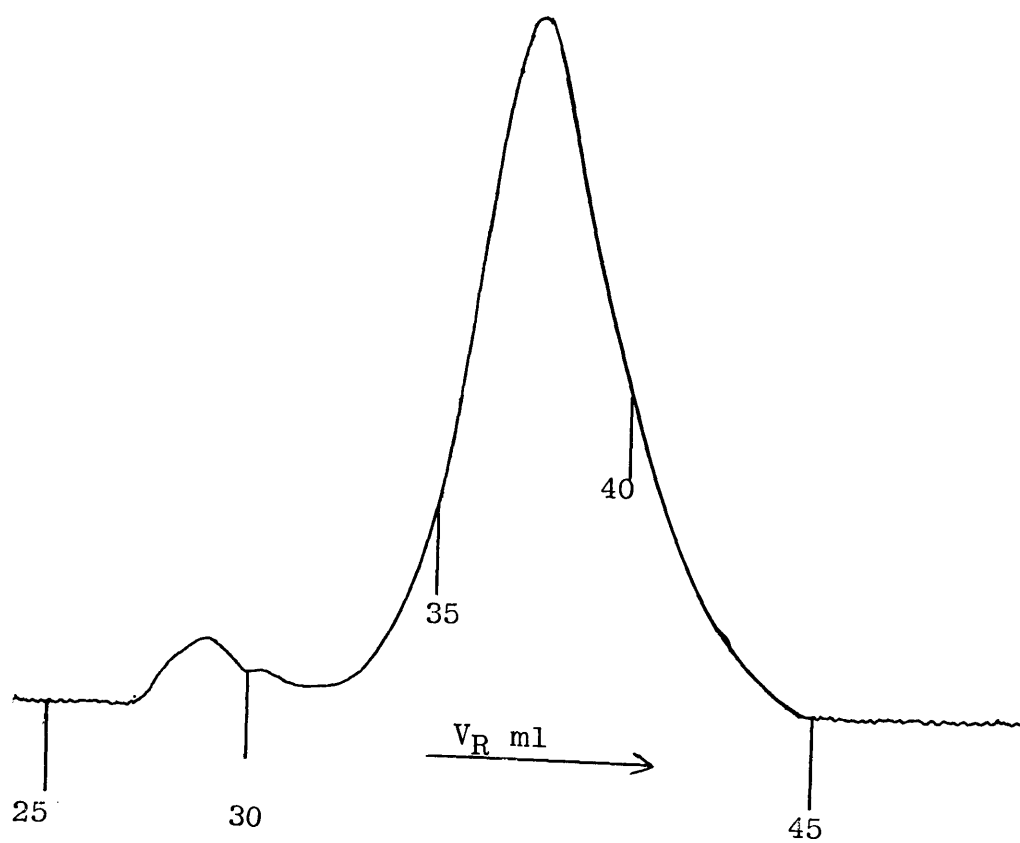


Fig 3.43 GPC chromatogram of PMMA prepared at 256 K

Initiation 195 K      Initiator - fluorenyl sodium

$[M]_0 = 0.2803 \text{ M/dm}^3$      $[I] = 3.7814 \times 10^{-4} \text{ M/dm}^3$

$[\text{Na(Ph)}_4\text{B}] = 1 \times 10^{-3} \text{ M/dm}^3$

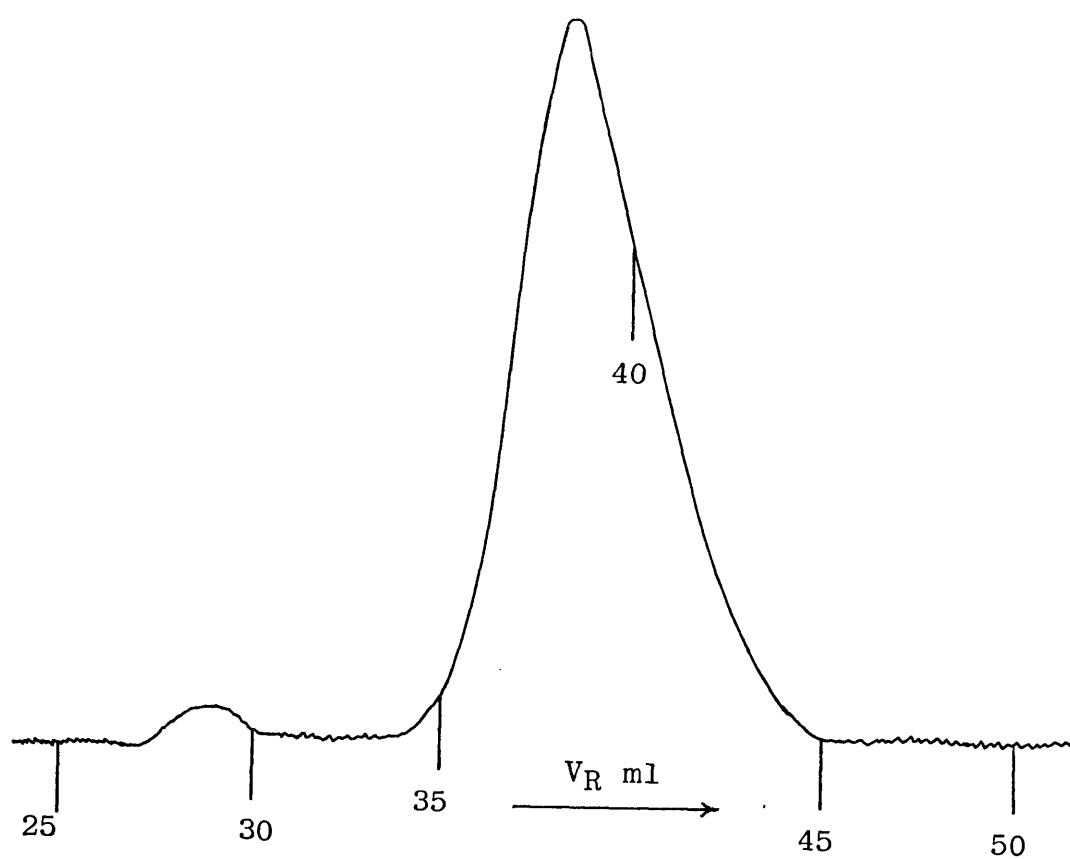


Fig 3.44 GPC chromatogram of PMMA prepared at 256 K  
 Initiation at 195 K. Initiator - Fluorenyl sodium  
 $[M]_0 = 0.2371 \text{ M/dm}^3$   $[I]_0 = 6.643 \times 10^{-4} \text{ M/dm}^3$   
 $[\text{Na(Ph)}_4\text{B}] = 1 \times 10^{-3} \text{ M/dm}^3$

(Fig 3.43 and 3.44). Fig 3.44 is the result of the same experiment as Fig 3.43 but repeated with double the concentration of initiator. As it is seen, the bimodal distribution, with a small high molecular peak (M.wt > 200,000) persists.

It was observed throughout all the low temperature polymerisations (200 K) with fluorenyl sodium that the living polymer solution was coloured. Only on termination with methanol did the colour of the polymer solution disappear. Even though the PMMA anion is colourless, the fact that almost 100% conversion was observed whenever the colour remained could be considered as an indication of the reactivity of the chain ends. When the propagation was carried out at 245 K and 256 K, the colour of the solution was lost within a period from a few seconds to 180 seconds. When the initiator concentration was increased keeping monomer concentration approximately the same, the time taken for disappearance of colour increased, along with the spreading of the low molecular tail of the curve. If the disappearance of colour of the polymer solution could be taken as a guide for the disappearance of reactivity, this directly shows that the rate of termination is increased with the increase in  $[M]/[I]$  ratio, at least at higher temperatures.



Table 3.25 Termination reactions of polymethyl methacryl potassium ion pairs in THF and MWD data for resultant polymers.

Initiator = fluorenyl potassium

$$[I]_0 = 4.4 \times 10^{-4} \text{ M dm}^{-3}$$

$$[M]_0 = 0.23 - 0.25 \text{ M dm}^{-3}$$

$$[K(Ph)_4B] = 1 \times 10^{-3} \text{ M dm}^{-3}$$

Expt No	$M_n$ from GPC	PDI	$\alpha$	Temp	Remarks
T7	140000	1.50	100	200	Colour remained
T8	86500	1.67	98	220	" "
T9	36000	1.64	98	245	" "
T10	34000	1.53	96	256	Small high molecular peak
T11	28650	1.71	93	270	Colour remained

With fluorenyl potassium, the change of MWD of polymers is not regular or orderly as with fluorenyl sodium. However, the GPC chromatograms show an increase in broadening as the temperature is increased (Fig 3.45 - 3.48). Except for experiment No T7 which is the control at 200 K, the high molecular side of the elution curves gradually spreads showing a continuous termination process. At 270 K an extremely broad, almost symmetrical curve, was obtained (Fig 3.48). At 245 K and 256 K, bimodal distributions as seen with fluorenyl sodium were observed. However, these second peaks are almost inconspicuous in proportion, appearing at retention volumes around 30 ml representing m.wts > 200,000.

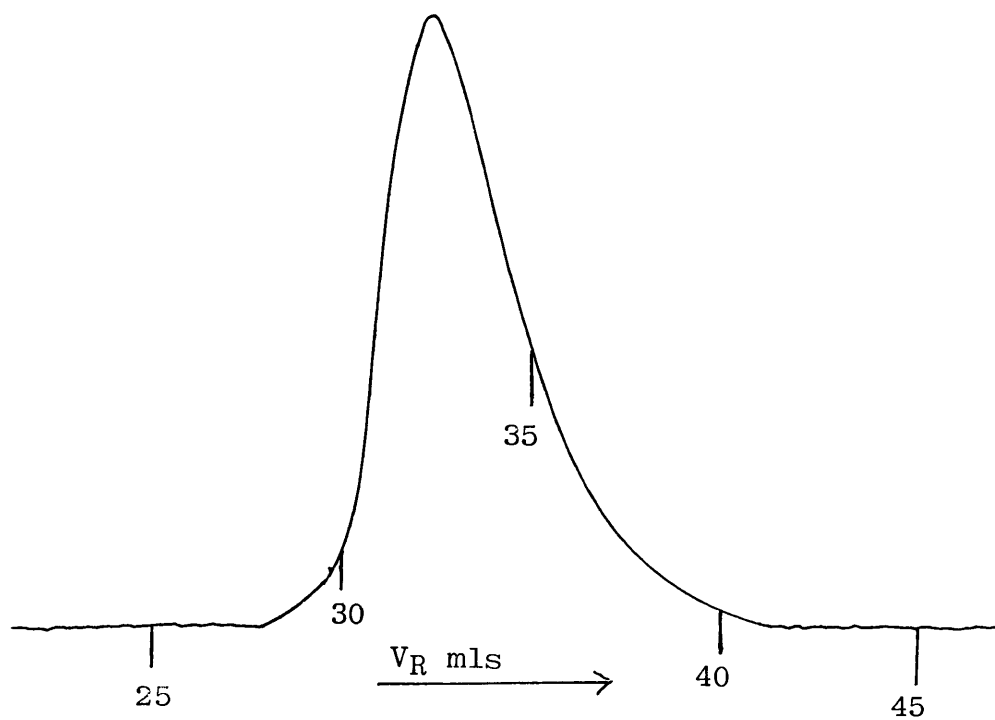


Fig 3.45 GPC chromatogram of PMMA prepared at 220 K.

Initiation at 195 K

Initiator - fluorenyl potassium

$$[M]_0 = 0.2461 \text{ M/dm}^3 \quad [I]_0 = 4.3 \times 10^{-4} \text{ M/dm}^3$$

$$[K(Ph)_4B] = 1 \times 10^{-3} \text{ M/dm}^3$$

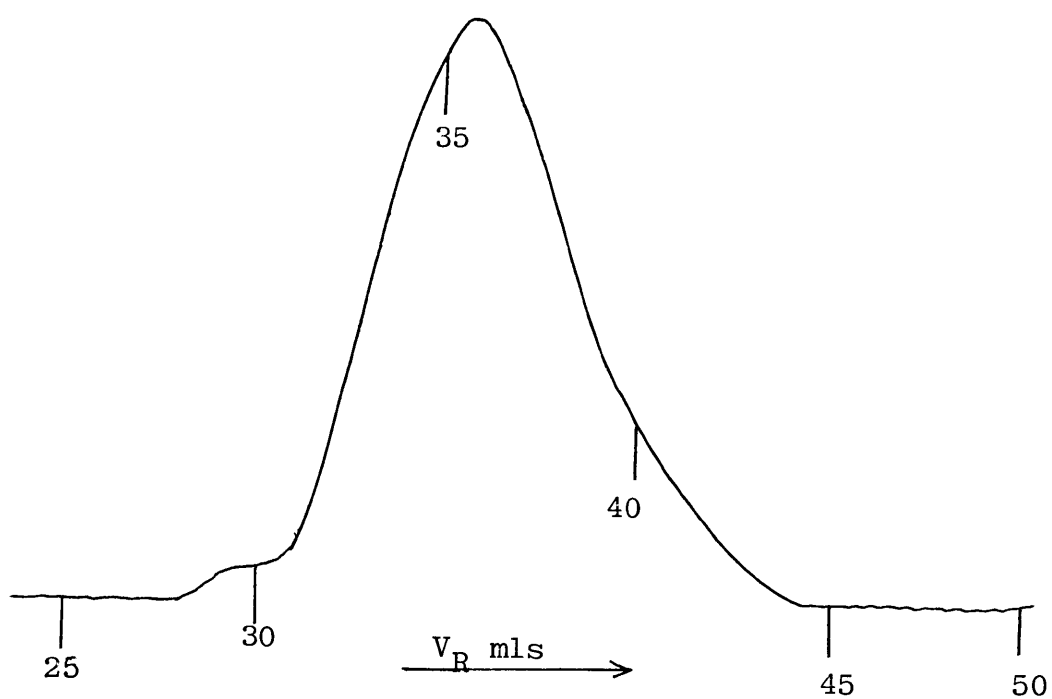


Fig 3.46 GPC chromatogram of PMMA prepared at 245 K.

Initiation 195 K                      Initiator - fluorenyl potassium

$[M]_0 = 0.2574 \text{ M/dm}^3$      $[I]_0 = 4.1091 \times 10^{-4} \text{ M/dm}^3$

$[K(Ph)_4B] = 1 \times 10^{-3} \text{ M/dm}^3$

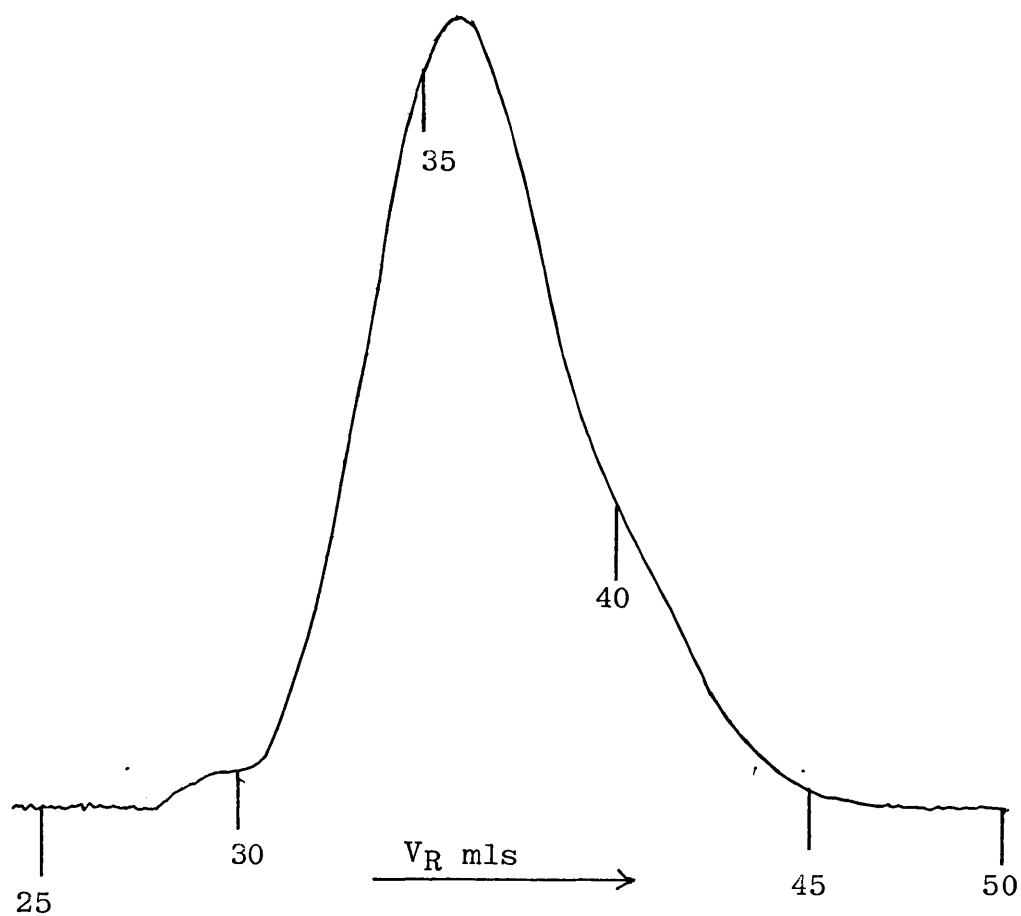


Fig 3.47 GPC chromatogram of PMMA prepared at 256 K.

Initiation 195 K                      Initiator - fluorenyl potassium

$[M]_0 = 0.2468 \text{ M/dm}^3$                        $[I] = 4.0037 \times 10^{-4} \text{ M/dm}^3$

$[K(Ph)_4B] = 1 \times 10^{-3} \text{ M/dm}^3$

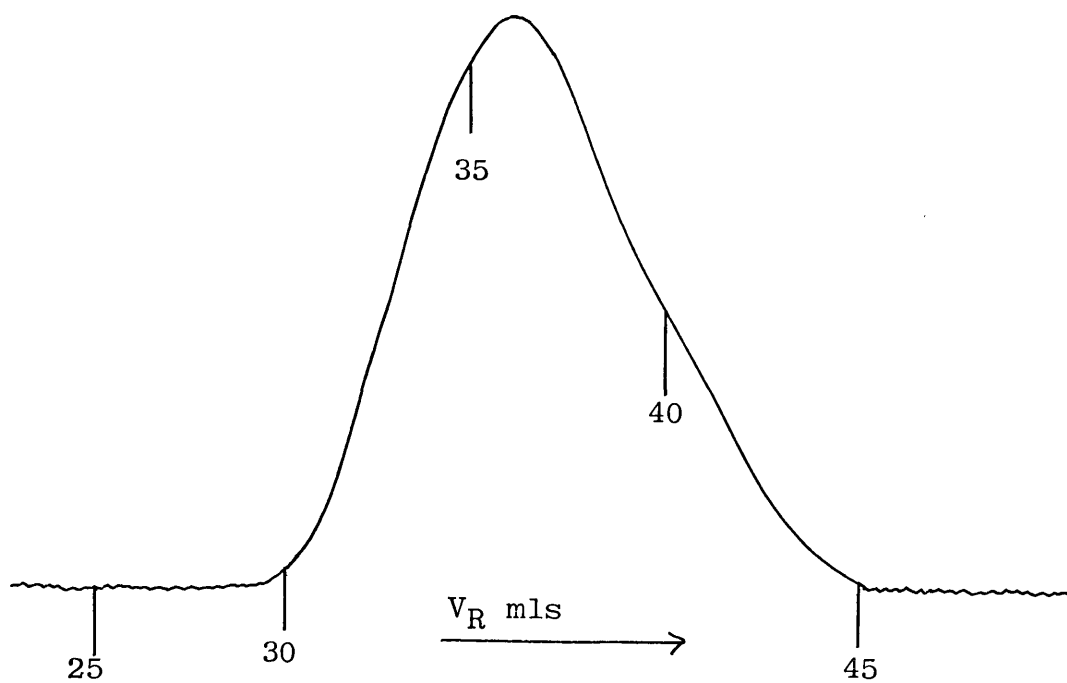


Fig 3.48 GPC chromatogram of PMMA prepared at 268 K.

Initiation at 195 K

Initiator - fluorenyl potassium

$$[M]_0 = 0.2326 \text{ M/dm}^3 \quad [I]_0 = 3.8056 \times 10^{-4} \text{ M/dm}^3$$

$$[K(Ph)_4B] = 1 \times 10^{-3} \text{ M/dm}^3$$

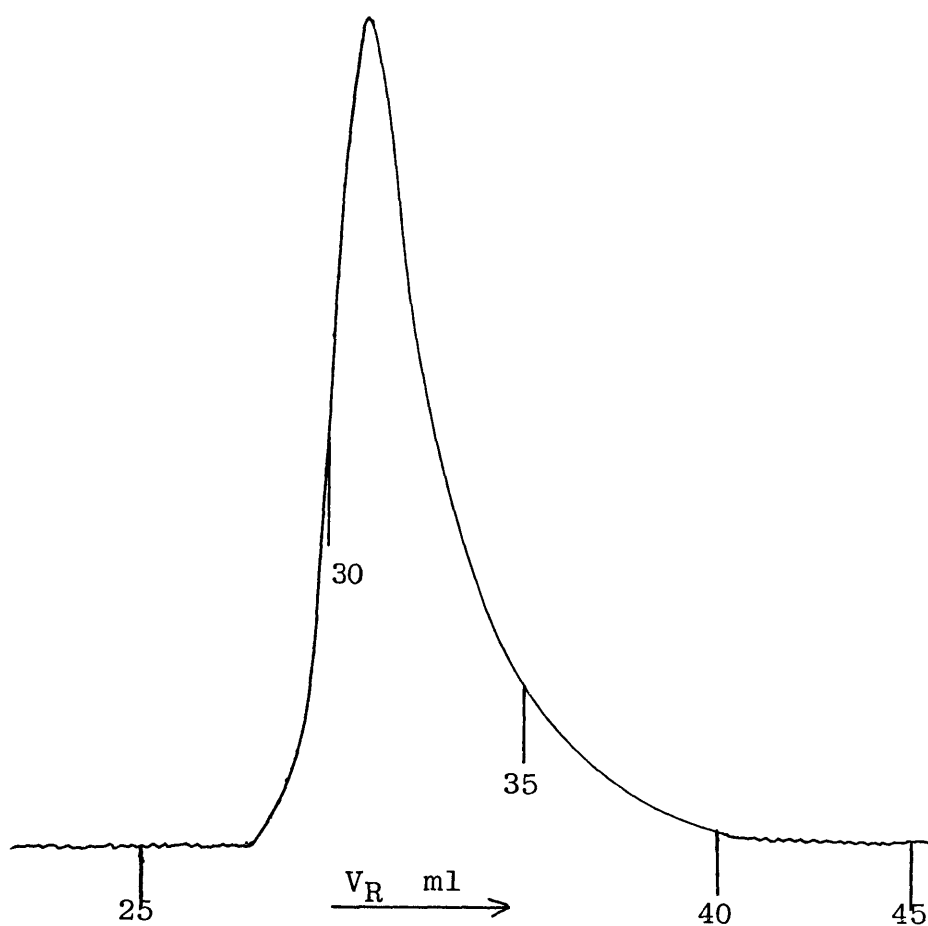


Fig 3.49 GPC chromatogram of PMMA prepared at 195 K.

Initiator - fluorenyl potassium

$$[M]_0 = 0.2409 \text{ M/dm}^3 \quad [I]_0 = 3.7809 \times 10^{-4} \text{ M/dm}^3$$

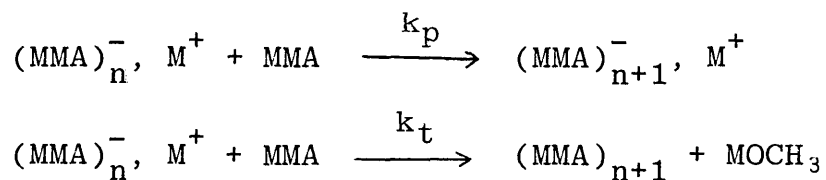
$$[K(Ph)_4B] = 1 \times 10^{-3} \text{ M/dm}^3$$

Although the range of monomer and initiator concentration used are the same, at temperatures above 200 K conversion values varying from 93-98 were obtained. It is unlikely that the less than quantitative conversion observed is due to experimental errors, even though it cannot be discarded as a possible reason. However, the persistence of the colour of the solution till terminated in all cases up to 270 K is difficult to explain.

Two models can be used for the calculation of termination rate constant  $K_t(\pm)$  (90, 134). The first model is due to Löhr and based on the following assumptions.

- (a) The initiation is very fast compared to propagation
- (b) The chain transfer reactions and reaction of the active centres with the ester group of the growing polymer chain or the deactivated chain are absent.

In the previous section, it was found that the termination reactions in the absence of monomer are very slow and in the order of  $2-2.5 \times 10^{-5} \text{ sec}^{-1}$ . Although all such reactions are operating in the presence of monomer too, considering the short reaction times (30 minutes) it would not introduce appreciable errors by not considering them. There was no evidence for appreciable chain transfer reactions during the propagation at low temperatures by ion pairs. It is assumed that at elevated temperatures, even if they come into operation, the effects are not very considerable. Hence, for the treatment of the results, given in Tables 3.24 - 3.25, only the following reactions are considered.



where  $k_p$  = rate constant of propagation by ion pairs

$k_t$  = rate constant of termination by ion pairs.

According to this kinetic scheme, the following differential equations can be written:

$$\frac{-d[\text{M}]}{dt} = (k_p + k_t) [\text{M}] [\text{I}] \quad (1)$$

$$\frac{-d[\text{I}]}{dt} = k_t [\text{M}] [\text{I}] \quad (2)$$

where  $[\text{M}]$  is the concentration of monomer

$[\text{I}]$  is the concentration of active chains. From equations (1) and (2).

$$\begin{aligned} \frac{[\text{M}]}{[\text{M}]_0} &= \frac{[\text{I}]}{[\text{I}]_0} \int \frac{k_p + k_t}{k_t} d[\text{I}] \quad (3) \end{aligned}$$

Subscript 0 indicates the original concentrations. Now, a parameter  $\alpha$  is defined as the product of termination ratio  $K$  and the ratio of  $[\text{M}]_0$  to  $[\text{I}]_0$

$$\alpha = K \frac{[\text{M}]_0}{[\text{I}]_0} \quad (4)$$

$$\text{where } K = \frac{k_t}{k_p + k_t} \quad (5)$$

The fractional conversion  $x_p$  is given as

$$x_p = 1 - \frac{[\text{M}]}{[\text{M}]_0}$$



Integrating equation (3)

$$[I] = [I]_0 (1 - \alpha) + K [M]$$

It can be shown that the maximum degree of polymerisation of the deactivated chains,  $P_m$ , for  $\alpha x_p < 1$  can be given as:

$$P_m = - \left\{ \frac{1}{K} \right\} \ln (1 - \alpha x_p) \quad (6)$$

At any instant during the propagation of polymerisation with simultaneous termination, the resultant polymer consists of two main fractions:

- (i) fraction of deactivated chains; denoted by  $\beta$
  - (ii) fraction of still active chains; denoted by  $1 - \beta$
- The distribution of these two fractions can be designated as  $h(P)_d$  and  $h(P)_a$  respectively. Hence the distribution of the whole polymer can be written as

$$h(P) = \beta h(P)_d + (1 - \beta) h(P)_a \quad (7)$$

It can be shown that the mole fraction of deactivated chains  $\beta = \alpha x_p$ .

The distribution of the deactivated chains is given by:

$$\begin{aligned} h(P)_d &= \frac{I}{\alpha x_p [I]_0} \left[ - \frac{d[I]}{dP} \right] \\ &= \frac{K}{\alpha x_p} e^{-kP} \quad \text{for } P \leq P_m \end{aligned} \quad (8)$$

The fraction of still active chains approaches poisson distribution and is given as

$$h(P)_a = \frac{1}{P_m \sqrt{2} U_i} \exp \left[ - \frac{(P - P_m)^2}{2 U_i P_m^2} \right] \quad (9)$$

where  $U_i$  = internal non-uniformity of the still active

chains having the number average degree of polymerisation  $P_m$ .

$$\therefore h(P) = \begin{cases} \alpha x_p \cdot h(P)_d + (1 - \alpha x_p)h(P)_a & \text{for } P < P_m \\ (1 - \alpha x_p)h(P)_a & \text{for } P \geq P_m \end{cases} \quad (10)$$

The number average degree of polymerisation  $D_{p_n}^-$  is defined as:

$$\begin{aligned} D_{p_n}^- &= \int_0^{\infty} P \cdot h(P) dP \\ &= \frac{[M]_0}{[I]_0} x_p \end{aligned} \quad (11)$$

The weight average degree of polymerisation  $D_{p_w}^-$  is defined as

$$\begin{aligned} D_{p_w}^- &= \frac{1}{M_n^-} \int_0^{\infty} P^2 \cdot h(P) dP \\ &= \frac{2}{\alpha K \cdot x_p} \left[ \alpha x_p + (1 - \alpha x_p) \ln(1 - \alpha x_p) - \frac{U_i}{2} \ln^2(1 - \alpha x_p) \right] \end{aligned} \quad (12)$$

Since  $\frac{D_{p_w}^-}{D_{p_n}^-} = \frac{M_w^-}{M_n^-} = \text{PDI}$  and  $\alpha = K \frac{[M]_0}{[I]_0}$ , from (10) and (11)

$$\text{PDI} = \frac{2}{(\alpha x_p)^2} \left[ \alpha x_p + (1 - \alpha x_p) \ln(1 - \alpha x_p) - \frac{U_i}{2} \ln^2(1 - \alpha x_p) \right]$$

Considering the low concentration of living ends and the fact that we have a well stirred solution with a uniform deactivation, it is reasonable approximation to assign the value of  $U_i$  as zero. Hence the resultant simplified equation can be written as:

$$\text{PDI} = \frac{2}{(\alpha x_p)^2} \left[ \alpha x_p + (1 - \alpha x_p) \ln(1 - \alpha x_p) \right]$$

The second model is similar to that proposed by Szwarc (134). This was proposed in order to examine the effect of continuous addition of monomer containing impurities, on the MWD of the resultant polymer.

It is assumed that the initiation is rapid and the very first portion of added monomer converts quantitatively the initiator to growing chains. Further addition of monomer causes initial uniform growth but the impurities terminate some growing chains. If the mole fraction of impurities in monomer is  $f$ , the addition of  $dm$  moles of monomer at time  $t$  terminates  $f.dm$  moles of living polymer, the degree of polymerisation of which can be given as:

$$j = \int_0^M (I_0 - fm)^{-1} dm \quad (14)$$

where  $M$  = total amount of monomer added

$I_0$  = number of moles of initiator originally present.

Denoting by  $d_{x_i}$  the mole fraction of terminated chains the degree of polymerisation of which is confined to the interval  $j, j + dj$ , the distribution of the terminated chain can be given as:

$$\frac{d_{x_i}}{dj} = f \exp(-fj) \quad (15)$$

Thus the MWD depends only on  $f$ , while the ratio  $M/I_0$  determines the highest degree of polymerisation,  $j_M$  which can be given as:

$$j_M = + \frac{1}{f} \ln \left( 1 - f \frac{[M]}{[I]_0} \right) \quad (16)$$

The number average degree of polymerisation ( $D_{p_n}^-$ ) is

$$D_{p_n}^- = \frac{[M]}{[I]_0}$$

The ratio of  $D_{p_w}^-$  to  $D_{p_n}^-$  is calculated to be:

$$\frac{D_{p_w}^-}{D_{p_n}^-} = 2 \left[ \frac{[I]_0}{f[M]} \right]^2 \left\{ \frac{f[M]}{[I]_0} + \left( 1 - f \frac{[M]}{[I]_0} \right) \ln \left( 1 - f \frac{[M]}{[I]_0} \right) \right\} \quad (17)$$

In this expression  $f \frac{[M]}{[I]_0}$  is the fraction of chains

terminated and is equal to the term  $\alpha x_p$  in the Lohrs expression (12).

The continuous termination of the living chains during propagation as a result of the continuous addition of impurities is comparable to the continuous termination of living ends by the monomer. This is also shown by the similarity of two expressions (13) and (17) for the MWDs of the resultant polymers.

$$\therefore \alpha x_p = f \frac{[M]}{[I]_0}$$

Substituting  $\alpha$  from equation (4)

$$K \cdot \frac{[M]}{[I]} \cdot x_p = f \cdot \frac{[M]}{[I]_0}$$

$$f = K \cdot x_p$$

for  $I_0 > f [M]$  the fractional conversion  $x_p = 1$

$$\therefore f = K$$

$\therefore f$  can be simply expressed as:

$$f = \frac{k_t}{k_p + k_t}$$

$$\text{Since } \alpha = K. \frac{[M]}{[I]_0} \quad \text{and} \quad \frac{D_{p_w}^-}{D_{p_n}} = \text{PDI}$$

the expression (17) for the MWD of the polymers according to this model can be given as:

$$\text{PDI} = \frac{2}{\alpha^2} (\alpha + (1 - \alpha) \ln (1 - \alpha))$$

In the present case, impurities if any, are introduced at once. Although a certain amount of termination in the very early phase of polymerisation at 198 K has been observed in some cases, it is assumed that all impurities are purged immediately and the termination process operating from that instant onwards is due to the interaction of monomer and reactive species alone and is a continuous process. Thus the two models given above are considered to describe satisfactorily the termination by the monomer in the anionic polymerisation of MMA by ion pairs.

Results of the termination rate constant calculations for fluorenyl sodium are given in Table 3.26.  $\alpha \cdot x_p$  values; were obtained from the MWD data by varying its value to obtain the best fit. The maximum degree of polymerisation  $D_{p_m}$  of the deactivated chains was obtained from GPC measurements and the calibration curve. As evident from the GPC chromatograms as well as dispersity indices, the broadening of MWD with increase in temperature is significant. Finally the polymerisation does not reach complete conversion at higher temperatures, indicating the total deactivation of living ends. This is well reflected in the increase in  $K_t(\pm)$  with the temperature. (Table 3.26 column 11). (Fig 3.50). From this, it is apparent that the

Table 3.26 Experimental conditions and calculated data for termination rate constant for MMA<sup>-</sup> Na<sup>+</sup> ion pairs (Initiator - Fluorenyl Sodium)

Expt No	Temp K	$[M]_0$ mol/dm <sup>3</sup>	$[I]_0 \times 10^4$ mol/dm <sup>3</sup>	$D_{pmax}$	PDI	Percentage Conversion	$\alpha \cdot x_p$	$K \times 10^3$	$K_p(\pm)$ dm <sup>-3</sup> /sc	$k_t(\pm)$ dm <sup>-3</sup> /sc
T1	195	0.235	3.2053	605	1.15	1.0	0.36	0.738	60	0.044
T2	220	0.269	3.6835	490	1.35	1.0	0.66	2.201	118	0.26
T3	245	0.167	3.4891	240	1.42	0.695	0.735	5.53	200	1.11
T5	245	0.174	5.6119	350	1.46	0.95	0.77	4.20	200	0.84
T4	255	0.280	3.7814	230	1.47	0.422	0.78	6.58	241	1.60
T6	255	0.237	6.643	195	1.42	0.66	0.74	6.90	241	1.61

$$[Na(Ph)_4B] = 1 \times 10^{-3} \text{ mol/dm}^{-3}/\text{sec}$$

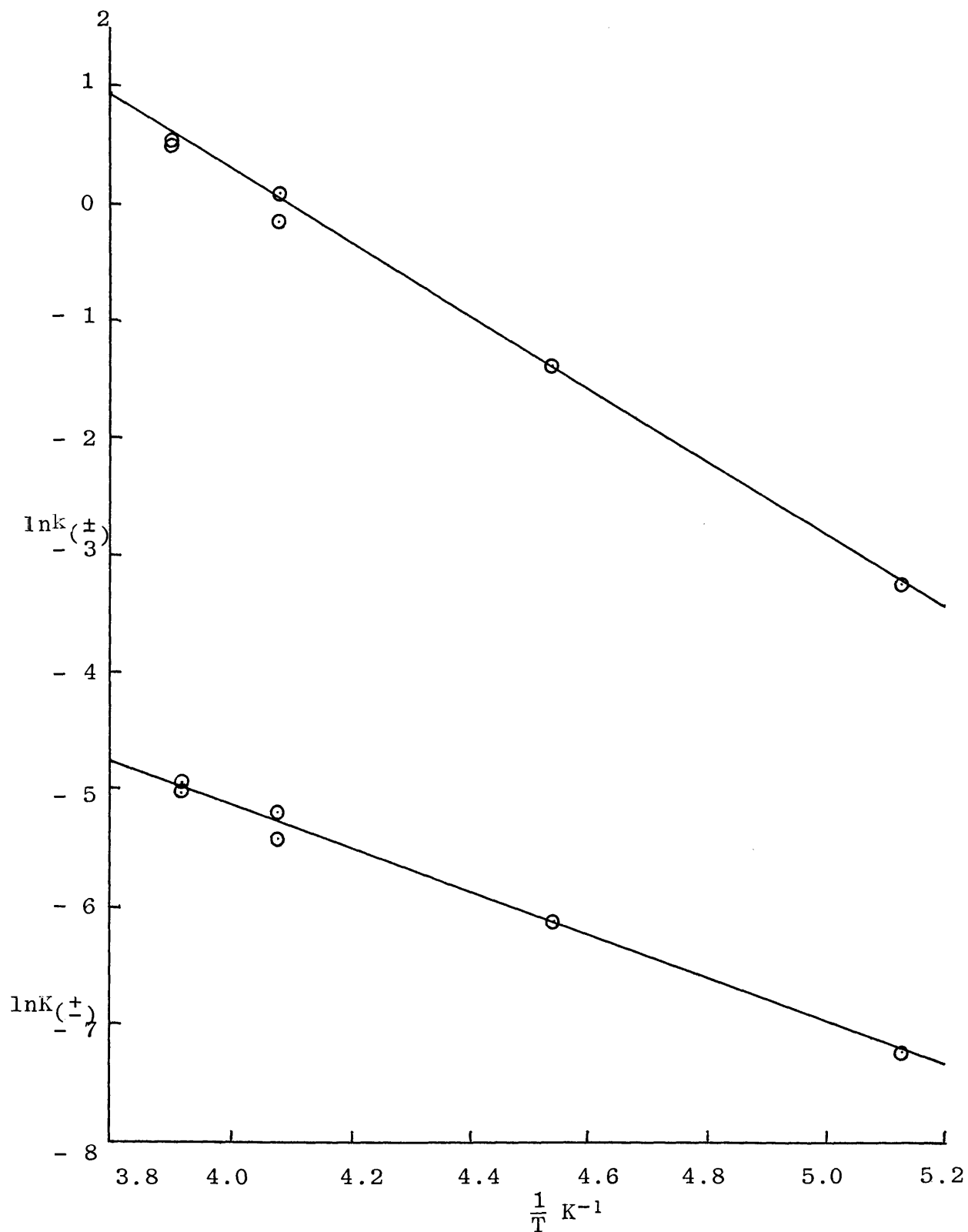


Fig 3.50 Arrhenius plots for the overall rate constant of termination,  $k_t(\pm)$  and  $K(\pm)$  for  $\text{MMA}^- \text{Na}^+$  ion pairs.

Initiator - Fluorenyl sodium

Reaction conditions are detailed in Table 3.26

termination reaction requires higher activation energy than the propagation reaction.

The Arrhenius plots for  $K_{(\pm)}$  (expression (5)) and  $k_{t(\pm)}$  are given in the Fig. 3.50.

From these plots the activation energy for the termination reaction can be calculated.

$$\begin{aligned} \text{From the plot of } \ln k_{t(\pm)} \text{ Vs } \frac{1}{T}, \\ \text{the slope} &= \frac{-3.3504 \times 10^{-3}}{1.1312 \times 10^{-6}} \\ &= -2.9618 \times 10^3 \end{aligned}$$

$$\text{From the expression } \ln k_{t(\pm)} = 2.303A - \frac{E_a}{RT}$$

where  $E_a$  = activation energy, and

$$R = \text{gas constant}$$

$$\therefore \text{the slope} = \frac{E_a}{R} = 2.9618 \times 10^3$$

$$\text{Since } R = 8.3143 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} E_a &= 2.9618 \times 10^3 \times 8.3143 \times 10^{-3} \text{ KJ mol}^{-1} \\ &= 24.63 \text{ KJ mol}^{-1} \end{aligned}$$

From the intercept, the frequency factor  $A$  can be calculated.

$$\text{Intercept} = 2.303A = 12.0092$$

$$\therefore A = 5.22$$

It is apparent from the expression (5) that the calculated values of  $k_{t(\pm)}$  from the experimental values of  $K_{(\pm)}$  are dependent on the values of  $k_{p(\pm)}$ . The published data show a set of controversial values. A recent publication (89) reports higher values for  $k_{p(\pm)}$  in the order of 2-3 times the originally accepted values (81). However, the



$k_p(\pm)$  values used here were selected based on our kinetic results. Since the low temperature kinetic measurements are in good agreement with Löhr's results, high temperature  $k_p(\pm)$  values have been taken from his published data. The linear Arrhenius plot obtained for  $K(\pm)$  which is independent of any outside results is compatible with that for  $k_t(\pm)$  indicating that the used values are satisfactory.

With cumyl cesium as indicator Löhr obtained a value of 46 KJ mol<sup>-1</sup> for the activation energy of the termination reaction and a frequency factor of 11. The difference in the activation energies of termination and propagation was 29 KJ mol<sup>-1</sup>. The calculated values of Arrhenius parameters from Fig 3.50, for PMMA<sup>-</sup> Na<sup>+</sup> ion pairs,  $E_a = 24.63$  KJ mol<sup>-1</sup> and  $A = 5.22$  are in very good agreement with the observed results. This explains the marked absence of side reactions with Cs<sup>+</sup> as counterion when they are significant with Na<sup>+</sup>. As would be expected, the termination rate constants for PMMA<sup>-</sup> Na<sup>+</sup> are significantly higher than those for PMMA<sup>-</sup> Cs<sup>+</sup> at a given temperature.

From the Arrhenius plot for  $K(\pm)$ , the difference in the activation energies of termination and propagation can be calculated. This is 15.21 KJ mol<sup>-1</sup> and hence the activation energy of propagation reaction is 9.42 KJ mol<sup>-1</sup>. This agrees well with the Lohr's reported value of 9.61 KJ mol<sup>-1</sup> (81).

Due to the experimental errors that could arise from MWD measurements as well as the possible internal non-uniformity

of the polymer, the calculated results could contain a certain factor of errors. Repetition of experiments were done often to minimise this factor and given values are considered to be satisfactory within experimental errors. From the results, it appears to be significant that the rate of termination of anions by reaction with the monomer ester function at 250 K is higher than the rate of intra molecular termination. The propagation rate in turn is much higher than both these processes.

From this, it is apparent that the most important termination reaction in a polymethyl methacrylate/THF system polymerised by ion pairs is the reaction of ion pairs with the ester function of MMA monomer. However, the significance of this reaction is most apparent at elevated temperatures due to the high activation energy needed.

### Section 3

#### 3.3 Stereo regulation and the Mechanism of Anionic Polymerisation of Methyl Methacrylate

The kinetics of the anionic polymerisation of methyl methacrylate was investigated in the previous two sections. Polymers were also produced at different levels of monomer concentrations, initiator concentration and temperature to determine the dependence of number average molecular weight and MWD on such conditions. These measurements provide a considerable amount of information concerning the active species. In order to obtain more information on the nature of active species and mode of their propagation, the polymer samples produced under known conditions as above were investigated by NMR spectroscopy. The polymers prepared can be basically classified into three categories:

- (i) polymers prepared by anionic mechanism in which ion pairs with  $\text{Na}^+$  as counterion dominate the mechanism;
- (ii) polymers prepared by anionic mechanism in which ion pairs with  $\text{Li}^+$  as counterion dominate the mechanism;
- (iii) polymers prepared by anionic mechanism in which ion pairs with  $\text{K}^+$  as counterion dominate the mechanism.

##### 3.3.1 Treatment of Results

The tacticities of these polymers were calculated following Bovey's (110) method and only the tactic triads are considered. The chemical shifts of  $\alpha$ -substituents in vinyl

polymers generally vary appreciably, with the relative configuration of the nearest neighbouring monomer units (110-b). Thus, in the polymethylmethacrylate, which is not stereochemically pure,  $\alpha$ -methyl group resonance could show three types, representing the central monomer units of isotactic, syndiotactic and heterotactic triads.

Polymerisation conditions and results of tacticity measurements are given in Tables 3.27-32, where I, S and H represent isotactic, syndiotactic and heterotactic triads respectively. From these values, it is possible to calculate the fractions of isotactic diad placement ( $\equiv$  meso),  $P_i$  and syndiotactic diad placement ( $\equiv$  racemic),  $P_s$  from the following relationships:

$$P_i = I + H/2$$

$$P_s = S + H/2$$

Average sequence lengths of isotactic and syndiotactic placements,  $\bar{l}_i$  and  $\bar{l}_s$  respectively are given by the following expressions:

$$\bar{l}_i = \frac{2P_i}{H}$$

$$\bar{l}_s = \frac{2P_s}{H}$$

It is convenient to compare the results with a simple random distribution model and study the deviations from it. The term persistence ratio, designated by  $\rho$ , is defined by:

$$\rho = \frac{2P_i P_s}{H}$$

This is the ratio of actual average sequence lengths to the theoretical average sequence lengths, assuming Bernoullian

statistics. For a Bernoullian type sequence distribution,  $\rho = 1$ .

It is possible to form four types of triad structures from diads. These probabilities can be represented as  $P_{is}$ ,  $P_{ii}$ ,  $P_{si}$  and  $P_{ss}$ , where:

$P_{is}$  = probability that an isotactic placement is followed by a syndiotactic placement;

$P_{ii}$  = probability that an isotactic placement is followed by an isotactic placement;

$P_{si}$  = probability that a syndiotactic placement is followed by an isotactic placement;

$P_{ss}$  = probability that a syndiotactic placement is followed by a syndiotactic placement.

The relationship of I, H and S triads,  $P_i$  and  $P_s$  diads and above probabilities can be given by the following expressions:

$$I = P_i \cdot P_{ii}$$

$$S = P_s \cdot P_{ss}$$

$$P_{ii} + P_{is} = 1$$

$$P_{ss} + P_{si} = 1$$

Hence, the four placement probabilities can be simply given as:

$$P_{is} = \frac{H}{2P_i}$$

$$P_{ii} = \frac{H}{P_i}$$

$$P_{si} = \frac{H}{2P_s}$$

$$P_{ss} = \frac{H}{P_s}$$

The calculated values of these probabilities along with the average sequence chain lengths are given in Tables. The values of  $P_{ii}/P_{Si}$  and  $P_{SS}/P_{is}$  ratios provide an indication of the dependence of polymer chain configuration on the penultimate effects.

The isotactic, heterotactic and syndiotactic values obtained from the spectra can also be fitted into a ternary diagram for each system. Here the loci of equal persistence ratio are given by single curved lines. Since the persistence ratio for a Bernoullian triad process is equal to 1.0, any deviation from it can be seen as separate curves outside the line representing  $\rho = 1.0$ . Individual diagrams for six initiator systems are given in Figures 3.55-57, 61, 65 & 66. Figures 3.58 & 3.67 are ternary diagrams for different polymer prepared with common counter ions. Computer graphics (genograph) was used for drawing the ternary diagrams and the broken line represents the best value of persistence ratio for the set of results in each system. The curves for all polymers prepared with  $\text{Na}^+$  as counterion lie very close to the curve representing  $\rho = 1$ , while those for  $\text{Li}^+$  and  $\text{K}^+$  deviate considerably towards lower values.

These results can also be fitted into probability diagrams similar to that given by Bovey (110). Considering diad structures, if the probability of generating a meso sequence ( $\equiv$  isotactic in triad sequence) whenever a new unit of monomer is added to the end of growing polymer chain is given by a single parameter  $P_i$ , but is not

influenced by any effect due to the structure of the preceding unit of the chain, then according to random process, following probabilities can be written:

$$I = P_i^2$$

$$S = (1 - P_i)^2$$

$$H = 2(P_i - P_i^2)$$

Figures 3.59, 62 & 68 are plots of these probabilities for three types of cations, as a function of isotactic placement. These are plotted by fitting syndiotactic values on the curve and allowing other values to fall wherever they may. If the distribution of tactic sequences follows Bernoullian behaviour, all the values for a given polymer would lie on a single vertical line for a given value of  $P_i$ . As is evident from the diagrams, it is only for polymers prepared with  $\text{Na}^+$  as counterion that tacticity values fall on a single vertical line (Figure 3.59) and this has the value  $P_i = 0.25$ .

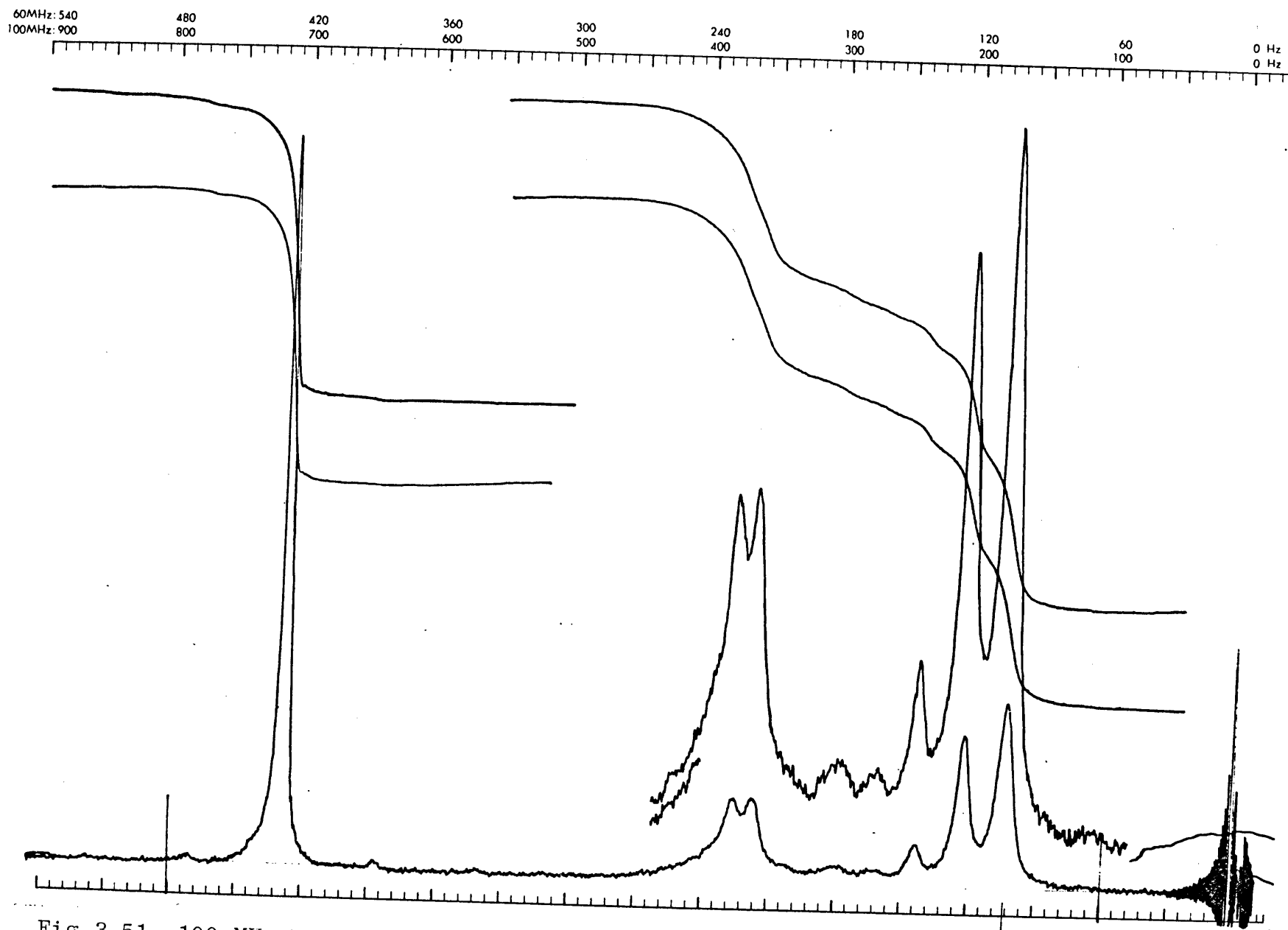


Fig 3.51 100 MHz NMR spectrum of polymethyl methacrylate prepared using sodium naphthalene in THF



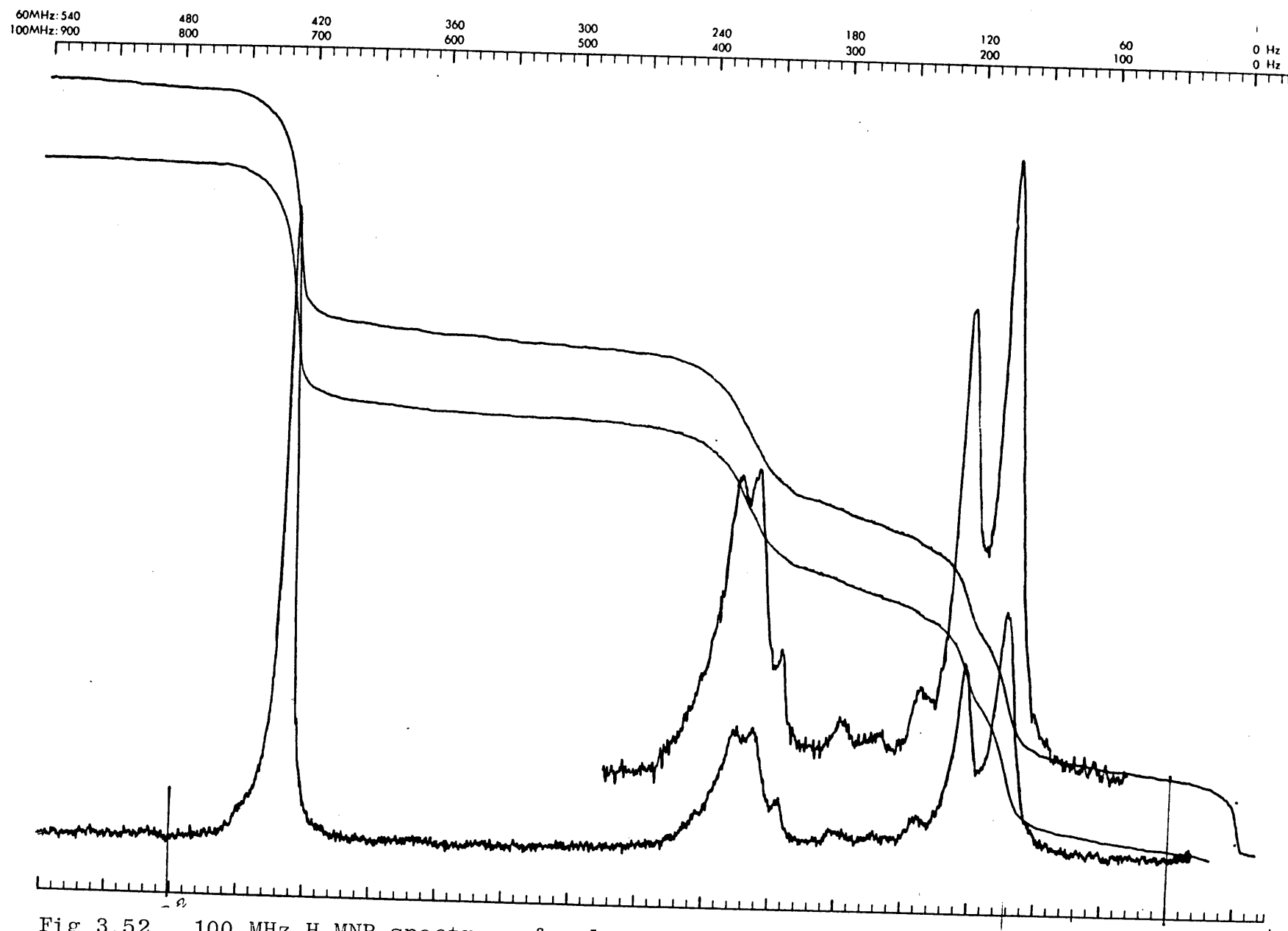


Fig 3.52 100 MHz  $^1\text{H}$  NMR spectrum of polymethyl methacrylate prepared using  $\alpha$ -methyl styryl sodium in tetrahydrofuran

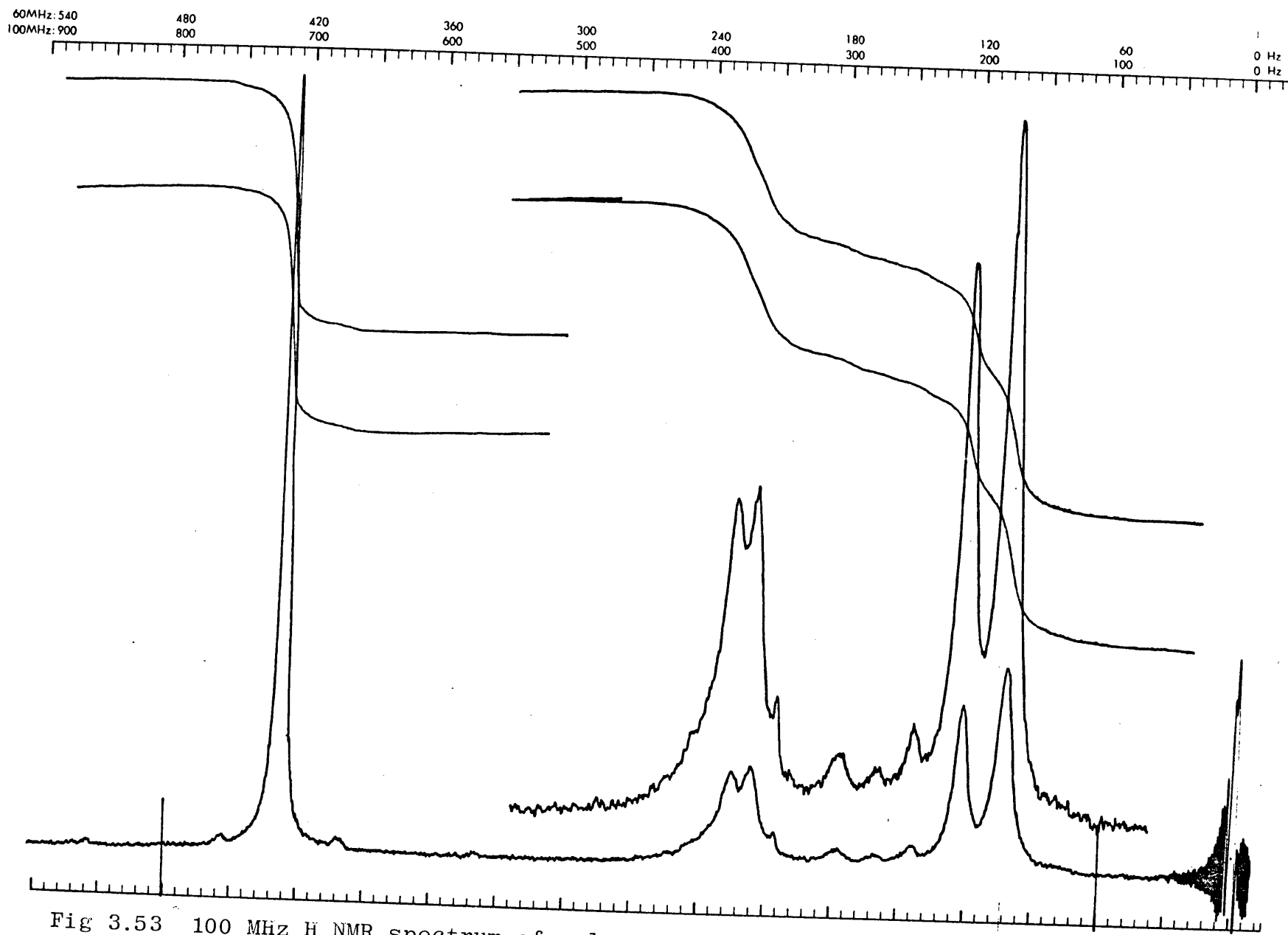


Fig 3.53 100 MHz  $^1\text{H}$  NMR spectrum of polymethyl methacrylate prepared using Fluorenyl sodium in THF

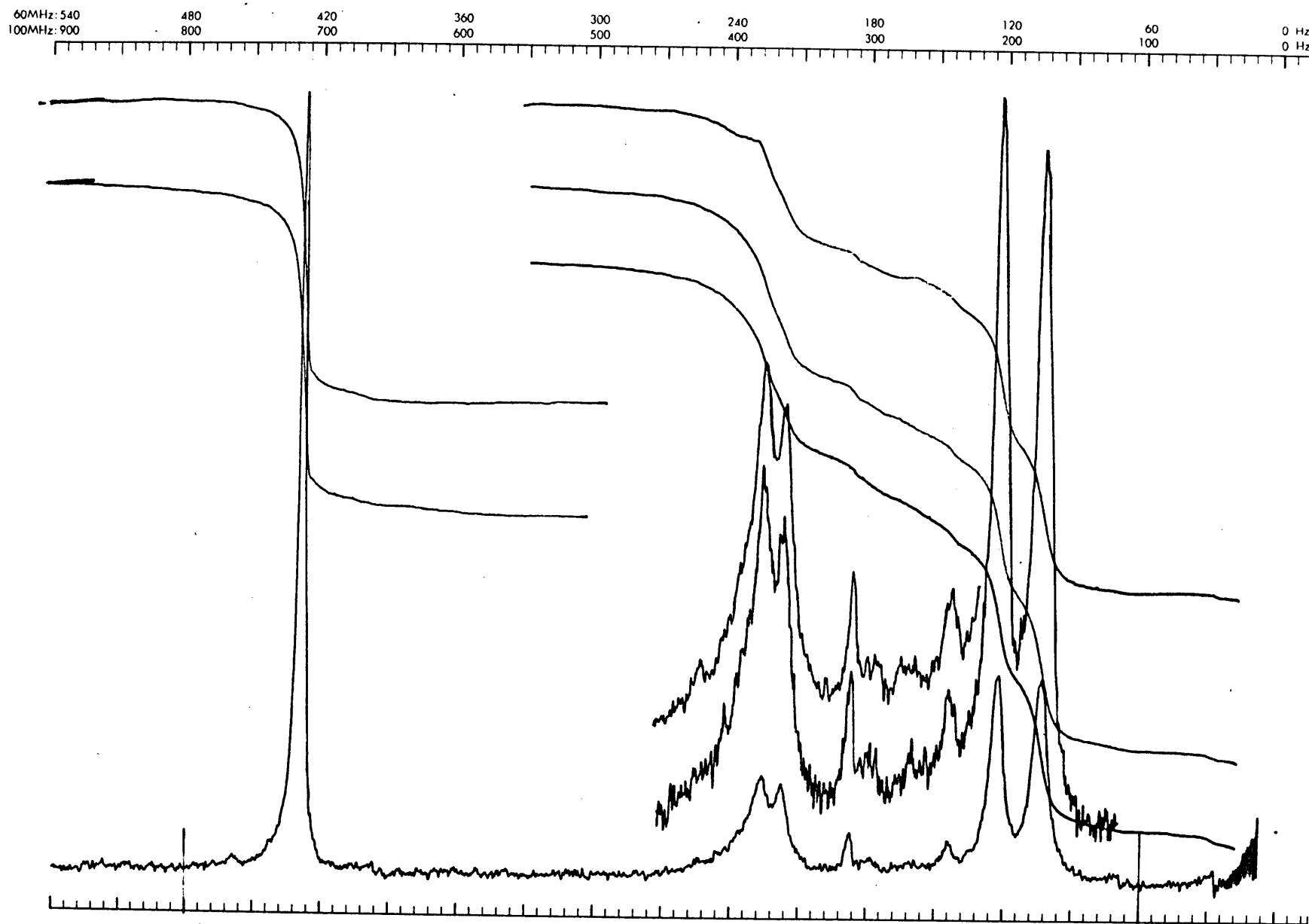


Fig-3.54 100 MHz  $^1\text{H}$  NMR spectrum of polymethyl methacrylate prepared using fluorenyl sodium in THF at 256 K.

Table 3.27 Experimental conditions and steric sequence distribution data for polymethyl methacrylate polymer prepared with sodium naphthalene as initiator in pure THF

Exp No	Temp K	$[I]_0 \times 10^3$ M/dm <sup>3</sup>	$[M]_0$ M/dm <sup>3</sup>	$D_{pn}^-$	Conversion	I	H	S	P
C-15	195	1.01	0.257	680	1.0	0.088	0.389	0.523	1.042
C-5	253	0.94	0.120	280	1.0	0.080	0.445	0.475	0.948
C-8	195	0.99	0.246	425	1.0	0.100	0.380	0.520	1.084
C-16	195	1.38	0.131	1,165	1.0	0.075	0.390	0.535	1.011
C-14	195	1.10	0.254	753	1.0	0.070	0.410	0.520	0.973

Table 3.27b

Exp No	$P_i$	$P_s$	$\bar{l}_i$	$\bar{l}_s$	$P_{ii}$	$P_{is}$	$P_{ss}$	$P_{si}$	$\frac{P_{ss}}{P_{is}}$	$\frac{P_{ii}}{P_{si}}$
C-15	0.282	0.717	1.452	3.689	0.312	0.688	0.729	0.271	1.059	1.149
C-5	0.302	0.697	1.360	3.135	0.264	0.736	0.681	0.319	0.926	0.829
C-8	0.290	0.710	1.520	3.737	0.345	0.655	0.732	0.268	1.118	1.289
C-16	0.270	0.730	1.385	3.744	0.278	0.722	0.733	0.267	1.015	1.040
C-14	0.275	0.725	1.341	3.537	0.255	0.745	0.717	0.283	0.962	0.900

Table 3.28. Experimental conditions and steric sequence distribution data for polymethyl methacrylate polymer prepared with sodium  $\alpha$ -methyl styrene as initiator in THF

Exp No	Temp K	$[I]_0 \times 10^3$ M/dm <sup>3</sup>	$[M]_0$ M/dm <sup>3</sup>	$D_{pn}^-$	Conversion	I	H	S	P
B-2	195	1.14	0.257	198	0.44	0.076	0.410	0.514	0.986
B-14	195	1.14	0.248	437	1.00	0.056	0.382	0.562	0.974
B-15	195	0.87	0.263	605	1.00	0.063	0.405	0.532	0.964
B-5	195	1.07	0.247	372	0.81	0.058	0.380	0.562	0.984
B-13	195	0.99	0.237	478	1.00	0.060	0.40	0.540	0.962

Table 3.28b

Exp No	$P_i$	$P_s$	$\bar{I}_i$	$\bar{I}_s$	$P_{ii}$	$P_{is}$	$P_{ss}$	$P_{si}$	$\frac{P_{ss}}{P_{is}}$	$\frac{P_{ii}}{P_{si}}$
B-2	0.281	0.719	1.371	3.507	0.270	0.730	0.715	0.285	0.980	0.949
B-14	0.247	0.753	1.293	3.942	0.227	0.773	0.746	0.254	0.965	0.894
B-15	0.265	0.735	1.311	3.627	0.237	0.763	0.724	0.276	0.950	0.861
B-5	0.248	0.752	1.305	3.958	0.234	0.766	0.747	0.253	0.975	0.926
B-13	0.260	0.740	1.30	3.70	0.231	0.769	0.730	0.270	0.949	0.854

Table3.29 Experimental conditions and steric sequence distribution data for polymethyl methacrylate polymer prepared with fluorenyl sodium as initiator in pure THF

Exp No	Temp K	$[I]_0 \times 10^3$ M/dm <sup>3</sup>	$[M]_0$ M/dm <sup>3</sup>	$D_{pn}$	Conversion	I	H	S	P
T1	195	0.321	0.235	605	1.0	0.050	0.400	0.550	0.980
T2	220	0.368	0.269	405	1.0	0.059	0.379	0.562	0.985
T5	245	0.561	0.174	242	0.95	0.057	0.362	0.581	1.002
T3	245	0.349	0.167	177	0.70	0.055	0.370	0.575	0.937
T6	256	0.664	0.237	142	0.66	0.080	0.434	0.486	0.962

Table 3.29b

Exp No	$P_i$	$P_S$	$\bar{I}_i$	$\bar{I}_S$	$P_{ii}$	$P_{is}$	$P_{ss}$	$P_{si}$	$\frac{P_{ss}}{P_{is}}$	$\frac{P_{ii}}{P_{si}}$
T1	0.250	0.750	1.250	3.750	0.200	0.800	0.733	0.267	0.917	0.750
T2	0.248	0.751	1.311	3.966	0.237	0.763	0.748	0.252	0.981	0.942
T5	0.238	0.762	1.315	4.210	0.239	0.761	0.762	0.238	1.003	1.008
T3	0.240	0.760	1.297	4.108	0.229	0.771	0.757	0.243	0.982	0.941
T6	0.297	0.703	0.369	3.24	0.269	0.731	0.691	0.309	0.946	0.873

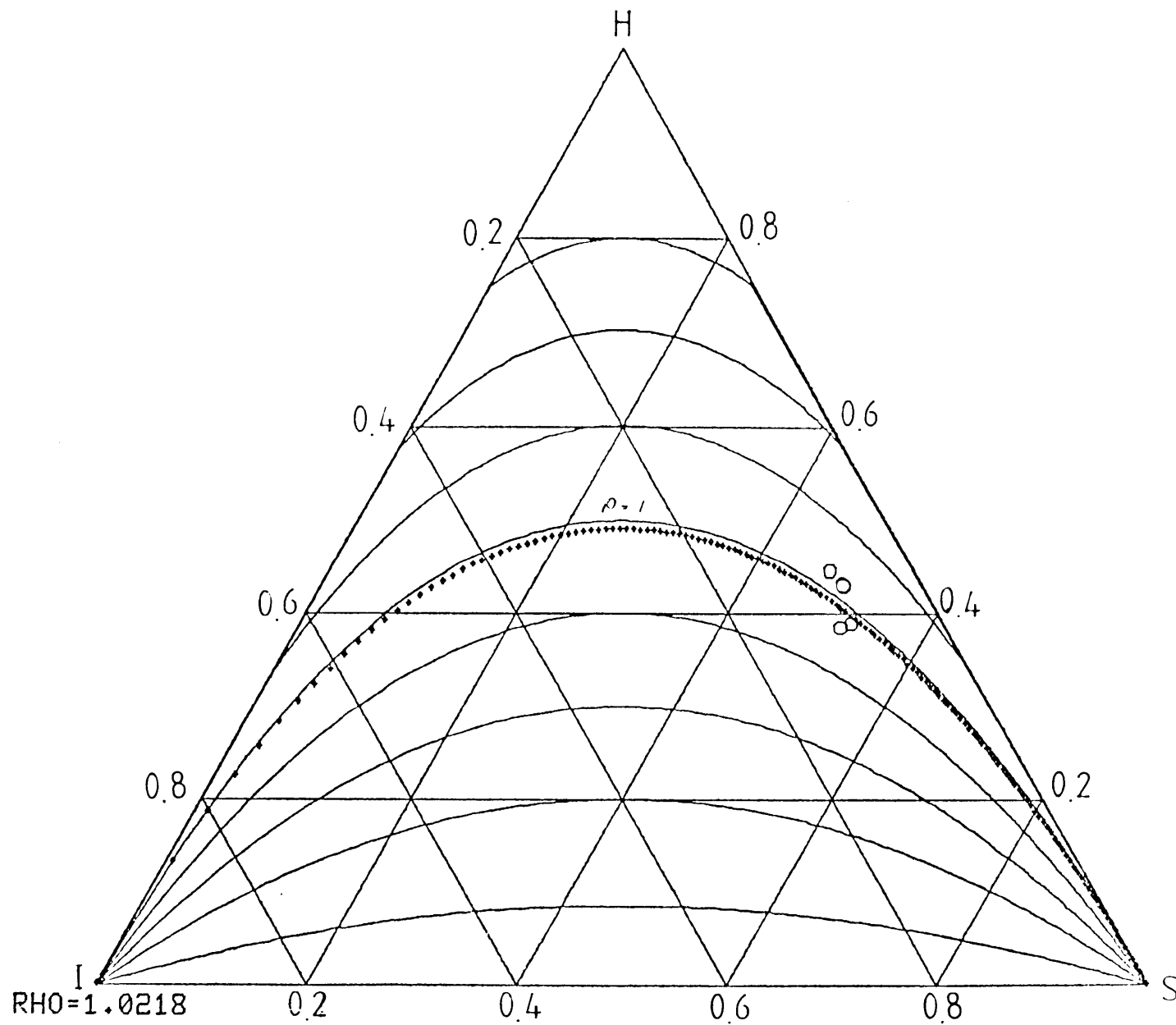


Fig 3.55 Ternary diagram for PMMA

Initiator - sodium naphthalene

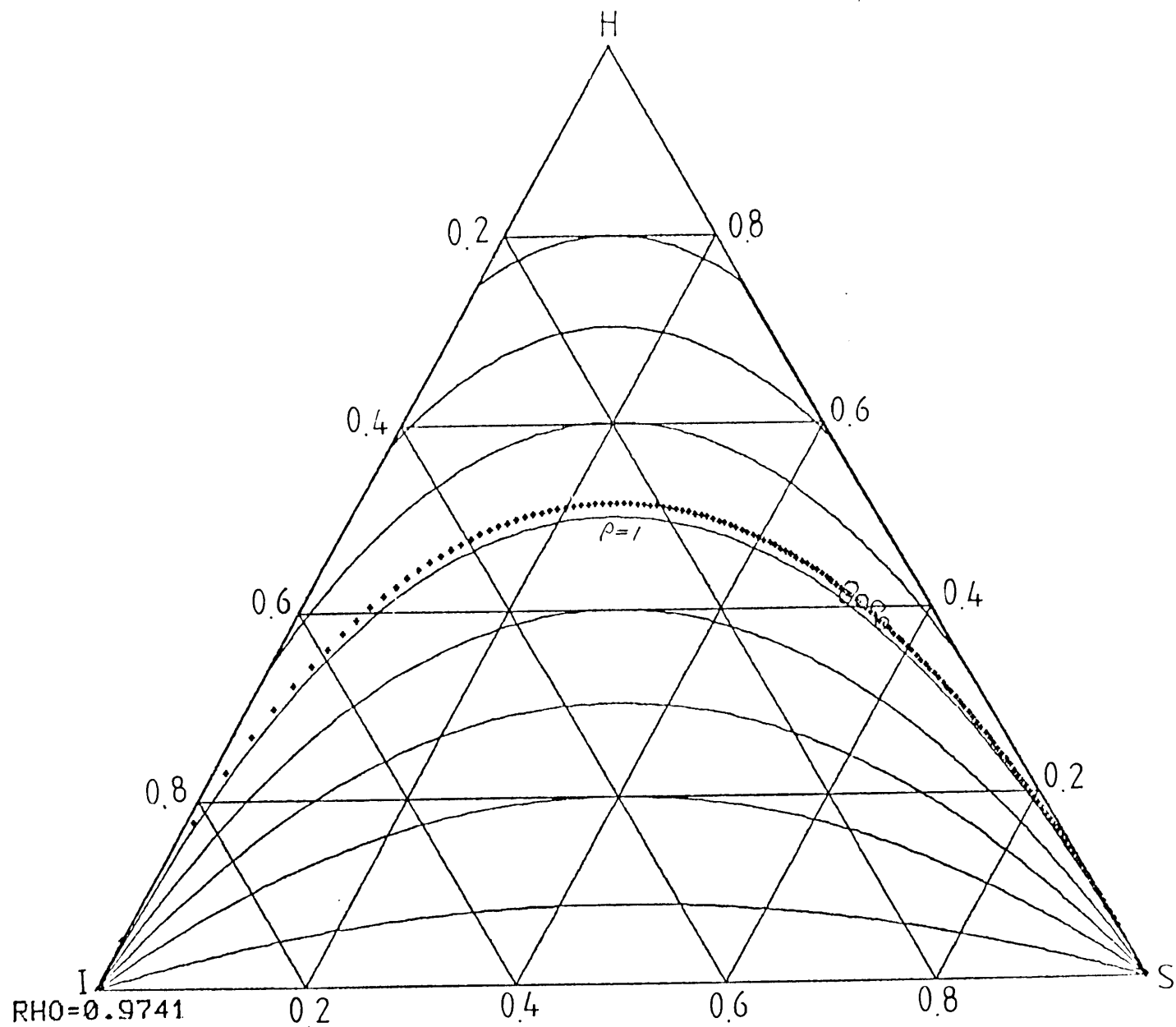


Fig 3.56 Ternary diagram for PMMA

Initiator - sodium  $\alpha$ -methyl styrene



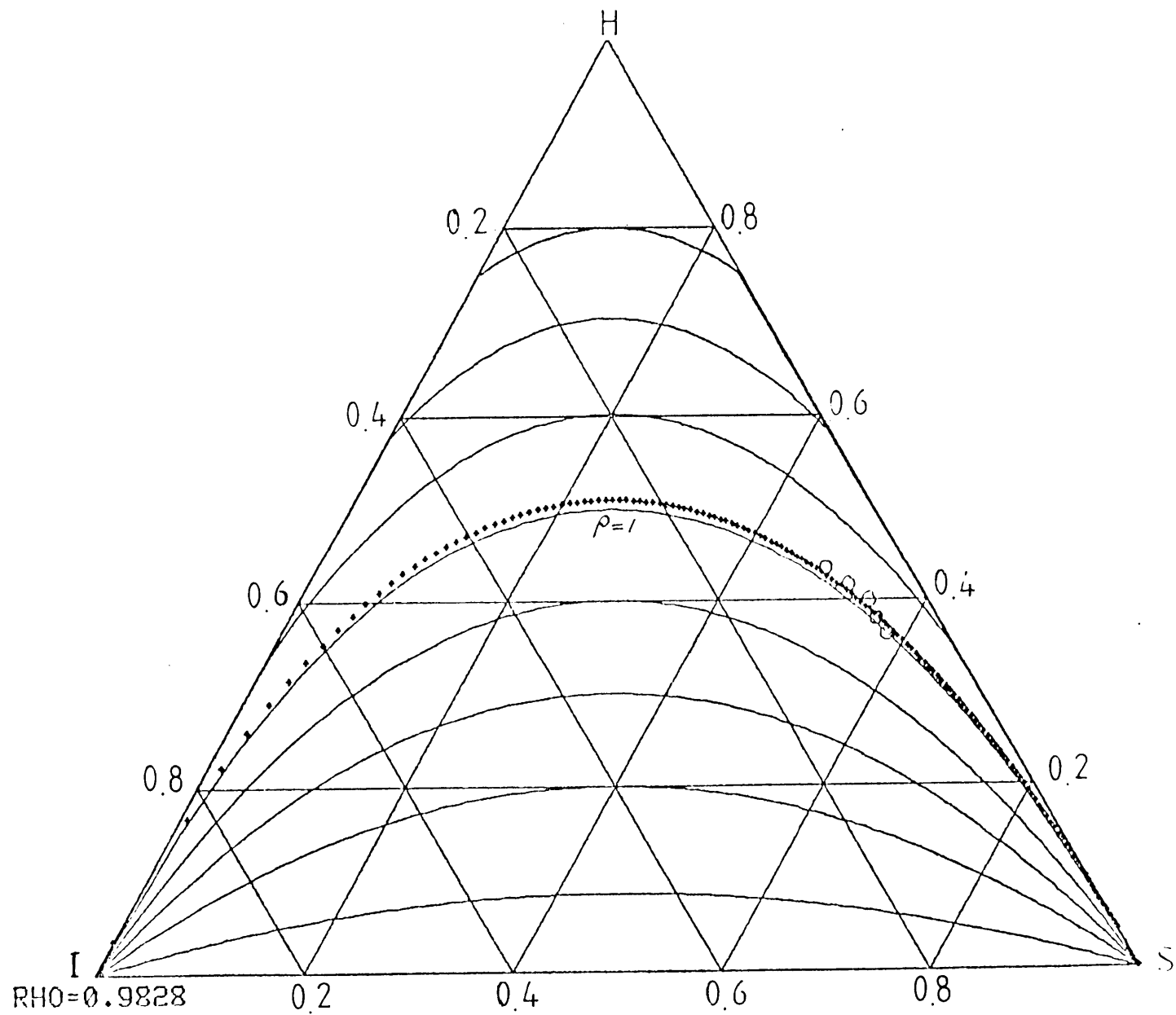


Fig 3.57 Ternary diagram for PMMA

Initiator - Fluorenyl sodium

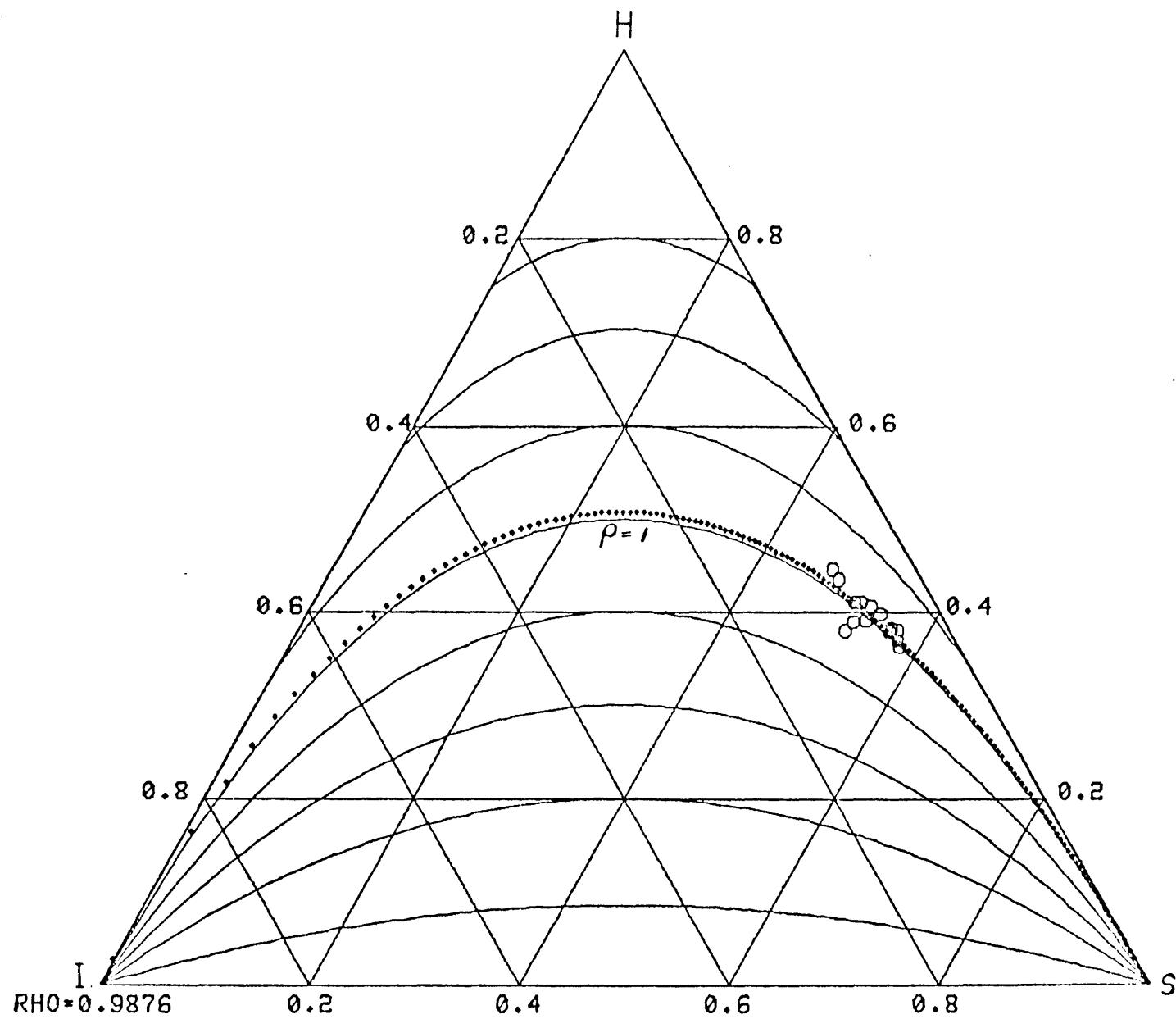


Fig 3.58 Ternary diagram PMMA, Na System

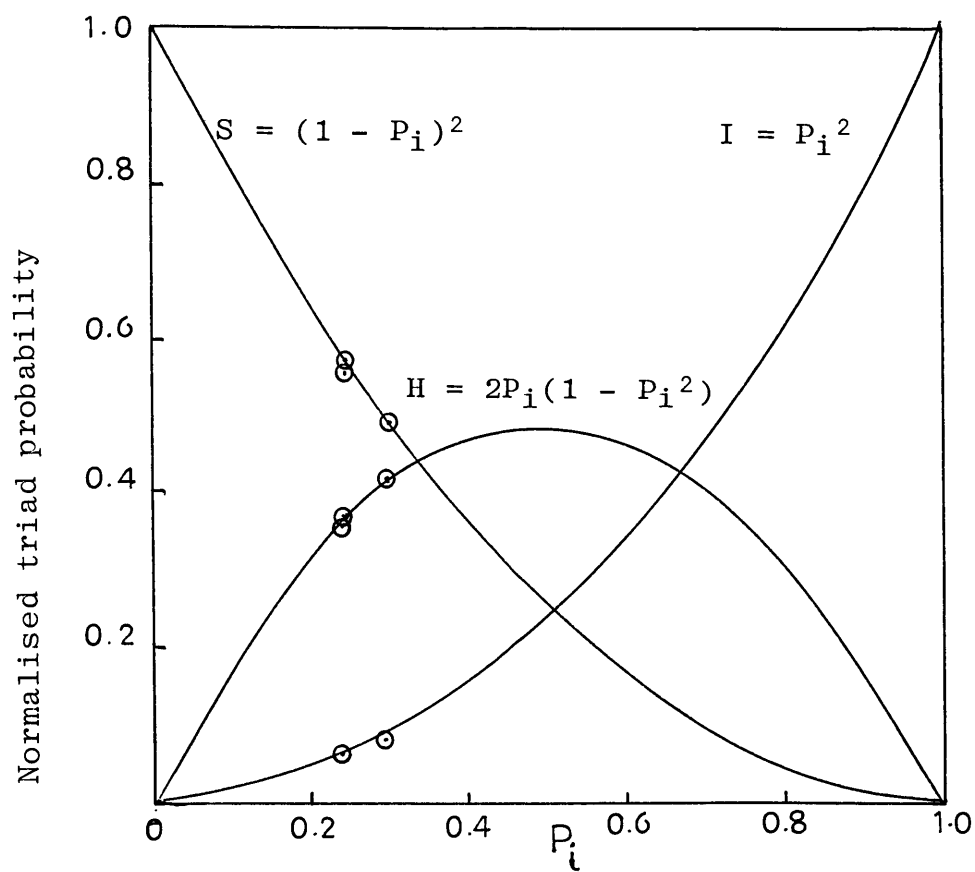


Figure 3.59 The probabilities of I, H and S triads as a function of  $P_i$  for PMMA

Initiator - fluorenyl sodium  
sodium  $\alpha$ -methyl styrene

3.3.2 Stereoregulation of polymethyl methacrylate prepared by anionic mechanism in which ion pairs with  $\text{Na}^+$  as counterion dominate

Three types of initiators were used for the preparation of polymers:

- (i) naphthyl sodium;
- (ii)  $\alpha$ -methyl styryl sodium;
- (iii) fluorenyl sodium;

Naphthyl sodium is a radical ion which dimerises on initiation to form dicarbanion which then propagates as a bifunctional initiator.  $\alpha$ -Methylstyrene is in the form of a tetramer which initiates and propagates as a difunctional initiator. Fluorenyl sodium is a monofunctional initiator. In all three cases, the free ion concentration was suppressed by the addition of the common cation  $\text{Na}(\text{Ph})_4\text{B}$  and only ion pairs are responsible for propagation. Separate reaction conditions and steric sequence distributions are given in Tables 3.27-29. 100 MHz  $^1\text{H}$  NMR spectra representing each of these initiator systems are given in Figures 3.51 - 3.53.

From these results, it is evident that the nature of the carbanion has no detectable effect on the propagating end. Not only are their triad sequence ratios identical, but the NMR spectra with the fine structures are almost super-imposable. Consequently the persistence ratios in all three cases are very close to 1. The best fit curve on the ternary diagram (Figure 3.58) gives a value  $P = 0.9876$ .

The effect of temperature is significant. When initiated at 195 K and propagated at 255 K, both monofunctional (NoC-5)

and bifunctional (No T-6) types show an identical increase in isotactic triads and heterotactic triads with a corresponding decrease in syndiotactic triads. Thus the effect of the increase in temperature of propagation is the same for both monofunctionally and bifunctionally initiated polymers and the NMR spectra are identical (Figure 3.54) This indicates that the reactive species in both cases probably have the same structure and the addition of monomer follows the same mechanism. Although the effect of temperature is detectable in the triad distribution as well as lower values of persistence ratios, the deviation from Bernoullian behaviour is not very significant. Hence, it appears that the sequence distribution of steric triads in the case of  $\text{Na}^+$  counterion is similar to that of polymers prepared with free radical initiators.

The operation of termination reactions along with the propagation of chains does not seem to have a significant effect on the triad distribution. Similarly, the concentration of initiator too does not seem to have any effect, at least in the range of initiator concentrations ( $< 10^{-3} \text{ m}^{-3}$ ) studied. This is apparent in the spectras of two polymers prepared at 255 K. In the case of No T6, all reactive species became deactivated within a short time, while No C5 had a longer deactivation time, and a higher conversion.

The effect of monomer concentration on the triad distribution is negligible. However, in the case of sodium  $\alpha$ -methylstyrene initiated polymer, in which kinetic studies

were carried out, there is an apparent increase of isotacticity and corresponding decrease in syndiotacticity in the initial phase of the polymerisation reaction (3 seconds, corresponding to a fractional conversion of 0.4). This polymer has a bimodal distribution but it is not possible to say whether this is a result of two types of reactive species or due to partial deactivation of bifunctional living ends.

From the ternary diagrams where  $P \approx 0.7876$  and the Bovey plot where all three tactic sequences fall on a single probability value ( $P_i = 0.25$ ), it is evident that sequence distribution of all polymers prepared with  $\text{Na}^+$  as counterion in THF can be described by Bernoullian statistics. The ratios  $P_{ii}/P_{si}$  and  $P_{ss}/P_{is}$ , both show values close to 1, ( $P_{ii}/P_{si} = 0.9819$ , S.D = 0.051) which again shows the agreement with Bernoullian behaviour. Average chain length of isotactic sequence is 1.36 with a standard deviation 0.08. For syndiotactic sequence, it is 3.66 with standard deviation = 0.24.

### 3.3.3 Stereo-regulation of polymethyl methacrylate prepared by anionic mechanism in which ion pairs with $\text{Li}^+$ as counterion dominate

Fluorenyl lithium was used for the preparation of polymers, and its kinetics were well-defined. (Section 1) Steric sequence distribution and experimental conditions are given in the Table 3.30 100 MHz  $^1\text{H}$  NMR spectrum of a standard polymer is shown in Figure 3.60 Ternary diagram for tactic triads gives a persistence ratio value of 0.889. This is

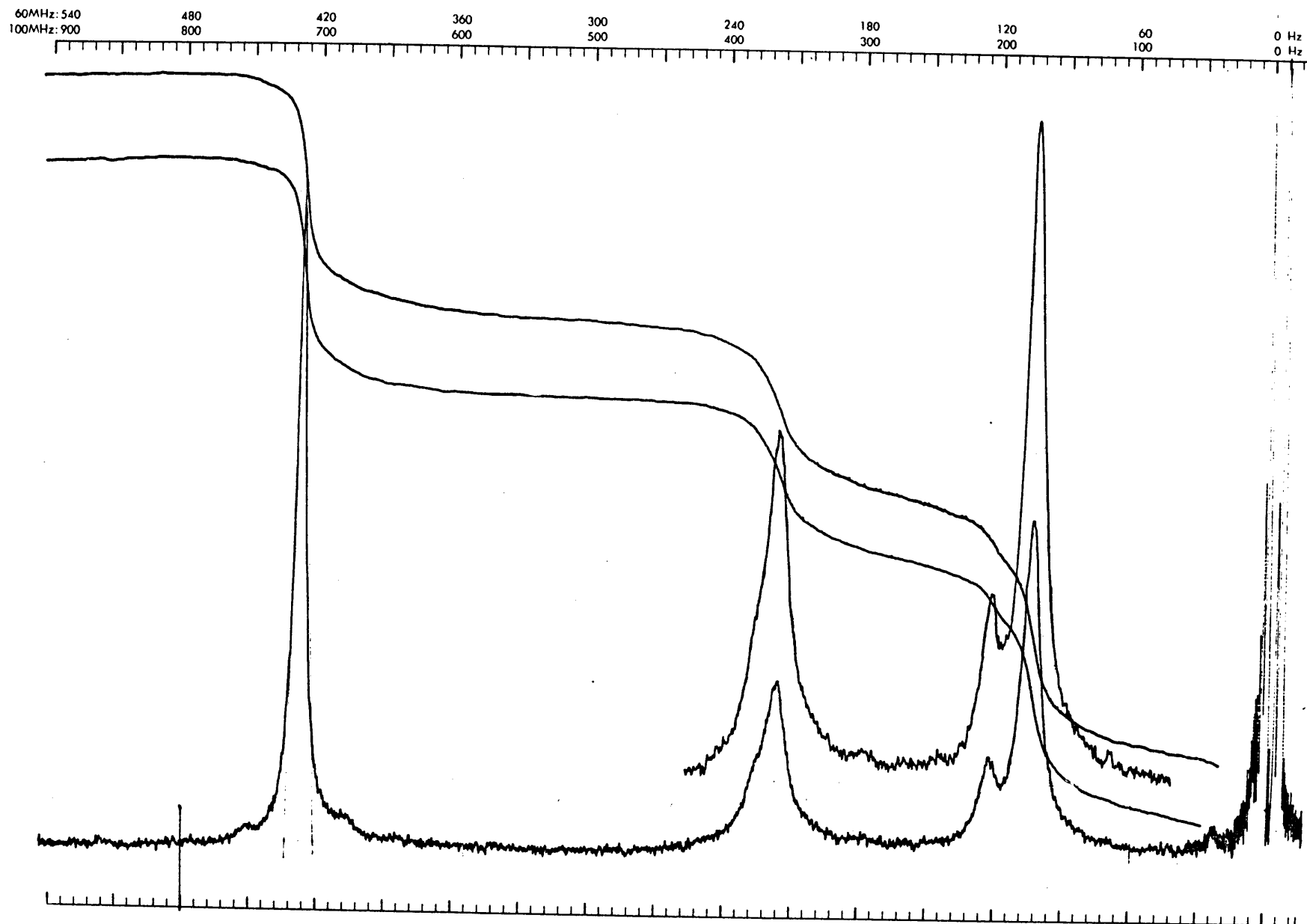


Fig 3.60 100 MHz  $^1\text{H}$  NMR spectrum of polymethyl methacrylate prepared using fluorenyl lithium in THF

Table 3.30 Experimental conditions and steric sequence distribution data for polymethyl methacrylate polymer prepared with fluorenyl lithium as initiator in THF

Exp No	Temp K	$[I]_0 \times 10^3$ M/dm <sup>3</sup>	$[M]_0$ M/dm <sup>3</sup>	$D_{Pn}$	Conversion	I	H	S	P
A-10	195	1.24	0.095	81	1.0	0.00	0.248	0.752	0.876
A-14	195	1.03	0.166	165	0.96	0.00	0.220	0.780	0.890
A-13	195	1.14	0.261	301	0.96	0.00	0.200	0.800	0.900
A-11	195	1.14	0.095	111	1.0	0.00	0.220	0.780	0.890
A-15	195	1.93	0.093	76	0.84	0.00	0.230	0.770	0.885

Table 3.30b

Exp No	$P_i$	$P_S$	$\bar{I}_i$	$\bar{I}_S$	$P_{ii}$	$P_{is}$	$P_{ss}$	$P_{Si}$	$\frac{P_{ss}}{P_{is}}$	$\frac{P_{ii}}{P_{Si}}$
A-10	0.124	0.876	1.00	7.065	0.00	1.00	0.858	0.142	0.858	0.00
A-14	0.110	0.890	1.00	8.091	0.00	1.00	0.876	0.124	0.876	0.00
A-13	0.100	0.900	1.00	9.000	0.00	1.00	0.889	0.111	0.889	0.00
A-11	0.110	0.890	1.00	8.091	0.00	1.00	0.876	0.124	0.876	0.00
A-15	0.115	0.885	1.00	7.696	0.00	1.00	0.870	0.130	0.870	0.00



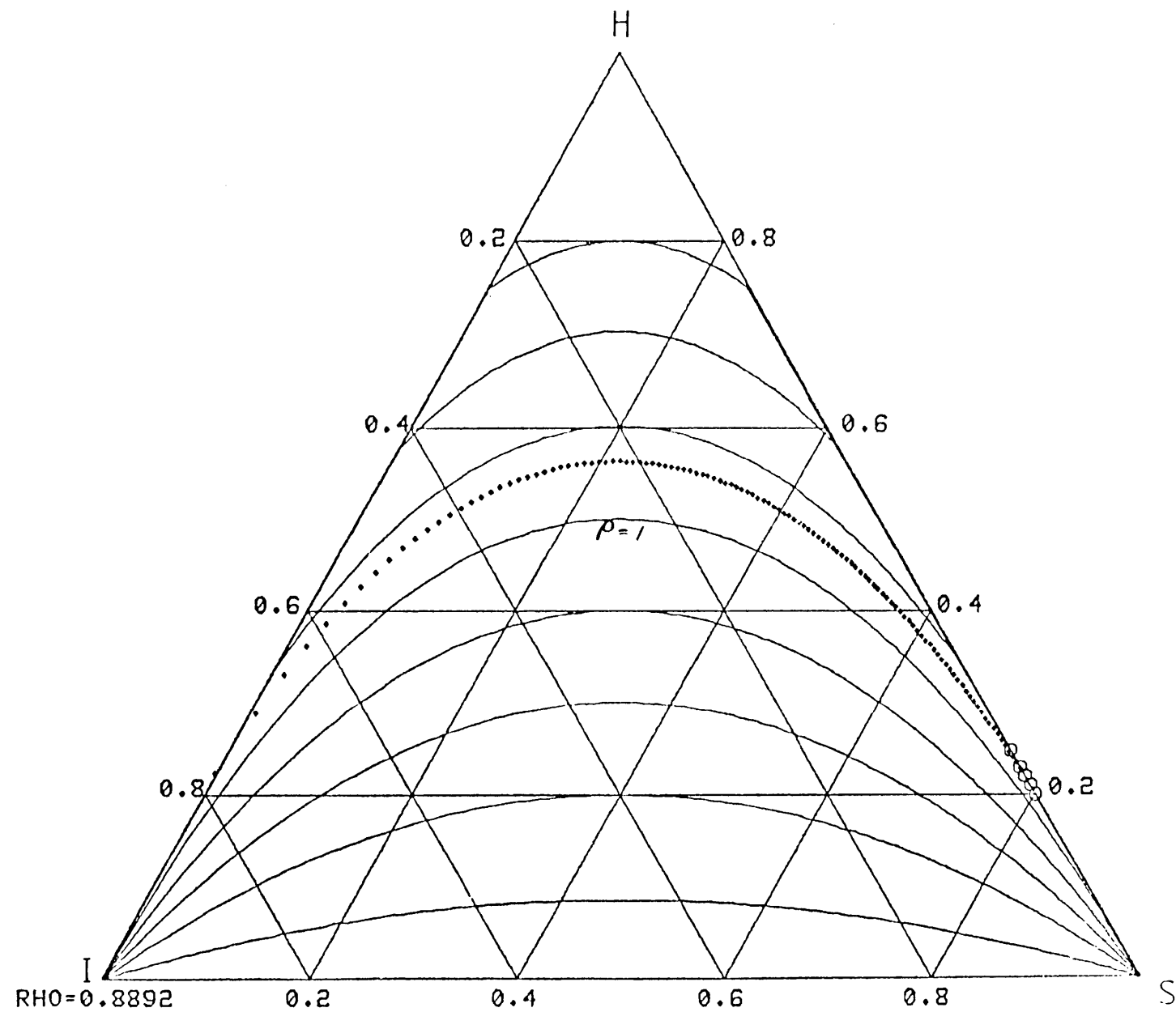


Fig 3.61 Ternary diagram. PMMA, Li System

indicative of a deviation from Bernoullian behaviour (Fig 3.61 ). These results are significantly different from Amerik's results (100) in which he observed Bernoullian statistics for polymers prepared using n-butyl lithium in THF. It is evident from Table 3.30 that polymers prepared with fluorenyl lithium in THF at 200 K do not show any isotactic triads (polymer nos A10 - A15) This is a significant result and could be possibly interpreted as due to the presence of a definite directive influence on the stereo-regulation of the polymer by the active species.

It is easy to understand the observation of Bernoullian statistics for polymers initiated by n-butyl lithium. In the polymerisation of methyl methacrylate by n-butyl lithium in THF, even at very low temperatures such as 200 K, side reactions are extensive (72) and propagation is disturbed. It is possible that by-products formed could influence the tactic placements and the overall distribution of triads could be different from that of an undisturbed system. Even in the case of polymers initiated with fluorenyl lithium, calculations show that the hypothetical inclusion of 2-3% fraction of isotactic triads brings the value of the persistence ratio close to 1.0. Hence with a little contribution towards isotactic placements, the distribution can be readily shifted towards a Bernoullian type. In the case of fluorenyl lithium initiated systems, no such disturbance could be detected.  $M_w/M_n < 1.10$  and molecular weights theoretically expected from  $[M]_0/[I]_0$  ratios are readily obtained. However, it must be pointed out that

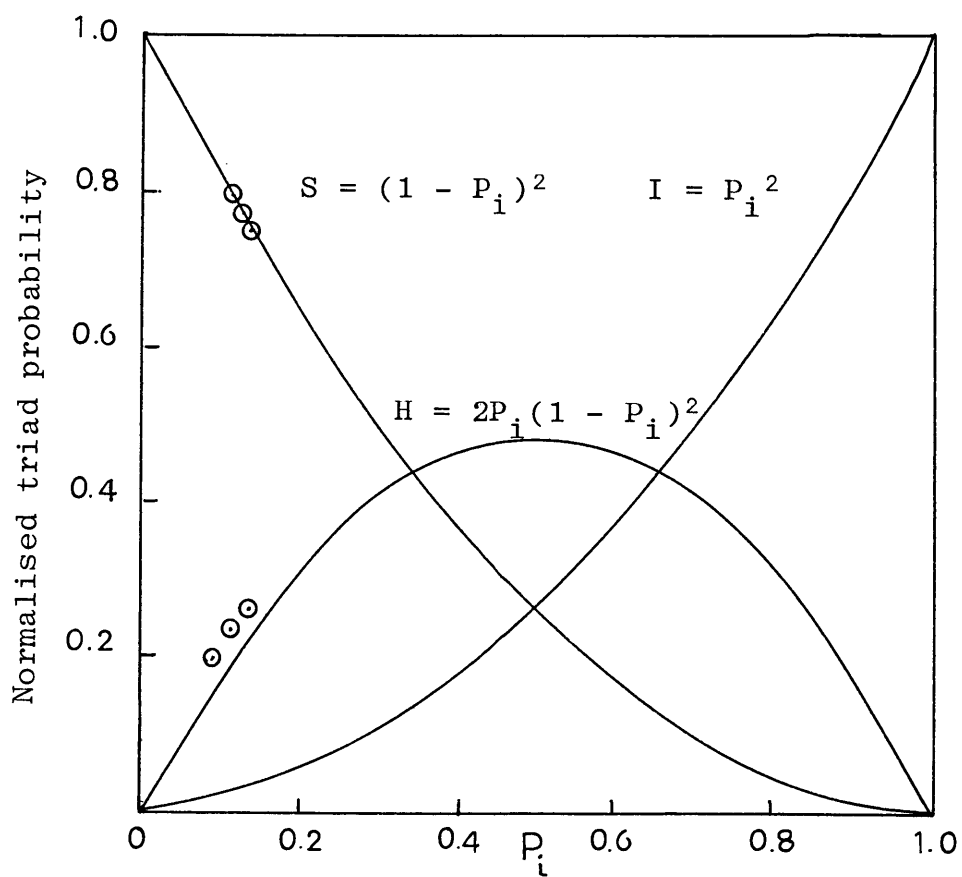


Figure 3.62 The probabilities of I, H and S triads as a function of  $P_i$  for PMMA

Initiator - Fluorenyl lithium

minute distribution levels of isotacticity up to 2% are difficult to detect from the  $\alpha$ -methyl resonance. This is due to the fact that the base line between the  $\alpha$ -methyl resonance peak and the  $\beta$ -methylene resonance peak does not come down to the zero level because of the residual effects of higher sequences (Fig 3.51 - 54). This difficulty can be avoided by considering the  $\beta$ -methylene resonance, which gives independent and more reliable information, if coupled with  $\alpha$ -methyl resonance. Fig 3.52 is the spectrum of a fluorenyl sodium initiated polymer with an isotactic triad content of 6% and  $P = 0.985$ . The  $\beta$  methylene resonance is clearly split due to the field of isotactic placements. In a syndiotactic polymer, this would have been a singlet and only a slight broadening would be expected due to residual effects. Inspection of Fig 3.60 shows, in fact, this is the case.

The average chain length of syndiotactic sequence is remarkably high and has a value of 8.00 with a standard deviation of 0.7, whereas that of isotactic sequence,  $\bar{l}_i$  is 1.0. By comparison,  $\bar{l}_s$  for  $\text{Li}^+$  counterion is more than twice that for  $\text{Na}^+$  counterion. The probability of isotactic addition of oncoming monomer to a isotactic placement is zero. This means that the isotactic addition is always followed by syndiotactic addition and some form of influence on the reversal of the direction of the oncoming monomer, interrupted by occasional isotactic placement is operating. This is reflected in the  $P_{ss}/P_{is}$  value, which is 0.87 with standard deviation of 0.1. Considering the zero probability of  $P_{ii}$  and very high probabilities of  $P_{is}$

and  $P_{SS}$ , it is apparent that this effect is penultimate and the deviation from Bernoullian behaviour is due to this.

3.3.4 Stereo-regulation of polymethyl methacrylate prepared by anionic mechanism in which ion pairs with  $K^+$  as counterion dominate

Two types of initiators were used for the preparation of polymers:

- (i) potassium  $\alpha$ -methyl styrene (bifunctional)
- (ii) fluorenyl potassium (monofunctional)

Experimental conditions and steric sequences are given in Tables 3.31 & 3.32 Calculated statistical data are given in Tables 3.31b & 3.32b 100 Mhz  $^1H$  NMR spectra representing each initiator system are shown in Figures 3.63 and 3.64

The most conspicuous characteristic of spectra of polymers prepared with  $K^+$  as counterion is that, the heterotactic triads have a greater distribution than the syndiotactic triads. This is in clear contrast to  $Na^+$  and  $Li^+$  counterion system in which as a rule, syndiotactic sequences are greater in distribution.

The comparison of triad sequence distribution also shows that polymers prepared with  $K^+$  as counterion have the lowest fraction of syndiotactic triads out of all three systems investigated.

Ternary diagram gives a persistence ratio value 0.833, again the lowest for all three types of polymers (Fig 3.67 It is interesting to note that I, H and S, triad ratios and

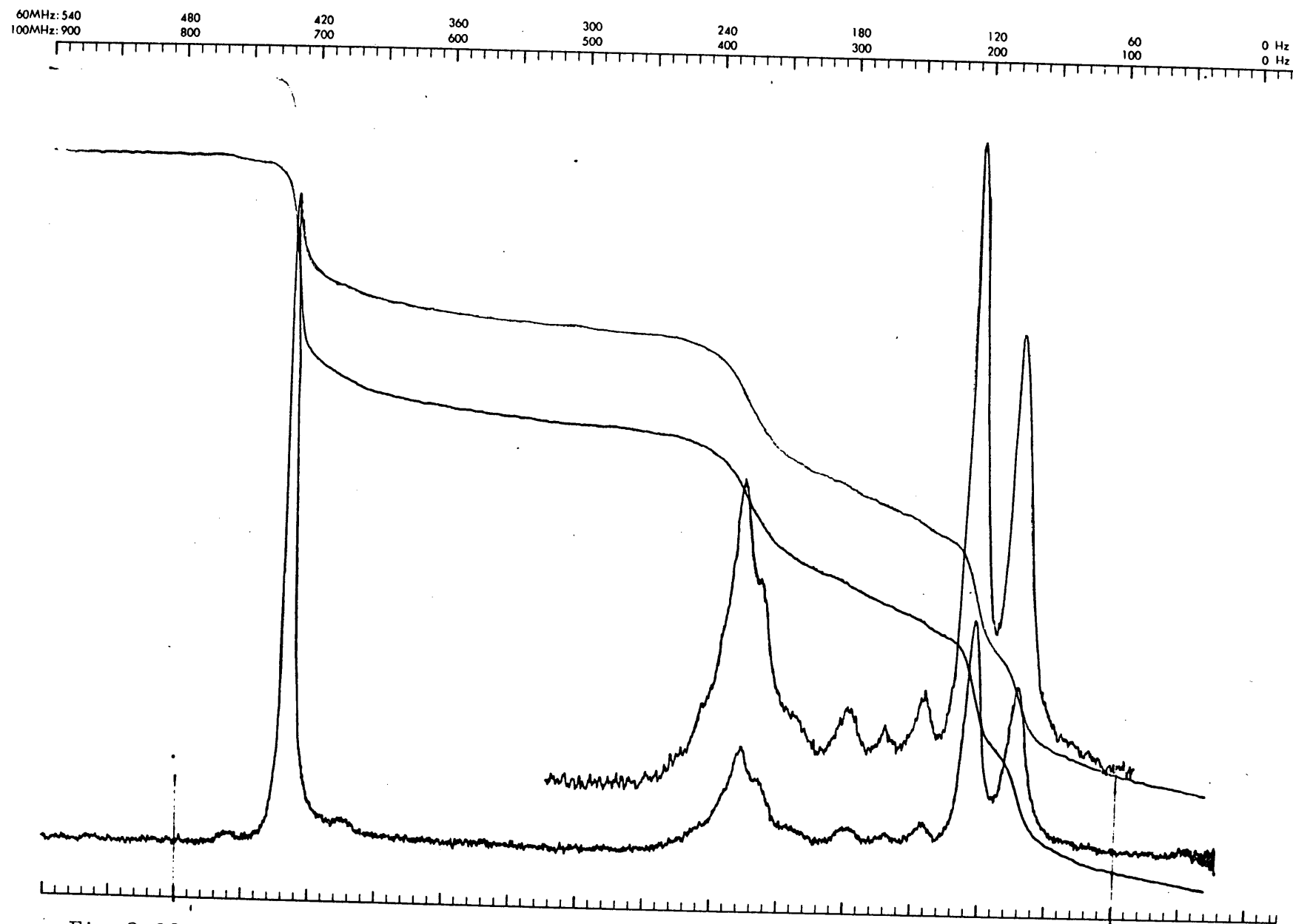


Fig 3.63 100 MHz  $^1\text{H}$  NMR spectrum of polymethyl methacrylate prepared using potassium  $\alpha$ -methyl styrene in THF

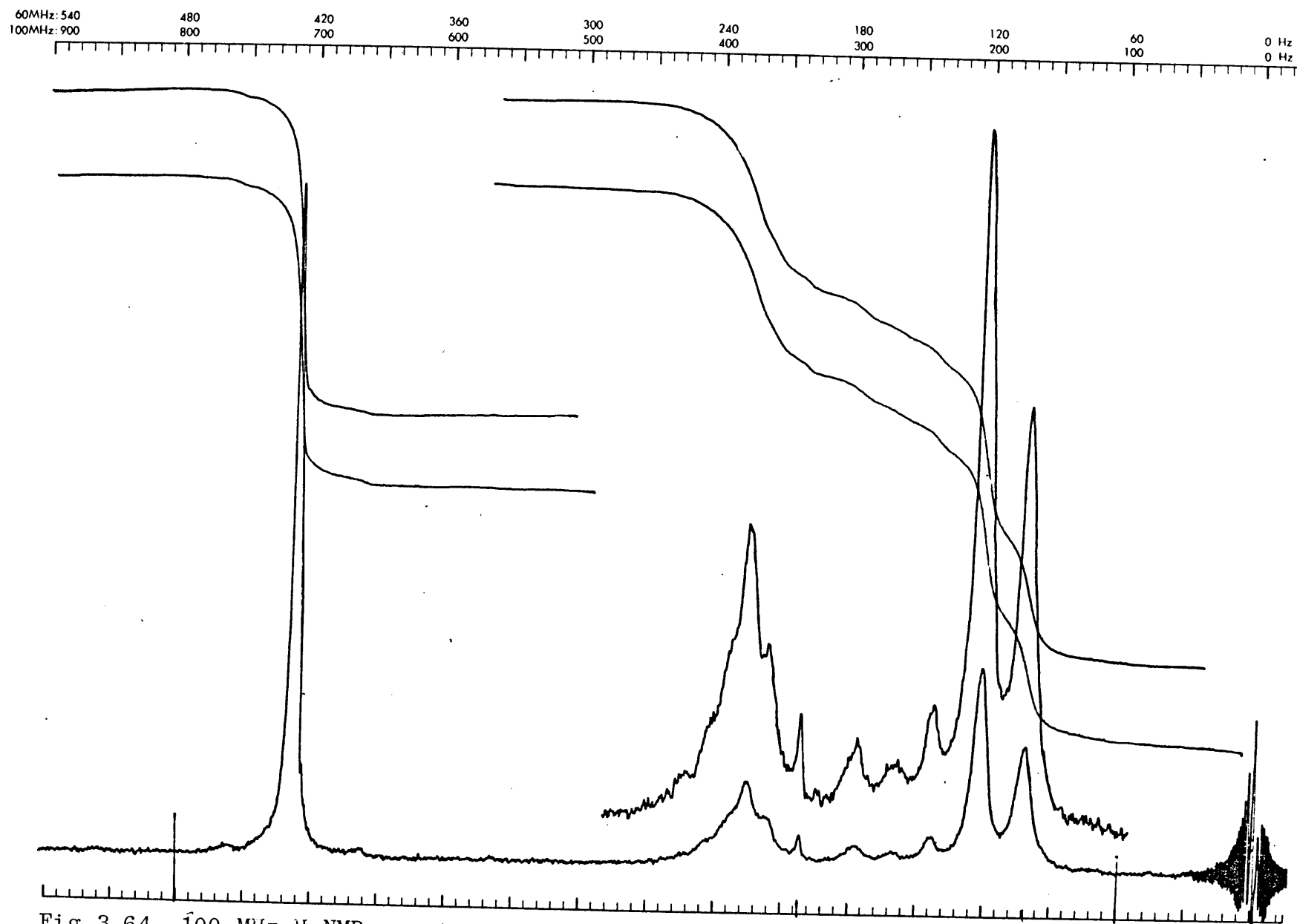


Fig 3.64  $^{100}$  MHz  $^1\text{H}$  NMR spectrum of polymethyl methacrylate prepared using fluorenyl potassium in THF

Table 3.31 Experimental conditions and steric sequence distribution data for polymethyl methacrylate polymer prepared with potassium  $\alpha$ -methyl styrene as initiator in THF

Exp No	Temp K	$[I]_0 \times 10^3$ M/dm <sup>3</sup>	$[M]_0$ M/dm <sup>3</sup>	$D_{p_n}^-$	Conversion	I	H	S	P
E-6	195	0.835	0.189	438	0.97	0.050	0.510	0.440	0.831
E-9	195	2.450	0.226	185	1.0	0.060	0.530	0.410	0.828
E-14	195	0.856	0.472	1,105	1.0	0.052	0.530	0.418	0.817
E-16	195	0.793	0.220	555	1.0	0.068	0.553	0.379	0.817
E-11	195	1.559	0.327	420	1.0	0.065	0.540	0.395	0.825

Table 3.31b

Exp No	$P_i$	$P_s$	$\bar{I}_i$	$\bar{I}_s$	$P_{ii}$	$P_{is}$	$P_{ss}$	$P_{si}$	$\frac{P_{ss}}{P_{is}}$	$\frac{P_{ii}}{P_{si}}$
E-6	0.305	0.695	1.196	2.725	0.164	0.836	0.633	0.367	0.757	0.447
E-9	0.325	0.675	1.226	2.547	0.185	0.815	0.607	0.393	0.745	0.470
E-14	0.317	0.683	1.196	2.577	0.164	0.836	0.612	0.388	0.732	0.423
E-16	0.344	0.655	1.246	2.371	0.197	0.803	0.578	0.422	0.720	0.468
E-11	0.335	0.665	1.241	2.463	0.194	0.806	0.594	0.406	0.737	0.478



Table 3.32 Experimental conditions and steric sequence distribution data for polymethyl methacrylate polymer prepared with fluorenyl potassium as initiator in THF

Exp No	Temp K	$[I]_0 \times 10^3$ M/dm <sup>3</sup>	$[M]_0$ M/dm <sup>3</sup>	$D_{p_n}^-$	Conversion	I	H	S	P
T-12	195	0.440	0.275	630	1.0	0.060	0.520	0.420	0.837
T-7	195	0.378	0.241	1440	1.0	0.050	0.524	0.426	0.819
T-8	220	0.430	0.246	545	0.95	0.070	0.530	0.400	0.841
T-9	245	0.411	0.257	618	0.98	0.079	0.536	0.385	0.845
T-11	268	0.381	0.233	570	0.93	0.090	0.520	0.390	0.875

Table 3.32b

Exp No	$P_i$	$P_s$	$\bar{l}_i$	$\bar{l}_s$	$P_{ii}$	$P_{is}$	$P_{ss}$	$P_{si}$	$\frac{P_{ss}}{P_{is}}$	$\frac{P_{ii}}{P_{si}}$
T-12	0.320	0.680	1.231	2.615	0.188	0.813	0.618	0.382	0.760	0.490
T-7	0.312	0.688	1.191	2.626	0.160	0.840	0.619	0.381	0.737	0.421
T-8	0.335	0.665	1.264	2.509	0.209	0.791	0.602	0.398	0.760	0.524
T-9	0.347	0.653	1.295	2.437	0.228	0.772	0.590	0.410	0.763	0.555
T-11	0.350	0.650	0.346	2.500	0.257	0.743	0.600	0.400	0.808	0.643

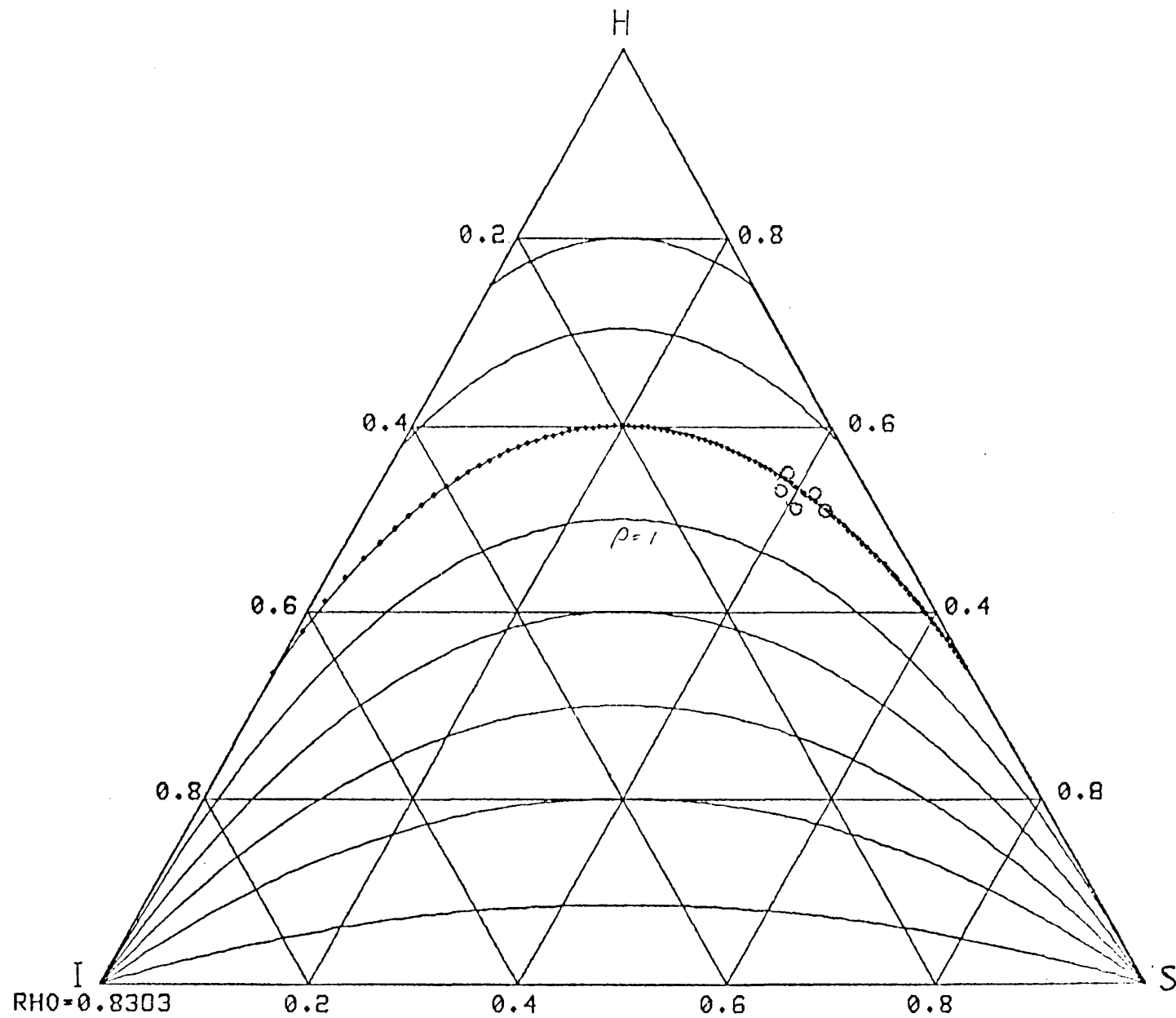


Fig 3.65 Ternary diagram for PMMA  
 Initiator - potassium  $\alpha$ -methyl styrene

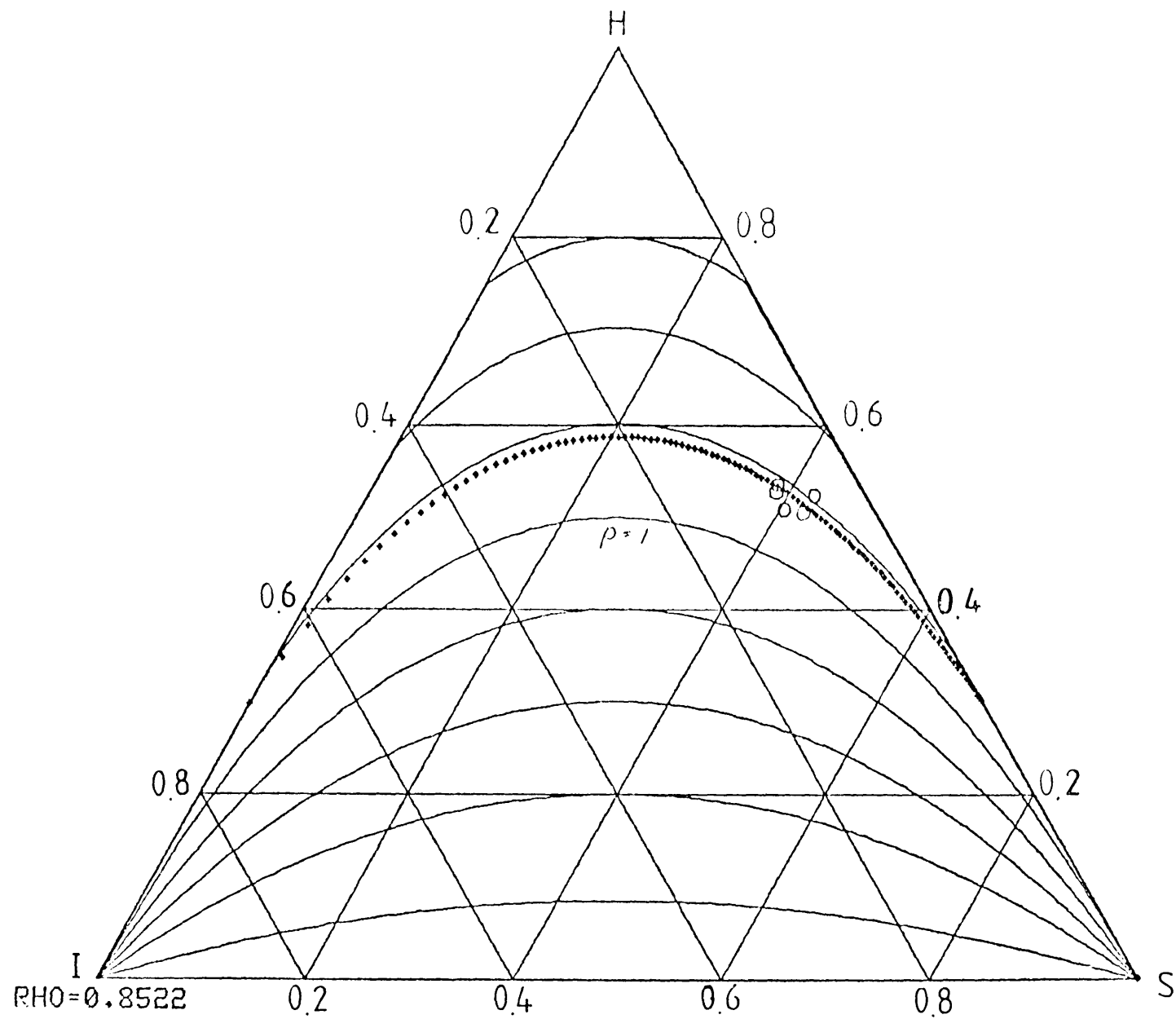


Fig 3.66 Ternary diagram for PMMA.  
 Initiator - fluorenyl potassium

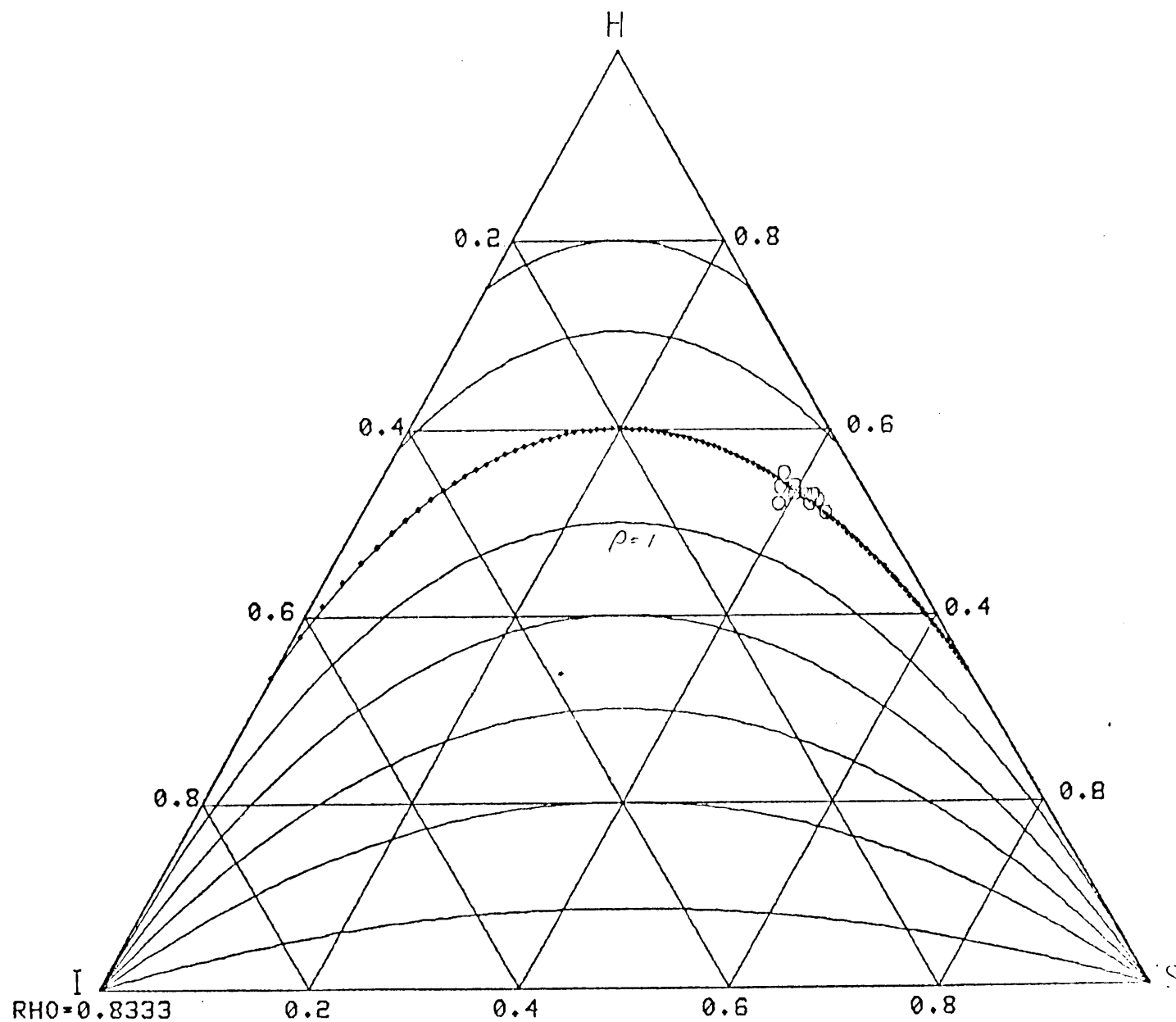


Fig 3.67 Ternary diagram, PMMA, K System

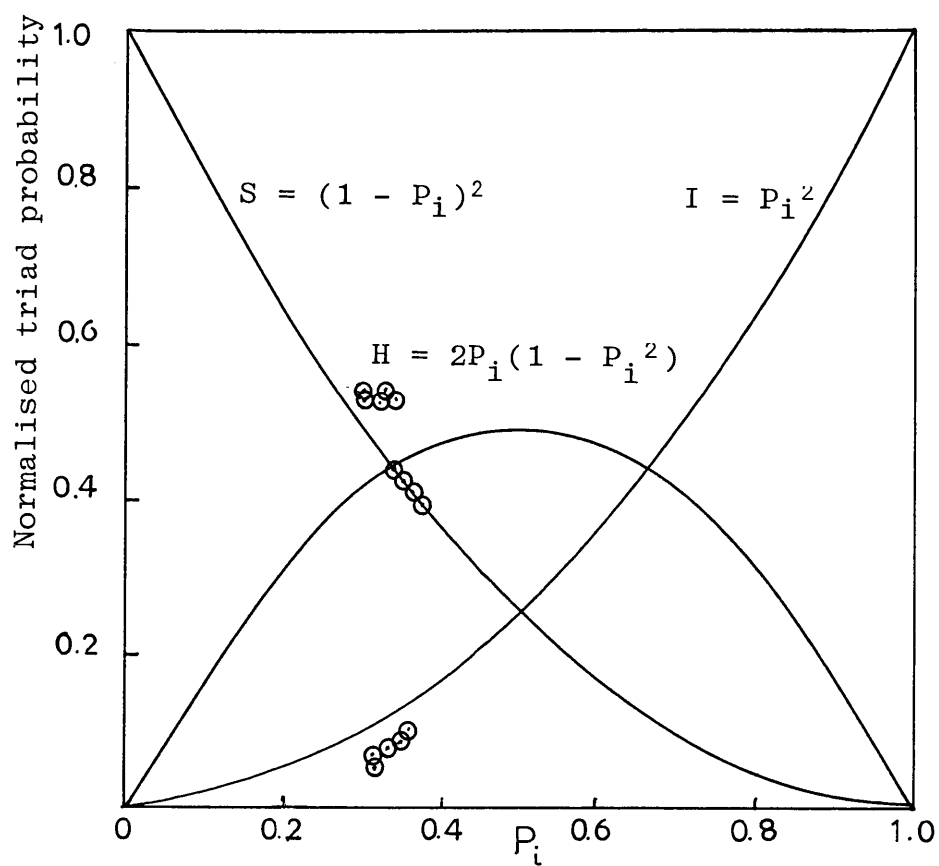


Figure 3.68 The probabilities of I, H and S triads as a function of  $P_i$  for PMMA

Initiator - Potassium  $\alpha$ -methyl styrene  
Fluorenyl potassium

hence the other statistical data for this system closely resemble those of polymers prepared with  $\text{Cs}^+$  as counterion when polymerisations are carried out in THF at 200-270 K (87). This could indicate that stereo-regulation of polymethyl methacrylate prepared anionically in THF depends on the size of the cation more than any other factor. This appears to be the case at least for ion pairs. Furthermore, monofunctional and bifunctional initiators both add monomer in a stereospecifically identical manner. NMR spectra of the respective polymers (Figures 3.63 & 3.64) have a similarity up to fine structures. Hence the suggestion that bifunctional chains add monomer in a different manner to that of monofunctional initiators (91) cannot be justified. Although the cyclisation of bifunctional chains is a possibility, there is no evidence for a different type of addition of monomer. Thus it may be safely stated that, irrespective of the types of carbanion, it is the counterion which plays a major role in stereoregulation.

The effect of temperature on the steric triad sequence distribution was investigated using fluorenyl potassium. (Table 3.32). There is a tendency for an increase in isotactic triads as the temperature increases, with an opposite effect on syndiotactic triads. This results in a decrease in the difference between isotactic and syndiotactic chain lengths (Table 3.32b)

However, these changes are not large enough to change the general distribution pattern which is non-Bernoullian.

The deviation from Bernoullian behaviour can also be seen in the Bovey plot (Fig 3.68 ). None of the polymers show tacticities that could be described by a single probability value. The average sequence length of syndiotactic placements is  $2.54 \pm 0.1$  which is much less than that for  $\text{Na}^+$  counterion, which in turn is almost half the value for  $\text{Li}^+$  counterion. Average sequence length for isotactic placement does not change significantly with the counterion. However, the probability of isotactic placement is clearly increased over that for  $\text{Na}^+$  counterion, even though masked by the increase in heterotactic triads. This is reflected in the low  $P_{SS}$  values observed for  $\text{K}^+$  counterion which also has characteristically low  $P_{SS}/P_{IS}$  and  $P_{II}/P_{IS}$  ratios. The latter values show the penultimate effects on the sequence distributions and the non-Bernoullion behaviour.

### 3.3.5 Discussion

From the results in Table 3.33 it is apparent that the change in steric sequence data as the counterion changes is regular, and conforms to a certain trend. The highest distribution of syndiotactic placements is seen with  $\text{Li}^+$  counterion while the lowest is the  $\text{K}^+$  counterion. The opposite is true for isotactic placements. Average sequence length of isotactic placement is minimal with  $\text{Li}^+$ , but the change with the counterion is not very large. However, the trend in the decrease in the average sequence length of syndiotactic placement is most significant. The probability that a syndiotactic placement is followed by a syndiotactic placement is highest with  $\text{Li}^+$  but decreases down the order, and is 0.6 with  $\text{K}^+$ . The opposite trend

Table 3.33 Comparison of stereo-regularity of polymethyl methacrylate polymers prepared by anionic mechanism in THF with  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  as counterions

Counter ion	I	H	S	$P_i$	$P_S$	$\bar{I}_i$	$\bar{I}_S$
$\text{Li}^+$	0.00	0.22	0.78	0.11	0.99	1.00	7.99
$\text{Na}^+$	0.06	0.40	0.54	0.26	0.74	1.32	3.75
$\text{K}^+$	0.06	0.53	0.41	0.33	0.67	1.22	2.54

Counter ion	P	$P_{ii}$	$P_{is}$	$P_{ss}$	$P_{si}$	$\frac{P_{ss}}{P_{is}}$	$\frac{P_{ii}}{P_{si}}$
$\text{Li}^+$	0.89	0.00	1.00	0.87	0.13	0.87	0.00
$\text{Na}^+$	0.98	0.24	0.76	0.73	0.27	0.96	0.90
$\text{K}^+$	0.82	0.18	0.82	0.60	0.40	0.74	0.46

(All values are averages of minimum of 5 samples)



is observed for the probability of isotactic addition to a syndiotactic placement. It is useful to interpret these observations in terms of the increasing ionic size. Thus it appears that there is a tendency for the discontinuation of syndiotactic addition, helped by the increased frequency of isotactic addition as the size of the counterion increases.

Any model proposed to explain these results has to satisfy the kinetics of propagation, as well as the kinetics of termination. In section one, it was seen that the order of reactivity of ion pairs increases with the size of cation,  $\text{Li} < \text{Na} < \text{K}$ , which is a complete reversal of the order of reactivity of polystyryl ion pairs under the same conditions. The inability of THF to yield similar solvated ion pairs with methyl methacrylate was attributed to the formation of cyclic structures, where the counterion is solvated by the last two or three ester groups of the growing polymer chain (Section 1). The cyclic structures given are comparable to those proposed by Fowell (88) and Schulz (85, 86).

The kinetic observation that  $\text{PMMA}^-\text{Li}^+$  has the lowest reactivity indicates that the interaction of its ion pair is greatest with respect to  $\text{Na}^+$  and  $\text{K}^+$ . Such a result is readily explained if it is assumed that the cyclic structure is a special form of contact ion pair, where the steric requirements allow smaller  $\text{Li}^+$  counterion closer approach to the carbanic site. This  $\text{K}^+$  and  $\text{Cs}^+$  will have the highest steric hindrance whereas the  $\text{Na}^+$  has an intermediate effect. Apparently such a process is being helped

by the external interaction of THF molecules. It appears that this form favours the syndiotactic monomer placement, while the linear contact ion pair, which is in equilibrium with the cyclic structure favours isotactic addition. However, since the major species of ion pairs is that of cyclic type (Section 1), the general tendency is always to invert the placement of oncoming monomer with respect to the placement of the last unit. Hence the probability of an isotactic placement followed by another isotactic placement does not change significantly, with the change of counterion. With the increase in the size of the counterion, the fraction of linear contact type of ion pair seems to increase. This is also reflected in the higher isotactic addition at elevated temperatures. Hence with  $K^+$  counterion relatively higher distribution of isotactic placements is observed, with the opposite for  $Li^+$  counterion. This could be supported by MWD data. With  $Li^+$  counterion, very narrow MWD's with  $M_w/M_n > 1.10$  are obtained while with  $K^+$  broad MWD is the normal result. With  $Na^+$  as counterion, intermediate results are obtained. The idea of a cyclic structure as the major propagating species agrees well with termination rates observed.

The termination rate constant for intramolecular termination has the highest value for  $\text{PMMA}^- \text{Li}^+$  ion pairs, while it is approximately 2 orders of magnitude lower for  $\text{PMMA}^- \text{K}^+$  ion pairs.

The effect of the preceding units of the active centre on the placement of monomer observed with  $\text{Li}^+$  and  $\text{K}^+$  counterions seems to be disturbed in the case of  $\text{Na}^+$ . Apparently this coincides with the increased probability of isotactic placement followed by isotactic placement ( $P_{ii}$ ) and the increased average sequence length of isotactic placement ( $l_i$ ) (Table 3.33). According to the proposed model, this may be related to a slight shift of equilibrium towards the linear type of ion pair (Section 1, Figure 3) which can be explained as being due to the increased size of the counterion. The highest value of isotactic diad placement ( $P_i$ ) observed for  $\text{K}^+$  counterion supports this view. Although the  $P_i$  value for  $\text{Na}^+$  is intermediate between those of  $\text{Li}^+$  and  $\text{K}^+$ , it is the  $P_{ii}$  value which appears to cause the deviation.

It is difficult to explain this increased probability of retention of isotactic placement when most of the other data are intermediate. (Lower value of  $P_{is}$  is the direct consequence of higher  $P_{ii}$  value.) However, because of the intermediate position of  $\text{Na}^+$  ion between the smaller  $\text{Li}^+$  ion and larger  $\text{K}^+$  ion, the factors involved in the equilibrium process such as external solvation by THF molecules, the number of ester groups involved, and the structure of reactive species etc may favour a retention

of isotactic placement at a certain point. Although the exact mechanism is not clear, this may explain the observed Bernoullian behaviour. Statistically a Bernoullian process is the limiting case of a Markov process, when only the last unit in the chain has the significant effect on the placement of the oncoming monomer. When the overall polymerisation process in the presence of alkali metal counterions is considered, the placement of oncoming monomer, according to the discussed model is dependent on the placement of the previous units. Hence, the steric triad sequence distribution appears to obey Markovian statistics. The fact that the polymers prepared with  $\text{Na}^+$  as counterion showed Bernoullian behaviour can be considered as a special case of Markovian statistics.

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## APPENDIX I

Computer Program for Sampling. Takes output from detector and stores on cassette

```
25 PRINT "B= SAMPLING RATE IN B/100 THS OF A SECOND.  
   B=";\INPUT B  
27 PRINT "K=NO OF DATA POINTS. INPUTK"; \ INPUT K  
40 PRINT "INPUTFILE NO ITO 6.IF G<0 PROGRAM STOPS"  
45 PRINT "G="; \ INPUT G  
50 IF G<=0 GO TO 500  
52 IF G>3 GO TO 65  
55 ON G GO TO 56,58,60  
56 OPEN "CT0:PVC" FOR OUTPUT AS FILE # 1  
57 GO TO 85  
58 OPEN "CT0:GPC1" FOR OUTPUT AS FILE # 1  
59 GO TO 85  
60 OPEN "CT0:GPC2" FOR OUTPUT AS FILE # 1  
62 GO TO 85  
65 LET L=G-3  
68 ON L GO TO 70, 75, 80  
70 OPEN "CT0:GPC3" FOR OUTPUT AS FILE # 1  
72 GO TO 85  
75 OPEN "CT0:GPC4" FOR OUTPUT AS FILE # 1  
77 GO TO 85  
80 OPEN "CT0:GPC5" FOR OUTPUT AS FILE # 1  
85 PRINT "READY FOR SCHMIDT-TRIGGER"  
90 DIM X (100),A(1800)  
100 USE (X)  
110 RTS(X,6,0,19,0)  
120 RDB(X,F)  
130 IF F<0GO TO 120  
150 PRINT "*"   
170 SETR (5,1,B)  
180 USE(A)  
190 RTS(A,6,0,30000,2)  
210 FOR N=1 to K  
215 LET S=0  
220 FOR I=1 TO 10  
260 PDB(A,Z)  
270 IF Z=-2 GO TO 260  
272 IF Z>=4095 GO TO 500  
275 LED(Z)  
280 LET S=S+Z  
290 NEXT I  
300 LET Y=S/10  
320 PRINT # 1,Y  
330 NEXT N  
340 CLOSE # 1  
500 PRINT "PROGRAM REACHED HERE AT I=";\PRINT N  
700 END
```

## APPENDIX II

Computer program for the calculation of MW averages,  
using data on cassette and using Universal Calibration  
method

```

5 PRINT "B=, K=,"; \ INPUT B,K
7 DIM Y(1500)
10 PRINT "V 1,V 2,V3,V4, DELINEATE THE PEAK. V5 to V3 IS THE
    TAIL"
11 PRINT "V 1=,V 2=, V3=, V4=,V5="; \ INPUT V1,V2,V3,V4,V5
12 PRINT "W = STARTING VOLUME. F1= FLOW RATE"
13 PRINT "W = F 1 =, "; \ INPUT W,F1
15 A=0 \ S=0 \ T=0 U=0 P=0
20 D1=0 \ D2=0 \ D3=0 \ D4=0 \ D5=0
25 D6=0 \ D7=0 \ D8=0
30 H1=0 \ H2=0 \ H3=0
42 LET K1=1.4290E-04 LET A1=.695
44 PRINT "K2,A2 ARE THE MARK-HOUWINK COEFFICIENTS OF THE
    SAMPLE"
50 PRINT "INPUT G=OTO6 FOR COMPUTATION. IF G<=0 PROGRAM STOPS"
55 INPUT G
57 PRINT "PROGRAM INPUTS DATA FROM CASSETTE"
60 IF G<=0 GO TO 700
63 IF G<=5 GO TO 80
65 LET L=G-3
67 ON L GO TO 70,74,77
70 OPEN "CT 0:G PO3" AS FILE # 1
72 GO TO 95
74 OPEN "CT 0:G PC4" AS FILE # 1
75 GO TO 95
77 OPEN "CT 0:G PO5" AS FILE # 1
79 GO TO 95
80 ON G GO TO 85,87,89
85 OPEN "CT 0:P VC" AS FILE # 1
86 GO TO 95
87 OPEN "CT 0:G PC1" AS FILE # 1
88 GO TO 95
89 OPEN "CT 0:G PC2" AS FILE # 1
95 LET J=0
98 LET D=K-5
100 FOR I=1 TO D
110 INPUT # 1,Y
120 LET X=W + ((I*B*F1)/600)
125 IF X>V 4 GO TO 230
130 IF X<V 1 GO TO 220
135 IF X>V 1 THEN IF X<V2 GO TO 175
140 IF X>V 3 GO TO 175
150 LET J=J+1
160 LET Y(J)=Y
170 GO TO 220
175 LET P=R+X *Y \ LET S=S+X \ LET T=T+Y
180 LET Y=Y + X ^ 2 \ LET A=A+1
220 NEXT I
230 LET C2=(A*R - S*T)/(A*U-S^2)
240 LET C1=(T - C2*S)/A
245 PRINT "PROGRAM IS NOW CALCULATING EQUATION OF BASELINE"
250 PRINT "C1-";C1,"C2=";C2

```

```

260 PRINT "I=";I;"A=";A;J=";J
264 PRINT "PROGRAM IS NOW FITTING PEAK TAIL TO A QUADRATIC"
265 FOR I=1 TO J
269 LET V=V2+( (I*B*F1)/600)
270 IF V<V6 GO TO 283
274 D1=D1+Y (I) \ D2=D2+V \ D3=D3+V 2
278 D4=D4+V 3 \ D5=D5+V 4 \ D6=D6+V*Y(I)
282 D7=D7+(V 2)*Y (I) \ D8=D8+1
283 NEXT I
284 E1=D8*(D3*D7-D4*D6) \ E2=D2*(D2*D7-D3*D6)
286 E3=D1*(D2*D4-D3 2) \ E1=D1-E2+E3
290 E2=D8*(D3*D5-D4 2) \ E3=D2*(D2*D5-D3*D4)
294 E4=D2*D3*D4-D3 3 \ E5=E2-E3+E4
298 H3=E1/E5
300 M=D6-H3*D4 \ N=D1-H2*D3
305 H2=(D2*N-D8*M) / (D2 2-D8*D3)
310 H1=(M-H2*D3) / D2
315 PRINT "H1=";H1;"H2=";H2;"H3=";H3
325 PRINT "PROGRAM NOW CALCULATES MOLECULAR WTS"
330 PRINT "K2=,A2="; \ INPUT K2,A2
333 PRINT "NO OF DATA PTS ON PEAK =J/C. INPUT C"; INPUT C:
335 T1=1.72-2.38*A1*A1^2 \ T2=1.72-2.38*A2+A2^2
340 T3=T2/T1 \ D2=1/(1 + A2) \ D3=(1 + A1)*D2
345 N1=0 \ N2=0 \ N3=0 \ O=0
347 N4=0
350 FOR I=1 TO J STEP C
355 LET V=V2 + ( (I*B*F1)/600)
358 IF V<V6 GO TO 360
359 LET Y(I) = H1+H2*V+H3*V^2
360 LET P=C1+C2*V
370 LET P1 = Y(I)-P
390 IF P1>0 GO TO 420
415 GO TO 455
420 LET N1=N1+P1
430 GOSUB 5 50
438 LET A=( (T3*K1/K2)^D2)*(A^D3)
440 N2=N2+P 1*A
450 N3=N3+P1 / A \ N4=N4+P1*(A A2)
453 GO TO 460
455 LET O=O+1
460 NEXT I
465 PRINT O
470 M1=(N1/N3) \ M2=N2/N1
473 A4=1/A2
475 M3=(N4/N1)^A4
480 P1=M3/M1 P2=M2/M1
490 PRINT "MN=NUMBER AVERAGE MOLECULAR WT.MN=";M1
500 PRINT "MW=WEIGHT AVERAGE MOLECULAR WT.MW=";M2
505 PRINT "MV=VISCOSITY AVERAGE MOLECULAR WT.MV=";M3
510 PRINT "MW;MV;MN=";P2":P1:";1"
520 GO TO 330
550 IF V<43.5 GO TO 580
560 LET A= 8.8608-.121904*V
570 GO TO 6 20
580 IF V<32.2 GO TO 610
590 LET A=9.75594-.141883*V
600 GO TO 620

```

```
610 LET A=12.467 - .22558*V
620 LET A=10 A
645 RETURN
700 END
```



APPENDIX III: COMPUTER PROGRAM FOR THE CALCULATION OF  
STEREO SEQUENCE DATA

\*MUSIC AT SHEFFIELD CITY POLYTECH SIGN ON.

/ID 36,D2T7N57,SENA

\*PASSWORD?

\*CODE LAST USED 14:45 04AUG80

\*WEEKLY CPU ALLOWANCE=NOLIMIT USED=00H:00M:01S

\*SIGN ON MON AUG 04, 1980 TIME=14:53 PORT=055 RESTART  
= 058

\*GO

/L TACTIC

/LOAD VSBASIC

/OPT LPREC

010 PRINT

020 PRINT

030 PRINT "THIS PROGRAM CALCULATES PROBABILITIES FROM  
TACTIC MIXTURES"

040 PRINT

050 PRINT "ENTER NUMBER OF SAMPLES YOU WISH TO PROCESS"

060 INPUT N

070 PRINT "ENTER IDENTITY NUMBERS IN FREE FORMAT"

080 MAT INPUT S(1,N)

090 PRINT "ENTER I, H, S VALUES IN FREE FORMAT"

100 DIM V (150)

110 MAT INPUT V(N,3)

120 PRINT "DO YOU WISH TO CHANGE ANY VALUES --- YES OR NO"

130 INPUT AS

140 IF AS="NO" GOTO 230

150 IF AS<>"YES" GOTO 120

160 PRINT "ENTER ROW NUMBER, COLUMN NUMBER AND NEW VALUE  
E.G. 5, 3, 0, 52"

170 INPUT X,Y,Z

180 V(X,Y)=Z

190 PRINT "DO YOU WISH TO CHANGE FURTHER VALUES --- YES OR  
NO"

200 INPUT BS

210 IF BS="YES" GO TO 160

220 IF BS<>"NO" GOTO 190

230 PRINT

240 PRINT

250 FORM POS2,C,POS9,C,POS15,C,POS21,C,POS26,C,POS32,C,  
POS38,C

250.1 POS44,C,POS50,C,POS56,C,POS62,C,POS68,C,SKIP 1

260 PRINT USING 250. "NUM","I","H","S","P-I","P-S","L-I",  
"L-S", "RHO"

260.1 "P-II", "P-IS", "P-SS"

270 PRINT

280 FOR J=1 TO N

290 N0=S(1,J)

300 I1=V(J,1)

310 H1=V(J,2)

320 S1=V(J,3)

330 T=I1+H1+S1

```

340 I=I1/T
350 H=H1/T
360 S=S1/T
370 P1=I+(0.5*H)
380 P2=S+(0.5*H)
390 L1=(2+P1)/H
400 L2=(2*P2)/H
410 R1=(2*P1*P2)/H
420 P3=I/P1
430 P4=H/(2*P1)
440 P5=S/P2
450 P6=H/(2*P2)
460 FORM POS2, PIC(ZZZ), POS7,PIC(###),POS13,PIC(###),
    POS19,PIC(###)
460.1 POS25,PIC(###),POS31,PIC(###),POS37,PIC(###),
    POS43,PIC(###),POS
460.2 49,PIC(###),POS55,PIC(###), POS61,PIC(###),
    POS67,PIC(###), S KIP 1
470 PRINT USING 460,N0,I,H,S,P1,P2,L1,L2,R1,P3,P4,P5
480 NEXT J
490 PRINT
500 PRINT
510 FORM POS2,C, POS8,C, POS14,C, SKIP 1
520 PRINT USING 510, "P-SI","P-SS/","P-II"
530 FORM POS8,C,POS14,C,SKIP 1
540 PRINT USING 530,"P-IS","P-SI"
550 PRINT
560 FOR K=1 TO N
570 I2=V(K,1)
580 H2=V(K,2)
590 S2=V(K,3)
600 T1=I2+H2+S2
610 I0=I2/T1
620 H0=H2/T1
630 S0=S2/T1
640 P8=I0+(0.5*H0)
650 P9=S0+(0.5*H0)
660 Q1=I0/P8
670 Q2=H0/(2*P8)
680 Q3=S0/P9
690 Q4=H0/(2*P9)
700 Q8=Q3/Q2
710 Q9=Q1/Q4
720 FORM POS1,PIC(###),POS7,PIC(###),POS13,PIC(###),
    SKIP 1
730 PRINT USING 720,Q4,Q8,Q9
740 NEXT K
750 PRINT
760 PRINT
770 END

```

## APPENDIX IV : COMPUTER PROGRAM TO PLOT TERNARY DIAGRAM

### FITTING THE TACTICITY DATA

```
/L TRIDIA
/SYS TIME=MAX
/LOAD FORTG1
    DIMENSION RHO(8)
    DATA RHO/0.625,0.71,0.83,1.00,1.25,1.67,2.50,5.85/
    DIMENSION PMAT(50.3)
23  WRITE (6,1)
1   FORMAT ('ENTER NUMBER OF SAMPLES')
    READ (9,*)NUM
    WRITE (6,2)
2   FORMAT('ENTER EACH I,H,S TRIPLE PER LINE')
    READ (9,*)((PMAT(I,K),K=1,3)I=1,NUM)
    WRITE (6,3)
3   FORMAT ('ENTER ANY NUMBER AND RETURN TO DRAW GRAPH
    .DITTO TO CONTINUE 1E')
    CALL NPRMPT
    READ(9,*)A
    CALL T4010
    CALL PICCLE
    CALL WINDOW (2)
    PEAK=(150.0*(0.75**0.5))+5.0
    CALL MOVTO2(17.0.5.0)
    CALL LINTO2(92.0.0.0)
    CALL LINTO2(167.0.5.0)
    CALL LINTO2(17.0.5.0)
    FACTOR = 0.75**0.5
    XS1=47.0
    XS2=77.0
    XS3=107.0
    XS4=137.0
    XI1=XS1-15.0
    XI3=XS2-15.0
    XH1=XS4+15.0
    XH3=XS3+15.0
    Y1=(FACTOR*30.0)+5.0
    Y2=(FACTOR*60.0)+5.0
    Y3=(FACTOR*90.0)+5.0
    Y4=(FACTOR*120.0)+5.0
    CALL MOVTO2(XS1,5,0)
    CALL LINTO2(XI1,Y1)
    CALL LINTO2(XH1,Y1)
    CALL LINTO2(XS4,5.0)
    CALL LINTO2(XS2,Y4)
    CALL LINTO2(XS3,Y4)
    CALL LINTO2(XS1,5.0)
    CALL MOVTO2(XS2,5.0)
    CALL LINTO2(XS1,Y2)
    CALL LINTO2(XS4,Y2)
    CALL LINTO2(XS3,5.0)
    CALL LINTO2(XI3,Y3)
    CALL LINTO2(XH3,Y3)
    CALL LINTO2(XS2,5.0)
    DO 5 I=1,8
    CALL MOVTO2(17.0.5.0)
```

```

DO 10 J=1,151
SYNDIO=(7-1.0)/150.0
HET=1.0-RHO(I)-(2.0*SYNDIO)
HETERO=HET+(((4.0*SYNDIO*RHO(I))-(2.0*RHO(I))+
(RHO(I)*RHO(I))
1+1.0)**0.5)
COMBIN=SYNDIO+HETERO
IF(COMBIN.GT.1.0)GOTO 10
XAXIS=SYNDIO+(HETERO/2.0)
XXAXIS=(XAXIS+150.0)+17.0
YAXIS=(HETERO*(0.75**0.5))
YYAXIS=(YAXIS*150.0)+5.0
CALL LINTO2(XXAXIS,YYAXIS)
10 CONTINUE
5 CONTINUE
RHO8=8
DO 50 L=1,NUM
AISO=PMAT(L,1)
AHET=PMAT(L,2)
ASYN=PMAT(L,3)
TOTAL=AISO+AHET+ASYN
BISO=AISO/TOTAL
BHET=AHET/TOTAL
BSYN=ASYN/TOTAL
RHOA=((2.0*BISO*BSYN)/BHET)+BISO+BSYN+(BHET/2.0)
RHOB=RHOB+RHOA
XAX=((BSYN+(BHET/2.0))*150.0)+17.0
YAX=(BHET*FACTOR*150.0).5.0
CALL MOVTO2(XAX,YAX)
CALL SYMBOL(7)
50 CONTINUE
RHOC=RHOB/NUM
CALL MOVTO2(17.0,5.0)
DO 25 M=1, 151
ASYNDI=(M-1.0)/150.0
AHET=1.0-RHOC-(2.0*ASYNDI)
AHETER=AHET+(((4.0*ASYNDI*RHOC)-(2.0*RHOC)+
1(RHOC*RHOC)+1.0**0.5)
ACOMBI=ASYNDI+AHETER
IF(ACOMBI.GT.1.0)GO TO 25
AXAXIS=ASYNDI+(AHETER/2.0)
BXAXIS=(AXAXIS+150.0)+17.0
AYAXIS= AHETER*(0.75**0.5)
BYAXIS=(AYAXIS*150.0)+5.0
CALL MOVTO2(BXAXIS-1.0BYAXIS)
CALL CHAHOL(3H.*.)
25 CONTINUE
CALL MOVTO2(0.0,-1.0)
CALL MOVTO2(0.0,140.0)
CALLCHAHOL(6H.*.)
WRITE (6,6)RHOC
6 FORMAT(10X,'RHO-',F6.4)
CALL DEVEND
CALL NPRMPT
READ(9,*)8
WRITE(6,21)
21 FORMAT('DO YOU WISH TO PROCESS FURTHER DATA. YES=1
NO=0')

```

```
READ(9,*)YESNO  
IF(YESNO.EQ.1)GO TO 23  
END
```

```
*END  
*GO
```

>006965512



