AN INVESTIGATION OF THE SYNTHESIS OF MONODISPERSE BLOCK COPOLYMERS OF PREDICTABLE MOLECULAR WEIGHT AND COMPOSITION

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SUMMARY:

Previous efforts to prepare block copolymers by anionic polymerisation have employed sodium or organo sodium initiators, which because an electron transfer mechanism operates in the initiation step, produces unbranched polymer chains containing three sequences due to the bifunctional character of the growing polymer. Addition of a second monomer to each end of this chain may also produce an unsymmetrical polymer, since adventitious termination may occur at one or both ends of the chain so that a mixed polymer results. Studies on the solution properties of block copolymers have amply demonstrated that both molecular weight and composition distributions are important factors. Most, if not all previous efforts to produce suitable model polymers of the desired characteristics have been unsuccessful.

In order that a model polymer be prepared free from extraneous homopolymer, strict tolerances must be imposed on homogeneity of the product, the molecular weight, the composition, and possibly even the microstructure. In this work, several

methods of producing simple blocks containing only two sequences have been investigated. It has long been known that butyllithium in benzene produces monofunctional polymer chains, and therefore this system was adopted since it seemed to offer the greatest chance of successful preparation. The monomers styrene and isoprene were chosen mainly because of the widely diverging physical properties of the homopolymers. On the one hand, polystyrene is hard and brittle, whereas polyisoprene is a rubber.

Homogeneity with respect to molecular weight requires that the initiation be complete before any significant propagation has occurred. Similarly, in the addition of the second monomer, the cross propagation must be fast compared with the propagation of the second monomer. The only relevant data in the literature concerns the polymerisation of styrene in benzene. The kinetics of the initiation of isoprene in benzene by butyllithium, the propagation of isoprene in benzene, and the cross propagation of polyisoprenyllithium to polystyryllithium therefore had to be investigated. The kinetics of initiation and cross propagation were studied spectrophotometrically, and the rate of propagation of isoprene was followed dilatometrically. The kinetics of the first stage of the preparation have been accepted for publication in Vol. 2 of the European Polymer Journal, 1966. The rate of initiation was found to be first order with respect to butyllithium after a slow initiation reaction. An acceleration of the rate as the polymer is generated, was observed even after the most rigorous purging of the reactants, and therefore the sigmoidal rate curve appears to be characteristic of the initiation step. The rate of polymerisation was shown to be half order with respect to the concentration of the growing chains, indicating a dimeric association of the polymer. The degree of association has defied several attempts to evaluate it, and this problem still remains unsolved. However, the kinetic study provided ample data, and allowed a choice to be made from the several methods of producing a block copolymer of the desired characteristics.

A high vacuum technique using break seals, and living polymer solutions as purging agents for glassware and starting materials was adopted after many trial runs and alterations to the all-glass reaction vessel. The method is versatile in that multiple blocks containing several sequences may be prepared by simply repeating the procedure for each sequence as many times as required, to give the following polymer structure.

---- BA ---- AB ---- BA ---- AB ---- BA ---- AB ----

The method may also be used to prepare block copolymers from several different monomers.

A ---- AB ---- BC ----C.

A second publication on cross propagation is now in the course of preparation.

This thesis contains no material previously submitted for a degree or diploma in any University and, to the best of my knowledge and belief, contains no material previously written by another person, except when due reference is made in the text.

Peter S. Lawry

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CHAPTER I.

1. Introduction

Block copolymers are relatively new compounds, and their physical properties, both in solution and bulk, are intrinsically interesting. However, despite the recent book by Ceresa(43) in which more than one thousand methods of block copolymer synthesis are listed, no successful synthesis of a narrow molecular weight distribution block copolymer has been reported in the literature. The interest aroused by these new polymers is reflected in the recent advancement of theories concerning their behaviour in dilute solution.(1-5) However, due to the lack of suitable model block copolymers, much of this theoretical treatment is experimentally unverified. Naturally, further theoretical developments will be hindered until the synthesis of suitable polymers is possible.

It is not unlikely that block copolymers will become important commercially. Indeed, block copolymers are recommended as cements for the bonding of films from different homopolymers. An excellent example of this application is found in the bonding of polyethylene and polypropylene films, in which a block copolymer from ethylene and propylene is used. No deformation occurs with this type of bonding, and undoubtedly, further commercial applications of block copolymers will follow.

There are numerous polymeric materials in commercial use today. Pure homopolymers offer a limited choice of properties, the only variation being due to differences in molecular weight. However, by adding "modifiers" to the pure polymer, a new and improved range of properties is often obtained. In broad terms, various fillers and plasticisers are used to modify the properties of polymers. Fillers consisting of finely divided solids, usually carbon blacks, alter the physical properties of polymers such as a noncrystallising vulcanised rubber in two principle respects: they increase the modulus of elasticity, and they also increase the ultimate tensile strength. On the other hand, the range over which any polymer shows useful rubber-like properties can be shifted to lower temperatures by incorporating into the network structure, an involatile liquid which is retained indefinitely. Such liquids are called plasticisers, and allow hard plastics such as polyvinyl chloride to show elastomeric properties at ordinary temperatures.

Frequently, it is desirable to produce polymers that combine certain properties of two or more homopolymers. For example, polyethylene has a low brittle point but a relatively poor surface hardness and a melting point that is too low for many applications. Polypropylene, on the other hand, has excellent hardness and a higher melting point, but an unsuitably high brittle point. In order to combine the favourable properties of two homopolymers, mixtures of the homopolymers may be employed. Although this method is satisfactory sometimes, in many cases, it is found that the desired combination of properties is not achieved. For example, mixtures of polyethylene and polypropylene are particularly brittle, and exhibit demixing phenomena over a broad range of mixing ratios. The possibility of solvent extraction of one of the polymeric constituents of the simple mixture also limits the use of this method of combining properties.

The classic method of combining the desirable properties of two homopolymers in one product is copolymerisation. However, often the properties of a random copolymer are unexpected on the basis of the properties of its parent homopolymers. The copolymerisation of ethylene and propylene, over a wide range of composition, yields amorphous products that are completely soluble in hydrocarbon solvents and that, after isolation, exhibit rubber-like properties. Their properties differ greatly from those of polyethylene and polypropylene, which are crystalline, hard, and insoluble at room temperature. Block copolymerisation has increased the possibility of combining the properties of different homopolymers in one product. Further scope is also provided by the fact that when block copolymers are mixed with homopolymers or random copolymers, incompatibility phenomena such as demixing and embrittlement are frequently reduced.

The reason for the differences in properties of mixtures, random copolymers, and block copolymers is closely related to the intramolecular and intermolecular interactions between the polymer molecules. For a random copolymer of monomers A and B, there are three different intermolecular interactions,. These are A-B, B-B, and A-B. The extent of the A-B interactions for copolymers is much greater than for mixtures of poly-A and poly-B, and accounts for some of the unexpected properties. The effects of these interactions in copolymers are not clearly understood, and a study of suitable model block copolymers should provide information which would allow a greater predictability of random copolymer properties. Kilb and Bueche (1) have predicted that for a simple block copolymer, the number of sequences in the chain should have little effect. In any case, the number of sequences will be very small compared with the number in a random copolymer, so that any worthwhile synthesis of block copolymers must be capable of producing "multiple blocks" of perhaps ten or twenty sequences if a study of their properties is to be of much value.

Burnett *et al.* (44) and Stearne and Urwin (45) have found that for simple A:B block copolymers, separation of the polymer chain into two distinct regions of poly-A and poly-B occurs in solution, and probably in the solid. In view of the limited experimental data available there is an urgent need for studies on well characterized block copolymers in a wide range of solvents.

Many previous attempts to produce block copolymers are reviewed in the literature,(6-10) and although few if any of these have succeeded in providing narrow molecular weight samples without the need for fractionation, a carefully considered combination of some of the suggested techniques can lead to a satisfactory synthesis. The ideal synthesis should be capable of producing block copolymers of narrow molecular weight distribution so that fractionation of the product is unnecessary. For simplicity, such polymers will be referred to as "monodisperse" block copolymers, although it is realised that even in the most successful synthesis, some inhomogeneity of molecular weight and composition must occur. The simplest block copolymer of monomers A and B has the structure shown in I.1.

AAAAA ---- AAAABBBB ---- BBBBB (I.1)

Previous attempts at synthesis have failed to produce this block of two sequences in a sufficiently pure state for examination, and it was the aim of the present work to investigate the means whereby such a sample could be synthesised directly, without the need to fractionate the product, and also, to find a method of producing "monodisperse multiple block copolymers" of predictable molecular weight and composition.

After an early attempt to synthesise the block copolymers by an emulsion technique as described in Chapter VI, it became evident that anionic polymerisation offered the best chance of success. The basic requirement for the production of a block copolymer is the formation of unterminated homopolymer, capable of adding a second monomer. This concept of "terminationless" anionic polymerisation was introduced by Szwarc,(11) and will be discussed in Section 2 of this Chapter. After some preliminary experiments, it became evident that the kinetics of each step in the synthesis should be examined if monodisperse block copolymers were to be produced. The steps referred to for a block copolymer of A and B are:

(a) Initiation of A, the creation of active centres

(b) Propagation of monomer A to form "living" poly-A

(c) Cross propagation, the addition of the first molecule of monomer B to the "living" poly-A

(d) Propagation of monomer B

(e) Termination of polymerisation unless a "multiple" block copolymer is to be synthesised.

A discussion of the results of the kinetic investigation of reactions (a) and (b) is contained in Chapter III of this thesis, while reaction (c) is discussed in Chapter IV.

By exercising the maximum control over the five processes listed above, it is possible to produce monodisperse block copolymers of predictable molecular weight and composition, at least in the system chosen. It is to be emphasised that a universal recipe for block copolymer synthesis is not given, and that each change of reactants or solvents will require a similar kinetic investigation to that described in this thesis, if model polymers are to be synthesised. A review of the most significant developments in anionic polymerisation is now given.

2. Anionic Polymerisation

The ability of alkali metals and their organo metal compounds to initiate polymerisation reactions has been known since the early part of this century.(12-14) However, the polymerisation of styrene in tetrahydrofuran (THF) initiated by sodium naphthalene without termination, which was described by Szwarc(11) for the first time in 1956, has aroused wide interest in anionic polymerisation. Szwarc found that yields of polymer were quantitative, and provided certain critical precautions were taken to purify monomer and solvent, it was possible to produce polystyrene of extremely narrow molecular weight distribution. He proposed the mechanism that initiation was by electron transfer from the naphthalene anion to a monomer molecule according to the equation:

$$\text{Naphthalene}^{\ominus} + \text{Styrene} \rightleftharpoons \text{Styrene}^{\ominus} + \text{Naphthalene} \qquad (\text{I.2})$$

The resulting activated monomer units can then add monomer by either a radical or an anion mechanism, but after addition of the first monomer unit, an actual separation of electrons occurs to produce true radical ions. At low temperatures, the radical ends dimerise to form the species

$$^{\ominus}\text{CHX} - \text{CH}_2 \quad \text{CH}_2 - \text{CHX}^{\ominus} \qquad (\text{I.3})$$

In the absence of terminating material, addition of monomer to both ends of this dianion continues until the monomer supply is exhausted. The resulting polymer was termed a "living polymer", to be consistent with prevailing terminology in which terminated polymer was referred to as "dead" polymer. The unterminated or "living" polymer was capable of further growth in the presence of a fresh supply of pure monomer. The homogeneity ratios

$(\overline{M_W}/\overline{M_N})$ for three polystyrene samples prepared in this way were reported to be 1.06, 1.12 and 1.06(15) (Szwarc has since admitted that these values were incorrect.)

In an attempt to repeat this work of Szwarc, Wenger(16,17) found that on slow addition of styrene monomer to sodium naphthalene in T.H.F. at -78°C, the initiator was consumed only gradually over an extended monomer addition time, thus violating one of the requirements for the synthesis of a monodisperse polymer. Wenger found that the homogeneity ratios of polymers prepared in this way were in the range 2.5 to 4.0. He therefore proposed a two stage polymerisation in order to improve this ratio, in which complete initiation was carried out at 0°C, followed by propagation at -78°C. Although no details of homogeneity ratios were given,(17) the molecular weight distribution was claimed to be very narrow.

Wenger(17) then proposed that the two stage polymerisation process could be avoided by the use of sodium biphenyl as initiator. This was explained on the basis that the equilibrium of the electron transfer initiation reaction was shifted far to the right in contrast to the sodium naphthalene reaction. Polystyrene of very narrow molecular weight distribution was claimed to have resulted from this preparation.(17) ($\overline{M_W}/\overline{M_N}$ = 1.02). Stearne and Urwin (18) used the sodium biphenyl initiation system to prepare living polystyrene as the first stage in preparing block copolymers with methyl methacrylate, and have reported a homogeneity ratio for the parent polystyrene as low as 1.12. The important point to observe here with regard to block copolymer synthesis is that both the naphthalene and biphenyl systems give rise to difunctional growing polymer chains. A block copolymer resulting from the use of either initiator must be of the "sandwich" type shown below.

AAA ---- AABB ---- BBBAAA ---- AAA (I.4)

There are several reasons why the use of a difunctional system for the synthesis of a model block copolymer is unsatisfactory. Apart from the fact that the resultant polymer has a minimum of three sequences and does not allow the synthesis of the simple two sequence polymer, inhomogeneity of both molecular weight and composition is inevitable unless termination is completely negligible. Most workers in the field of anionic polymerisation now recognise the difficulty of removing all terminating material from glassware, solvents and monomers. The small amount of termination occurring in a difunctional initiator system gives rise to the existence of three polymers species in solution. These are unterminated difunctional chains, monofunctional chains in which termination has occurred at one end of the chain, and dead polymer from termination of both reactive centres. The rate of addition of monomer to the dianion will be double that of the monofunctional species, and a broadening of molecular weight distribution must occur. Since termination in THF is rapid, the molecular weight of dead polymer would generally be low. The terminated polymer should therefore be readily separated from the polymer mixture. However, it would be expected that difunctional chains growing for the same times as monofunctional chains would have twice their molecular weight. Stearne and Urwin(18) and McCormick(19) have verified the presence of these two species by turbidimetric titrations. When a second monomer is added to form a block copolymer, inhomogeneity further increases. Monofunctional chains can add the second monomer to one end only, while difunctional chains can propagate from both ends. Furthermore, the addition of the second monomer to both ends of the difunctional chains need not be symmetrical. Therefore, unless all terminating material is removed from the system, block copolymers of narrow distribution of molecular weights, and known composition cannot be synthesised. Schlick and Levy's report(20) of the successful preparation of block copolymers of styrene and isoprene, using sodium biphenyl in THF must therefore be regarded with suspicion, and this may well be the reason that their experimental results on dilute solution behaviour contradict the theoretical predictions of Kilb and Bueche.(21)

A further development in the production of monodisperse polymers resulted from studies using ∝-methylstyrene. Wenger(22,23) used ∝-methylstyrene tetramer, formed by reaction of metallic sodium with the monomer in THF above the ceiling temperature, as the initiator. He also used a similar solution of "living" polymer to purge his reaction vessels. From osmotic pressure and light scattering data, he derived a homogeneity ratio of 1.03 for these polymers. Since the tetramer is also difunctional, and the removal of impurities from the system was not complete, the differential mass distribution curves showed two maxima occurring at molecular weights differing by a factor of two. However, the percentage of low molecular weight material was only a fraction of the total yield of polymer, so that termination of one end of the dianionic species was only slight. This synthesis showed that if sufficient care was taken to remove terminating material, and if the reaction was carried out at the right temperature, the ideal of monodispersity could be almost achieved. Since dianions are the active species in this polymerisation, it was not really suitable for the preparation of a simple two sequence model polymer, but the introduction of the purging process by Wenger(23) represented a valuable contribution to improving homogeneity.

The stereospecific nature of lithium initiated polymerisations has been recognised for a long time.(24-29) It has been shown(28,29) that the course of the reaction is determined largely by the solvent used, and in an attempt to elucidate the mechanism operating in this reaction, O'Driscoll and Tobolsky(29) conducted a series of experiments using n-butyllithium as initiator. Their work stimulated interest in polymerisation with this initiator, and recently a number of papers have been published(30-34) concerning its use as an initiator in several systems. It was immediately apparent from this work that n-butyllithium offered many advantages as an initiator system for the synthesis of model block copolymers, and the reasons behind the ultimate choice of this initiator, and the monomers styrene and isoprene are now discussed.

3. The Choice of the System

Styrene and isoprene monomers were chosen partly on the grounds that their homopolymers have widely diverging physical properties. On the one hand, polystyrene is hard and brittle, whereas cis - 1:4 polyisoprene is a rubber. Furthermore, polymerisation of isoprene does not suffer from the difficulties of monomers such as methyl methacrylate, which has also been used in previous block copolymer syntheses,(18) and which is either self terminating as suggested by Szwarc,(35) or more likely, is extremely difficult to purify. An advantage in the use of isoprene is the visible colour of the isoprenyl ion, unlike the anions of polymethylmethacrylate which are colourless, so that removal of terminating material by "titration" with "living" polymer is not possible. The fact that "living" polymethylmethacrylate is also incapable of initiating styrene polymerisations was considered a further reason for rejection of this monomer as unsuitable for the present work, since the synthesis of multiple blocks is not feasible. The choice of the solvent benzene, with n-butyllithium as initiator was made after careful consideration of the literature.

The discovery that lithium and its alkyls produce polyisoprene with a high cis - 1:4 content in hydrocarbon solvents(24) has led to a wide interest in lithium and lithium alkyl polymerisations. Tobolsky(29) and Overberger(36) postulated that for lithium metal, electron transfer took place from lithium to monomer, in a similar way to the sodium naphthalene initiation described by Szwarc.(11) The result was that a difunctional polymer anion was produced. It was found, however, that an entirely different mechanism operated in the case of the lithium alkyls. Initiation was by addition of lithium alkyl to monomer molecules, and though the reaction is complex, it is essentially that suggested by Ziegler(37) as long ago as 1936, and represented in equation I.5, where R is an alkyl group.

$$R\text{-}Li \xrightarrow{+M} R.M_1\text{-}Li \xrightarrow{+M} R.M_2\text{-}Li \rightarrow etc. \quad (I.5)$$

The nature of the C-Li bond in the resulting polymer chain is open to some doubt, although it most certainly is highly polar.(34) The reason for the high proportion of stereoregular polymer formed by lithium alkyls in some solvents, is thought to be due to some special bonding characteristics of lithium,(34) although no convincing proof for this exists at present. Polymerisation is by an anionic mechanism, the most outstanding feature being that the growing polymer chains are monofunctional. This initiator system offered for the first time, a means of producing a simple block of two sequences by anionic polymerisation.

Benzene was chosen as a suitable solvent for a number of reasons apart from the high cis - 1:4 isoprene formed. Propagation is slow in benzene, and this is important. Systems resulting in rapid polymerisation have inherent disadvantages when a polymer of narrow molecular weight is desired. Such a polymer can only grow under homogeneous reaction conditions. In the case of fast polymerisations, this can be most closely achieved only by the continuous slow addition of monomer, preferably from the vapour phase, to the initiator. On the other hand, homogeneous reaction conditions can be obtained easily for slow polymerisations, by using a simple batch technique in which all reactants are thoroughly mixed together and stirred throughout the course of reaction. Anionic polymerisation of both styrene and isoprene in benzene takes place over several hours, so that a batch technique is applicable.

The slow rate of polymerisation in benzene offers a further advantage. Probably the most difficult single step in controlled anionic polymerisation is the removal of impurities from reaction vessels and starting materials, particularly the monomer. Even after the most careful degassing and drying techniques, terminating material will remain in the monomer. When a high molecular weight polymer is desired, the initiator concentration must be low, so that even the smallest trace of impurities in the system will have a deleterious effect on the product. The purging technique first introduced by Wenger,(22,23) in which vessels are washed with living polymer immediately prior to use, and impurities in the monomer and solvent are purged with living polymer, has considerably helped to overcome this problem of adventitious termination. As will become evident in Chapter II, the removal of impurities from monomer and solvent by "titration" with living polymer is easier if polymerisation is slow. Of course, if termination is also extremely slow, the method is invalidated, but Wenger(31) has claimed that in the purging of styrene in benzene, using a solution of short chain polystyryl ions, the termination by impurities is fast at ambient temperatures, requiring a small energy of activation. By contrast, the energy of activation for chain propagation is high.(38) The purging efficacy would therefore be expected to increase with decreasing temperature. The same applies for isoprene in benzene, since propagation of isoprene in benzene is also slow.

In the preparation of block copolymers of styrene and isoprene, a further decision had to be made. Should the first stage of the synthesis involve the production of living polyisoprene or living polystyrene? Wenger(31) has reported that spectrophotometric determinations of styryl ion concentrations as well as bromide titrations after reaction of styryl ions with butyl bromide, indicate only approximately 30% conversion of butyllithium to styryllithium. However, Morton(32) has shown that for the preparation of polyisoprenyllithium "seed" in hexane, 100% conversion of the butyllithium occurred. On this basis, it was decided that living polyisoprenyllithium should be prepared as the first stage of the block copolymer synthesis. Wenger reacted the butyllithium with styrene monomer in the molar ratio of 1:4 at 60°C, and it is now realised that the reason for the low percentage conversion of butyllithium is due solely to the lack of sufficient monomer for complete reaction.

Although a greater knowledge of the detailed processes involved in this type of polymerisation has been gained in recent years, a number of problems remain unsolved. Thus, reference to the literature revealed that n-butyllithium, polystyryllithium and polyisoprenyllithium are associated in benzene solution. It is now generally agreed(38-42) that in hydrocarbon solvents, n-butyllithium is associated as hexamers. The degree of association of polystyryllithium is generally accepted as two,(32,33) i.e. dimers exist in solution. For polyisoprenyllithium, some doubt exists. Thus, the viscosity work of Morton(32) supports dimeric association, while light scattering results of Worsfold and Bywater(46) suggest tetramer formation. Other authors(47,48) agree with the tetramic association, but some doubt still exists on this point.

For the successful synthesis of a model block copolymer, initiation must be completed before a significant degree of propagation has occurred. Polymerisation of the first monomer must be complete, and result in the formation of living polymer, so that terminating material must be completely removed from the system. The second monomer must also be completely free from terminating material, and must be added to the living polymer solution without termination occurring. Cross propagation, the addition of the first monomer molecule to each living polymer chain, is similar to initiation of the first stage, and this must also be complete before the second monomer has propagated significantly. On completion of this stage, a living block copolymer should exist, and this can then either be terminated, or polymerised further. Obviously, if negligible termination occurs in the course of reaction, this method of synthesis offers many possibilities and these are discussed in Chapter V. However, the homogeneity of the simple block copolymer will depend on the degree of control attainable for the initiation of isoprene by n-butyllithium and the subsequent propagation, the cross propagation of polyisoprenyllithium to polystyryllithium and the styrene propagation. Of special importance is the temperature dependence of these reactions. Since relative data were either missing from the literature altogether, or in some instances confusing, it was apparent that a complete kinetic investigation of the separate steps in the synthesis was necessary. Chapter III deals with the kinetics of initiation of isoprene by n-butyllithium, and the propagation of isoprene which follows. Chapter IV is concerned with the cross propagation reaction.

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CHAPTER II

EXPERIMENTAL:

1. Introduction

The most satisfactory choice of method for the synthesis of block copolymers by an anionic technique, using n-butyllithium as initiator, was made after many preliminary experiments. Some details of earlier attempts to develop satisfactory preparative methods are discussed in Chapter VI. The method finally adopted will be discussed in Chapter V, and was chosen after careful consideration of the minimum number of operations, and having taken into account all the necessary precautions to control initiation, propagation cross propagation and termination. The experimental technique for examining the kinetics of initiation of isoprene by n-butyllithium and the subsequent propagation step, was also improved and simplified.

As is to be expected, the more experience gained in the handling of solutions in high vacuum, the more sophisticated and generally the simpler were the techniques evolved. Obviously, the early work was of an exploratory nature.

2. The Vacuum Line

Although a number of methods have been tried, it is now generally agreed that the only satisfactory method for studying anionic polymerisation is by using high vacuum techniques. During the early development of this project, a vacuum of approximately 10^{-3} to 10^{-4} Torr. was used, the pressure being indicated on a McLeod gauge when a "sticky" vacuum was obtained. After much work had been carried out using this system, since slow termination of dilute living polymer solutions always occurred, it was realised that a new pumping system was required in order to produce lower pressures (in the range 10^{-5} to 10^{-6} Torr.) This fact was highlighted by a claim of Bywater(2) that in a greaseless high vacuum system, under conditions where the glassware as well as monomer and solvents are pretreated with butyllithium or its equivalent, the concentration of reactive impurities is normally about 3×10^{-6} molar. The need to improve the vacuum obtainable and thereby decrease the amount of gaseous impurities in the system was obvious, since this work required that the living polymer solutions investigated be dilute.

The vacuum line was therefore modified. The two stage silica diffusion pump was replaced by an all metal three stage Speedivac model 2M3D mercury diffusion pump. The McLeod gauge was replaced by a Metrovac ionisation vacuum gauge head (type 29D2) in conjunction with a Metrovac VC9 ionisation gauge measuring unit. This new system was capable of producing pressures of 10^{-6} Torr. The new pressure gauge also demonstrated the importance of using dry, degassed grease on the vacuum taps. Using grease directly from the manufacturer's container, a low pressure was recorded only after prolonged pumping of the system. On exposing a fresh area of grease by slight rotation of a tap, the pressure in the line rose sharply, returning to its original value after a further period of pumping. The performance of the system was much improved by using grease which had been stored over phosphorus pentoxide in a vacuum dessicator. As a consequence of this behaviour of the grease, whenever a reaction vessel was sealed off the line under vacuum, pumping was continued during the sealing off process, instead of first isolating the vessel from the line by closing a tap. All reactions were carried out between 10^{-5} and 10^{-6} Torr. in this way.

Benzene, the solvent used throughout this investigation, was required in large quantities. It was stored on the vacuum line, and freed from impurities by adding a "living" polystyrene solution. In order to degas such a large volume of solvent, the usual technique of repeated freeze-pump-thaw cycles was hazardous and time consuming. The large reservoir of benzene was therefore attached to the line through a vacuum condenser which was cooled by refrigerated water.

This allowed rapid degassing of the solvent, since it was unnecessary to freeze the benzene during the first rough degassing. Vapours from the solvent were condensed and returned to the storage vessel during this operation. For the final degassing, the benzene was frozen and pumping continued for two hours.

3. Purification of Reagents

(a) Benzene

Univar A.R. grade benzene was dried over sodium wire for twenty four hours. It was then refluxed over calcium hydride for five hours, and fractionally distilled through a 3 ft. column packed with stainless steel turnings. A proportionating head was fitted to the column, and the fraction boiling between 79.5°C and 80.5°C was collected at a 1/10 take off rate. The benzene was then placed on the line and degassed. Styrene monomer was distilled into the flask, and the contents allowed to warm to room temperature. A quantity of n-butyllithium in benzene was added by means of a break seal. Slowly, after stirring with a magnetic stirrer, the red colour of living polystyrene appeared in the solution. The benzene was assumed to contain no terminating material as long as this colour persisted.

(b) The Monomers

In the early stages of the work, before adoption of the technique of purging impurities in the monomer with living polymer solution, conventional means were used to purify the monomer. It was later considered that nothing was gained by removal of inhibitor by alkali washing rather than direct distillation, since both processes yield "wet" monomer, requiring further vigorous drying. After removal of inhibitor, the monomer was allowed to stand over calcium hydride for twenty four hours. It was then degassed on the vacuum line, and vacuum distilled on to fresh calcium hydride, the middle fraction being collected. After periodic shaking of the flask for six hours, the middle fraction was once again distilled on to fresh calcium hydride and allowed to stand for six hours. This process was repeated three times, after which the monomer was stored in a refrigerator at -10°C. Prior to use, the monomer was flash distilled three times on to sodium mirrors.

With the introduction of the purging step, the monomer purification process was not only much simpler, but more satisfactory. Monomer was merely dried over calcium hydride, flash distilled three times on to fresh calcium hydride, the middle fraction being collected each time, and stored in the dark at -10°C. Final purification was carried out by purging in the reaction vessel.

(c) Methyl Iodide

Methyl iodide was used to estimate the concentration of n-butyllithium and living polymer solutions. For accurate estimates, the methyl iodide had to be pure. Univar A.R. grade was therefore dried with calcium hydride, degassed, and flash distilled three times on to fresh calcium hydride. The middle fraction was collected each time.

4. Preparation of n-Butyllithium

Two methods were used to prepare n-butyllithium. In the preliminary experiments, it was prepared in an atmosphere of dry, oxygen-free nitrogen. Dried benzene was placed in a 100 ml. round bottom flask, which was flushed with a continuous stream of nitrogen. An excess of clean lithium shavings was added, and by means of a dropping funnel, a solution of benzene and n-butylchloride was added through a side arm, over a period of one hour. Red spots appeared on the surface of the lithium, and bubbles of gas were evolved, indicating that the reaction had commenced. The flask was cooled in an ice-water bath, and after five hours, a rubber suba-seal, which allowed sampling of the solution with a syringe, was fitted into the neck of the flask. The butyllithium was thus stored in an atmosphere of nitrogen, and

<u>FIG. II.1</u>

Vessel for preparation of n-butyllithium

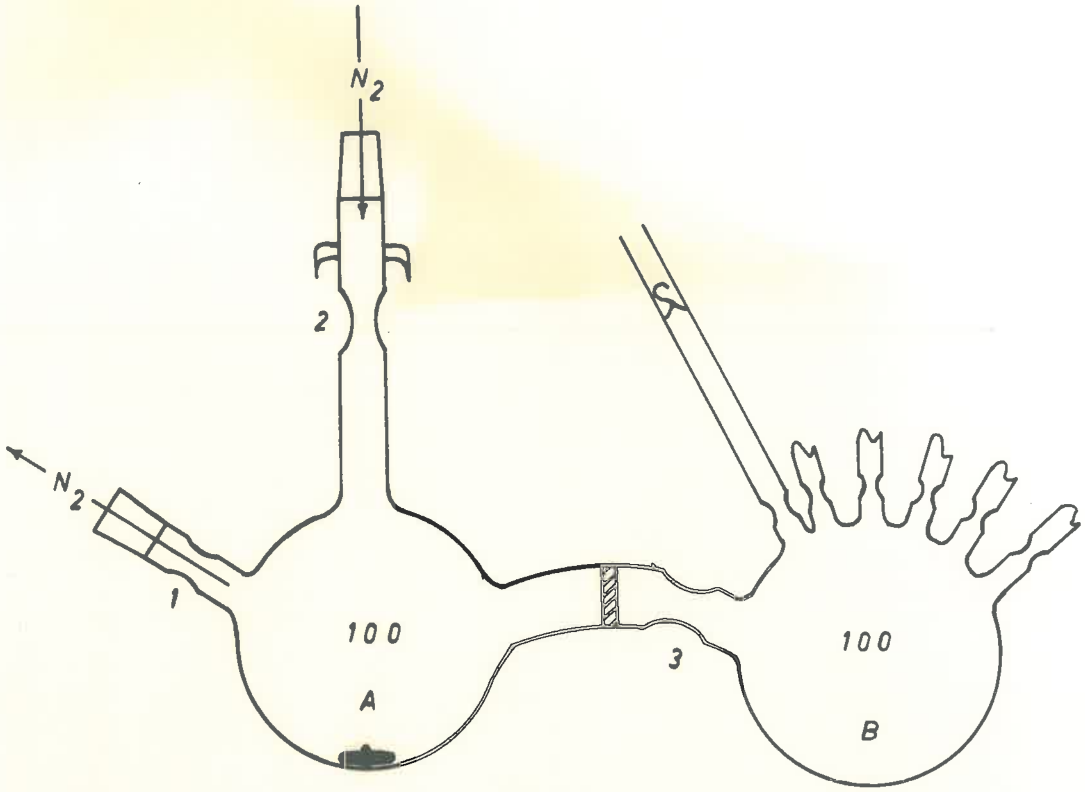


FIG. II.1.

remained active for several weeks. However, an extremely fine precipitate was formed in the course of the preparation, having a greyish-white appearance. Only after several days, did the supernatant liquid become clear. When samples were removed in a syringe, great care had to be exercised not to disturb the precipitate. An aqueous solution of this fine precipitate was found to be strongly alkaline. It was considered to have been a mixture of lithium, lithium oxide, lithium hydroxide and lithium chloride.

In later preparations, steps were taken to remove this precipitate. The reaction was performed under vacuum, using the apparatus shown in Fig.II.1. A steady stream of dry, oxygen-free nitrogen was flushed through the vessel, and clean shavings of lithium metal were added through the B_{24} side arm on flask A. Flask A was then stoppered, and the apparatus attached to the vacuum line at the B19 standard cone. The vessel was evacuated and sealed off at constriction 1. Pumping was continued for one hour after which about 50 ml. of pure benzene and a calculated volume of n-butylchloride were distilled in. While pumping was continued, the vessel was sealed off at constriction 2. Soon after the contents of the flask had warmed to room temperature, red spots appeared on the surface of the lithium metal, and in order to prevent boiling, it was necessary to cool the flask in an ice-water bath. The reaction mixture was periodically stirred by a magnetic stirrer. Once again, the fine precipitate formed. Twenty four hours after the reaction was commenced, the vessel was tipped so that filtration could occur through the number 4 filter between flasks A and B. Up to three days were required for the 70 ml. of solution to pass into flask B as a perfectly clear, faintly yellow solution. Flask B was then sealed off at constriction 3. The sampling ampoules were filled to the required level and also sealed off. Filters of greater porosity were tried in an effort to speed up this filtration, but the fine suspension passed through filters coarser than

No. 4. One ampoule of n-butyllithium was used to determine its concentration. Generally, this preparation produced approximately 0.5M butyllithium.

5. Preparation of Purging Solutions

The purging solutions were simply benzene solutions of either living polystyrene or polyisoprene. These were prepared by reaction of n-butyllithium with a benzene solution of the monomer, in a vessel with break seal ampoules attached. On completion of reaction, measured volumes of purging solution were sealed off in ampoules.

6. Preparation of Initiator Solutions

There were really two initiator systems used in this work. In the kinetic study of initiation of isoprene in benzene by n-butyllithium, and the ensuing propagation of isoprene, a standardised

FIG. II.2

Vessel for preparation of polyisoprenyllithium "seed"

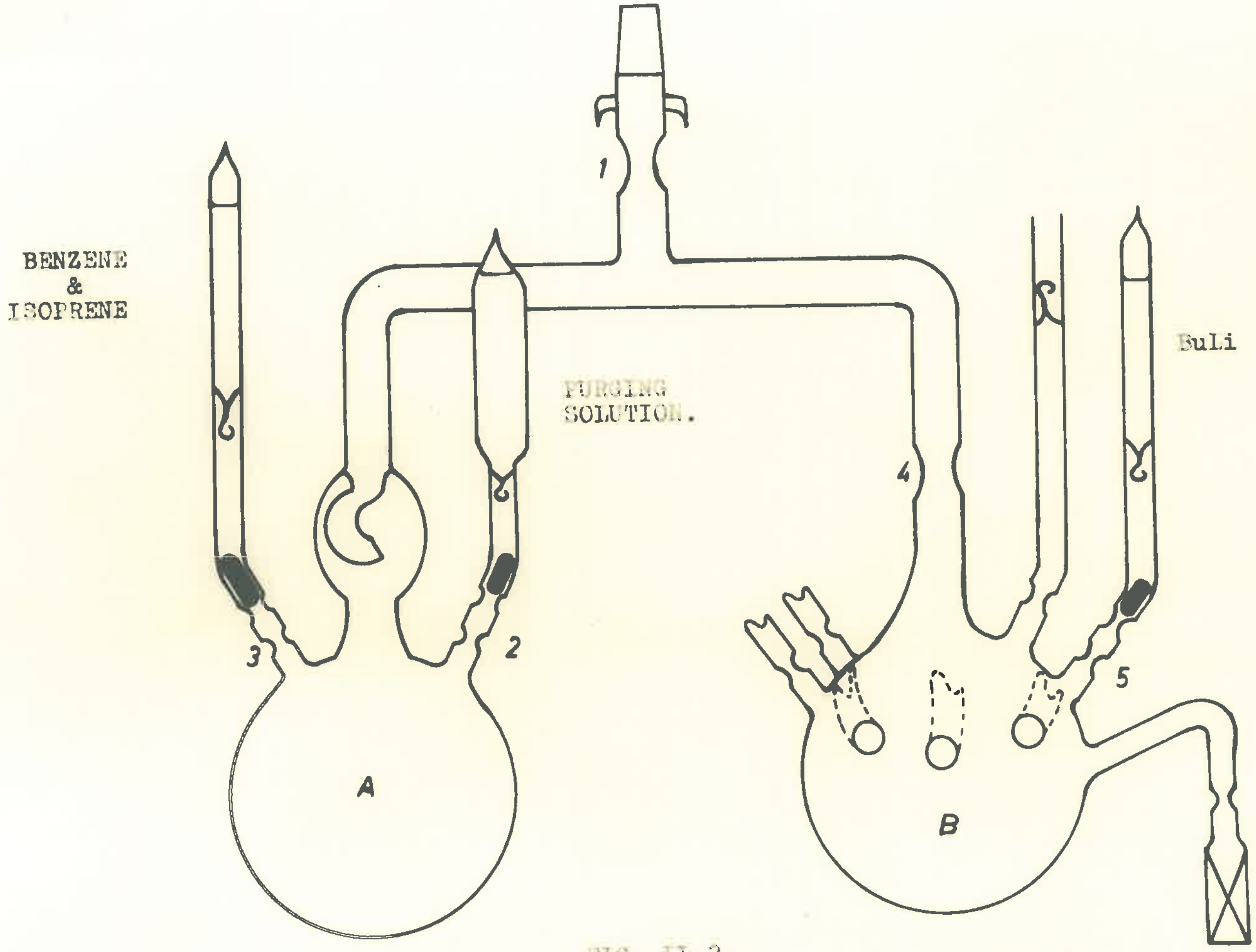


FIG. II.2.

solution of n-butyllithium was used. The second initiation system used was polyisoprenyllithium "seed" in benzene. This was used to examine the kinetics of cross propagation to polystyryllithium, and as initiator for the block copolymer syntheses. The best method of preparing the "seed" was derived from the kinetic study of n-butyllithium initiation of isoprene. The relevant kinetic data are discussed in Chapter III. If n-butyllithium was reacted with isoprene in benzene at +5°C, all of the lithium alkyl was converted to polyisoprenyllithium when the number average molecular weight was approximately 3,000.

The "seed" was prepared in a vessel similar to that shown in Fig. II.2. The vessel was placed on the line and flamed out with continuous pumping. When the pressure registered in the range 10^{-5} to 5×10^{-6} Torr, the reaction vessel was sealed off at constriction 1. A purging solution of living polymer in a known volume of benzene (approximately 100 mls.) was added to flask A through a breakseal, and the empty ampoule was sealed off at constriction 2. This purging solution was washed around the entire inside surface of the vessel for one day, after which it was tipped back into bulb A. Pure benzene was then distilled from A into B, and washed around to remove any "living ends" remaining in this section of the apparatus. The splash head above bulb A reduced the risk of "bumping" into bulb B, during the distillation. The benzene was then tipped back into flask A. This washing process was repeated three times before all the benzene was distilled across into Bulb B. Thus the reaction flask B was completely free from terminating material as was the benzene. A sticky mass of living polymer remained in A, and this was cooled to +5°C. The small volume of benzene plus isoprene monomer was added to this living polymer, the empty ampoule being sealed off at constriction 3. At this reduced temperature, purging of impurities in the monomer and benzene was effected, while propagation of isoprene was only slight. After fifteen minutes, the monomer and benzene solution was completely transferred to B by distillation. The apparatus was then sealed off at constriction 4, and the contents cooled to +5°C in an ice-water bath. A calculated quantity of n-butyllithium was added, and sealing off at constriction 5 completed the steps in the preparation. The temperature was maintained at +10°C for thirty hours, when measured volumes of initiator were sealed off in the ampoules attached to B. A 1 cm. optical cell was also included in order to estimate the concentration of polyisoprenyllithium. Estimation of concentrations above 10^{-4} molar by spectrophotometric analysis could be made.

FIG. II.3

Vessel for determination of
Initiator concentrations.

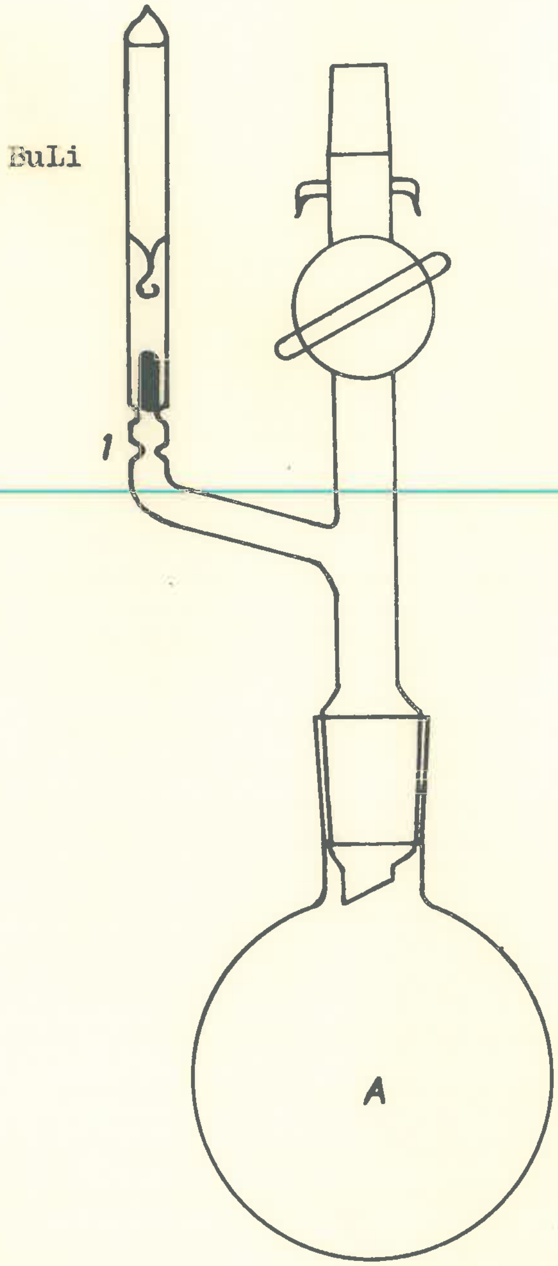


FIG. II.3.

7. Analyses of Initiator Solutions

(a) n-Butyllithium

An approximate estimate of lithium alkyl concentration was obtained by adding a known volume of its benzene solution to distilled water. The lithium hydroxide formed was titrated against standard hydrochloric acid. The value obtained in this way was likely to be too high, since lithium hydroxide formed by adventitious termination reactions with water during preparation or subsequent handling, would also be titrated by the acid. This quick method nevertheless gave a useful guide to concentration.

The most accurate determination of n-butyllithium concerned its conversion to lithium iodide by reaction with methyl iodide. The apparatus used is shown in Fig. II.3. The vessel was flamed out under continuous evacuation on the vacuum line. An excess of methyl iodide (1-2 mls) was distilled into flask A, and the vessel isolated from the line by means of a vacuum tap. The benzene solution of butyllithium was added through the break seal, the empty ampoule being sealed off at constriction 1. Lithium iodide was formed according to equation (II.1).

$$C_4H_9Li + MeI \longrightarrow C_4H_9Me + LiI \qquad (II.1)$$

The vacuum tap was reopened, and pumping continued for three hours to remove the excess methyl iodide. Estimation of the lithium iodide resulting from this reaction, yielded the concentration of butyllithium.

Flask A was removed from the apparatus, and about 100 ml. of distilled water were added, together with a further 100 ml. of 5% nitric acid. Two titration procedures were used for the estimation of iodide. The Volhard procedure was found to be satisfactory above a 10^{-3} molar concentration of iodide. An excess of 0.1N silver nitrate was added to the acidic iodide solution.

Using ferric alum as indicator, the excess silver nitrate was titrated with 0.1N ammonium thiocyanate. Thus the number of moles of silver nitrate reacting with the lithium iodide was found, which is directly related to the concentration of n-butyllithium. Below 10^{-3} molar lithium iodide solution, this procedure was subject to considerable experimental error, since the difference between the volume of silver nitrate added and the titration figure of ammonium thiocyanate became too small. However, a simpler and more accurate potentiometric titration technique was used, in which the silver nitrate was titrated against the lithium iodide directly.

(b) Polyisoprenyllithium "Seed"

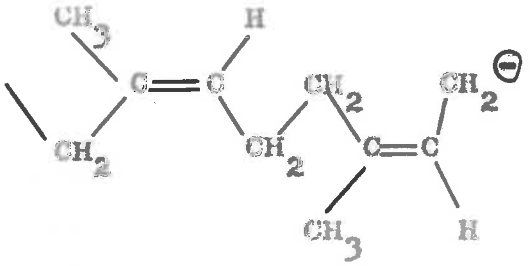
Three methods of analysis were attempted.

(i) Titration

Either the Volhard analysis or the potentiometric method was used. After the excess methyl iodide was distilled off, a few mls. of benzene were added to dissolve the polyisoprene remaining in the flask. This was necessary because lithium iodide became trapped in the polymer as the solvent was removed. Water and acid were then added as before, and the titration carried out. The presence of benzene made determination of the end point for the Volhard analysis difficult, so that potentiometric titration was preferred.

(ii) Nuclear Magnetic Resonance (n.m.r.)

The polyisoprenyl anion has the structure shown below.


(II.2)

This anion should show a characteristic peak in the n.m.r. spectrum at a high τ value due to the high electron density around the "living end".

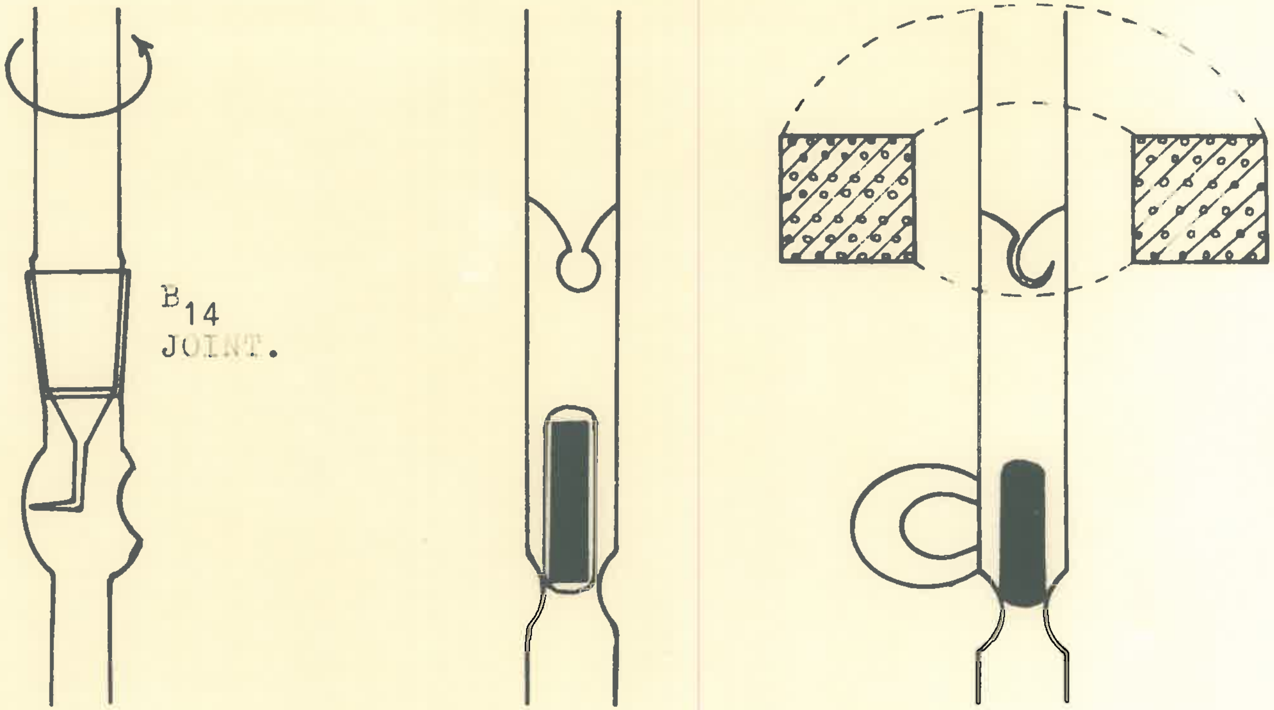
This peak would vary with the concentration, and it was hoped to obtain a graph of the area of the integrated peak against concentration. However, a peak was not obtained. The method might be applicable when the concentration of the "living ends" is higher and the molecular weight of the polymer is lower. Failure to comply with these conditions rendered the method unsuitable for this particular analysis.

(iii) Visible Spectrophotometry

Polyisoprenyllithium solutions were analysed from their optical density at the maximum absorption in the range 320 to 330 mμ. Beer's Law was not obeyed, and it was necessary to prepare calibration curves for this analysis. Details of the method will be described later in this Chapter.

FIG. II.4

Types of Break seals used.



(a) TWIST TYPE.

(b) BULB TYPE.

(c) WHISKER TYPE.

FIG. II.4.

8. Break Seals

During the course of the work, three types of break seal were used. They are shown in Fig. II.4. The twist break seal was easy to operate and was used in the study of isoprene initiation and in early attempts at block copolymer synthesis. Its main disadvantage was that it required the use of a greased joint, and this introduced two complications. In the first case, unless the grease was completely degassed and free from moisture, a vacuum better than 5 x 10^{-5} Torr. was not attainable. Secondly, purging of the reaction vessels was difficult and incomplete, since the purging solution had to be kept away from the joint. There was also the possibility that the greased joint could streak and therefore leak if sufficient care was not exercised in the greasing process.

This type of breakseal was therefore replaced by a bulb breakseal, using a glass encased soft iron breaker in conjunction with a solenoid. The breaking operation proved hazardous for a number of reasons. Often the inherent strength of the bulb was too great, so that instead of the seal breaking, the glass envelope of the breaker fractured. When very dilute solutions of living polymer were in use, the terminating material introduced by this mishap was sufficient to ruin the experiment. This was found to be so, even if the soft iron core was clean, and sealed into the glass envelope under vacuum. When handling concentrated living polymer solutions, the problem was not so serious.

The third type of break seal was found to operate faultlessly provided a few simple precautions were taken. The seal consisted of a fine whisker of glass which was easily broken on operation of the solenoid. The breakers used were small (3/4" long and 3/16" in diameter), and were made from magnetisable 2.20 stainless steel rod. It was therefore possible to operate the solenoid at a reduced voltage, and by inclining the ampoules so that the movement of the breaker was almost horizontal, the likelihood of fracture of vessels by too rapid movement of breakers in either direction, was remote. Since the stainless steel breaker was so light, it could be easily held away from the whisker by a small magnet taped around the glass tubing on the receiving side of the seal. This was most useful during purging operations, since the glassware could be held at any angle without fear of inadvertant fracture of a seal. The breaker itself was thoroughly washed with purging solution in situ, and always remained untarnished.

9. Cleaning of Glassware

All glassware was cleaned with a 5% solution of hydrofluoric acid. A half an hour in this solution was sufficient to provide excellent cleaning. Repeated washings with distilled water removed traces of acid. The glassware was then dried in an oven.

FIG. II.5

Vessel for synthesising block copolymer using Morton's viscometric method for following the course of reaction.

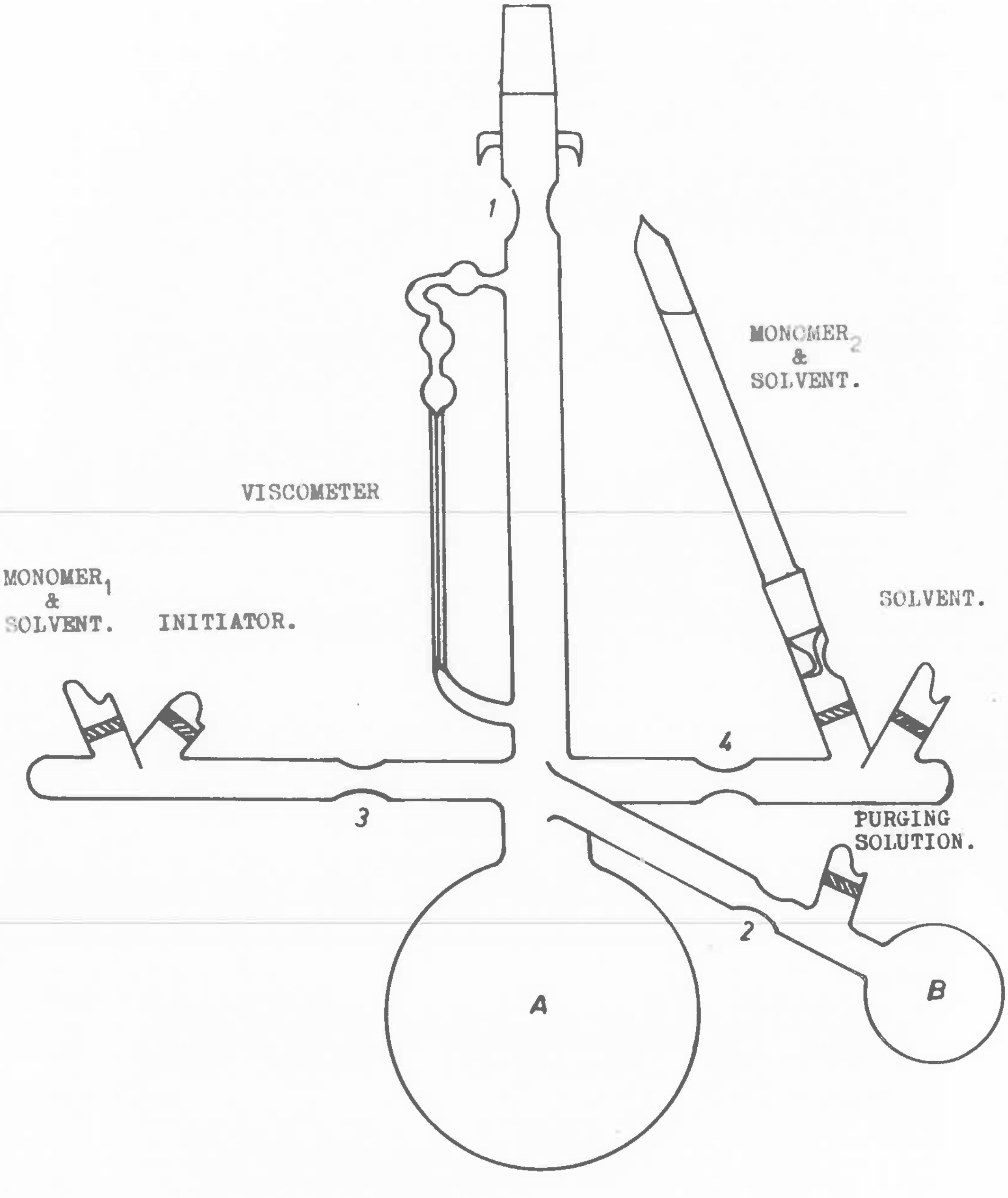

1
MONOMER$_2$ & SOLVENT.
VISCOMETER
MONOMER$_1$ & SOLVENT.
INITIATOR.
SOLVENT.
4
3
PURGING SOLUTION.
2
A
B

FIG. II.5

10. An early attempt at synthesis using Viscometric analysis

It was considered highly desirable that the progress of the reaction be followed at every stage of the synthesis, and since the viscometric method can be used to follow the growth of the polymer chain, a preparative method based on the vacuum viscometer apparatus of Morton(1) was therefore adopted. The attachment of a viscometer to the reaction vessel allows one to follow the increase in flow time of the polymerising solution until a steady value is reached, at which point it can be assumed that all of the first monomer has been polymerised. On addition of the second monomer, further growth of the polymerizing chains would be indicated by the increased viscosity. The apparatus used is shown in Fig. II.5.

Five ampoules were prepared containing the following solutions. Benzene, isoprene plus benzene, styrene plus benzene, purging solution, and initiator solution (polyisoprenyllithium "seed"). The benzene was distilled directly into the ampoules from a living polymer solution. The monomers were flash distilled from sodium mirrors according to the method of Morton.[1] With all ampoules sealed in place, the vessel was evacuated and flamed out until the McLeod gauge on the vacuum line registered a "sticky" vacuum. The apparatus was removed from the line by sealing off at constriction 1. Purging solution was added through a twist break seal, washed around the entire vessel for several hours, then tipped back into bulb B. Benzene was carefully distilled back into A, the main reaction flask, and washed around to remove traces of purging material. It was then tipped back into bulb B which was sealed off at constriction 2. Solvent and isoprene monomer were introduced to the reaction vessel, and the initiator added to it. The side arm was then sealed off at constriction 3.

That polymerisation had commenced was indicated by the increasing flow times in the viscometer. However, since the initiator concentration was low, it was impossible to tell visually whether the polymer remained unterminated, as polyisoprenyllithium is only pale yellow even in concentrated solutions. When a steady flow time was recorded, the fresh solvent and styrene plus solvent samples were added and thoroughly mixed in the reaction vessel. The side arm was sealed off at constriction 4. Observations of flow time showed no increase, so that termination of the "living" polymer had obviously occurred. Several possible sources of terminating material were considered, and it was decided to adopt a procedure whereby the monomer and solvent could be freed from impurities by purging with "living" polymer immediately prior to use.

The sintered glass filters which were used in the first attempt, and designed to trap chips of

FIG. II.6

Modified vessel for block copolymer synthesis.

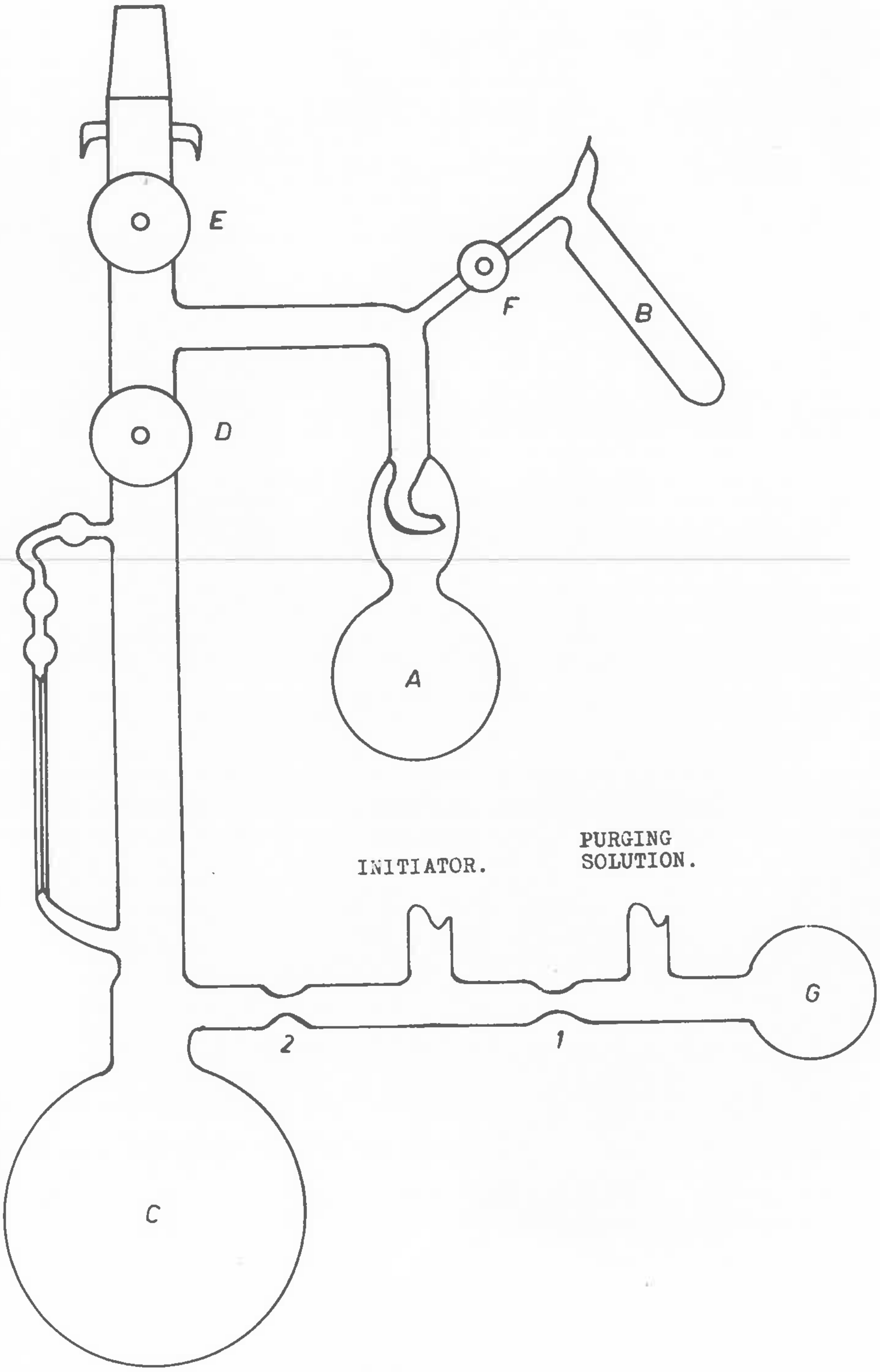


FIG. II.6.

glass from the break seals were removed. This was made necessary since it was extremely difficult to purge the reaction vessel properly while they were present. Large greaseless vacuum taps with Viton A diaphragms were employed at this time as their use promised to simplify the transfer of material considerably. It was generally considered that they could maintain a high vacuum for an extended period, and allow solutions to be poured through them. A new reaction vessel (Fig. II.6) was therefore constructed. The small vessel B contained a concentrated solution of living polystyrene in benzene. It was attached through a greaseless tap to a splash head and a 150 ml. flask A.

An initiator ampoule and a purging solution ampoule were fitted to the side arm above reaction vessel C. The apparatus was evacuated and flamed out. When a "sticky" vacuum was obtained, the greaseless tap D was closed, and the apparatus removed from the line. Purging solution was introduced to the reaction vessel through a twist break seal, washed throughout the viscometer and reaction vessel, and tipped back into bulb G. The reaction vessel C was rinsed with benzene distilled from G, and the purging solution sealed off at constriction 1. The apparatus was returned to the vacuum line, and with tap D still tightly closed, flask A was evacuated and flamed out. Calculated volumes of isoprene and benzene were distilled into A, tap E was tightly closed, and the impurities in the monomer-solvent solution "titrated" until a faint yellow colour persisted, by adding living polymer solution through the small greaseless tap F. The assembly was again removed from the line, and the upper portion of the apparatus above tap D was washed with the living polymer solution which was then returned to flask A. Tap D was carefully opened, when the monomer-solvent mixture distilled into the reaction flask. Bumping over into C was avoided by using a splash head above A.

Tap D was tightly closed, and initiator added from the side arm, which was then sealed off at constriction 2.

Polymerisation was followed by periodic reading of flow times through the viscometer. On completion of the first stage, the apparatus was returned to the line. Styrene monomer and benzene were distilled into A, titrated as before, and carefully distilled through tap D into reaction vessel C. After the contents of C had thawed, further polymerisation was observed. However, termination occurred before all of the second monomer was consumed, and although some block copolymer was produced, the method was not entirely satisfactory. Small chips of glass from the break seals occasionally blocked the capillary of the viscometer, so that no satisfactory kinetic data was obtainable from this method. The flow times increased from 100 seconds to 3,000 seconds during the polymerisation. However, when the apparatus contained a living polystyrene solution, no dramatic decrease in flow time was observed on termination. Morton$^{(1)}$ has used this technique to determine the degree of association of polystyryllithium in a number of solvents, and found that in some cases, flow times decreased ten-fold on termination of the living polymer solutions. The failure of our experiments to show any indication of this behaviour is puzzling.

In view of the unsatisfactory state of affairs at this point, the approach to the problem was reviewed. Emphasis was shifted from techniques employed in the synthesis itself, to the kinetics of each stage of the reaction. It is now realised that proper control of experimental conditions is impossible without this knowledge. Since viscometry alone could not provide the required information, a system involving spectrophotometric analysis of the initiation process, and dilatometric analysis of the propagation step for the reaction between n-butyllithium and isoprene

FIG. II.7

Vessel for spectrophotometric study of polystyryllithium and polyisoprenyllithium.

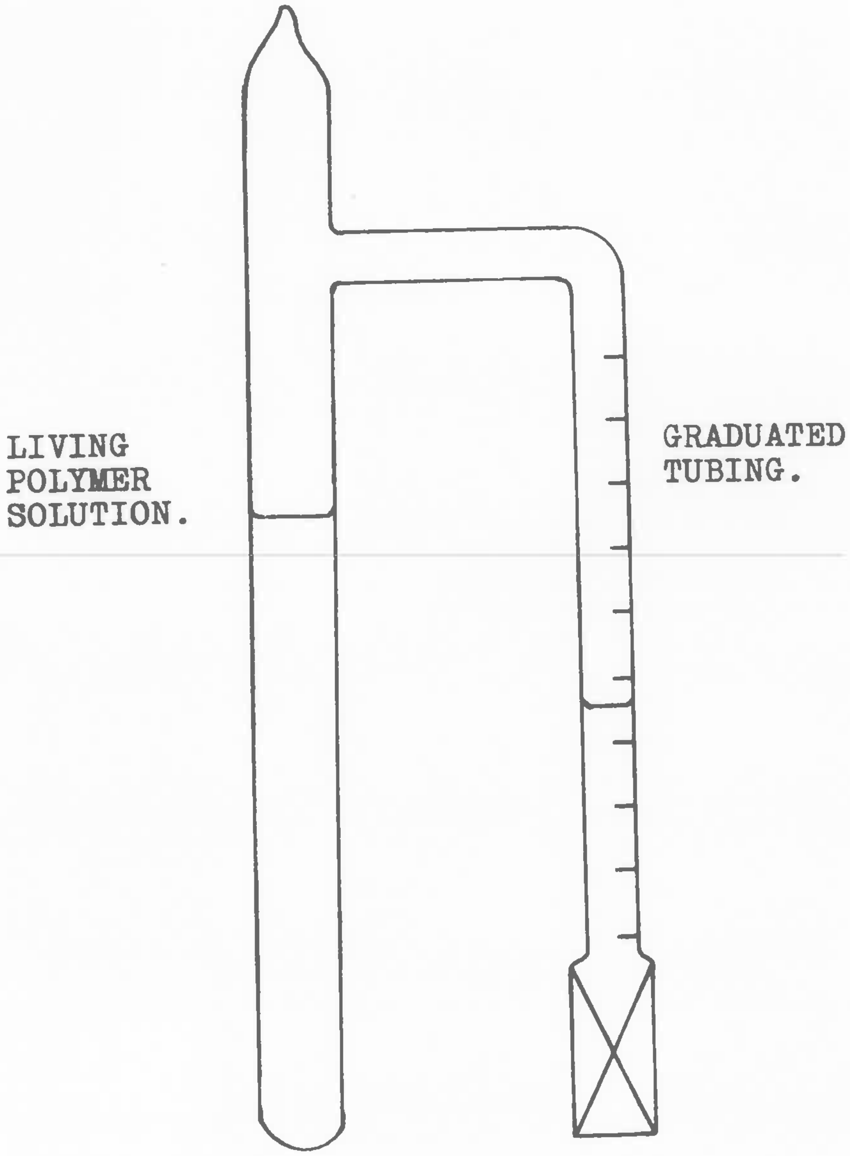


FIG. II . 7.

in benzene, was devised to study the first step in the synthesis. A discussion of the results of this investigation is contained in Chapter III.

The visible spectra of solutions of polystyryllithium and polyisoprenyllithium were studied first, and the experimental details are now given.

11. Spectrophotometry

The apparatus for studying the spectra of polystyryllithium and polyisoprenyllithium is shown in Fig. II.7. A concentrated solution of living polymer was isolated in the vessel and sealed off under vacuum. In a separate experiment, the concentration of this solution was accurately determined by potentiometric titration. A measured volume of solution was then tipped into the 1 cm. pyrex optical cell, and its optical density measured in a Unicam SP 700 spectrophotomer. A special cover for the cell compartment was constructed to allow the apparatus to fit into the instrument. The vessel was removed from the spectrophotometer, and pure benzene was distilled across into the graduated tube. Careful shaking of the vessel caused thorough mixing of the solution. The optical density was recorded once again. This process was repeated several times, and since the volume and concentration of the original solution was known, by measuring the volume of benzene distilled across for each dilution step, it was possible to construct a graph of optical density as a function of concentration. The results of this investigation are contained in Chapter III. Polystyryllithium in benzene was found to obey Beer's Law at 334 mμ, whereas polyisoprenyllithium dd not obey a Beer's Law relationship at 328 mμ.

FIG. II.8

Apparatus for preparing solutions for kinetic study of the initiation and propagation reactions for isoprene

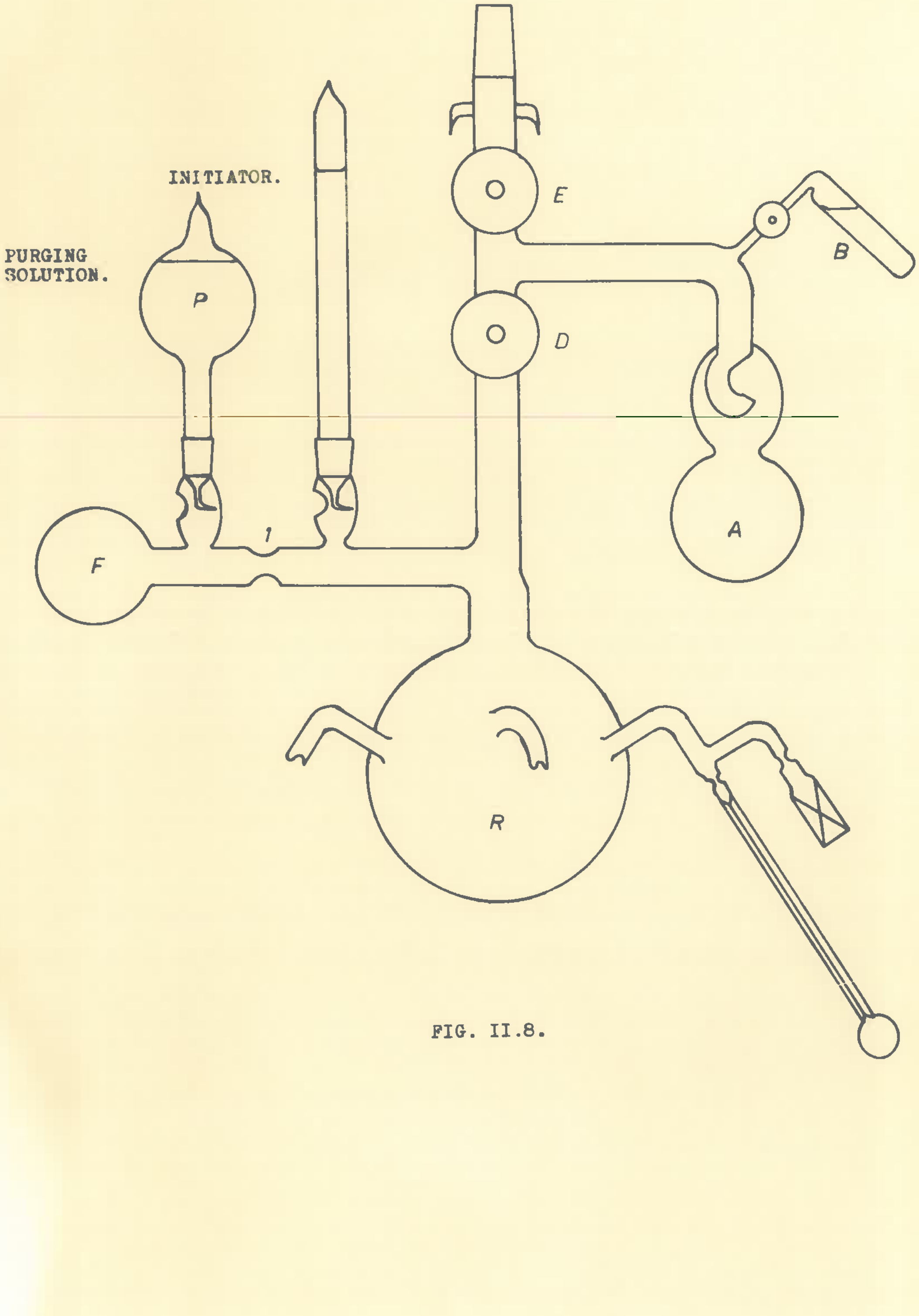


FIG. II.8.

12. Kinetics of Isoprene Polymerisation

The apparatus used is shown in Fig. II.8. A measured volume of n-butyllithium of known concentration was sealed into an ampoule fitted with a twist break seal. It was then attached to the apparatus alongside of an ampoule of purging solution P. The reaction vessel was evacuated and flamed out, greaseless tap D was closed tightly, and the vessel removed from the vacuum line. Purging solution was introduced, and the vessel was thoroughly purged, washed with benzene as described previously, and the purging solution sealed off in flask F at constriction 1. The vessel was once again attached to the vacuum system, and the section above tap D evacuated and flamed out. The required volume of isoprene monomer and benzene was distilled into flask A, the greaseless tap E was closed, and the vessel removed from the line. The monomer-solvent mixture was titrated with living polymer solution from tube B as mentioned before, and then carefully distilled into the reaction flask A through tap D. The butyllithium initiator was added, mixed thoroughly with the monomer solution, and the three optical cells and three dilatometers filled and sealed off from the apparatus. An optical cell (pyrex 10mm x 10mm) and a dilatometer were placed in each of two water baths set at 30°C and 40°C. The remaining cell and dilatometer were kept in an air conditioned room at 20°C.

An automatic recording Unicam SP 700 spectrophotometer was used to measure the optical density of the solutions in the cells at regular intervals, and the contraction of solutions in the dilatometers was periodically measured using a cathetometer. The optical density in the three cells was found to increase slowly until it reached a steady value, at which point all n-butyllithium was converted to polyisoprenyllithium and initiation was therefore complete. The results of this spectrophotometric analysis yielded valuable information on the kinetics of initiation, and further discussion follows in the next chapter. A combination of the spectra and dilatometer results indicated the average molecular weight of the polyisoprenyllithium at completion of initiation, so that useful information was acquired concerning the preparation of polyisoprenyllithium "seed". The dilatometer data also provided information concerning the propagation step. Conducting the same experiment at three different temperatures yielded information which was essential for maximum control of the reaction in the block copolymer synthesis.

13. Kinetics of Cross Propagation

The conversion of polyisoprenyllithium to polystyryllithium is known as cross propagation. This reaction is faster than the initiation step, so that a new technique had to be devised to examine its kinetics. Less concentrated solutions of polyisoprenyllithium were required, since the optical density of polystyryllithium is considerably higher than that of a solution of the isoprene compound of the same concentration. The spectrophotometer was not capable of measuring solutions of optical density greater than 2, and since the only suitable measuring cells available had a minimum path length at 10 mm., care had to be exercised in choosing a suitable concentration of polyisoprenyllithium initiator. The previous work with twist break seals and greaseless taps was satisfactory, but it was seen that the system could be simplified and improved greatly by using an all glass system with "whisker" type break seals. The principle attributes of the new technique are that termination was practically eliminated, and spectra could be measured within thirty seconds of commencing the reaction. It was necessary to have an excess of styrene monomer, so that the monomer concentration remained essentially constant throughout the course of the cross propagation. Furthermore, rate constants could not be calculated unless the monomer concentration was accurately known. The previous method of titrating impurities in the monomer was

FIG. II.9

Vessel for prepurging
samples of monomer.

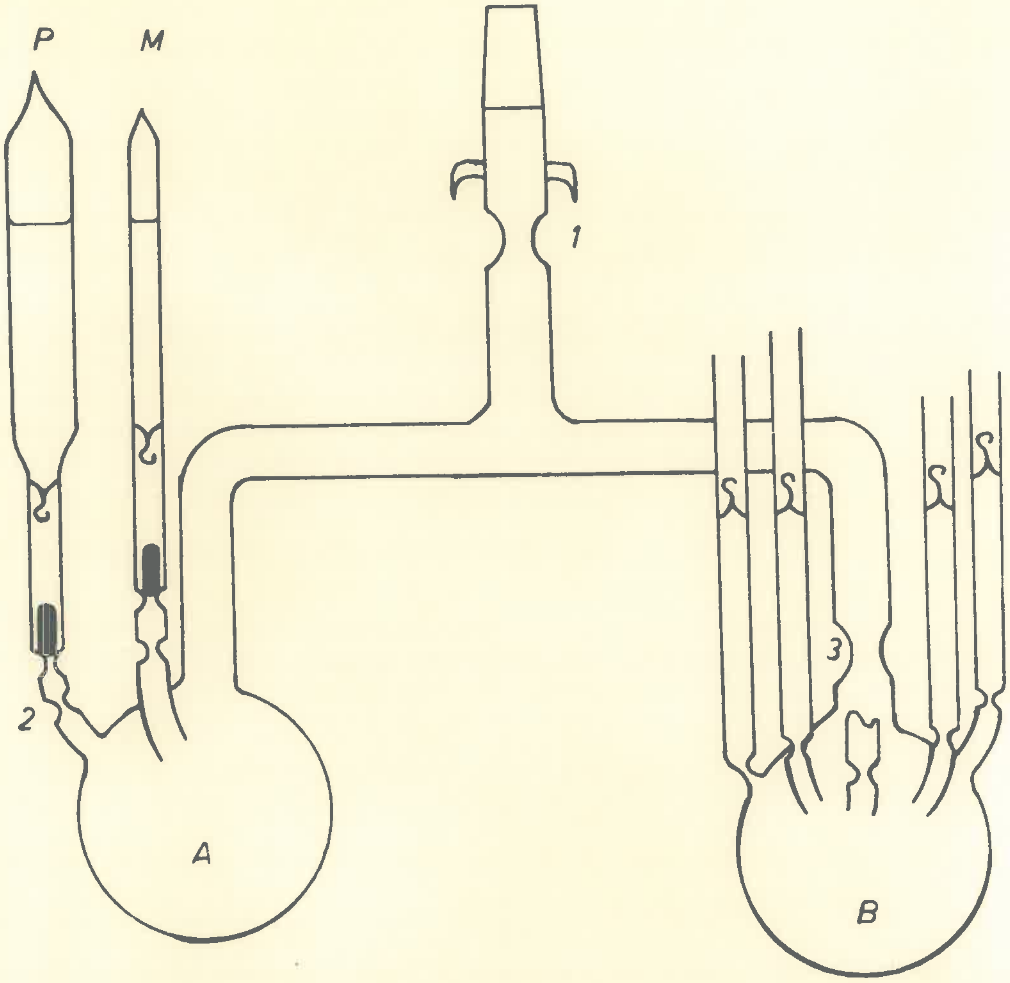


FIG. II.9.

therefore not applicable, since it was not possible to estimate the amount of monomer polymerised during this operation. The only solution to this problem was to prepurge a monomer-solvent solution, and estimate its concentration before sealing it on to the reaction vessel. The apparatus used for this process is shown in Fig. II.9.

Seven sampling ampoules were fixed to flask B. Two ampoules were sealed on to flask A. One (P) contained a measured volume of purging solution, and the other (M), contained a solution of styrene monomer in benzene. The vessel was flamed out, evacuated, and sealed off at constriction 1. Purging solution was added, and ampoule P sealed off at constriction 2. The apparatus was purged by repeated washing over a period of six hours. Special care was taken to ensure that the sampling ampoules were purged. The solution was returned to flask A and benzene distilled from it into flask B. This section of the vessel had to

FIG. II.10

Vessel for study of cross

propagation reaction

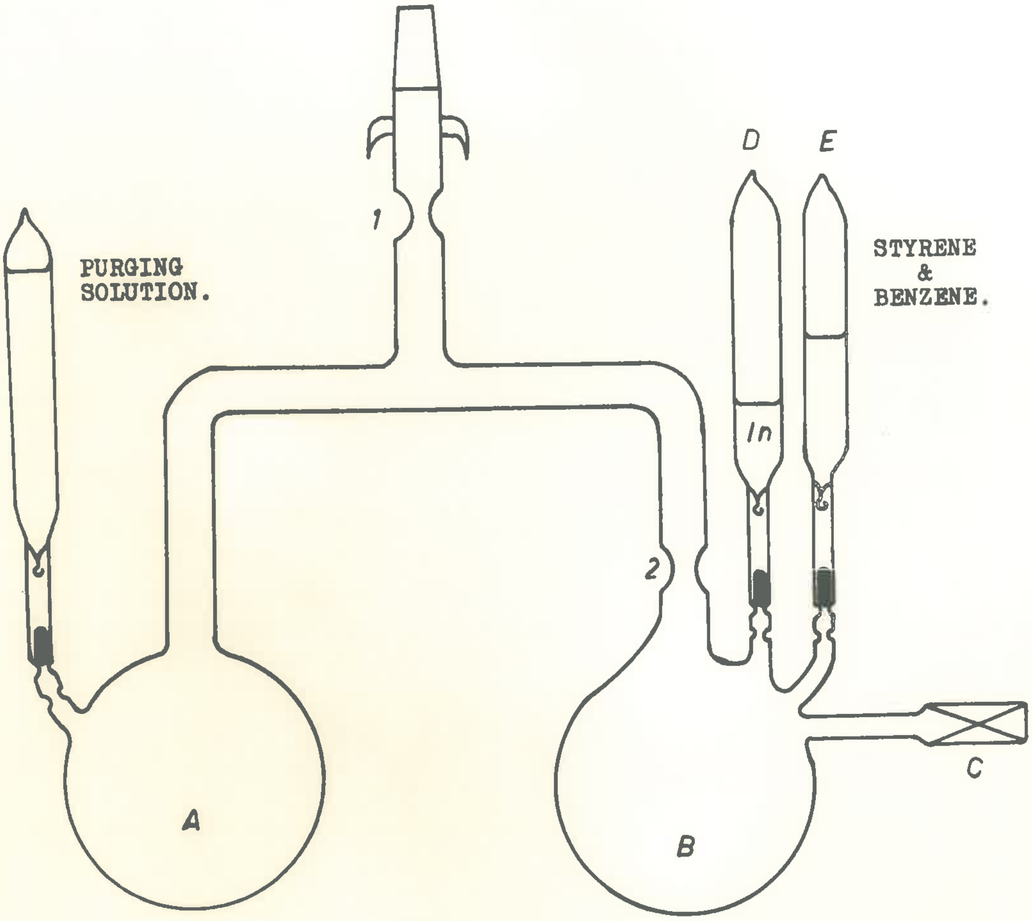


FIG. II.10.

be completely freed from residual purging solution, so that washing with pure benzene was performed six times. The benzene was distilled once more into B, and the small volume of monomer solution in benzene added from ampoule M on to the living polymer left in flask A. During this purging process, the temperature was maintained at +5°C to minimise polymerisation. After ten minutes, the monomer and solvent were distilled into B, which was then sealed off at constriction 3. A measured volume of purged monomer solution was sealed off in each of the seven sampling ampoules. These were kept in a refrigerator until required.

The cross propagation reaction was conducted in a similar vessel, which is shown in Fig. II.10. The vessel was evacuated and purged as described previously, the benzene from the purging solution being distilled into flask B before sealing off at constriction 2. The polyisoprenyllithium "seed" was then added through the break seal, and its contribution to the optical density of the solution at 334 $m\mu$ measured. The vessel was then removed from the spectrophotometer and the temperature of the solution in B adjusted to coincide with the temperature of the run. The prepurged solution of monomer and benzene was added from ampoule E, and thoroughly mixed in flask B. A stop clock was started, the vessel transferred to the SP 700 spectrophotometer, and with the wavelength set at 334 $m\mu$, a trace of the rate of increase of polystyryllithium anion concentration was automatically recorded. The reaction was carried out over a range of temperature and initiator concentrations.

References to Chapter II

1) M. MORTON and L.J. FETTERS. J. Polymer Sci., A2, 3311 (1964)

2) S. BYWATER. Adv. Polymer Sci., 4, 66 (1965)

FIG. III.1

Plot of concentration of polyisoprenyllithium against wave number.

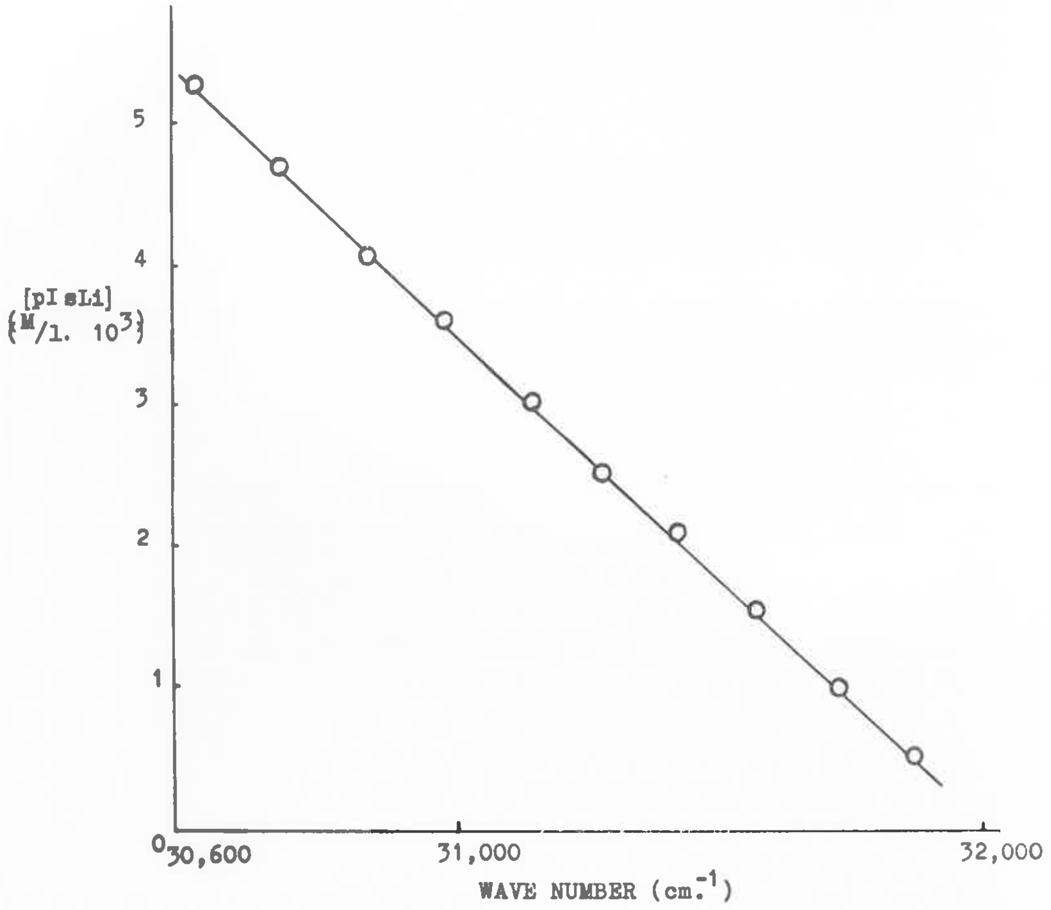
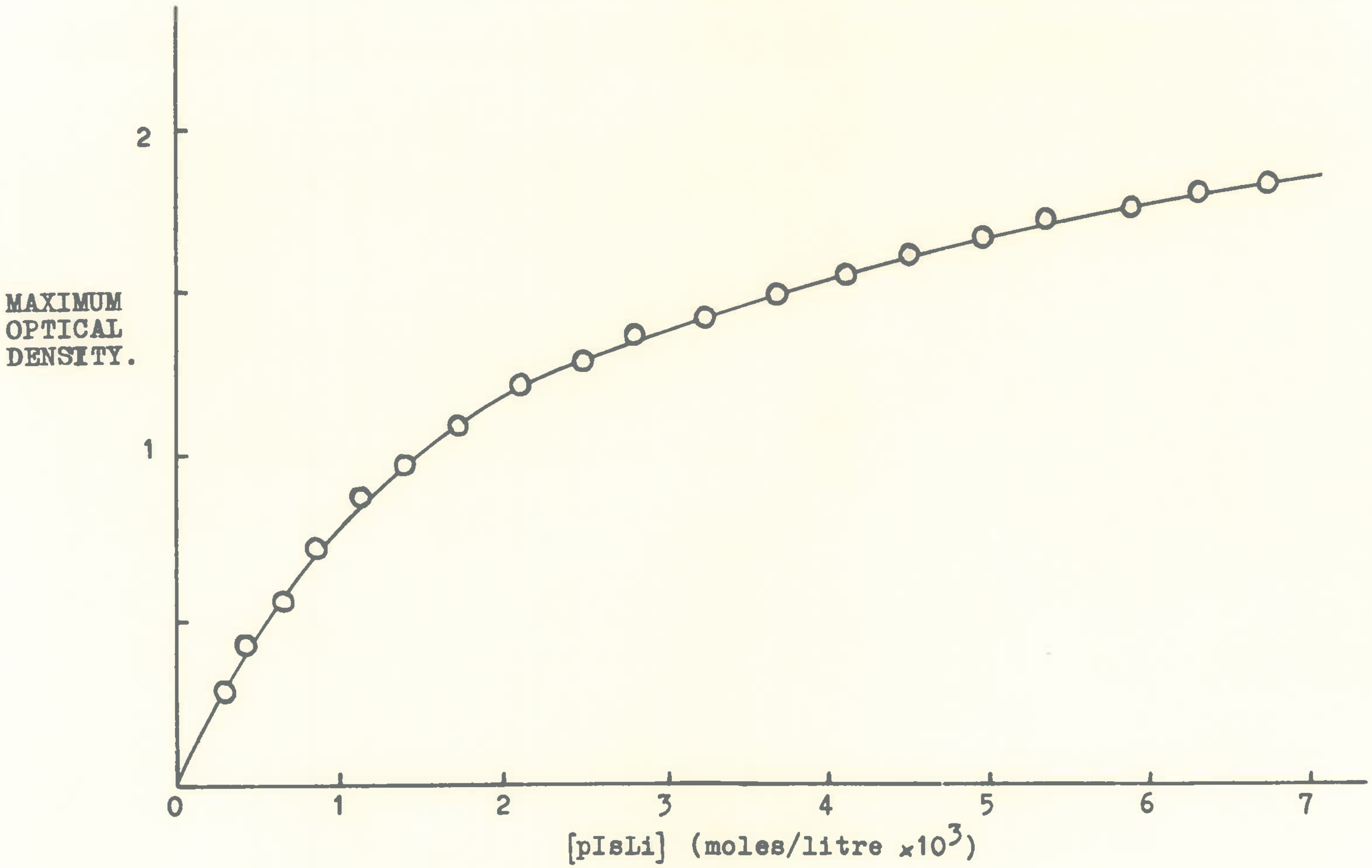


FIG.III.1.

FIG. III.2

Plot of maximum optical density against polyisoprenyllithium concentration



MAXIMUM OPTICAL DENSITY.
2
1
0
1
2
3
4
5
6
7
[pIsLi] (moles/litre x10^3)

FIG. III.2.

CHAPTER III

RESULTS AND DISCUSSION OF INITIATION AND PROPAGATION

1. Spectrophotometry

(a) Polyisoprenyllithium

Spectrophotometric studies on the pale yellow polyisoprenyllithium showed a hypsochromic shift of the maximum absorption. Within the concentration range studied (5×10^{-4}M. to 5×10^{-3}M.), the shift was linear as shown in Fig. III.1.

Figure III.2 was used for interpretation of the kinetic data. This is a graph of the maximum optical density of the polyisoprenyllithium at the absorption peak regardless of its wavelength, as a function of the polyisoprenyllithium concentration. The concentration of polyisoprenyllithium at any stage of a polymerisation was computed by simply noting the maximum optical density of the solution and reading

FIG. III.3

Plot of optical density at 328 mμ against polyisoprenyllithium concentration

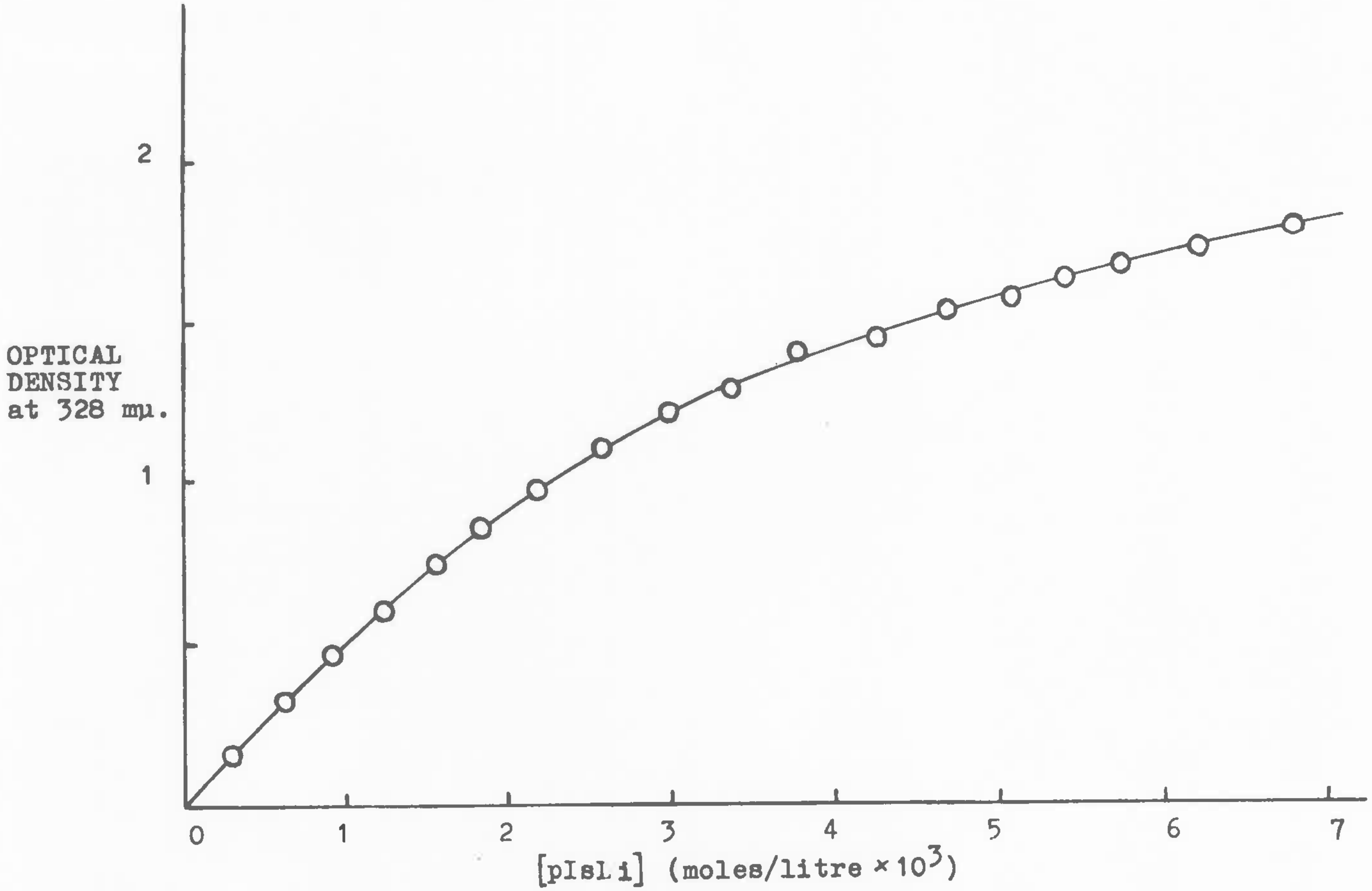


FIG. III.3.

off the corresponding concentration from Fig. III.2.

To test whether polyisoprenyllithium obeys Beer's Law at a fixed wavelength, a third curve was constructed and is shown in Fig. III.3. This is a plot of the optical density at 328 mμ as a function of concentration. No isosbestic point could be located for the benzene solution of polyisoprenyllithium.

Some interesting points arise from this spectrophotometric investigation. The concentration dependence of the position of the absorption peak shown in Fig. III.1, suggests that a whole range of polymerisation intermediates, possibly complexed with the solvent, is involved. Reference to Fig. III.2 supports this view. In a recent review, Cubbon and Margerison(2) summarised the results of various workers in this field. In order to explain all the results reported in the literature, they found it necessary to assume that different degrees of association of polyisoprenyllithium are found at different concentrations. Thus the results of Morton *et al.*(3) imply dimerisation of the active centres of polymerisation, Worsfold and Bywater's(1) results imply a four-fold association, while those of Sinn's(4) group suggest an equilibrium involving monomeric, trimeric and hexameric polyisoprenyllithium. Bywater, Johnson and Worsfold(24) have reported that polyisoprenyllithium in cyclohexane obeys Beer's Law at 270 mμ within an error of ± 5%. However, as shown in Fig. III.3, the present work indicates that in benzene, polyisoprenyllithium does not obey a Beer's Law relationship at 328 mμ. The curve appears to have two distinct sections which correspond to an extinction coefficient $\varepsilon = 500$ at concentrations of polyisoprenyllithium up to 2.5×10^{-3}M, and an $\varepsilon = 280$ at concentrations in the range 3.5×10^{-3}M to 1×10^{-2}M. Comparing this data with the kinetic results, the average association number for the growing chains appears to change from the dimeric form in dilute solution to trimer or tetramer in more concentrated solution. Sinn(5) has reported the existence of the monomeric form at very low concentrations and an even higher association number of six for concentrated solutions in n-heptane. Conductivity studies in n-heptane. Conductivity studies in these solutions indicate the virtual absence of free ions.(6) It is assumed that the species with $\varepsilon = 280$ is the tetramer, and that with $\varepsilon = 500$ is dimer. Thus there can be no doubt that polyisoprenyl-lithium is associated in solution, although the degree of association will depend on the concentration of the solution. A question naturally arising from this conclusion is, "Do all the polymerisation intermediates, regardless of degree of association, form active centres for polymerisation?" Discussion of this question will follow in the section dealing with the kinetics of polymerisation.

FIG. III.4

Spectrum of "isomerised" polystyryllithium

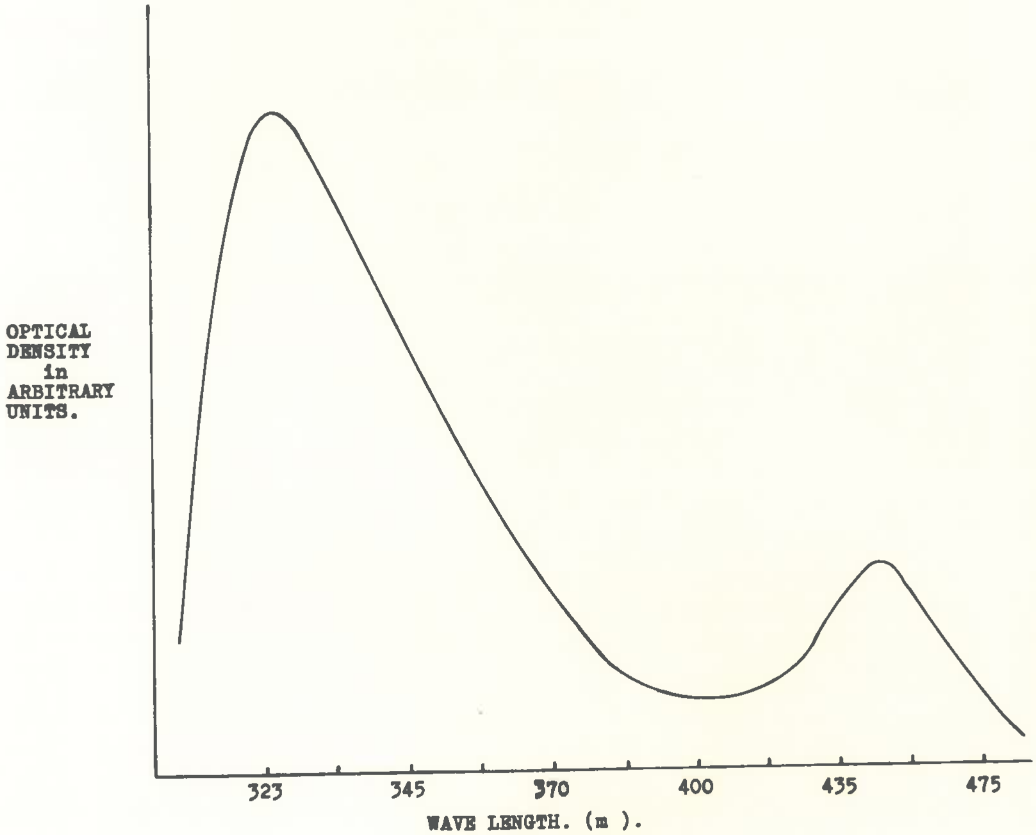

OPTICAL DENSITY in ARBITRARY UNITS.
323
345
370
400
435
475
WAVE LENGTH. (m).

FIG. III. 4.

(b) Polystyryllithium

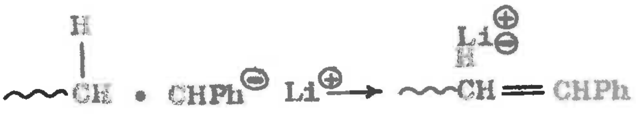
Solutions of polystyryllithium in benzene were found to obey Beer's Law in the concentration range 10^{-5} to 10^{-3}M. at 334 mμ. No change in position of the peak was observed at varying concentrations, suggesting that the polystyryllithium exists predominantly in one form. From kinetic data of other workers,(7,8,9) it is postulated that this absorption peak is due to an associated dimeric species.

The polystyrene solution was kept in its measuring vessel for twelve months, over which period, the deep blood red colour was found to change to a brownish red colouration. The colour of solutions of polystyryl anions in THF was also found to change, this time to a more magenta colour. Figure III.4 shows a spectrum of the twelve month old solution.

In the complete spectrum of the fresh polystyryllithium, there was an absorption peak at 334 mμ, with no sign of a peak at 450 mμ. However, this same solution, after being kept for twelve months, had not only changed colour, but had developed a strong absorption at 450 mμ. Recent work by Szwarc(10,11) has elucidated the mechanism and species involved in this change known as "isomerisation", thereby explaining the anomalies in the polystyryl anion spectrum suggested by Kuwata(12).

(c) Isomerisation of polystyryl anions

The possibility of isomerisation of solutions of living polystyrene must be considered in a discussion of the synthesis of block copolymers by anionic polymerisation. Some interesting features of this curious reaction were reported by Szwarc.(10,11) The reaction was found to be much slower in benzene than in tetrahydrofuran. Isomerisation was also found to be faster when the molecular weight of the polymer was low. The fact that solutions of "living" poly-α-methylstyrene do not undergo this change seems to indicate that the α-hydrogen of polystyrene is involved. Szwarc has proposed that the reaction results from two consecutive reactions.



$$\sim\sim\overset{H}{\overset{|}{CH}} \cdot CHPh^{\ominus}\ Li^{\oplus} \longrightarrow \sim\sim\overset{\overset{Li\substack{\oplus\\\ominus}}{H}}{CH}=CHPh \qquad (III.1)$$

and

$$\sim\sim CH_2 \cdot CHPh^{\ominus}\ Li^{\oplus} + CHPh=CH \cdot CHPh \cdot CH_2\sim\sim$$

$$\longrightarrow \sim\sim CH_2 \cdot CH_2Ph + Li^{\oplus}\ CHPh=CH \cdot \overset{\ominus}{C}Ph \cdot CH_2\sim\sim$$

(III.2)

The second reaction followed the first rapidly, the formation of the 1,3-diphenylallyl ions causing the observed spectral changes. Their stability accounted for the inability of "isomerised" polystyrene to sustain further polymerisation, and this property of isomerised polystyrene has two important consequences for the present work.

Firstly, if a "living" polystyrene solution was to be used for further polymerisation, it had to be kept in a refrigerator until required, since isomerisation was much slower at reduced temperatures. Secondly, if solutions of "living" polystyrene were deliberately isomerised by storage at an elevated temperature, they became useful purging solutions for freeing monomers from impurities. The isomerised polymer retained its extreme reactivity to terminating material present in the monomer. Thus the monomer was allowed to react with such a solution for a long time, efficient purging of impurities taking place while no polymerisation occurred.

2. Kinetics

(a) Introduction

The primary aim of this kinetic study was to obtain information on the rates of initiation and propagation, and in particular, to study the temperature dependence of these reactions so that control of the polydispersity of the block copolymers could be controlled. The polymerisation of isoprene in benzene using butyllithium as initiator was examined as two distinct reactions, namely initiation and propagation. The initiation step was followed spectrophotometrically, and the propagation step by dilatometry. The two reactions were examined simultaneously, so that the increase in molecular weight of the "living" polymer and the increase in concentration of polyisoprenyllithium could be followed simultaneously. A series of five experiments were carried out at different butyl-

FIG. III.5

Plot showing increase in number average molecular weight and increase in polyisoprenyllithium during initiation.

The molecular weight of the "seed" at completion of initiation is seen to be 3,000.

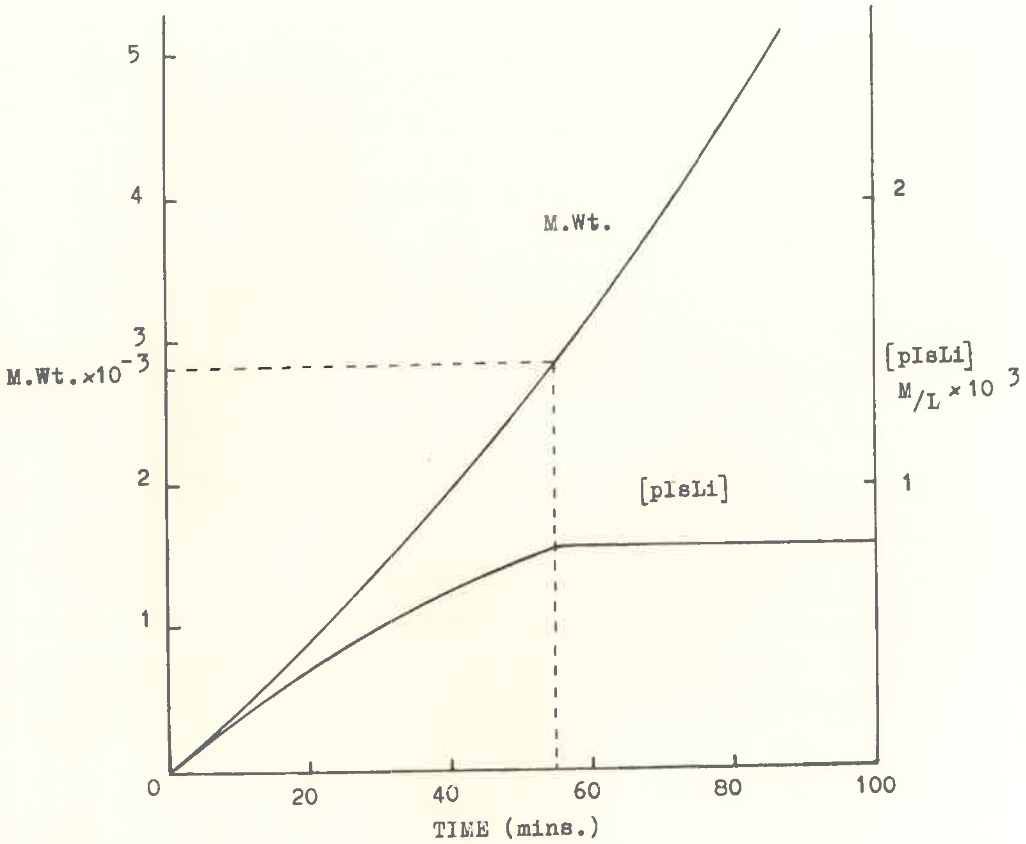

5
4
3
2
1
0
M.Wt.×10^{-3}
M.Wt.
[pIsLi]
[pIsLi]
M/L × 10 3
2
1
20
40
60
80
100
TIME (mins.)

FIG. III.5.

lithium concentrations, and the results of each run are typified by Fig. III.5. The molecular weight curve was calculated from dilatometry results which will be discussed fully under the heading of propagation. In Fig. III.5, it can be seen that for a solution containing 8×10^{-4} molar butyllithium, initiation was complete after 55 minutes at 20°C, the number-average molecular weight of the polyisoprene being approximately 3,000. Thus, for initiation to be complete at room temperature, approximately 40 monomer units were required for each molecule of butyllithium. This value was calculated from the ratio of the total monomer consumed at complete initiation $[M]o$, to the total initiator generated, a_o. It is interesting to note that this value is considerably lower than the 200 to 300 monomer excess reported by Worsfold and Bywater(1) using cyclohexane as solvent. Cubbon and Margerison(2) have stated that the critical ratio of $[M]o/a_o$ seems to be about 100 for the usual concentrations and temperatures employed, but this value depends on the solvent used. This seems to be the reason why Wenger$^{(13)}$ found only 30% conversion of butyllithium to styryllithium, in view of the ratio $[M]o/a_o$ of only 4 used by him.

A solution of polyisoprenyllithium free from n-butyllithium is often used as initiator, and is usually referred to as "the seed". This procedure is exemplified in the work of Morton, Bostick and Clarke,$^{(14)}$ who thereby obtained not only the simple stoichiometry of one lithium atom to every chain, but also the sharp molecular weight distribution expected on statistical grounds. When this "seeding" process was not used, they found that polyisoprenes prepared at 29°C in n-hexane were polydisperse. Although it was convenient to use a polyisoprene "seed" as initiator for the block polymerisation, the kinetic data obtained in this work shows that this is not necessary provided the initiation reaction is performed in benzene under the right conditions. The polydispersity of the polymer produced will depend largely on the ratio $[M]o/a_o$. Initiation is complete after the last molecule of butyllithium has added its first monomer molecule. The polymer present at this stage will be polydisperse and the larger the value of the ratio $[M]o/a_o$ the greater will be the range of molecular weights present. If only a small amount of monomer is required to complete initiation, i.e. if $[M]o/a_o$ is small, on the further addition of sufficient monomer to produce a high molecular weight polymer, the polydispersity of the final product will not be much affected by the small range of molecular weights produced during initiation.

The ratio $[M]o/a_o$ must be kept as low as possible therefore, and can be controlled if values of the initiation rate constant k_i, the propagation rate constant k_p, and the activation energies of these steps are known. The faster the rate of

FIG. III.6

Plot of increase in polyisoprenyllithium concentration with time during initiation.

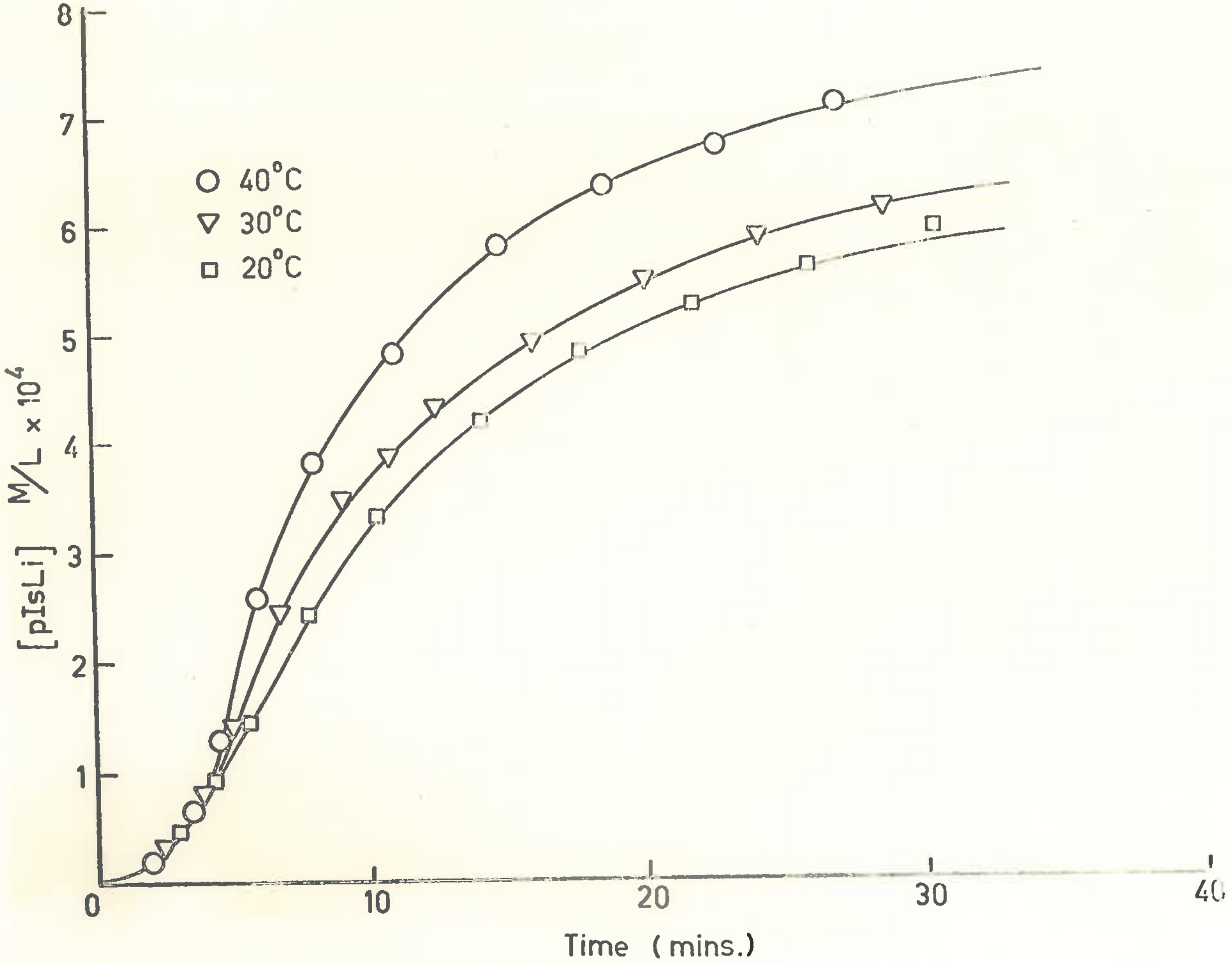


FIG. III 6.

initiation (R_i) compared with the rate of propagation R_p, the smaller will be the value of $[M]_o/a_o$. A knowledge of the activation energies of these steps will allow adjustment to be made to these rates by choosing the appropriate temperature for reaction. It was the primary aim of the ensuing kinetic investigation to find experimental values for k_i, k_p, R_i, R_p and the activation energies.

(b) Initiation Reaction

Figure III.6 shows typical initiator time-conversion curves. As indicated, polymerising solutions of the same concentration were examined at 20°C, 30°C and 40°C. It was found from five separate experiments conducted at different concentrations of n-butyllithium, that the increase in concentration of polyisoprenyllithium with time was not linear, but exhibited a sigmoidal curve similar to that reported by Worsfold and Bywater(1) for the same reaction in cyclohexane. The slow induction period occurred despite the most rigorous purging of vessels and solutions.

The exact cause of this behaviour is not clear, but Worsfold and Bywater(1) have suggested that traces of lithium salts due to fortuitous termination of butyllithium may be the cause. Johnson and Worsfold(9) have reported that less rigorously purified samples of butadiene do not show this induction period, the initial reaction rate with butyllithium being about three times the maximum rate shown by the pure monomer. Evidently impurities may act as catalysts in the initiation reaction. In the present work, however, when rigorous purging techniques were employed, the induction period still existed. The fact that the concentration of butyllithium initially added to the system was found to correspond with the final concentration of polyisoprenyllithium led to the conclusion that the induction period is a characteristic of the complex initiation step.

Johnson and Worsfold(9) have made the plausible suggestion that the reaction is auto catalytic. The nature of the carbon-lithium bond in butyllithium is still largely in doubt, but it quite possibly is less ionic than that in polyisoprenyllithium, as there is less possibility of delocalising the charge. The fact that butyllithium is strongly associated in hydrocarbon solvents still indicates a highly polar molecule. It is therefore not unexpected that butyllithium shows a reluctance to form the more highly polar isoprenyllithium molecule in solvent of low dielectric constant. Johnson and Bywater(1) have therefore concluded that a complex of the polyisoprenyllithium and butyllithium is the active polymerisation agent. In the present work, the energy of activation and pre-exponential factor were obtained from the temperature dependence of the rate of initiation. The apparent rate constant

FIG. III.7

First order plots of initiation rate with respect to butyllithium

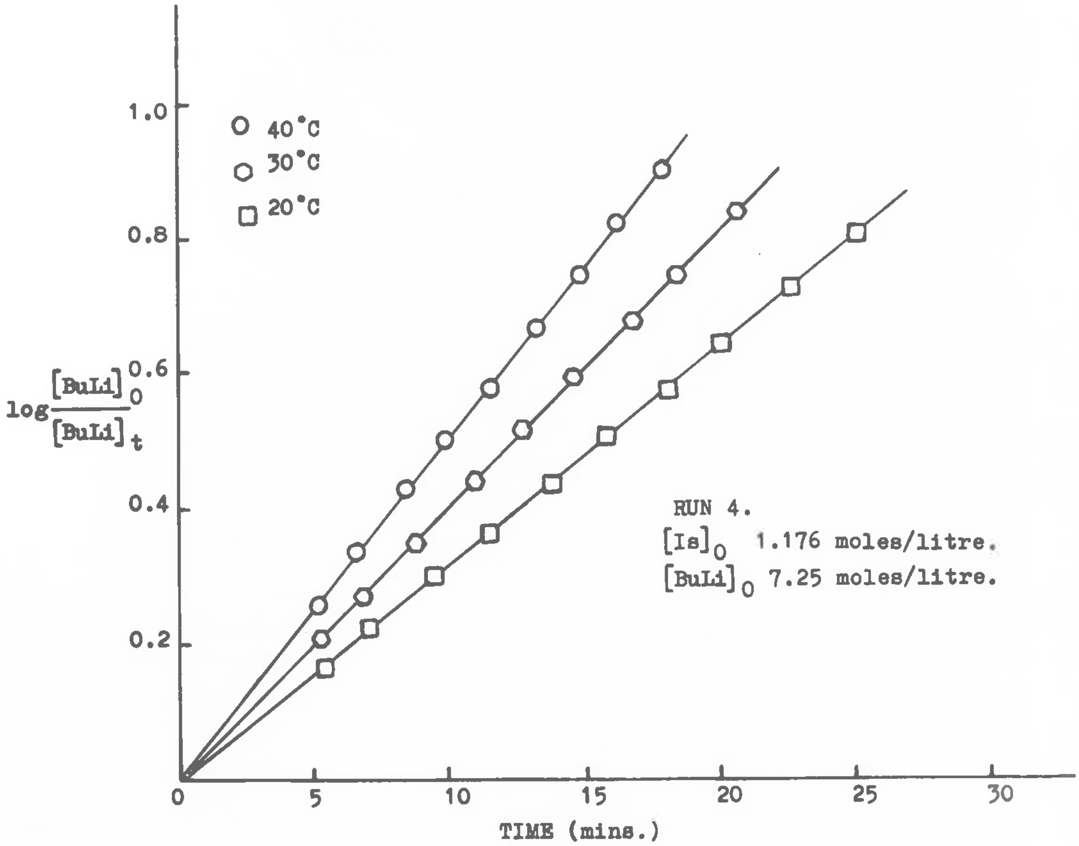

1.0
0.8
0.6
0.4
0.2
$\log \frac{[BuLi]_0}{[BuLi]_t}$
○ 40°C
⬡ 30°C
□ 20°C
RUN 4.
$[Is]_0$ 1.176 moles/litre.
$[BuLi]_0$ 7.25 moles/litre.
0
5
10
15
20
25
30
TIME (mins.)

FIG. III. 7.

for initiation was found to be

$$k_i = 10^{2.04}\, e^{-\frac{4,300}{RT}} \text{ litres/mole/min, and at}$$

30°C, is 8.04×10^{-2} litre mole^{-1} min.^{-1} The low pre-exponential factor observed here is consistent with the large negative entropy to be associated with the formation of such a complex as suggested by Worsfold and Bywater.(1) It seems plausible that the undissociated or monomeric ion pairs $[\text{Bu}^{\ominus}\ \text{Li}^{\oplus}]$ may begin the initial slow reaction which is rapidly catalysed by the complex being formed. The sharp increase in reaction rate on addition of small amounts of polar solvents such as THF is easily explained on this basis.

First order plots of the initiation rate with respect to butyllithium were obtained, and are shown in Fig. III.7. The reaction is likely to be first order in monomer, but the order with respect to butyllithium is unexpected, since butyllithium has been shown to exist as a hexamer in hydrocarbon solvents.(7,15,16) Worsfold and Bywater(1) have deduced an order of 0.7 with respect to butyllithium from their work in cyclohexane. However, in both cases, initiation is almost certainly more complicated than this, as is indicated by the sigmoidal shape of the initiation curve.

If a sufficiently large excess of monomer is used, its concentration will remain sensibly constant during initiation. The rate of initiation is given by equation III.3.

$$R_i = -\frac{d[\mathrm{BuLi}]}{dt} = k_i [\mathrm{BuLi}]^x [M] \quad \text{(III.3)}$$

If $[M]$ is constant and $x = 1$,

$$-\frac{d[\mathrm{BuLi}]}{dt} = k [\mathrm{BuLi}] \quad \text{where } k = k_i [M]$$

Integrating

$$\log \frac{[\mathrm{BuLi}]_o}{[\mathrm{BuLi}]_t} = kt/2.303 \qquad (\mathrm{III.4})$$

If the reaction is first order with respect to butyllithium, a plot of log $[\mathrm{BuLi}]_o / [\mathrm{BuLi}]_t$ against t should produce a straight line of slope k/2.303. The initial concentration of butyllithium was obtained from the concentration of polyisoprenyllithium determined spectrophotometrically at the end of reaction. The concentration of butyllithium at any time t, was calculated from the difference between the optical density of the solution finally and at time t. The optical density was converted to concentration by reference to Fig. III.3.

From the first order constants found at several temperatures, the Arrhenius constants were

FIG. III.8

Arrhenius plot for Initiation reaction.

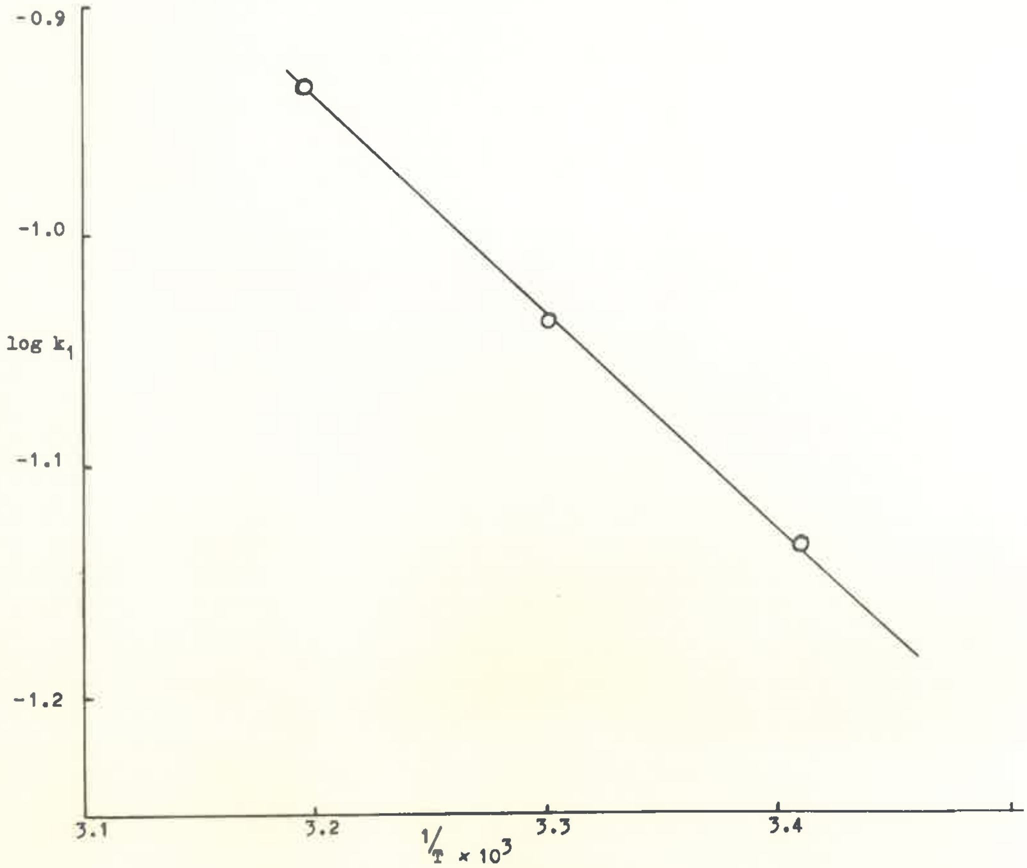


FIG. III.8.

determined according to

$$k = Ae^{-\frac{Ea}{RT}} \qquad (III.5)$$

A plot of log k against $\frac{1}{T}$ yields a straight line of slope-E/2.303R. The Arrhenius plot is shown in Fig. III.8, and the complete expression for the experimental rate constant for initiation is therefore

$$k = 10^{2.04} e^{\frac{-4,300}{RT}} \qquad (III.6)$$

The maximum rate of initiation in benzene appears to be nearly four powers of ten higher than in cyclohexane as determined by Worsfold and Bywater(1), indicating the reluctance of the initiation reaction to proceed in a solvent of only slightly lower dielectric constant. This effect of the dielectric constant of the solvent has also been observed in the initiation of styrene by butyllithium in benzene(7) and cyclohexane(9). In this case, the reaction is some hundreds of times faster in benzene. From the data available at present, it is not possible to propose with certainty a mechanism for initiation. However, the present work has made it possible to suggest a likely course for the reaction.

(c) Suggested Mechanism of Initiation

The following experimental details are relevant to a discussion of the mechanism of initiation. Apart from the work of Piotrovski and Ronina,(17) molecular weight studies have shown that n-butyllithium is hexameric in hydrocarbon solvents.(7,15,16) It has also been established that the rate of initiation is increased, sometimes enormously, by increasing the dielectric constant of the solvent. The work of Bywater, Johnson and Worsfold,(1,9) in cyclohexane has shown that the initiation curve is sigmoidal, but Bywater(18) has specifically stated that this behaviour is not found for the reaction in benzene.

Our work is in disagreement with this statement. The reaction is first order with respect to monomer, and would appear from the present work, to be first order with respect to butyllithium. Worsfold and Bywater⁽¹⁾ have deduced an order of 0.7 with respect to butyllithium in cyclohexane, and since the experimental rate constant is determined from the logarithmic plot in Fig. III.7 which will be relatively insensitive to small changes in the order with respect to butyllithium, our results would appear to agree satisfactorily with those of Worsfold and Bywater. A further important factor to consider is that polyisoprenyllithium in hydrocarbon solvents is associated. It is generally assumed to exist as a tetramer, although dimers,⁽³⁾ monomers, trimers and hexamers⁽⁴⁾ have also been proposed. The final point to note before discussing the initiation reaction is the value of the A factor of $10^{2.04}$ and the activation energy of 4.3

Kcals/mole. Both these values are lower than expected.

Of particular significance is the state of the alkyllithium compound in solution. If the alkyl group is polystyryl or polyisoprenyl, the degree of association is reduced below the hexameric state of butyllithium. In solvents of high dielectric constant such as tetrahydrofuran, butyllithium is still hexameric, but polyisoprenyl and polystyryllithium are completely dissociated. In general, increasing the bulkiness of the alkyl group tends to decrease the association of alkyl lithium. Increasing the solvating power of the solvent also tends to decrease the association of the alkyllithium. One obvious question arising from the first generalisation is whether the number of monomer units in the polyisoprenyllithium determines the stability of the complexes in which it participates. As yet, there is no definite answer to this question.

The present state of knowledge concerning the individual steps in the polymerisation is confused. Most workers are agreed that both the initiation and propagation process involve the following two elementary reactions.

$$\mathrm{BuLi} + \mathrm{M} \longrightarrow \mathrm{BuM_1Li} \qquad \text{Initiation} \qquad (\text{III.7})$$

$$\mathrm{BuM_1^{Li}} + \mathrm{M} \longrightarrow \mathrm{BuM_2Li}$$

$$\text{Propagation} \qquad (\text{III.8})$$

$$\mathrm{BuM_i} + \mathrm{M} \longrightarrow \mathrm{BuM_{i+1}Li}$$

Only the monomeric forms of butyl and isoprenyl lithium are involved in reaction with isoprene monomer. The main difficulty obscuring the contemporary picture of the overall reaction is the lack of knowledge concerning the role played by the association of polyisoprenyllithium molecules with each other, and possibly with butyllithium.

The reaction scheme generally accepted for the butyllithium polymerisation of styrene in hydrocarbons is based on the following information.

The degree of association of butyllithium is independent of its concentration, implying that butyllithium exists in solution predominantly as a single hexameric species, and that the intermediates in the following equilibria must be present in very low concentration.

$$\begin{array}{lll}
(\mathrm{BuLi})_6 \rightleftharpoons (\mathrm{BuLi})_5 + \mathrm{BuLi} & & \\
(\mathrm{BuLi})_5 \rightleftharpoons (\mathrm{BuLi})_4 + \mathrm{BuLi} & & (\mathrm{III.9}) \\
\qquad\quad \vdots & & \\
(\mathrm{BuLi})_2 \rightleftharpoons 2\mathrm{BuLi} & &
\end{array}$$

There is in fact, no direct evidence for these equilibria other than the kinetic evidence obtained in polymerisation studies. It is possible that the hexamer dissociates completely on removal of one molecule, although this possibility is not generally accepted. Worsfold and Bywater and Cubbon and Margerison have agreed that for styrene, the rate of initiation is one sixth order with respect to butyllithium, over the range of concentrations studied (5 x 10^{-5} Molar to 4 x 10^{-2} Molar.). This result can only be explained in the following terms.

$(BuLi)_6 \overset{K_1}{\rightleftharpoons} 6\ BuLi$ dissociation

$BuLi + M \xrightarrow{k_i} BuMLi$ initiation

$$\text{Since BuLi} = K_1^{1/6} ([\text{BuLi}])^{1/6}$$

$$= K_1^{1/6} a_o^{1/6}$$

$$R_i = k_i K_1^{1/6} a_o^{1/6} M. \qquad (\text{III.10})$$

It is at once apparent that the initiation of isoprene is much more complex than this, since the order with respect to butyllithium is close to unity. Dissociation of hexameric to monomeric butyllithium shown in III.9 involving pentamers, tetramers, trimers and dimers may partly explain the unexpected order in butyllithium. However, it is more likely that a still more complex reaction scheme applies. All the results reported to date can only be explained if it is assumed that different degrees of association of polyisoprenyl lithium molecules are found at different concentrations. Morton, Bostick and Livigni(3) have shown that n-butyllithium associates with the active polyisoprenyllithium centres themselves. Consequently one has to consider a whole range of complexes of the type

$$h\mathrm{BuLi} + k\mathrm{Is}_x\mathrm{Li} \rightleftharpoons (\mathrm{BuLi})_h(\mathrm{Is}_x\mathrm{Li})_k \qquad \text{(III.11)}$$

where all values of h and k which together total six, are permissible. It seems that the essential reaction is the conversion of hexameric n-butyllithium into an "n-meric" polyisoprenyllithium through a whole series of mixed complexes as follows

$$(\mathrm{BuLi})_6 \rightleftharpoons (\mathrm{BuLi})_5 + \mathrm{BuLi}$$

$$\vdots$$

$$(\mathrm{BuLi})_2 \rightleftharpoons 2\mathrm{BuLi}$$

$$(\mathrm{BuLi})_5(\mathrm{Is}_x\mathrm{Li}) \rightleftharpoons (\mathrm{BuLi})_5 + \mathrm{Is}_x\mathrm{Li}$$

$$\vdots$$

$$(\mathrm{BuLi})(\mathrm{Is}_x\mathrm{Li}) \rightleftharpoons \mathrm{BuLi} + \mathrm{Is}_x\mathrm{Li}$$

$$\begin{tikzcd}
(\mathrm{BuLi})_4(\mathrm{Is}_x\mathrm{Li})_2 & \rightleftharpoons \arrow[d, dash, dashed] & (\mathrm{BuLi})_4(\mathrm{Is}_x\mathrm{Li}) + \mathrm{Is}_x\mathrm{Li} \\
(\mathrm{BuLi})(\mathrm{Is}_x\mathrm{Li})_2 & \rightleftharpoons & (\mathrm{BuLi})(\mathrm{Is}_x\mathrm{Li}) + \mathrm{Is}_x\mathrm{Li}
\end{tikzcd}$$

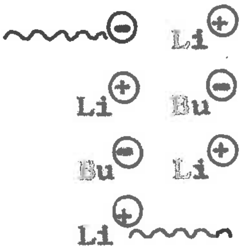
$$\begin{tikzcd}
(\mathrm{Is}_x\mathrm{Li})_6 & \rightleftharpoons \arrow[d, dash, dashed] & (\mathrm{Is}_x\mathrm{Li})_5 + \mathrm{Is}_x\mathrm{Li} \\
(\mathrm{Is}_x\mathrm{Li})_2 & \rightleftharpoons & 2\ \mathrm{Is}_x\mathrm{Li}
\end{tikzcd} \qquad \text{(III.12)}$$

Support for this view was found in the spectroscopic investigation of the initiation reaction. Soon after commencement of reaction, the absorption peak was broad, indicating the possible presence of several species in solution. At completion of initiation, the absorption peak was much narrower, and possibly corresponded to the single species $(\mathrm{Is}_x\mathrm{Li})_4$. The fact that the position of the peak changed during the initiation period also supports this view.

The autocatalytic nature of the reaction can easily be understood on this basis. Early workers discovered that polar materials present in amounts comparable to the concentration of n-butyllithium led to more rapid polymerisations in non polar solvents. Since only the overall polymerisation rates were measured, it was not clear whether this was due to an acceleration of initiation or propagation or both processes. Kropacheva and associates(20) showed that THF markedly increased the rate of initiation, while the propagation rate increased only slightly. Bywater(18) has interpreted the effect of THF to be due to solvation of the active centres to a monoetherate, having a greater reactivity than an associated complex, but less reactivity than a dissociated ion pair. Solvation of active centres can lead to different products. Thus Smid(21) has differentiated between contact or intimate ion pairs which are peripherally solvated, and solvent-separated ion pairs. The reactivity of the latter type would approach that of free carbanions, accounting for the higher reaction rates in more polar solvents. As conductivity studies in THF have shown ion pairs to be the major species, it is possible that these persist in solvents of lower dielectric constant, although in extensively aggregated form (self solvation). Since it is well known that the nature of the counterion has a pronounced effect on the microstructure of the polymer, ion pairs rather than free anions and cations are likely to be involved.

It is proposed that during the induction period, hexameric butyllithium is completely destroyed; a whole series of associated complexes between butyllithium and isoprenyllithium being formed as shown in III.12. As the small number of

$[\mathrm{Bu}^{\ominus}\ \mathrm{Li}^{\oplus}]$ ion pairs present initially, react with monomer to form the more polar isoprenyllithium, further decomposition of hexamer is promoted, so that the rate of decomposition of hexamer increases with time. The initiation rate will therefore increase until all hexamer is decomposed, the associated complexes in solution being of the form



(III.13)

The rate of dissociation of $\mathrm{Bu}^{\ominus}\ \mathrm{Li}^{\oplus}$ from these complexes must be more rapid than the rate of addition of an isoprene molecule so that the rate is first order with respect to monomer. The rate of initiation will then decrease as the butyllithium is consumed.

The possibility that free cations and anions may exist in solution has been proposed by Sinn,(6) who measured the conductivity of n-butyllithium in n-heptane. Although he found some evidence of free cations and anions, their concentration was far too low to explain the observed initiation rates. Sinn has suggested that for isoprenyllithium concentrations below 10^{-4} M, the following reactions occur to a limited extent

$$\begin{aligned} &LiR \rightleftharpoons R^{\ominus} + Li^{\oplus} \\ &(LiR)_3 \rightleftharpoons (Li_2R_3)^{\ominus} + Li^{\oplus} \\ &(LiR)_6 \rightleftharpoons (Li_5R_6)^{\ominus} + Li^{\oplus} \end{aligned} \qquad \text{(III.14)}$$

On the basis of Bywater's findings, considerable doubt must be placed on Sinn's suggestion of free ions in solution. Bywater has demonstrated that in a greaseless high vacuum system, under conditions where the glassware as well as solvent and monomer are pretreated with butyllithium or its equivalent, the concentration of reactive impurities is normally in the region of 3×10^{-6} M. It is therefore most likely that the conductivity measured by Sinn was due to these impurities rather than to free ions.

(d) Propagation

The rate of propagation was followed by dilatometry. The dilatometers were filled, sealed off, and placed in a water bath at the appropriate temperature. The height of the liquid in the capillary was accurately recorded at two minute intervals using a cathetometer. From these readings, a height versus time curve was constructed, and this allowed the height at zero time to be found by extrapolation. Generally, approximately five minutes were necessary for temperature equilibrium to be established. Knowing the height at zero time, it was then possible to construct a contraction versus time curve, which was essentially a monomer concentration against time plot since the initial monomer concentration was known. Once again,

FIG. III.9

First order plots for the propagation reaction.

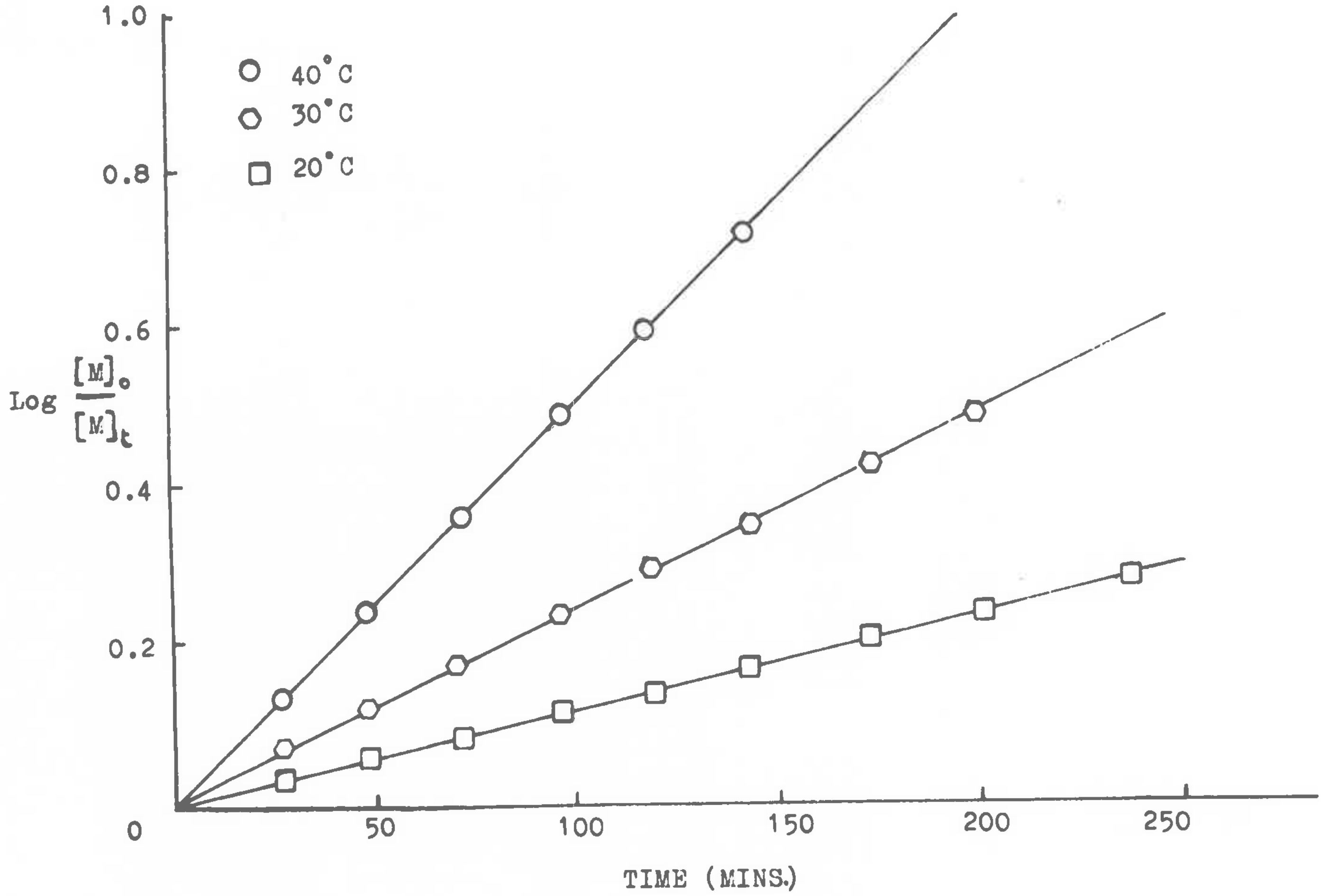

1.0
0.8
0.6
0.4
0.2
0
Log $\frac{[M]_o}{[M]_t}$
○ 40°C
⬡ 30°C
□ 20°C
50
100
150
200
250
TIME (MINS.)

FIG. III. 9.

this curve was sigmoidal, but on completion of initiation, good first order plots were obtained for the consumption of monomer over at least four half life times. These plots are shown in Fig. III.9 for three runs at 20°C, 30°C and 40°C. The rates were more reproducible than those of initiation. The rate of propagation is therefore given by equation III.15

$$-\frac{d[M]}{dt} = k_2 [\text{polyisoprenyllithium}]^{n} [\text{isoprene}]^{1.0} \tag{III.15}$$

in accordance with the mechanism

$$[\text{Bu}(M)_x\text{Li}]_n \overset{K_2}{\rightleftharpoons} n\text{Bu}(M)_x\text{Li}$$

$$\text{Bu}(M)_x\text{Li} + M \xrightarrow{k_p} \text{Bu}(M)_{x+1}\text{Li} \tag{III.16}$$

in which the growing chain is assumed to be strongly associated. The apparent rate constant is therefore a function of the equilibrium constant.

FIG. III.10

A plot of $\text{Log}\left[-\frac{1}{[M]}\ \frac{d\,[M]}{dt}\right]$ as a function of $\text{Log}\left[\text{pIsLi}\right]$

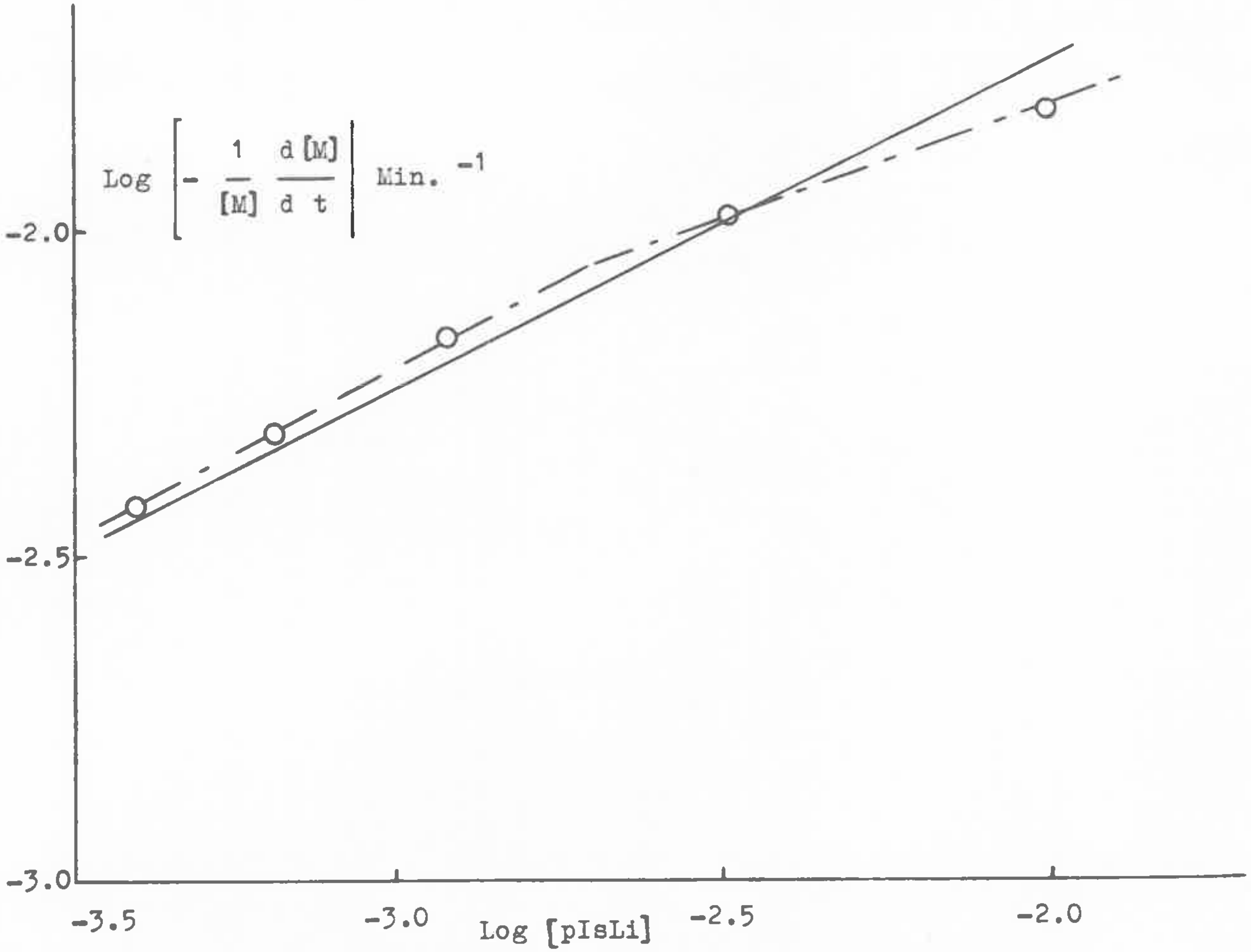

Log $\left[-\frac{1}{[M]}\frac{d[M]}{dt}\right]$ Min.$^{-1}$
-2.0
-2.5
-3.0
-3.5
-3.0
-2.5
-2.0
Log [pIsLi]

FIG. III. 10.

Since the propagation reaction is governed by equation III.15, a plot of $\log(-\frac{1}{[M]}\frac{dM}{dt})$ as a function of [polyisoprenyllithium] will have a gradient n equal to the order of the reaction with respect to polyisoprenyllithium. This graph is shown in Fig. III.10. The slope of the line drawn through the experimental points is 0.5 corresponding to a half order with respect to polyisoprenyllithium. The points suggest that a change in slope to a value of 0.25 might be expected at higher concentrations (shown by dotted line), but the present data are inconclusive on this point. Further experiments are needed at higher polyisoprenyllithium concentrations in order to determine whether this effect is real.

It is interesting to note that this change in order appears to commence at a concentration of about 3×10^{-3} M, suggesting the possibility of tetramers above this concentration. It has been previously mentioned that the spectrophotometric analysis of

FIG. III.11

A plot of Log $\left[- \frac{1}{[M]} \quad \frac{d\,[M]}{dt} \right]$ versus log $\left[\text{pIsLi} \right]$ showing the results of a number of authors.

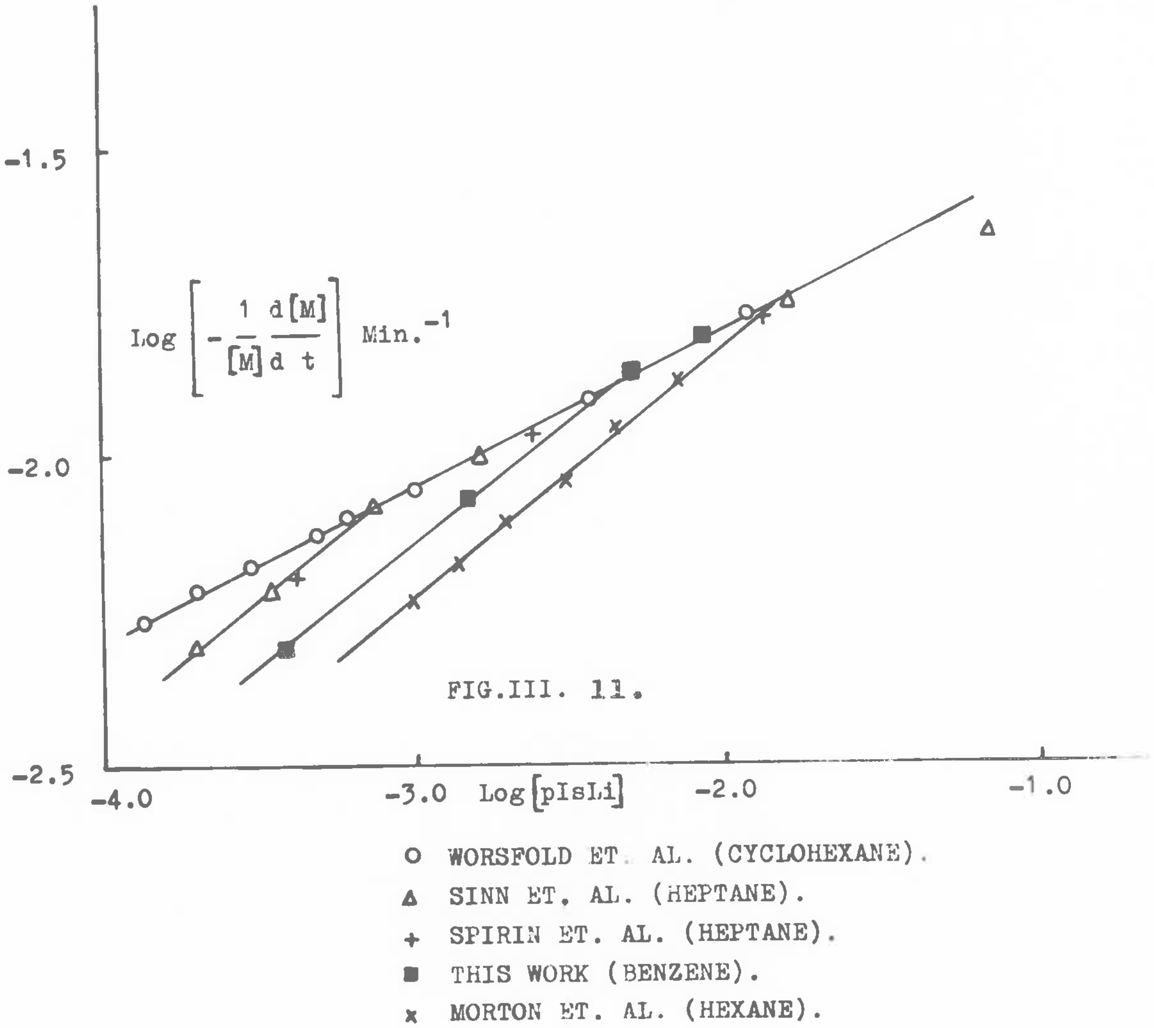

-1.5
-2.0
-2.5
Log $\left[-\frac{1}{[M]}\frac{d[M]}{dt} \right]$ Min.$^{-1}$
-4.0
-3.0
Log [pIsLi]
-2.0
-1.0
○ WORSFOLD ET. AL. (CYCLOHEXANE).
△ SINN ET. AL. (HEPTANE).
+ SPIRIN ET. AL. (HEPTANE).
■ THIS WORK (BENZENE).
× MORTON ET. AL. (HEXANE).

FIG.III. 11.

polyisoprenyllithium suggests a change from dimers to tetramers in this region. As can be seen from Fig. III.11, this change in order has also been observed at approximately the same concentration by Sinn and Patat(22) and by Spirin, Gantmakher and Medvedev(8) who used n-heptane as solvent. However, Morton *et al.*(23) observed this change in order at a higher concentration of approximately 10^{-2}M using n-hexane as solvent. Worsfold and Bywater(1), on the other hand, found no change in order, throughout the concentration range 5 x 10^{-5}M to 5 x 10^{-2}M using cyclohexane as solvent. Bywater, Johnson and Worsfold(24) also found that in cyclohexane, polyisoprenyllithium obeyed Beer's Law, indicating no significant change in the species measured throughout this concentration range.

An association number of four has been found for polyisoprenyllithium in cyclohexane(1) using light scattering, and also in heptane(5) at millimolar concentrations by a viscometric method. However, Morton and Fetters(25) found dimeric

FIG. III.12

Effect of dielectric constant on propagation rate.

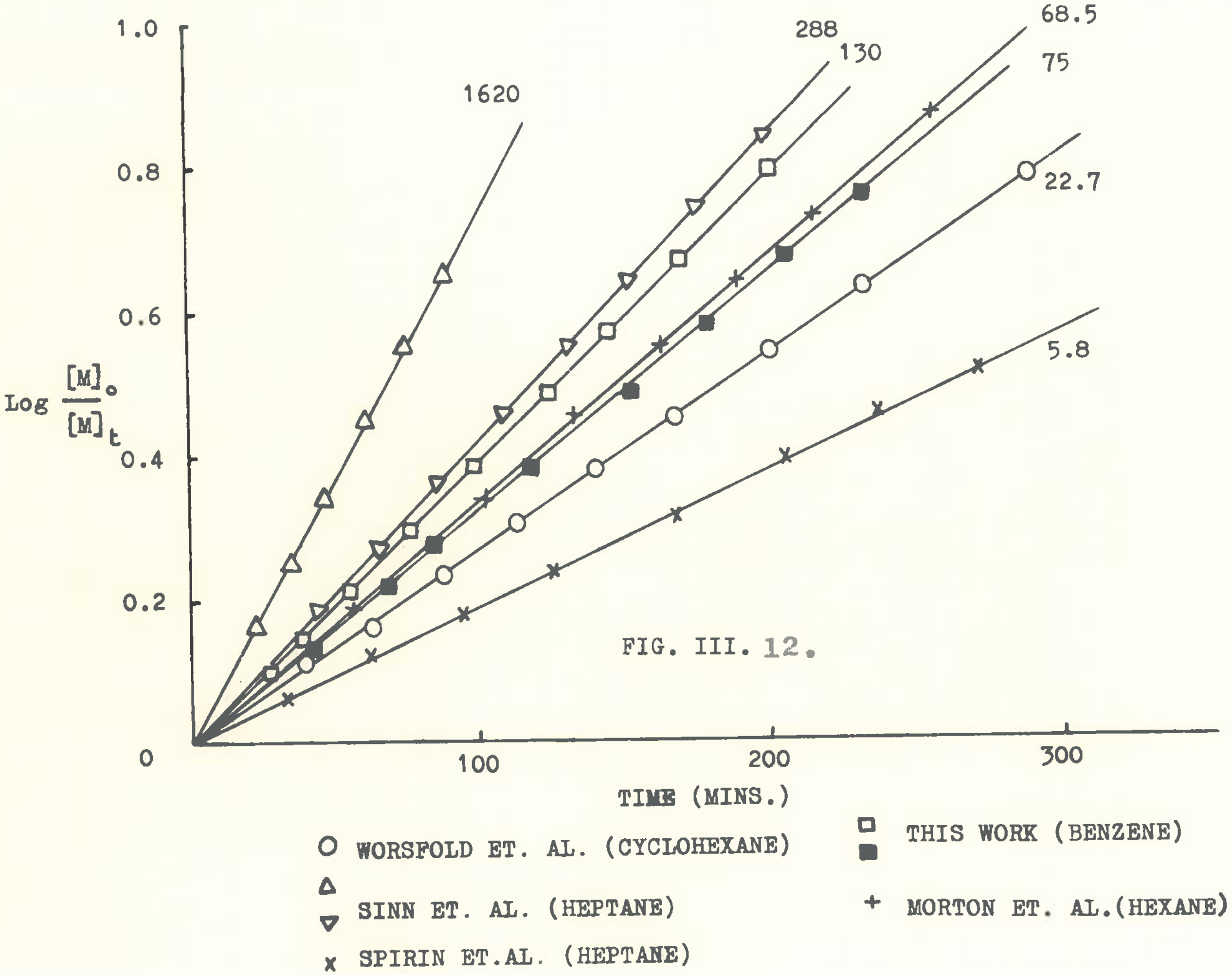

1.0
0.8
0.6
0.4
0.2
0
Log $\frac{[M]_o}{[M]_t}$
100
200
300
TIME (MINS.)
1620
288
130
68.5
75
22.7
5.8
WORSFOLD ET. AL. (CYCLOHEXANE)
SINN ET. AL. (HEPTANE)
SPIRIN ET.AL. (HEPTANE)
THIS WORK (BENZENE)
MORTON ET. AL.(HEXANE)

FIG. III. 12.

association in n-hexane by viscometry studies.

There appears to be a genuine difference between the results of Worsfold and Bywater and those of other authors. It is unlikely that the use of cyclohexane as solvent rather than the other hydrocarbons can account for this disparity. The dielectric constants of these solvents are as follows

Benzene	2.274
Cyclohexane	2.015
n-Heptane	1.931
n-Hexane	1.898

It can be seen that the differences are small, cyclohexane occupying no significant position in the table. A possible explanation for these differences is that the rates of propagation and the degree of association are sensitive to small amounts of lithium salts which are produced by

FIG. III.12

Effect of dielectric constant on propagation rate.

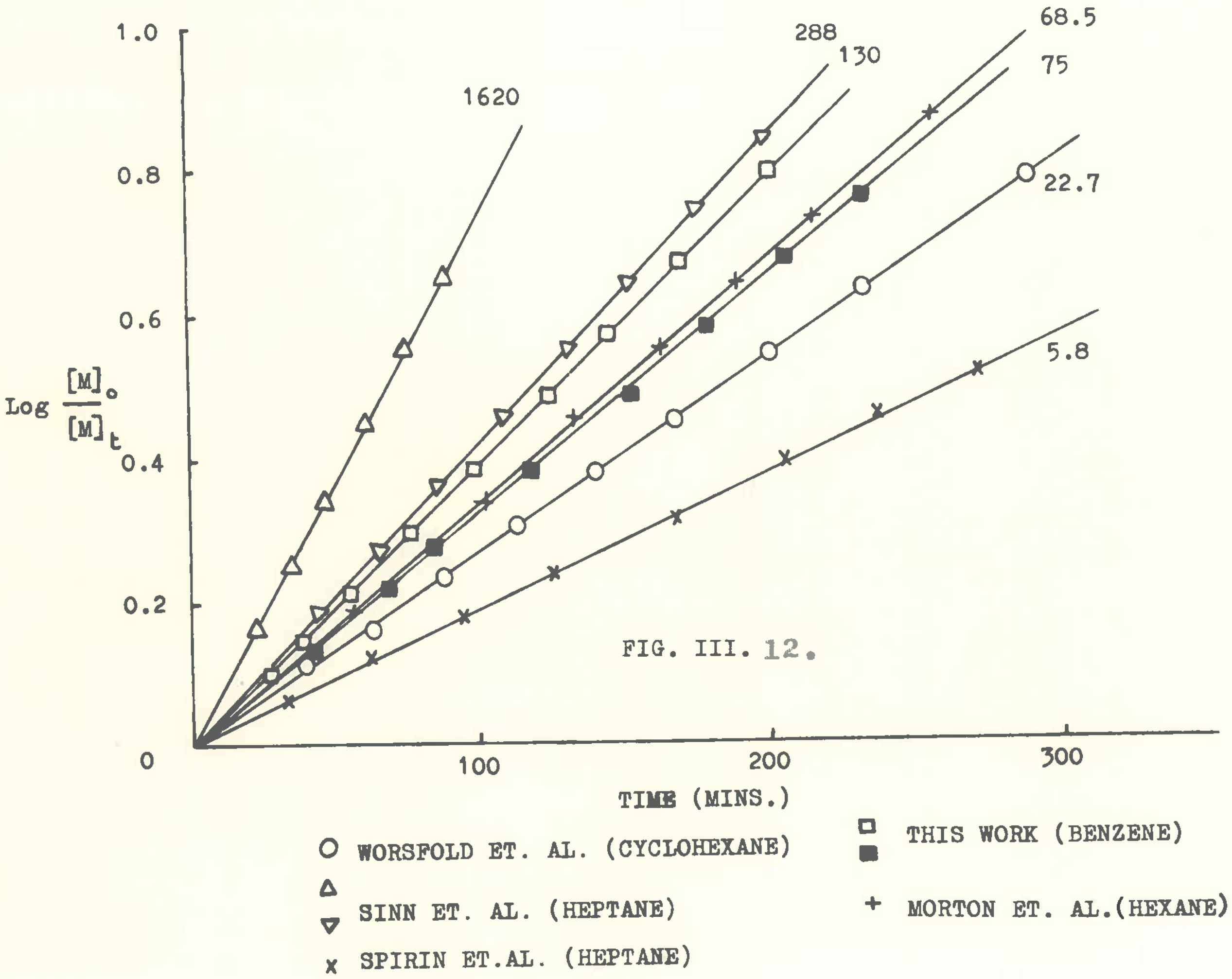

1.0
0.8
0.6
0.4
0.2
0
$\text{Log} \frac{[M]_o}{[M]_t}$
100
200
300
TIME (MINS.)
1620
288
130
68.5
75
22.7
5.8
○ WORSFOLD ET. AL. (CYCLOHEXANE)
△
▽ SINN ET. AL. (HEPTANE)
x SPIRIN ET.AL. (HEPTANE)
□
■ THIS WORK (BENZENE)
+ MORTON ET. AL.(HEXANE)

FIG. III. 12.

termination due to incomplete purging of the apparatus and reactants.

Reference to Fig. III.12 shows that the dielectric constant of the solvent appears to have little effect on reaction rates, the first order plots depending only on the "living end" concentration. This behaviour is in sharp contrast to that found for initiation, where only small changes in the dielectric constant of the solvent cause large differences in initiation rate.

The propagation reaction is governed by the relation

$$R_p = k_2 \left[\text{isoprene}\right]\left[\text{polyisoprenyllithium}\right]^{\frac{1}{2}} \qquad \text{(III.17)}$$

and is a pseudo first order reaction since the polyisoprenyllithium concentration remains constant throughout. The Arrhenius constants have been determined from the temperature dependence of the rates, and the apparent rate constant for propagation is:

$$k_2 = 10^{9.0} \exp - \frac{13,300}{RT} \qquad \text{(III.18)}$$

At 30°C, the experimental value is 7.7×10^{-2} litre mole^{-1} min.$^{-1}$ This value obviously includes the equilibrium constant K_2. Morton$^{(25,26)}$ has attempted to determine the value of K_2 by an independent method, but Bywater claims that no accurate value for k_2 has yet been obtained.

Despite this handicap, it is essential to determine the apparent rate constants of initiation and propagation, as it was the purpose of this kinetic study to determine the temperature dependence of these reactions in order to control the polydispersity of the block copolymer. The results of this study will appear in press shortly.(27)

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CHAPTER IV

CROSS PROPAGATION

1. Introduction

In the case of block copolymer synthesis from monomers A and B in which "living poly-A" is produced as the first step, the following reaction must take place.

$$\text{poly } A^{\ominus} + B \longrightarrow \text{poly } AB^{\ominus} \qquad \text{(IV.1)}$$

This addition of the first B monomer molecule is called cross propagation. In order that a Poisson distribution of molecular weights for the block copolymer be obtained, it is essential that the cross propagation reaction be fast compared with the propagation reaction for monomer B. In free radical polymerisations, an indication of the relative rates of these two processes is provided by a determination of the reactivity ratios of the monomer in question. However, in anionic polymerisation, the propagation steps are highly discriminatory, and since the value of the reactivity ratio is determined from copolymer composition, the method will fail for monomers of widely differing polarity. The polymethylmethacrylate ion pair, for instance, will not add styrene,(1) so that no copolymer can be formed by anionic polymerisation of a mixture of these two monomers.

In more conventional anionic copolymerisation, it is still necessary to enquire whether the standard methods developed for free radical reactions can be applied to the determination of cross propagation and propagation rates in these anionic systems. In the copolymerisation of two monomers M_1 and M_2, four propagation steps are involved. These are:

1) $P_1^* + M_1 \xrightarrow{k_{11}} P_1^*$

2) $P_1^* + M_2 \xrightarrow{k_{12}} P_2^*$

3) $P_2^* + M_2 \xrightarrow{k_{22}} P_2^*$

4) $P_2^* + M_1 \xrightarrow{k_{21}} P_1^*$ (IV.2)

where P_x^* represents an active polymer chain having an 'x' unit at the active centre. The concentration of P_x^* will be the concentration of the free ion-pair in solvents where the active species are associated. The system is usually analysed in terms of two reactivity ratios, $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$, these ratios being determined from the copolymer composition by equation (IV.3)

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]\quad r_1\,[M_1] + [M_2]}{[M_2]\quad r_2\,[M_2] + [M_1]} \qquad \text{(IV.3)}$$

where $\frac{d[M_1]}{d[M_2]}$ represents the relative rate of incorporation of the two monomers into the copolymer, and $[M_1]$ and $[M_2]$ are the concentrations of the two monomers in the mixture. In his recent review, Bywater(2) has shown that the copolymer composition equation is a reasonable approximation if the composition is measured for a polymer of high molecular weight containing several sequences of each monomer in the chain. Since the monomer concentrations change continuously except under the special conditions where $r_1 = r_2$, the copolymer composition is usually extrapolated to zero conversion. Bywater(2) has suggested that this procedure is dangerous for anionic systems since it is equivalent to extrapolation to low molecular weight where preferential initiation to one monomer can influence the copolymer composition.(1)

In hydrocarbon solvents, most of the growing chains are associated, so that the reactivity ratios are strongly dependent on the solvent system,(3,4,5) in particular, the nature of the solvation around the ion-pairs. Bywater(2) has pointed out that interesting effects are observed in the copolymerisation of butadiene-styrene, isoprene-styrene, and isoprene-butadiene in hydrocarbon solvents. In each case, the copolymerisation rate during the first half of the reaction is essentially that of the monomer which homopolymerises more slowly. The initial copolymer formed is richer in this monomer. Korotov(6) has suggested that this is due to a preferential solvation of the growing chain end by one of the two monomers, so that the copolymerisation rate becomes equal to the homopolymerisation rate of this monomer. Despite these difficulties, a number of reactivity ratios have been determined from initial copolymer composition data, but Bywater(2) has suggested that these are of unknown accuracy in view of the uncertainties involved in their determination from the copolymer composition equation IV.3.

It was therefore realised that a study of the cross propagation reaction was necessary in order to determine the conditions under which this reaction should be performed in the block copolymer synthesis. It is to be emphasised that this aspect of the work was not a complete kinetic study aimed at the elucidation of the full mechanism of this step in the synthesis, but was merely undertaken in order to find the best method for producing a monodisperse block copolymer.

2. Kinetic Investigation

The apparatus and method used for this investigation have been briefly outlined in Chapter II. The increase in optical density at 334 mμ due to the formation of polystyryllithium was measured in an SP 700 spectrophotometer, the optical density of the solution then being converted to concentration of polystyryllithium. A set of five experiments was designed to provide information on the concentration and temperature dependence of the cross propagation reaction. Table (IV.1) gives the details of these experiments.

TABLE IV.1

Run	Temp.	Conc. of isoprenyl-lithium in moles/litre	Conc. of styrene monomer in moles/litre
CP_1	21°C	2×10^{-4}	0.52
CP_2	21°C	1×10^{-4}	0.52
CP_3	21°C	3×10^{-4}	0.52
CP_4	27°C	1×10^{-4}	0.52
CP_5	13°C	1×10^{-4}	0.52

The styrene monomer was prepurged with isomerised polystyryllithium prior to sealing on to the reaction vessel. The apparatus described in Chapter II was then evacuated, flamed out, sealed off from the vacuum line, and washed with "living" polystyrene purging solution. The benzene from this solution was then distilled into the reaction bulb which was subsequently sealed off from the complete vessel previously described. The reaction flask was thermostatted, the isoprenyllithium introduced, and its small contribution to the optical density measured. The styrene monomer was then added, mixed thoroughly, and a stop clock started in order to time the reaction. On addition of the monomer, the faint orange colour of polystyryllithium appeared almost instantaneously, and grew in intensity over a short period. Using this technique, it was possible to begin measuring the increase in optical density within 30 secs. of mixing, and with the wavelength set at 334 mμ, a trace of optical density versus time was automatically recorded. That the cross propagation reaction is rapid compared with

FIG. IV.1

Plot of optical density versus time for a typical cross propagation reaction.

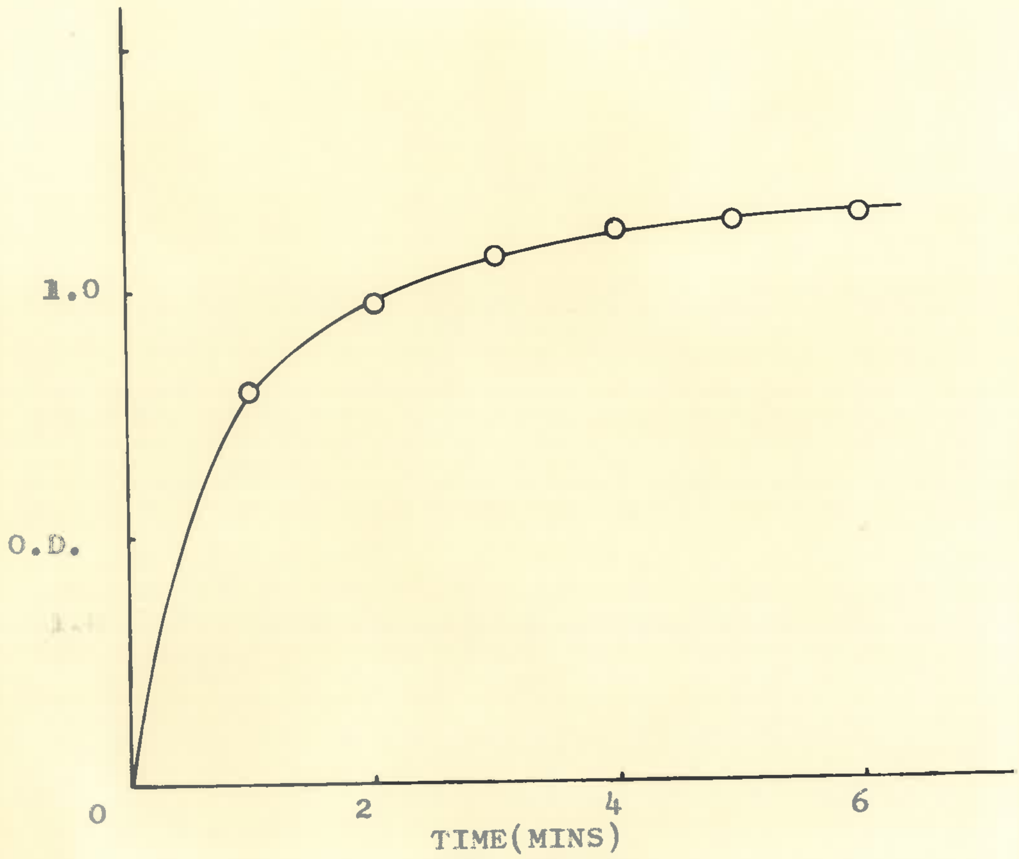

FIG. IV. 1.

propagation of styrene in benzene, was evident from the fact that although the optical density of the solution reached a steady value within minutes, the viscosity of the solution increased slowly over a period of several hours. During cross propagation, the monomer concentration remained sensibly constant since it was present in excess to the extent of 10,000/1 at the start of the reaction.

3. Results and Discussion

(a) Introduction

In each of the five runs, a graph similar to the one for run CP_3 and shown in Fig. IV.1 was obtained. The virtual absence of termination was apparent once again, and the ratios of the final optical density of the solutions for each run coincided with the concentration of isoprenyllithium added. The optical densities were converted to concentrations of polystyryllithium so that a styryllithium concentration versus time curve was obtained for each run. The study of the concentration dependence of the reaction will be discussed first.

(b) Concentration dependence

The reaction studied is given by Equation (IV.4)

$$\mathrm{p\overset{\ominus}{I}s\overset{\oplus}{L}i} \quad + \quad \mathrm{S} \quad \xrightarrow{k_{I.S.}} \quad \mathrm{pIs\overset{\ominus}{S}\ \overset{\oplus}{Li}} \qquad (IV.4)$$

where S refers to styrene monomer and k_{IS} is the cross propagation constant. This reaction has been over simplified, since it is known that isoprenyllithium is associated in benzene. The rate of reaction is given by equation (IV.5)

$$\text{Rate} = \frac{d\left[S^{\ominus}\right]}{dt} = \frac{d\left[Is^{\ominus}\right]}{dt} = k_{I.S.}\left[Is^{\ominus}\right]^{x}\left[S\right] \qquad (IV.5)$$

The assumption is made that the reaction is first order with respect to styrene monomer. The two values to be determined are x and $k_{I.S.}$.

In view of the strong evidence for dimeric association of isoprenyllithium, a half order dependence on concentration of isoprenyllithium might be expected according to the scheme;

$$(Is^{\ominus}Li^{\oplus})_2 \overset{K_2}{\rightleftharpoons} 2\,(Is^{\oplus}Li^{\ominus}) \qquad (IV.6,1)$$

$$Is^{\ominus}Li^{\oplus} + S \xrightarrow{k_p} IsS^{\ominus}Li^{\oplus} \qquad (IV.6,2)$$

$$IsS^{\ominus}Li^{\oplus} + S \xrightarrow{k_p} IsS_2^{\ominus}Li^{\oplus} \qquad (IV.6,3)$$

The concentration of isoprenyllithium present initially was known, so that the concentration at any time t could be found by subtraction of the polystyryllithium concentration obtained from the spectrophotometric measurements.

A plot of $\log \dfrac{[Is^{\ominus}_o]}{[Is^{\ominus}_t]}$ versus t gave a straight line graph for all five runs, the value of the gradient being equal to $k_{IS}[S]/_{2.303}$. Good agreement was found for runs CP_1, CP_2 and CP_3, the value for the cross propagation constant at 21°C being 2.09 litre mole^{-1} min^{-1} assuming this first order dependence on monomer.

(c) Proposed Mechanism

The first order dependence of the cross propagation with respect to "living ends" can be explained in terms of the following reaction scheme, assuming dimeric association of isoprenyllithium.

$$(\text{Is}^{\ominus}\text{Li}^{\oplus})_2 + \text{S} \xrightarrow{k^1_{IS}} \text{IsS}^{\ominus}\text{Li}^{\oplus} + \text{Is}^{\ominus}\text{Li}^{\oplus}$$

$$\text{Is}^{\ominus}\text{Li}^{\oplus} + \text{S} \xrightarrow{k_{IS}} \text{IsS}^{\ominus}\text{Li}^{\oplus} \qquad \text{(IV.8)}$$

$$\frac{d(\text{IsS}^{\ominus}\text{Li}^{\oplus})}{dt} = k^1_{IS}[\text{S}]\left[(\text{Is}^{\ominus}\text{Li}^{\oplus})_2\right] + k_{IS}[\text{S}]\left[\text{Is}^{\ominus}\text{Li}^{\oplus}\right] \qquad \text{(IV.9)}$$

where k^1_{IS} refers to the reaction of a styrene monomer molecule with associated isoprenyllithium, and k_{IS} refers to the reaction with the monomeric form. From equation (IV.9),

$$\frac{1}{[S]} \frac{d\left[(IsS^{\ominus}Li^{\oplus})\right]}{dt} = k\left[(Is^{\ominus}Li^{\oplus})_2 + (Is^{\ominus}Li^{\oplus})\right]$$

$$= k\left[IsLi\right]_{total} \qquad (IV.10)$$

on the assumption that there is little difference between k'_{IS} and k_{IS}; k is then the measured first order rate constant in $min.^{-1}$

(d) Temperature Dependence

The three runs CP_5, CP_2 and CP_4 were identical in all respects except that they were carried out at 13°C, 21°C and 27°C respectively. Temperature control in runs CP_5 and CP_4 was difficult, since only the measuring cell could be thermostatted during the time of the experiment, which was of the order of ten minutes. However, useful information was derived from the temperature dependence study, and this is contained in Table IV.2.

TABLE IV.2

Temp. °C	k l. mole^{-1} min^{-1}	log. k.
13	1.978	0.296
21	2.09	0.3201
27	2.591	0.4135

A plot of log k versus 1/T gave an energy of activation of 5 ± 1.5 K cals, and an A factor of the order of 10^5.

For polystyryllithium in benzene at 30°C, $k_p > 30$ according to Worsfold.(7) From the values summarised in Table 1 of reference 2 in this Chapter, no A factor is given, and the energy of activation is $<$ 14 K cals/mole. Since the energy of activation for cross propagation is 5 ± 1.5 K cals, the cross propagation reaction should be performed at a low temperature, say 10°C, in order to yield a narrow distribution of molecular weights for the block copolymer synthesis.

As in the case of the initiation of isoprene by n-butyllithium, the A factor is lower than normal, consistent with the large negative entropy of formation of an associated intermediate complex. The results of this investigation will be published shortly.

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CHAPTER V

BLOCK COPOLYMER SYNTHESIS

1. Introduction

A model block copolymer would be homogeneous in molecular weight and composition. For the simplest block copolymer of isoprene and styrene, all polyisoprene segments would be of the same length, as would be the polystyrene segments. No homopolymer would be present, and the microstructure of the polymer chains would be the same in each polymer molecule. Thus the polyisoprene would be say all cis or all trans form. If this hypothetical polymer molecule was to be synthesised, all polyisoprene chains must begin to grow at the same time, so that initiation must be complete before any propagation occurred. The polyisoprene molecules must grow at the same rate and continue growing until all isoprene monomer polymerised. The chains must then stop growing at the one instant, but remain unterminated. Without a single anion being destroyed, the styrene monomer must be added. Each polyisoprene molecule should then add one styrene molecule before any styrene propagation occurred. The rate of addition of styrene monomer must be the same for each polymer molecule until all monomer polymerised. Immediately the molecules had grown fully, they must be terminated.

Obviously such a synthesis is an impossibility, but one should be able to exercise the maximum control over each step in the synthesis, thereby producing a polymer which approximated this ideal. Thus k_i/k_{11}, the ratio of the rate of initiation to the rate of propagation of isoprene must be as large as possible, as must be k_{12}/k_{22}, the ratio of the rate of cross propagation to the rate of propagation of styrene. The kinetic study of the individual steps in the synthesis indicated how these conditions could best be satisfied.

2. Synthesis

The synthesis involved three separate steps. These were the preparation of polyisoprenyllithium "seed", the polymerisation of isoprene, and the addition of styrene. Each reaction was carried out in a separate vessel, and the experimental details are now given.

(a) Formation of initiator "seed"

The results discussed in Chapter III show that if a "seed" of molecular weight 3,000 is produced, the complete conversion of butyllithium to polyisoprenyllithium is assured. A solution of butyllithium in benzene of known concentration was reacted with a solution of isoprene monomer in benzene. The concentration of isoprene was such as to yield a number average molecular weight for the "seed" of approximately 3,000. The reaction was performed in a vessel similar to that shown in

FIG. V.1

Effect of temperature on k_i and k_p.

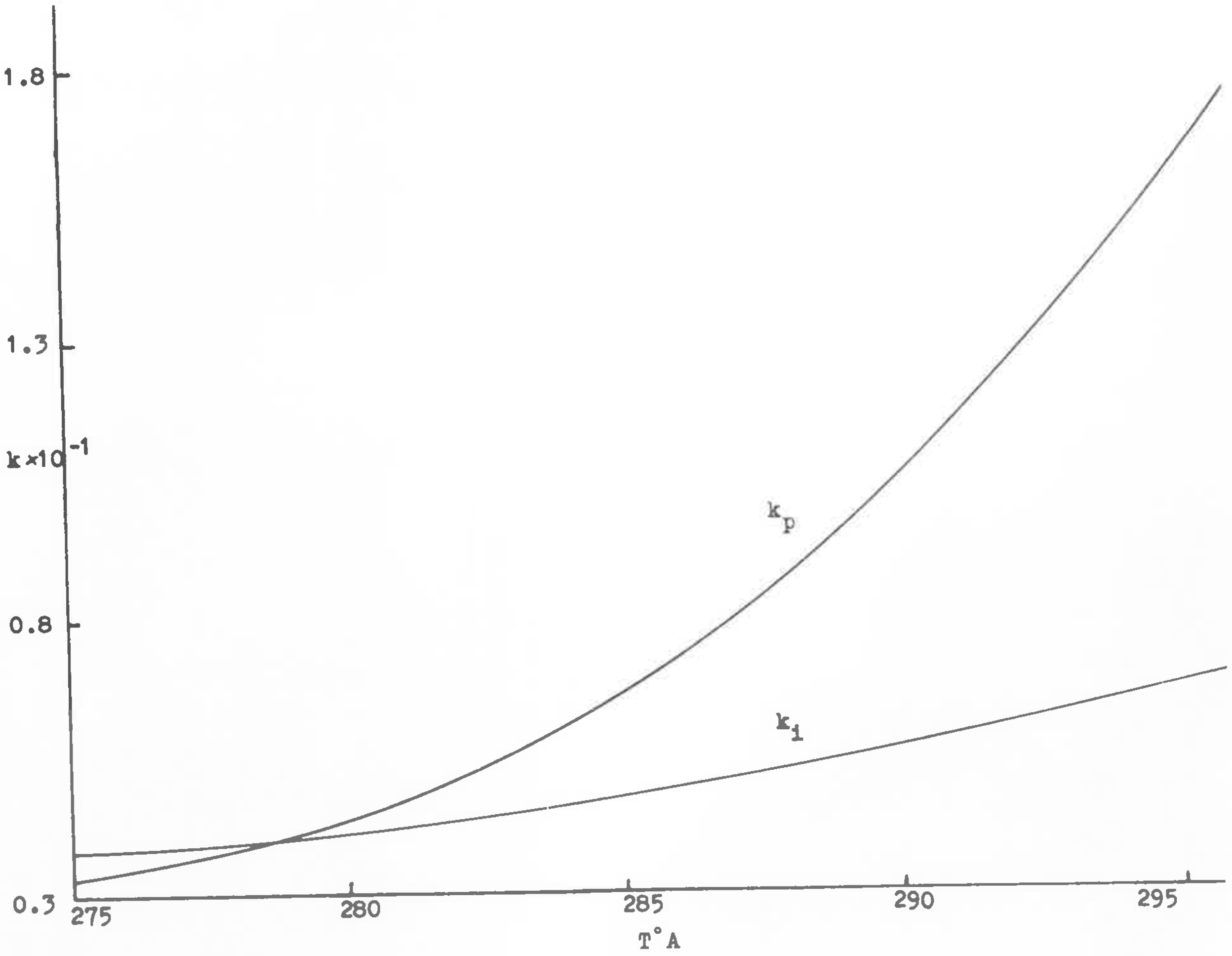


FIG. V.1.

Fig.II.2. The kinetic study of isoprene polymerisation in benzene discussed in Chapter III yielded values for the energy of activation of initiation and propagation of 4.3 Kcals. and 13.3 Kcals. respectively. Since the polydispersity of the polymer depends largely on the rate of initiation compared with the rate of propagation, performing the initiation step at a low temperature will provide the most favourable conditions for the production of a narrow molecular weight distribution "seed". The effect of temperature on the rates of initiation and propagation is seen in Fig.V.1. The rate constants k_i and k_p are plotted as a function of temperature. The values of k_i and k_p are calculated from the expressions $k_i = 10^2 e^{\frac{-4,300}{RT}}$ and $k_p = 10^9 e^{\frac{-13,300}{RT}}$. It can be seen at once from the graph, that the propagation rate constant is much more temperature dependent than the initiation rate constant. At approximately 6.5°C, $k_i = k_p$, but the rates of initiation are not equal at this temperature. The rates of expression are determined by the following expressions.

$$R_i = k_i \left[BuLi \right] \left[M \right]$$

and

$$R_p = k_p \left[pIsLi \right]^{\frac{1}{2}} \left[M \right]$$

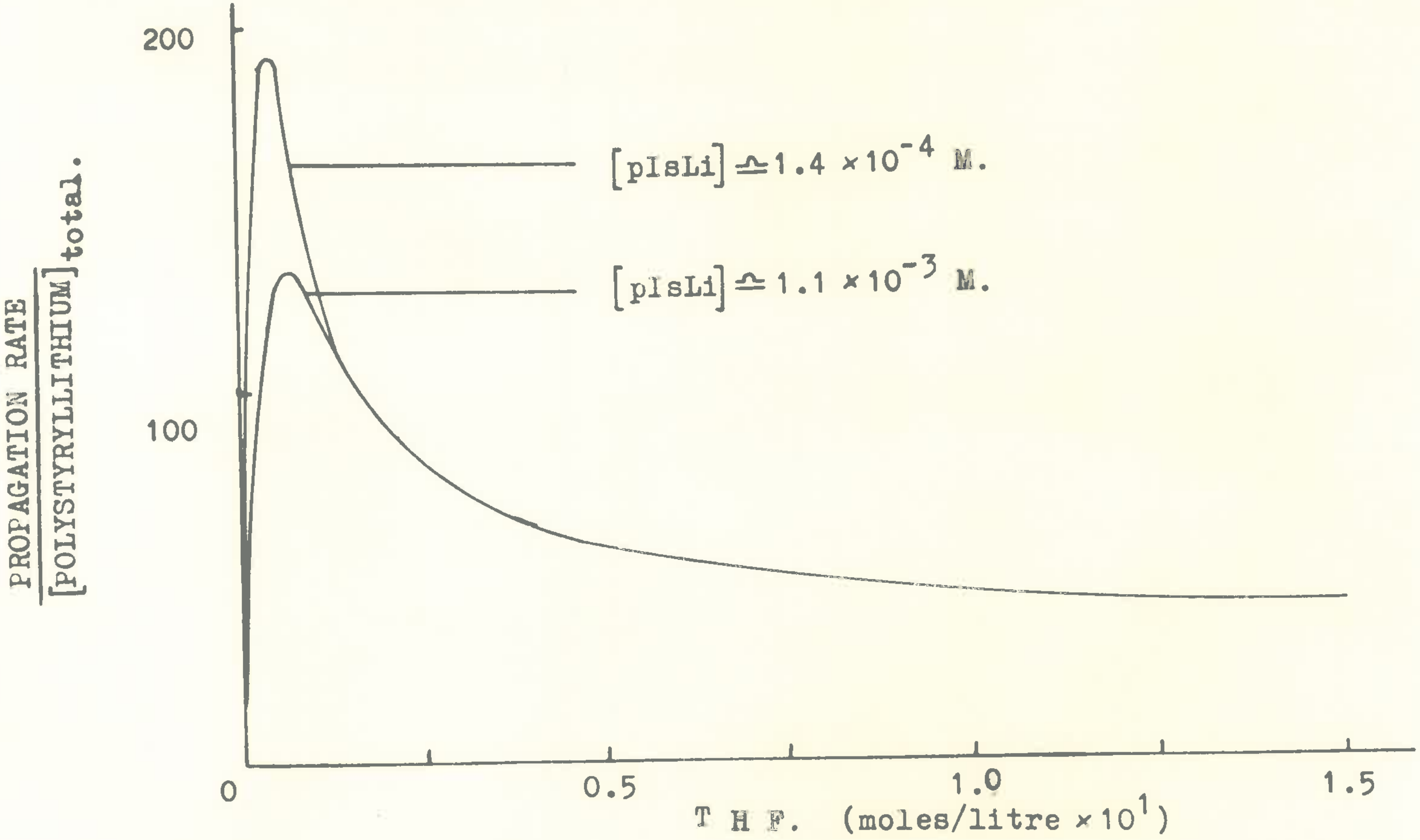
$$\therefore \quad \frac{R_i}{R_p} = \frac{k_i \left[BuLi \right]}{k_p \left[pIsLi \right]^{\frac{1}{2}}}$$

Although at 5°C, $k_i \simeq k_p$, $\left[BuLi \right] \neq \left[pIsLi \right]^{\frac{1}{2}}$. These two values will change continuously throughout initiation. In the early stages of initiation, pIsLi is very small, so that $R_i \gg R_p$. Towards the end of initiation, $\left[BuLi \right]$ is very small, so that the rate of propagation may become greater than the rate of initiation, causing a broadening in the molecular weight distribution of the "seed". However, since benzene freezes at +4°C, it is not possible to perform the initiation reaction at a temperature lower than +5°C, so that the seed must have some degree of inhomogeneity of molecular weight. In the system chosen, however, it is impossible to choose reaction conditions which will produce a better product.

Once the "seed" was prepared, its concentration was determined by potentiometric titration. Measured volumes were then sealed off in breakseal ampoules ready for the synthesis of block copolymers of varying molecular weight and composition. Although it is possible to exercise the same control over the initiation step by simply allowing butyllithium to react at 5°C with all of the isoprene required to complete the first stage of the block copolymer synthesis, it was found more convenient to use the "seeding" technique. The propagation reaction was allowed to proceed at room temperature.

FIG. V.2.

Effect of THF on propagation rate of styrene in benzene.



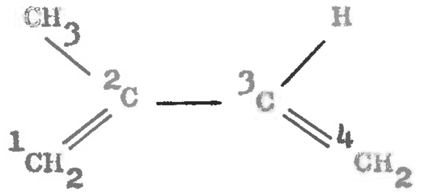
200
100
$\frac{\text{PROPAGATION RATE}}{[\text{POLYSTYRYLLITHIUM}]_{\text{total}}}$.
$[\text{pIsLi}] \simeq 1.4 \times 10^{-4}$ M.
$[\text{pIsLi}] \simeq 1.1 \times 10^{-3}$ M.
0
0.5
1.0
1.5
T H F. (moles/litre $\times 10^{1}$)

FIG. V.2.

One further method of exercising control over initiation so that it is more rapid than propagation is to add small amounts of a highly polar solvent. Kropacheva and associates(1) showed that the increased rate of polymerisation on addition of THF in amounts similar to the concentration of butyllithium was due to a dramatic increase in initiation rate by comparison with propagation. Bywater studied this effect for styrene(2), as well as isoprene(3) polymerisations. This effect of traces of THF on isoprene polymerisations was also studied by Morton and associates.(4)

Except at very low THF concentrations, chain initiation becomes too rapid to be measured by conventional means. The effect on the propagation reaction for styrene in benzene is complex, as shown by Fig. V.2. This figure was obtained from reference (5) of this Chapter. Bywater interpreted his results as indicating the presence of at least four different polymer species in labile equilibrium: the normal polymer ion-pair dimer $(RM_xLi)_2$, its dissociation product RM_xLi, a monoetherate RM_xLi, THF, and a dietherate $RM_xLi2THF$. The ion-pair dimer was assumed to be unreactive, the other species having varying degrees of activity. When sufficient THF has been added to produce mainly dietherate, the propagation reaction was slowest. Bywater claims(5) that at about 0.15 molar THF, all the polystyryllithium is in the form $RM_xLi.2THF$. The overall propagation rate at this point is not greatly different from that observed in pure benzene, nor is the dielectric constant of the solvent. The initiation reaction at this point, however, is far too rapid to allow its measurement. The same effect has been observed for isoprene by Morton and co-workers(6,7), and Worsfold and Bywater.(3) No maximum was found in the propagation rate as the concentration of THF was increased, suggesting that only a monoetherate exists in this case. A higher concentration of THF was necessary to dissociate polyisoprenyllithium ion-pair aggregates than for polystyryllithium aggregates. Thus, performing the polymerisation of isoprene by n-butyllithium in a mixed solvent of benzene and THF (0.2 to 0.3 moles/litre), should produce a polyisoprene sample of narrow molecular weight distribution.

The main objection to the use of this technique lies in its effect on the microstructure of the polyisoprene. Isoprene monomer has the following structure



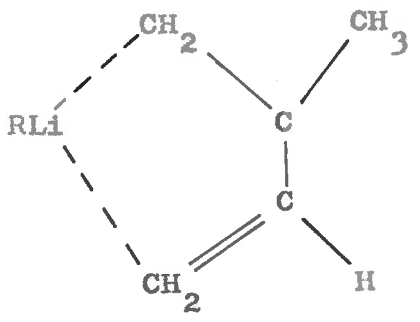
(V.1)

As a result of this, four different isomers of polyisoprene are possible. These are 1:2, 3:4, cis-1:4 and trans-1:4 polyisoprene. Lithium and its compounds are unique amongst the alkali metal catalysts in polymerising isoprene to the cis-1:4 isomer. Cooper(8) has suggested a reason for the stereospecificity of this reaction. Lithium alkyls add to the monomer to form a polymer containing one end group derived from the catalyst. For example, with isoprene

$$\mathrm{LiR} + \mathrm{CH_2{=}C(CH_3)-CH{=}CH_2} \rightarrow \overset{\oplus}{\mathrm{Li}}\overset{\ominus}{\mathrm{C}}\mathrm{H_2-C(CH_3){=}CH-CH_2R}$$

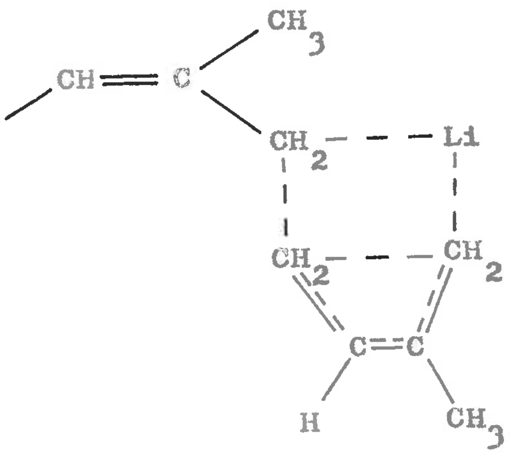
Representation of the initiation reaction in this way does not emphasize the characteristics which distinguish lithium from other alkali metals. Lithium possesses much stronger complexing power than sodium or potassium, exhibiting some of the characteristics of a polyvalent atom. This enables it to form cyclic complexes and thus maintain a considerable degree of steric control in its reactions.

In the case of isoprene, it has been proposed that a complex is formed of the structure V.2.



(V.2)

This complex can rearrange to a cyclic activated complex (V.3) prior to addition of the monomer molecule.(9)



(V.3)

Continuation of this process would produce all cis polymer. Head-to-tail addition in the polymer is ensured by the difference in electron density at the two terminal carbon atoms of the isoprene molecule.

The effect of ethers such as THF on the polymerisation is to alter the microstructure of polyisoprene, the percentages of each isomer changing according to table (V.1). If sufficient THF is added to benzene to convert all polyisoprenyllithium ion-pair aggregates to the monoetherate, the product of polymerisation is the same as if pure THF was used as solvent.

TABLE (V.1)

Solvent	% cis-1:4	% trans-1:4	% 1:2	% 3:4
Benzene	93	0	0	7
T.H.F.	0	30	16	54

The reason for the change of microstructure from 93% cis-1:4 to the mixture of isomers for THF shown in Table (V.1) is that complexing of THF with the lithium alkyl to form the monoetherate prevents formation of intermediates of type (V.2) Donation of electrons from the oxygen atom of the ether facilitates charge separation of the partly ionic lithium-carbon bond. The reaction therefore becomes more like a normal anionic polymerisation and gives polymers of essentially the same structure as the other alkali metals. Earlier work by Hsieh and Tobolsky(10) demonstrated that the temperature at which the polymerisation is performed has a small effect on the microstructure of the polymer. Reducing the temperature under otherwise constant conditions reduced the proportion of trans-1:4 isomer, the increase in 1 : 2 addition being greater than the increase in 3 : 4 additions.

(b) Polymerisation of isoprene

The first stage of the block copolymer synthesis was the polymerisation of isoprene to "living" polyisoprenyllithium. For a block copolymer of total molecular weight 5×10^{-5}, containing 50% isoprene and 50% styrene, the molecular weight of each segment will be 2.5×10^{5}.

Knowing the concentration of polyisoprenyllithium seed, it was possible to calculate the volume of initiator and isoprene monomer required to produce 5 gms. polyisoprene of molecular weight 2.5×10^{5}. The total weight of block copolymer produced would be 10 gms. in the present case. As polymerisation occurred, the solution became viscous, and this was the factor controlling the weight of polymer prepared, since it was considered inadvisable to have higher than a 3% solution of block copolymer at the end of the synthesis. In order to comply with this restriction, very large vessels would be required for synthesis of more than 10 gms. of polymer.

FIG. V.3.

Vessel for polymerisation of isoprene as the first step in block copolymer synthesis.

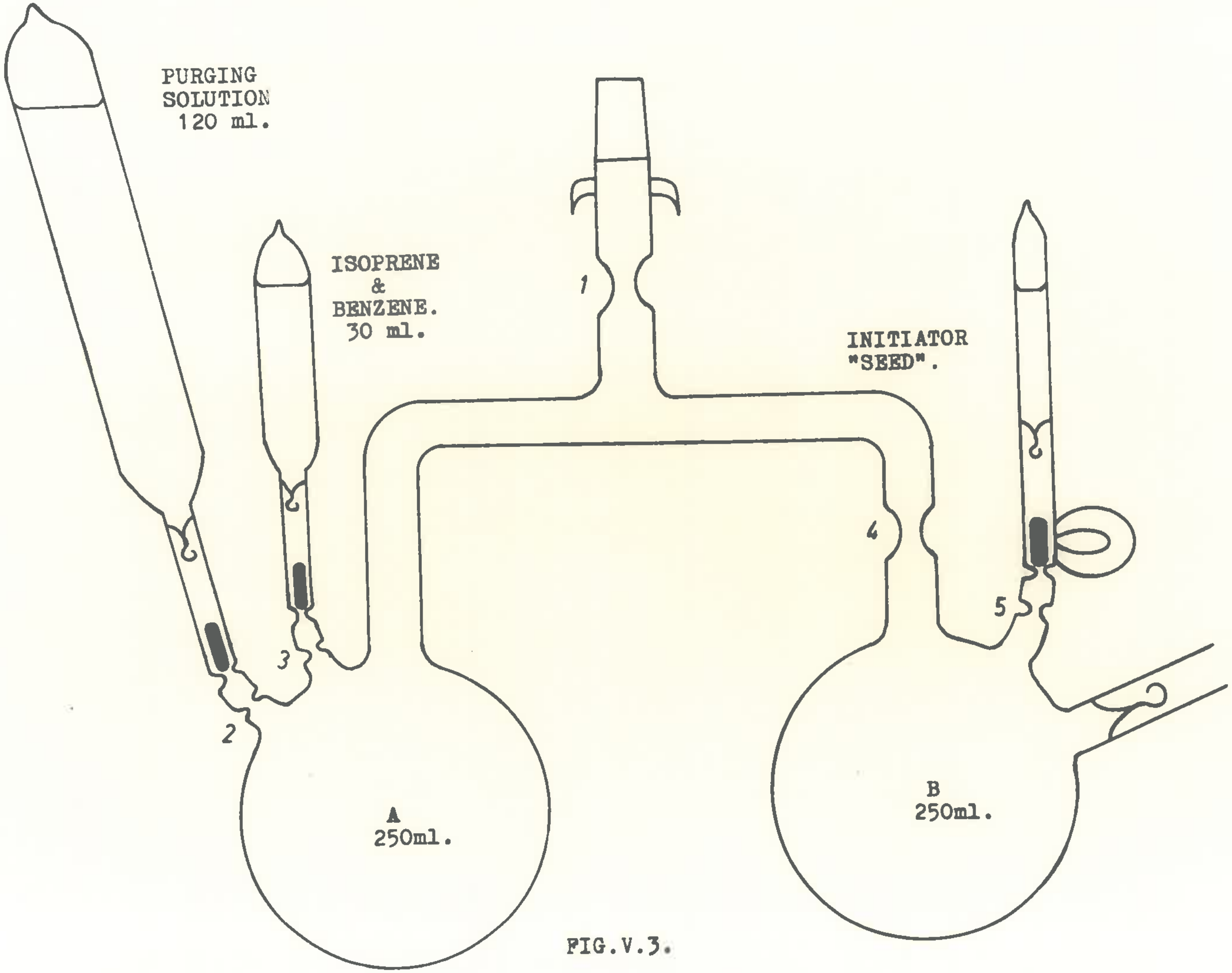

PURGING
SOLUTION
120 ml.
ISOPRENE
&
BENZENE.
30 ml.
1
INITIATOR
"SEED".
2
3
4
5
A
250ml.
B
250ml.

FIG.V.3.

The apparatus is shown in Fig. V.3. Two ampoules were sealed on to flask A. One contained 150 mls. benzene solution and isomerised polystyryllithium. This solution was used to purge the reaction vessel, the benzene then being used in the reaction. The other ampoule contained 5 gms of isoprene monomer in benzene, the total volume being 30 mls. Flask B was the reaction flask. An ampoule containing a calculated volume of initiator "seed" was sealed on to this vessel. A large break seal was also sealed on so that the polyisoprenyllithium produced in this first stage could be used to produce the block copolymer.

The apparatus was placed on the vacuum line and degassed. Pumping was continued as the apparatus was flamed out several times. When the pressure in the vessel was below 5×10^{-6}, the apparatus was sealed off at constriction 1. The purging solution was introduced and the empty ampoule sealed off at constriction 2. The breakers in the remaining two ampoules were held in place by a horseshoe magnet taped on as shown, so that the purging solution could be tipped around the entire apparatus with no fear of accidental fracture of a break seal. This washing process was continued over a period of twelve hours, after which the solution was tipped back into flask A. The benzene was then distilled back into B and washed around to remove traces of purging material, and tipped back into A. This process was repeated four times, after which the benzene was distilled completely into B, leaving a red-brown mass of isomerised polystyryllithium in A. Since the benzene was distilled from living polymer, it must be free from terminating material. The isoprene plus benzene was introduced into A, the empty ampoule being sealed off at constriction 3. Since the polystyryllithium in A was isomerised, no polymerisation of the isoprene monomer occurred, but terminating material was removed from the solution. After one hour, the benzene and isoprene solution was distilled into B, which was then sealed

FIG. V.4

Vessel for addition of styrene to living polyisoprene as the second stage in block copolymer synthesis.

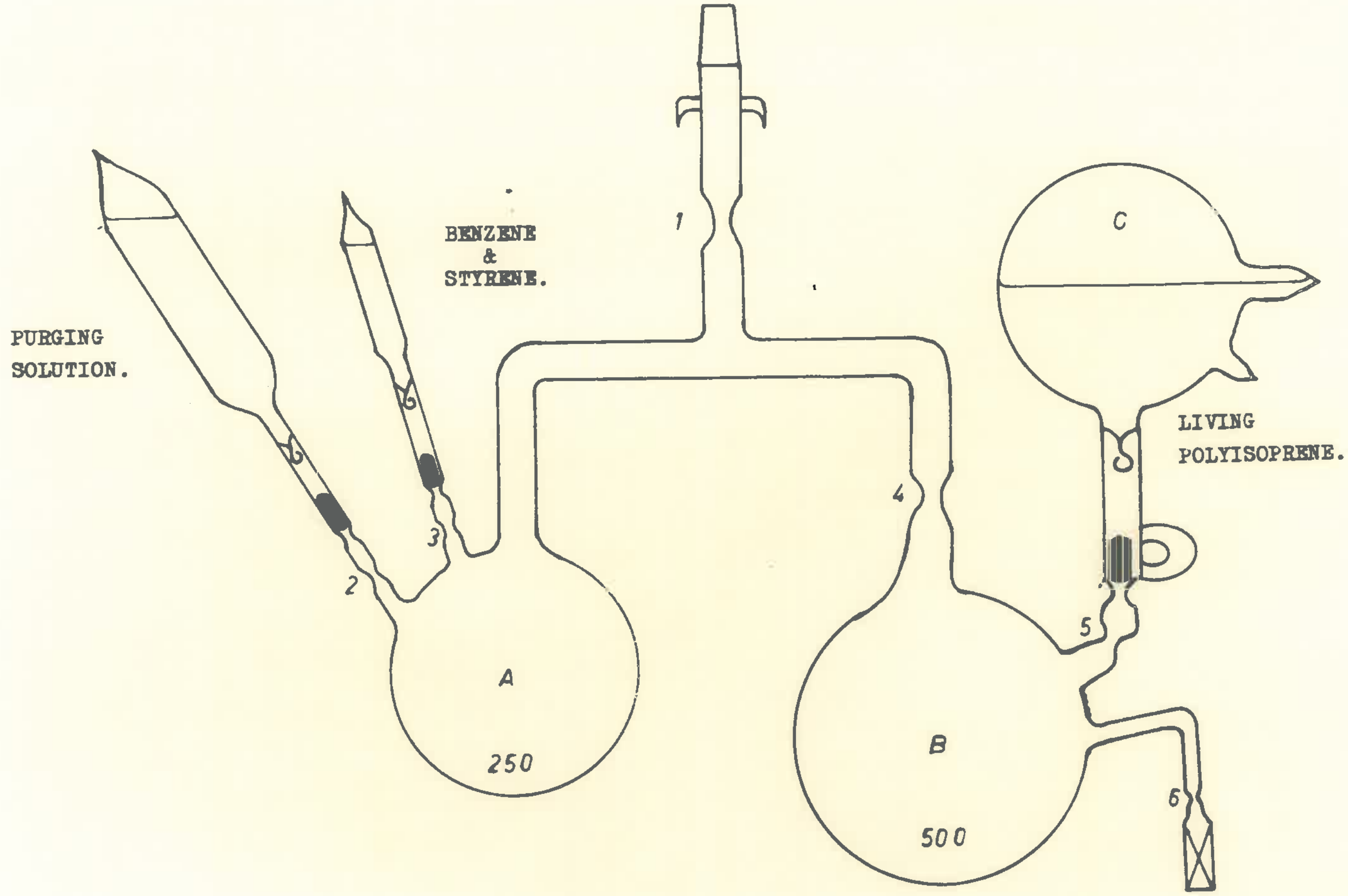

PURGING SOLUTION.
BENZENE & STYRENE.
1
2
3
4
5
6
A
250
B
500
C
LIVING POLYISOPRENE.

FIG. V.4.

off at constriction 4. The initiator was added, its ampoule sealed off at constriction 5, and the reaction allowed to proceed at room temperature until complete. The flask was periodically shaken to ensure homogeneous reaction conditions, the time for complete reaction being calculated from the rate equation.

(c) Addition of styrene

The cross propagation study showed that this reaction should be performed at a low temperature of say 10°C. The propagation step was carried out at room temperature. This step in the synthesis was performed in the apparatus shown in Fig. V.4. In this case, the same procedure was adopted as in the case of the isoprene polymerisation, except that the "seed" was replaced by the "living" polyisoprenyllithium prepared in the first stage. On completion of the cross propagation, the faint orange-red colour of the styryl ions persisted throughout the propagation step. When sufficient time had elapsed for the styrene monomer to be consumed, the 1 cm. optical cell was sealed off at constriction 6, and the concentration of polystyryllithium checked in a spectrophotometer . No loss of concentration of lithium complex was detected, indicating that the entire process was conducted in the absence of any detectable termination. On completion of polymerisation, air was admitted to the reaction flask so that the polymer was terminated. The reason for terminating the polymer soon after completion of the reaction was to avoid a broadening of the molecular weight distribution due to depropagation.

3. Depropagation of living polymers

In discussing the depropagation reaction, a general case of anionic polymerisation is referred to, as by Szwarc(11) in his original treatment of the problem. The propagation reaction involves the following stages

$$M_1^* + M \longrightarrow M_2^*$$

$$M_2^* + M \longrightarrow M_3^*$$

$$M_j^* + M \longrightarrow M_{j+1}^*$$

M_1^* is a growing polymer molecule and M is a monomer molecule. It is assumed that the rate constants of these reactions are independent of j, and equal to k_p. The principle of microscopic reversibility demands the occurrence of the reverse reactions, and the unimolar rate constant of this depropagation reaction, assumed again to be independent of j, is denoted by k_d.

Since there is no termination, the system must eventually reach an equilibrium state, the equilibrium concentration M_e of the monomer being determined by the equation

$$\frac{dM}{dt} = -k_p M_e \sum_{1}^{\infty} M^*_j - k_d \sum_{2}^{\infty} M^*_j = 0 \qquad (V.1)$$

where M denotes concentrations. If the initial concentration of all active species is denoted by C, then

$$\sum_{1}^{\infty} M^*_j = C \quad \text{and} \sum_{2}^{\infty} M^*_j = C - M^*_{1,e}$$

where $M^*_{1,e}$ denotes the equilibrium concentrations of the active species M^*_1. For a polymerisation proceeding to a high molecular weight product, $M^*_{1,e}$ is negligible compared with C, so that

$$M_e \simeq k_d/k_p = K_e \qquad (V.2)$$

The equilibrium concentration of monomer is thus independent of the initial concentrations of the monomer and catalyst, and is determined uniquely by the temperature, and by the nature of the monomer, the polymer, and the solvent.

The equilibrium molecular weight distribution of "living" polymers may be calculated, and is given by equation (V.3)

$$M^*_{j,e} = M^*_{1,e}\,(1 - M^*_{1,e}/C)^{j-1} \qquad (V.3)$$

Thus, the equilibrium molecular weight distribution is given by the usual function named by Flory "the most probable distribution", and leads to $\bar{N}_n = M_T/C$ and $\bar{N}_W/\bar{N}_N = 2$ (M_T, the total amount of monomer polymerised, is given by the equation $M_T = M_{initial} - M_e$) Although the equilibrium molecular weight of "living" polymers is the same as that characterised by many conventional processes, an entirely different distribution of molecular weight may be formed immediately after completion of the polymerisation process. For example, if $k_p \gg k_d$, and the half-life time of the depropagation is long compared with the time of the experiment, then a rapid dispersion of all the active species M_1^* in the monomer yields a product with a Poisson distribution, the polymer being essentially monodisperse.

Wherever a high molecular weight product is obtained, the concentration of unpolymerised monomer is minute compared with the total amount of monomer. Hence the total amount of polymerised monomer is essentially constant, say M_t, the total number of polymer molecules is also constant, C, and therefore the number average degree of polymerisation $\bar{N}_n$ is also approximately constant, namely $\bar{N}_n = {M_t}/C$. On the other hand, the higher average, $\bar{N}_W$, the weight average degree of polymerisation varies with time.

The weight average degree of polymerisation is given by equation (V.4)

$$\bar{N}_W = \left(\sum_1^\infty j^2 M_j^*\right)/M_t \qquad (V.4)$$

Assuming constancy of M_t according to the steady state approximation, $dM_t/dt = 0$, so that

$$\frac{d\bar{N}_W}{dt} = \left(\sum_1^{\infty} j^2 \, dM^*_j/dt \right) / M_t \qquad (V.5)$$

This leads to equation (V.6)

$$\frac{d\bar{N}_W}{dt} = \frac{2k_d}{\bar{N}_n} \cdot (1 - X_1 \bar{N}_n) \qquad (V.6)$$

where X_1 is the mole fraction of M^*_1

At equilibrium, $M^*_{1_e} = C/\bar{N}_n$, and $X_1 = \frac{1}{\bar{N}_n}$ so that $\frac{d\bar{N}_W}{dt} = 0$. If the steady state assumption is abolished then M_T and $\bar{N}_n$ are no longer constant, and $d\bar{N}_W/dt$ is given by equation (V.7)

$$\frac{d\bar{N}_W}{dt} \bumpeq k_d \frac{(\bar{N}_W)(X_{1,e} - X_1)}{(\bar{N}_n)} \qquad (V.7)$$

which agrees with equation (V.6) when $\bar{N}_W/\bar{N}_n = 2$, that is, when the system is close to the most probable distribution. If the non-equilibrium distribution is of the Poisson type, then the approximate equation (V.6) gives a rate of change twice as high as the more correct equation (V.7) Thus, while a rapid mixing of active species M_1^* with monomer leads initially to a Poisson distribution if $kp \gg kd$, unless the polymer is terminated at this stage, the "most probable distribution" of molecular weights will occur in time.

Following Szwarc's original treatment of the problem, Miyake and Stockmayer(12) have published a full treatment of the effect of depropagation on the molecular weight distribution. They have shown that the time required for the initial narrow Poisson distribution to charge to the final "most probable" distribution is proportional to the square of the average chain length. When initiation is at least as fast as propagation, a Poisson distribution may be obtained, but a less narrow distribution will be achieved when initiation is slow. By purely theoretical means, Stockmayer has shown that a polymerisation may be divided into three separate stages. These are (1), a well defined initial stage during which free monomer concentration, initiator concentration, and the average chain lengths all follow the characteristic of irreversible polymerisation; (2), a stage of transient behaviour, during which the free monomer concentration falls off to essentially its equilibrium value M_e given for long chains by $M_e \hat{=} {}^{k}d/_{k_p}$, while number and weight average chain lengths each stay near their Poisson values of ${}^{M}o/I_o$; and (3), the stage of redistribution, during which initiator concentration and weight average chain length slowly reach their equilibrium values. It was shown that the time for completion of the first two stages is ofthe order of $\frac{1}{kIo}$, while the time for completion of the redistribution process is of the order

$\frac{1}{k_d(\frac{Io}{Mo})^2}$. Stockmayer used the results of Szwarc(13) for the styrene polymerisation in THF at 25°C, and found that the first two stages were over in a few seconds, whereas the final stage required almost a century to proceed to completion.

Obviously, in the present case, it is not a serious mistake to allow the "living" polymer to remain unterminated for a day or so, since the molecular weight distribution will not change detectably. However, for some polymerisations, e.g. α-methylstyrene, the depropagation rate constant will be sufficiently large for the problem to become serious. It is therefore necessary, when synthesising these polymers, to re-examine the problem of the distribution of molecular weights.

4. Synthetic Possibilities

Using the present technique, a wide range of block copolymers of varying molecular weight and composition may be synthesised. Any monomer which will propagate by anionic polymerisation may be incorporated into the polymer chain. Thus, as well as simple block copolymers of type

AA ----- AB ----- B,

by carrying out the required number of operations, a block copolymer of many sequences may be produced e.g.

A --- AB --- BA --- AB --- BA --- AB --- B --- etc.

Our work has shown that if proper precautions are observed, no detectable termination occurs at each addition of monomer. This technique for making multiple blocks from two monomers gives much better predictability of molecular weight and composition than the techniques employed by other authors such as Schlick and Levy.(14) They reported the successful synthesis of homogeneous multiple block copolymers using sodium naphthalene as initiator in THF. The active species produced would be a dianion capable of propagation in two directions, so that even if reaction could be performed in the absence of termination, the likelihood of an equal distribution of monomer at both ends of the polymer molecule, is remote.

It is also possible to extend the technique to the synthesis of block copolymers with more than two different polymer segments in the chain, to yield the following type of polymer.

— A —— AB —— BC —— C —

Providing the terminal sequence remains unterminated and is capable of promoting the polymerisation of another monomer, the process can be used to produce a wide variety of polymers of varied composition.

A further interesting synthetic possibility concerns the microstructure of polyisoprene. In pure benzene, isoprene polymerises as the cis-1:4 isomer. In benzene plus THF, no cis-1:4 polymer is produced, a mixture of trans-1:4, 1:2, and 3:4 isomers resulting. By adding THF to the reaction mixture on completion of an isoprene polymerisation in benzene, the second batch of isoprene monomer added will polymerise in such a way that no cis-1:4 isomer results. Thus a "structural" or "stereo" block polymer will result.

$$\mathrm{Is}\underset{\text{produced in benzene}}{\overset{\text{cis 1:4}}{\underline{\qquad\qquad\qquad}}}\mathrm{Is} - \mathrm{Is}\underset{\text{produced in benzene plus THF}}{\overset{\substack{\text{mixture of isomers} \\ \text{no. cis 1:4}}}{\underline{\qquad\qquad\qquad}}}\mathrm{Is}$$

A "stereo" block polymer of these two isomers should possess interesting properties. However, the reasons for undertaking this study of block copolymer synthesis were not just to produce interesting polymers. Since present theories of the properties of block copolymers in dilute solution remain largely unsubstantiated due to the lack of experiments carried out on suitable polymer samples, the need to find suitable methods of producing "model" block copolymers is obvious. The properties of random copolymers are due largely to the interaction of different segments in the chain, and should be related to both the size of the segments containing like molecules, and to the number of segments in the chain. The exact dependence on these two variables can only be evaluated if a series of block copolymers of from two to say ten segments is available for study, since the simplest block copolymer and a random copolymer represent extreme cases of copolymer molecules.

It is felt that the present investigation has indicated the best possible method for producing a variety of block copolymers of styrene and isoprene. The synthesis of block copolymers of any other monomers must be preceded by a similar study if polymers worth investigation are to be produced.

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CHAPTER VI

A. EMULSION POLYMERISATION TECHNIQUE

1. Introduction

In 1957, Bianchi, Price and Zimm(1) published a paper titled "Monodisperse Polystyrene". They claimed to have successfully prepared large amounts of practically monodisperse polymer of high molecular weight using an emulsion technique. Coupled with the fact that most of the published syntheses of block copolymers produce small yields, it was considered that, assuming the proposed mechanism was valid, and in the light of the generally accepted Smith-Ewart theory of emulsion polymerisation, an extension of this technique might produce large quantities of block copolymer of narrow molecular weight distribution. The decision to attempt such a synthesis was not taken without reservation, but the technique appeared to be easy by comparison with other methods, and the promise of high yield was attractive.

The chances of success appeared good and therefore the challenge was accepted. Before describing the details of the method employed in the synthesis, the main features of emulsion polymerisation will be briefly discussed.

2. Emulsion Polymerisation

Aqueous emulsions of monomers can be formed in the presence of emulsifying agents such as Manoxol O.T. (dioctyl sodium sulphosuccinate). An initiator, soluble in the aqueous (or external) phase, is added, and on the formation of free radicals by thermal, or photochemical breakdown, causes polymerisation of the emulsified monomer. In emulsion reactions, the rates and degrees of polymerisation are very much higher than those found in the bulk reaction, so that a knowledge of the kinetics and location of each individual step in the process is necessary for an understanding of the process as a whole.

The work of McBain(3) and of Harkins(4-6) greatly aided the elucidation of the course of the reaction. They were able to obtain good X-ray diffraction patterns of strong soap solutions, and reported that lamellar micelles were present, consisting of a pile of three or more double layers of oriented soap molecules. On the addition of a hydrocarbon, the double layers of soap split as the hydrocarbon penetrated the micelle, so that the micelles then consisted of single layers of soap separated by water and oil. On the other hand, Hartley(14) proposed that the micelles were spherical in dilute solution, and rod-like structures in more concentrated solutions. This structure for the micelle is favoured on energetic grounds. Light scattering data obtained by Debye(15) and streaming birefringence measurements by Sheraga and Backus(16) supported this view, and showed that the micelles were from 1000 to 3000A° long, their diameters being approximately twice the length of the detergent molecule. Debye(17) also discovered that the effect of adding an inorganic salt was to lower the electrostatic energy of the polar layers in the micelle, and thus allow the formation of longer micelles.

The proportion of monomer initially present in an emulsion polymerisation mixture is much greater than can be accounted for by the micelles, since the soap solutions are usually only 1 to 3% with respect to soap concentrations. Hence, most of the monomer occurs as droplets much larger in size (a micron or more in diameter), which may be stabilised by a portion of the soap. Thus, while most of the monomer initially present is in macroscopic droplets, most of the soap occurs in the micelles. More important still, the micelles present a much greater total surface area than the droplets, although the total volume of the micelles in considerably less than that of the droplets.

3. The Locus of Emulsion Polymerisation

The immediate question which must be resolved in advance of a detailed enquiry into the mechanism of emulsion polymerisation concerns the locus of initiation and propagation in these complex systems. Conceivably, polymerisation may occur in the aqueous phase, in the monomer droplets, within the micelles, at an interface, or else different steps in the process may occur in different loci. The qualitative investigations of Harkins (4-8) showed that after only a small percentage of the monomer had been converted to polymer, the initially low surface tension of the aqueous phase rose sharply, indicating a decrease in soap concentration in this phase. The soap concentration was then too low to maintain micelles, so these were eliminated as the locus for further polymerisation. On the disappearance of micelles, the monomer droplets became unstable and coalescence of the oil phase occurred.

The polymer which had been formed at this stage was found to occur in numerous polymer particles, no more than 200 to 400 A^{o} in diameter. These particles appeared to have acquired nearly all the soap, which was absorbed on their surface. As polymerisation progressed, these polymer particles grew in size, but their number remained sensibly constant, as did the rate of polymerisation from about 20% to 80% conversion. At 80% conversion, all the monomer was absorbed by the polymer particles, and the rate of polymerisation gradually decreased. Harkins therefore concluded that it was necessary to postulate two loci for polymerisation.

At the beginning of polymerisation, the micelles were assumed to be much swollen by water. This would greatly facilitate the diffusion of water soluble initiator fragments into the micelle. The added fact that no new polymer particles were formed after the disappearance of the micelles led to the conclusion that the principal locus for initiation was in the micelles(5-7,9,18) As more and more micelles were converted to polymer particles which rapidly grew to sizes surpassing the dimensions of the initial micelles, the soap was rapidly acquired by the polymer particles, and the micelles disappeared. Careful X-ray studies have shown that the polymer molecules are ejected from the micelles when they reach a certain size, the dimensions of the micelles returning to their original value. If more monomer was available, the micelles filled up again so that the sequence of solubilization, initiation, and initial propagation was repeated. The polymer-monomer particles ejected were surrounded by adsorbed soap, so that at about 20% conversion, all micellar soap had disappeared. Further polymerisation took place almost exclusively in the polymer particles. Vinograd(10) has presented data showing that diffusion of monomer from the emulsified droplets or oil phase, to the micelles or polymer particles, is sufficiently rapid to maintain the observed rate of polymerisation. The concentration of monomer in the polymer particles appears to be restricted by the surface tension at the particle-water interface, which opposes swelling of the small polymer particles. If this was not so, the particles might be expected to swell indefinitely until all the supernatant monomer was absorbed.

4. The Smith-Ewart theory

The quantitative theory of Smith and Ewart(2) is based on the observations of Harkins. Initiation of polymerisation is assumed to occur within the micelles due to the penetration of free radicals from the aqueous phase. Propagation is assumed to occur in the polymer particles swollen with monomer and surrounded by adsorbed soap. No attempt is made to give a detailed account of the Smith-Ewart theory, but the main features of the calculations are discussed.

The basis of the calculations is that no new polymer particles are formed after the disappearance of the micellar soap. In the "ideal" case of emulsion polymerisation, it is assumed that a radical, having once entered a micelle, is incapable of leaving it, so that termination of the growing polymer chain can only be accomplished by the entry of another radical. The derived expression for the rate of polymerisation under these conditions is

$$-\frac{d[M]}{dt} = \frac{1}{2} k_p [M] N$$

where [M] is the monomer concentration and N is the number of isolated reaction nuclei per ml. of aqueous phase.

Thus the rate of reaction is proportional to the number of particles present, and independent of all other variables except temperature. This theory has been supported by experimental evidence,$^{(11-12)}$

and it is found that the rate of polymerisation per particle remains constant up to about 10^{14} particles/ml, after which it falls off slightly.

5. "Monodisperse Polystyrene"

Bianchi, Price and Zimm(1) claimed to have controlled the chain initiation and termination processes, thereby producing a "monodisperse" polymer. The four important processes in a polymerisation by a free radical mechanism are (1) Initiation, (2) Propagation, (3) Termination, and (4) Transfer, the abstraction of a hydrogen atom by a radical from some other molecule to produce a polymer molecule and a new radical. Normally all four processes proceed at once and the molecular weight of the polymer formed is determined statistically by the competition of process (2) with processes (3) and (4). The resulting molecular weight distribution is quite broad. Zimm *et al.* tried to achieve intermittent initiation and termination, so that once initiated, the chains could grow until they were terminated by entry of a second radical into the polymer-monomer particle. Transfer was assumed to be negligible, since the reaction was performed at a low temperature. The most successful method of initiation involved the photochemical decomposition by ultraviolet light from a sun lamp, of α,α^1-azo-bisisobutyramide (AIBA). Termination occurred only when a large number of new radicals were produced, i.e., when the light was on. Thus the termination of one set of polymer chains and the initiation of a new set occurred in the same burst of light. Under these conditions, the time of growth of a polymer was equal to the time between exposures to light (transfer being neglected), and for styrene at 0°C, a molecular weight of 10^6 should be produced in about two minutes. The use of two 275 watt. G.E. Sun lamps placed either side of a "pancake" cell containing the emulsion, produced the most satisfactory results, and it was claimed that large fractions of "monodisperse" polystyrene were synthesised. It was also claimed that polymers with molecular weights between 5×10^5 and 2.5×10^6 could be prepared by this method.

6. Block Copolymer Synthesis

According to Zimm et al.(1), if chain terminating material (e.g. oxygen) is removed from the emulsion and if chain transfer reactions are reduced to negligible proportions, termination of the growing polymer chains within the latex particles can only be caused by the entry of a second radical. Thus, if there is a large excess of micelles at the start of the reaction compared with the number of free radicals produced by a single burst of light from a powerful ultra-violet light source, most of the radicals should enter separate micelles. Initiation, followed by propagation should occur, and since no new radicals are produced, propagation without termination should occur. Propagation should continue until all solubilized monomer is depleted, and a "living" polymer is formed.

If a second emulsion containing a different monomer is added and thoroughly mixed with "living polymer" suspension, further propagation should occur as the second solubilized monomer diffuses into the latex particles. The resultant product should be a simple block copolymer of the type

AAA ---- A ---- ABBB ---- B ----B (VI.1)

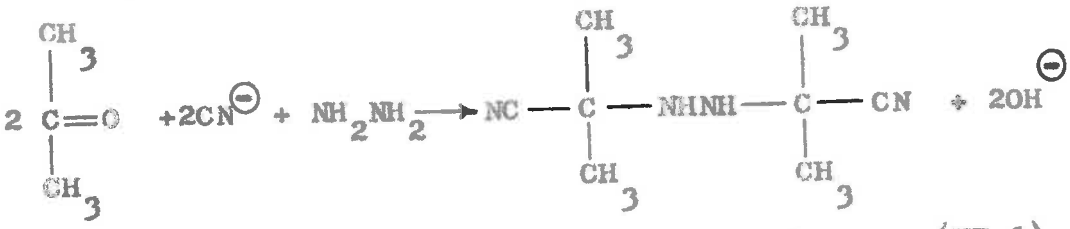
As previous efforts to synthesize block copolymers by anionic polymerisation had failed to produce satisfactory model polymers for characterisation in dilute solution, and since the quantity of polymer produced anionically was usually small, an attempt at preparation by an emulsion technique seemed justified.

7. Experimental

A flow technique was devised in which an emulsion of styrene monomer was polymerised by photochemical decomposition of AIBA. After sufficient time had elapsed for all the monomer to be theoretically converted into "living" polystyrene, a second emulsion containing solubilised methyl methacrylate was added. After thorough mixing, a further period of time was allowed for polymerisation of the second monomer. The resulting suspension of polymer was collected in a solution of saturated brine, which broke the emulsion, and allowed the polymer to separate out.

(a) Preparation of AIBA

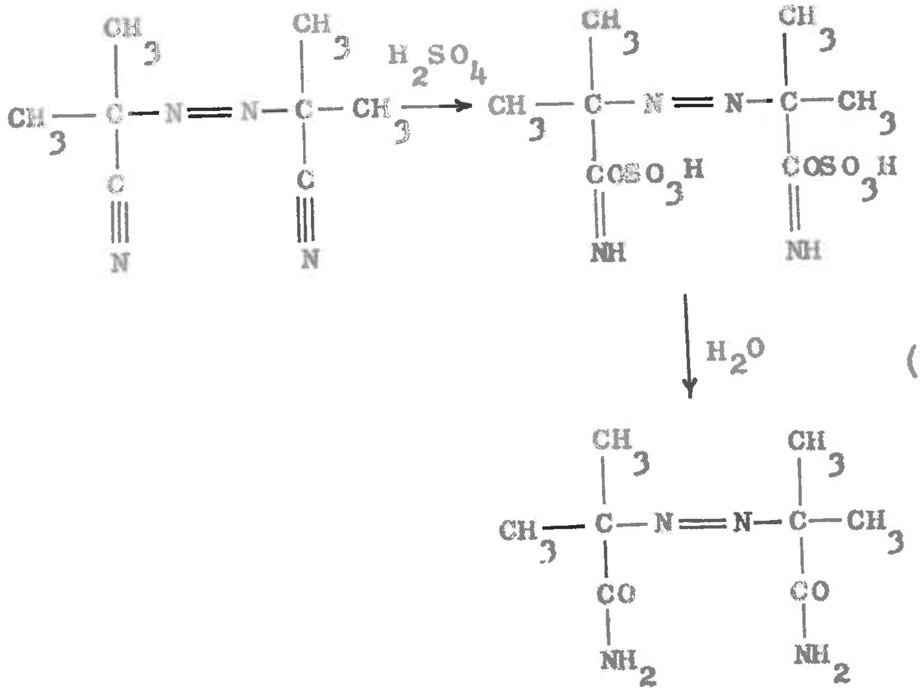
Acetone, sodium cyanide, and hydrazine sulphate were shaken vigorously in water. An hydrazo compound was formed according to the equation(VI.1)



$$2\ CH_3-\overset{}{C}(=O)-CH_3 + 2CN^{\ominus} + NH_2NH_2 \longrightarrow NC-C(CH_3)_2-NHNH-C(CH_3)_2-CN + 2OH^{\ominus}$$

hydrazo compound (VI.1)

The fine crystals of hydrazo compound were filtered from solution, and oxidised by the Bichel-Waters oxidation using bromine. The product of this reaction was α-α^1-azo-bisisobutyronitrile. The more soluble amide was prepared by reaction with concentrated sulphuric acid. After fifteen hours, the mixture was poured into a beaker containing crushed ice and solid potassium carbonate. The aqueous layer was decanted and extracted with chloroform. Solid AIBA crystallised out from the chloroform fraction.



(VI.2)

AIBA

(b) Treatment of Monomers

The inhibitor was removed from the monomers by washing with 10% caustic soda solution and water. Rough drying was effected by calcium chloride, and the monomers distilled under a reduced pressure of nitrogen.

FIG. VI.1

Emulsion Polymerisation Apparatus.

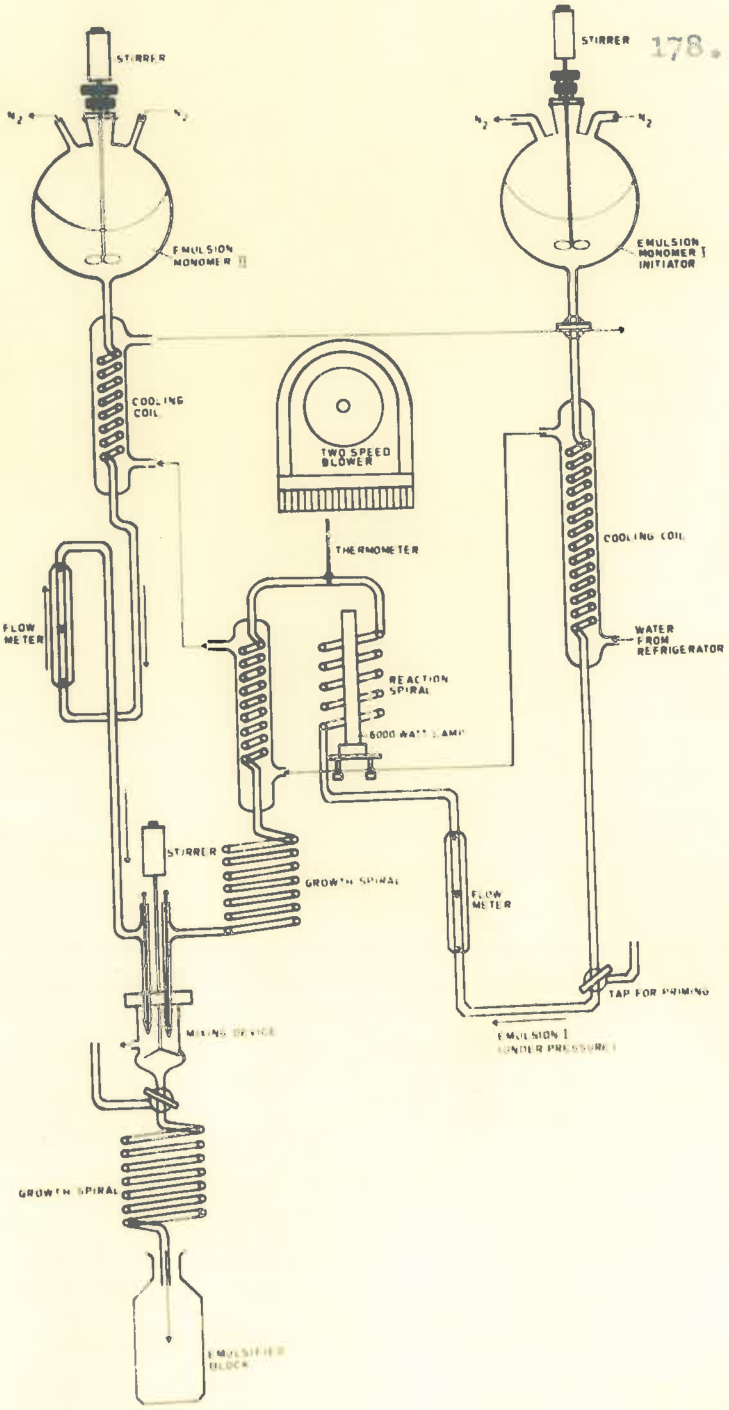

STIRRER
N_2
N_2
EMULSION MONOMER II
STIRRER
N_2
N_2
EMULSION MONOMER I INITIATOR
COOLING COIL
TWO SPEED BLOWER
COOLING COIL
THERMOMETER
FLOW METER
WATER FROM REFRIGERATOR
REACTION SPIRAL
6000 WATT LAMP
STIRRER
GROWTH SPIRAL
FLOW METER
TAP FOR PRIMING
MIXING DEVICE
EMULSION I (UNDER PRESSURE)
GROWTH SPIRAL
EMULSIFIER BLOCK

FIG.VI.1.

(c) Preparation of Emulsions

The water used to make the emulsions had to be free of oxygen. Distilled water was therefore boiled vigorously for fifteen minutes, then allowed to cool slowly as a stream of oxygen-free nitrogen was bubbled through it. Two emulsions were required for the preparation of the block copolymer. One contained water, styrene, manoxal O.T. (1-3%) and initiator, while the other emulsion contained water, methyl methacrylate, and manoxol O.T. (¼-1%). Less manoxol was required for the second emulsion, since it was only necessary to stabilise the oil phase without the production of micelles.

(d) The Synthesis

The apparatus is shown in Fig. VI.1. A water-cooled 6,000 watt Xenon arc lamp was used as the source of irradiation. This intense light source emitted a spectrum of light similar to that of sunlight, so that as well as the shorter wavelengths required for the photodecomposition of initiator, much infra red radiation was also emitted. So much heat was generated, in fact, that if a sufficiently fast flow of water was not maintained through the cooling jacket of the lamp, the water boiled. To overcome this problem, a powerful fan was mounted above the lamp so that a cooled stream of air was directed over it. A solution of copper sulphate was also circulated through a jacket placed between the lamp and the reaction spiral. In this way the temperature of emulsions passing through the reaction spiral increased only about 5°C.

Each emulsion was placed in a 5litre storage vessel above the lamp, and was continuously stirred in an inert atmosphere of nitrogen. The styrene emulsion first flowed through a cooling condenser in which its temperature was reduced to approximately 10°C. The rate of flow was measured by a flow meter.

Since the volume of the reaction spiral was known, the time of irradiation of the emulsion could be varied as desired by adjusting the flow rate. On passing the lamp, bubbles of nitrogen were formed in the emulsion, indicating a break down of the initiator. The volume of gas evolved during the course of the experiment was directly related to the number of free radicals produced. This number could be varied by either altering the time of irradiation, or the concentration of initiator in the emulsion. Initiation having occurred, the emulsion was once again cooled by flowing through a cooling condenser. It was necessary to reduce the temperature of the emulsion at this stage in order to minimise chain transfer. The emulsion then passed through a long hold-up spiral which allowed sufficient time for propagation of the styrene. The hold up time could be satisfactorily varied from five to twenty five minutes, according to the rate of flow.

At this stage, it was thought that under the right reaction conditions, large fractions of "living" polystyrene should have existed in suspension, and that the monomer supply would have been exhausted. The suspension was admitted to a mixing vessel, and the precooled emulsion of methyl methacrylate was introduced at the appropriate rate. Following thorough mixing, the emulsion flowed into another hold-up spiral to allow time for propagation of methyl methacrylate, with the formation of block copolymer. The emulsified polymer was collected in a solution of saturated sodium chloride, and floated to the surface to form a flocculent aggregate. This was collected and washed several times to remove soap. Each synthesis was designed to produce up to 100 gms. of polymer from a total volume of four litres of emulsion, but a continual replenishing of the emulsion reservoirs offered the possibility of a yield up to 50 gms. of block copolymer per hour.

8. Results and Discussion

The success of this technique depended largely on its ability to produce "living" polystyrene of narrow molecular weight distribution. This first stage of the synthesis was investigated in some detail. The first prerequisite to success was that the number of micelles swollen with monomer should greatly exceed the number of free radicals produced. The number of free radicals produced was directly related to the volume of nitrogen liberated on irradiation. This number could be easily altered by either changing the flow rate past the light source, or by changing the concentration of initiator in the emulsion. The number of micelles present could not be so easily computed, but Burnett(13) has derived an approximate expression for the number of particles (N)

$$N = k(\rho/\mu)^{2/5} (a_s S)^{3/5}$$

where k is a numerical constant whose values lie between 0.37 and 0.53

ρ = rate of radical production

μ = rate of change of volume of the particle

a_s = specific area of the soap

S = total weight of soap

Using a soap concentration of 1% in water, the number of particles to be expected is approximately 10^{15} particles/ml. of 10^{17} particles/gm. of soap. Smith also found that the production of polymer particles was more efficient for a given weight of soap in dilute solution. The volume of emulsion was 2 litres, so that a 1% soap solution should form 2000 x 10^{15} or 2 x 10^{18} particles.

Many experiments were conducted in an effort to find reaction conditions which allowed the production of "living" polystyrene of narrow molecular weight distribution. The concentration of soap was varied from 0.5 to 5%, the emulsifying agent itself was changed, the concentration of styrene in the emulsion was varied from 0.25 to 2.5%, the concentration of initiator (AIBA) was subjected to a similar ten-fold change, diacetyl was used as initiator instead of AIBA, and flow rates were altered. No really satisfactory results were derived from this technique, and it is difficult to say why this should be. There was no doubt that large quantities of high molecular weight polystyrene were produced. There is also no doubt that large fractions of block copolymer were produced. The most disturbing feature of the synthesis was that no matter what changes in reaction conditions were made, complete consumption of the monomer was never achieved. This factor alone is sufficient to invalidate the method as a possible source of 'model' block copolymers.

Arising out of the mass of results obtained, a few conclusions were drawn. Whenever the soap concentration was in excess of 4%, the emulsion always broke on passing the light source, with the formation of an abundance of flocculent precipitate. No attempt was made to identify this species. One factor which greatly improved the yield of polymer was the degassing of monomer prior to use, and the addition of sodium sulphite to the emulsion to act as a scavenger for oxygen. It appears therefore that complete removal of oxygen from the system is necessary, and the failure of the technique may have been partly due to the lack of fulfillment of this condition. However, using two litres of emulsion containing 50 gms. of styrene monomer, up to 80% yields of polymer were obtained. Viscosity measurements showed that the molecular weight of the polystyrene was of the order of 10^6.

The recipe producing the above sample of polystyrene was used in an attempt to synthesise a block copolymer by addition of an emulsion containing 50 gms. of methyl methacrylate monomer. Once again, the total yield of polymer was about

80%. Solvent extraction of the polymer and U.V. analysis showed that the polystyrene content was approximately 40%, and that a block copolymer had definitely been produced. However, there were large fractions of polystyrene and polymethyl methacrylate homopolymer also present. The presence of the polymethyl methacrylate was surprising, and can only have arisen from chain transfer reactions. If too many free radicals were produced as the emulsion passed the light source, it is most unlikely that they would have remained unreacted by the time methyl methacrylate was added. It is also unlikely that a high molecular weight polymer as produced, would be formed in the presence of an excess of free radicals, if the growing polymer particles were to capture all the radicals. The possibility of free radicals escaping from a polymer particle before reacting with monomer is negligible, so the only explanation for the presence of polymethyl methacrylate in the synthesis is in terms of chain transfer.

Although Zimm(1) claimed that at 0°C, no appreciable chain transfer occurred, at 10°C, the temperature at which this synthesis was conducted, there must be considerable transfer. If the Harkins qualitative theory is correct, the methyl methacrylate monomer is added when only polymer particles are present, so that the second monomer must diffuse through the aqueous phase into the polymer particles in order to polymerise, unless chain transfer to some component of the aqueous phase had occurred previously. Since the emulsifier has a relatively acidic hydrogen atom, it is possible that a free radical could abstract this atom, creating a soap free radical in the aqueous phase. This may then be adsorbed on the surface of a polymer particle so that its likelihood of mutual termination with other such radicals is reduced. However, when the second monomer is added, this may well be polymerised by these soap free radicals.

Reproducibility of results was poor, so that no conclusive evidence for the above suggestion was possible. The only conclusions that could be drawn from the mass of results obtained, were that block copolymers could be prepared in this way, but yields were not quantitative, and a mixture of polymers resulted. It thus seemed obvious that further work in this field would not lead to block copolymers suitable for studies of solution behaviour, so that an entirely different mode of synthesis was called for. It is perhaps significant that Zimm has published no further work in this field, despite his claims that good samples of monodisperse polymer could be obtained from the emulsion technique.

B. EARLY ATTEMPTS AT SYNTHESIS BY ANIONIC POLYMERISATION

1. Introduction

The failure of the emulsion system to produce large quantities of block copolymers suitable for solution property investigations, forced a reappraisal of anionic techniques. Since a reasonable degree of success had been demonstrated using sodium biphenyl initiator in THF in this laboratory(20), it seemed that the best approach to the problem was by an anionic polymerisation, but with a different approach in order to improve on the yields previously obtained using vacuum line techniques. In 1961, Wenger and Shiao-Ping S. Yen(19) published the first paper on the use of n-butyllithium in the preparation of monodisperse polystyrene. They described an elaborate process carried out under high vacuum, which produced polystyrene with a heterogeneity ratio of 1.05.

They investigated the effect of atmospheric contamination on the synthesis and showed that the principle of purging impurities in situ, prior to polymerisation, was completely satisfactory. The following quotation is found on page 10 of their paper.

> "The apparatus and techniques described have been found convenient for the preparation of small samples. Details of the techniques described were of importance only during this initial investigation and can be simplified or omitted in future applications. Specifically, it is suggested that the polymerisation be carried out under an inert atmosphere, and that the monomer be introduced into the reaction vessel by ordinary means. In larger scale polymerisations it would be of advantage also to use a single metering device for the controlled addition of catalyst during purging and in the subsequent initiation".

This statement by Wenger, suggested that it might be worth while to investigate block copolymer synthesis in an inert atmosphere of nitrogen. Commercial dry oxygen-free nitrogen was subject to further purification by passing the gas through two simple commercial deoxygenating units which converted traces of oxygen in the presence of small quantities of hydrogen, into water vapour. The gas was then passed through two chromous chloride scrubbing towers to ensure complete removal of oxygen. The stream of wet nitrogen was next dried by passing successively through towers containing anhydrous calcium chloride, concentrated sulphuric acid, and phosphorus pentoxide. To remove any acid fumes or vapour, it was passed through a tower containing solid sodium hydroxide pellets, thence into an anhydrous potassium carbonate tower. Before emerging for use, it was passed through a long tube packed with silica gel. This purified stream of nitrogen was used in two attempts to synthesise the block copolymers which will be dealt with in turn.

2. Vacuum Line and Nitrogen Line Method

A second line was incorporated into the vacuum line to carry purified nitrogen. The nitrogen was stored under pressure in a 20 litre flask mounted on the metal framework supporting the two lines. A system was devised in which preparation of

FIG. VI.2.

Apparatus for block copolymer synthesis by the vacuum line and nitrogen line techniques.

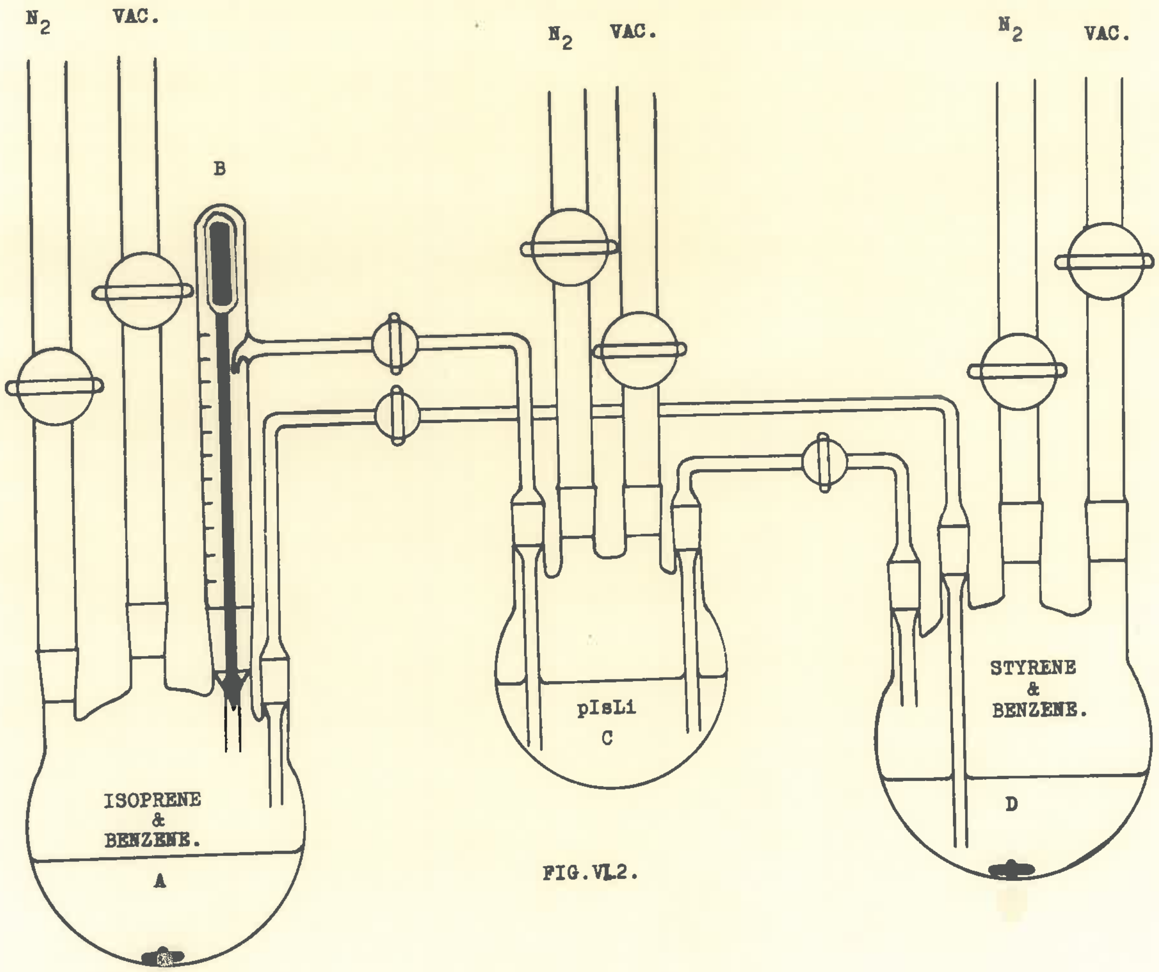

N_2
VAC.
N_2
VAC.
N_2
VAC.
B
ISOPRENE
&
BENZENE.
A
pIsLi
C
STYRENE
&
BENZENE.
D

FIG.VI.2.

butyllithium initiator, purging of benzene and monomer solutions, initiation of styrene polymerisation, and addition of a prepurged solution of benzene and isoprene could be performed in an atmosphere of nitrogen. Solutions were transferred in bulk through tubes from one vessel to another, by adjusting the pressures in the different parts of the system. Pressures could be increased by nitrogen pressure, or decreased by evacuation.

The apparatus is shown in Fig. VI.2. A clean sample of isoprenyllithium was introduced into flask C. Calculated quantities of isoprene and benzene were distilled into the reaction flask A, and isoprenyllithium forced into the graduated vessel B under nitrogen pressure. The valve in B was operated by means of a powerful magnet, and the contents of flask A freed from impurities by titration. Mixing was achieved by means of a magnetic stirrer. On completion of titration, a measured volume of initiator was added from B, and polymerisation allowed to proceed. Styrene and benzene were distilled into flask D, titrated with initiator until the faint yellow colour persisted, and forced over into reaction flask A to form block copolymer.

The results of this method were most encouraging. The living polymer solutions retained their activity in the inert atmosphere, and block copolymer was produced. However, the quality of the product was poor, since over titration of the second monomer was difficult to avoid. Polystyrene homopolymer would result in the case of over-titration, while under-titration would cause termination of living polyisoprenyllithium in A, producing polyisoprene homopolymer. Perhaps the worst feature of all was the need to incorporate greased taps and joints in the system. These were found to be attacked by the reactants with the result that the system developed leaks. Had greaseless taps been available at the time, the method may have proved more successful.

3. Dry Box Method

Since it seemed likely that the synthesis could be performed in an atmosphere of nitrogen, it was decided to make a further attempt under these conditions. The previous method suffered from technological difficulties, so the simplest possible method of handling solutions in an inert atmosphere was adopted. The reaction was carried out in a dry box. Solutions were sampled and transferred by means of syringes which were washed out in the dry box with living polymer solution. The whole process of synthesis was relatively simple; the use of syringes making titration and addition of one solution to another, easy. Provided sufficient vessels and starting materials were placed in the box to begin with, there appeared to be no reason why a whole series of polymers having a range of molecular weight and composition could not be synthesised at the same time. On testing the efficacy of the method, however, it was found to be unsatisfactory. Despite persistent efforts and modifications to the system, the dry box could not be completely freed from atmospheric contamination. Air was expelled from the box by inflating a large balloon with nitrogen a number of times inside the box. Nitrogen was "sprayed" into the box from a number of points, but terminating material was still not completely removed. Exposure of living polymer solutions resulted in their slow termination. With some reluctance, this method was abandoned in preference for the high vacuum technique. By this time it was obvious that model block copolymers could only be produced if proper control is exercised over each single step in the synthesis. The method described in Chapter V has successfully demonstrated that such an approach is absolutely essential.

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