

# KINETIC STUDIES AND REACTION MECHANISMS IN HOMOGENEOUS ANIONIC POLYMERIZATION

S. BYWATER

*Applied Chemistry Division, National Research Council, Ottawa, Canada*

## INTRODUCTION

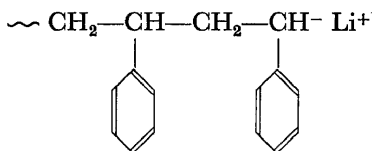
Interest in anionic polymerization has grown remarkably in the last few years. Much of the early work was confined to qualitative studies on the effect of metal gegenion and solvent on polymer microstructure and copolymer composition. More recently, kinetic studies have been made on several polymerizing systems, and it seems appropriate to consider how they have contributed to our knowledge of the mechanism of anionic polymerization.

Although base-catalyzed polymerizations can be carried out in liquid ammonia, and many early studies were carried out in this solvent<sup>1-3</sup>, the polymerizations are complicated by chain-transfer to the solvent. Recent work has, therefore, been concentrated on polymerizations carried out in hydrocarbons and ethers where chain-termination is absent or negligible if the systems are rigorously purified and the reactions carried out in the absence of moisture or air. Catalyst concentrations are usually in the millimolar range, so that the concentration of reactive impurities must be reduced to about  $10^{-5}$  molar for reliable kinetic results. This requires not only rigorous purification and drying of the reactants but also the removal of adsorbed moisture from the surface of the glass vessels.

Marked differences in rates and kinetics of polymerization and in the microstructure of the resultant polymers are observed between polymerizations carried out in hydrocarbons and in ethers. Some authors<sup>4, 5</sup> have considered that only the polymerizations carried out in ethers of relatively high dielectric constant are true anionic reactions ("classical anionic"), and that in hydrocarbon solvents (where the counter-ion is usually lithium owing to the solubility of alkyllithium catalysts) the intermediates are largely covalent in character. Alternatively, prior complex formation of the Li—C bond with a monomer molecule has been considered necessary<sup>6</sup> to increase its ionic character before monomer addition. There is little convincing evidence in the literature as to the degree of covalency of the C—Li bond. Coates<sup>7</sup> has suggested that the general properties of alkyllithium compounds, particularly their solubility in hydrocarbons, indicates a considerable degree of covalency. It is more probable that the solubility of n-butyllithium in hydrocarbons is due to association with the formation of an "inverted micelle" structure<sup>8</sup> which is made soluble by the hydrocarbon chains. Moreover, methylithium and the alkydilithium compounds are just as insoluble in hydrocarbons as the alkylsodium series. Micellar structures of the type required for solubilization would be less likely to form with these compounds. Warhurst<sup>8</sup> in fact assigns an 80 per cent ionic character to the C—Li bond. The ionic character of this bond

will depend somewhat on resonance stabilization in the alkyl or aryl anion. Differences in ionic character might also be expected in different solvents, but this factor may be less important than is often supposed. In a non-polar solvent, the loss of stabilization energy due to solvation may well be offset by the increased coulombic interaction energy of the ion-pair, together with additional interaction energy from ion-pair dimerization. At a charge separation of 4 Å, extra stabilization energy of approximately 50 kcal is available from these sources on changing from tetrahydrofuran to benzene as solvent.

Aryllithium compounds seem to be almost entirely ionic in character. Wittig and Stahnecker<sup>9</sup> have shown that the spectra of lithium, sodium and potassium benzhydrylphenyl ethers are identical in tetrahydrofuran. A sharp absorption band is observed at 450 m $\mu$ , which must be attributed to the substituted benzhydryl anion, and which is in fact very similar to that observed for the triphenylmethyl anion. A similar comparison can be made in polymer systems. The ultra-violet absorption spectra of polystyryllithium:



in benzene and polystyrylsodium in tetrahydrofuran are remarkably similar and show a maximum in the region 340–343 m $\mu$  (Figure 1). The observed colour difference in the two solvents is entirely due to a broadening of the absorption band for polystyrylsodium. These bands lie close to the wavelength predicted theoretically<sup>10</sup>, and must be attributed to the benzyl type anion, large unaffected by ion association phenomena. The integrated extinction coefficients of the two bands are similar, and suggest that the

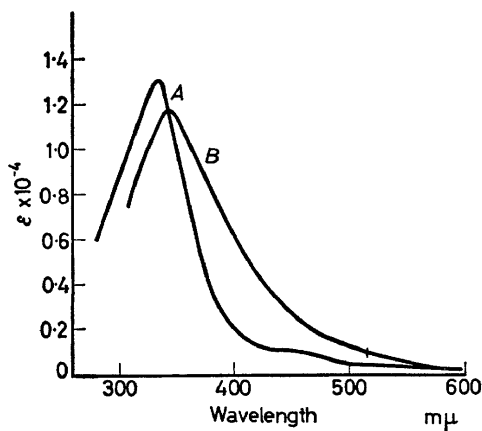


Figure 1. Ultra-violet absorption spectra of: A, polystyryl lithium in benzene; and B, polystyryl sodium in tetrahydrofuran

## HOMOGENEOUS ANIONIC POLYMERIZATION

ionic characters are similar. The longer wavelength bands reported by Kuwata<sup>11</sup> and attributed to the polystyrene anion in toluene and the benzyl anion in tetrahydrofuran are similar to those reported<sup>12, 13</sup> to be produced slowly from polystyrylsodium solutions, and are presumably due to subsequent reaction to produce a more stable anion.

In tetrahydrofuran ( $\epsilon = 7.6$ ), the ions would be expected to exist mainly as ion-pairs. This supposition has been confirmed for sodium polystyryl by Worsfold and Bywater<sup>13</sup>. In this system, a plot of  $\log \Lambda$  versus  $\log c$  is linear with a gradient of  $-\frac{1}{2}$  over an ion concentration range of  $5 \times 10^{-5}$  to  $10^{-2}$  molar. This result indicates that the conductivity is governed by a simple dissociation of ion-pairs to free ions, which are the conductors of the current. The dissociation constant is low, so that only about 1 per cent of free ions will exist at millimolar concentrations. Thus it is probable that the ion-pair is the reactive species in polymerization in tetrahydrofuran at about millimolar catalyst concentrations. If, despite their low concentration, free ions were much more reactive than ion-pairs, and hence responsible for chain propagation, the propagation rate would be of half order in active centres. In this solvent a first-order law is always observed.

In benzene or hexane ( $\epsilon \sim 2$ ), ion-pair aggregation is important even at low concentrations, as is shown by the extensive conductivity studies on quaternary ammonium salts reported mainly by Fuoss and Kraus and reviewed by the latter author<sup>14</sup>. In these solvents, the quaternary ammonium salts show the same behaviour as polystyrylsodium in tetrahydrofuran only at concentrations of about  $10^{-5}$  molar; ion-pair aggregation is extensive at a concentration of  $10^{-4}$  molar. We may assume, by analogy, that growing polymer ion-pairs are highly associated in these solvents, and that the aggregates are probably not active in polymerization; for instance, the polarizing effect of a quadrupole falls off very rapidly with distance. These suppositions appear to be borne out by kinetic studies on anionic polymerization in benzene and n-hexane.

The dielectric constant alone will not be a completely reliable guide to ion-association phenomena, for, in polymerizations carried out in benzene containing a little tetrahydrofuran (where the dielectric constant is very little higher than that of benzene), kinetic evidence shows that free ion-pairs are again the predominant species. This suggests that, if a material which solvates the ions sufficiently strongly is present, preferential association with it will occur, and the ion-pair aggregates will be broken down. This normally requires only a few molecules of ether per ion-pair. Similar considerations may apply if the polymer contains polar groups. Association of ion-pairs in non-polar solvents may be inhibited by preferential association of the counter-ion with the polar groups.

The ionic nature of the active species in the polymerization of isoprene or butadiene by alkyllithium compounds in solvents of low dielectric constant is at present less well-established. It is possible that the C—Li bond in these growing polymer chains is somewhat more covalent in character owing to the smaller resonance stabilization in alkenyl ions. However, kinetic studies show that the polymerization behaviour is very similar to that exhibited by styrene, and it seems reasonable to suppose that the active intermediate is still basically an ion-pair and that the complexities of the

polymerization are due to ion-pair aggregation. The relative slowness of the polymerization is caused mainly by association of catalyst molecules and of polymer ion-pairs, as a result of which the concentration of reactive molecules is effectively reduced.

A more detailed discussion of some interesting areas of investigation can now be made on the basis of the principles discussed above.

## STYRENE

Electron-transfer-initiated polymerization in ethers catalyzed by sodium naphthenide was first described by Szwarc<sup>15</sup>. Chain-initiation forms a styrene ion-radical; any radical ends dimerize quickly and chain propagation proceeds from ionic centres at each end of the chain. Termination is negligible under ideal conditions<sup>16</sup>. If chain-initiation is rapid and chain propagation is slow, the rate of polymerization measured will be that of chain-propagation. In dioxan, propagation occurs at a measurable rate and the polymers formed have the narrow molecular weight distribution<sup>17</sup> expected for rapid initiation.  $\alpha$ -Methylstyrene shows the same behaviour in tetrahydrofuran<sup>18</sup> since the propagation rate is lower. In the styrene-tetrahydrofuran system, chain-propagation occurs more rapidly but the propagation rate can be measured by preforming polystyryl anions and then reacting them with monomer in a flow system<sup>19</sup>. The propagation rate is first order in both monomer concentration and concentration of ionic ends in all these systems, if the concentration of the latter species is in the range 0.4–4 millimolar. These results suggest that, at these concentrations, chain-propagation occurs directly by the interaction of a monomer molecule with a polymer ion-pair. At 25°,  $k_p$  for styrene was found to be 5 l. mole<sup>-1</sup> sec<sup>-1</sup> in dioxan and 560 l. mole<sup>-1</sup> sec<sup>-1</sup> in tetrahydrofuran. This difference is presumably mainly due to the increase in energy required for charge separation in the solvent of lower dielectric constant. The activation energy of 9.2 kcal in dioxan is surprisingly high, and is to be compared with a value of 2–3 kcal for  $\alpha$ -methylstyrene propagation in tetrahydrofuran. The latter monomer has a  $k_p$  of about 2 l. mole<sup>-1</sup> sec<sup>-1</sup> in tetrahydrofuran.

The system styrene-benzene-*n*-butyllithium has been extensively studied. Initiation consists of the addition of *n*-butyllithium across the monomer double bond<sup>20</sup>: one polymer chain is produced by each initiator molecule<sup>21</sup>. Chain-termination is negligible, but initiation and propagation proceed at comparable rates<sup>21, 22</sup>. If the monomer/catalyst ratio is high, chain-initiation will be complete before all the monomer has been consumed, and the later stages of the polymerization will give a measure of the rate of the propagation reaction. However, it is difficult to confine the experimental observations to this region. *Figure 2* shows the simultaneous appearance of chain anions and disappearance of styrene in a polymerization carried out at a low monomer/catalyst ratio. At all times, the rate of styrene consumption is a complex function of initiation and propagation rates under these particular conditions. Subsequent monomer additions will, however, facilitate the measurement of a true propagation rate once the number of active chains has reached its maximum value.

O'Driscoll and Tobolsky<sup>23</sup> measured the polymerization rates at high catalyst concentrations. They found that the rate at the apparently linear

## HOMOGENEOUS ANIONIC POLYMERIZATION

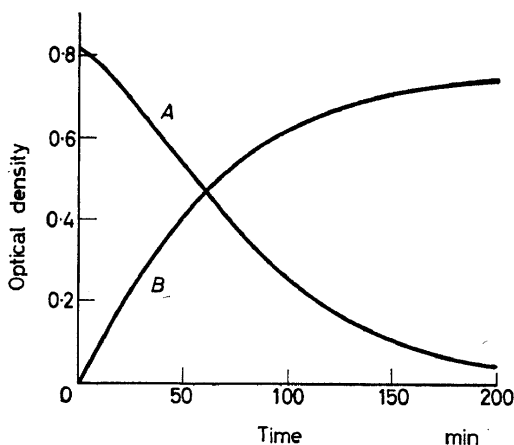
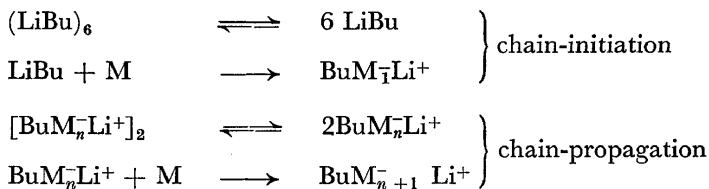


Figure 2. *A*, rate of disappearance of styrene; and *B*, rate of formation of polymer ion-pairs, as measured spectrophotometrically. Polymerization catalyzed by *n*-butyllithium in benzene solution. (Reproduced by permission from *Can. J. Chem.*)

portion of the rate curve was proportional to the square of the monomer concentration, and was almost independent of catalyst concentration. The former result is to be expected, for this portion of the rate curve is dependent on initiation and propagation rates, both of which depend on the monomer concentration. Welch<sup>24</sup> measured only the rate in the later stages of reaction, and showed that the propagation step was first order in monomer concentration and almost independent of catalyst concentration above 0.02 M *n*-butyllithium. The results at high catalyst concentration were presumably influenced by incomplete initiation; this is certainly indicated by the published rate curve at the highest catalyst concentration. A more detailed investigation by Worsfold and Bywater<sup>21</sup> involved simultaneous determinations of styrene and ionic intermediate concentrations by means of ultra-violet absorption measurements. The rate of chain-initiation, measured from the initial rate of formation of ionic intermediates, was found to be first order in monomer concentration and of low order (1/6) with respect to *n*-butyllithium. The propagation rate was only measured when the concentration of ionic intermediate indicated that initiation was complete. This often necessitated the addition of extra monomer. The rate of chain-propagation was found to be half order in active centre and first order in monomer concentration. These observations are consistent with a mechanism of the following type, where the extent of dissociation in the two equilibria must be small:



The activation energies observed for initiation and propagation, 18.0 kcal and 14.3 kcal respectively, are, therefore, composite values involving a preliminary dissociation step and an actual reaction step.

Confirmatory evidence for the mechanism is obtained from several authors<sup>25-27</sup>, who have observed that alkyllithium compounds are associated approximately to hexamers in solvents of low dielectric constant. Ethyllithium shows no evidence of dissociation in benzene in the concentration range  $7 \times 10^{-2}$  to  $3 \times 10^{-1}$  M<sup>28</sup>, and these data suggest that dissociation would be small at even lower concentrations. The concentration range used in the polymerization experiments is, however, much lower, and it is necessary to assume that association is predominant down to concentrations of  $10^{-4}$  M. At lower concentrations, the polymerization experiments show divergencies which could be due to further dissociation of n-butyllithium. The association of the growing ion-pairs is to be expected in solvents of low dielectric constant.

Morton, Bostick and Livigni<sup>29</sup> have argued that n-butyllithium is not associated in n-hexane at the low concentrations of n-butyllithium used in polymerizations. The experiments presented in support of this argument, however involve, free n-butyllithium concentrations up to  $10^{-1}$  M where cryoscopic measurements indicate extensive association. The origin of this discrepancy is not clear.

On addition of very small amounts of tetrahydrofuran to the benzene, the polymerization rates increase<sup>23, 30</sup>. Other Lewis bases produce similar results. Welch<sup>30</sup> measured the effect of tetrahydrofuran on the rate in the later stages of reaction, and showed that the rate levelled off at a tetrahydrofuran/n-butyllithium ratio of 2 : 1. The author assumes that the lithium counter-ion forms strong complexes with two molecules of tetrahydrofuran. Association constants were measured from the variation in rate which occurred on the addition of tetrahydrofuran.

The calculated equilibrium constants will be inaccurate because a first-order dependence of propagation rate on ionic-centre concentration was assumed even in pure benzene. As shown above, the propagation rate is half order in active-centre concentration in benzene, although recent work in this laboratory has shown<sup>31</sup> that, with a few tenths of a per cent of tetrahydrofuran in benzene, the order does change from one half to unity. The variation of rate on the addition of tetrahydrofuran appears to be more complex than previously reported, and we find no evidence for the exclusive formation of a 2 : 1 complex. The results, however, do indicate that strong complexes are formed preferentially by alkali metal ions with basic solvents, and are also consistent with the idea that a solvated ion-pair is the major species in benzene in the presence of quite low concentrations of tetrahydrofuran. The increase in rate on addition of tetrahydrofuran is not as large as might be expected from a very low ion-pair concentration in benzene. This suggests that the solvated ion-pair could be less reactive in the mixture than the relatively unsolvated ion-pair in pure benzene.

## ISOPRENE

Isoprene polymerization appears to proceed in a similar manner to styrene, in benzene<sup>32</sup> or n-hexane<sup>29, 32</sup> or in bulk<sup>22</sup> monomer; alkyllithium

catalysts produce characteristic S-shaped rate curves. The low initiation rate which causes this behaviour was demonstrated for bulk polymerization<sup>22</sup>, and certainly occurs in other solvents of low dielectric constant. Polymers of narrow molecular weight distribution are formed, particularly if the broadening due to slow initiation is circumvented by a pre-initiation technique<sup>29</sup>, and the average molecular weights are those expected if one molecule of alkyllithium initiates each polymer chain. The chain-propagation step is first order in monomer concentration. Lundborg and Sinn<sup>33</sup> established this fact by studying the later stages of reaction where chain initiation is complete, and Morton and co-workers<sup>29</sup> by pre-initiating the reaction with a small amount of monomer at a higher temperature. The latter workers found that the propagation step is half order in active-centre concentration and has an activation energy of 22 kcal in n-hexane. The initiation step has not been studied directly, but it seems likely that it is similar to that for styrene. Lundborg and Sinn<sup>33</sup> reported that the "over-all rate" was proportional to  $[\text{Li—}]^{1/n}$  with  $n$  values of 6 at  $10^{-2}$  molar and 3 at  $10^{-5}$  M and where  $[\text{Li—}]$  is the concentration of organically-bonded lithium. The meaning of "over-all rate" is not clear, but the quoted results are closely similar to those given for the dependence of the initiation rate on n-butyllithium concentration, found previously for styrene.

Korotkov and co-workers<sup>32</sup> reported the "rate" (the apparently linear portion of the S-shaped curve) to be between first and second order in monomer concentration, a result to be expected in a period where initiation and propagation are proceeding simultaneously. Their proposed polymerization scheme, which does not consider association of n-butyllithium and involves bimolecular termination between chain ends, is not likely to be correct. The use of the stationary state principle in a reaction of this type is not justified, and the difficulties in this interpretation are shown in the final numerical values of the derived rate constants which are inconsistent with the original approximations made.

Morton and co-workers<sup>29</sup> have suggested that the half-order dependence of the propagation rate on the active-centre concentration is due to association of the polymer ion-pairs, and that only dissociated products are active in polymerization. Ion-pair aggregation was also demonstrated by the sharp decrease in the solution viscosity on the addition of chain-terminating agents and consequent destruction of ionic centres. Addition of n-butyllithium to the solution of active polymers also reduces the solution viscosity; this suggests that an n-butyllithium molecule can replace a polymer chain end in the associated complex. Some association of n-butyllithium with the active chain ends is thus possible, particularly in the early stages of polymerization where the ratio of n-butyllithium to active polymer is high.

If an equilibrium process of the type:



is assumed, the decrease in solution viscosity on addition of n-butyllithium can be satisfactorily explained. However, no association of n-butyllithium with itself can be assumed even at  $10^{-1}$  M concentration (see *Table 6* in the paper by Morton, Bostick and Livigni<sup>29</sup>). This interpretation is thus

not in agreement either with cryoscopic data at the higher concentrations or with the comparative insensitivity of the polymerization rate to *n*-butyllithium concentration at lower concentrations. This discrepancy requires further investigation.

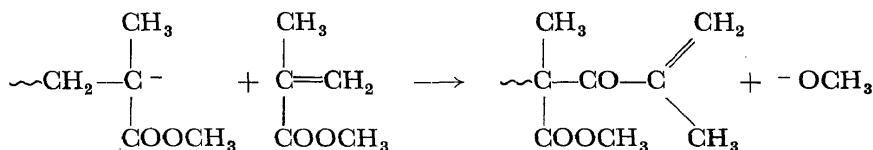
In tetrahydrofuran, the polymerization catalysed by *n*-butyllithium is faster and the rate curve is no longer sigmoidal in shape<sup>29</sup>. Thus initiation is somewhat faster in this system. The over-all rate, which will correspond to the propagation rate if initiation is rapid, is first order in monomer and active-centre concentrations. This indicates that the propagation consists of a simple ion-pair reaction with monomer. The over-all activation energy is 7 kcal. Some attack of *n*-butyllithium on the solvent occurs, as is to be expected from the experiments of Gilman and Gaj<sup>34</sup>.

### BUTADIENE

From a kinetic standpoint, butadiene has received less attention than isoprene. Reaction orders and activation energies in the propagation step in tetrahydrofuran and *n*-hexane<sup>29</sup> were similar to those found for isoprene, and the results indicate a similar mechanism. In *n*-hexane solution, initiation by *n*-butyllithium is somewhat more rapid than for isoprene and the maximum rate is established at an early stage in the reaction. It must be emphasized, however, that the absence of a period of increasing rate does not automatically imply that initiation is instantaneous or that initiation is complete when the maximum rate is attained. *Figure 1* shows that this is not always so, for, in this particular case, chain-initiation is still proceeding rapidly at the period of maximum rate. Pre-initiation by addition of a small amount of monomer at a higher temperature may not result in completion of the initiation step either, for larger amounts of monomer may be necessary<sup>21</sup>. Thus, there is a possibility that, in the experiments with butadiene and isoprene, the measured rates were not simply that of chain-propagation but included a small contribution from chain-initiation.

### METHYL METHACRYLATE

The mechanism of methyl methacrylate polymerization is undoubtedly more complex than that of unsaturated hydrocarbons. Early reports<sup>35</sup> suggested that the methacrylate anion undergoes rapid termination in tetrahydrofuran solution even at  $-78^{\circ}$ . Later experimenters have shown that this is not so<sup>36, 37</sup>, although they do not definitely exclude the possibility of some termination. Rempp and co-workers<sup>38</sup> have reported that deactivation in tetrahydrofuran occurs rapidly at room temperature if excess monomer is present, but that the ions are stable if polymerization is completed at low temperature and the mixture is subsequently warmed up. Hence, they suggest that, at room temperature, termination occurs by attack of the carbanion on the ester group of a monomer molecule:

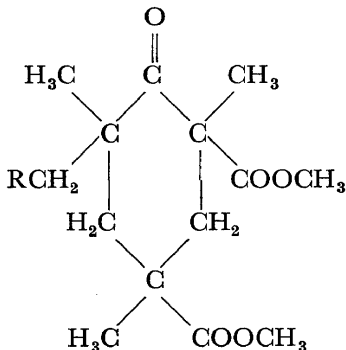




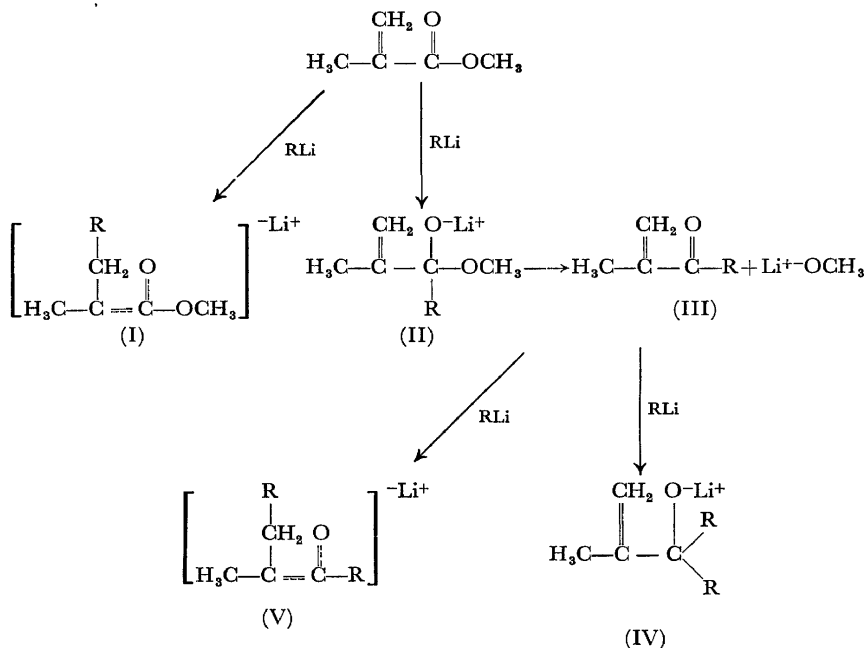
HOMOGENEOUS ANIONIC POLYMERIZATION

This termination mechanism has also been proposed by Schreiber<sup>39</sup>. A similar attack of the active end on polymeric ester groups is not observed<sup>38</sup>.

In toluene solution at low temperatures<sup>40</sup>, almost all the high polymer chains are active towards <sup>14</sup>CO<sub>2</sub> or CH<sub>3</sub>COO<sup>3</sup>H, which indicates that chain-termination is negligible under these conditions. Low polymer isolated from phenyl magnesium bromide or fluorenyllithium catalysis contains some cyclic trimer:

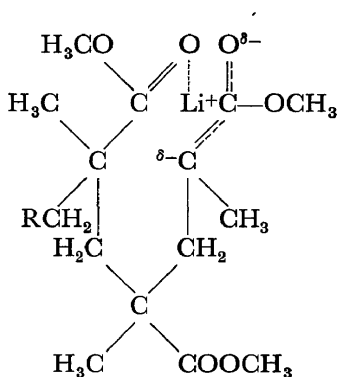


where R may be the initiator fragment or a short polymer chain. It has not been proved conclusively whether the cyclization occurs in the polymerization<sup>41</sup> or in the isolation procedure<sup>42</sup>. A more complex problem exists in that the monomer has an ester group which can be attacked by organo-metallic compounds. Possible initial reactions involving attack on the ester group and the double-bond are shown in *Scheme 1*. A product correspond-

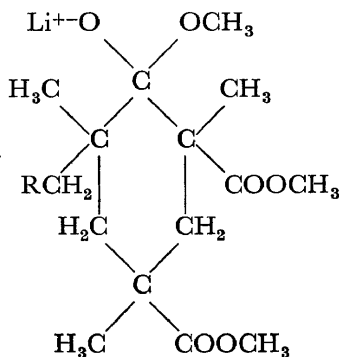


*Scheme 1*

ing to (V) was isolated in the polymerization of methyl methacrylate, catalysed by phenyl magnesium bromide in toluene<sup>41</sup>, and one corresponding to (IV) by the action of phenyllithium in ether<sup>39</sup>. The alkoxide ions are presumably inactive in causing further polymerization, although Goode and co-workers<sup>43</sup> have demonstrated that sodium methoxide is an effective catalyst for the polymerization of methyl methacrylate in liquid ammonia. Products (I) and (V) are basically resonance-stabilized carbanions and should act as initiating centres. The extent to which the ester group is attacked will obviously depend on the reactivity of the catalyst used, and will be least for the relatively stable carbanions such as fluorenyl, where in fact no products of this type have been isolated. In all cases, however, in toluene solution a considerable number of initiator molecules are found in low molecular weight products which include the above products, the cyclic ketone, and polymers of molecular weight below about 2,000. Polymer of molecular weight above 1,000 was shown to have one initiator fragment per chain in the polymerization catalysed by phenyl magnesium bromide at 0°, or by fluorenyllithium at -60°. Thus, structure (I) would appear to be the effective initiator for high polymer chains. The polymerization mechanism is apparently restricted to chain-initiation and chain-propagation. Leaving aside for the moment the low molecular weight products, the high polymer would be expected to have a narrow molecular weight distribution, particularly since fluorenyllithium, at least, initiates rapidly<sup>40</sup>. The high polymer formed in toluene solution has, however, a very wide molecular weight distribution, and it is necessary to postulate the occurrence of some special features in the propagation step which allow different over-all rates of growth. It has been postulated<sup>41, 42</sup> that isotactic placements proceed rapidly *via* a cyclic<sup>41</sup> intermediate or one involving lithium complexed to the carbonyl groups of the last two monomer units<sup>42</sup>. Chain growth is slowed down from time to time by random non-isotactic addition groups which lead to formation of a more stable ring structure involving three monomer units in the form of a complex<sup>42</sup>:



or of a real cyclic structure<sup>41</sup>:



It is proposed that these structures are converted to the linear form and add monomer slowly until enough isotactic segments are produced to re-form a rapidly propagating helical structure. More exact details are given in the original papers. It is difficult to assess whether this mechanism would give the expected wide distribution of molecular weights.

Glusker and co-workers<sup>42</sup> reported that the fluorenyllithium-catalysed polymerizations in toluene-ether (10 per cent) solutions at low temperature show first-order dependence on monomer concentration to high conversions if allowance is made for the almost immediate formation of cyclic trimer. A more complex dependence on monomer concentration, particularly at low catalyst concentrations, has been observed by Korotkov and co-workers<sup>44</sup> and in this laboratory<sup>45</sup> in the *n*-butyllithium-catalysed polymerization in toluene solution at low temperatures. The former workers proposed a mechanism which involved chain-initiation, wastage of initiator by attack on the ester function of the monomer, and monomer termination. The last reaction does not seem likely in view of the evidence given above on lack of termination reactions. Otherwise the validity of the scheme is difficult to assess, as the approximate solution of the differential equations given is only valid at low conversions. In this region, much of the product formed is of quite low molecular weight, so that the behaviour is not typical of the reaction as a whole. We have found that low molecular weight material is formed almost exclusively in the first few minutes in this system, and that its amount then remains constant through the reaction. At high catalyst concentrations, the monomer consumption is approximately first order in monomer concentration internally over much of the reaction, but the apparent first-order constant is a function of initial monomer concentration. This variation seems to be connected with variations in the amount of low molecular weight products. At low catalyst concentrations, the monomer consumption curves are more complex, and a distinct break occurs at the point where low molecular weight material ceases to form. There are strong grounds for the supposition that formation of low molecular weight polymer and high molecular weight polymer occur in different stages of the reaction when *n*-butyllithium is used as catalyst, and that the former material cannot grow into high polymer later. Further monomer is poly-

merized rapidly if added after the polymerization of the original monomer sample is complete, and no additional low molecular weight polymer is formed. Therefore, low molecular weight polymer formation seems to depend on the mechanism of *n*-butyllithium initiation or on abnormal behaviour of polymer ions of low molecular weight. Thus, no simple kinetic scheme is likely to cover both stages of the polymerization adequately.

### COPOLYMERIZATION

The study of anionic copolymerization has received some attention, and certain difficulties in the interpretation of the results are apparent. Graham and co-workers<sup>46</sup> have emphasized that it is necessary to ensure that the experiments measure only the relative rates of monomer addition in the propagation step and are uninfluenced by the initiation reaction. This is particularly important if the over-all conversion is small or the experimental results are extrapolated to zero conversion. For example, with certain initiators, a few styrene units may be introduced into the polymer in the copolymerization of styrene and methyl methacrylate owing to preferential initiation to styrene. Similarly, O'Driscoll and Tobolsky<sup>47</sup> have shown that in the same system with lithium metal initiation in non-polar solvents, some styrene is incorporated into the polymer. This was attributed to initiation proceeding by electron-transfer to monomer and the addition of appreciable amounts of styrene by the free radical ends before dimerization. This factor is of negligible importance in systems where the anions add monomer much more rapidly.

Similar caution is required in the interpretation of alkyllithium initiated polymerizations in non-polar solvents. Rakova and Korotkov<sup>48</sup> have studied the polymerization of isoprene-butadiene mixtures in *n*-hexane, catalysed by *n*-butyllithium. They found that butadiene is preferentially incorporated into the polymer and that the "rate" is that of butadiene homopolymerization, rather than that of isoprene which is faster. Preferential adsorption of one monomer around the chain ends was postulated to explain these results. Copolymerization is, however, a complex simultaneous reaction consisting of two initiation steps and four propagation steps. A better understanding of the rates of all six in conjunction with experiments carried out under conditions where chain-initiation is known to be complete is necessary before detailed mechanisms are postulated. The "rate" of the homopolymerizations and the copolymerizations are usually expressed as the maximum rate, and, as seen previously, chain-initiation is often important at this stage, so that a comparison of these rates is relatively meaningless. In the butadiene-isoprene system, it seems likely that initiation to butadiene occurs more rapidly than to isoprene, and, if the butadienyl anion is more stable than the isoprenyl anion, then butadiene will continue to be preferentially incorporated into the chain\*.

### STEREOSPECIFICITY

Many theories of the stereo-regulating effect, particularly of lithium compounds, exist in the literature. It will be difficult to make a decision

\* Polarographic measurements indicate that butadiene has a higher electron affinity than isoprene.

## HOMOGENEOUS ANIONIC POLYMERIZATION

on their relative merits from an experimental point of view. The special stereo-regulating effect of lithium compounds disappears when low concentrations of ethers are added, and corresponds to the point at which the reaction order in active centres changes and ion-pair aggregation presumably is destroyed. Since, however, in the associated systems the experimental evidence indicates that the active entity is the free ion-pair, it does not seem likely that ion-pair dimerization causes the special stereo-regulating effect. Morton<sup>49</sup> has proposed that the active dissociation product of the ion-pair dimer is a triple-ion of the type  $(RLiR)^-$  rather than an ion-pair. Steric requirements in the triple-ion could then cause stereo-specificity in the propagation step for certain monomers. Conductivity studies on salts in benzene indicate that, where the quadrupole concentration is high, the concentration of free ions and triple-ions is vanishingly small. The major dissociation product is, therefore, more likely to be a simple ion-pair. It seems that specific effects must be connected with polar interaction of the  $Li^+$  counter-ion with adjacent centres of high electron density on the polymer chain. Both this effect and ion-pair association seem to disappear for similar reasons on addition of small amounts of ethers, due to preferential association with the more electronegative groups on the added solvent.

### Summary

Studies on anionic polymerization continue to increase in scope. Recent work in this field is discussed with particular reference to kinetic studies. Kinetic studies on the polymerization of styrene,  $\alpha$ -methylstyrene, methyl methacrylate and isoprene have recently been carried out. In some cases the investigations are still in the preliminary stage, but useful information on the mechanism of the reaction can be obtained. The nature of the reactive intermediates in the reactions is also discussed particularly in terms of conductivity studies in solvents of low dielectric constant, and measurements of ultra-violet absorption spectra.

### Note added in proof (5.2.62)

Recent work in the laboratory has shown that the chain-propagation step in the polymerization of isoprene in cyclohexane, catalyzed by *n*-butyllithium, is of low order in active chain concentration (1/5 to 1/6). Similar results would be expected in *n*-hexane. It seems probable that the poly-isoprene anions are more highly associated in solvents of low dielectric constant than is suggested in the text, and that previous results were indeed affected by incomplete chain initiation.

*The author is indebted to Dr D. J. Worsfold and Dr D. M. Wiles for the experimental work they have carried out and for frequent discussions.*

### References

- <sup>1</sup> M. G. Evans, W. C. E. Higginson and N. S. Wooding. *Rec. trav. chim.*, **68**, 1069 (1949)
- <sup>2</sup> J. J. Sanderson and C. R. Hauser. *J. Am. Chem. Soc.*, **71**, 1595 (1949)
- <sup>3</sup> W. C. E. Higginson and N. S. Wooding. *J. Chem. Soc.*, **1952**, 760
- <sup>4</sup> R. S. Stearns and L. E. Forman. *J. Polymer Sci.*, **41**, 381 (1959)
- <sup>5</sup> A. V. Tobolsky and C. E. Rogers. *J. Polmer Sci.*, **40**, 73 (1959)
- <sup>6</sup> Y. L. Spirin, A. R. Gantmakher and S. S. Medvedev. *Vysokomolekulyarnye Soedineniya*, **1**, 1258 (1959)
- <sup>7</sup> G. E. Coates. *Organometallic Compounds*, p. 1, Methuen, London (1956)
- <sup>8</sup> E. Warhurst. *Discussions Faraday Soc.*, **2**, 239 (1947)
- <sup>9</sup> G. Wittig and E. Stahnecker. *Ann. Chem., Liebigs's*, **605**, 69 (1957)
- <sup>10</sup> W. Bingel. *Z. Naturforsch.*, **10A**, 462 (1955)
- <sup>11</sup> K. Kuwata. *Bull. Chem. Soc. Japan*, **33**, 1091 (1960)
- <sup>12</sup> M. Levy, M. Szwarc, S. Bywater and D. J. Worsfold. *Polymer*, **1**, 515 (1960)
- <sup>13</sup> D. J. Worsfold and S. Bywater. *J. Chem. Soc.*, **1960**, 5234

## S. BYWATER

- <sup>14</sup> C. A. Kraus. *J. Phys. Chem.*, **60**, 129 (1956)  
<sup>15</sup> M. Szwarc. *Nature*, **178**, 1168 (1956)  
<sup>16</sup> M. Szwarc. *Fortschr. Hochpolymer. Forsch.*, **2**, 275 (1960)  
<sup>17</sup> G. Allen, G. Gee and C. Stretch. *J. Polymer Sci.*, **48**, 189 (1960)  
<sup>18</sup> D. J. Worsfold and S. Bywater. *Can. J. Chem.*, **36**, 1141 (1958)  
<sup>19</sup> C. Geacintov, J. Smid and M. Szwarc. *J. Am. Chem. Soc.*, **83**, 1253 (1961)  
<sup>20</sup> R. C. P. Cubbon and D. Margerison. *Proc. Chem. Soc.*, **1960**, 146  
<sup>21</sup> D. J. Worsfold and S. Bywater. *Can. J. Chem.*, **38**, 1891 (1960)  
<sup>22</sup> E. N. Kropacheva, A. Dolgoplosk and E. M. Kuznetsova. *Doklady Akad. Nauk S.S.S.R.*, **130**, 1253 (1960)  
<sup>23</sup> K. F. O'Driscoll and A. V. Tobolsky. *J. Polymer Sci.*, **35**, 259 (1959)  
<sup>24</sup> F. J. Welch. *J. Am. Chem. Soc.*, **81**, 1345 (1959)  
<sup>25</sup> F. Hein and H. Schramm. *Z. physik. Chem.*, **151**, 234 (1930)  
<sup>26</sup> G. Wittig, F. J. Meyer and G. Lange. *Ann. Chem., Liebigs*, **571**, 167 (1951)  
<sup>27</sup> T. L. Brown and M. T. Rogers. *J. Am. Chem. Soc.*, **79**, 1859 (1957)  
<sup>28</sup> M. T. Rogers and T. L. Brown. *J. Phys. Chem.*, **61**, 366 (1957)  
<sup>29</sup> M. Morton, E. E. Bostick and R. Livigni. *Rubber & Plastics Age*, **42**, 397 (1961)  
<sup>30</sup> F. J. Welch. *J. Am. Chem. Soc.*, **82**, 6000 (1960)  
<sup>31</sup> D. J. Worsfold and S. Bywater. Unpublished results  
<sup>32</sup> A. A. Korotkov, N. N. Chesnokova and L. B. Trukhmanova. *Vysokomolekulyarnye Soenineniya*, **1**, 46 (1959)  
<sup>33</sup> C. Lundborg and H. Sinn. *Makromol. Chem.*, **41**, 242 (1960)  
<sup>34</sup> H. Gilman and B. J. Gaj. *J. Org. Chem.*, **22**, 1165 (1957)  
<sup>35</sup> M. Szwarc and A. Rembaum. *J. Polymer Sci.*, **22**, 189 (1956)  
<sup>36</sup> F. Wenger. *Chem. & Ind. (London)*, **1959**, 1094  
<sup>37</sup> R. K. Graham, D. L. Dunkelberger and E. S. Cohn. *J. Polymer Sci.*, **42**, 501 (1960)  
<sup>38</sup> P. Rempp, V. I. Volkov, J. Parrod and C. Sadron. *Bull. soc. chim. France*, **1960**, 1919  
<sup>39</sup> H. Schreiber. *Makromol. Chem.*, **36**, 86 (1959)  
<sup>40</sup> D. L. Glusker, E. Stiles and B. Yoncoskie. *J. Polymer Sci.*, **49**, 297 (1961)  
<sup>41</sup> W. E. Goode, F. H. Owens and W. L. Myers. *J. Polymer Sci.*, **47**, 75 (1960)  
<sup>42</sup> D. L. Glusker, I. Lysloff and E. Stiles. *J. Polmer Sci.*, **49**, 315 (1961)  
<sup>43</sup> W. E. Goode, W. H. Snyder and R. C. Fettes. *J. Polymer Sci.*, **42**, 367 (1960)  
<sup>44</sup> A. A. Korotkov, S. P. Mitsengender and V. N. Krasulina. Paper presented at Symposium on Macromolecules, Moscow (1960)  
<sup>45</sup> D. M. Wiles and S. Bywater. *Polymer*, in press  
<sup>46</sup> R. K. Graham, D. L. Dunkelberger and W. E. Goode. *J. Am. Chem. Soc.*, **82**, 400 (1960)  
<sup>47</sup> K. F. O'Driscoll and A. V. Tobolsky. *J. Polymer Sci.*, **38**, 363 (1959)  
<sup>48</sup> G. V. Rakova and A. A. Korotkov. *Doklady Akad. Nauk S.S.S.R.*, **119**, 982 (1958)  
<sup>49</sup> M. Morton. *Chem. Eng. News*, **38**, No. 39, 55 (1960)