Mechanism of initiation of anionic polymerization by alkali metals

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In most reviews and books dealing with the mechanisms of anionic initiation and polymerization, the modes of initiation in good solvents like tetrahydrofuran (THF) by alkali metals and by electron transfer catalysts have been bracketed together as if they were mechanistically identical and the latter were merely a solubilized form of the former[1-3]. Clearly, since initiation by alkali metal is heterogeneous and that by electron transfer catalysts is homogeneous there must be significant differences between the two, but these have not been adequately developed. In this communication these differences are examined and a proposal is made of a mechanism for anionic initiation by alkali metals which, hopefully, is adequately supported by experimental evidence.

The mechanism developed for initiation in solvents like THF by electron transfer catalysts and subsequently assumed to hold also for alkali metal initiation, is shown in equations (1) to (3) with styrene as monomer.

The initial process involves a one electron transfer equilibrium to form the radical anion I. This species may subsequently dimerize to form the dimer dianion II or may react with monomer to form a 'true' radical anion dimer III. In both cases the reaction involves a tail-to-tail linkage to generate the resonance stabilized benzyl anion or radical. Species II then propagates with further monomer by a head-to-tail addition to perpetuate the benzylic anion, while species III may propagate anionically in the same manner at one end and free radically at the other until termination by combination of two of the latter species yields a polymeric dianion. Although the existence of III has not been experimentally verified (see below) and the author believes that at best it makes only a very small contribution to the total propagating species, there seems to be little doubt that the picture given

by equations (1) and (2) at least is essentially correct.

Objections arise from the direct application of this scheme to alkali metal initiation. This process, being heterogeneous, almost certainly involves initial adsorption of the monomer on to the metal surface, and the following mechanism is proposed, illustrated schematically for styrene in equation (4), which takes this extra parameter into account. In this scheme the monomer, which is highly polarizable due to its conjugate double bond system, is assumed to adsorb on to the metal surface. The further assumption is then made that the adsorbed monomer molecules are mobile enough to rotate, and do so until the methylene groups from adjacent molecules are sufficiently close to allow a coupling reaction to occur to form an adsorbed dimer dianion. The resulting concentration of the anionic charges on the methine carbons creates an attractive force strong enough to remove the metal cations from the lattice, the powerful cation solvating power of the solvent (THF) greatly aiding this process. This mechanism therefore requires that adsorption of the monomer takes
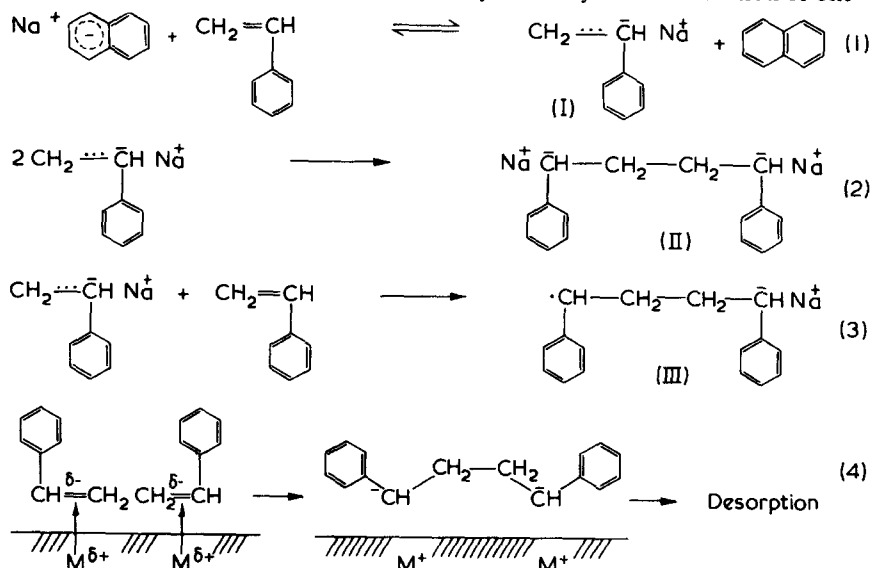
place prior to reaction, and that reaction takes place to form the dimer dianion directly, i.e. no radical intermediates of type I or III are postulated. The experimental evidence which supports this mechanism is now presented in itemised form.

(a) The synthesis of the α-methylstyrene tetramer by direct reaction of a THF solution of the monomer with sodium metal under controlled conditions of concentration and temperature provided the strongest evidence for the intermediate formation of radical anions[4]. The tetramer was originally thought to have structure IV and to be formed by the dimerization of radical anion intermediates of structure analogous to III[5].
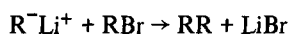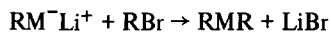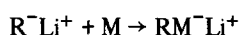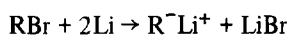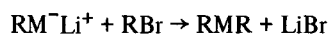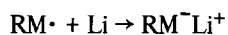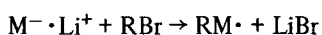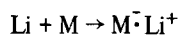

(IV)

(V)
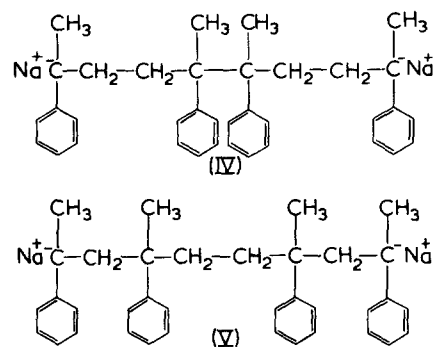
However, it was more recently shown to have the structure V, and its formation has been explained as the thermodynamically allowed addition of one

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monomer molecule at each end of the dimer dianion of structure II[6]. The resulting head-to-tail terminal configuration thereby increases steric hindrance to a point where further propagation may not occur under the monomer concentrations specified. Thus the existence of a dimer radical anion need not be invoked to explain tetramer formation.

(b) A very vigorous reaction takes place when THF solutions of alkyl halides are brought into contact with alkali metal and Wurtz condensation products are formed. However, if a monomer such as styrene is introduced into this system, the violence of the reaction is immediately very much reduced and a smoother but different reaction ensues. The latter process involves the initial formation of dimer dianions as in equation (4), and their subsequent addition of further monomer units until capped by the alkyl halide molecules[7].

It is reasonable to assume that this less vigorous reaction comes into prominence because of the superior adsorptive power of the monomer. Thus the monomer with its easily polarisable π electron system forms a monolayer on the metal surface which prevents access to the σ-bonded but potentially more reactive alkyl halides. These are then consumed principally by reaction with the desorbed oligomeric dianions.

(c) When equimolar amounts of monomer (M) and alkyl bromide (RBr) in THF are reacted with alkali metal, greater than 90% yield of RMMR is obtained, about 5% RMR and the remainder being RMMMR and RR[7]. It has been shown by ^{1}H n.m.r. analysis that the dimer and the trimer adducts contain a tail—tail linkage and so are derived from an initially generated dimer dianion of structure II. It is possible that the monomer adduct could be formed by one of two routes, equations (5) or equations (6).

$$Li + M \rightarrow M^{\cdot} Li^+$$

$$M^- \cdot Li^+ + RBr \rightarrow RM \cdot + LiBr$$

$$RM \cdot + Li \rightarrow RM^- Li^+$$

(5)

$$RM^- Li^+ + RBr \rightarrow RMR + LiBr$$

$$RBr + 2Li \rightarrow R^- Li^+ + LiBr$$

$$R^- Li^+ + M \rightarrow RM^- Li^+$$

(6)

$$RM^- Li^+ + RBr \rightarrow RMR + LiBr$$

$$R^- Li^+ + RBr \rightarrow RR + LiBr$$

The former requires the intermediate formation and desorption of a monomer radical anion, whilst the latter assumes a small amount of direct reaction of the alkyl bromide with the alkali metal.

Of the two alternatives equations (6) are preferred as they alone explain the small amount of RR formed. Furthermore, it has been found that if alkyl chlorides are used in place of alkyl bromides the amounts of RMR and RR generated are greatly increased[8]. Evidently the greater strength and stability of the carbon—chlorine bond allows the alkyl chloride to penetrate further through the dimer dianions desorbing from the surface, and consequently the possibility of direct reaction with the metal to form the alkali metal alkyl is enhanced. The increase in RMR is accompanied by an increase in head—tail linked dimer formed, supporting this view. Thus there is no concrete evidence produced from these wide ranging studies on the direct reaction of monomer with alkali metal that supports the formation of either a monomer or a dimer radical anion.

(d) When equimolar amounts of aryl halide and monomer are reacted with alkali metal in THF, only very small yields of the dimer diadducts are formed and the main products are oligomeric material and the coupled product of the Wurtz reaction[9]. In this case the polarizability of the halide, derived from its aromaticity, allows it to compete effectively with the monomer for adsorption sites on the alkali metal surface, and so the Wurtz condensation process becomes predominant.

An interesting extension of this picture is provided by the behaviour of the aralkyl dihalide, p-xylylene dibromide under similar conditions. Experiments in which butadiene was used as monomer produced copolymers with compositions which were governed by the initial monomer: dihalide molar ratio[10]. N.m.r. examination of these products showed all to give a sharp singlet at 7.2 τ which was ascribed to the methylene units in the grouping

$$\underset{\text{(structure)}}{} -CH_2-CH_2- \underset{\text{(structure)}}{}$$
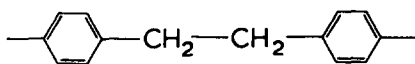
and quantitative analysis of the spectra demonstrated that the p-xylylyl units existed exclusively as dimer moieties in the polymer chain regardless of the initial reactant ratio.

Presumably the p-xylylene dibromide is able to adsorb effectively until

dimerisation occurs on the surface after which the loss in configurational entropy required to hold this species to the metal is too great and it desorbs to react in the normal way with the oligomeric dianions being generated simultaneously (equation 7).

$$BrCH_2-\langle\rangle-CH_2Li \quad BrCH_2-\langle\rangle-CH_2Br$$

$$BrCH_2 \underset{CH_2-CH_2}{\overset{\downarrow}{}} CH_2Br \qquad (7)$$
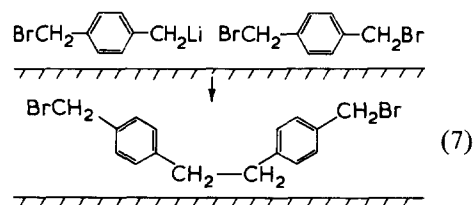
(e) The reactivities of ethyl bromide and ethyl tosylate (ethyl p-toluene sulphonate) to carbanions have been compared under a variety of conditions[9]. The alkyl tosylates are as susceptible to nucleophilic attack as the alkyl iodides, and indeed when ethyl tosylate was reacted with living polymers quantitative capping of the polymer chains was achieved. Ethyl bromide gave similar results. When, however, these reagents were each reacted with equimolar monomer and excess alkali metal in THF, their behaviours were markedly different. Virtually quantitative formation of the dimer diadduct was obtained with ethyl bromide whilst only about 10% of this product was generated by the tosylate and a gas, possibly butane, was seen to be evolved during the course of the reaction.

Again, the polarizable and dipolar character of the tosylate ligand allows this species to compete successfully for the adsorption sites on the metal surface, and therefore allows the Wurtz reaction a prominent role. In contrast, the alkyl bromide, being entirely σ-bonded, cannot interact as effectively and so the generation of dimer dianions can proceed virtually uninterruptedly.

It is to be expected that different monomers are adsorbed to differing degrees by the alkali metal surface, and this concept can be developed to provide an explanation for the observation that significant quantities of styrene are found in polymers produced in the first few percent reaction of equimolar quantities of styrene and methyl methacrylate with a dispersion of lithium metal[11]. The amount is dependent on the presence and the nature of the solvent (*Table 1*), and has to be contrasted with the composition of less than 1% styrene in polymer prepared using an equimolar mixture of the same ingredients when initiated by n-butyllithium.

Table 1 Styrene composition of polymers formed by reacting equimolar mixtures of styrene and methyl methacrylate with a lithium dispersion in various reaction media[11]

Solvent	Styrene (%)
Bulk	28
Heptane	15
THF	7
$(C_2H_5)_3N$	3
$(C_2H_5)_2NH$	1
NH_3	0

Tobolsky and coworkers[12-14] originally proposed that lithium initiated by a one electron transfer to monomer to produce a radical anion species of type I, and that this propagated anionically at one end and by a free radical mechanism at the other until termination occurred. The anionic mechanism propagates methyl methacrylate exclusively whereas free radical propagation in equimolar styrene—methacrylate mixtures yields a 50/50 random copolymer. Segments of the latter composition should therefore appear in the product from lithium dispersion initiation if such a mechanism were to hold. This process was, however, later disproved by Overberger and Yamamoto[15] who showed by [1]H n.m.r. examination that the styrene component of these polymers was present as homopolymer sequences and that there was no evidence of random sequences of both monomers. They proposed that styrene was adsorbed on to the surface in preference to methyl methacrylate and homopropagated anionically until the oligomer detached itself and reacted with methyl methacrylate in the monomer mixture.

Work carried out in these laboratories confirms the hypothesis that the adsorptive power of styrene is greatly superior to that of methyl methacrylate

on lithium metal. Under conditions which, with styrene alkyl halide and lithium metal in THF, yield significant quantities of the dimer adduct, methyl methacrylate and the same reagents form a carbinol almost exclusively (90%)[16,17]. The reaction has been shown to proceed by initial reaction of alkyl halide with lithium metal to generate alkyl lithium [first equation (6)] which then attacks methyl methacrylate in the manner of a Grignard reagent to yields first the ketone and then the carbinol. Thus the adsorption of methyl methacrylate on to lithium metal must be very small compared with that of styrene, and this adds support to Overberger's theory.

It is interesting to note from *Table 1* that the amount of styrene incorporated decreases as the solvating power of the solvent and its ability to interact directly with the metal increases. The concept that the dimer dianion is desorbed on its formation need apply only in the presence of a good solvating solvent like THF; in bulk or in inert solvents like heptane the free energy gain due to solvation on desorption is largely lost, and so the probability of further propagation on the surface with adsorbed styrene monomer is increased. Eventually the polystyrene oligomer grows to a chain length sufficient to create a favourable free energy change on desorption, and passes into solution where it subsequently reacts exclusively with methyl methacrylate. With the amine Lewis bases, their strong cation solvating powers support early desorption of oligomers and introduce direct competition by these solvents for the available adsorption sites. Furthermore, direct reaction with alkali metal yields

lithium amides which initiate homogeneously and so polymerize methyl methacrylate exclusively.

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Dilatometric investigations of the terpolymerization of benzyl methacrylate, styrene and methyl methacrylate

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INTRODUCTION

Investigations on the terpolymerization field are mainly dealing with the examination of the validity of the well

known Alfrey—Goldfinger equation[1]:

$$d[M_1] : d[M_2] : d[M_3] =$$

$$m_1 : m_2 : m_3$$

$$= M_1 \left[\frac{M_1}{r_{31} r_{21}} + \frac{M_2}{r_{21} r_{32}} + \frac{M_3}{r_{31} r_{23}} \right] \times$$

$$\left[M_1 + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}} \right]$$

$$: M_2 \left[\frac{M_1}{r_{12} r_{31}} + \frac{M_2}{r_{12} r_{32}} + \frac{M_3}{r_{32} r_{13}} \right] \times$$