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The Mechanism of Alkaline Catalytic Polymerisation of Hydrocarbon Monomers

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In contrast to free-radical polymerisation, there is no single theory of anionic polymerisation which could explain all the observed phenomena, these being treated usually from different standpoints. In the present review an attempt is made at a critical analysis of the existing hypotheses in this field. The bibliography includes 90 references.

The polymerisation of vinyl and divinyl compounds under the influence of alkali metals and their organic compounds is regarded by the majority of investigators as successive organometallic synthesis[1-5]. As a result of repeated stepwise addition of monomer molecules to the initial organometallic compound, a polymer with a high molecular weight is formed. If a fresh portion of monomer is added to such a polymeric organometallic compound, the former adds to the macromolecule and polymerisation is restarted. Szwarc very aptly called such growing polymer chains "living" polymers[6].

The growth of a "living" polymer occurs of course in the absence of impurities from the reaction medium (water, alcohol, aldehydes) and in the absence from the monomer of functional groups which could interact with the organometallic compounds.

In 1928 Ziegler[1,2] concluded, on the basis of his own experimental data and those of Schlenk[7] and other investigators, that the polymerisation of butadiene under the influence of sodium is a complex consecutive reaction in which the monomer adds to the organic disodium compound at each stage:

$$2\,Na + CH_2{=}CH{-}CH{=}CH_2 \rightarrow NaCH_2{-}CH{=}CH{-}CH_2Na \quad \text{or} \quad NaCH_2{-}\underset{\displaystyle CH{=}CH_2}{\underset{|}{CHNa}},$$

$$NaCH_2{-}CH{=}CH{-}CH_2Na + CH_2{=}CH{-}CH{=}CH_2 \rightarrow$$

$$\rightarrow NaCH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na,$$

$$NaCH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na + CH_2{=}CH{-}CH{=}CH_2 \rightarrow,$$

$$\rightarrow NaCH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na,$$

etc.

If an organosodium compound is used instead of metallic sodium, the mechanism of the growth of the polymeric chains does not change, only the monomer now adds to the monosodium compound:

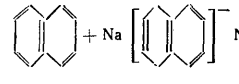
$$RNa + CH_2{=}CH{-}CH{=}CH_2 \rightarrow R{-}CH{-}CH{=}CH{-}CH_2Na\ .$$

Ziegler succeeded in isolating the intermediate products and in showing the stepwise occurrence of polymerisation. A characteristic feature of such stepwise reactions is the gradual growth of the molecular weight of the polymer with time. At low temperatures it is possible to terminate the chain growth at any stage. The degree of polymerisation is determined by the ratio of the amounts of monomer and catalyst consumed.

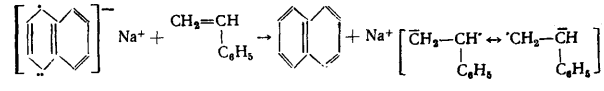
Ziegler[8,9], Medvedev[10], and Morton[11-13] pointed out the unusual form of the polymerisation reactions of vinyl monomers under the action of organic derivatives of alkali metals. For example, triphenylmethylsodium and diphenylethylpotassium polymerise butadiene and styrene with formation of polymers having relatively high molecular weights. Even in the presence of a large excess of the catalyst it is impossible to isolate the primary addition products of butadiene or styrene to the organometallic compound. When solutions of the monomer and the organometallic compound are mixed, the colour of the latter fades or disappears completely, but after the completion of polymerisation it is restored[10], i.e. the organometallic compound is hardly consumed and is regenerated. In contrast to the stepwise reactions, these processes were called catalytic. It was postulated that such catalytic polymerisation reactions must take place by a mechanism different from that of stepwise polymerisation. Contrary views were put forward on this subject: in his catalytic polymerisation Ziegler also isolated intermediate low-molecular products and thereby showed that the mechanism of the catalytic and stepwise polymerisation is the same[9].

Using an Alfin catalyst (typical) for catalytic polymerisation) and butyl-lithium (typical for stepwise polymerisation), Korotkov[14,15] obtained copolymers with the same composition. This confirmed that the reaction mechanism is the same in both cases. The observed differences in stepwise and catalytic polymerisation are related, according to Ziegler[9] and Korotkov[14], to the difference in the relative rates of initiation of polymerisation and of chain propagation and termination.

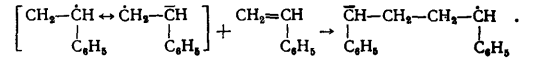
In recent years Szwarc and coworkers[3,16-18] put forward a new view concerning the mechanism of similar reactions. On dissolving in tetrahydrofuran in the presence of condensed aromatic compounds, metallic sodium forms a coloured complex[19,20]:



According to Szwarc, when a monomer is added to this compound, an electron is transferred from naphthalene-sodium to the monomer with formation of a radical-ion in which the unpaired electron is not localised, i.e. the compound formed is neither a true anion nor a true radical:

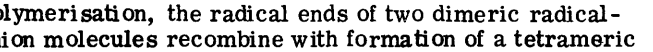


It was suggested that the radical-anion is formed only after the addition of a second styrene molecule without direct interaction between the three electrons:

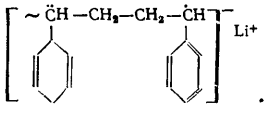


This structure of the dimer is the most likely, since both the anion and the radical are stabilised by the phenyl group. The dimeric radical-anion formed can, in principle, combine with styrene both by an anionic and a radical mechanism. As a rule, under the conditions of low-temperature

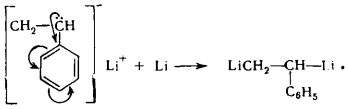
polymerisation, the radical ends of two dimeric radical-anion molecules recombine with formation of a tetrameric dianion, which becomes the sole active centre for polymerisation



Electron transfer from naphthalenesodium to the monomer takes place very rapidly in tetrahydrofuran but not at all in hydrocarbon media. Tobolsky's work [21-26] on the copolymerisation of styrene and methyl methacrylate in the presence of dispersed metallic lithium constitutes an experimental confirmation of Szwarc's hypothesis. The copolymers formed had in some cases an enchanced content of styrene units instead of being virtually pure poly(methyl methacrylate), which is obtained with other anionic catalysts, for example butyl-lithium. To account for the anomalous composition of the polymer, it was assumed that initiation with lithium is analogous to the reaction with naphthalenesodium, i.e. an electron is transferred from lithium to styrene with formation of a radical-anion with separated electrons:



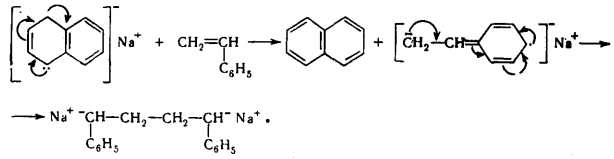
Such an active centre gives rise to further chain propagation by a radical mechanism at one end and by an anionic mechanism at the other. The enhanced styrene content in the resulting copolymer is due to polymerisation by a radical mechanism. In polar solvents the content of styrene units is sharply reduced. However, Korotkov and coworkers[27] obtained similar results in the polymerisation of styrene with methyl methacrylate in the presence of a typical anionic catalyst—solid methyl-lithium. It is suggested that the characteristic features of the reaction involving electron transfer from naphthalenesodium to styrene in solution should not apply to reactions with electron transfer from the surface of the metal, which occurs in the interaction of styrene with metallic lithium. Tobolsky's data are interpreted as follows: since, as a result of the primary initiation step, a radical-ion (styryllithium) is formed on the surface of the metal, its electron unsaturation must be immediately compensated by the electrons of the metal, which are highly mobile. As a result of the interaction between styrene and lithium, a dilithium compound should form:



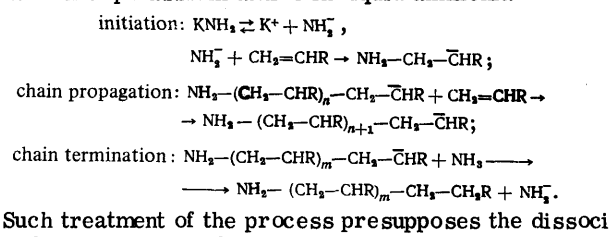
Because of the low solubility of the latter, chain propagation on the surface of the metal takes place preferentially with participation of the more readily adsorbed monomer. In this case styrene is evidently such a monomer.

After the polymeric chains reach a sufficiently large size and dissolve in the form of a dianion, the usual anionic polymerisation begins, in which virtually methyl methacrylate alone is incorporated in the polymeric chain. This leads to the formation of block polymers. On the other hand, in the copolymerisation of monomers with similar adsorption properties (for example, butadiene and styrene), the composition of the copolymer is independent of the heterogeneity of the catalyst or medium. Thus Tobolsky's results cannot serve as an unambiguous confirmation of Szwarc's hypothesis of the formation of a radical-anion with separated electrons.

On the basis of data on the copolymerisation of styrene and methyl methacrylate in the presence of anionic catalysts, Korotkov and coworkers[27] suggest that in polymerisation under homogeneous conditions the stage involving the formation of a radical-anion with separated electrons is absent. Dianions are formed by dimerisation in the initial initiation stage:

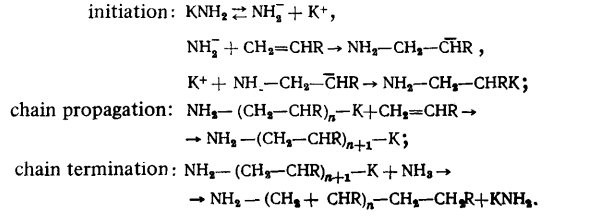


Price[28] was the first to suggest that alkaline polymerisation be regarded as an anionic process in which the active centre is trivalent negatively charged carbon (carbanion). Subsequently Sounderson and Hauser[29] and Higginson and Wooding[30] attempted to confirm experimentally the suggested mechanism. For example, the following mechanism was proposed for the polymerisation of styrene under the action of potassium amide in liquid ammonia[30]:



Such treatment of the process presupposes the dissociation of potassium amide into a free anion and cation. The attacking anion dissociates the double bond of the monomer with formation of a covalent bond at one end of the molecule and an active centre (carbanion) at the other. It is suggested that, within the limits of Coulombic attraction, the anion acts as an independent species, which is not bound to the counterion.

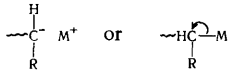
The mechanism quoted above was confirmed by kinetic studies on polymerisation carried out by Higginson, who showed that the rate of polymerisation is proportional to the concentration of the monomer and the amide ion, and that each polymer molecule contains the NH_2 group, while the molecular weight is independent of the concentration of the catalyst and is proportional to the concentration of the monomer. However, the results obtained can be explained with equal success on the basis of Ziegler's hypothesis by postulating the following mechanism for this reaction[31]:



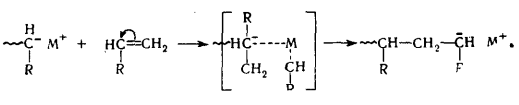
In this type of stepwise mechanism the equation for polymerisation kinetics and the dependence of the average molecular weight on the kinetic constants and the reactant concentrations are consistent with Higginson's relations obtained on the basis of an ionic mechanism of the reaction. Furthermore, Shatenshtein[32] showed that styrene polymerises on the surface of solid potassium amide, when the latter is not dissociated, and that this reaction cannot therefore be used as an unambiguous confirmation of Price's hypothesis.

Extensive experimental data confirm that the counterion always participates in the polymeric chain propagation steps. If the polymerisation centre were a free carbanion, the nature of the catalyst cation could affect only the rate of initiation of polymerisation centres but not the elementary chain propagation reaction. According to experimental data, the microstructure and properties of polymers, i.e. all the factors that are determined by the nature of the reaction, depend on the cation. For example, it is known that the content of 1,2- and 3,4-units in polydienes depends strongly on the nature of the cation[10,14,33,34] and that the stereoregularity of the polymer also depends on the latter[35,36]. Likewise the composition of the copolymers changes sharply on going from organolithium and organosodium compounds to organopotassium compounds[14,21,35,37]. The above differences in the structure of polymers and the composition of copolymers are sometimes explained by differences in the mechanism of the process. For example, it is believed that polymerisation in the presence of organolithium and organopotassium compounds takes place both by a radical and by an anionic mechanism, the relative contributions of which depend on the polymerisation conditions (the nature of the metal and medium)[5,34-42].

The experimental data on the effect of the catalyst metal on the rate and mode of polymerisation led the majority of investigators to the conclusion that in a hydrocarbon medium the active polymerisation centre is an ion pair or dipole[5,43-47]:



which is regenerated at the ends of the polymeric chains after the addition of each monomer molecule in the propagation step:



In polymerisation in the presence of catalysts which are readily ionised, for example, organosodium and organopotassium compounds in a strongly solvating or polar solvent, it is assumed that the degree of ionisation of the dipole is greatly enhanced and the active centre is regarded as a carbanion.

The hypotheses enumerated above have common features despite the apparent differences. The common features are that the polymerisation is regarded as a stepwise reaction involving consecutive addition of monomeric molecules to active centres, which may be anions or ion pairs, and therefore the nature of the active centres is analogous to that of the initial organometallic compounds.

Such treatment constitutes essentially a development of Ziegler's hypothesis with the sole difference that in the latter the C–M bond was regarded as covalent while in the new treatment it is regarded as ionic or of the ion–dipole type. A further difference is that, in the examination of actual reactions, account is now taken of the polarity of the bond in the terminal groups as a function of the structure of the monomer, the solvent, the nature of the metal, and other reaction conditions.

The experimental data which have accumulated in recent years cannot be accounted for from the standpoint of the stepwise polymerisation mechanism. To interpret the observed deviations, auxiliary hypotheses and assumptions are introduced. Some of the most typical cases are described below.

Thus regeneration of the catalyst after the completion of the polymerisation of butadiene or styrene in the presence of organic derivatives of alkali metals[8-10] (the reappearance of the initial colour of the solution) cannot be explained by regarding polymerisation as organometallic synthesis. For example, in the polymerisation of butadiene Ziegler[8,9] explained the reappearance of the colour of the initial catalyst (triphenylmethylsodium) by the metallation of traces of triphenylmethane. However, it is not clear why the metallation of the mobile hydrogen of triphenylmethane begins only after the completion of the polymerisation of butadiene. A similar case of regeneration of the catalyst in the polymerisation of butadiene in the presence of phenylisopropylpotassium in ethyl ether was accounted for by the possibility of the occurrence of a special case of "chain catalysis", but the mechanism of polymerisation and catalyst regeneration was not given[10].

In the polymerisation of isoprene[48], butadiene[49], and styrene[5,43] under the influence of butyl-lithium in a hydrocarbon medium and also of α-methylstyrene in the presence of naphthalenesodium in tetrahydrofuran[50] an anomalous variation of the reaction rate with the initial concentration of the organometallic compound was observed. The rate of reaction is independent of the initial concentration of the catalyst (n_0) when the latter is high and the resulting relation – $dm/dt = f(n_0)$ is represented by a curve exhibiting saturation.

This anomalous behaviour is explained by the specific properties of the organolithium compounds, namely the formation by the latter of association complexes in the hydrocarbon medium which are inactive in polymerisation[51-60]. For example, Welch[43] postulates the presence in the hydrocarbon medium of a dynamic equilibrium between the inactive associated molecules of the organolithium compounds and their monomeric active form:

$$(RLi)_n \overset{k}{\rightleftarrows} n\,RLi,$$

where R is butyl or polymeric radicals. In this case the rate of polymerisation reaction must be proportional to the sixth or seventh root of the initial concentration of butyllithium (for $n = 6$ or 7) and the variation of the rate of polymerisation of styrene with catalyst concentration will be represented by a curve exhibiting saturation. The hypothesis of the presence of association complexes combined with various assumptions makes it possible to explain for a number of cases the results of many investigations[53] and therefore it has found wide application and acceptance[5,52-64]. However, the proposed interpretation still requires a quantitative test. The adherents of the stepwise polymerisation mechanism, who assume that the nature of the active centres is the same as that of the initial organometallic compound, believe that the stability of the association complexes of the growing chains depends on the nature of the monomer, which explains the differences in the activity of monomers in polymerisation[68]. The higher activity of styrene compared with isoprene or butadiene when these are polymerised separately is attributed to the greater tendency of the growing polydiene chains towards association. However, the much lower activity of styrene compared with the above dienes in copolymerisation then becomes incomprehensible. Furthermore, it is known that the degree of association of organolithium compounds falls with increase in the size of the alkyl radical[46,65]. Therefore, on going from ethyllithium to polymeric lithium alkyls the anomaly in the dependence of the rate of polymerisation on the concentration of lithium alkyls should become less pronounced. However, this is not observed. For this reason, in the

formation of association complexes of mixed organolithium compounds (initial and high-molecular) the polymeric lithium alkyls should be present predominantly in the dissociated state. This must lead to the incomplete utilisation of the initial catalyst (for example butyl-lithium, even at relatively low concentrations of the latter), which should result in the formation of a polymer with a wide molecular weight distribution and a high number-average molecular weight. In anionic polymerisation the polymers obtained have as a rule a narrow molecular weight distribution and the degree of polymerisation is equal to the ratio of the concentrations of the monomer and the catalyst, i.e. all the initial organolithium compounds participate in the process. The evidence in favour of the presence of association complexes of "living" lithium polyalkyls, based on the observation that the viscosity of solutions of "living" polydienes falls on addition of butyl-lithium[66], tetrahydrofuran, or alcohol[67–69], cannot be regarded as unambiguous proof. The postulate that the anomalous relation $dm/dt = f(n_0)$ is due to the association of the organometallic compound in the hydrocarbon medium is inconsistent with the data of Podolsky and Korotkov[50] on the polymerisation of α-methylstyrene under the action of naphthylsodium in tetrahydrofuran. It was shown that in tetrahydrofuran, where organometallic compounds are not associated[43,57–67,70,71], the rate of polymerisation is also independent of the initial concentrations of the catalyst when the latter are high. A similar anomalous relation was observed by Szwarc and coworkers and Schulz and coworkers[72–75] in the polymerisation of styrene in tetrahydrofuran under the influence of "living" polystyrene. They found that the polymerisation rate constant decreases with the initial concentration of the "living" polymer. The rate constant was calculated on the hypothesis that the reaction takes place without termination by a stepwise mechanism. Since it was assumed that the concentration of the active ends of the "living" polymer does not change during the reaction, the calculation was based on the equation for the kinetics of a pseudounimolecular reaction. To account for the anomalous relation, the authors put forward additional postulates, directly opposed to those discussed earlier, assuming that "living" polymers are dissociated in tetrahydrofuran:

$$\sim\!CH_2-\underset{C_6H_5}{\bar{C}H}\sim Na^+ \rightleftarrows \sim\!CH_2-\underset{C_6H_5}{\bar{C}H} + Na^+,$$

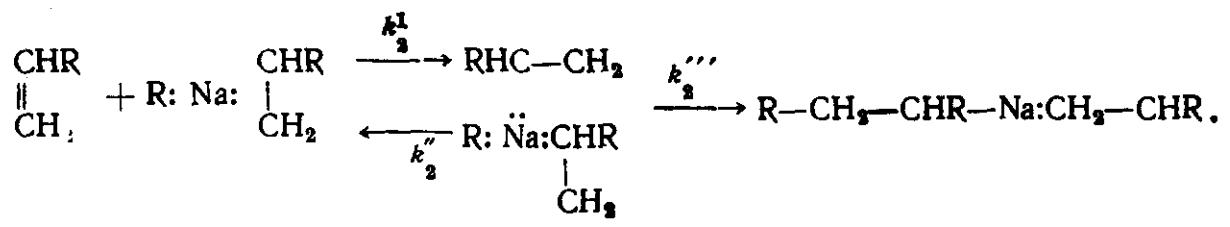
and that both the ion pair and the free carbanion behave as polymerisation centres but of course with different activities. This conclusion was based on the observed electrical conductivity of the "living" polystyrene in tetrahydrofuran[76] and also the finding that the addition of tetraphenylboronsodium led to a sharp reduction of the reaction rate constant, which depended little on the initial concentration of the "living" polystyrene[76–78]. The sharp decrease of the rate of polymerisation was regarded as evidence that at the ends of the growing chains there are free anions, whose concentration falls very appreciably on introduction of tetraphenylboronsodium, due to a sharp increase of the concentration of the counterions as a result of the dissociation reaction

$$[(C_6H_5)_4B]Na \rightleftarrows [(C_6H_5)_4B]^- + Na^+.$$

Fundamentally new hypotheses concerning the mechanism of homogeneous catalytic polymerisation in the presence of organometallic compounds were put forward by Korotkov[48, 50, 79–84]. On the basis of an analysis of the polymerisation kinetics and also by studying the dependence of the average molecular weight of the polymer and its molecular weight distribution on the concentrations of the initial reactants and the rate constants of the elementary reactions, he justified the hypothesis that anionic polymerisation is of a coordination type and that it takes place in a much more complex manner than would appear on the basis of the stepwise mechanism. In the suggested hypothesis the active polymerisation centres are regarded not as organometallic compounds but as more reactive complexes of the monomer and the organometallic compounds, formed using the π-electrons of the unsaturated compound and the p-electrons of the valence shell of the metal:

$$RNa + \begin{matrix}CH_2\\ \| \\ CHR\end{matrix} \overset{k_1}{\rightleftarrows} R{:}Na{:}\begin{matrix}CH_2\\ | \\ CHR\end{matrix}\ . \qquad (1)$$

In such complex compounds with a coordination number of two the disposition of ligands relative to the central atom (the metal) must be close to linearity, which ensures their relative stability. On the other hand, owing to the weakening and the polarisation of the C–M bond and also the coordination unsaturation of the central atom (alkali metal), the reactivity of these compounds increases and the addition of a second monomer molecule (chain propagation) should take place at a much higher rate:



(I) (II) (2)

The alternation of the charges of the adjacent carbons atom within the coordination sphere of complex(II) is responsible for the ease of charge redistribution and hence the higher rate of the isomerisation reaction with regeneration of complex (I), which is the active polymerisation centre.

Frequent repetition of the elementary steps involving the formation of the intermediate compounds (II) and their isomerisation to the active centres leads ultimately to the formation of polymeric molecules. A second distinctive feature of the proposed mechanism is the occurrence of kinetic termination of the growing chains. The latter are capable of becoming deactivated spontaneously (a), on collision with the initial organometallic compound (b), or with participation of the monomer (c), forming polymeric organometallic compounds—the "living" polymer:

$$\begin{aligned}
&(a)\ RNaM_i \xrightarrow{k_{31}} RM_iNa,\\
&(b)\ RNaM_i + RNa \xrightarrow{k_{32}} RM_iNa + RNa,\\
&(c)\ RNaM_i + RNa + M \xrightarrow{k_{33}} \begin{cases} RM_iNa + RMNa \\ RM_{i+1}Na + RNa. \end{cases}
\end{aligned} \qquad (3)$$

These may again combine with the monomer, with the rate constants k_1 or k_1', and can again become polymerisation centres:

$$RM_i\,Na + M \overset{k_1}{\rightleftarrows} RM_i\,NaM^{*}. \qquad (4)$$

After the addition of a certain number of monomeric molecules, these secondary active centres can be again deactivated, etc., until the monomer is exhausted. The authors suggest that $k_1 = k_1'$ only in a special case. Thus, according to this hypothesis, the polymerisation reaction consists of not less than three elementary reactions[81], in contrast to the stepwise mechanism.

Korotkov's hypothesis of a coordination mechanism of "anionic" polymerisation presupposes two modes of reaction: the first, which the authors call a stepwise coordination mechanism, in which the initial organometallic compound loses its individuality in the propagation stage after

the addition of the first monomer molecule [Eqn. (2)] and the second, the catalytic coordination reaction, in which the initial organometallic compound retains its individuality in the propagation stage, i.e. participates in its entirety in the construction of the polymerisation active centre[81]:

$$RNa + M \xrightarrow{k_3} RNaM^*, \qquad (5)$$

$$RNaM_i^* \xrightarrow{k_3} RNaM_{i+1}^*,$$

but loses its individuality in the termination stage† [see mechanism(3)].

The organometallic compounds formed by reaction (3) (a, b, c) are capable of again initiating polymerisation, but now by the stepwise coordination mechanism.

On the basis of these postulates, Korotkov derived an equation for the kinetics of non-steady-state reactions and the degree of polymerisation using a new variable φ, which is called the effective time and which is related to the true time by the expression $d\varphi = mdt$, i.e. $\varphi = \int_0^t \bar{m}dt$, where m is the concentration of the monomer and t the reaction time.

The relations obtained explain the observed phenomena in the region of catalytic polymerisation. Thus it was shown that the complex relation between the rate of polymerisation and catalyst concentration described above, which is represented by a curve exhibiting saturation, is associated with the occurrence of kinetic chain termination [reaction (3)] and the complex form of the $x-\varphi$ kinetic curves is due to the nature of the termination [reaction (3) (a, b, c)]. While direct proportionality between the extent of polymerisation and x and φ is characteristic of the stepwise mechanism, i.e. $x = f(\varphi)$, in the coordination mechanism at a high degree of conversion the kinetic curves as a rule "bend" to the right in the presence of termination, in accordance with mechanisms (3a) and (3b) and to the left in termination by mechanism (3c). Since the propagation of the polymeric chain alternates with "rest periods" (kinetic termination), such a mechanism should result, in contrast to the stepwise mechanism, in the formation of polymers with a fairly narrow molecular weight distribution, approaching the Gaussian distribution, with a slow fall-off at high molecular weights. It has been shown for the polymerisation of φ-methylstyrene under the action of naphthylsodium in tetrahydrofuran at −78 °C as an example[50] that the experimental data for the kinetics $[x = F(t, \varphi)]$, the number-average molecular weight $[\bar{M} = F(n_0)]$, and the molecular weight distribution are in good agreement with the results calculated on the hypothesis that the polymerisation takes place consecutively by the catalytic coordination and stepwise coordination mechanisms. It is suggested[83] that the decrease of the polymerisation rate constants with increasing catalyst concentration observed by Szwarc and coworkers[77, 78] is not due to the fact that the polymerisation centres are both free ions and ion pairs but is caused by the kinetic termination of the growing chain, which becomes more pronounced in the presence of $[(C_6H_5)_4B]Na$.

According to the coordination mechanism, the effect of electron-donor additives (tetrahydrofuran, ethyl ether, amines) on the rate of polymerisation, the polymer structure, and also the composition of the copolymers[14,50,81-84] is not attributed to the dissociation of the organilithium compounds but to the capacity of these additives to form fairly stable complexes with the organometallic compounds, for example:

$$R^1 : Li + 2(C_2H_5)_2O \rightleftharpoons R^1 : Li \begin{matrix} :O(C_2H_5)_2 \\ :O(C_2H_5)_2 \end{matrix}.$$

Esters and amines are more powerful bases than any unsaturated hydrocarbon capable of polymerisation. Therefore the formation of intermediate lithium (or sodium) complexes with a higher coordination number is postulated in the presence of such bases[82,84,85]:

$$R^1 : Li \begin{matrix} :O(C_2H_5)_2 \\ :O(C_2H_5)_2 \end{matrix} \rightleftharpoons R^1 : Li \begin{matrix} :O(C_2H_5)_2 \\ :O(C_2H_5)_2 \\ H_2C{-}CHR \end{matrix}.$$

Nor can one exclude the possibility of the formation of mixed complexes resulting from the displacement of an ether molecule by the monomer:

$$R^1 : Li \begin{matrix} :O(C_2H_5)_2 \\ :O(C_2H_5)_2 \end{matrix} + \begin{matrix} CH_2 \\ \| \\ CHR \end{matrix} \longrightarrow R^1 : Li \begin{matrix} :O(C_2H_5)_2 \\ :CH_2 \\ CHR \end{matrix} + (C_2H_5)_2O.$$

In such compounds the R′–Li bond is more strongly polarised than in complex hydrocarbon compounds and the group R′ is more reactive. This is responsible for the low stability of the compound as a whole and therefore also for the higher rate of intramolecular isomerisation. We believe that all these factors are decisive in the acceleration of polymerisation according to the mechanism

$$\sim CH_2{-}\underset{R}{CH} : Li \begin{matrix} :O(C_2H_5)_2 \\ :O(C_2H_5)_2 \end{matrix} + \begin{matrix} CH_2 \\ \| \\ CHR \end{matrix} \longrightarrow \sim CH_2{-}\underset{R}{CH} : Li : O(C_2H_5)_2 \begin{matrix} H_2C{-}CHR \\ O(C_2H_5)_2 \end{matrix} \longrightarrow$$

$$\longrightarrow \sim CH_2{-}\underset{R}{CH}{-}CH_2{-}\underset{R}{CH} : Li \begin{matrix} :O(C_2H_5)_2 \\ :O(C_2H_5)_2 \end{matrix}.$$

The hypothesis that elementary reactions, in particular the chain propagation reaction, take place via relatively stable intermediate complexes, explains satisfactorily the observed change in the activity of two monomers on transition from separate polymerisation to copolymerisation[82,86-90]. For example, styrene, which is more reactive than butadiene in separate polymerisation, becomes relatively inactive in the copolymerisation of these monomers[87]. This is because butadiene forms relatively more stable intermediate complexes than styrene and the composition of these complexes in fact determines the composition of the copolymer. On the other hand, the isomerisation of the intermediate complex to an active centre affects only the overall rate but not the composition of the copolymer. In copolymerisation in a hydrocarbon medium butadiene is 400 times more reactive than styrene. In a strongly solvating medium, for example in tetrahydrofuran, the capacity for the formation of the butadiene complex decreases and its reactivity falls relative to styrene[84].

It follows from the above that in the field of catalytic "anionic" polymerisation of vinyl and diene monomers in the presence of organometallic compounds, two main hypotheses concerning the nature of the active centres exist so far. In one of these the active centres are regarded as ion pairs capable of dissociation in the limit into ions and it is supposed that the process takes place by a stepwise mechanism, i.e. via two elementary reactions. In the second hypothesis polymerisation is regarded as a coordination process proceeding via intermediate complexes of the monomers with the initial organometallic compounds. The polymerisation then consists of not less than three elementary reactions.

†The regeneration of the catalyst after the completion of polymerisation observed in the experiments of Ziegler, Medvedev, and Morton described above (see Russ. p. 277), can be explained from the standpoint of this hypothesis by a reaction according to the catalytic coordination mechanism.

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