present study the rate was followed gravimetrically but a more accurate method for obtaining the rate data will be desirable for precise analyses regarding the latter two subjects. The application of the present quantitative treatment to other 1:1 alternating radical copolymerization systems is now in progress to verify the generality of the proposed mechanism and to make quantitative analyses of individual systems.

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Importance of Mixed Dimerization in Copolymerizations Involving Lithium Salts of Living Polymers in Benzene. Comments and New Interpretation of the Work of O'Driscoll and Patsiga

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ABSTRACT: The importance of mixed dimerization of lithium salts of living polymers in benzene is shown by the results obtained for the styrene–butadiene system and for the styrene–*p*-methylstyrene system studied by O'Driscoll and Patsiga. In their work the kinetics of monomer consumption was shown to be governed by first-order law, i.e., $M_1 = M_{10}\exp(-\gamma_1 t)$ and $M_2 = M_{20}\exp(-\gamma_2 t)$, with $\gamma_1 \neq \gamma_2$. The treatment invoking mixed dimerization of living polymers predicts such relations and shows that γ_1 and γ_2 are uniquely determined by the total concentration of all living polymers and are independent of the initial composition of the feed. This conclusion is confirmed by the data reported in the literature.

As is well known, lithium salts of many living polymers exist in benzene solution in the dimeric, unreactive form. The polymerization in such systems is propagated by the minute fraction of monomeric polymers that are in equilibrium with the dimers. For example, in the polystyrene system, $\sim\text{S}^-$, Li^+, the rate of polymerization is given by

$$-\text{d}\ln S/\text{d}t = k_\text{p}K^{1/2}[\sim\text{S}^-,\text{Li}^+{}_\text{total}]^{1/2}$$

$$[\sim\text{S}^-,\text{Li}^+] = K^{1/2}[\sim\text{S}^-,\text{Li}^+{}_\text{total}]^{1/2}$$

The problem becomes more complex in copolymerization. In previous papers from this laboratory[1,2] the rate of cross-propagation was studied, namely,

$$\sim\text{S}^-,\text{Li}^+ + \text{D} \rightarrow \sim\text{D}^-,\text{Li}^+$$

and

$$\sim\text{D}^-,\text{Li}^+ + \text{S} \rightarrow \sim\text{S},\text{Li}^+$$

where D denotes 1,1-diphenylethylene and $\sim\text{D}^-,\text{Li}^+$ is $\sim\text{CH}_2\text{C(Ph)}_2{}^-,\text{Li}^+$. It was found that the conversions of $\sim\text{S}^-,\text{Li}^+$ into $\sim\text{D}^-,\text{Li}^+$ in the first system, the reverse conversions of $\sim\text{D}^-,\text{Li}^+$ into $\sim\text{S}^-,\text{Li}^+$ in the second system, are first-order reactions, provided that the concentration of monomers is virtually constant. This condition is fulfilled if monomer concentration greatly exceeds that of living polymers. Moreover, the slopes of the first-order plots, say in the first system $\text{d}\ln[\sim\text{D}^-,\text{Li}^+{}_\text{total}]/\text{d}t$ or $-\text{d}\ln[\sim\text{S}^-,\text{Li}^+{}_\text{total}]/\text{d}t$, are given by $(\text{constant})[\text{D}]_0/[\sim\text{S}^-,\text{Li}^+]_0{}^{1/2}$, where $[\text{D}]_t \approx [\text{D}]_0$ and $[\sim\text{S}^-,\text{Li}^+{}_\text{total}]_0$ = total concentration of all living polymers $[\sim\text{S}^-,\text{Li}^+]_t + [\sim\text{D}^-,\text{Li}^+]_t$.

This kinetic relation was accounted for by the following mechanism.

$$2\sim\text{S}^-,\text{Li}^+ \rightleftarrows (\sim\text{S}^-,\text{Li}^+)_2 \quad (1/2)K_1$$

$$\sim\text{S}^-,\text{Li}^+ + \sim\text{D}^-,\text{Li}^+ \rightleftarrows (\sim\text{S}^-,\text{Li}^+,\sim\text{D}^-,\text{Li}^+) \qquad K_{12}$$

$$2\sim\text{D}^-,\text{Li}^+ \rightleftarrows (\sim\text{D}^-,\text{Li}^+)_2 \qquad (1/2)K_2$$

$$\sim\text{S}^-,\text{Li}^+ + \text{D} \xrightarrow{k_\text{p}} \sim\text{D}^-,\text{Li}^+$$

Denoting by u and v the concentrations of the monomeric polymers, by x, y, and z the concentration of the respective dimers, by α the ratio v/u, and by f the ratio $[\sim\text{S}^-,\text{Li}^+{}_\text{total}]_t/[\sim\text{S}^-,\text{L}^+{}_\text{total}]_0$, one finds

$$-\text{d}\ln f/\text{d}t = \{k_\text{p}[\text{D}]_0/[\sim\text{S}^-,\text{Li}^+{}_\text{total}]_0{}^{1/2}\}\{(K_1 + 2K_{12}\alpha + K_2\alpha^2)/(K_1{}^2 + 2K_1K_{12}\alpha + K_{12}{}^2\alpha^2)\}^{1/2}$$

Only for $K_{12}{}^2 = K_1K_2$ this expression is reduced to

$$-\text{d}\ln f/\text{d}t = k_\text{p}[\text{D}]_0/K_1{}^{1/2}[\sim\text{S}^-,\text{Li}^+{}_\text{total}]_0{}^{1/2}$$

that agrees with experimental results.

We wish to emphasize that the first-order character of this reaction, i.e., the linear relation of $\ln[\sim\text{S}^-,\text{Li}^+{}_\text{total}]_t$ vs. time, demands the relation $K_{12}{}^2 = K_1K_2$. Indeed, we have shown in a subsequent paper[3] that the above plots

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become curved for systems not obeying the condition $K_{12}^2 = K_1K_2$. Moreover, the "memory" effect, the dependence of the slope on the *initial* concentration of living polystyrene, is the result of mixed dimerization.

A somewhat similar system, a conversion of living lithium polybutadiene in benzene into living lithium polystyrene, was investigated by Morton and Ells.[4] Like in the systems studied by us, the conversion of one kind of living ends into the other followed first-order kinetics—a result the authors were unable to explain. The observed first-order constants, k_u, normalized for styrene concentration, i.e., $k_u/[S]$, claimed to be linear with the square root of concentration of all living polymers, the latter being given by $[BuLi]_0^{1/2}$ (see Figure 2 of ref 4). However, examination of their data suggests that $k_u/[S]$ is inversely proportional to $[BuLi]_0^{1/2}$. In fact, an explicit statement to this effect was made in their paper.

The first-order kinetics and the inverse proportionality $k_u/[S] \sim 1/[BuLi]_0^{1/2}$ are predicted by our treatment that takes into account mixed dimerization of living polymers, provided that $K_{12}^2 = K_1K_2$. Thus, the work of Morton and Ells furnishes another example of a system fulfilling that relation.

Another example suggesting the importance of mixed dimerization of lithium salts of living polymers in benzene and the validity of the relation $K_{12}^2 = K_1K_2$ is provided by the work of O'Driscoll and Patsiga.[5] These workers studied copolymerization of styrene (S) and *p*-methylstyrene (pS) initiated in benzene with BuLi. Concentrations of both monomers decreased according to first-order kinetics, i.e., $[S] = [S]_0 \exp(-\gamma_1 t)$ and $[pS] = [pS]_0 \exp(-\gamma_2 t)$ with $\gamma_1 \neq \gamma_2$. This inequality is stressed. Following the approach of Stearns and Foreman,[6] the course of the investigated reaction was described by two differential equations

$$-d[S]/dt = \{k_{11}P_S^{1/2} + k_{21}P_{pS}^{1/2}\}[S]$$

and

$$-d(pS)/dt = \{k_{12}P_S^{1/2} + k_{22}P_{pS}^{1/2}\}[pS]$$

where P_S and P_{pS} denote the concentrations of living polymers terminated by $-S^-,Li^+$ and $-pS^-,Li^+$ end groups, respectively. Implicit in this treatment is the assumption that the respective polymers form only the inactive, dormant homodimers, the polymerization being propagated by the monomeric polymers present in minute concentrations in equilibrium with the homodimers. Mixed dimerization was not considered.

The observed first-order kinetics led O'Driscoll to the conclusions that

$$k_{11}P_S^{1/2} + k_{21}P_{pS}^{1/2} = \gamma_1 = \text{constant}$$

and

$$k_{12}P_S^{1/2} + k_{22}P_{pS}^{1/2} = \gamma_2 = \text{constant}$$

and since under their conditions $P_S^{1/2} + P_{pS}^{1/2}$ appeared to be approximately constant, at least up to 50% conversion, they deduced the following equalities,

$$k_{11} = k_{21} \text{ and } k_{12} = k_{22}$$

These were interpreted as an indication of equal reactivity of either anion toward a monomer. This interpretation is not correct. Their approach implies that $k_{11} = (K_1/2)^{1/2}k_{11}'$, $k_{21} = (K_2/2)^{1/2}k_{21}'$, $k_{12} = (K_1/2)^{1/2}k_{12}'$, and $k_{22} = (K_2/2)^{1/2}k_{22}'$, where $K_1/2$ and $K_2/2$ are the dissociation constants of the respective homodimers into the active, monomeric living polymers, and the primed k_{ij}' are the proper rate constants of homo- and cross-propagation. There is no compelling reason for K_1 to be equal to K_2 and hence $k_{11}' \neq k_{21}'$ and $k_{12}' \neq k_{22}'$, even if $k_{11}'/k_{21}' = r_1 = k_{21}'/k_{22}' = 1/r_2$, i.e., $r_1 \cdot r_2 = 1$.

What are the consequences of O'Driscoll and Patsiga's findings if living polymers undergo homodimerization as well as mixed dimerization? Let us consider a general system of two copolymerizing monomers M_1 and M_2 forming living polymers P_1 and P_2 that undergo homo- and mixed dimerization. Denote again by u and v the concentrations of the active, monomeric polymers, i.e., $(K_1/2)u^2 = [P_1]_2$, $K_{12}uv = [P_1,P_2]$, and $(K_2/2)v^2 = [P_2]_2$. The total concentration, C_0, of all living polymers is given by

$$K_1u^2 + 2K_{12}uv + K_2v^2 = C_0 \quad (1)$$

because u and v are negligible when compared with $[P_1]_2$, $[P_2]_2$, and $[P_1,P_2]$. Obviously, $-dM_1/dt = (k_{11}u + k_{21}v)M_1$ and $-dM_2/dt = (k_{12}u + k_{22}v)M_2$. The first-order kinetics requires therefore

$$\begin{aligned} k_{11}u + k_{21}v &= \gamma_1 = \text{constant} \\ k_{12}u + k_{22}v &= \gamma_2 = \text{constant} \end{aligned} \quad (2)$$

with γ_1 and γ_2 being independent of time and of u and v.

Equations 1 and 2 cannot be independent, because they determine the same two variables, u and v. Only two cases are then possible: (a) eq 2 are independent of each other; and (b) eq 2 are identical, one being multiple of the other. In the first case u and v are uniquely determined by eq 2, i.e., by the fixed values of k's and γ's. Therefore, in each run u and v have to be constant and independent of time. Since the concentration of all P_1's is $K_1u^2 + K_{12}uv$ and of all P_2's is $K_{12}uv + K_2v^2$, they should also be constant in each run and independent of time, i.e.,

$$-d[\text{all } P_1\text{'s}]/dt = d[\text{all } P_2\text{'s}]/dt = 0$$

However, $d[\text{all } P_1\text{'s}]/dt = -d[\text{all } P_2\text{'s}]/dt = -k_{12}uM_2 + k_{21}vM_1$. Hence,

$$M_2/M_1 = (k_{21}/k_{12})(v/u) = \text{contant}$$

On the other hand, the experimental data show M_2/M_1 to be time dependent, namely,

$$M_2/M_1 = (M_{20}/M_{10}) \exp(\gamma_1 - \gamma_2)t \text{ with } \gamma_1 \neq \gamma_2$$

This inconsistency proves that case (a) is unacceptable. Thus we are left only with case (b), i.e.,

$$k_{11}/k_{12} = r_1 = k_{21}/k_{22} = 1/r_2 = \gamma_1/\gamma_2$$

Hence, γ_1/γ_2 should be independent of the initial composition of the feed, and furthermore $r_1 \cdot r_2 = 1$. Our deduction goes further. To avoid the fixed, time-independent values of u and v, and therefore to avoid the previously discussed inconsistency, we have to conclude that eq 1 and 2 are *not independent* of each other. This is only possible if $K_{12}^2 = K_1K_2$, and then eq 1 acquires the form

$$K_1^{1/2}u + K_2^{1/2}v = C_0^{1/2}$$

with

$$K_1^{1/2}/k_{11} = K_2^{1/2}/k_{21} = C_0^{1/2}/\gamma_1$$

$$K_1^{1/2}/k_{12} = K_2^{1/2}/k_{22} = C_0^{1/2}/\gamma_2$$

Hence, γ_1 and γ_2 are uniquely determined by C_0 and increase proportionally with $C_0^{1/2}$. Let us stress that for a constant C_0 the values of γ_1 and γ_2, and not only their ratio, are independent of the initial composition of the feed. The results of O'Driscoll and Patsiga appear to confirm this conclusion.

It should be stressed that our treatment, in contrast to the treatment of O'Driscoll and Patsiga, does not introduce the questionable condition $[\text{all } P_1]^{1/2} + [\text{all } P_2]^{1/2} =$ constant but is based on the proper condition $[\text{all } P_1] + [\text{all } P_2] =$ constant.

Finally, the lack of consideration of the highly probable mixed dimerization casts doubt on the calculations of O'Driscoll and Kuntz[7] pertaining to copolymerization of styrene and butadiene initiated in benzene by alkyllithium. It would be advisable to reconsider this kinetics with proper consideration of the mixed dimerization.

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On the Structure of the Propagating Species in the Anionic Polymerization of Methyl Methacrylate. Kinetic Investigations in Tetrahydrofuran Using Monofunctional Initiators

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ABSTRACT: The kinetics of the propagation step in the anionic polymerization of methyl methacrylate in THF were investigated over the temperature range of +20 to −100 °C with cumylcesium and at −25 °C with monofunctional oligomeric α-methylstyrylsodium as initiators. A flow tube reactor and a stirred tank reactor were used. At low temperatures the termination is nearly avoided, but it gains in importance at higher temperatures especially when sodium is used as a counterion. The Arrhenius plots of the rate constants for the monomer addition to ion pairs of PMMA–Cs and PMMA–Na are linear; presumably the reacting ion pairs exist in one form only. The Arrhenius parameters for both counterions are identical within experimental errors: Cs$^+$, A = 7.7, E_a = 4.9 kcal/mol = 21 kJ/mol; Na$^+$, A = 7.4, E_a = 4.7 kcal/mol = 20 kJ/mol. These results are in strong contrast to the kinetics of the polymerization of styrene. They can be explained by the assumption of an "intramolecular solvation" of the counterion by the penultimate or antepenultimate ester group of its own polymer chain.

The nature of the active species in the anionic polymerization of styrene has been disclosed to a high degree. The picture revealed, however, has proven not to be transferable to polar monomers such as methyl methacrylate. Here, in addition, termination reactions complicate the kinetics and broaden the molecular weight distributions of the polymers. Although these side reactions are less pronounced in polar solvents than in nonpolar ones only very few investigations dealt with the kinetics of the anionic polymerization of methyl methacrylate (MMA) in polar solvents. According to Löhr and Schulz[2,3] and to Mita et al.[4] little or no termination is observed when the reaction proceeds in THF at $T \le -75$ °C, whether Na$^+$ or Cs$^+$ is used as a counterion. The rate of propagation is first order with respect to the monomer and the number average degree of polymerization is a linear function of conversion. Moreover, the molecular weight distributions are narrow. At higher temperatures termination reactions gain in importance as indicated by deviations from the first-order kinetics, by broadening of the molecular weight distribution,[5] and by the generation of alkali methoxide.[4]

Conductance studies of Löhr and Schulz[2,3] and of Figueruelo[6] show that the dissociation constants of PMMA–alkali metal ion pairs are low as compared with ion pairs involving polystyryl or fluorenyl anions. Mita et al.[4] attributed this fact to the exclusive existence of contact ion pairs. The kinetic results of Löhr and Schulz[2,3] prove that at least two different kinds of species are involved in the propagation, i.e., free anions and ion pairs. Their experiments, however, give no evidence on the nature of the ion pairs.

It is known that two kinds of ion pairs, i.e., contact and solvent separated ion pairs, participate in the anionic polymerization of styrene with Na$^+$[7] or Cs$^+$[8] as counterions. They are in equilibrium with each other and propagate with different rates. The Arrhenius plot of the ion pair rate constants taken over a wide temperature range exhibits a distinct curvature.

The kinetic data reported for the polymerization of MMA with Na$^+$ as a counterion are questionable because they were obtained with bifunctional initiators, i.e., naphthalenesodium[4] or oligomers of α-methylstyrylsodium.[3] According to Warzelhan and Schultz,[9] when bifunctional initiators are employed intramolecular association of the chain ends occurs. This results in a deviation from first-order kinetics. The analogous intermolecular association has not been observed within the investigated range of concentrations of living ends ($10^{-4} \le c^* \le 10^{-3}$ mol/L).

Therefore, we decided to reinvestigate the kinetics of the polymerization of MMA with monofunctional initiators, such as benzyloligo(α-methylstyryl)sodium[23] and cumyl cesium, over a wide temperature range. Cs$^+$ was chosen as a counterion since termination reactions seem

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