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Effect of Complexing Agents on the Rate of Polymerization in Systems Involving Dormant Aggregated Polymers and Living Nonaggregated Polymers

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Lithium salts of polystyrene or polydienes are aggregated in hydrocarbon solvents. The aggregates are inert and the polymerization is carried out by a minute amount of unassociated polymers which are in equilibrium with the aggregates. Various solvating agents may dissociate the aggregates by being complexed with the unassociated polymers. The resulting complexes have usually a 1:1 stoichiometry and contribute to propagation; however, their rate of growth is, on the whole, different from that of the unassociated polymers.

Let us consider polymerization of lithium polystyrene, denoted here by P*, in a hydrocarbon solvent. In such solvents the polymers form dimeric aggregates P^*_2 which are in equilibrium with P*, i.e.,

$$P^*_2 \rightleftharpoons 2P^* \qquad K_{diss}$$

while

$$P^*_{n\text{-mer}} + M \rightarrow P^*_{(n+1)\text{-mer}} \, k_p$$

with M denoting the monomer. In the presence of a complexing agent denoted by C an additional equilibrium is assumed to be established: namely,

$$P^* + C \rightleftharpoons (P^*,C) \qquad K_c$$

yielding a 1:1 complex propagating with a rate constant k_c. The observed rate of propagation, R, per monomer, should be given therefore by

$$R = -\mathrm{d} \ln [M]/\mathrm{d}t = k_p[P^*] + k_c[(P^*,C)] \tag{1}$$

Obviously, R increases with increasing C for $k_c > k_p$, but the dependence on C is more complex when $k_c < k_p$. It is our intention to examine such a dependence and to derive an expression giving R as a function of [C] and of X—the total concentration of the polymers in whatever form.

From the following balanced equation

$$2[P^*]^2/K_{diss} + [P^*] + K_c[C][P^*] = X \tag{2}$$

one finds, for a constant X, the derivative

$$\mathrm{d}[P^*]/\mathrm{d}[C] = -K_c[P^*]/(1 + 4[P^*]/K_{diss} + K_c[C]) \tag{3}$$

to be negative demonstrating, as expected, that [P*] decreases with increasing [C]. In view of eq 1, one gets for a constant X

$$\mathrm{d}R/\mathrm{d}[C] = K_c[P^*][k_c - (k_p + k_cK_c[C])/(1 + K_c[C] + 4[P^*]/K_{diss})]$$

and hence the initial slope of R plotted as a function of [C] is

$$(\mathrm{d}R/\mathrm{d}[C])_{[C]=0} = K_c[P^*][k_c - k_p/(1 + 4[P^*]/K_{diss})]$$

i.e., the rate of polymerization increases with [C] when

$$(k_c/k_p)(1 + 4[P^*]/K_{diss}) > 1$$

and decreases when

$$(k_c/k_p)(1 + 4[P^*]/K_{diss}) < 1$$

Note, these inequalities are independent of the value of [C] since they refer to the effect caused by the addition of very small amounts of the complexing agent.

For most of the studied systems $[P^*] \ll X$ and then the approximation $[P^*] \sim (^1/_2 K_{diss}X)^{1/2}$ is justified when the concentration of the complexing agent is low. Under such conditions the rate of polymerization decreases on addition of small amounts of C when

$$(k_c/k_p)[1 + (4/2^{1/2})X^{1/2}/K_{diss}^{1/2}] < 1$$

or, since $(4/2^{1/2})X^{1/2}/K_{diss}^{1/2} \gg 1$ under conditions prevailing in polymerization, the rate of propagation decreases when

$$X < (k_p/k_c)^2K_{diss}/8$$

provided that $k_c < k_p$.

In conclusion, initial addition of a complexing agent to a dimerically aggregated lithium polystyrene, or to another similarly aggregated living polymer, increases the rate of polymerization when the total concentration of polymers, in all its forms, exceeds $(k_p/k_c)^2K_{diss}/8$ and decreases it when the inequality is reversed, provided that $k_c < k_p$.

The results reported by Hélary and Fontanille[1,2] provide an illustration of the above principle. Coordination of lithium polystyrene with tetramethylethylenediamine in cyclohexane increases the rate of propagation for $X = 8.3$ mM and decreases it when $X = 0.93$ mM. Their studies led to $k_c = 0.15$ M^{-1} s^{-1} at 25 °C, hence the constant $k_p(K_{diss}/2)^{1/2}$ could be calculated on the basis of our treat-

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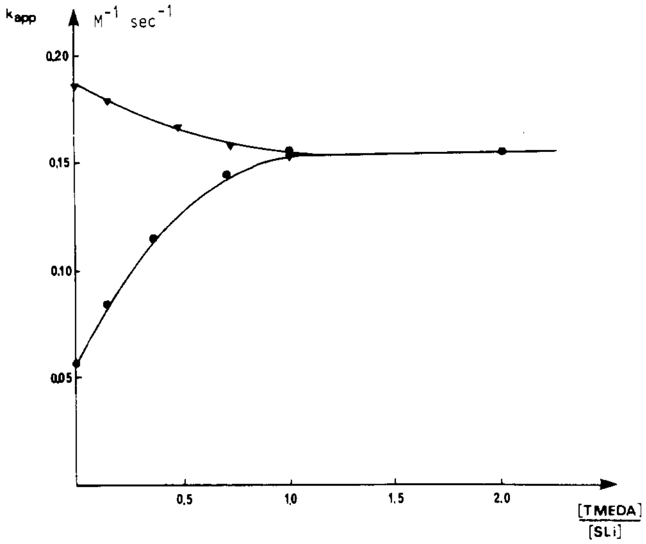

Figure 1. Effect of tetramethylethylene diamine on the apparent rate constant of propagation of polystyryllithium in cyclohexane: (▼) $[S^-,Li^+] = 9.2 \times 10^{-4}$ M; (●) $[S^-,Li^+] = 8.3 \times 10^{-3}$ M.

ment by assuming that at a reasonable value of $X = 1$ mM the addition of the complexing agent does not affect the rate of polymerization. Thus

$$k_p(K_{diss}/2)^{1/2} = 9.4 \times 10^{-3}\ M^{-1/2}\ s^{-1} \quad \text{at} \quad 25\ °C$$

compared with the reported, and directly determined, values of $5.3 \times 10^{-3}\ M^{-1/2}\ s^{-1}$ (ref 1) or $7.5 \times 10^{-3}\ M^{-1/2}\ s^{-1}$ (extrapolated from ref 3).

The above discrepancy may reflect experimental uncertainties or it may indicate a more complex structure of the studied system. Indeed we may consider a system in which the complexing agent is associated with the aggregated P^*_2 as well with the unaggregated P^*, i.e.,

$$P^* + C \rightleftarrows (P^*,C) \qquad K_{c^1}$$

$$P^*_2 + C \rightleftarrows (P^*_2,C) \qquad K_{c^2}$$

and assume that P^* and (P^*,C), but not P^*_2 or (P^*_2,C), are propagating. The balance equation aquires now the form

$$2[P^*]^2/K_{diss} + 2K_{c^2}[C][P^*]^2/K_{diss} + [P^*] + K_{c^1}[C][P^*] = X$$

Proceeding like previously we find

$$d[P^*]/d[C] = -(K_{c^1}[P^*] + 2K_{c^2}[P^*]^2/K_{diss})/ (1 + 4[P^*]/K_{diss} + K_{c^1}[C] + 4K_{c^2}[C][P^*]/K_{diss})$$

and

$$dR/d[C] = k_cK_{c^1}[P^*] - (k_p + k_cK_{c^1}[C])(K_{c^1}[P^*] + 2K_{c^2}[P^*]^2/K_{diss})/ (1 + 4[P^*]/K_{diss} + 4K_{c^2}[C][P^*]/K_{diss} + K_{c^1}[C])$$

For $[C] = 0$ the respective $dR/d[C]_{[C]=0}$ is given by

$$K_{c^1}[P^*] \times [k_c - k_p(1 + 2K_{c^2}[P^*]/K_{c^1}K_{diss})/(1 + 4[P^*]/K_{diss})]$$

Applying again the approximation $[P^*] \sim (K_{diss}/2)^{1/2}X^{1/2}$ and keeping in mind that $(4/2^{1/2})X^{1/2}/K_{diss}{}^{1/2} \gg 1$, we find that the plot of R versus [C] initially turns down when

$$X < (k_p/k_c)^2K_{diss}/8[1 - \tfrac{1}{2}(k_p/k_c)(K_{c^2}/K_{c^1})]^2$$

provided that $k_c < k_p$. This result, as expected, is identical with the previous one for $K_{c^2} = 0$. It leads on the whole to higher values of X for $K_{c^2} > 0$, but it demonstrates that K_{c^2}/K_{c^1} has to be smaller than $2k_p/k_c$. Provided that for $X = 1$ mM the addition of the complexing agent does not affect the rate of polymerization and taking the values of $k_c = 0.15\ M^{-1}\ s^{-1}$ and $k_p(K_{diss}/2)^{1/2} = 5.3 \times 10^{-3}\ M^{-1/2}\ s^{-1}$ one finds

$$(k_p/k_c)(K_{c^2}/K_{c^1}) = 0.86$$

Since k_p/k_c is at least 500, one concludes that K_{c^2}/K_{c^1} is at the most 1.7×10^{-3}; i.e., the association of tetramethylethylenediamine with the dimer is expected to be considerably weaker than with the unaggregated polymer.

Consideration of still more complex systems is not warranted at this stage. Extention of these considerations to lithium polydienes may be interesting.

A Remark. C denotes the free complexing agent. The concentration of the added complexing agent, $[C_0]$, is given by $[C](1 + K_c[P^*])$ for the simple approach or by $[C](1 + K_{c^1}[P^*] + K_{c^2}[P^*_2])$ for the more elaborate one. However, $(dR/d[C_0])_{[C_0]=0} = 0$ only when $(dR/d[C])_{[C]=0}$ is also 0.

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Communications to the Editor

^{15}N Solid-State NMR Characterization of Aramid-Containing Nylon-6 by in Situ Polymerization with Benzoyl Caprolactam Derivatives

Polyamides and aramids are two important structural materials noted for their toughness, high modulus, and tensile strength.[1] They are currently used in a wide variety of applications as structural plastics and as reinforcing fibers in high-performance composites.

Natural abundance ^{15}N NMR spectroscopy has been used to characterize polyamides in solution.[2-5] ^{15}N NMR spectroscopy has several advantages over ^{13}C NMR including larger spectral width and simpler spectra. Characterization of polyamides by solution ^{15}N NMR is, however, hampered by the limited solubility of many polyamides, especially homo- and copolymers containing aromatic moieties. Polyamide nitrogens are subject to large chemical shift changes in the solvents needed to dissolve them.[6,7] Moreover, solution studies cannot duplicate the crystalline structure or hydrogen bonding in solid polyamides.

Recently, polyamic acid precursors to polyimides have been characterized by solid state ^{15}N CP-MAS NMR.[8] We had previously prepared and characterized several aliphatic/aromatic copolyamides based on caprolactam and several *N*-benzoyl caprolactam initiators (Figure 1).[9] In

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