Mixed Dimerization of Living Polymers Having Li$^+$ Counterions. Kinetics of the Addition of 1,1-Diphenylethylene to Living Lithium Polystyrene in Benzene

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ABSTRACT: Kinetic studies of the addition of 1,1-diphenylethylene (D) to living lithium polystyrene ($\sim\!\sim S^-$, Li$^+$) in benzene demonstrated that the reaction is first order in the olefin (D). For an excess of D the rate of conversion of $\sim\!\sim S^-$, Li$^+$ into $\sim\!\sim SD^-$, Li$^+$ is proportional to the unconverted $\sim\!\sim S^-$, Li$^+$, but the apparent rate constant is invertially proportional to $[\sim\!\sim S^-, Li^+]_0^{1/2}$. Denoting by f the ratio $[\sim\!\sim S^-, Li^+]_t/[\sim\!\sim S^-, Li^+]_0$ one finds $df/dt = \text{const}\cdot([D]/[\sim\!\sim S^-, Li^+]_0^{1/2})f$. Analysis of this result indicates that the following reversible reactions, $2(\sim\!\sim S^-, Li^+) \rightleftarrows (\sim\!\sim S^-, Li^+)_2$, $1/2K_1$; $(\sim\!\sim S^-, Li^+) + (\sim\!\sim SD^-, Li^+) \rightleftarrows (\sim\!\sim S^-, Li^+, \sim\!\sim SD^-, Li^+)$, K_{12}; and $2(\sim\!\sim SD^-, Li^+) \rightleftarrows (\sim\!\sim SD^-, Li^+)_2$, $1/2K_2$, maintain minute equilibrium concentrations of the unassociated $\sim\!\sim S^-$, Li$^+$ and $\sim\!\sim SD^-$, Li$^+$. The former reacts with D in a bimolecular fashion, $\sim\!\sim S^-, Li^+ + D \rightarrow \sim\!\sim SD^-, Li^+$ and the observed kinetics is then accounted for if $K_{12}^2 = K_1K_2$.

In hydrocarbon solvents anionic polymerization is often complicated by the aggregation of living ends, a phenomenon frequently encountered in systems involving Li$^+$ counterions. For example, living lithium polystyrene forms in benzene the unreactive, dimeric associates, $(\sim\!\sim S^-, Li^+)_2$, and only the unassociated living chains propagate the polymerization.[1] The problem of agglomeration becomes even more intricate in anionic copolymerization because mixed aggregates, *e.g.*, $(\sim\!\sim A^-, Li^+)_n(\sim\!\sim B^-, Li^+)_m$ as well as homoassociates may be present in such systems.

To learn more about mixed aggregates and their role in the over-all reaction we investigated the addition of 1,1-diphenylethylene, D, to lithium polystyrene, $\sim\!\sim S^-$, Li$^+$, in benzene. Although the olefin reacts readily with the living polymer, *viz.*

$$\sim\!\sim S^-, Li^+ + D \rightarrow \sim\!\sim S\cdot CH_2\cdot \bar{C}(Ph)_2, Li^+ = \sim\!\sim SD^-, Li^+$$

no further addition of D to $\sim\!\sim SD^-$, Li$^+$ takes place, since the latter reaction is prevented by the substantial steric strain arising from the crowding of four bulky phenyl groups on two carbon atoms separated by a CH$_2$ group.

Polymerization involving living polymers proceeds on until an equilibrium is established between the monomer and living polymers. The equilibrium concentration of the monomer may be very low and then the polymerization is virtually irreversible. In our system the absorption of $\sim\!\sim S^-$, Li$^+$ eventually disappears indicating that the addition of D to $\sim\!\sim S^-$, Li$^+$ is essentially irreversible if an excess of D is used.

Experimental Section

The procedures used in the purification of benzene and styrene were described elsewhere.[1,2] Commercial 1,1-diphenylethylene was freed from benzophenone, which is always present in unpurified samples, by vacuum distillation of the liquid kept over a small amount of sodium. The distilled olefin was sealed in ampoules and never exposed to the atmospheric air.

The progress of the reaction was monitored spectrophotometrically following the decay of the 334-mμ peak (λ_{max} $\sim\!\sim S^-$, Li$^+$ in benzene). The conversion of $\sim\!\sim S^-$, Li$^+$ into $\sim\!\sim SD^-$, Li$^+$ leads to the formation of a new absorption band at about 460 mμ. Stop-flow technique[3] and batch technique[4] were used in these investigations. To simplify the kinetic studies a large excess of the olefin was used in each experiment.

Results

The conditions maintained in the individual experiments are given in Table I. All the experiments were performed at 19°. In each run the plot of log (o.d. 334)$_t$/(o.d. 334)$_0$ *vs.* time was linear, as exemplified by the two graphs shown in Figure 1. Note that the ratio $[D]_0/[\sim\!\sim S^-, Li^+]_0$ was smaller in these two experiments than in other runs. Nevertheless, the reaction followed the first-order law even when the conversion exceeded 90%. The copolymerization behaves, therefore, as if it were first order in $[\sim\!\sim S^-, Li^+]$ and the slopes of the

Table I

$\sim\!\sim S^-, Li^+ + D \rightarrow \sim\!\sim SD^-, Li^+$, in Benzene at 19°

$[\sim\!\sim S^-, Li^+]_0 \times 10^4$, M	$[D]_0 \times 10^4$, M	$k_u \times 10^2$, sec^{-1}	$k_u/[D]_0$, M^{-1} sec^{-1}	$(k_u/[D]_0)[\sim\!\sim S^-, Li^+]_0^{1/2} \times 10^{-2}$ $M^{-1/2}$ sec^{-1}
1.2	750	6.30	0.84	0.92
1.3	1500	12.50	0.83	0.94
3.6	190	0.95	0.50	0.95
4.6	1300	5.85	0.45	0.96
4.7	1400	5.75	0.41	0.89
5.0	25	0.11	0.44	0.98
5.0	74	0.28	0.38	0.85
5.3	500	1.75	0.35	0.81
6.0	1300	4.66	0.36	0.88
6.0	1900	6.83	0.36	0.88
6.2	1800	6.30	0.35	0.87
6.5	5000	17.50	0.35	0.89
			Av	0.90 ± 0.05

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[2] D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

[3] J. Jagur, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2168 (1962).

[4] T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 796 (1967).

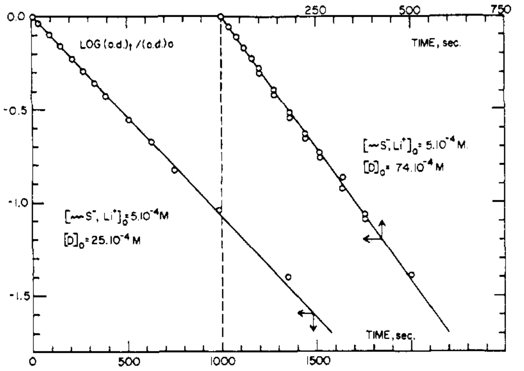

Figure 1. Plot of log $\{o.d.(334)_t/o.d.(334)_0\}$ *vs.* time. The slope of the line gives k_u. $\sim S^-, Li^+ + D \rightarrow \sim SD^-, Li^+$ in benzene at 19°.

lines giving log $[\sim S^-, Li^+]$ *vs.* t yield the apparent first-order rate constant denoted by k_u.

Comparison of k_u's observed for constant *initial* concentrations of $\sim S^-, Li^+$ and variable $[D]_0$ shows that k_u is proportional to $[D]_0$, *i.e.*, the reaction is also first order in D. However, $k_u/[D]_0$ is invertially proportional to $[\sim S^-, Li^+]_0^{1/2}$. This is seen in Figure 2 as well as from inspection of the last column of Table I. Hence

$$d[\sim S^-, Li^+]_t/dt = k[\sim S^-, Li^+]_0^{-1/2}[D]_t[\sim S^-, Li^+]_t$$

Substitution of $[D]_t$ for $[D]_0$ is justified since $[D]_0 \gg [\sim S^-, Li^+]_0$.

Discussion

It was established that $\sim S^-, Li^+$ is dimeric in benzene; however, the anionic polymerization is propagated by minute fraction of the monomeric species present in equilibrium with the dimers.[1] Let us assume that $\sim SD^-, Li^+$ forms also dimers and mixed dimers with $\sim S^-, Li^+$ in benzene. Furthermore, we shall assume that the relevant rates of dissociations and associations are very rapid. Consequently, during the whole course of the reaction the equilibria between the small fractions of the unassociated $\sim S^-, Li^+$ and $\sim SD^-, Li^+$ on one hand, and the respective dimers, $(\sim S^-, Li^+)_2$, $(\sim SD^-, Li^+)_2$, and $(\sim S^-, Li^+, \sim SD^-, Li^+)$, on the other, are maintained. This assumption was confirmed by some preliminary experiments performed in this laboratory. Thus

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

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

$$2(\sim SD^-, Li^+) \rightleftarrows (\sim SD^-, Li^+)_2,\ 1/2K_2$$

Let us denote by u and v, respectively, the concentrations of the monomeric species, and by x, y, and z those of the relevant dimers. It appears that the addition of D takes place only to the unassociated $\sim S^-, Li^+$, *i.e.*

$$\sim S^-, Li^+ + D \xrightarrow{k_a} \sim SD^-, Li^+$$

Under our conditions u or v are much smaller than x, y, or z. Hence

$$1/2K_1u^2 = x$$

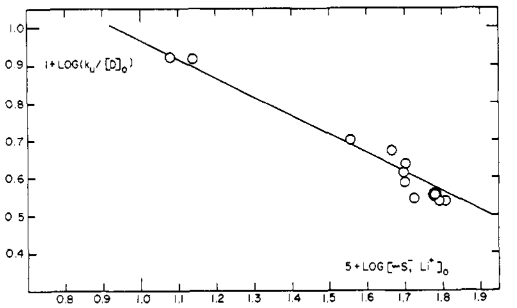

Figure 2. Plot of log $(k_u/[D]_0)$ *vs.* log $[S^-, Li^+]_0$. The drawing gives the "best" line with slope $^1/_2$.

$$K_{12}uv = y$$

$$1/2K_2v^2 = z$$

Since the reaction does not involve termination

$$K_1u^2 + 2K_{12}uv + K_2v^2 = 2[(\sim S^-, Li^+)_2]_0 = C_0 = \text{const}$$

Denote v/u by α and $(2x + y)/C_0$ by f. Then fC_0 gives the concentration of all the $\sim S^-, Li^+$ present in all the forms, *i.e.*, $f = (\text{o.d. }334)_t/(\text{o.d. }334)_0$. It follows that

$$u^2(K_1 + 2K_{12}\alpha + K_2\alpha^2) = C_0$$

or

$$u = C_0^{1/2}/(K_1 + 2K_{12}\alpha + K_2\alpha^2)^{1/2}$$

However, $(K_1 + K_{12}\alpha)/(K_1 + 2K_{12}\alpha + K_2\alpha^2) = f$ and therefore α is a function of K_1, K_2, K_{12}, and f, *viz.*

$$\alpha = \frac{K_{12}(1 - 2f) + \{K_{12}^2(1 - 2f)^2 + 4K_1K_2f(1 - f)\}^{1/2}}{2K_2f}$$

Now, d[all $\sim S^-, Li^+$]/dt = $k_a[D]u$ and because $[D] \approx [D]_0$ and [all $\sim S^-, Li^+$] = fC_0, one finds

$$df/dt = (k_a[D]_0/C_0^{1/2})/(K_1 + 2K_{12}\alpha + K_2\alpha^2)^{1/2}$$

Let us introduce one more assumption, namely $K_{12}^2 = K_1K_2$, *i.e.*, the equilibrium constant of the mixed dimerization (apart from the statistical factor of 2) is a geometrical average of the equilibrium constants of homodimerization. This simplifies the expression for the rate of conversion, *viz.*, $K_1 + 2K_{12}\alpha + K_2\alpha^2 = K_1/f^2$ and hence

$$df/dt = (k_a/K_1^{1/2})([D]_0/C_0^{1/2})f$$

The reaction is, therefore, first order in [D], first order in f, *i.e.*, in $[\sim S^-, Li^+]$, but the apparent rate constant is invertially proportional to $C_0^{1/2}$. The experimental findings are therefore accounted for and substance is provided for the claim that, at least in this system, the equilibrium constant of the mixed dimerization is the geometrical average of the equilibrium constants of homodimerizations.

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