pendent propagation. This may result from a high stability of the propagating species derived from *p*-methoxystyrene and the relatively high reaction temperature (30 °C) employed here.

Interesting is a recent stopped-flow study[8,9] on the styrene polymerization by perchloric acid, in which an increase of $k_p$ values was observed on addition of a perchlorate salt in methylene chloride. Decreasing solvent polarity in our work and the salt addition in the polar solvent in that study may have induced similar suppression of the ionic dissociation of the propagating species to give the "invisible" species. The nature of this species cannot be unambiguously described at present, although Pepper et al.[8,9] proposed covalent esters. However, since it has no absorption in the UV–visible region from 320 to 450 nm, it should be quite different in nature from free ionic carbocations.

**Acknowledgment.** Financial support from the Ministry of Education, Japanese Government is gratefully acknowledged.

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# Kinetics of Styrene Addition in Benzene Solution to Living Lithium Polymers Terminated by 1,1-Diphenylethylene Units. The Effect of Mixed Dimerization of Monomeric Polymers

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ABSTRACT: The kinetics of addition of styrene to living polymers terminated by $-CH_2C(Ph)_2^-,Li^+$ was investigated in benzene. Under these conditions the reaction involves monomeric species; however, almost all the polymers exist in dimeric form. In our system the homodimers of lithium polystyryl and $Li-C(Ph)_2^-$ coexist in equilibrium with mixed dimers. The value of the association constant $K_{12}$ characterizing the mixed dimerization is shown to be equal to $(K_1{\cdot}K_2)^{1/2}$, where $K_1/2$ and $K_2/2$ are the association constants of the respective homodimers. This relation is responsible for the first-order character of the addition, i.e., $-\{d \ln [\sim C(Ph)_2^-,Li^+]/dt\}/[\text{styrene}] = k_{21}/K_2^{1/2}{\cdot}C_0^{1/2}$, where $k_{21}$ is the bimolecular rate constant of addition of styrene to the monomeric $\sim C(Ph)_2^-,Li^+$ and $C_0$ is the *total* concentration of *all* the living polymers, i.e., $C_0$ = [lithium polystyryl] + $[\sim CH_2C(Ph)_2^-,Li^+]$. The importance of mixed dimers in other living systems involving Li salts in benzene is discussed.

On addition of an excess of 1,1-diphenylethylene, D, to lithium polystyryl in benzene, $\sim S^-,Li^+$, a pseudo-first order reaction ensues,[1] its rate being monitored by the decay of $\sim S^-,Li^+$ absorbance or by the appearance of absorption of $\sim CH_2{\cdot}C(Ph)_2^-,Li^+$ pairs. Since D does not homopolymerize the reaction arising from

$$\sim S^-,Li^+ + D \xrightarrow{k_{12}} \sim CH(Ph){\cdot}CH_2{\cdot}C(Ph)_2^-,Li^+ = \sim D^-,Li^+$$

does not proceed further. The kinetics is peculiar in that the normalized pseudo-first-order constant, $k_u = -\{d \ln [\text{total } \sim S^-,Li^+]/dt\}/[D]$, has been found to depend on the *initial* concentration of $\sim S^-,Li^+$, namely $k_u \sim 1/[\text{total } \sim S^-,Li^+]_0^{1/2}$. In other words, the rate $R_t$ determined at constant concentration of D and measured at a time when the *total* concentration of lithium polystyryl has a fixed value depends also on the initial $[\text{total } \sim S^-,Li^+]_0$, viz., $R_t$ increases proportionally to $[\text{total } \sim S^-,Li^+]_0^{1/2}$.

This peculiarity was accounted for by the following mechanism.[1] Lithium polystyryl is present in benzene in a dimeric, unreactive form which remains in equilibrium with the reactive monomeric species,[2]

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

The observed addition of D involves this monomeric form, but as $\sim D^-,Li^+$ is formed additional equilibria become established. It has been assumed that $\sim D^-,Li^+$ homodimerizes as well as codimerizes with $\sim S^-,Li^+$, i.e.,

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

and

$$(\sim D^-,Li^+,\sim S^-,Li^+) \overset{1/K_{12}}{\rightleftarrows} \sim D^-,Li^+ + \sim S^-,Li^+$$

It was deduced[1] that

$$k_u = -\{d \ln [\text{total } \sim S^-,Li^+]/dt\}/[D] = k_{12}/K_1^{1/2}C_0^{1/2}$$

where $C_0$ = $[\text{total } \sim S^-,Li^+]_t$ + $[\text{total } \sim D^-,Li^+]_t$ = $[\text{total } \sim S^-,Li^+]_0$, provided that $K_{12} = (K_1{\cdot}K_2)^{1/2}$ and that the

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concentrations of the monomeric species are minute as compared with the concentrations of the dimers. Thus, the equilibrium concentration of the reactive monomeric ~~S⁻,Li⁺ is determined not only by the concentration of the polystyryl dimers, (~~S⁻,Li⁺)₂, but by the concentration of *all* the dimers, i.e., (~~S⁻,Li⁺)₂ + (~~D⁻,Li⁺)₂ + (~~S⁻,Li⁺,~~D⁻,Li⁺).

We wish to reemphasize again that this simple first-order kinetics is observed because $K_{12} = (K_1 \cdot K_2)^{1/2}$. Otherwise a plot of ln [total ~~S⁻,Li⁺]$_t$ vs. time becomes curved. In a forthcoming publication[3] we shall describe systems for which $K_{12} \neq (K_1 \cdot K_2)^{1/2}$ and show how such an inequality affects the kinetics. However, since the relation $K_{12} = (K_1 \cdot K_2)^{1/2}$ has been proved valid in the system ~~S⁻,Li⁺ + D, it has to be also valid in the system ~~D⁻,Li⁺ + S. We investigated, therefore, the kinetics of styrene addition to ~~D⁻,Li⁺ in benzene.

Since styrene homopolymerizes one cannot maintain the simplifying conditions keeping [S] virtually constant. This complication forced us to limit our study to the initial rate of conversion of ~~D⁻,Li⁺ into ~~S⁻,Li⁺. We determined the normalized, pseudo-first-order rate constant, $k_0$, of the addition of styrene to ~~D⁻,Li⁺ by monitoring the decrease of absorbance at 440 nm, i.e., at $\lambda_{max}$ of ~~D⁻,Li⁺ pairs. Fortunately, ~~S⁻,Li⁺ does not contribute to the absorbance at this wavelength. In agreement with expectation we found indeed that

$$k_0 = -\{d \ln [\text{total } \sim\sim D^-,Li^+]/dt\}/[S]_0$$

is proportional to ([total ~~S⁻,Li⁺]$_0$ + [total ~~D⁻,Li⁺]$_0$)$^{-1/2}$. The proof was provided by the results of experiments in which styrene was added to benzene solutions of a mixture of ~~D⁻,Li⁺ and ~~S⁻,Li⁺, paying special attention to those runs in which [total ~~D⁻,Li⁺]$_0$ was approximately constant while [total ~~S⁻,Li⁺]$_0$ was varied. The results are summarized in Table I.

**Brief Derivation of the Kinetic Relations.** Denote by $u$ and $v$ the equilibrium concentrations of the monomeric ~~S⁻,Li⁺ and ~~D⁻,Li⁺, respectively. The concentrations of the pertinent dimers are given by $(K_1/2)u^2$, $(K_2/2)v^2$, and $K_{12}uv$, and therefore $K_1u^2 + K_{12}uv$ gives the concentration of ~~S⁻,Li⁺ in whatever form, and the concentration of ~~D⁻,Li⁺ in the homo- and mixed dimers is given by $K_2v^2 + K_{12}uv$ (the contributions of the monomeric species, given by $u$ and $v$, can be neglected because they are small). The rate of reaction is given by $k_{21} \cdot v \cdot [S]$. Now, for $K_{12} = (K_1 \cdot K_2)^{1/2}$ one finds

$$K_2^{1/2}v + K_1^{1/2}u = \{K_2v^2 + 2K_{12}uv + K_1u^2\}^{1/2} = C_0^{1/2}$$

$C_0$ denoting the *total* concentration of living polymers, i.e., [total ~~S⁻,Li⁺]$_t$ + [total ~~D⁻,Li⁺]$_t$ = [total ~~S⁻,Li⁺]$_0$ + [total ~~D⁻,Li⁺]$_0$. Thus the total concentration of ~~D⁻,Li⁺ = $K_2^{1/2} \cdot v(K_2^{1/2}v + K_1^{1/2}u) = K_2^{1/2} \cdot v \cdot C_0^{1/2}$, and therefore $v$ = [total ~~D⁻,Li⁺]$/K_2^{1/2}C_0^{1/2}$. Hence, the rate of the reaction $-$d[total ~~D⁻,Li⁺]/d$t$ = $(k_{21}/K_2^{1/2}C_0^{1/2})$ [total ~~D⁻,Li⁺][S] and $k_0 = -\{d \ln$ [total ~~D⁻,Li⁺]/d$t\}_0/[S]_0 = k_{21}/K_2^{1/2}C_0^{1/2}$. In conclusion, $k''_0 = k_0$([total ~~D⁻,Li⁺]$_0$ + [total ~~S⁻,Li⁺]$_0$)$^{1/2} = k_{21}/K_2^{1/2}$, and not $k'_0 = k_0$[total ~~D⁻,Li⁺]$_0^{1/2}$, is the observed rate constant of the reaction. This deduction is verified by the data presented in the last two columns of Table I.

## Experimental Section

Styrene was dried by refluxing it over $CaH_2$. Thereafter it was distilled on high vacuum line and the distillation was repeated again after addition to the previously distilled monomer of a few milliliters of benzene solution of lithium polystyrene. The preparation and purification of 1,1-diphenylethylene was described elsewhere;[4] it suffices to stress that the purified hydrocarbon was free of benzophenone. Purification of benzene utilized the high vacuum technique, well known by now.

**Table I**
**Initial Rate of Conversion of ~~D⁻,Li⁺ into ~~S⁻,Li⁺ [d]**

~~D⁻,Li⁺ + S $\xrightarrow{k_{21}}$ ~~S⁻,Li⁺

| $10^4$[~~D⁻, Li⁺]$_0$, M | $10^4$[~~S⁻, Li⁺]$_0$, M | $10^2$[S]$_0$, M, | $k_0$,[a] M/s | $10^4k'_0$,[b] M$^{1/2}$ s | $10^4k''_0$,[c] M$^{1/2}$ s |
|---|---|---|---|---|---|
| 0.98 | 3.8 | 1.4 | 0.036 | 3.6 | 7.9 |
| 1.5 | 5.5 | 5.0 | 0.028 | 3.4 | 7.8 |
| 4.0 | 10.0 | 2.7 | 0.022 | 4.4 | 8.1 |
| 6.3 | 5.7 | 3.1 | 0.021 | 5.15 | 7.1 |
| 7.7 | 17.3 | 3.8 | 0.015 | 4.3 | 7.5 |
| 8.0 | 28.0 | 2.0 | 0.011 | 3.2 | 6.8 |
| 14.0 | 40.0 | 4.2 | 0.013 | 4.8 | 9.5 |
| 28.8 | 80.0 | 1.4 | 0.0069 | 3.75 | 7.2 |
| 29.5 | 19.3 | 1.8 | 0.0109 | 5.9 | 7.6 |
| | | | | Av | 7.7 ± 0.8 |

[a] $k_0 = -\{d \ln$ [~~D⁻,Li⁺]/d$t\}_0/[S]_0$. [b] $k'_0 = -\{d \ln$ [~~D⁻,Li⁺]/d$t\}_0 \cdot$[~~D⁻,Li⁺]$_0^{1/2}/[S]_0$. [c] $k''_0 = -\{d \ln$ [~~D⁻,Li⁺]/d$t\}_0 \cdot$ ([~~D⁻,Li⁺]$_0$ + [~~S⁻,Li⁺]$_0$)$^{1/2}/[S]_0$. [d] For the sake of briefness the word "total" is omitted in these notations.

All the operations and kinetic studies were carried out in evacuated all-glass equipment and an attached quartz cell allowed us to determine by spectrophotometry the concentrations of the reagents and the progress of the reaction. The spectra were recorded on a Beckman Acta M spectrometer using the appropriate range of optical densities.

Lithium polystyryl was prepared in benzene solution using *sec*-butyllithium as an initiator. Its $\lambda_{max}$ 335 nm and the respective value of its molar absorbance, viz. $1.3 \times 10^4$, was taken from the literature.[2] Quantitative conversion of ~~S⁻,Li⁺ into ~~D⁻,Li⁺ was achieved by adding a small excess of D to ~~S⁻,Li⁺ in benzene. The absence of any destruction of living ends was demonstrated by an isosbestic point through which passed the spectra of the solution recorded at different stages of the reaction. The results established that the $\lambda_{max}$ of ~~D⁻,Li⁺ lies at 440 nm and its molar absorbance is $2.2 \times 10^4$.

The conversion of ~~D⁻,Li⁺ into ~~S⁻,Li⁺ was monitored at 440 nm after adding a desired amount of styrene to benzene solution of a mixture of ~~S⁻,Li⁺ and ~~D⁻,Li⁺ both at known initial concentrations. The initial rate was calculated from Δ(od) measured at 100 s after the start of the reaction. In these early stages of conversion Δ(od) was virtually linear with time, this facilitating the determination of $(\Delta(od)/\Delta t)_0$.

## Results and Discussion

The results summarized in Table I show that the normalized pseudo-first-order constant $k_0 = -\{d \ln$ [total ~~D⁻,Li⁺]/d$t\}_0/[S]_0$ decreases as the initial concentration of ~~D⁻,Li⁺ increases. However, its value depends on the initial concentration of ~~S⁻,Li⁺. This is evident on inspecting the results of the last two runs where the total concentration of ~~D⁻,Li⁺ is kept virtually constant while the concentration of lithium polystyryl is decreased by a factor of 4. Similar conclusions may be drawn from the results of three runs in which the concentration of ~~D⁻,Li⁺ varied from 6.3 to $8.0 \times 10^{-4}$ M while the concentration of ~~S⁻,Li⁺ increased from 5.7 to $28 \times 10^{-4}$ M. The last two columns of Table I demonstrate that it is not the $k'_0 = k_0$[total ~~D⁻,Li⁺]$_0^{1/2}$ that is constant but the $k''_0 = k_0$([total ~~D⁻,Li⁺]$_0$ + [total ~~S⁻,Li⁺]$_0$)$^{1/2}$.

According to our treatment $k''_0$ is given by $k_{21}/K_2^{1/2}$ where $k_{21}$ is the bimolecular rate constant of styrene addition to *monomeric* ~~D⁻,Li⁺ and $K_2/2$ is the association constant of homodimerization of the monomeric ~~D⁻,Li⁺ into (~~D⁻,Li⁺)₂. Its value is $k_{21}/K_2^{1/2} = (7.7 \pm 0.8) \times 10^{-4}$ M$^{-1/2}$ s$^{-1}$.

It is interesting to compare it with $k_{12}/K_1^{1/2} = (2.1 \pm 0.1) \times 10^{-2}$ M$^{-1/2}$ s$^{-1}$ deduced from studies of Laita and Szwarc,[1] where $k_{12}$ refers to the bimolecular rate constant of addition of 1,1-diphenylethylene to *monomeric* polystyryllithium and

$K_1$ is its association constant to dimers.[6] The 30-fold decrease of $k_{21}/K_2^{1/2}$ compared with $k_{12}/K_1^{1/2}$ is due to two opposing factors. The more reactive 1,1-diphenylethylene should add more rapidly to the more reative ~S⁻,Li⁺ than the less reactive styrene to the less reactive ~D⁻,Li⁺, i.e., $k_{12}$ is expected to be much larger than $k_{21}$. On the other hand, the more bulky ~D⁻,Li⁺ is expected to be less extensively associated than the less bulky ~S⁻,Li⁺, i.e., $K_1$ is probaby greater than $K_2$.

We may also compare $k_{11}/K_1^{1/2}$ with $k_{12}/K_1^{1/2}$, $k_{11}$ denoting the bimolecular rate constant of styrene addition to monomeric lithium polystyryl. The value of $k_{11}/K_1^{1/2}$ is given[2] as $0.94 \times 10^{-2}$ $M^{-1/2}$ $s^{-1}$ implying that 1,1-diphenylethylene is twice as reactive as styrene in its addition to monomeric lithium polystyrene.

The importance of mixed dimerization in copolymerization involving Li cations and benzene solvent is shown again in studies of copolymerization of styrene and butadiene. In a paper[7] describing the kinetics of this reaction it was reported that the conversion of lithium butadienyl end group into lithium styryl end group obeys the first-order law. The authors could not explain this result. Apparently even in this system the association constant of ~S⁻,Li⁺ and ~B⁻,Li⁺ (butadienyl group) is again given by the square root of the association constants of the respective homodimerizations. In such a case the treatment outlined in ref 1 and in this paper accounts for the reported kinetic results.

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# Dependence on Molecular Weight of the Chain Expansion Factor of Polystyrene in Dilute Solutions[1]

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ABSTRACT: Accurate light-scattering and viscosity measurements were made in toluene at 30 °C on five polystyrene samples with narrow distribution in molecular weight. In the range of studied molecular weight, 1.3 million to 15.9 million, it was shown that the double logarithmic plot of $(\langle S^2\rangle/M)$ against $M^{1/2}$ gave a curve concave downward and that the penetration function $\Psi$ in the expression of $A_2$ decreased with the expansion factor $\alpha_s$ with a tendency to level off. The dependence of $\alpha_s$ on the parameter $z$ of the excluded-volume effect was deduced from the experimental data in a straightforward way by using the slope $F$ in the double logarithmic plot of $(\alpha_s^3 - 1)$ vs. $M^{1/2}$. It was concluded that $F$, starting from unity at $\alpha_s = 1$, decreased monotonously with $\alpha_s$. This conclusion was shown to be supported by the data of numerical computations on nonintersecting random walks on three-dimensional lattices. An empirical equation of $z$ was suggested as a function of $\alpha_s$, which yielded a constant value of $1.28 \times 10^{-3}$ for $z/M^{1/2}$ for the present polystyrene–toluene system regardless of molecular weight.

## I. Introduction

For flexible macromolecules perturbed by the excluded-volume effect, the mean-square radius of gyration $\langle S^2\rangle$ is not proportional to molecular weight $M$ but to $M$ to a power greater than unity. To avoid confusion, let us first define the parameter $\gamma$ for this property as

$$\gamma = \mathrm{d} \ln \langle S^2\rangle / \mathrm{d} \ln M \quad (1)$$

The perturbation may vanish at the theta temperature at which the second virial coefficient $A_2$ becomes zero. Of experimentally observable quantities, most directly related to the excluded-volume effect is the expansion factor,[3] which is denoted as $\alpha_s$ and defined by the ratio of $\langle S^2\rangle^{1/2}$ to its unperturbed value $\langle S^2\rangle_0^{1/2}$.

Considerable experimental effort has been directed toward elucidating this effect since Flory introduced this concept in 1949,[4] but for the last 5 years essentially no work was published. This never means that the effect has been analyzed in so much detail that the expansion factor is uniquely and universally related to the parameter

$$z = (3/2\pi a^2)^{3/2} \beta n^{1/2} \quad (2)$$

as the theory predicts.[5] Indeed, Yamakawa undeniably described in a recent review[6] that "as for the detailed deductions and conclusions about this effect, there is not as yet a complete consensus of all polymer physical chemists and physicists". In experimental studies difficulty lay in the luck of accuracy despite the fact that important improvements were made.[7,23]

However, there are now sufficient reasons to believe that we can obtain more accurate light-scattering data. (1) There is available an improved light-scattering photometer.[8] The reduced scattered intensity on dilute polymer solutions can routinely be determined correct to 0.5–1.0% over the range of the scattering angle from 9 to 150°. Both the geometrical correction and the correction for the Fresnel reflection can be ignored. Quick temperature equilibration of the sample liquid, as well as the accurate temperature control, is possible. The stray light level is low enough to obtain the correct angular dependence of the scattering from benzene to 20°. It should be mentioned that the quality of light-scattering data can be

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