Spectroscopic and Kinetic Studies of Addition of Double 1,1-Diphenylethylenes to Lithium Polystyryl in Benzene

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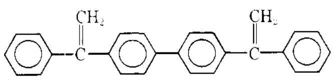
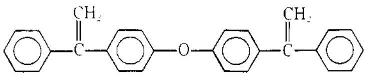
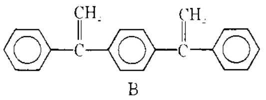
ABSTRACT: Addition of lithium polystyryl dissolved in benzene to the following "double 1,1-diphenylethylenes" was investigated: D-D, DOD, and B.



D-D



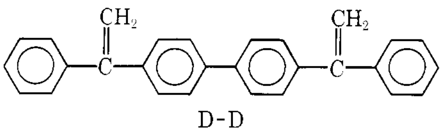
DOD



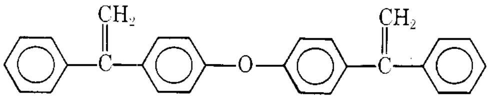
B

We demonstrated that the addition to only one C=C bond, observed in the presence of an excess of "double 1,1-diphenylethylene", follows the mechanism outlined by Laita and Szwarc.[3] This mechanism assumes that the active monomeric lithium polystyryl is the reagent added to the C=C bond but its concentration is determined by the equilibria of two homodimerizations and a mixed dimerization. As a result the reaction shows an interesting memory effect. The monoadducts as well as the diadducts were characterized spectroscopically, and a startling difference is observed between the spectra of mono- and diadducts of D-D. The kinetics of all these additions was unravelled. The dimerization and further aggregation of the adducts were studied by viscometry. Finally, kinetics of initiation of styrene polymerization by the diadducts sheds light on its structure. It seems that the diadducts form cyclic dimers which are in equilibrium with their open-chain form. The latter are the true initiators of styrene polymerization.

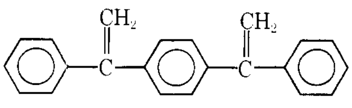
The dimeric nature of lithium polystyryl in benzene[2] leads to some pecularities in its addition to 1,1-diphenylethylene.[3] We extended recently the previously reported study to "double 1,1-diphenylethylenes", i.e., compounds possessing two 1,1-diphenyl moieties in one molecule. The following "double 1,1-diphenylethylenes" were synthesized:



D-D



DOD



B

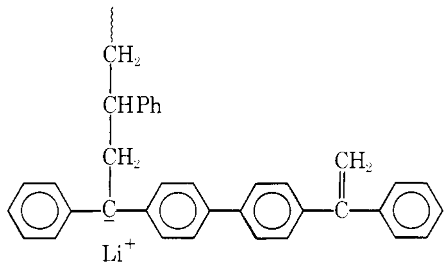
Their preparation and characterization will be reported elsewhere.[4] In this paper we shall describe the kinetics of their addition to lithium polystyryl in benzene, the spectra of the respective adducts, and the conclusions drawn about their state of aggregation.

The preparation of low molecular weight lithium polystyryl (DP ~ 20) and its addition to D–D, DOD, and B were performed on high vacuum line using the now well-known technique utilizing breakseals and constrictions. The polymerization was initiated by secondary butyllithium added to benzene solution of styrene. Spectroscopic studies were performed in quartz cells sealed to the reactors. The spectra were recorded on a Beckman Acta M-VI spectrophotometer.

The initial concentrations of lithium polystyryl were determined spectrophotometrically. The concentrations of D–D, DOD, and B were calculated from the known weights of the added monomers and the total volume of the investigated solutions.

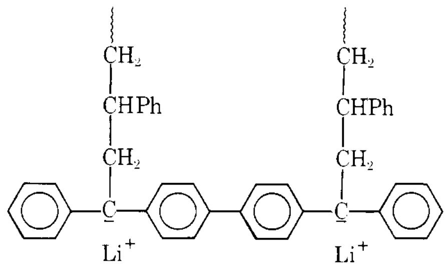
Spectroscopic and Kinetic Studies of D–D

Absorption Spectra of Addition Products of Lithium Polystyrene to D–D in Benzene Solution. Addition of a large excess of D–D to benzene solution of lithium polystyryl leads to the formation of a red monoadduct (I^-,Li^+), probably in a dimeric form $(I^-,Li^+)_2$ of a similar nature as the dimeric lithium polystyryl.[2] Its absorption spectrum is shown in Figure 1, λ_{max} 522 nm, $\epsilon = 2.2 \times 10^4$.



($I^-.Li^+$)

Further addition of lithium polystyryl eventually converts (I^-,Li^+) into a blue diadduct ($II^{2-},2Li^+$), absorbing at λ_{max} 598 nm, $\epsilon = 14 \times 10^4$, i.e., its molar absorbance is six times higher than the molar absorbance of (I^-,Li^+). The spectrum of ($II^{2-},2Li^+$) is also shown in Figure 1. The conversion of D–D to the diadduct is quantitative in the presence of an excess of lithium polystyryl. Under these conditions ($II^{2-},2Li^+$) is probably associated with two lithium polystyryl chains.



($II^{2-}, 2Li^+$)

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Table I
$\sim S^-,Li^+$ + Excess of D–D → (I^-,Li^+) (k_a) in Benzene

$10^4[\sim S^-,Li^+]_0$, M	$10^4[D\text{–}D]_{ex}$, M	$10^2 s_1$, s	$10^2 s_2$, s	s_1/s_2	$s_1/[D\text{–}D]_{ex}$, M s	$(10^2 k_a/K_1^{1/2})$, $M^{1/2}$ s^a
1.22	14	1.3	0.68	1.9	9.3	10.3
2.20	20	0.96	0.46	2.1	4.8	7.1
2.05	24	1.4	0.78	1.8	5.8	8.3
2.13	38	2.3	1.2	1.9	6.1	8.9
3.02	60	2.9	1.2	2.3	4.8	8.3
2.14	96	6.0	2.7	2.2	6.3	9.1
5.01	100	3.5	1.6	2.2	3.5	7.8
15.2	100	1.9	1.0	1.9	1.9	7.4
			Av	2.0 ± 0.2		8.4 ± 1.0

[a] $k_a/K_1^{1/2} = s_1 C_0^{1/2}/[D\text{–}D]_{ex}$.

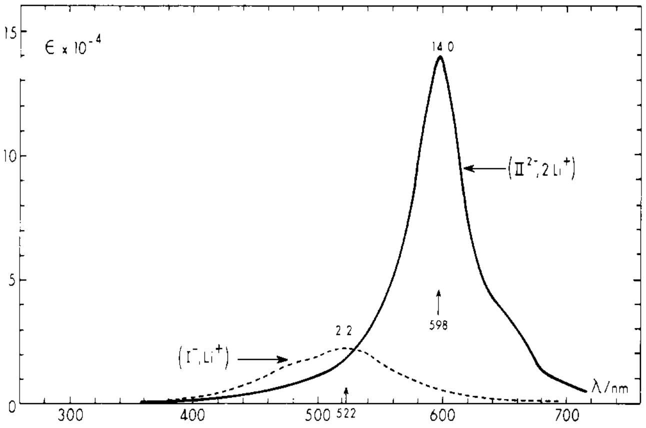


Figure 1. Spectra of (I^-,Li^+) and $(II^{2-},2Li^+)$ in benzene.

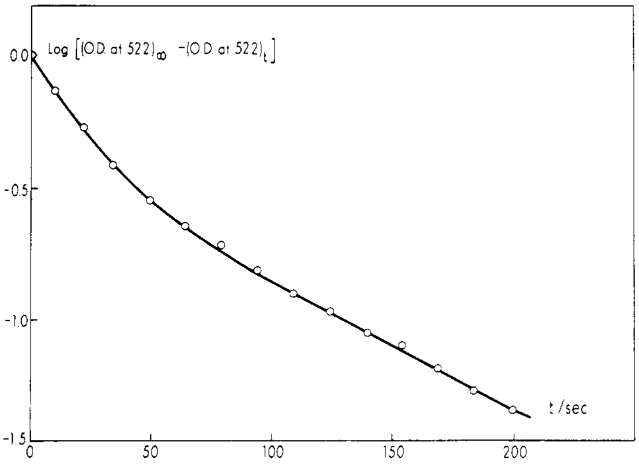


Figure 2. Plot of log $\{1 - (\mathrm{OD}\ 522)_t/(\mathrm{OD}\ 522)_\infty\}$ vs. time for the addition of lithium polystyryl to an excess of D–D (decimal log scale).

Kinetics of Lithium Polystyryl Addition to D–D

Kinetics of lithium polystyryl addition to D–D was studied in benzene under two extreme conditions: (a) in the presence of a large excess of D–D, and (b) in the presence of a large excess of lithium polystyryl.

The kinetic results obtained in the presence of a large excess of D–D are summarized in Table I. The reaction was monitored by the increase of absorbance at 522 nm, i.e., at λ_{max} of (I^-,Li^+). The absence of the diadduct was demonstrated by scanning the whole spectrum after completion of the addition. Plots of ln $\{\mathrm{OD}(522)_\infty - \mathrm{OD}(522)_t\}/\mathrm{OD}(522)_\infty$ vs. time are slightly curved, as exemplified by Figure 2. The initial slopes, s_1, and those of the asymptotes, s_2, could be determined with a reasonable accuracy and their values are listed in Table I.

The kinetics of the addition

$$\sim S^-,Li^+ + D\text{–}D \xrightarrow{k_a} (I^-,Li^+)$$

seems to be governed by the mechanism proposed by Laita and Szwarc.[3] The reactive monomeric lithium polystyryl, $(\text{–}S^-,Li^+)$, coexisting in equilibrium with its unreactive dimer $(\text{–}S^-,Li^+)_2$ and the mixed dimer $(\text{–}S^-,Li^+)(I^-,Li^+)$ is the reagent responsible for the observed reaction. The following equilibria seem to be maintained during the addition:

$$2(\text{–}S^-,Li^+) \rightleftarrows (\text{–}S^-,Li^+)_2 \qquad \tfrac{1}{2}K_1 \qquad (1)$$

$$(\text{–}S^-,Li^+) + (I^-,Li^+) \rightleftarrows (\text{–}S^-,Li^+)(I^-,Li^+) \qquad K_{1,2} \qquad (1,2)$$

$$2(I^-,Li^+) \rightleftarrows (I^-,Li^+)_2 \qquad \tfrac{1}{2}K_2 \qquad (2)$$

However, the concentrations of (I^-,Li^+) and $(\text{–}S^-,Li^+)$ are negligibly small compared with the concentrations of the dimeric species. The rate of addition, i.e., the rate of formation of (I^-,Li^+) in whatever form (homo- or heterodimers),[7] is given by

$$\mathrm{d}(\mathrm{OD}\ 522)_t/\mathrm{d}t = (\epsilon l)k_a[D\text{–}D]_{ex}[\text{–}S^-,Li^+]$$

where (ϵl) is the product of the molar absorbance of (I^-,Li^+) and the length of the cell, $[D\text{–}D]_{ex}$ denotes the concentration of D–D considered to be constant in each run in view of its excess, and $[\text{–}S^-,Li^+]$ is the concentration of the monomeric $\text{–}S^-,Li^+$ maintained by the previously discussed equilibria. Let us denote by C_0 the initial total concentration of polystyryl and by f its fraction remaining at time t. Obviously $C_0 = (\mathrm{OD}\ 522)_\infty/\epsilon l$ and $f = \{(\mathrm{OD}\ 522)_\infty - (\mathrm{OD}\ 522)_t\}/(\mathrm{OD}\ 522)_\infty$.

Laita and Szwarc[3] have shown that $[\text{–}S^-,Li^+] = C_0^{1/2}/\{K_1 + 2K_{12}\alpha + K_2\alpha^2\}^{1/2}$ where $\alpha = [I^-,Li^+]/[\text{–}S^-,Li^+]$, i.e., the ratio of the concentrations of the monomeric (I^-,Li^+) and $(\text{–}S^-,Li^+)$ maintained by the equilibria 1, 1,2, and 2, and

$$f = (K_1 + K_{1,2}\alpha)/(K_1 + 2K_{1,2}\alpha + K_2\alpha^2)$$

Since

$$-\mathrm{d}(\mathrm{OD}\ 522)_t/\mathrm{d}t = \mathrm{d}\{(\mathrm{OD}\ 522)_\infty - (\mathrm{OD}\ 522)_t\}/\mathrm{d}t = (\mathrm{OD}\ 522)_\infty \mathrm{d}f/\mathrm{d}t$$

and

$$-\mathrm{d}f/\mathrm{d}t = k_a[D\text{–}D]_{ex}[\text{–}S^-,Li^+]/C_0$$

we find

$$-\mathrm{d}f/\mathrm{d}t = k_a[D\text{–}D]_{ex}/C_0^{1/2}(K_1 + 2K_{1,2}\alpha + K_2\alpha^2)^{1/2}$$

and

$$-\mathrm{d}\ln f/\mathrm{d}t = (k_a[D\text{–}D]_{ex}/C_0^{1/2})\{(K_1 + 2K_{1,2}\alpha + K_2\alpha^2)/(K_1^2 + 2K_1K_{1,2}\alpha + K_{1,2}^2\alpha^2)\}^{1/2} \qquad (3)$$

This is a modified equation of Laita and Szwarc.[3] In their system (addition of 1,1-diphenylethylene to lithium polystyryl

Table II
$(I^-,Li^+)(-S^-,Li^+)$ + Excess of $\sim\!\sim S^-,Li^+ \rightarrow (II^{2-},2Li^+)(-S^-,Li^+)$ (k_b) in Benzene

$10^4[\sim\!\sim S^-, Li^+]_0$, M	$10^4[D\text{--}D]_0$, M	$10^4 k_u$, s	$(10^2 k_u/[\sim\!\sim S^-, Li^+]_0{}^{1/2})$ $M^{1/2}s = 10^2 k_b/K_1{}^{1/2}$
2.39	0.24	2.50	1.64
2.40	0.17	2.76	1.78
4.40	0.19	4.45	2.08
5.00	0.13	4.41	1.96
11.8	0.12	6.35	1.84
15.7	0.14	9.5	2.40(?)
18.1	0.19	7.6	1.80
31.3	0.13	10.5	1.80
		Av	1.85 ± 1.4

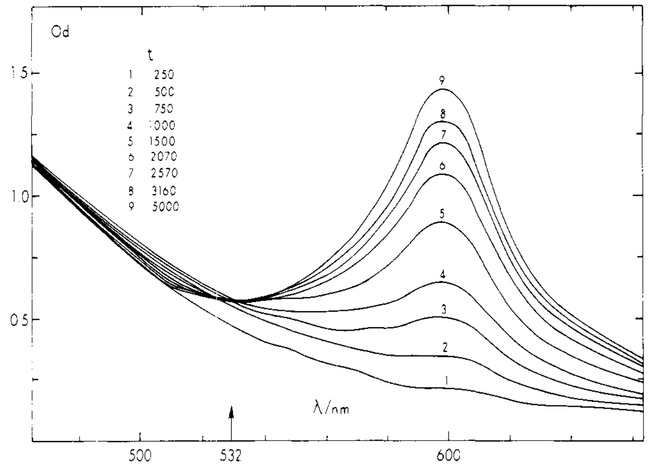


Figure 3. Spectra of a mixture of D–D with an excess of lithium polystyryl in benzene recorded at different times (time given in s). Note the appearance of the isosbestic point (532 nm) at later stages of the reaction.

in benzene) further simplification was possible because $K_{1,2}{}^2 = K_1K_2$. In such a case the last factor

$$(K_1 + 2K_{1,2}\alpha + K_2\alpha^2)^{1/2}/(K_1{}^2 + 2K_1K_{1,2}\alpha + K_{12}{}^2\alpha^2)^{1/2} = 1/K_1{}^{1/2}$$

and hence in their study ln f was linear with time, its slope being given by $k_a[D\text{–}D]_{ex}/K_1{}^{1/2}C_0{}^{1/2}$. In our system the plots of ln f vs. time are slightly curved (see Figure 2) implying that the relation $K_{1,2}{}^2 = K_1K_2$ is not obeyed. Nevertheless, inspection of eq 3 shows that the initial slopes of such plots (i.e., for $\alpha \ll 1$) are given by $k_a[D\text{–}D]_{ex}/K_1{}^{1/2}C_0{}^{1/2}$ whereas the slopes of the asymptotes ($\alpha \rightarrow \infty$) are $k_aK_2{}^{1/2}[D\text{–}D]_{ex}/K_{1,2}C_0{}^{1/2}$.

The data collected in Table I give $k_a/K_1{}^{1/2} = (8.4 \pm 1.0) \times 10^{-2}$ $M^{-1/2}$ s^{-1}, a value larger than $(2.1 \pm 0.1) \times 10^{-2}$ $M^{-1/2}$ s^{-1} reported by Laita and Szwarc[3] for the similar addition to 1,2-diphenylethylene.[8] Taking the statistical factor of 2 into account, one finds D–D to be about twice as reactive as the diphenylethylene, a trend concordant with the generally observed increase of reactivity with increasing conjugation of aromatic substrates.

From the ratios s_1/s_2 listed in the fifth column of Table I we get $\gamma = K_{1,2}/(K_1K_2)^{1/2}$. Its deviation from unity is a measure of curvature of the ln f vs. time plot. For γ larger than 1 the tendency to form a mixed dimer is greater than geometric average of homodimerizations and the curve is concave. This is the case in our system, $\gamma = 2.0 \pm 0.2$.

Kinetics of lithium polystyryl addition to D–D when the former is in excess was also investigated by spectrophotometric technique. The absorption spectra of the reacting solution taken at successive times are shown in Figure 3. Its inspection reveals two stages of the process. At early stages of the reaction the monoadduct (I^-,Li^+) is rapidly formed; the conversion of D–D into (I^-,Li^+) appears to be completed in about 15 min. The conversion of (I^-,Li^+) into $(II^{2-},2Li^+)$ is slow and revealed at later stages of the reaction when virtually all D–D has been converted into (I^-,Li^+). At this stage of the process the concentration of (I^-,Li^+) decreases and an equivalent amount of $(II^{2-},2Li^+)$ is formed. This is confirmed by the appearance of an isosbestic point at about 532 nm (see Figure 3). The slow reaction was found to be pseudo-first-order, i.e., ln $\{(OD\ 598)_\infty - (OD\ 598)_t\}$ (λ_{max} of $II^{2-},2Li^+$) is perfectly linear with time as shown in Figure 4, the slope being proportional to $C_0{}^{1/2}$ where C_0 denotes the virtually constant concentration of lithium polystyrene in each run. The pertinent results are collected in Table II, the average value of the pseudo-first-order rate constant $k_u/C_0{}^{1/2}$ is $(1.85 \pm 0.14) \times 10^{-2}$ $M^{-1/2}$ s^{-1}, i.e., the bimolecular rate constant k_b of the addition of the monomeric $\sim\!\sim S^-,Li^+$ to (I^-,Li^+) is only slightly lower than the respective constant found for the addition to 1,1-diphenylethylene.

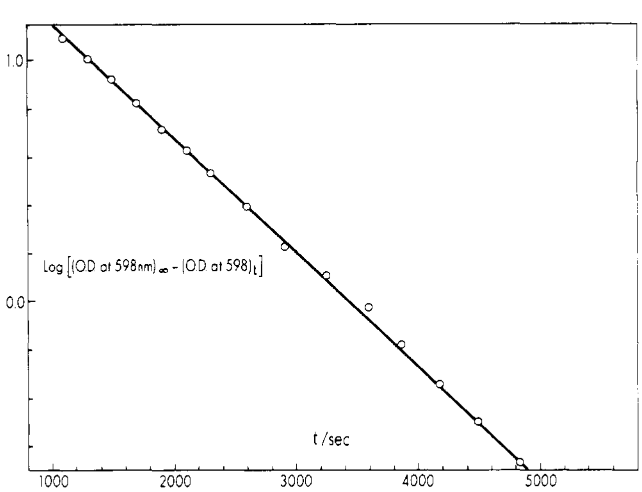


Figure 4. Plot of $-\log\ [(OD\ 598)_\infty - (OD\ 598)_t]$ vs. time for later stages of the reaction taking place between excess of lithium polystyryl and D–D in benzene (decimal log).

The results of the previous series of experiments imply that under conditions prevailing in the present series of runs (I^-,Li^+) is associated with $(-S^-,Li^+)$ forming a mixed dimer $(I^-,Li^+)(-S^-,Li^+)$. One could expect therefore the conversion of (I^-,Li^+) into $(II^{2-},2Li^+)$ to be a truly unimolecular reaction

$$(I^-,Li^+)(-S^-,Li^+) \xrightarrow{k_c} (II^{2-},2Li^+)$$

However, the results presented in Table II demonstrate that such a reaction, if it occurs, is much slower than the bimolecular addition observed here

$$(I^-,Li^+)(-S^-,Li^+) + (-S^-,Li^+) \xrightarrow{k_b} (II^{2-},2Li^+)(-S^-,Li^+)$$

The product of this addition becomes later associated with another $(-S^-,Li^+)$, thus forming the final adduct $(II^{2-},2Li^+)(-S^-,Li^+)_2$.

The validity of the proposed mechanism of addition is further confirmed by monitoring at 532 nm (the isosbestic point at later stages of the reaction) the early progress of the reaction taking place in the presence of an excess of lithium polystyryl. At this wavelength the molar absorbances of (I^-,Li^+) and $(II^{2-},2Li^+)$ are identical. Hence,

Table III
$\sim S^-,Li^+$ + Excess of DOD → (III^-,Li^+) (k_a') in Benzene

10^4[DOD], M[a]	$10^4[\sim S^-,Li^+]_0$, M	$10^3k_u'$, s	$\{k_u'/[DOD]\}[\sim S^-,Li^+]_0^{1/2}$ $M^{1/2}$ s $\times 10^2 = 10^2k_a'/K_1^{1/2}$
85	12.1	4.12	1.68
145	1.67	21.3	1.90
172	3.17	17.9	1.85
179	16.6	8.51	1.93
218	5.16	18.2	1.89
389	19.9	15.7	1.80
640	16.7	26.7	1.70
		Av	1.82 ± 0.10

[a] Note that for a constant [DOD] (the third and fourth experiments) k_u' decreases with $[\sim S^-,Li^+]_0$ and for a constant $[\sim S^-,Li^+]_0$ (the fourth and the last experiment) it increases with increasing [DOD].

$$d(OD532)/dt = (\epsilon' l)\cdot d\{[I^-,Li^+] + [II^{2-},2Li^+]\}/dt$$

Since

$$d[I^-,Li^+]/dt = (C_0/K_1)^{1/2}(k_a[D\text{–}D] - k_b[I^-,Li^+])$$

$$d[II^{2-},2Li^+]/dt = (C_0/K_1)^{1/2}(k_b[I^-,Li^+])$$

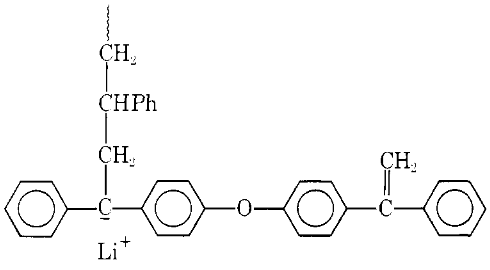
and $(OD\ 532)_\infty = \epsilon' l[D\text{–}D]_0$, we find

$$-\ln\{(OD\ 532)_\infty - (OD\ 532)_t\}/(OD\ 532)_\infty = (k_a/K_1^{1/2})C_0^{1/2}t$$

This relation is again obeyed and a typical plot of ln $\{(OD\ 532)_\infty - (OD\ 532)_t\}$ vs. time is shown in Figure 5. From its slope divided by $C_0^{1/2}$ we find $k_a/K_1^{1/2}$ to be 8.9×10^{-2} $M^{-1/2}$ s^{-1} in agreement with the value derived from the experiments with an excess of D–D.

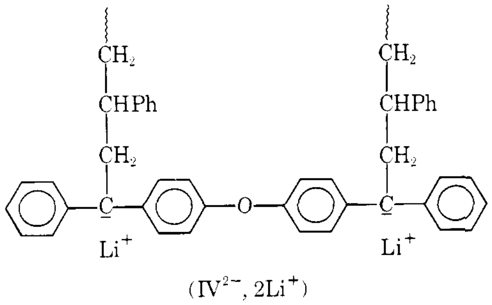
Spectroscopic and Kinetic Studies of DOD

Absorption Spectra of the Addition Products of Lithium Polystyryl to DOD in Benzene Solution. Addition of benzene solution of lithium polystyrene to an excess of DOD yields an orange-red monoadduct (III^-,Li^+) presumably present in a dimeric form.



(III^-,Li^+)

Its spectrum, shown in Figure 6, reveals a broad band with λ_{max} 417 nm and $\epsilon = 1.6 \times 10^4$. The increasing absorbance below 350 nm, revealed by Figure 6, arises from the presence of the unreacted DOD. Further addition of lithium polystyrene eventually results in the formation of a diadduct ($IV^{2-},2Li^+$). The latter is presumably associated with the unreacted lithium polystyrene present in excess, and its spectrum, also drawn in Figure 6, only slightly differs from that of (III^-,Li^+). Its λ_{max} is shifted to 428 nm and $\epsilon = 3.2 \times 10^4$ is, as could be expected, twice as high as that of the monoadduct. These results strongly contrast with those observed in the D–D system and imply that the interaction between the two chromophores is weak, both in DOD and in its adducts.



($IV^{2-},2Li^+$)

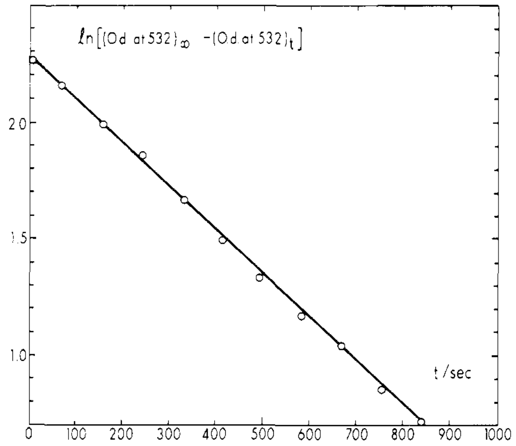


Figure 5. Plot of $-\ln (OD\ 532)_\infty - (OD\ 532)_t)$ vs. time for the reaction between excess of lithium polystyryl and D–D in benzene. At 532 nm the molar absorbances of (I^-,Li^+) and ($II^{2-},2Li^+$) are identical.

Kinetics of $\sim S^-,Li^+$ Addition to DOD

Kinetics of $\sim S^-,Li^+$ addition to an excess of DOD was followed by monitoring the absorbance at 417 nm. The reaction obeyed first-order law, ln ($OD_\infty - OD_t$), being linear with time. The resulting pseudo-first-order constants, k_u', are listed in Table III and, as shown by the last column of this table, $\{k_u'/[DOD]\}[\sim S^-,Li^+]_0^{1/2}$ is virtually constant. This could be expected on the basis of the mechanism proposed by Laita and Szwarc[3] discussed in the preceding section, provided that the equilibrium constants of the dimerizations, K_1, K_2, and $K_{1,2}$, obey the relation $K_{1,2} = (K_1K_2)^{1/2}$. The deduced value of $\frac{1}{2}k_a'/K_1^{1/2} = 0.9 \times 10^{-2}$ $M^{-1/2}$ s^{-1} ($\frac{1}{2}$ accounts for the statistical factor of 2) is substantially smaller than the rate constant found by Laita and Szwarc[3] for the addition of lithium polystyrene to 1,1-diphenylethylene, implying that the reactivity is reduced when phenoxy group is substituted for H.

The reaction performed with an excess of lithium polystyryl and monitored at λ_{max} of the products mixture obeyed again first-order law. The pseudo-first-order rate constant was proportional to $[\sim S^-,Li^+]^{1/2}$, this being demonstrated by the data collected in Table IV. Since $(OD)_\infty$ corresponds to a quantitative conversion of DOD into ($IV^{2-},2Li^+$), a simple first-order kinetics implies that the rate constant of the reaction

$$DOD + \sim S^-,Li^+ \rightarrow (III^-,Li^+) \qquad k_a'$$

Table IV
Excess of $\sim\!\!\sim S^-,Li^+$ + DOD → (III^-,Li^+) and $(IV^{2-},2Li^+)$ $(k_{av}')^a$

$10^4[DOD]_0$, M	$10^4[\sim\!\!\sim S^-,Li^+]_0$, M	$10^4k_u'$, s	$(k_u'/[\sim\!\!\sim S^-,Li^+]_0^{1/2})\ M^{1/2}\ s \times 10^2 = 10^2k_{av}'/K_1^{1/2}$
0.82	5.9	2.87	1.06
1.0	29.0	4.51	0.84
1.2	19.2	4.26	0.97
3.8	78.5	7.19	0.81
6.7	120	10.3	0.93
		Av	0.92 ● 0.10

[a] k_{av}' is the average of $\frac{1}{2}k_a'$ and k_b'.

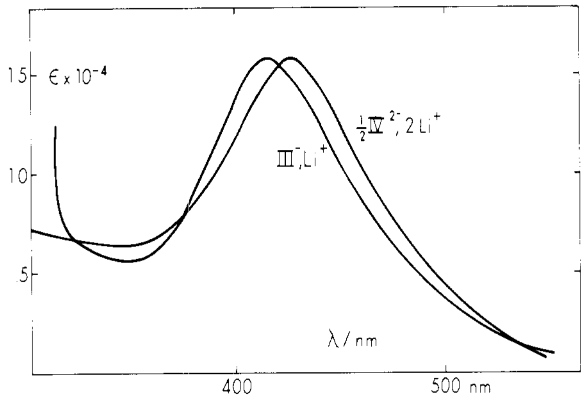


Figure 6. Spectra of (III^-,Li^+) and $\frac{1}{2}(IV^{2-},2Li^+)$ in benzene.

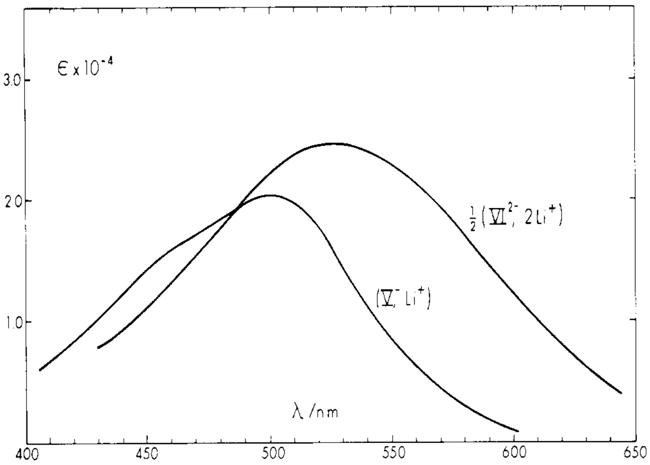


Figure 7. Spectra of (V^-,Li^+) and $(VI^{2-},2Li^+)$ in benzene.

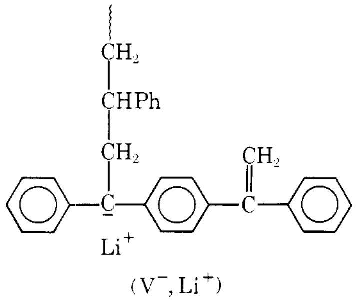
is twice as high (due to the statistical factor of 2) as that of the reaction

$$(III^-,Li^+) + \sim\!\!\sim S^-,Li^+ \rightarrow (IV^{2-},2Li^+) \qquad k_b'$$

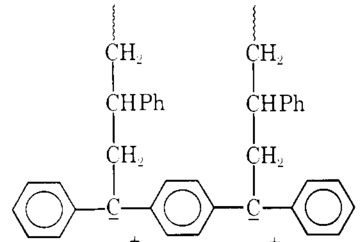
Moreover, since the spectra of (III^-,Li^+) and $\frac{1}{2}(IV^{2-},2Li^+)$ closely overlap (see Figure 6) and ϵ at λ_{max} of (III^-,Li^+) is $\frac{1}{2}$ of ϵ at λ_{max} of $(IV^{2-},2Li^+)$, the pertinent pseudo-first-order rate constant could be determined from a plot of ln $(OD_\infty - OD_t)$ vs. time, where OD_t is measured at the momentary λ_{max}. The constant k_u' refers to the conversion of all the C=C bonds into the adducts and therefore the value of $k_u'/[\sim\!\!\sim S^-,Li^+]_0^{1/2}$ derived from this series of experiments should be $\frac{1}{2}$ of that of $\{k_u'[DOD]\}/[\sim\!\!\sim S^-,Li^+]_0^{1/2}$ deduced from the preceding series of runs, provided that the reactivity of each C=C bond in DOD is virtually the same as that of the C=C bond in III^-,Li^+. This conjecture is verified.

Spectroscopic and Kinetic Studies of B

Absorption Spectra of the Addition Products of Lithium Polystyrene to B in Benzene. Addition of benzene solution of lithium polystyrene to an excess of B yields a reddish adduct (V^-,Li^+). Its spectrum is shown in Figure 7, λ_{max} 500 nm, $\epsilon = 2.2 \times 10^4$. Further addition of lithium polystyrene converts the monoadduct (V^-,Li^+) into diadduct $(VI^{2-},2Li^+)$.



(V^-, Li^+)



$(VI^{2-}, 2Li^+)$

Its spectrum, also shown in Figure 7, reveals a slight bathochromic shift in λ_{max} from that of (V^-,Li^+), namely to 530 nm with $\epsilon = 4.4 \times 10^4$. Thus, the molar absorbance of $(VI^{2-},2Li^+)$ is only twice as high as that of (V^-,Li^+), a result similar to that observed in the DOD system, but strikingly different from the observed spectral changes in the D–D system. The expected interaction, so dramatically revealed in the D–D adducts, does not affect the molar absorbance of $(VI^{2-},2Li^+)$.

Kinetics of $\sim\!\!\sim S^-,Li^+$ Addition to B

Addition of benzene solution of $\sim\!\!\sim S^-,Li^+$ to an excess of B leads to a reaction monitored at 500 nm. Plots of ln $\{(OD\ 500)_\infty - (OD\ 500)_t\}$ were curved as exemplified by Figure 8. We concluded that this addition is governed by the mechanism discussed in the section dealing with D–D, i.e., $K_1K_2 < K_{1,2}^2$. Utilizing the previously outlined approach we found from the initial slopes of the curves the respective value of $k_a''/K_1^{1/2}$.

$$B + \sim\!\!\sim S^-,Li^+ \xrightarrow{k_a''} (V^-,Li^+)$$

The pertinent data are collected in Table V and lead to $k_a''/K_1^{1/2} = (7.2 \pm 0.6) \times 10^{-2}\ M^{-1/2}\ s^{-1}$, and $\gamma'' = s_1''/s_2'' = 2.8 \pm 0.4$.

Table V
$\sim\!\sim S^-,Li^+$ + Excess of B → (V^-,Li^+) (k_a'') in Benzene

$10^4[\sim\!\sim S^-,Li^+]_0$, M	$10^4[B]_{ex}$, M	$10^2 s_1''$, s	s_1''/s_2''	$(s_1''/[B]_{ex})$, M s	$10^2 s_1'' C_0^{1/2}/[B]_{ex}$ $= (10^2 k_a''/K_1^{1/2})$ $M^{1/2}$ s
1.6	49.3	2.56	2.8	5.2	6.6
7.5	111	2.61	2.4	2.4	6.4
4.2	117	4.42	3.4	3.8	7.7
6.7	151	4.34	3.2	2.9	7.4
7.6	266	7.42	2.3	2.8	7.7
24.3	313	4.60	2.4	1.5	7.2
				Av 2.8 ± 0.5	7.2 ± 0.6

Table VI
Excess of $\sim\!\sim S^-,Li^+$ + (V^-,Li^+) → $(VI^{2-},2Li^+)$ (k_b'') in Benzene

$10^4[\sim\!\sim S^-, Li^+]_0$, M	$10^4[B]_0$, M	$10^4 k_u''$, s	$(10^2 k_u''/C_0^{1/2})$ $M^{1/2}$ s $= 10^2 k_b''/K_1^{1/2}$ $M^{1/2}$ s
8.1	0.10	1.55	0.55
40.8	0.28	3.77	0.49
96.9	7.4	4.42	0.45
254	0.70	9.27	0.58
628	11	14.4	0.57
		Av	0.55 ± 0.06

The reaction observed in the presence of an excess of lithium polystyrene shows the characteristic feature of the similar addition to D–D. A fast step is followed by a slow one, and an isosbestic point at about 480 nm appears during the later stage of the addition. The latter process is governed by the first-order kinetics and is conveniently monitored by the optical density at 560 nm. From the slopes of the respective lines (see the data collected in Table VI) we determined $k_b''/K_1^{1/2}$ to be 0.55×10^{-2} $M^{-1/2}$ s^{-1}. Hence, the addition of the second lithium polystyrene is substantially slower than that of the first one, as in the D–D system.

$$(V^-,Li^+) + \sim\!\sim S^-,Li^+ \xrightarrow{k_b''} (VI^{2-},2Li^+)$$

Effect of Diphenyl Ether on the Rate of Addition of $\sim\!\sim S^-,Li^+$ to 1,1-Diphenylethylene

Our study of kinetics of addition of $\sim\!\sim S^-,Li^+$ to DOD raised the question of whether this kind of ether affects the reactivity and perhaps also the state of aggregation of lithium polystyryl in benzene. To resolve it we reinvestigated the kinetics of addition of 1,1-diphenylethylene to lithium polystyryl, keeping the latter reagent in large excess, and then repeated these experiments with 0.15 M diphenyl ether added to benzene solution of living polystyrene ([lithium polystyryl] was varied from 10^{-3} to 10^{-2} M).

The kinetic results obtained in the absence of diphenyl ether showed that the reaction follows the pseudo-first-order law, the pseudo-first-order constant, k_f, being proportional to $[(\sim\!\sim S^-,Li^+)_2]^{1/2}$. Thus, the ratio $k_f/[(\sim\!\sim S^-,Li^+)_2]^{1/2}$ identified with $k_{ad}/K_1^{1/2}$ was found to be $(1.8 \pm 0.1) \times 10^{-2}$ $M^{-1/2}$ s^{-1} in fair agreement with the findings of Laita and Szwarc[3] and confirmed recently by Busson and Van Beylen.[5] Neither the kinetics nor the rate was affected by the addition of PhOPh ([PhOPh] ~ 0.15 M). Hence, we have to conclude that the lower reactivity of DOD observed in our study is due to the intrinsic effect of OPh substituent on the reactivity of the parent hydrocarbon and not to the effect of Ph–O–Ph acting as a solvating agent on the reactivity or state of aggregation of lithium polystyryl in benzene.

Our findings do not contradict the claims of Tobolsky and Rogers.[6] They found that substitution of hydrocarbon solvent by *bulk* diphenyl ether affects the copolymerization of styrene and isoprene initiated by BuLi and the microstructure of polyisoprene. We presume that such effects would be undetectable had the concentration of that ether been reduced from ~5 to ~0.15 M.

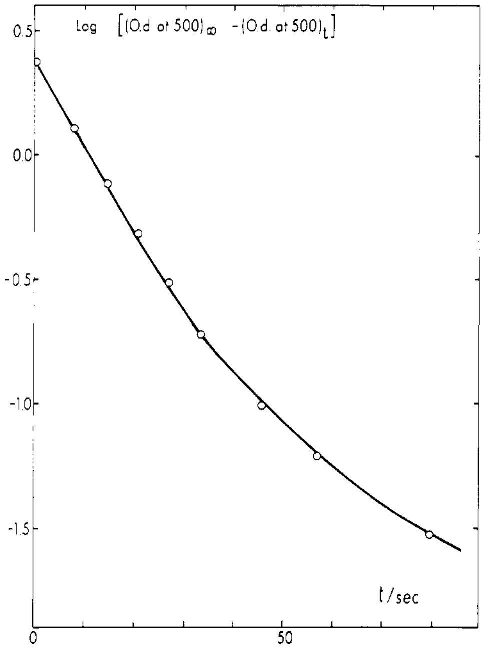


Figure 8. Plot of log {(OD 500)$_\infty$ − (OD 500)$_t$} vs. time for the reaction of lithium polystyryl with excess of B in benzene.

The Effect of D–D or DOD Addition on the Viscosity of Lithium Polystyryl in Benzene

The previously discussed kinetic results demonstrated that polystyryls possessing the D–D, DOD, or B end groups associated with Li^+ counterions undergo in benzene solution either a homodimerization or form mixed dimers with lithium polystyryl. To substantiate this conclusion we investigated the effect of addition of these diphenylethylene derivatives on the viscosity of benzene solution of lithium polystyryl.

The equipment used in this work is shown in Figure 9. Low molecular weight living polystyrene (DP ~ 20) dissolved in benzene was kept in ampule A, rigorously purified styrene in ampule B, and a required amount of D–D or DOD in ampule C. The unit was evacuated on a high-vacuum line and, after closing the stopcock S, the breakseal of A was crushed and its content transferred into bulb F terminated by an optical cell (2 mm optical path) by tilting the apparatus. The concentration of living ends was then determined by their absorbance. The breakseal of ampule B was then crushed and a few drops of the solution of living polystyrene was transferred to it in order to destroy any undesirable impurities contaminating the monomer. The monomer was then distilled to the

Table VII
The Effect of Addition of D–D or DOD on the Viscosity of Lithium Polystyrene in Benzene[a]

Expt no.	$10^3[\sim S^-,Li^+]_0$, M	$[S]/[\sim S^-,Li^+]$	Substance added	Flow time, s
1	0.8	3800		3460
			MeOH	335
2	1.1	1600		202
			Excess D–D	213
			+ MeOH	30
3	0.7	1700		428
			0.5 equiv of D–D	1210
			+ MeOH	434
4	2.5	690		24.5
			Excess DOD	25.0
			+ MeOH	6.1
5	3.1	790		48.3
			0.5 equiv of DOD	116
			+ MeOH	33.4

[a] The living polystyrene used to produce the higher molecular weight polymer had DP ~ 20.

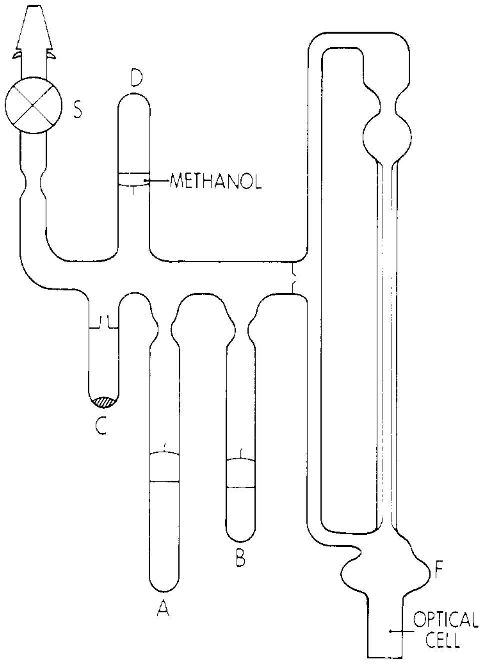


Figure 9.

chilled bulb F and thereafter ampules A and B were sealed off the unit. The contents of bulb F were melted, thoroughly mixed, and left overnight at ambient temperature to allow for completion of the polymerization. The unit was reattached to the vacuum line and rigorously purified nitrogen was admitted (at a pressure of a few hundred Torr). The viscosity of thus prepared solution was measured by transferring it to the upper bulb and determining the time of flow through the capillary. Thereafter the breakseal of ampule C was crushed, some solvent distilled from F to C, and D–D or DOD kept in C dissolved, and its solution returned to F. After completion of the reaction the viscosity was redetermined.

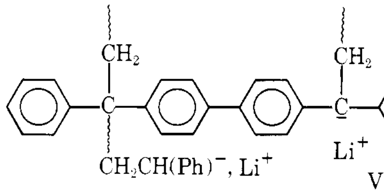
In experiment 1 the viscosity of living polymers was determined and thereafter the polymers were protonated by adding a drop of methanol from ampule D to their solution and then the viscosity of dead polymers was redetermined. The results are shown in Table VII. The expected decrease of viscosity confirmed the well-known dimeric nature of lithium polystyryl in benzene.[2]

For technical reasons dilute solutions of polymers of lower molecular weight had to be used in the following experiments and hence the approximate 3.4 exponential relation of viscosity on DP is not applicable to these systems. The results of experiment 2 demonstrate that the polymers terminated by monocarbanions produced by the addition of an excess of D–D are still dimeric. The viscosity of the solution of lithium polystyryl did not change on addition of an excess of D–D, but it again decreased after methanol addition.

In experiment 3 the same procedure was followed; however, only 0.5 equiv of D–D solution was slowly added to the polystyryl solution. The large increase of viscosity demonstrates that the resulting dianions become aggregated apparently forming a four-armed star-shaped unit, or perhaps even larger aggregates. Significantly, the viscosity of the solution returned to that of the original polystyryl solution after protonation. The dimeric living polystyryl was converted into polymer in which two chains are linked through a D–D bridge forming dianions which eventually became protonated. Experiments 4 and 5 show similar results obtained with DOD. All of these results confirm the dimeric nature of the polymers formed by the addition of an excess of D–D or DOD and the more extensive association of the dianions formed on addition of 0.5 equiv of D–D or DOD to lithium polystyryl.

Kinetics of Polymerization of Styrene Initiated by $II^{2-},2Li^+$ or $IV^{2-},2Li^+$

Addition of styrene to $II^{2-},2Li^+$ leads to polymerization of that monomer and the formation of $VII^{2-},2Li^+$. Since the initiation is slow while the propagation is relatively fast, the conversion of virtually all $II^{2-},2Li^+$ into $VII^{2-},2Li^+$ is not feasible, even when a large excess of styrene is used. The absorption spectrum recorded after completion of the polymerization arises from the absorbance of the unreacted $II^{2-},2Li^+$ and that of the formed $VII^{2-},2Li^+$. It appears that $VII^{2-},2Li^+$ does not absorb at λ >600 nm. This is evident from the determination of the ratios OD(λ after polymerization)/OD(λ before styrene addition). These ratios remain constant for λ >600 nm and therefore they provide a measure of the fraction of the unreacted $II^{2-},2Li^+$. Knowing the absorption spectrum of $II^{2-}2Li^+$ over the whole range of accessible wavelengths we can subtract now the contribution of unreacted $II^{2-},2Li^+$ from the absorption spectrum of the reacted mixture and thus obtain the absorption spectrum of $VII^{2-},2Li^+$ shown in Figure 10.



VII^{2-}, 2Li

Table VIII
Polymerization of Styrene Initiated by $II^{2-},2Li^{+}$

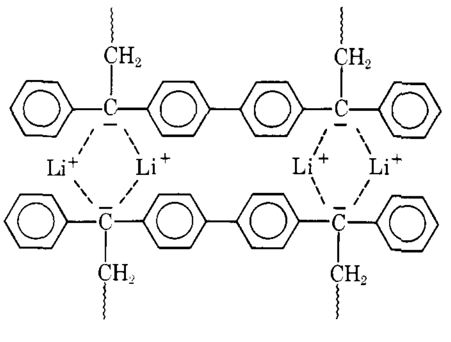
t, s	(OD 598)	(OD 291)	$10^4\Delta(OD\ 598)/\Delta t$	10^4k_{it}	$10^4\Delta(OD\ 291)/\Delta t$	k_{pt}
			Run 1			
0	4.06	0.80				
600	3.89	0.69	2.83	3.52	1.83	1.31
1200	3.73	0.58	2.67	4.06	1.83	0.79
2220	3.55	0.46	1.76	3.40	1.18	0.40
3780	3.36	0.33	1.22	3.41	0.83	0.28
			Run 2			
0	3.21	1.88				
840	2.84	1.57	4.40	3.10	3.69	0.52
1680	2.62	1.28	2.62	2.49	3.45	0.37
2640	2.45	1.02	1.77	2.23	2.71	0.31
3600	2.34	0.80	1.15	1.94	2.29	0.26
4860	2.25	0.56	0.71	1.66	1.90	0.26
			Run 3			
0	1.24	2.90				
300	1.17	2.73	2.33	2.52	5.67	2.58
900	1.04	2.43	2.17	2.78	5.00	0.87
1500	0.93	2.09	1.83	3.04	5.67	0.73
2100	0.85	1.78	1.33	2.81	4.33	0.51
2700	0.77	1.44	1.33	3.74	5.67	0.68
3300	0.71	1.14	1.00	3.82	5.00	0.65
			Run 4			
0	0.293	1.85				
660	0.272	1.77	0.318	2.26	1.21	2.84
1320	0.250	1.68	0.333	2.69	1.36	1.64
2220	0.224	1.58	0.289	2.74	1.11	0.94
3120	0.203	1.49	0.233	2.62	1.00	0.65
4020	0.184	1.40	0.211	2.74	1.00	0.57
6000	0.156	1.23	0.141	2.29	0.86	0.43
10920	0.100	0.86	0.114	2.77	0.75	0.34
			Run 5			
0	4.05	0.90				
600	3.96	0.79	1.50	1.63	1.83	2.17
1200	3.87	0.69	1.50	1.89	1.67	1.12
2460	3.70	0.55	1.35	2.10	1.11	0.46
3300	3.60	0.49	1.19	2.56	0.71	0.27
4200	3.49	0.42	1.22	2.80	0.77	0.28
5100	3.40	0.37	1.00	2.72	0.56	0.20
			Av[a]	$(3.01 \pm 0.54) \times 10^{-4}\ M^{-1}\ s^{-1}$		

[a] Only Runs 1, 3, and 4 were used to calculate the average value of k_i. Runs 2 and 5 were rejected because the results showed a trend of k_{it} with conversibn.

The spectrum of $VII^{2-},2Li^{+}$ resembles that of I^{-},Li^{+} shown in Figure 1. Its λ_{max} is slightly shifted to shorter wavelength when compared with that of I^{-},Li^{+}, namely it appears at 490 nm instead of 522 nm. The molar absorbance of $VII^{2-},2Li^{+}$ seems to be lower than that of I^{-},Li^{+}, namely 1.3×10^4 compared to 2.2×10^4. These observations suggest that the addition of styrene takes place mainly on one of the ends of $II^{2-},2Li^{+}$, the subsequent addition to the other end being much slower. The lack of addition to the other end was checked by comparing the increase of OD at 334 nm (measuring the total concentration of lithium polystyryl formed in the reaction) with the decrease of OD at 598 nm monitoring the consumption of $II^{2-},2Li^{+}$. Using the appropriate molar absorbances we found a 1:1 stoichiometry. However, the large difference in the respective ϵ's introduces about 20% of uncertainties in this finding.

The data collected in Table VIII allow us to determine the concentrations of the unreacted $II^{2-},2Li^{+}$ and of the monomer at each time interval t to $t + \Delta t$. The rates of initiation, r_{it}, are calculated from the data listed in the fourth column of Table VIII and these lead to the formal bimolecular rate constants of initiation, $k_{it} = r_{it}/[II^{2-},2Li^{+}]_t[\text{styrene}]_t$. Their values, listed in the fifth column of Table VIII, seem to be approximately constant and independent of $[II^{2-},2Li^{+}]$ (compare the results of runs 1 and 4). There are trends observed in runs 2 and 5, namely k_{it} decreases with time in the former and increases in the latter, but the considerable experimental difficulties perhaps distorted the results and rendered them unreliable.

The apparent constancy of k_{it} might be accounted for by the following mechanism. It was shown in the previous section that $II^{2-},2Li^{+}$ is aggregated and presumably present in dimeric ring form,



(closed dimer)

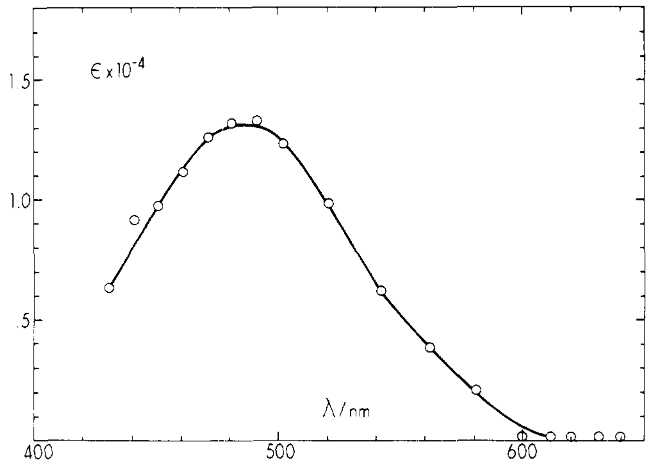
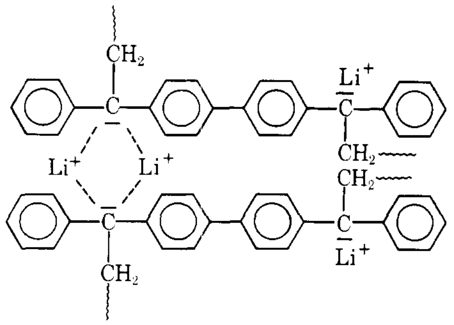


Figure 10. Absorption spectrum of VII^{2-},2Li$^+$.

This supposedly unreactive species may exist in equilibrium with its reactive open form that initiates the polymerization.



The fraction of such an open form should be constant and independent of the total concentration of II^{2-},2Li$^+$ and thus the proposed mechanism would account for the reported findings.

Similar calculations based on the rates of propagation r_{pt} calculated from the data listed in all but the last column of Table VIII leads to formal bimolecular rate constants of propagation, $k_{pt} = r_{pt}/[\sim\!\sim S^-,Li_{total}^+]_t[\text{styrene}]_t$, listed in the last column of Table VIII. Their values show definite trends, decreasing with time by large factors. We account for these results by recalling that only the free, nonassociated $\sim\!\sim S^-,Li^+$ propagate the polymerization, and as more chains are formed the fraction of the free chains decreases. Moreover, as the reaction progresses the intramolecular looser mixed dimerization is probably gradually replaced by a tighter intermolecular homoassociation.

Discussion and Recapitulation

The results reported here conclusively demonstrate that the additions of D–D, DOD, and B to lithium polystyryl in benzene proceed only with the monomeric form of $\sim\!\sim S^-,Li^+$. Moreover, the concentration of the reactive monomeric $\sim\!\sim S^-,Li^+$ is governed by three equilibria, viz.,

$$2\sim\!\sim S^-,Li^+ \rightleftarrows (\sim\!\sim S^-,Li^+)_2 \qquad \tfrac{1}{2}K_1 \qquad (1)$$

$$\sim\!\sim S^-,Li^+ + \text{adduct} \rightleftarrows (\sim\!\sim S^-,Li^+)(\text{adduct}) \qquad K_{1,2} \qquad (1,2)$$

$$2\ \text{adduct} \rightleftarrows (\text{adduct})_2 \qquad \tfrac{1}{2}K_2 \qquad (2)$$

maintained during the studied reactions. "Adduct" denotes here (I$^-$,Li$^+$), (III$^-$,Li$^+$), or (V$^-$,Li$^+$). In the D–D and B systems $K_1K_2 < K_{1,2}^2$ whereas the equality $K_1K_2 = K_{1,2}^2$ holds for the DOD system.

The three equilibria are important in determining the kinetics of addition when the substrate, D-D, DOD, or B, is in large excess relative to lithium polystyryl. Under these conditions the observed kinetics shows a kind of a memory effect. This means that the momentary rate of formation of the adduct between the substrate and lithium polystyryl measured at any time t is determined not only by the concentrations of substrate and living polystyryl present at that time but also it depends on the *initial* concentration of the polystyryl at the onset of the addition. Thus the rates of addition may be different in two runs although the concentrations of the nominal reagents, lithium polystyryl and D–D, DOD, or B, are the same at the times of the respective measurements, provided that the *initial* concentrations of living polystyrene were different at the onset of the respective runs.

This memory effect, fully accounted for by the proposed mechanism, is not exhibited in experiments performed with large excess of living polystyryl. This is obvious because under those conditions the kinetics of the addition is virtually governed only by equilibrium 1.

In the systems D–D and B the addition to the first C=C bond is much faster (allowing for the statistical factor of 2) than the addition to the second one. The conjugation spreads the negative charge into the other C=C bond and diminishes its reactivity. In the DOD system the conjugation is virtually eliminated and hence both bonds, in DOD and (III$^-$,Li$^+$), are equally reactive. The lack of conjugation in DOD is evident on comparing the spectra of (III$^-$,Li$^+$) and (IV^{2-},2Li$^+$). The small bathochromic shift observed in (IV^{2-},2Li$^+$) relative to (III$^-$,Li$^+$) is probably due to chromophore–chromophore splitting.

Introduction of the second negative center in D–D is dramatically manifested by the spectral changes as (I$^-$,Li$^+$) is converted into (II^{2-},2Li$^+$). The very large increase of the molar absorbance is the most significant. We expected to observe a similar spectral behavior in the B system, as (V$^-$,Li$^+$) becomes converted into (VI^{2-},2Li$^+$), and we are surprised to find the spectra of the adducts (V$^-$,Li$^+$) and (VI^{2-},2Li$^+$) to be alike. No explanation for this observation can be offered at this time. In spite of this, the kinetic behaviors of the D–D and B system are similar, as has been expected.

The dimerization of the lithium monoanions obtained from living polystyrene by the addition of an excess of D–D or DOD is verified also by the viscosity studies described in this paper. This technique reveals also the higher degree of aggregation in the systems involving dianions. Moreover, the kinetics of styrene polymerization initiated by the lithium dianions implies that they form cyclic aggregates which are in equilibrium with an open form. The latter are responsible for the initiation of polymerization.

In conclusion, the first two authors wish to thank the National Science Foundation for their generous support of this investigation and the Dow Chemical Co. for an unrestricted grant.

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(6) (a) A. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.*, **38**, 205 (1959); (b) *ibid.*, **40**, 73 (1959).
(7) It is tacitly assumed that the absorption spectrum of (I$^-$,Li$^+$) is not affected by its association with (–S$^-$,Li$^+$) or another (I$^-$,Li$^+$).
(8) A factor 2.3 was omitted in the k_u values listed in Table I of ref 3. The k_u value was rechecked in this work and found to be $(1.8 \pm 0.1) \times 10^{-2}\ M^{-1/2}\ s^{-1/2}$ in agreement with the corrected value reported in ref 3.