variable transmission upon shear and, therefore, are thermotropic. Using wide angle X-ray diffraction, optical microscopy, and a variety of other techniques, one can demonstrate that, upon cooling, the bulk of the polymer retains its nematic texture and morphology.[1] Consequently, the rheological and mechanical behavior of the material as well as its structure resembles more closely that of a glass than that of a semicrystalline polymer.

Upon annealing below the glass transition temperature, highly oriented AQ polymer fibers relax toward their equilibrium structure in much the same way as conventional unoriented glasses. Although no changes in density have been found to accompany enthalpic relaxation, fibers have a lower (20%) strain-to-fall after annealing as well as a more linear stress–strain curve.

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Kinetics of 1,1-Diphenylethylene Addition to Lithium Polyhexa-1,4-dienyl in Benzene

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Addition of 1,1-diphenylethylene (D) to lithium polystyryl ($\sim S^-,Li^+$) in benzene was studied in the past[1] and similar reactions of this kind were investigated later.[2] The following mechanism accounts for the findings. The addition involves the monomeric, nonassociated form of the polystyryl, viz.,

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

However, the monomeric salt of polystyryl and that of the $\sim SD^-$ anions are in equilibrium with the respective homo and mixed dimers, i.e.,

$$2\sim S^-,Li^+ \rightleftarrows (\sim S^-,Li^+)_2 \qquad {}^1/_2K_1$$

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

$$2\sim SD^-,Li^+ \rightleftarrows (\sim SD^-,Li^+)_2 \qquad {}^1/_2K_2$$

Concentrations of the monomeric species are assumed to be much smaller than those of the dimeric ones, and the absorbance of the latter, per unit of the pertinent anion, seems to be unaffected by the mode of dimerization, i.e., whether homo or mixed type.

Progress of the addition was followed spectrophotometrically by monitoring the absorbance at λ_{max} of either of the respective anions. The proposed mechanism predicts the conversion to be first order, provided that D is in large excess and $K_{12} = (K_1K_2)^{1/2}$, i.e.,

$$d \ln [\sim S^-,Li^+]/dt = k[D]/K_1^{1/2}[\sim S^-,Li^+]_0^{1/2}$$

The first-order plot becomes curved when $K_{12} \neq (K_1K_2)^{1/2}$, but the initial slope is still inversely proportional to $[\sim S^-,Li^+]_0^{1/2}$.

Table I

$[\sim\sim H^-,Li^+]_0 \times 10^4$,[a] M	$[D] \times 10^4$,[b] M	$k_i \times 10^4$,[c] s^{-1}	$(k_i/[D])$, $M^{-1}\ s^{-1}$
1.0	74	80	1.09
1.1	217	208	0.96
2.0	64	58	0.91
3.6	54	35	0.65
3.6	327	235	0.72
7.2	104	55	0.53
8.5	246	93	0.38
10.1	78	33	0.42
13.1	186	61	0.33

[a] $[\sim\sim H^-,Li^+]_0 = [\sim\sim D^-,Li^+]_\infty$; $\epsilon_{435}(\sim\sim D^-,Li^+) = 2.2 \times 10^4$. [b] [D] determined by gas chromatography. [c] $k_i = 2.3$ (initial slope of the plot of log $(OD_\infty - OD_t)_{435}$ vs. time).

Our approach has been applied lately by the Akron team to the system lithium polyhexadienyl in benzene.[3] The reported results intrigued us and it was decided to re-investigate this problem. Our findings, however, diverge from those reported by the other group.

Experimental Section

2,4-Hexadiene (mixture of isomers, Aldrich) was distilled twice from calcium hydride, and 1,1-diphenylethylene was freed from traces of benzophenone by vacuum distillation of the compound kept for a few hours over sodium mirror. The distilled olefins were sealed in ampules and never exposed to the air.

Lithium polystyryl was prepared in benzene using *sec*-butyl lithium as the initiator. Its molar absorbance at $\lambda_{max} = 335$ nm is 1.3×10^4, while that of $\sim SD^-,Li^+$ at $\lambda_{max} = 435$ nm is 2.2×10^4. The molar absorbance of polyhexadienyl salt is $\sim 1.0 \times 10^4$ at 290 nm, based on the ϵ_{435} of $\sim SD^-,Li^+$.

The lithium polystyryl capped by 2,4-hexadiene was prepared by adding about 100-fold excess of the diene (in respect to the concentration of living polystyryl) to the solution of lithium polystyryl in benzene and observing the decay of the original absorbance. It disappears in a few hours and thereafter the reagents were kept for about 24 h before being used in the kinetic or viscometric studies.

All the operations and kinetic studies were carried out in evacuated all-glass equipment with an attached quartz cell that allowed us to determine the initial concentrations of the reagents and to follow the progress of the reaction spectrophotometrically. The viscosity measurements were carried out following the procedures reported by Yamagishi and Szwarc.[2]

Purification of Diphenyl Ether. The degassed phenyl ether (Aldrich Chemical Company) was stirred and vacuum pumped over potassium mirror for about 24 h. The color of the solvent turned greenish-brown. Next diphenyl ether was slowly distilled under high vacuum pumping at ~70 °C into evacuated vials with break seals.

Results

For each run the plots of log $(OD_\infty - OD_t)_{435}$ vs. time are curved as exemplified by Figure 1. The values of $k_i = 2.3$(initial slope) are listed in Table I. The nonlinearity of the plots implies the inequality $K_{12} \neq (K_1K_2)^{1/2}$. The ratios of the initial slope to the respective, extrapolated slope at infinity are substantially greater than unity, implying a high tendency for formation of the mixed dimers.

All the kinetic results are summarized in Table I, and the plot of the log of normalized pseudo-first-order constants determined at the onset of the reaction, i.e., $(k_i/[D])$, vs. the log of $[\sim H^-,Li^+]$ is shown in Figure 2. The slope

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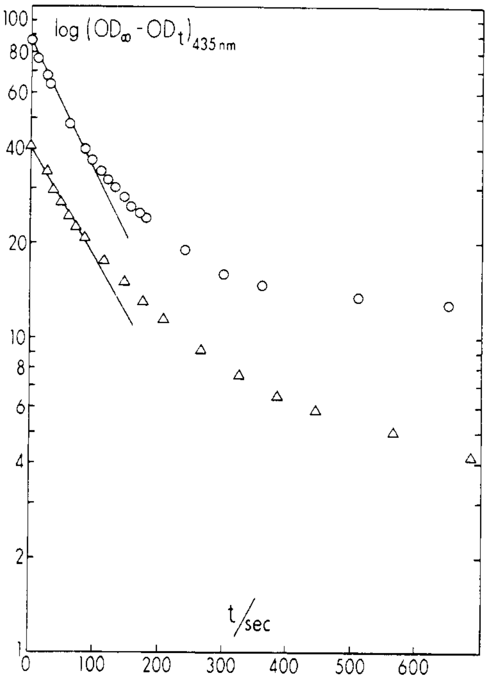

Figure 1. Plot of log $(\mathrm{OD}_\infty - \mathrm{OD}_t)_{435}$ vs. time.

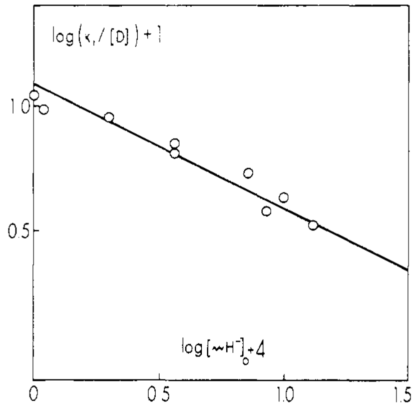

Figure 2. Plot of log $(k_i/[\mathrm{D}])$ vs. log $[\sim\sim\mathrm{H}^-,\mathrm{Li}^+]_0$; slope 0.43.

is 0.43, slightly less than 0.5. Accepting the previously proposed mechanism we conclude that for this system

$$k/K_1^{1/2} = (1.2 \pm 0.1) \times 10^{-2}\ (\mathrm{M}^{1/2}\ \mathrm{s})^{-1}$$

i.e., it is slightly smaller than $(2.1 \pm 0.1) \times 10^{-2}\ (\mathrm{M}^{1/2}\ \mathrm{s})^{-1}$ reported[1,2] for the similar addition of D to $\sim\sim\mathrm{S}^-,\mathrm{Li}^+$.

The viscosity data are collected in Table II. Apparently the $\sim\sim\mathrm{H}^-,\mathrm{Li}^+$ pairs dimerize in benzene. The small decrease in N is attributed to some destruction of the anions by 2,4-hexadiene which probably acts as a weak proton donor.

Table II[a]

end group	time of flow/s	N with exp 3.3	N with exp 3.4	N with exp 3.5
	First Series			
-S⁻,Li⁺	2387			
	2341			
	av. 2364	2.02	1.97	1.94
-H⁻,Li⁺	1875			
	1975			
	1848			
	av. 1899	1.89	1.85	1.82
-D⁻,Li⁺	1892			
	1817			
	av. 1854	1.87	1.84	1.81
dead	235			
	236			
	232			
	av. 234[d]	1.00	1.00	1.00
	Second Series			
-S⁻,Li⁺	1247			
	1200			
	1225			
	av. 1224	2.02	1.98	1.94
-H⁻,Li⁺	1007			
	1042			
	av. 1025	1.92	1.88	1.85
-D⁻,Li⁺	946			
	900			
	958			
	av. 935	1.87	1.83	1.80
dead	121			
	118			
	119			
	av. 119.3[d]	1.00	1.00	1.00

[a] Solvent, benzene; $T = 24$ °C. [b] First series: $[\text{-S}^-,\mathrm{Li}^+] = 1.2 \times 10^{-3}$ M; $[\mathrm{S}]_0 = 4.5$ M. [c] Second series: $[\text{-S}^-,\mathrm{Li}^+] = 1.5 \times 10^{-3}$ M; $[\mathrm{S}]_0 = 3.4$ M. [d] Assumed.

Table III
Effect of Diphenyl Ether on the Degree of Association of Lithium Polystyryl in Benzene at 24 °C[a]

T1[b]	T2[c]	T3[d]	N before	N after
	exp 1			
1563	1390	161		
1609	1385	160		
1585	1342	160		
av. 1585	av. 1372	av. 160	1.96	1.88
	exp 2			
2252	2018	212		
2270	2048	210		
2222	2046	212		
av. 2248	av. 2037	av. 212	2.0	1.95

[a] $10^3[\sim\sim\mathrm{S}^-,\mathrm{Li}^+]/\mathrm{M} = 0.87$; $[\mathrm{S}]/\mathrm{M} = 3.5$; $[\mathrm{PhOPh}]/\mathrm{M} = 0.15$; after addition of PhOPh $[\sim\sim\mathrm{S}^-,\mathrm{Li}^+] = 0.82.10^{-3}$ M. [b] Time of flow(s) before addition of PhOPh. [c] Time of flow(s) after addition of PhOPh. [d] Time of flow(s) of dead polymer.

Comparison of Our Findings with the Results Reported in Reference 3. Our values of $k_i/[\mathrm{D}]$ agree fairly well with those reported in ref 3, within the 10^{-4}–10^{-3} M range of $[\sim\sim\mathrm{H}^-,\mathrm{Li}^+]$.[4] However, our slope of the line log $(k_i/[\mathrm{D}])$ vs. log $[\sim\sim\mathrm{H}^-,\mathrm{Li}^+]$ is substantially lower than that claimed in ref 3, vis., ~0.5 compared to ~1.0. The slope of ~1.0 reported in ref 3 implies a constant rate of reaction, *independent* of the concentration of lithium polyhexadienyl. Such a result could be rationalized for a high degree of aggregation of $\sim\sim\mathrm{H}^-,\mathrm{Li}^+$ whereas the degree of association claimed by the authors is lower than 2, namely, ~1.6. Strangely enough, the degree of association determined in the past for the same salt in the same laboratory was reported to be 1.3–1.45, with no explanation being offered for these conflicting results. The low degrees of association are even more puzzling in view of the explicit statement by the authors: "Through the use of this procedure (measurement of viscosity) the vinyl biphenyl-, 2,3-dimethyl-1,3-butadienyl-, 1,3-pentadienyl-, 2-, 3-, 4-methyl-1,3-pentadienyl- and 2,4-dimethyl-1,3-pentadienyllithium species have been shown to be dimerically associated". Surely these observations make it improbable to involve electron delocalization or steric hindrance as the reasons for the claimed low degree of association of the 2,4-hexadienyllithium species.

In conclusion, the system $\sim\sim\mathrm{H}^-,\mathrm{Li}^+ + \mathrm{D}$ in benzene seems to behave like those previously studied in our laboratory.

Acknowledgment. The generous financial support of this investigation by the National Science Foundation is gratefully acknowledged.

Appendix

The following remark was made by the Akron group: "The fallacy involved in uncritically relating reaction orders to association states can be seen in the following. Yamagishi et al.[5] examined the reaction between polystyryl lithium and 1,1-diphenylethylene in benzene in the presence of about 0.15 M diphenyl ether. . . . based solely on kinetic results they concluded that the presence of the ether failed to influence the association state of these polymers. . . . . Our measurements (determination of viscosity, our addition) on poly(styryllithium) and the 1,1-diphenylethylene capped poly(styryllithium) show that their average degree of association is considerably less than 2 in the presence of diphenyl ether, i.e., 25–60% of the chains can be present in the unassociated state under the conditions used by Yamagishi et al."

We checked this claim. Our results, shown in Table III, prove that the degree of association of lithium polystyryl in benzene is unaffected by the presence of diphenyl ether (0.15 M). This conclusion was confirmed by the independent study of Professor M. Van Beylen (The University, Leuven, Belgium), viz., flow time of benzene solution of polystyryl, concentration 5×10^{-3} M, dp 320: before diphenyl ether addition 628 s (average of six experiments); immediately after the addition (0.15 M) 624 s (average of four experiments). Two points need stressing. (1) Purified, and not commercial, ether has to be used, otherwise some carbanions are destroyed. (2) Prolong action of the ether gradually destroys the carbanions as revealed by the decrease of optical absorption at 334 nm.

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Carbon-13 NMR Spin-Lattice Relaxation Times of Inverted Monomeric Units in Polypropylene

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^{13}C NMR spectroscopy has proved quite useful in determinations on both the stereochemical structure[3] and the chain dynamics[4,5] of polypropylene. Recently, we have demonstrated that ^{13}C NMR is sensitive to a specific sequence structure of propylene units resulting from propylene inversion along the chain of polypropylene.[6-8] The chemical shift assignment for ^{13}C resonances arising from head-to-head propylene units [$-CH_2-CH(CH_3)-CH(CH_3)-CH_2-$] and tail-to-tail propylene units [$-CH(CH_3)-CH_2-CH_2-CH(CH_3)-$] was made by using the Lindeman and Adams relationship.[9] More recently, the effect of stereosequence on the chemical shift of methyl-carbon resonances in the head-to-head propylene units was examined from the ^{13}C NMR analysis of model compounds of polypropylene and 30% enriched poly([3-^{13}C]-propylene) by Zambelli et al.[10,11]

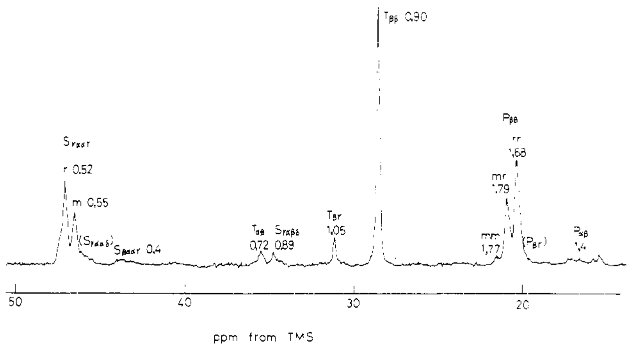
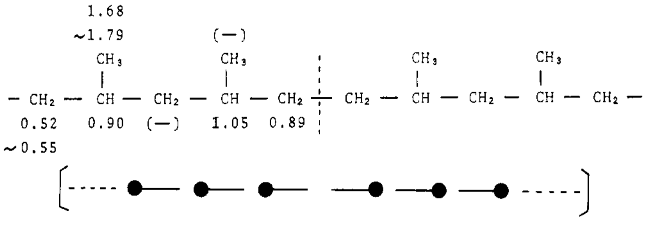


Figure 1. ^{13}C NMR spectrum of polypropylene at 123 °C in 100% w/v *o*-dichlorobenzene. The number of transients accumulated was 128.

Tail-to-Tail Sequence



Head-to-Head Sequence

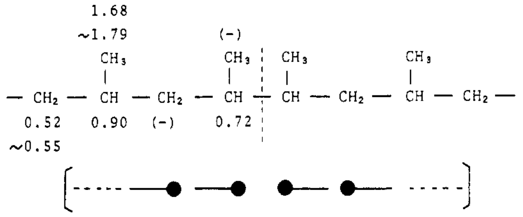


Figure 2. T_1 map of the polypropylene containing tail-to-tail and head-to-head units in 100% w/v *o*-dichlorobenzene at 123 °C (in seconds).

In the present study, the ^{13}C NMR spin–lattice relaxation times (T_1's) for specific carbon species of a polypropylene containing head-to-head and tail-to-tail units have been determined to confirm the previous chemical shift assignment and to obtain information on the main-chain motion near the reversal points in the polypropylene chain.

Figure 1 shows a ^{13}C NMR spectrum of the predominantly syndiotactic polypropylene ([*rr*] = 0.55, [*mr*] = 0.38, and [*mm*] = 0.07), together with the T_1 value in seconds for each peak.[12] For convenience, the T_1 map of polypropylene is given in Figure 2, based on the chemical shift assignments[6] as shown in Figure 1.

The methylene carbon in tail-to-tail units has a T_1 which is 62–71% longer than the methylene carbon T_1 in head-to-tail units. Similarly, the methine carbon T_1 in tail-to-tail units is 17% longer than the methine carbon T_1 in head-to-tail units. In contrast, the methine carbon T_1 in head-to-head units is 20% shorter than the methine carbon T_1 in head-to-tail units. Thus the tail-to-tail units are more mobile (longer NT_1) while the head-to-head units are less

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