at least 8% heterotactic and isotactic triads, structures which could account for another few per cent hydrolysis required to produce 85% conversion with this model. Besides explaining the observed maximum extent of hydrolysis, this model also predicts triad fractions very nearly equal to those of a purely random process for all degrees of hydrolysis, which is in agreement with the nmr data.[12,13]

The hydrolysis models presented above for the isotactic and syndiotactic polymers are consistent with the relative rates of hydrolysis. If the two polymers are assumed to react at a similar rate at 0% hydrolysis, where both reactions are assumed to be random, the faster reaction of the isotactic polymer can be attributed to the activation of a neighboring ester by each hydrolyzed group.

Kinetic Studies of Anionic Polymerization of Polystyryl Salts in Tetrahydropyran and 2-Methyltetrahydrofuran

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ABSTRACT: Kinetics of homopropagation of the living polystyryl salts were investigated in tetrahydropyran (THP) and 2-methyltetrahydrofuran (MeTHF). Conductance studies of the lithium and sodium polystyryls in THP showed that their dissociation constants, K_d, increase from about 2×10^{-10} M at 25° to about 5×10^{-10} and 12×10^{-10} M, respectively, at $-40°$. The relevant propagation constants, k_{obsd}, were determined in THP over a wide concentration range of living polymers, [LE], at 25, 0, -20, and $-40°$ and from the plots k_{obsd} *vs.* $1/[LE]^{1/2}$ the respective values $k_-K_d^{1/2}$ were calculated; k_- denotes the propagation constant of the free $\sim\!\sim S^-$ ions. By combining these kinetic data with the conductance findings the values of k_- were determined over the investigated temperature range. The linear Arrhenius plot led to $E_- = 4.8$ kcal/mol, $A_- = 2 \times 10^8$ M^{-1} sec^{-1}, and $k_- = 60000$ M^{-1} sec^{-1} at 25°, the values obtained from the studies of the lithium salt being consistent with those derived from the investigation of the sodium salt. It appears, therefore, that the reactivity of the free $\sim\!\sim S^-$ ions is virtually the same in DME, THF, THP, and THF–dioxane or THF–benzene mixtures. The reactivity of the $\sim\!\sim S^-,Li^+$ and $\sim\!\sim S^-,Na^+$ ion pairs in THP is discussed and our results are compared with those obtained by other investigators. The reactivities of the Li^+, Na^+, K^+, and Cs^+ salts of $\sim\!\sim S^-$ in MeTHF were studied at 25° only. Some undesirable properties of MeTHF are discussed.

Reactions involving ionic species are usually greatly affected by the nature of the solvent. For example, a change from dioxane to dimethoxyethane increases the rate of propagation of polystyrylsodium by a factor of 1000.[1,2] Moreover, the change of solvent may reverse the reactivity order for the polystyryl salts. While in dioxane the propagation rate constant of the polystyryl ion pair increases with the size of the alkali counterion,[1] in tetrahydrofuran[3] and in dimethoxyethane[2] the cesium ion pairs are much less reactive than the lithium and sodium ion pairs.

The understanding of these effects calls for systematic studies of the properties of ethereal solvents, their ability to dissociate ion pairs and to solvate ionic species. Much information on this problem may be obtained from the kinetic studies of anionic polymerization.

Kinetics of homopolymerization of polystyryl salts in dioxane,[1] tetrahydrofuran,[3,4] and dimethoxyethane[2] have been reported recently, and the physical properties of these solvents are described in ref 5. Here we report our findings concerned with anionic propagation of living polystyrenes possessing Li^+, Na^+, K^+, and Cs^+ counterions in methyltetrahydrofuran and tetrahydropyran.

Experimental Section

Commercial 2-MeTHF or THP (Aldrich Chemicals) was refluxed overnight on Na-K alloy, then fractionated and the middle fraction was distilled into the flask containing Na-K alloy and small amounts of benzophenone. The solvent, whenever needed, was redistilled under high vacuum into the required containers.

The one-ended $\sim\!\sim S^-,Li^+$ was prepared at 0° by adding a styrene solution in MeTHF or THP to the commercial ethyllithium (Foot Co.) freshly purified by repeated crystallization from benzene. The reaction was over in about 0.5 hr and thereafter the aliquots were stored at $-78°$ to avoid any decomposition. All the subsequent manipulations were rapidly performed at low temperatures, and eventually the required solution was brought up to the desired temperature just prior to the kinetic run. The runs lasted a few minutes for [LE] $\sim 10^{-3}$ M, and at higher dilution, [LE] $\sim 10^{-5}$ M, the conversion exceeded 90% in 1 hr.

Two types of sodium salts of living polystyrene were investigated. The one-ended $\sim\!\sim S^-,Na^+$ was prepared in

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(1) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).

(2) T. Shimomura, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 5743 (1967).

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

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

(5) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *ibid.*, **87**, 5548 (1965).

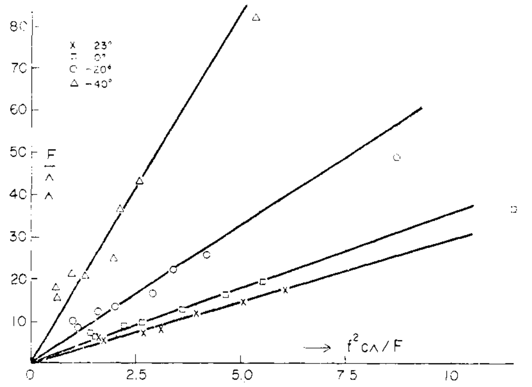

Figure 1. Fuoss plots of conductivity of $\sim S^-,Li^+$ in THP at various temperatures: ×, 23°; □, 0°; ○, 20°; △, −40°.

THF using benzylsodium for the initiation as described in ref 4. The THF was then distilled off under vacuum and replaced by MeTHF or THP, the newly added solvent was in turn evaporated, and finally the polymer was redissolved in a fresh portion of the desired ether. The two living-ended polystyrylsodium (DP ~20–25) was prepared in the conventional way[3] in THF and then the solvent replaced by MeTHF. The solution of the two-ended polystyrylsodium in THP was prepared directly in this solvent by adding at 0° a styrene–THP solution to the sodium α-methylstyrene tetramer dissolved in THP.

The lithium and sodium salts are unstable in MeTHF, the two-ended sodium polymer being slightly more stable than the one ended. About 20% of the living polymers decomposed in the first 30 min. Therefore, the prepared solutions had to be used immediately and the necessary corrections accounting for the destruction were introduced in the calculations as described in ref 3.

The potassium and cesium salts of living polystyrene were investigated only in MeTHF; the one living-ended salts were used in these studies. The salts were prepared by adding the monomer to the appropriate cumyl salt in THF. These polymers are also unstable in MeTHF and, therefore, they were kept in THF until needed. Just prior to the kinetic runs THF was replaced by MeTHF. Only the lithium and sodium polystyryls were investigated in THP. Their stability in this solvent was satisfactory.

The kinetics of propagation were investigated by following the disappearance of the monomeric styrene as monitored by the optical density at 291.4 mμ. The concentration of active ends was determined spectrophotometrically (λ_{max} 340 mμ in MeTHF but 337 mμ in THP), using the extinction coefficients reported in Table I of ref 3. Low-temperature runs in THP were performed using a quartz dewar provided with optical windows and filled with precooled methanol. The temperature could be kept constant with ±0.5° by adjusting the flow of air cooled by liquid air and carried through a coil fitted inside the optical dewar. The temperature was recorded with a thermocouple placed approximately 0.5 cm from the reaction cell. Further details of the experimental procedures are described in ref 3 and 4.

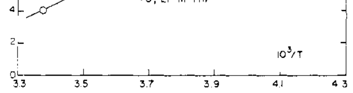

Figure 2. Log K_d as a function of $1/T$ for polystyryllithium in THP.

Table I
Conductance of Polystyryllithium in Tetrahydropyran

T, °C	Λ_0[a]	Slope × 10^{-6}	$K_d \times 10^{10}$ M
23	37.1	2.92	2.57
10	29.1	3.26	3.63
0	25.1	3.60	4.41
−10	20.8	4.49	5.15
−20	16.9	6.50	5.40
−30	13.6	9.87	5.47
−40	10.7	16.5	5.26

[a] Λ_0's calculated by applying the Walden rule on the Λ_0 values reported in THF (ref 4 and D. Nicholls, C. Sutphen, and M. Szwarc, *J. Phys. Chem.*, **72**, 1021 (1968).

Conductivity measurements for $\sim S^-,Li^+$ and $\sim S^-,Na^+$ in THP were carried out over a temperature range of −40 to 25°. The apparatus for measuring conductance of living polymers has been described elsewhere.[3,4] The instability of polystyryl salts in MeTHF prevented us from determining their conductance in this solvent.

Results

Conductance Studies. Two sets of measurements with two different samples were carried out on polystyryllithium dissolved in THP. A series of resistance *vs.* temperature plots were obtained at various living end concentrations in the range of 10^{-3} to 10^{-6} M. The data were combined for the calculation of the Fuoss plots shown in Figure 1. At low temperatures the high resistance of the cell reduced the accuracy of the relevant experimental data. K_d was calculated in the usual way, the required Λ_0 values were obtained by the Walden rule from those found in THF.[4] The redetermined[6] values of $\lambda_0(Li^+)$ were used in these calculations. The final results are listed in Table I and presented graphically in Figure 2. The dissociation constant increases as the temperature decreases from 25 to −20°, and thereafter its value appears to remain constant. However, the low-temperature data are less accurate and should be considered as tentative.

The conductance of two-ended polystyrylsodium in THP was also determined for the concentration range of 10^{-3}–10^{-5} M, and the Fuoss plots were calculated assuming $\Lambda_0(\sim S^-,Li^+)_{THP} = \Lambda_0(\sim S^-,Na^+)_{THP}$. This assumption is justified by the observation[6] that in THF and MeTHF $\Lambda_0^+(Li^+) = \Lambda_0^+(Na^+)$. The results obtained at ambient temperatures are shown in Figure 3. All the Fuoss lines show pronounced curvatures; the plots begin to deviate from linearity at concentrations as low as 10^{-5} M. Curvature of this type is not unexpected in solvents with low dielectric constants and has been observed in other systems.

The high curvature of the Fuoss plots for the two-ended $\sim S^-,Na^+$ in THP prompted us to investigate the conductance of $\sim S^-,Na^+$ endowed with one growing end only. This study was performed at 20° and the results are included in Figure 3. At low concentrations the conductance of both polymers is virtually identical, although divergence is observed at higher concentrations.

The dissociation constants, K_d, were calculated on the basis of initial tangents to Fuoss curves accepting the previously discussed values of Λ_0. The results

TABLE II
DISSOCIATION OF SODIUM SALT OF LIVING POLYSTYRENE (TWO-ENDED) IN THP

T, °C	[LE] × 10^5 M	Λ_0	Λ	$K_d \times 10^{10}$ M, conductance
25	1.08	38.5	0.168	2.05
15	1.09	32.4	0.162	2.73
5	1.10	26.9	0.154	3.60
−5	1.11	22.1	0.144	4.72
−15	1.12	17.9	0.132	6.08
−25	1.14	14.2	0.118	7.88
−35	1.15	11.0	0.103	10.1
−45	1.16	8.4	0.089	13.0

TABLE III
ANIONIC POLYMERIZATION OF POLYSTYRYLLITHIUM AND POLYSTYRYL SODIUM IN TETRAHYDROPYRAN $[S]_0 \approx 10^{-2}$–10^{-3} M

[LE] × 10^4 M	k_{obsd}, M^{-1} sec^{-1}	[LE] × 10^4 M	k_{obsd}, M^{-1} sec^{-1}	[LE] × 10^4 M	k_{obsd}, M^{-1} sec^{-1}
S^-,Li^+ (A),[a] $T = 23^\circ$		S^-,Li^+ (A),[a] $T = -20^\circ$		S^-,Na^+, $T = 0^\circ$	
6.58	45.1	8.54	13.0	7.93	23.5
6.41	36.6	2.23	23.2	6.99	20.8
6.41	38.9	1.28	36.1	3.59	35.4
4.75	41.0	1.17	34.7	1.15	58.3
4.25	44.3	0.91	38.4	S^-,Na^-, $T = -20^\circ$	
2.60	49.9	0.81	45.9	11.1	14.7
2.33	59.7	0.64	60.8	7.71	18.2
2.04	62.1	0.57	59.3	5.96	15.5
1.69	62.9	S^-,Li^+ (A),[a] $T = -40^\circ$		3.59	22.6
1.57	72.0	10.0	5.06	2.74	27.6
1.41	85.3	8.58	7.04	1.51	40.4
1.02	102.0	8.12	6.18	1.39	34.6
0.92	104.0	4.08	8.10	0.87	53.4
0.65	125	2.61	7.41	0.78	57.3
0.53	143.0	1.78	12.4	S^-,Na^+, $T = -40^\circ$	
S^-,Li^+ (B),[a] $T = 23^\circ$		1.64	14.8	8.78	10.2
9.55	35.4	1.48	10.1	7.76	10.3
5.96	46.4	0.93	16.1	5.35	12.7
2.20	77.5	0.56	20.5	2.53	17.6
1.68	91.9	S^-,Na^+, $T = 23^\circ$		1.32	23.5
1.16	85.3	21.3	24.4	0.87	30.1
0.93	117.0	10.4	29.3	0.65	37.2
0.53	173.0	7.84	33.3		
S^-,Li^+ (A),[a] $T = 0^\circ$		7.23	32.5		
9.32	24.1	6.09	41.7		
5.80	35.6	4.00	52.2		
2.07	45.8	3.71	52.3		
1.36	61.1	2.37	60.7		
1.22	66.5	2.32	67.8		
0.83	84.5	1.71	75.3		
0.60	90.7	1.30	91.7		
		0.74	126.0		
		0.74	127.0		
		0.40	170.0		

[a] Test notations A and B refer to two different batches of polystyryllithium.

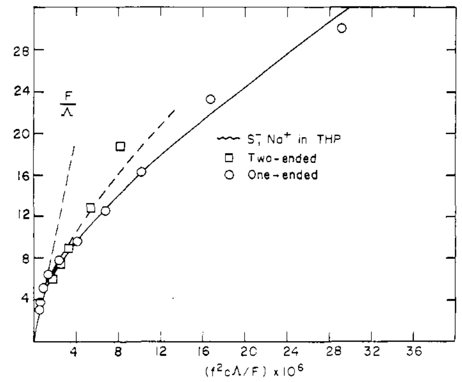

Figure 3. Fuoss plots of conductivity of $\sim\sim S^-,Na^+$ in THP at room temperature: □, two-ended polymer; ○, one-ended polymer.

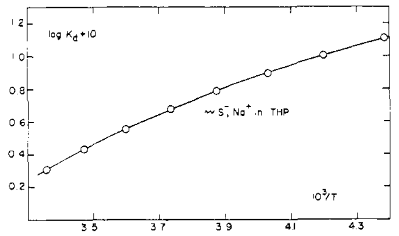

Figure 4. Log K_d as a function of $1/T$ for polystyrylsodium in THP.

are summarized in Table II. The lowest values of Λ used for the calculation of the tangents are given in the fourth column of this table. The plot of log K_d $vs.$ $1/T$ is given in Figure 4.

Kinetics of Propagation. The kinetic data for homopropagation of the lithium and sodium salts in THP are collected in Table III. Our studies covered a temperature range from −40 to 25°. At each temperature the observed propagation constants, k_{obsd}, were obtained for a sufficiently large range of concentration of growing polymers, [LE], to permit a reliable derivation of the linear relation between k_{obsd} and $1/[LE]^{1/2}$. Such linear relations are presented in Figures 5 and 6 and their slopes, rendering the values of $k_-K_d^{1/2}$ are listed in Table IV. Here k_- denotes the propagation constant of the free $\sim\sim S^-$ ions and K_d the dissociation constant of the respective salt.

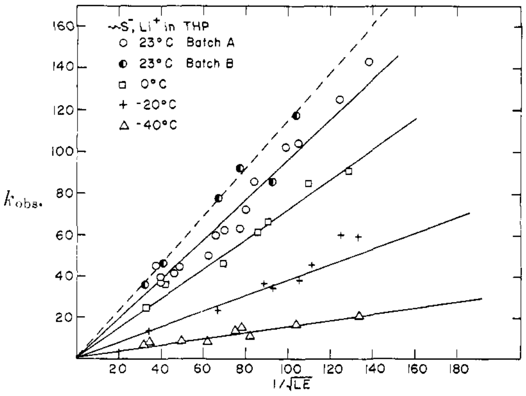

Figure 5. Plots of the apparent rate constants of propagation, k_{obsd}, of $\sim\sim S^-,Li^+$ in THP $vs.$ $1/\sqrt{LE}$: ○, 23° (batch A); ◐, 23° (batch B); □, 0°; ×, −20°; △, −40°.

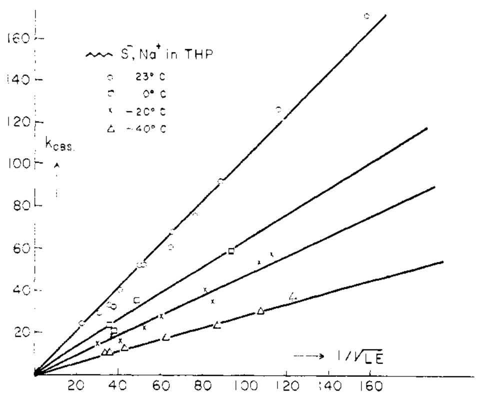

Figure 6. Plots of the apparent rate constants of propagation, k_{obsd}, of ∿S$^-$,Na$^+$ (two-ended) in THP *vs.* $1/\sqrt{LE}$: ○, 23°; □, 0°; ×, −20°; △, −40°.

TABLE IV
KINETIC CONSTANTS FOR POLYSTYRYLLITHIUM AND POLYSTYRYLSODIUM IN TETRAHYDROPYRAN[a]

T, °C	$k_-K_d^{1/2}$, $M^{-1/2}$ sec^{-1}	$K_d \times 10^{10}$ M	k_-, M^{-1} sec^{-1}
	∿S$^-$,Li$^+$		
23 (A)	0.97	2.57	61,000
23 (B)	1.15	2.57	72,000
0 (A)	0.70	4.41	33,300
−20 (A)	0.39	5.40	16,800
−40 (A)	0.16	5.26	7,000
	∿S$^-$,Na$^+$		
26	1.13^b		
23	1.01^c	2.15	68,800
0	0.60^c	4.10	29,700
0	0.37^b (0.65)^b		
−19	0.37^b		
−20	0.47^c	6.93	17,800
−40	0.27^c	11.4	8,000

[a] The notations A and B in the first column refer to different batches of polystyryllithium. [b] W. K. R. Barnikol and G. V. Schulz, *Makromol. Chem.*, **68**, 211 (1963); *Z. Physik. Chem.*, **47**, 89 (1965). [c] This paper.

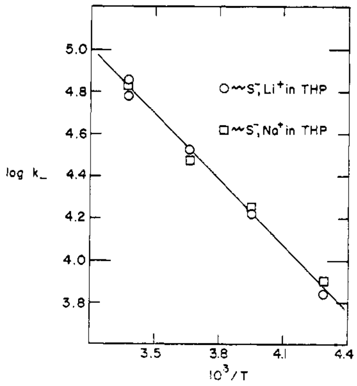

Figure 7. Arrhenius plot of the propagation constant of the free ∿S$^-$ ions, k_-, derived from the data obtained for ∿S$^-$,Li$^+$ (○) and ∿S$^-$,Na$^+$ (□) in THP.

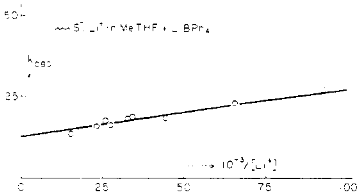

Figure 8. Polymerization of ∿S$^-$,Li$^+$ in MeTHF at 25° in the presence of LiBPh$_4$.

Accepting the K_d values for ∿S$^-$,Li$^+$ and ∿S$^-$,Na$^+$ given in Tables I and II, we calculated the values of k_- shown in the last column of Table IV. The plot of log k_- *vs.* $1/T$ is presented in Figure 7; the activation energy $E_- = 4.8$ kcal/mol and $A_- = 2 \times 10^8$ M^{-1} sec^{-1}. The self-consistency of these data is gratifying; it justifies the calculation of K_d for ∿S$^-$,Na$^+$ from our conductance studies which were hindered by the pronounced curvature of Fuoss plots.

The propagation constants, $k_\pm$, of the ion pairs ∿S$^-$,Na$^+$ or ∿S$^-$,Li$^+$ are very low. In fact, our data allow us only to estimate their upper limit, *viz.*, $k_\pm < 5$ M^{-1} sec^{-1} for the propagation at 25°, and at lower temperatures $k_\pm$ appears to be even smaller. Thus, our extrapolation is somewhat at variance with the data reported by other investigators[6,7] who claimed the propagation constant of ∿S$^-$,Na$^+$ in THP at 25° to be in the range 10–14 M^{-1} sec^{-1}.

The kinetics of propagation in MeTHF was investigated for the Li$^+$, Na$^+$, K$^+$, and Cs$^+$ polystyryls at one temperature only (25°). The results obtained for the Li$^+$ and Na$^+$ salts are somewhat questionable, because the spontaneous destruction of these salts in MeTHF is too rapid. We believe, however, that the data obtained in the presence of the relevant tetraphenyl boride salts are acceptable, and these are collected in Table V. We conclude that $k_\pm$ for ∿S$^-$,Li$^+$ and ∿S$^-$,Na$^+$ in MeTHF at 25° are 12 and 11 M^{-1} sec^{-1}, respectively. The dependence of k_{obsd} on $1/[Li^+]$ for

TABLE V
POLYMERIZATION OF POLYSTYRYLLITHIUM AND SODIUM IN 2-METHF AT 25° IN THE PRESENCE OF TETRAPHENYLBORIDE SALT; $[S]_0 \sim 10^{-2}$–10^{-3} M

[LE] × 10^4 M	[Boride] × 10^4 M	10^{-3}/[cation]	k_{obsd}, M^{-1} sec^{-1}
	∿S$^-$,Li$^+$ + LiBPh$_4$		
2.75	4.18	15.4	13.5
3.20	3.08	18.2	14.7
2.40	1.97	23.3	15.8
2.90	1.59	26.4	17.4
2.40	1.46	27.6	16.2
2.78	1.07	33.0	18.2
2.06	0.99	34.4	18.6
2.90	0.64	44.6	18.5
3.10	0.35	65.5	22.7
3.02	0.21	92.6	27.0
	∿S$^-$,Na$^+$ + NaBPh$_4$		
14.0	1.32		12.5
36.3^a	1.00		10.1
5.19^a	1.87		11.8

[a] Two-ended polystyrylsodium.

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(6) (a) See Table IV, footnote *b*; (b) L. Böhm, W. K. R. Barnikol, and G. V. Schulz, *Makromol. Chem.*, **110**, 222 (1967).

(7) F. S. Dainton, G. C. East, G. A. Harpell, N. R. Hurworth, K. J. Ivin, R. T. LaFlair, R. H. Pallen, and K. M. Hui, *Makromol. Chem.*, **89**, 257 (1965).

TABLE VI
PROPAGATION CONSTANTS, k_{obsd}, FOR $\sim\mathrm{S}^-,\mathrm{K}^+$ and $\sim\mathrm{S}^-,\mathrm{Cs}^+$ IN METHF AT 25°; $[\mathrm{S}]_0 \sim 10^{-2}$–$10^{-3}$ M

$[\sim\mathrm{S}^-,\mathrm{K}^+] \times 10^4$ M	k_{obsd}, M^{-1} sec^{-1}	$[\sim\mathrm{S}^-,\mathrm{Cs}^+] \times 10^4$ M	k_{obsd}, M^{-1} sec^{-1}
30.0	20	12.5	31.7
29.0	18	8.2	33.0
12.5	19	7.3	34.4
4.60	27	6.5	35.3
2.12	47	5.1	37.8
0.88	61	3.8	40.1
		1.85	44.0
		1.69	46.0
		0.79	60.5

the $\sim\mathrm{S}^-,\mathrm{Li}^+$ propagation is depicted in Figure 8. The concentration of Li$^+$ ions was calculated on the basis of K_{d} value of Li$^+$,BPh$_4^-$ reported in ref 8. The slope of the line shown in Figure 8 gives $k_-K_{\mathrm{d}} = 14 \times 10^{-5}$ sec^{-1} and, hence, if k_- in MeTHF is arbitrarily assumed to be 40,000 M^{-1} sec^{-1} the K_{d} is calculated to be about 3×10^{-9} M. This is a reasonable estimate for the dissociation constant of $\sim\mathrm{S}^-,\mathrm{Li}^+$ in MeTHF.

The results obtained for the K$^+$ and Cs$^+$ salts in MeTHF are given in Table VI, and the plots k_{obsd} *vs.* $1/[\mathrm{LE}]^{1/2}$ are shown in Figures 9 and 10. The relevant propagation constants, $k_\pm$, are obtained from the intercepts, *viz.*, 7.5 and 22 M^{-1} sec^{-1} for the K$^+$ and Cs$^+$ ion pairs, respectively. The slopes of the lines are 0.52 and 0.33 $M^{-1/2}$ sec^{-1}, and if the value of k_- is again assumed to be 40,000 M^{-1} sec^{-1} the K_{d}'s are calculated to be 1.7×10^{-10} and 0.6×10^{-10} M for $\sim\mathrm{S}^-,\mathrm{K}^+$ and $\sim\mathrm{S}^-,\mathrm{Cs}^+$ ion pairs, respectively. These results are plausible.

Discussion

The data presented in the preceding section show that the propagation constant of the free $\sim\mathrm{S}^-$ ions in THP is about 60,000 M^{-1} sec^{-1} at 25°. The relevant activation energy and frequency factor are 4.8 kcal/mol and 2×10^8 M^{-1} sec^{-1}, respectively, *i.e.*, not much different from those found in THF[4] (E = 5.9 kcal/mol, $A = 1 \times 10^9$ M^{-1} sec^{-1}) or DME[2] ($E \sim 5$ kcal/mol, $A = 2 \times 10^8$ M^{-1} sec^{-1}). Thus, another argument is provided to justify the claim that the reactivity of the free $\sim\mathrm{S}^-$ ions are only slightly affected by the nature of the ethereal solvent in which the polymerization is performed.[9,10] This observation implies that the interaction of molecules of the ethereal solvents with $\sim\mathrm{S}^-$ ion is rather weak.

Although the lower dielectric constant of THP, when compared with THF or DME, does not affect substantially the reactivity of the $\sim\mathrm{S}^-$ ions, the dissociation constants of the sodium or lithium salts are appreciably lower in THP than in the other two solvents. It is probable that the dissociation of ion paris in MeTHF is higher than in THP although much lower than in THF or DME. This is indirectly indicated by our data.

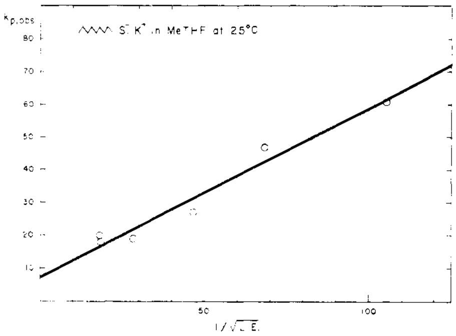

Figure 9. Concentration dependence of k_{obsd} for $\sim\mathrm{S}^-,\mathrm{K}^+$ in MeTHF at 25°.

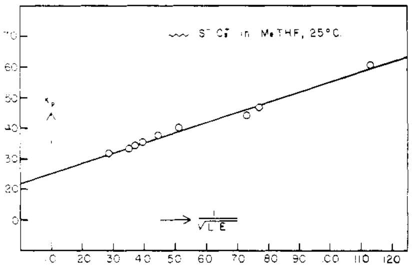

Figure 10. Concentration dependence of k_{obsd} for $\sim\mathrm{S}^-,\mathrm{Cs}^+$ in MeTHF at 25°.

It is known that ion pairs may undergo further agglomeration in solvents of low dielectric constants.[11] Triple ions, quadrupoles or still higher agglomerates are formed under those conditions. Although the shape of the Fuoss curves shown in Figure 3 might be considered as evidence for the formation of triple ions,[12] no clear argument for this phenomenon could be deduced from the analysis of the kinetic data. Nevertheless, it is possible that various agglomerations affect somehow the observed rate constants and this could modify the slopes and intercepts of lines giving k_{obsd} as a function of $1/[\mathrm{LE}]^{1/2}$. The problem is further complicated by the probable association of growing polymers with alkoxides, or other products of decomposition of living polymers, which may affect the rate of polymerization. Indeed, it was noted that aged solutions of living polystyrene are less reactive than the fresh ones, *i.e.*, the kinetic data led to higher k_{obsd} for the latter than for the former. Similar observation was made by the workers in Professor Schulz' laboratory (private communication).

Comparison of our data obtained at 23° with those reported by Barnikol and Schulz[6a] is nearly perfect; our $k_-K_{\mathrm{d}}^{1/2} = 1.01$ determined at 23° compares favorably with the value of 1.13 reported in ref 6a for 26°. It should be noted that the latter value was derived on the assumption $k_\pm = 0$, and our extrapolation leads also to $k_\pm \approx 0$. The comparison is poorer at 0°. At this temperature Barnikol and Schulz[6a] determined k_{obsd} over a wide concentration range of living polymers. The propagation constants reported by them for higher

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(8) See Table I, footnote *a*.

(9) M. van Beylen, D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **70**, 157 (1966).

(10) S. Bywater and D. J. Worsfold, *ibid.*, **70**, 162 (1966).

(11) R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, **55**, 2387 (1933).

(12) However, if triple ions are responsible for the curvature shown in Figure 3, one would expect the conductance of two-ended polymers to be more affected by this phenomenon than the conductance of polymers endowed with one growing end only. The results appear to be reversed, and we cannot offer any explanation for these findings.

TABLE VII
KINETIC CONSTANTS FOR THE HOMOPOLYMERIZATION OF POLYSTYRYL SALTS IN 2-METHYLTETRAHYDROFURAN AT 25°

Counterion	$k_\pm$ (MeTHF), M^{-1} sec^{-1}	$k_\pm$ (dioxane),[a] M^{-1} sec^{-1}	$k_\pm$(THF),[a] M^{-1} sec^{-1}	$k_\pm$(DME),[a] M^{-1} sec^{-1}
Li$^+$	12.0	0.9	160	
Na$^+$	11.0	4.0	80	3600
K$^+$	7.5	20.0	70	
Cs$^+$	22.0	24.5	22.0	150

[a] Data taken from ref 1 (dioxane), 3 (THF), and 2 (DME).

[LE], *viz.*, 10^{-3} down to 2×10^{-4} M, agree perfectly with our data. However, at lower [LE], less than 1×10^{-4} M, the propagation constants determined by us are by 30–50% higher than those reported by Schulz. It is probable that the effect of impurities, which is amplified at the low concentration range, reduced the value of the propagation constant determined by the Mainz group.

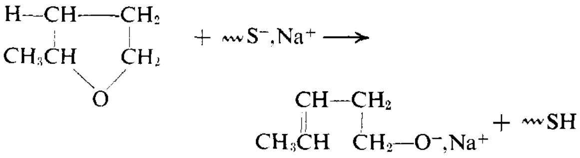
In their paper, Barnikol and Schulz[6a] reported also the temperature dependence of $k_-K_d^{1/2}$ to be about 3.8 kcal/mol. We determined $E_- = 4.8$ kcal/mol and inspection of Figure 4 indicates that $-\Delta H_d$ = 4.8-3.0 kcal/mol. Again, the agreement between both sets of data is reasonable.

The problem of reactivity of ion pairs in THP is perplexing. For $\sim$S$^-$,Na$^+$ ion pair in THP the propagation constant was determined by Schulz and his coworkers[6b] and independently by Ivin and his associates[13] over a wide temperature range (from −42 up to 48°). The agreement between both sets of data is excellent. Moreover, $k_\pm$ for the same salt was determined in our laboratory by Dr. Shinohara at 25° and again his data ($k_\pm$ = 12 M^{-1} sec^{-1}) agree well with those reported by Schulz ($k_\pm$ = 13 M^{-1} sec^{-1}) and by Ivin ($k_\pm \sim 15$ M^{-1} sec^{-1}).

All these results were obtained in the presence of sodium tetraphenyl boride to depress the dissociation of living polymers. Our extrapolated data are definitely lower, especially at 23 and 0°. The question arises, therefore, whether or not the presence of sodium tetraphenyl boride affects the reactivity of ion pairs. For example, it might be argued that a fraction of living polymers may associate with BPh_4^- anions and form more reactive triple ions. On the other hand, the extrapolation of the plots k_{obsd} *vs.* $1/[LE]^{1/2}$ are usually less reliable than the data obtained directly in the presence of the boride. Hence, the problem remains unsolved, and further work might be desirable.

Finally, it is interesting to note the deviations of the plots of $k_\pm$ *vs.* $1/T$ from the Arrhenius line.[6b] These are attributed by Barnikol and Schulz to the formation of the more reactive solvent separated pairs which become abundant at lower temperatures. Their conclusion is supported by our conductance data (see Figures 2 and 4) which show a decrease in the heat of dissociation at lower temperatures.

The destruction of living polymers which takes place in MeTHF calls for some comments. All the attempts to purify this solvent did not lead to satisfactory results. Is it possible that MeTHF is sufficiently acidic to react with $\sim$S$^-$ carbanions? It has been shown recently[14] that THF protonates the dianions of diphenylacetylene even at temperatures as low as −60°, although no protonation of monoradical ions (PhC≡CPh·$^-$) is observed at 25°. We suggest, therefore, tentatively that the reaction



is responsible for the destruction of living polystyrene in MeTHF.

In view of the above complications the results obtained in MeTHF should be considered as tentative. Nevertheless, it seems that the sequence of reactivities of Li$^+$, Na$^+$, K$^+$, and Cs$^+$ ion pairs observed in MeTHF (see Table VII) is plausible.

It is interesting to compare these values with those found in dioxane, THF, and DME, all of which are included in Table VII. It appears that only the $k_\pm$ for the cesium salt is not affected by a change of solvent DME being an exception. It is precisely in this solvent where the free Cs$^+$ ion was found to be solvated,[5] whereas no tight solvation shell is formed around the Cs$^+$ cation in THF, as shown by its high mobility.[5] Because MeTHF and dioxane are poorer solvating agents than THF, it is safe to conclude that only the contact $\sim$S$^-$,Cs$^+$ ion pairs exist in all these media,[15] their reactivities being apparently independent of the nature of their surroundings. On the other hand, the solvation of the Li$^+$ ions, and to a lesser extent the Na$^+$ ions, is stronger and increases in the order dioxane < MeTHF < THF < DME. The observed increase in the ion pair rate constants in these series of solvents is probably due to an increase in the fraction of very reactive solvent separated ion pairs.

In dioxane, no solvent separated ion pairs are present for any of the salts, and the $k_\pm$ value increases with increasing cation radius, due to a decreased Coulombic interaction between carbanion and counterion. This order is completely reversed in THF and DME where the increased fractions of solvent separated ion pairs is the dominating factor. In solvents of intermediate solvating ability like THP and MeTHF one may conceivably find that a plot of ion pair reactivity with cation size shows a minimum, due to the opposing factors which control the ion pairs reactivity. The extent of solvent separated ion pair formation was reported to be very similar in these solvents for fluorenyllithium.[15]

Acknowledgment. We gratefully acknowledge the financial support of this study by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society.

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(13) K. J. Ivin, private communication to us and to Professor Schulz.

(14) G. Levin, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, in press.

(15) L. L. Chan and J. Smid, *ibid.*, **90**, 4654 (1968).