volts of onset. From the present quality of our data, no consistent correlations can be made between the observed intensities of the various fragment currents and the breaks which are observed in the ionization efficiency curves.

Acknowledgments. The authors are indebted to Mr. Dave Erbeck who provided the computer program for calculating the ionization potentials and to Dr. P. L. Tappel, University of California, Davis, who kindly furnished the sample of pure selenomethionine.

Energy and Entropy of Activation of Propagation by the Free Polystyryl Anions and Their Ion Pairs. The Phenomenon of "Negative" Activation Energy.

T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc

Contribution from the Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210. *Received September 15, 1966*

Abstract: The anionic polymerization of sodium and cesium salts of living polystyrene was investigated in tetrahydrofuran between -70 and $+25°$. Under these conditions both salts are partially dissociated into free ions, and the respective dissociation constants, K_{dis}, were determined from conductance studies of their solutions. For the sodium salt, K_{dis} increases from 1.5×10^{-7} at 25° to 300×10^{-7} M at $-70°$, the heat of dissociation being -8 kcal/mole in the interval -30 to $+25°$ and about -6 kcal/mole at $-70°$. The cesium salt is less dissociated, K_{dis} being 0.047×10^{-7} at 25° and 0.1×10^{-7} M at $-60°$; thus the respective ΔH is -1.8 kcal/mole only. The kinetic data showed that the free $\sim\!\!\sim\mathrm{S}^-$ ions and the respective ion pairs participate in the propagation. Studies of either salt led to concordant results for the propagation constant, k_-, of the free ions, *viz.*, $k_- = 65{,}000$ at 25° and about 1000 M^{-1} sec^{-1} at $-70°$. Thus, $E_- \approx 6$ kcal/mole and $A_- \approx 10^9$ M^{-1} sec^{-1}. The cesium ion pair behaves conventionally; its propagation rate constant, $k_{\pm,\mathrm{Cs}}$, decreases from 25 at 25° to about 1 M^{-1} sec^{-1} at $-60°$. However, $k_\pm$ for the sodium ion pair *increases* from 80 at 25° to about 270 M^{-1} sec^{-1} at $-60°$. The reasons for this negative "activation energy" are fully discussed. The $\sim\!\!\sim\mathrm{S}^-,\mathrm{Na}^+$ might exist in two forms, a virtually unreactive contact ion pair and a highly reactive solvent-separated ion pair. The equilibrium favors the latter at lower temperatures, and this may account for the results. However, such an interpretation is not unique, and an alternative hypothesis has been also proposed.

Propagation of anionic polymerization in ethereal solvents involves free ions and ion pairs. For example, in tetrahydrofuran (THF) the free polystyrene ion, $\sim\!\!\sim\mathrm{S}^-$, grows with a rate constant $k_- = 65{,}000$ M^{-1} sec^{-1} at 25°, whereas the respective rate constants of the ion pairs seem to be 160, 80, and 25 M^{-1} sec^{-1} for the Li^+, Na^+, and Cs^+ salts.[1]

We have now determined the activation energy and the entropy of activation for the propagation of the free $\sim\!\!\sim\mathrm{S}^-$ ion and of its sodium and cesium salts (ion pairs) in THF. This was accomplished by investigating the kinetics of the over-all propagation over a wide temperature range (-70 to $+25°$) and by determining the dissociation constants of $\sim\!\!\sim\mathrm{S}^-,\mathrm{Na}^+$ and $\sim\!\!\sim\mathrm{S}^-,\mathrm{Cs}^+$ salts in THF.

Experimental Section

Purification of the monomer and the solvent and details of preparation of the living polystyrenes were previously reported.[1b,2] Benzylsodium was used for the preparation of "one-living-end" polystyrene. The initiator was synthesized on a high-vacuum line by treating dibenzylmercury (1 g dissolved in 70 cc of THF) with a sodium mirror at $-20°$. The reaction was completed in about 4 hr, and the resulting brownish red solution of $\mathrm{PhCH_2^-,Na^+}$ was filtered from the excess of the alkali metal and then treated with 1.9 g (about sevenfold excess) of α-methylstyrene. A direct addition of styrene was found unsatisfactory, since the propagation is then faster than the initiation.[3] The propagation of α-methylstyrene is slow and reversible, and hence the conversion of $\mathrm{PhCH_2^-,Na^+}$ into $\mathrm{PhCH_2CH_2C(Ph)(CH_3)^-,Na^+}$ is quantitative. The addition of styrene to the latter species is faster than the homopropagation of living polystyrene,[4] and therefore its conversion into $\sim\!\!\sim\mathrm{S}^-,\mathrm{Na}^+$ is quantitative.

Dropwise addition of 4 g of styrene dissolved in $\sim$10 cc of THF (distilled from benzylsodium) to the vigorously stirred solution of $\mathrm{PhCH_2CH_2C(Ph)(CH_3)^-,Na^+}$ kept at $-50°$ was followed by a vacuum distillation of an additional 1 g of styrene into the reacting mixture. The final yield of living polystyrene, based on the dibenzylmercury, was about 75%; the average degree of polymerization (DP) of the resulting "one-living-end" polystyrene was calculated to be about 12.

The one-ended polystyrylcesium salt was prepared from cumylcesium.[1b] The cumyl ether used in the preparation of cumylcesium must be freshly prepared, because it slowly decomposes into α-methylstyrene and methanol even if kept in sealed ampoules under vacuum in a freezer. The presence of α-methylstyrene leads to formation of the undesirable two-ended polystyrylcesium.

Recrystallized $\mathrm{Na^+,BPh_4^-}$ was dissolved in rigorously dried THF, and the required amounts were introduced into ampoules equipped with breakseals. The solvent was then slowly evaporated on a high-vacuum line, the residue was dried by pumping, and after a few hours the ampoules were sealed off. An appropriate ampoule was sealed to the reaction vessel whenever needed.

Studies of Conductance of the Living Polystyrenes. A detailed description of the technique used in the conductance studies is given elsewhere.[1,5] The conductance was measured for a series of con-

---

[1] (a) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *Polymer*, **5**, 54 (1964); (b) *J. Phys. Chem.*, **69**, 612 (1965).

[2] C. Geacintov, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 2508 (1962).

[3] M. Szwarc, *Makromol. Chem.*, **35**, 132 (1960).

[4] D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 533 (1963).

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

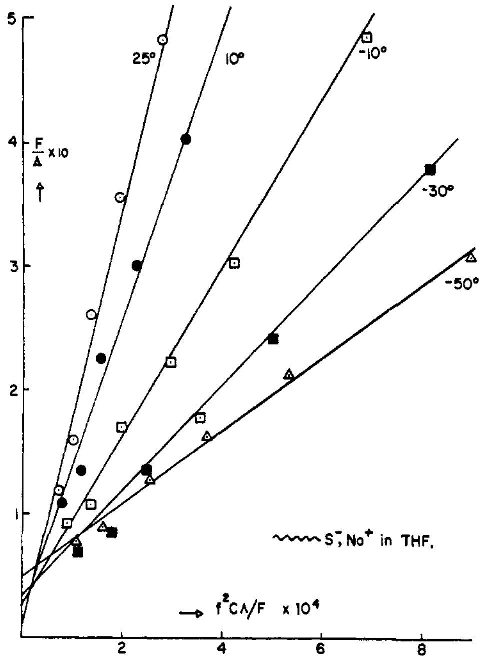


Figure 1. Plot of F/Λ *vs.* $f^2C\Lambda/F$ for living polystyrene at temperatures varying from 25 to −50°.

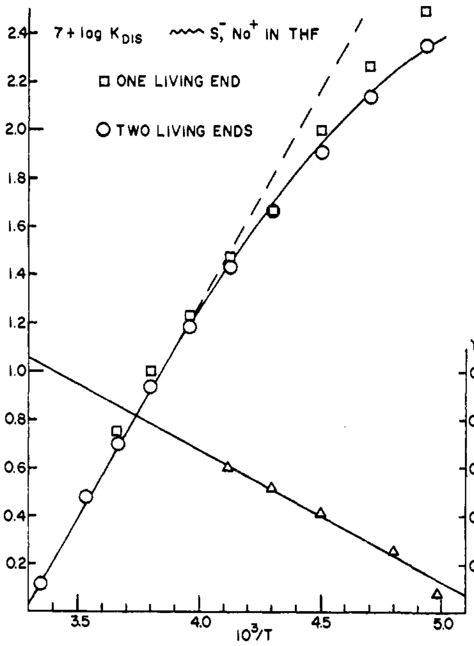


Figure 2. Plot of log K_{dis} of $\sim\sim S^-,Na^+$ in THF *vs.* $1/T$: ○, polymers possessing two living ends; □, polymers possessing one living end; △, Walden product $\eta\Lambda_0$ calculated from the experimentally determined Λ_0.

centrations, and for each concentration the measurements were made at temperatures ranging from −70 up to +25°. The results were corrected for the contraction of volume and used to calculate F/Λ and $f^2c\Lambda/F$ at a series of fixed temperatures.[5] Representative plots of F/Λ *vs.* $f^2c\Lambda/F$ are shown in Figure 1, and the resulting values of Λ_0 and K_{dis} are given in Tables I and II. Plots of log K_{dis} and of $\Lambda_0\eta$ *vs.* $1/T$ are shown in Figures 2 and 3.

Determination of the Propagation Rate Constant of Styrene Polymerization. The kinetics of polymerization were investigated spectrophotometrically, the conversion of the monomer into polymer being monitored by the decrease of optical density at 291.5 mμ (λ_{max} of styrene). The apparatus is shown in Figure 4. Ampoules containing the reagents and the rinsing solution (concentrated living polystyrene in THF) were attached to the main unit which was evacuated, flamed, and sealed off. Rinsing the apparatus with the concentrated solution of living polystyrene kept in ampoule A removed the reactive impurities adsorbed on its walls. By external cooling, which condenses the solvent on the inside surface, the residual polymer and the impurities were washed from the walls and collected in ampoule A. The latter was then sealed off after freezing its contents.

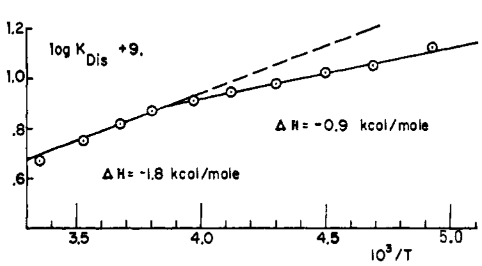


Figure 3. Plot of log K_{dis} of $\sim\sim S^-,Cs^+$ in THF *vs.* $1/T$.

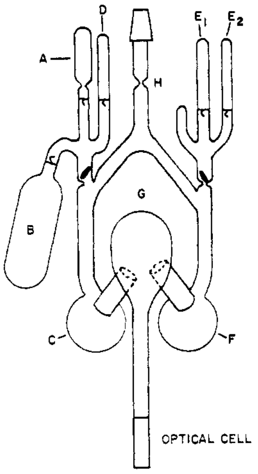


Figure 4. The apparatus developed for studies of kinetics of polymerization, suitable even at temperatures as low as −80°.

Table I. Dissociation of the Sodium Salt of Living Polystyrene in THF[a]

	Two-living-ends polymer				One-living-end polymer		
Temp, °C	Slope × 10^{-3}	Λ_0, cm²/ohm equiv	$\eta\Lambda_0$	K_{dis} × 10^7, *M*	Slope × 10^{-3}	Λ_0, cm²/ohm equiv	K_{dis} × 10^7, *M*
25	1.66	(63.5)	(0.294)	1.50	...	...	...
10	1.18	(53.0)	(0.288)	3.02	...	...	...
0	0.913	(46.5)	(0.284)	5.05	0.825	...	5.6
−10	0.694	(40.5)	(0.280)	8.8	0.635	...	9.6
−20	0.540	(34.7)	(0.275)	15.4	0.490	...	17
−30	0.423	29.5	0.270	27.1	0.383	28.6	30
−40	0.350	24.7	0.266	46.8	0.350	25.0	47
−50	0.295	20.4	0.261	81.5	0.245	20.0	98
−60	0.270	16.3	0.253	139	0.196	16.3	190
−70	0.267	12.8	0.244	228	0.186	12.8	325

[a] The apparently lower K_{dis} values observed for the two-living-ends polymer cannot be due to intramolecular association of the living ends. Such an association would make them larger.[1b] The values $\eta\Lambda_0$'s given in parentheses were extrapolated from the directly determined $\eta\Lambda_0$'s found for −30, −40, −50, −60, and −70°. The extrapolation was based on a linear relation between $\eta\Lambda_0$ and $1/T$. The extrapolated $\eta\Lambda$'s led to the extrapolated Λ_0's given in parentheses. For the one-ended polymer K_{dis} was calculated from the slopes of the respective Fuoss' lines and the Λ_0's given for the two-living-ends polymer. Viscosities of THF at various temperatures are given in Table II of ref 5.

Table II. Dissociation of Cesium Salt of Living Polystyrene (One End) in THF

Temp, °C	$\Lambda_0{}^a$	Slope of Fuoss line $\times 10^{-4}$	$K_{dis} \times 10^8$, M
+25	92.5	2.48	0.47
+10	77.5	2.95	0.56
0	68.5	3.24	0.66
−10	59.5	3.77	0.75
−20	51.5	4.61	0.81
−30	45.0	5.79	0.86
−40	38.0	7.32	0.95
−50	31.0	9.68	1.07
−60	26.5	12.65	1.12
−70	19.4	19.2	1.40

[a] Λ_0 calculated by using the data on $\lambda_0{}^+$ of Cs^+ in THF reported by Szwarc, *et al.*,[5] and adding $\lambda_0{}^-$ for the $\sim\sim S^-$ ion computed from the Walden product on the basis of $\lambda_0{}^-$ (25°) ≈ 14.

The investigated living polymer solution was then partially transferred from ampoule B into bulb C and its concentration adjusted by distilling the residual solvent from B into C. If required, a salt ($Na^+,BPh_4{}^-$) sealed in ampoule D was added to the polymer solution.

The monomer kept in ampoule E_1 was introduced into bulb F and diluted by distilling some solvent from C into F. The whole unit was immersed in a large dewar flask filled with methanol maintained at the desired temperature. After reaching thermal equilibrium, the unit was quickly withdrawn and the reagents were mixed in G by turning the apparatus upside down. The unit was then returned to its original position, thereby filling the optical cell with the reacting mixture, and the cell quickly immersed in a second small dewar equipped with optical windows properly fixed in the cell compartment of a Cary-14 spectrophotometer. All these operations could be performed in 15 sec. The small dewar had been previously filled with methanol kept at the same temperature as the thermostatic liquid in the large dewar. The optical density at 291.5 mμ was then continuously recorded giving, thereby, the monomer concentration as a function of time. The concentration of living ends was determined at various intervals by turning the monochromator to the absorption maximum of living polystyrene. The described technique permits us to study the kinetics of the polymerization in the temperature range −75 to +25°.

Results of the Conductance Studies

As shown in Figure 1, the plots of F/Λ *vs.* $f^2c\Lambda/F$ are linear, giving well-defined slopes, equal to $1/K_{dis}\Lambda_0{}^2$. The experimental reliability of the intercept depends on the ratio Λ/Λ_0, where Λ is the equivalent conductance at concentrations essential for an accurate determination of the slope. This ratio decreases with decreasing K_{dis}, preventing a direct determination of Λ_0 for the sodium salt of living polystyrene above −30°, although reliable values are obtained at lower temperatures. A comparison of the third and seventh columns of Table I shows a gratifying agreement between Λ_0's found for the "one-living-end" and "two-living-ends" polymers.

The Walden product, $\eta\Lambda_0$, is approximately constant, although a slight decrease is observed at lower temperatures,[5] usually amounting to less than 15% as the temperature varies from 25 to −70°. It seems that $\eta\Lambda_0$ is linear with $1/T$, and our data obtained in the range −70 to −30° confirm this empirical relation (see Figure 2). Hence, $\eta\Lambda_0$'s, and therefore also Λ_0's, may be calculated for higher temperatures by linear extrapolation of the low-temperature data, and thus at 25° one finds Λ_0 = 63.5 cm²/ohm equiv. This value was confirmed by two independent methods.

(1) A phenomenological relation, $u = D/kT$, correlates the mobility, u, of an ion with its self-diffusion constant, D. Since $u = 6.47\lambda_0{}^-$, $\lambda_0{}^-$ for the $\sim\sim S^-$ ion may be calculated if its diffusion constant is known. One expects an insignificant difference between the self-diffusion constant of a living polystyrene (DP ~ 25) and that of a dead polymer of the same degree of polymerization. From the data of Benoit,[6] *viz.*, $D = 3.9 \times 10^{-6}$ cm²/sec for DP = 25 in THF, $\lambda_0{}^-$ for the $\sim\sim S^-$ ion was calculated to be 14.4 cm²/Ω equiv. Since $\lambda_0{}^+$ for Na^+ was found[5] to be 45.2 cm²/Ω equiv, Λ_0 for $\sim\sim S^-,Na^+$ is calculated as 60 cm²/Ω equiv.

(2) Studies of the kinetics of $\sim\sim S^-,Na^+$ polymerization, carried out in the absence and in the presence of $Na^+,BPh_4{}^-$, led to a K_{dis} of the $\sim\sim S^-,Na^+$ ion pair of 1.5×10^{-7} M. This value, which agrees with that reported earlier by Worsfold and Bywater,[7] combined with the slope of the respective Fuoss line, leads to $\Lambda_0 = 61.7$ for $\sim\sim S^-,Na^+$ at 25°.

Therefore, the Λ_0's given in Table I appear to be reliable within 3–5%, and these were used in computing the corresponding K_{dis}'s listed in Table I and presented graphically in Figure 2. The K_{dis}'s obtained for the one-living-end and two-living-ends polymers are nearly identical. Certainly, the two living ends located on the same chain are not associated, because such a phenomenon would lead to reverse deviations than those observed in Figure 2 (see ref 1b and 8).

The dissociation of $\sim\sim S^-,Na^+$ is strongly exothermic, $-\Delta H$ = 8.2 kcal/mole at 25°, its value decreasing to 5–6 kcal/mole at −70°.

The dissociation of the cesium salt of polystyrene endowed with one living end is much lower than that of the sodium salt, and hence, the intercepts of the Fuoss lines are indistinguishable from zero. The values listed in Table II were obtained, therefore, by combining the $\lambda_0{}^-$'s of $\sim\sim S^-$ ions with the $\lambda_0{}^+$'s of Cs^+ ions.[5] $\lambda_0{}^-$ at 25° was found to be 14.4 cm²/Ω equiv; its values at lower temperatures were calculated from the relation

$$\lambda_0{}^-(T)/\lambda_0{}^-(25°) = \lambda_0{}^+(T)/\lambda_0{}^+(25°)$$

Because $\lambda_0{}^+(Cs^+)$ is much greater than $\lambda_0{}^-(\sim\sim S^-)$, this procedure should be satisfactory if $\Lambda_0 = \lambda_0{}^- + \lambda_0{}^+$ is our goal.

The slopes of the Fuoss lines were determined from five experiments performed at concentrations ranging from 1×10^{-5} up to 7×10^{-5} M. The experimental points and the respective calculated $1/\Lambda_0$'s formed good straight lines. The slopes and the dissociation constants are listed in Table II, and the van't Hoff plot is shown in Figure 3.

The dissociation is again exothermic, $-\Delta H$ = 1.8 kcal/mole within the −10 to +25° region, and decreases to about 0.9 kcal/mole at lower temperatures.

Results of Kinetic Studies

Kinetic studies of propagation show that

$$[\text{living polymer}]^{-1} \log \{(\text{OD } 291.5)_0 - (\text{OD } 291.5)_\infty\}/\{(\text{OD } 291.5)_t - (\text{OD } 291.5)_\infty\}$$

is linear with time, the slope giving the respective apparent k_p of propagation. All the results are listed in Tables III–V.

---

(6) H. Benoit, private communication.

(7) D. J. Worsfold and S. Bywater, *J. Chem. Soc.*, 5234 (1960).

(8) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **86**, 5024 (1964).

Table III. Propagation of $\sim\!\!S^-,Na^+$ in THF at 25°[a]

Series	[Living ends] × 10^4, M	[Na^+,B^-] × 10^4, M	$10^{-3}/[Na^+]$, M^{-1}	k_p (apparent), M^{-1} sec^{-1}
B	1.02	123	1.02	102
B	1.08	110	1.08	104
B	0.93	40.4	1.82	122
B	0.41	40.1	1.83	107
B	0.83	37.7	1.91	115
B	0.97	36.3	1.95	112
B	1.00	23.4	2.47	123
B	0.69	23.4	2.47	118
A	0.71	13.2	3.3	114
B	0.91	8.8	4.3	115
A	1.50	5.9	5.4	137
A	1.70	5.5	5.5	127
A	1.80	2.9	8.2	163
B	0.76	2.6	8.8	160
B	0.56	2.7	8.6	144
B	1.01	2.5	9.0	167
A	1.10	2.2	10.0	184
B	0.79	2.0	10.7	176
B	0.76	2.0	10.7	175
A	1.6	1.35	14.0	210
B	0.62	0.87	18.4	249
B	0.79	0.86	19.5	269
B	0.80	0.83	18.5	225
A	3.1	0.70	22.0	280
No salt	181	...	19.3	315 (?)
No salt	100	...	26.3	396
No salt	75.0	...	30	434
No salt	49.0	...	37	538
No salt	30.0	...	47	550
No salt	10.0	...	82	900
No salt	1.65	...	200	2050
No salt	1.10	...	248	2450
No salt	0.73	...	310	3560
No salt	0.62	...	335	3620
Calculated on the basis $K_{B^-,Na^+} = 8 \times 10^{-5}$ M				

[a] Series A, performed by Dr. Tölle; series B performed by Mr. Shimomura. Experiments without salt are taken from ref 1. Experiments linked by braces represent two consecutive runs performed in the same solution. The decrease in [living ends] in the second run reflects some killing of the living polystyrene arising from the addition of more monomer.

Table IV. $\sim\!\!S^-,Na^+ + S$ in THF at Other Temperatures than 25°

Temp, °C	Series	[Living, ends] × 10^4, M	[Na^+, BPh_4^-], 10^4 M	f	k_p (apparent), M^{-1} sec^{-1}
0	A	1.6	13.8	0.0014	113
0	A	1.7	2.9	0.0040	155
0	A	1.5	1.2	0.0069	200
0	A	1.5	1.0	0.0077	213
0	A	1.7	0.0	0.055	1100
Calculated on the basis $K_{S^-,Na^+} = 5.05 \times 10^{-7}$ M $K_{B^-,Na^+} = 12 \times 10^{-5}$ M					
−33	B	1.2	35.0	0.0054	151
−33	B	1.1	35.0	0.0054	160
−33	A	2.1	10.0	0.0104	154
−33	B	1.0	7.0	0.0130	170
−33	B	0.8	7.0	0.0130	199 (?)
−33	A	1.0	5.3	0.0150	181
−33	B	1.1	4.4	0.0175	200
−33	B	1.0	4.4	0.0175	198
−33	B	1.2	2.2	0.028	232
−33	B	1.1	2.2	0.028	249
−33	A	1.5	1.5	0.036	248
−33	B	1.4	1.4	0.038	252
−33	B	1.2	1.4	0.038	296
−33	A	1.1	1.2	0.040	280
Calculated on the basis $K_{S^-,Na^+} = 34 \times 10^{-7}$ M $K_{B^-,Na^+} = 16 \times 10^{-5}$ M					
−60	B	1.1	36	0.023	270
−60	B	0.9	36	0.023	307
−60	A	1.4	11.0	0.045	324
−60	A	1.2	5.5	0.070	374
−60	B	1.4	4.7	0.076	332
−60	B	1.2	4.7	0.076	396
−60	A	1.25	2.3	0.12	384
−60	B	1.5	2.1	0.13	387
−60	B	1.4	2.1	0.13	406
−60	A	1.0	1.8	0.15	408
−60	B	1.3	1.2	0.165	459
−60	B	1.2	1.2	0.165	510
−60	B	1.4	0.9	0.185	494
−60	B	1.4	0.9	0.185	521
Calculated on the basis $K_{S^-,Na^+} = 160 \times 10^{-7}$ $K_{B^-,Na^+} = 16.5 \times 10^{-5}$ M					
−75	A	1.8	0.0		790
−75	A	0.67	0.0		1260
−75	A	0.43	0.0		1380
Calculated on the basis $K_{S^-,Na^+} = 3.0 \times 10^{-5}$ M					
−80	B	1.64	9.70	0.0835	358
−80	B	1.06	4.52	0.128	370
−80	B	1.33	5.83	0.112	412
−80	B	1.68	10.98	0.077	336
−80	B	1.43	54.40	0.033	280
−80	B	1.06	1.74	0.219	460
−80	B	0.885	4.87	0.123	372
−80	B	0.612	4.87	0.123	394
−80	B	1.37	2.87	0.186	404
−80	B	1.02	2.87	0.186	428
−80	B	0.942	2.28	0.190	476
−80	B	1.32	84.70	0.026	292
−80	B	1.26	84.70	0.026	308
−80	B	0.438	21.40	0.054	356
Calculated on the basis $K_{S^-,Na^+} = 3.2 \times 10^{-5}$ M $K_{B^-,Na^+} = 1.75 \times 10^{-4}$ M					

The observed rate constant of propagation, k_p, is given by the sum of two terms, *viz.*

$$k_p = k_\pm + (k_- - k_\pm)f$$

where f denotes the fraction of the living ends present in the form of free ions. According to the mass law, $f/(1-f) = K_{dis}/[Na^+]$, where $[Na^+]$ is the concentration of free sodium ions. In most experiments $f \ll 1$ and $1 - f \approx 1$, justifying the approximation

$$k_p = k_\pm + (k_- - k_\pm)K_{dis}/[Na^+]$$

The concentration of sodium ions is determined by three simultaneous equations

$$[Na^+] = x + y$$

$$x([LE] - x)^{-1} = K_{dis}/[Na^+]$$

$$y([Na^+,BPh_4^-]_0 - y) = K_{B^-,Na^+}/[Na^+]$$

$[Na^+,BPh_4^-]_0$ denotes the total concentration of the added salt (dissociated and undissociated), K_{B^-,Na^+} is its dissociation constant,[5] x and y are the concentrations of the free $\sim\!\!S^-$ and BPh_4^- ions, respectively, and [LE] is the total concentration of living polystyrene. In most experiments it is permissible to neglect the contribution of $\sim\!\!S^-,Na^+$ to the formation of sodium ions, and then the concentration of the latter is determined by the single equation

$$\frac{[Na^+]^2}{[Na^+,BPh_4^-]_0 - [Na^+]} = K_{B^-,Na^+}$$

The computed values of $10^{-3}/[Na^+]$ are given in the fourth column of Table III and those of f in the fifth column of Table IV. Plots of the observed k_p *vs.*

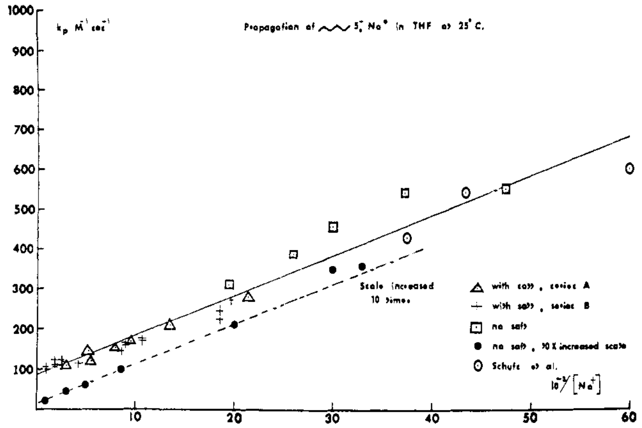


Figure 5. Plot of the apparent rate constant of propagation of $\sim\!S^-,Na^+$ in THF at 25° *vs.* $1/[Na^+]$: △, experiments performed in the presence of Na^+,BPh_4^-, series A; +, experiments performed in the presence of Na^+,BPh_4^-, series B; ⊡, experiments performed in the absence of salt; ●, experiments performed in the absence of salt at extremely low concentrations of $\sim\!S^-,Na^+$ (To accommodate these results on the graph, it was necessary to increase 10 times the scale. Thus, the shifted solid line becomes transformed into a parallel dashed line which passes through an intercept $^1/_{10}$th of the original one. Note that the solid circle points fit excellently this line, proving the linear relation to be valid for a 300-fold range in sodium ion concentration.); ⊙, experiments reported by Schulz.[8]

$10^{-3}/Na^+$, or *f*, are shown in Figures 5 to 9. The intercepts of the least-squares straight lines give the respective $k_\pm$'s, and from their slopes the propagation constant k_- of the free $\sim\!S^-$ ion is calculated. The results are summarized in Table VI and shown in the form of an Arrhenius plot in Figure 10.

Table V. Polymerization of $\sim\!S^-,Cs^+$ in THF

[Living ends] × 10^4, *M*	k_p (apparent), M^{-1} sec^{-1}	[Living ends] × 10^4, *M*	k_p (apparent), M^{-1} sec^{-1}
25°		25°	
0.68	562	3.76	227
1.00	450	6.10	195
1.55	365	6.8	179
1.62	351	8.35	175
2.34	324	17.3	131
2.55	296	22.2	113
0°		0°	
1.11	196	1.84	135
1.16	177	3.32	114
1.26	168	3.50	109
1.60	149	11.3	70
−30°		−30°	
1.12	56.5	2.33	37.4
1.33	55.0	4.00	32.3
1.45	52.5	5.68	26.0
1.87	42.5	10.0	24.2
2.24	38.8	10.2	20.4
		11.6	20.9
−60°		−60°	
1.41	11.1	5.9	5.9
1.98	9.4	7.45	5.45
3.0	7.8	11.2	4.4
5.2	6.3	13.5	4.2

The experiments performed at 25° were conducted in the presence and in the absence of sodium tetraphenylboride, and both sets of data are compatible. Such data permit us to calculate k_- and K_{dis} of $\sim\!S^-,Na^+$ (see ref 1), and the agreement with K_{dis} derived from the conductance study is most gratifying. The results of Schulz, *et al.*,[9] are also plotted in Figure 5 (open circles) and agree well with ours.

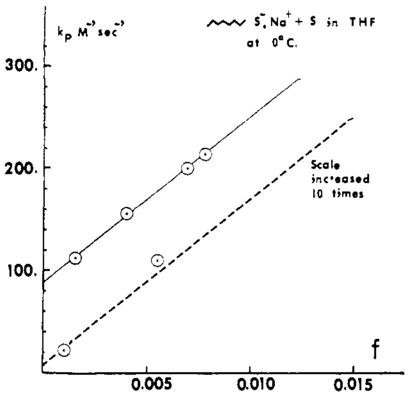


Figure 6. Plot of the apparent rate constant of propagation of $\sim\!S^-,Na^+$ in THF at 0° *vs.* fraction of free ions (*f*). Again, the scale is increased 10 times to accommodate the last two points, $f = 0.0077$ and $f = 0.055$. The linear relation holds, therefore, for a 50-fold change in *f*.

Table VI. Propagation of Anionic Polymerization of Living Polystyrene in THF

Counterion	Temp, °C	$K_{dis} \times 10^7$, *M* Na⁺	Cs⁺	k_-, M^{-1} sec^{-1}	$k_\pm$, M^{-1} sec^{-1} Na⁺	Cs⁺
Na⁺	25	1.5		65,000	80	
Cs⁺	25		0.047	63,000		21
Na⁺	0	5.0		16,000	90	
Cs⁺	0		0.066	22,000		9
Na⁺	−33	34		3,900	130	
Cs⁺	−30		0.086	6,200		2.4
Na⁺	−60	160		1,460	250	
Cs⁺	−60		0.112	1,100		1.0
Na⁺	−80	320		1,030	280	

For $\sim\!S^-$ Free Ion
$E_- = 5.9$ kcal/mole ± 0.5, $\log A_- = 9.05\ M^{-1}\ \text{sec}^{-1}$

For $\sim\!S^-,Na^+$ Ion Pair
$E_{\pm,Na^+} = -1.5$ kcal/mole,

For $\sim\!S^-,Cs^+$ Ion Pair
$E_{\pm,Cs^+} = 5.7$ kcal/mole, $\log A_{\pm,Cs^+} = 5.35\ M^{-1}\ \text{sec}^{-1}$

Determinations of the intercepts, *i.e.*, of $k_\pm$, are important to some of our conclusions. To minimize the uncertainties of the extrapolation, these studies were extended to as low values of *f* as were feasible. The results of experiments performed with sodium polystyrene having two living ends agreed with those in which polymers endowed with one growing end were employed.

In dealing with the cesium salt of living polystyrene, it is imperative to assure that the preparation contains only the polymers endowed with one growing end. The two-living-ends cesium polymers are intramolecularly associated, and this appreciably affects their conductance and reactivity.[1b,8]

Polymerization of $\sim\!S^-,Cs^+$ is relatively slow; hence, the addition of cesium tetraphenylboride was superfluous. The results are summarized in Table V. The plots of k_p (apparent) *vs.* $1/[\sim\!S^-,Cs^+]^{1/2}$ were linear,

---

[9] (a) H. Hostalka and G. V. Schulz, *Z. Physik. Chem.* (Frankfurt), **45,** 286 (1965); (b) H. Hostalka, R. V. Figini, and G. V. Schulz, *Makromol. Chem.*, **71,** 198 (1964).

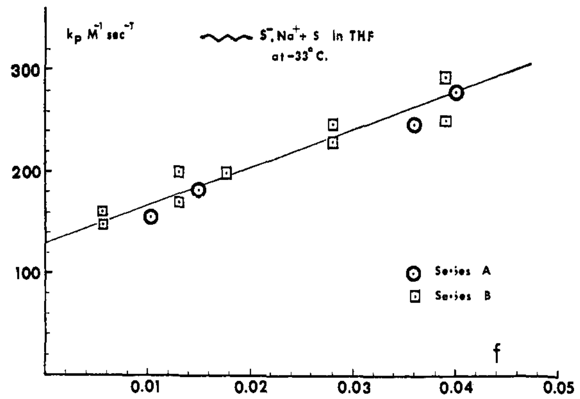


Figure 7. Plot of the apparent rate constant of propagation of $\sim S^-,Na^+$ in THF at $-33°$ *vs.* f (fraction of free ions): ⊙, series A; ⊡, series B.

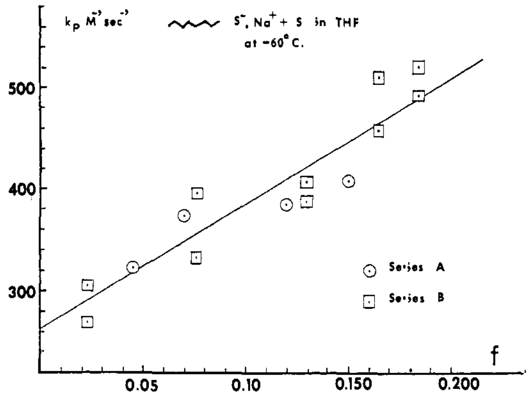


Figure 8. Plot of the apparent rate constant of propagation of $\sim S^-,Na^+$ in THF at $-60°$ *vs.* f (fraction of free ions): ⊙, series A; ⊡, series B.

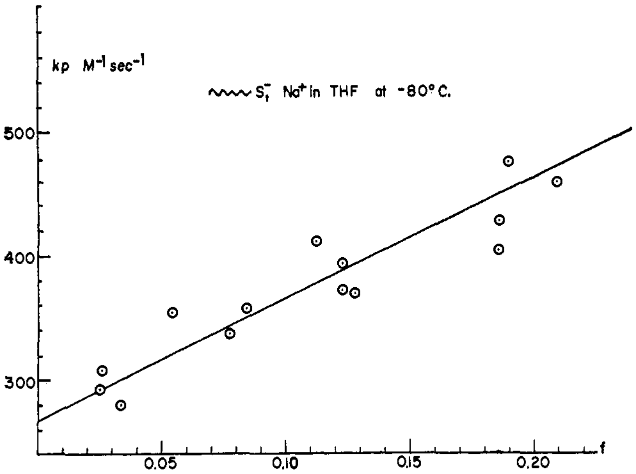


Figure 9. Plot of the apparent rate constant of propagation of $\sim S^-,Na^+$ in THF at $-80°$ *vs.* f (fraction of free ions). The high value of the intercept seems to be indisputable.

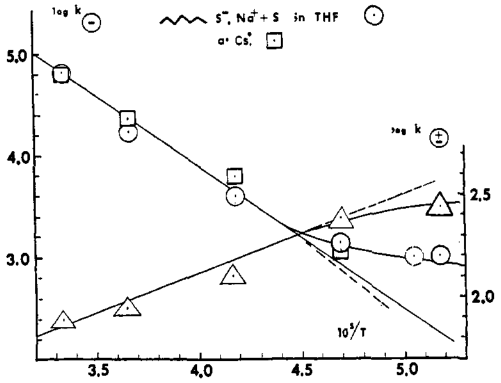


Figure 10. Arrhenius plots of k_- (propagation constant of the free $\sim S^-$ ions) and of $k_{\pm,Na^+}$ (propagation constant of the $\sim S^-,Na^+$ ion pairs) in THF: ⊙, k_- values derived from the studies of the sodium salt; ⊡, k_- values derived from the studies of the cesium salt; △, $k_{\pm,Na^+}$. The deviation at the lowest temperatures from the linear relation are not surprising. On the whole, such deviations are observed for many ionic reactions in solution if studied over a sufficiently large range of temperatures.

and from their intercepts and slopes the respective values of k_- and $k_\pm$ for the cesium ion pairs were calculated. These are given in Table VI together with the analogous data derived from the studies of the sodium salts. The agreement between the k_- constants calculated from both sets of experiments (Na^+ and Cs^+) is most satisfactory.

Discussion

a. Conclusions from the Studies of Conductance. The conductance data show striking differences in the behavior of the sodium and cesium salts of living polystyrene in THF. At 25° the dissociation constant of the former salt is about 30 times larger than that of the latter. Moreover, the exothermicity of the dissociation, $-\Delta H$, is 8.2 kcal/mole for $\sim S^-,Na^+$, decreasing to about 5–6 kcal/mole at -60 or $-70°$, whereas for the cesium salt the corresponding values are 1.8 and 0.9 kcal/mole, respectively. Studies of the conductance of sodium and cesium tetraphenylborides[5] showed that the free sodium ions are coordinated with THF molecules while the free cesium cations are not. The association of the latter with anions leads, therefore, only to contact ion pairs, and their dissociation provides no additional gain in energy arising from the coordination of the solvent with the cation. The heat of dissociation of cesium polystyrene may be calculated, therefore, from Ramsey's equation,[10] *viz.*

$$\Delta H = (Ne^2/Da)(1 + \mathrm{d}\ln D/\mathrm{d}\ln T)$$

and this leads to the separation distance at contact, a, of about 4.1 A. The Stokes radius of Cs^+ in THF was found to be[5] 2.2 A, while its crystal radius is 1.7 A. Therefore, a reasonable value of about 2 A is obtained for the effective radius (or half-thickness) of the -CH-(Ph)⁻ ion.

The high heat of dissociation of $\sim S^-,Na^+$ proves that this species forms, also, a contact ion pair, at least in the temperature region of -30 to $+25°$, which, however, dissociates into a THF-coordinated sodium ion. This substantially increases the exothermicity of dissociation of the sodium salt when compared with the cesium. Similar results were reported for the salts of fluorenyl carbanion[11] and for the tetraphenylethylene dianion.[12]

---

(10) J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, 77, 2615 (1955).

(11) T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 318 (1966).

(12) R. C. Roberts and M. Szwarc, *ibid.*, 87, 5542 (1965).

The decrease in the heat of dissociation at lowest temperatures may be attributed to the partial conversion to a solvent-separated ion pair.[11] According to this interpretation the fraction, γ, of solvent-separated ion pairs at −70° may be computed from the equation

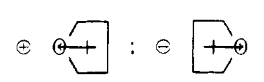
$$-\Delta H_{\mathrm{dis}}(\text{at } -70°) = 6 = (1-\gamma)8.2 + \gamma\Delta H''$$

where $\Delta H''$ is the heat of dissociation of solvent-separated pairs. The most probable value of the latter is 1–2 kcal/mole (see ref 11 and 13), and hence, $\gamma \approx 0.3$ at −70°. The heat or entropy of any process involving ions in solution need not, however, be constant if the process is studied over a sufficiently wide range of temperatures.

b. Discussion of the Kinetic Data. The propagation constant of the polystyryl anion is much greater than that of the corresponding free radical; *e.g.*, the respective rate constants are 65,000 and 27 M^{-1} sec^{-1} at 25°. Two factors contribute to this result: (1) the activation energy of the free-anion propagation (5.9 kcal/mole) is lower than that of the free radical (~7.8 kcal/mole[14]); (2) the entropy of activation is less negative for the former process ($A \sim 10^9$ M^{-1} sec^{-1}) than for the latter[14] ($A \sim 10^7$ M^{-1} sec^{-1}).

The lower activation energy could be expected. The approaching monomer is polarized by the anion, and this generates a relatively long-range attraction force, reducing the repulsion responsible for the potential-energy barrier. The larger A factor is also plausible. The negative charge of the anion becomes dispersed in the transition state. Consequently, the degree of polarization of the neighboring solvent molecules is reduced, increasing, thereby, the entropy of the system. Moreover, the incipient C–C bond in the transition state of the ionic propagation is probably longer than in the radical addition, and this increases the freedom of the attached monomer molecule. The combined effects increase ΔS by about 9 eu.

Negative ions are not *coordinated* with THF molecules,[13] whereas a strong coordination is observed, *e.g.*, for Na$^+$ ions.[5] This is explained by the following diagram.



The dipole is associated with the O atom and it approaches closely the positive, but not the negative, ion. Consequently, the nature of the ether is expected to affect only slightly the reactivity of the $\sim$S$^-$ ion, and indeed k_- at 25° was found to be 60,000 M^{-1} sec^{-1} in a 50:50 THF-dioxane mixture,[15] 40,000–80,000 M^{-1} sec^{-1} in a series of THF-benzene mixtures[16] (dielectric constant changing from 4.6 to 5.8), 60,000–70,000 M^{-1} sec^{-1} in THF, and apparently about 20,000 M^{-1} sec^{-1} in methyltetrahydrofuran.[17]

The propagation constant, $k_\pm$, of ion pairs is greatly affected by the nature of counterion and solvent. For example, at 25°, $k_\pm$ (in M^{-1} sec^{-1}) for $\sim$S$^-$,Na$^+$ was found to be about 80–90 in THF, 3–6 in dioxane,[18–20] about 10 in tetrahydropyran,[21] and 11 in methyltetrahydrofuran.[17] Interestingly, much smaller variations were found for the cesium salt. Thus, in THF $k_\pm$ is 20–25 M^{-1} sec^{-1} (this work and ref 1b), again about 15–25 M^{-1} sec^{-1} in dioxane,[19,20] and 49 M^{-1} sec^{-1} in tetrahydropyran.[20]

The striking difference between the propagation of $\sim$S$^-$,Cs$^+$ and $\sim$S$^-$,Na$^+$ is revealed by the temperature dependence of their rate constants. The behavior of the Cs$^+$ ion pair is normal, the rate constant decreases with decreasing temperature, and the activation energy appears to be about 5.7 kcal/mole corresponding to a low A factor of $\sim 2 \times 10^5$ M^{-1} sec^{-1}. This value compares reasonably well with E = 6–9 kcal/mole reported for $\sim$S$^-$,Na$^+$ in dioxane,[18,20] or with E = 5–6 kcal/mole reported for $\sim$S$^-$,Cs$^+$ in dioxane[20] and tetrahydropyran.[20] On the other hand, $k_\pm$ for the sodium salt in THF *increases* with decreasing temperature (see Figure 10), its value being ~80 at +25° and ~270 at −80°.

c. The "Negative" Activation Energy of $\sim$S$^-$,Na$^+$ Propagation. The potential-energy barrier for any elementary process cannot be negative; and, therefore, a "negative" activation energy must indicate some complexity of the process. At least three possibilities should be considered.

(1) The reaction A + B → C proceeds by two steps: a fast reversible complex formation producing minute amounts of (AB), the equilibrium constant being K_a

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{(AB)}$$

and a rate-determining unimolecular rearrangement, having rate constant k_r.

$$\mathrm{(AB)} \longrightarrow \mathrm{C}$$

The over-all rate constant, k, is given then by the equation $k = K_a k_r$, and if the complex formation is exothermic, *viz*, ΔH_a is negative, and $-\Delta H_a > E_r$, then the over-all "activation energy" would be negative, too.

(2) One of the reagents, say A, forms a mixture of two species, say A′ and A″, which coexist in a rapidly established equilibrium. The over-all reaction is determined, therefore, by two simultaneous reactions

$$\mathrm{A}' + \mathrm{B} \longrightarrow \mathrm{C}\ (\text{or } \mathrm{C}')\quad k'$$

$$\mathrm{A}'' + \mathrm{B} \longrightarrow \mathrm{C}\ (\text{or } \mathrm{C}'')\quad k''$$

in conjunction with the equilibrium

$$\mathrm{A}' \rightleftarrows \mathrm{A}''\quad K_s$$

The above rearrangement may or may not involve solvent. The apparent rate constant, k, of such a reaction is given by

$$k = \gamma k' + (1-\gamma)k'' = k'/(1+K_s) + K_s k''/(1+K_s)$$

where γ and $1-\gamma$ denote the fractions of A′ and A″ at equilibrium. For $k' \ll k''$ and for a not too small K_s, this approximates to

$$k = K_s k''/(1+K_s)$$

An apparent negative activation energy is observed if ΔH_s is negative and E'' sufficiently low.

---

(13) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, 70, 3180 (1966).

(14) M. S. Matheson, E. E. Auer, E. B. Berilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, 73, 1700 (1951).

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

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

(17) Unpublished results from this laboratory.

(18) (a) G. Allen, G. Gee, and C. Stretch, *J. Polymer Sci.*, **48**, 189 (1960); (b) C. Stretch and G. Allen, *Polymer*, **2**, 151 (1961).

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

(20) F. S. Dainton, *et al.*, *Makromol. Chem.*, **89**, 257 (1965).

(21) W. K. R. Barnikol and G. V. Schulz, *ibid.*, **86**, 298 (1965).

(3) The rate of a reaction in solution, and especially of an ionic reaction, depends on solvent; a large change may be observed when the environment is modified. In the language of transition-state theory, one explains the solvent effect in terms of solvation of the initial and the transition state.

Temperature affects the properties of solvents and, therefore, a solvent at 25° forms a very different medium than the same solvent at, say, −75°. Therefore, the potential energy barrier at 25° may be higher than at −75°; *e.g.*, if it amounts to 8 kcal/mole at the former temperature and to 5 kcal/mole at the latter, the rate would increase by a factor of 3. Hence, a "negative" activation energy may reflect, *e.g.*, an increasing degree of solvation of the transition state at lower temperature.

Let us apply these approaches to the kinetics of $\sim\!\sim\mathrm{S}^-,\mathrm{Na}^+$ propagation.

(1) The first hypothesis may be interpreted in terms of the following mechanism

$$\sim\!\sim\mathrm{S}^-,\mathrm{Na}^+ + \mathrm{S} \rightleftarrows \sim\!\sim\mathrm{S}^-(\mathrm{Na}^+\mathrm{S})$$

$$\sim\!\sim\mathrm{S}^-(\mathrm{Na}^+\mathrm{S}) \longrightarrow \sim\!\sim\mathrm{SS}^-,\mathrm{Na}^+$$

S denotes here styrene and ($\mathrm{Na}^+\mathrm{S}$) a sodium ion (or ion pair) coordinated with styrene. This type of mechanism has been considered by several workers,[22] but no sound evidence in its favor was provided yet. Spectrophotometric studies of Dr. Subhash in this laboratory failed to reveal any complex formation between styrene and sodium or lithium salts even at temperatures as low as −80°.

(2) The second hypothesis is the most attractive in view of other findings reported from this laboratory. It was shown[23] that the sodium salt of fluorenyl carbanion exists in THF in two forms identified as contact and solvent-separated ion pairs. The two forms are recognized by their different optical spectra, the former absorbing at $\lambda_{\max}$ 356 mμ, the latter at 373 mμ.

Careful studies of the absorption spectra of concentrated ($\sim 10^{-2}$ M) solutions of $\sim\!\sim\mathrm{S}^-,\mathrm{Na}^+$ and $\sim\!\sim\mathrm{S}^-,\mathrm{Cs}^+$ in THF revealed that the former salt absorbs at $\lambda_{\max}$ 340 ± 2 mμ at 25° and at 347 ± 2 mμ at −80°, whereas the spectrum of the latter has an absorption maximum at 344 ± 2 mμ at 25° which only shifts to 346 ± 2 mμ at −80°. The concentration of free ions is negligible in either solution both at 25 and −80°. Hence, the spectroscopic evidence, although not quite conclusive, supports the hypothesis of solvent-separated $\sim\!\sim\mathrm{S}^-,\mathrm{Na}^+$ ion pairs.

Let us postulate that only the solvent-separated pair contributes appreciably to the polymerization. The argument presented a part a of the Discussion suggests that the fraction of solvent-separated ion pairs is 0.3–0.4 at −70°, leading to a K_s of about 2 and $k'' = 800$ M^{-1} sec^{-1}. The heat of conversion of contact into solvent-separated pairs is at least −6 kcal/mole; therefore, K_s must be much smaller than unity at 25°, and hence the observed "activation" energy of −1.5 kcal/mole is given by the equation, $-1.5 = E'' + \Delta H_s$.

Obviously, $-\Delta H_s$ is less than 8 kcal/mole, its most probable value being $\sim$7 kcal/mole; hence, $E'' \leqslant 6$ kcal/mole. However, it is implausible that E'' (activation energy of propagation of solvent-separated $\sim\!\sim\mathrm{S}^-,\mathrm{Na}^+$) is *lower* than E_- (activation energy of propagation of free $\sim\!\sim\mathrm{S}^-$ ions), and, therefore, $E'' \geqslant 6$ kcal/mole. It follows therefore that $E'' = E_-$ and the heat of dissociation of solvent-separated pairs is about −1 kcal/mole. Consequently, $K_s = 3 \times 10^{-3}$ at 25°, leading to $\gamma = 3 \times 10^{-3}$ and $k'' = 30{,}000$ M^{-1} sec^{-1}.

(3) The third approach is somewhat similar to the second. It implies that the reaction involves contact ion pair, but the transition state of propagation becomes progressively more solvated as the temperature is lowered. In essence, this approach visualizes a partial dissociation of ion pairs in the transition state, and the process is facilitated by coordination of the solvent with Na^+ ion. This effect does not operate in the propagation of the cesium salt, because even a free Cs^+ ion is not coordinated with THF.

In conclusion, according to the second approach the enhanced reactivity of $\sim\!\sim\mathrm{S}^-,\mathrm{Na}^+$ at low temperatures is attributed to the presence of a highly reactive, thermodynamically distinct species, *viz.*, solvent-separated ion pairs, the proportion of which increases on lowering the temperature of polymerization. According to the last hypothesis, an increase in the degree of solvation of the transition state, resulting in a gradual lowering of the potential-energy barrier, accounts for the increase in the $k_\pm$ with decreasing temperature. Finally, it should be stressed that the concept of contact and solvent-separated ion pairs as distinct thermodynamic entities is restricted to some special situations;[13,24] there are others where such a distinction is not warranted.

Acknowledgment. The financial support of this investigation by the National Science Foundation and partially by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

---

[22] See, *e.g.*, (a) C. M. Fontana and G. A. Kidder, *J. Am. Chem. Soc.*, **70**, 3745 (1948); (b) G. V. Rakova and A. A. Korotkov, *Dokl. Akad. Nauk SSSR*, **119**, 982 (1958); (c) Y. L. Spirin, A. R. Gantmakher, and S. S. Medvedev, *Vysokomolekul. Soedin.*, **1**, 1258 (1959); (d) Yu. L. Spirin, A. A. Arest-Yakubovich, D. K. Polyakov, A. R. Gantmakher, and S. S. Medvedev, *J. Polymer Sci.*, **58**, 1181 (1962).

[23] T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).

[24] M. Szwarc, *Makromol. Chem.*, **89**, 44 (1965).