then the solution was diluted to the mark with water. The absorbance at 454 nm[16] was used to determine the concentration of Cu^{2+}

After the adsorption experiment, the column was washed with 200 ml of water. An eluting agent (1 *N* HCl aqueous solution) was passed through the column at a flow rate of SV 2.5. The content of Cu^{2+} in every 10 ml of eluate was determined by chelatometry.

Acknowledgment. This work was supported by a Grant in Aid for Scientific Research, the Ministry of Education, Japan. The authors are grateful to the Mitsubish Chemical Industries Co. Ltd. for a gift of cross-linked PSt-CH_2Cl samples.

References and Notes

(1) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, **3**, 35 (1972).
(2) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 108 (1972).
(3) D. A. Tomalia and D. P. Sheetz, *J. Polym. Sci., Part A-1*, **4**, 2253 (1966).
(4) T. Saegusa, H. Ikeda, S. Kobayashi, and A. Yamada, unpublished results.
(5) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, **4**, 87 (1973).
(6) T. Saegusa and H. Ikeda, *Macromolecules*, **6**, 808 (1973).
(7) T. Saegusa, S. Kobayashi, and A. Yamada, to be reported.
(8) M. Litt, *J. Macromol. Sci., Chem*, in press.
(9) G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950).
(10) H. Egawa and H. Saeki, *Kogyo Kagaku Zasshi*, **74**, 772 (1971).
(11) H. Egawa and K. Sugahara, *Kogyo Kagaku Zasshi*, **74**, 1026 (1971).
(12) H. Egawa and M. Takehara, *Nippon Kagaku Kaishi*, 1786 (1973).
(13) I. Noda and T. Kagawa, *Kogyo Kagaku Zasshi*, **66**, 854 (1963).
(14) Y. Ubemiya, T. Tabata, and H. Hisayama, *Kobunshi Kagaku*, **25**, 419 (1968).
(15) C. H. Bamford and H. Lindsay, *Polymer*, **14**, 330 (1973).
(16) G. F. Smith and W. H. McCurdy, *Anal. Chem.*, **24**, 371 (1952).

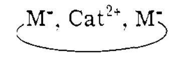
Anionic Polymerization of the Barium Salt of One-Ended Living Polystyrene. I. Conductance and Kinetic Studies

B. De Groof, M. Van Beylen,* and M. Szwarc[1]

University of Leuven, Laboratory of Macromolecular and Organic Chemistry, B-3030 Heverlee, Belgium. *Received February 13, 1975*

ABSTRACT: The barium salt of *one-ended* living polystyrene was prepared by converting on a barium mirror dibenzylmercury into dibenzylbarium; the latter was reacted with α-methylstyrene and the resulting oligomer with styrene. This procedure yields the required salt. The conductance of the barium polystyryl was determined in THF in the temperature range −70 to +20°. The results indicate that two equilibria are simultaneously maintained: $Ba^{2+},(\text{poly-S}^-)_2 \rightleftarrows Ba^{2+},(\text{poly-S}^-) + \text{poly-S}^-$ (K_1) and $2Ba^{2+},(\text{poly-S}^-)_2 \rightleftarrows Ba^{2+},(\text{poly- S}^-) + Ba^{2+},(\text{poly-S}^-)_3$ (K_2), and for all the investigated temperatures the values of K_1 and K_2 were calculated from the experimental data. The propagation involving the free poly-S^- anions accounts for the observed kinetics of polymerization, the contribution of the other species to the reaction being negligible. This mechanism predicts, in accordance with our observations, that the pseudo-first-order rate constant of propagation is virtually independent of the total concentration of the salt and provides, therefore, an alternative explanation of the results reported earlier by Francois et al.

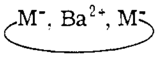
It is well established[2] that several distinct reactive species are involved in the propagation of alkali salts of living polymers. For example, in ethereal solvents ion pairs, $—M^-,Cat^+$, as well as the free $—M^-$ anions, contribute to the propagation,[3-5] and the contribution of intra- or intermolecular triple ions has been observed[6-9] at least in some of the investigated systems. The behavior of the alkaline-earth salts of living polymers is less documented. Their description requires a sharp delineation between the salts formed from polymers endowed with two growing end groups and those possessing one living end group only. The former may exist either in a cyclic form



M^-, Cat^{2+}, M^-

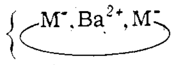
or as polymer-linked aggregates, $—M^-,Cat^{2+},M^-—M^-,Cat^{2+},M^-—$, etc., whereas the latter are composed from two living polymers linked to one bivalent cation, i.e., $\{X—M^-,Cat^{2+},{}^-M—X\}$.

Kinetic studies of polymerization of the barium salt of living polystyrene have been reported recently by Francois and his coworkers.[10] They claim that their system involves polymers terminated by carbanions on both of their ends and that the salt is cyclic in nature. The rate of propagation in THF, studied over a wide range of temperatures, was found to be independent of living end concentration when the latter was varied by two powers of ten, i.e., from about 10^{-5} to 10^{-3} *M*. This observation was accounted for by a mechanism postulating the existence of a minute fraction of single cyclic species, viz.



M^-, Ba^{2+}, M^-

which remain in equilibrium with large aggregates



$\{M^-,Ba^{2+},M^-\}_n$

However, our study of the polymerization of the barium salt of living polystyrene endowed with one growing end casts some doubt on their suggestion and leads to an alternative explanation for their findings. Moreover, our results allow us to compare the reactivities of the neutral salt, $Ba^{2+}(M^-—X)_2$, and of the pair $(X—M^-),Ba^{2+}$ with that of the free $X—M^-$ anions.

Preparation of the Barium Salt of One-Ended Living Polystyrene. The preparation involves three steps. (1) Conversion of mercury dibenzyl into barium dibenzyl, $Ba^{2+}(PhCH_2^-)_2$, by prolonged contacting of a THF solution of $Hg(PhCH_2)_2$ with a barium mirror freshly prepared in vacuum according to the procedure of Sigwalt et al.[11] The yield is quantitative. After filtering the resulting solution from the excess of metallic barium its spectrum was examined (λ_{max} = 343 nm and the decimal $\epsilon = 1.31 \times 10^4$ per mol of $PhCH_2^-$ anions).

(2) The addition of a 3.5-fold excess of α-methylstyrene (α-MeS) to the solution of $Ba^{2+}(PhCH_2^-)_2$ yields the barium salt of living α-MeS oligomer, $Ba^{2+}(PhCH_2\cdots\alpha\text{-MeS}^-)_2$. Although the reacting mixture was kept for 20 hr at 40°, about 5% of the benzyl carbanions and 10% of the added α-MeS were left unreacted. The presence of the unreacted $PhCH_2^-$ anions was revealed by the formation of toluene

Table I
Conductance of the Barium Salt of One-Ended Living Polystyrene, $Ba^{2+},(poly\text{-}S^-)_2$, in THF[a]

Ser	[Ba salt] × 10^4, M	Λ, cm^2 mol^{-1} Ω^{-1}	Ser	[Ba salt] × 10^4, M	Λ, cm^2 mol^{-1} Ω^{-1}
		$T = 20°$			
A	5.12	0.124 (0.093)[b,c]	A	0.50	0.156
B	3.48	0.120	B	0.296	0.193
A	2.3	0.124	A	0.236	0.180
B	1.64	0.138	B	0.164	0.223 (0.249)[b]
A	1.11	0.139	A	0.106	0.239
B	0.96	0.150	B	0.081	0.272
B	0.58	0.154 (0.174)[b]	A	0.050	0.313 (0.355)[b]
			B	0.036	0.34
		$T = 0°$			
A	5.22	0.124	A	0.24	0.160
A	2.36	0.128	A	0.11	0.209
A	1.18	0.130	A	0.051	0.264
A	0.50	0.140			
		$T = -20°$			
A	5.42	0.113	A	0.26	0.121
A	2.44	0.110	A	0.11	0.153
A	1.18	0.108	A	0.052	0.168
A	0.52	0.114			
		$T = -40°$			
A	5.56	0.0905	A	0.27	0.089
A	2.60	0.0803	A	0.12	0.105
A	1.22	0.0810	A	0.053	0.140
A	0.53	0.0849			
		$T = -60°$			
A	5.76	0.0634	A	0.27	0.0637
A	2.64	0.0582	A	0.13	0.0755
A	1.26	0.0580	A	0.054	0.101
A	0.544	0.0612			

[a] Approximate $M_n = 4000$ was determined by vapor-pressure osmometry after protonation of the salt. [b] The values in parentheses refer to the equivalent conductances of the polymers prepared by Francois et al., who reacted styrene with highly dispersed metallic barium. The conductance was determined at 25° (unpublished data of Francois et al. kindly provided to us). [c] Determined at the salt concentration of 4.43×10^{-4} M.

when alcohol was added to an aliquot of the solution of $Ba^{2+},(PhCH_2\cdots\alpha\text{-}MeS^-)_2$. The barium salt of α-MeS oligomer absorbs again at $\lambda_{max} = 343$ nm but the decimal $\epsilon = 0.6 \times 10^4$ per mol of $PhCH_2\cdots\alpha\text{-}MeS^-$ anion. The lower ϵ of the living α-MeS$^-$ oligomer, when compared with that of the $PhCH_2^-$ salt, is due to a broader absorption band of the former than of the latter.

(3) The salt of the α-MeS$^-$ oligomer was converted into the barium salt of one-ended living polystyrene, $Ba^{2+}(poly\text{-}S^-)_2$, by five successive additions of styrene to its THF solution. An eightfold excess of styrene was added in each step, and the residual α-MeS, present in the original solution of the living oligomer, was consumed in this process. The absorption maximum of $Ba^{2+}(poly\text{-}S^-)_2$ is at 360 nm, the decimal $\epsilon = 1.25 \times 10^4$ per mol of poly-S$^-$, being similar to that of $Ba^{2+}(PhCH_2^-)_2$.

The bathochromic shift of the λ_{max} of $Ba^{2+}(poly\text{-}S^-)_2$ when compared with the λ_{max} of the free poly-S$^-$ anion is contrary to expectation. However, the preparation involving 1,1-diphenylethylene instead of α-MeS as the intermediate led to the same result, and virtually an identical value of $\lambda_{max} = 359$ nm was reported by Francois et al.,[10] who prepared the barium salt of living polystyrene by reacting the THF solution of styrene with a highly dispersed metallic barium. No explanation of this anomaly is offered at present.

Results

Conductance Measurements. Conductances were determined in high vacuum in an all-glass apparatus, carefully purged with a concentrated solution of $Ba^{2+},(poly\text{-}S^-)_2$ and repeatedly rinsed by condensing the solvent on its walls through external cooling. Conductances were measured for a series of concentrations using a Wayne Kerr B221A universal bridge operating at 1592 cycles per second. For each concentration the measurements were made over a temperature range, from −70 up to +20°. Concentrations were varied in the usual way by the technique of internal dilution described elsewhere[2] and their values were determined spectrophotometrically at 360 nm, accepting the extinction coefficient mentioned previously. The experimental data are collected in Table I and displayed graphically in Figure 1, the procedure of Kraus and Bray being adopted. Two series of measurements, denoted by A and B, were carried out on two separately prepared batches of $Ba^{2+},(poly\text{-}S^-)_2$.

The deviation from linearity is pronounced, and this is attributed to the formation of triple ions.

Kinetic Measurements. The kinetics of polymerization was studied spectrophotometrically using a Cary 17 instrument, the disappearance of the monomer being monitored by the decrease of its optical density at 291.5 nm (a characteristic peak of styrene). The details of the procedure and

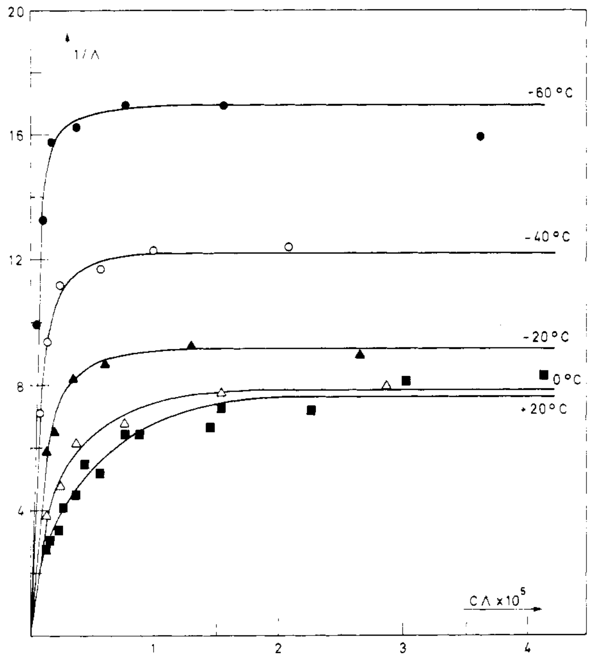


Figure 1. Kraus and Bray conductance plot for $Ba^{2+}(poly\text{-}S^-)_2$ at different temperatures in THF.

the apparatus used in the kinetic runs are given in ref 3.

The plots of log ($OD_t - OD_\infty$) vs. time are linear, their slope giving the pseudo-first-order rate constants k_{obsd} of the polymerization. It should be stressed at this point that k_{obsd} is obtained without recurrence to the concentration of active centers and that its value therefore is independent of the extinction coefficient or the way in which the concentration of $Ba^{2+},(poly\text{-}S^-)_2$ is expressed.

The pertinent results are summarized in Table II and a plot of the pseudo-first-order rate constants k_{obsd} as a function of the carbanion concentration is shown in Figure 2. In spite of some scatter, it seems justified to conclude that the value of k_{obsd} is independent of the concentration of active centers, provided that their concentration is higher than 10^{-5} *M*.

Discussion of the Conductance Data. The results reported here imply that the ionization of $Ba^{2+},(poly\text{-}S^-)_2$ is due not only to its dissociation into $Ba^{2+},(poly\text{-}S^-)$ cations and the free poly-S^- anions but also to the creation of $Ba^{2+},(poly\text{-}S^-)_3$ triple ions. Hence, two ionic equilibria have to be simultaneously maintained

$$Ba^{2+},(poly\text{-}S^-)_2 \rightleftharpoons Ba^{2+},(poly\text{-}S^-) + poly\text{-}S^- \quad (K_1) \quad (1)$$

and

$$2Ba^{2+},(poly\text{-}S^-)_2 \rightleftharpoons Ba^{2+},(poly\text{-}S^-) + Ba^{2+},(poly\text{-}S^-)_3 \quad (K_2) \quad (2)$$

It is advantageous to represent the formation of the triple ions by eq 2, rather than by the conventional equation

$$poly\text{-}S^- + Ba^{2+},(poly\text{-}S^-)_2 \rightleftharpoons Ba^{2+},(poly\text{-}S^-)_3$$

whenever only *one kind* of triple ions is produced. Equation 2 makes it obvious that the fraction of the salt converted into triple ions becomes independent of its nominal concentration, *C*, provided that *C* is sufficiently large to make insignificant the degree of dissociation (eq 1). In that range of concentrations the equivalent conductance, Λ, should remain constant and independent of *C*, its value being given by

$$\Lambda_l = \{K_2^{1/2}/(1 + K_2^{1/2})\}\lambda_0$$

where λ_0 is the sum of the limiting conductances of $Ba^{2+},(poly\text{-}S^-)$ and $Ba^{2+},(poly\text{-}S^-)_3$. Inspection of Table I shows that Λ is indeed independent of *C* for $C > 10^{-4}$ *M*, its value $\Lambda_l = 0.12$ cm^2 Ω^{-1} mol^{-1} at 20°.

The literature data[4a] permit us to estimate λ_0, viz., for our system $\lambda_0 \approx 25$ cm^2 Ω^{-1} mol^{-1}, and hence $K_2 \approx 2.5 \times 10^{-5}$ at 20°. In a similar way the values of K_2 at lower temperatures are calculated, using the Walden rule to determine the relevant λ_0's. The results are collected in Table III and displayed in Figure 3 in the form of a van't Hoff plot.

The dissociation constant K_1 may be calculated provided that we know the concentration C_i of the salt solution in which

$$[Ba^{2+},(poly\text{-}S^-)_3] = [poly\text{-}S^-]$$

since then $K_1 = K_2C_i$. At this concentration of the salt the equivalent conductance Λ_i is given by

$$\Lambda_i = f_i(\Lambda_0 + \lambda_0)$$

where f_i denotes the fraction of the salt converted into the free poly-S^- anions, i.e., $f_i = [poly\text{-}S^-]/C_i = [Ba^{2+},(poly\text{-}S^-)_3]/C_i = \frac{1}{2}[Ba^{2+},(poly\text{-}S^-)]/C_i$. It follows from eq 2 that

$$2f_i^2/(1 - 3f_i) = K_2$$

and for $3f_i \ll 1$ the approximation $f_i = (K_2/2)^{1/2}$ is valid. Since $K_2^{1/2} = \Lambda_l/\lambda_0$ one finds

$$\Lambda_i = \Lambda_l(1 + \Lambda_0/\lambda_0)/(2^{1/2})$$

The value Λ_0 is estimated to be 35 cm^2 Ω^{-1} mol^{-1} at 20° and therefore $\Lambda_i = 0.205$ cm^2 Ω^{-1} mol^{-1} since $\Lambda_l = 0.12$ cm^2 Ω^{-1} mol^{-1}. Using the data collected in Table I, one finds by interpolation the corresponding $C_i = 0.20 \times 10^{-4}$ *M* and

$$K_1 = K_2 \cdot C_i = 4.8 \times 10^{-10}\ M$$

Alternatively, the constants K_1 and K_2 may be calculated by applying a relation derived by Wooster[12] for the systems

Table II
Pseudo-First-Order Rate Constants of Polymerization at 20°

$C \times 10^4$, *M*	$k_{obsd} \times 10^3$, sec^{-1}	$C \times 10^4$, *M*	$k_{obsd} \times 10^3$, sec^{-1}
7.62	5.75	0.58	3.02
4.40	3.06	0.44	2.72
3.13	3.83	0.42	2.27
2.64	4.6	0.32	2.98
1.80	2.34	0.29	3.98
1.24	3.13	0.204	4.04
0.69	2.93	0.2	3.3
0.655	2.37		

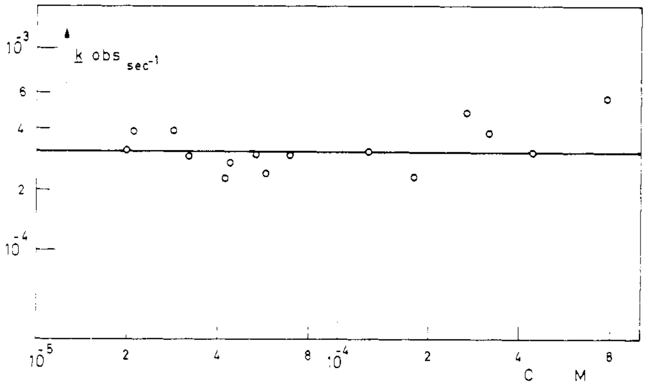


Figure 2. Plot of pseudo-first-order rate constant of propagation k_{obsd} of Ba salt of living polystyrene in THF vs. log of the concentration of $Ba^{2+},(poly\text{-}S^-)_2$ at 20°.

Table III
Equilibrium Constants K_1 and K_2 Computed on the Assumptions $\lambda_0 = 25$ and $\Lambda_0 = 35$ at 20°

T, °C	$K_1 \times 10^{+10}$, M	$K_2 \times 10^5$
+20	3.7 (4.8)	2.4
+10	3.9	2.9
0	3.9 (3.2)	3.9
−10	3.3 (3.3)	4.7
−20	3.2 (3.6)	5.1
−30	3.0 (3.5)	5.0
−40	2.5 (3.5)	5.0
−50	2.4 (3.7)	5.3
−60	2.4 (3.9)	5.5
−70	2.1 (4.0)	5.5

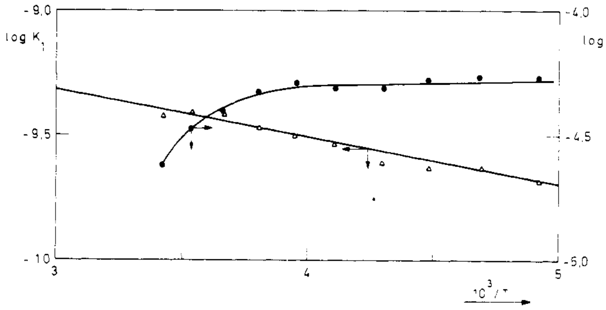


Figure 3. Temperature dependence of the dissociation constant K_1 and the constant of triple ion formation for $Ba^{2+},(poly\text{-}S^-)_2$ in THF: (●) K_2; (▵) K_1.

involving unilateral triple ions, viz.

$$C\Lambda^2 = \Lambda_0^2K_1 + (2\Lambda_0\lambda_0 - \Lambda_0^2)K_2C$$

This relation is valid for the concentrations C sufficiently large to make the fraction of the salt converted into ions appreciably smaller than 1, and it requires $(1 - \lambda_0/\Lambda_0)^2 \ll 2\lambda_0\Lambda_0 - 1$. For the λ_0 and Λ_0 values chosen for our system $(1 - \lambda_0/\Lambda_0)^2 = 0.08$ and $2\lambda_0\Lambda_0 - 1 = 0.43$, hence the Wooster approach seems acceptable since, as shown a posteriori, the fraction of the salt converted into the ions is less than 0.01 at the lowest concentration of the salt (3×10^{-6} M) used in this study.

A Wooster plot derived from the data obtained at 20° is shown in Figure 4. Its linearity is trivial because it reflects simply the constancy of Λ for $C > 1 \times 10^{-4}$ M, coupled with the smallness of the intercept. Nevertheless, the intercept is well determined since the linearity is retained down to the lowest investigated concentrations and the experimental points closely approach the y axis. For sufficiently low salt concentrations the Wooster plot has to curve and eventually it reaches the origin at $C = 0$. Therefore the linear extrapolation to $C = 0$ may be erroneous if the deviations from the linearity occur at too high concentrations. The value of the intercept provides us with K_1 subject only to the uncertainty of our estimate of Λ_0. The K_1 values obtained by this procedure are listed in Table III and presented graphically in Figure 3, whereas those derived by the previously outlined method are given in the same column in parentheses.

The reliability of the computed values of K_1 and K_2 should be examined. Our first method of determining K_2 leads to an uncertainty arising from the uncertainty in our estimate of λ_0. The chosen value is reliable within 25% or less, and hence the reliability of K_2 determined by the first method is better than 50%. In contrast, the uncertainty of 25% in our estimate of λ_0 and Λ_0 affects the slope of the Wooster line and therefore also K_2 determined by that method by ~150%. Nevertheless, K_1 determined from the Wooster plot is reliable within less than 50%, while the alternative method may lead to errors as large as 200% due to sensitivity of C_i on the value of Λ_i.

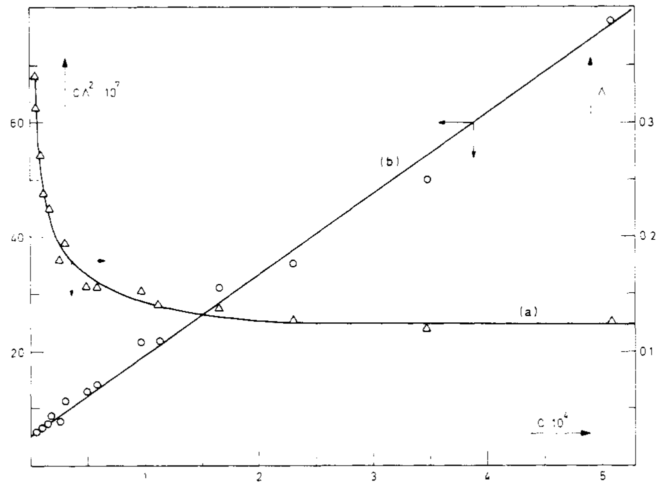


Figure 4. (a) Plot of equivalent conductance as a function of concentration for $Ba^{2+},(poly\text{-}S^-)_2$. (b) Wooster plot for unilateral triple ion formation in the system $Ba^{2+},(poly\text{-}S^-)_2$

Discussion of the Kinetic Data. The pseudo-first-order rate constants, k_{obsd}, listed in Table II and shown graphically in Figure 2, seem to be independent of the concentration of the barium salt when the latter is varied from 2×10^{-5} to 7×10^{-4} M. This remarkable behavior of the polymerization was observed previously by Francois et al.[10]

Four distinct species might contribute to the investigated polymerization: $Ba^{2+},(poly\text{-}S^-)_2$; $Ba^{2+},(poly\text{-}S^-)$; $Ba^{2+},(poly\text{-}S^-)_3$; and the free poly-S⁻ anions. Let us denote by k_0, k_1, k_2, and k_- the respective bimolecular rate constants of propagation, and introduce the notation

$$f = [\text{poly-S}^-]/C$$

$$g = [\text{Ba}^{2+}, (\text{poly-S}^-)]/C$$

$$h = [\text{Ba}^{2+}, (\text{poly-S}^-)_3]/C$$

The condition of electric neutrality requires $g = f + h$, and the stoichiometry demands $(1 - f - 2h)C$ to be the concentration of the un-ionized salt.

Since the equilibria 1 and 2 have to be maintained

$$fgC = K_1(1 - f - 2h)$$

$$gh = K_2(1 - f - 2h)^2$$

The conductance studies indicate that $1 - f - 2h \approx 1$ under the conditions of our kinetic investigations and therefore $fgC = K_1$, $gh = K_2$, and $f + h = g$. Solution of these equations leads to

$$f = K_1/C(K_1C + K_2)^{1/2}$$

$$g = (K_1/C + K_2)^{1/2}$$

and

$$h = K_2/(K_1/C + K_2)^{1/2}$$

and therefore

$$k_{obsd}/C = k_0 + (K_1/C + K_2)^{1/2}k_1 + \{K_2/(K_1/C + K_2)^{1/2}\}k_2 + \{K_1/C(K_1/C + K_2)^{1/2}\}k_-$$

The kinetic results obtained in the presence of barium tetraphenylboride, $Ba^{2+}(BPh_4^-)_2$, to be reported later, demonstrate that the contribution to the polymerization of all the species but the free polystyryl anions is negligible, and hence

$$k_{obsd} = \{K_1/(K_1/C + K_2)^{1/2}\}k_-$$

Thus, in agreement with our results k_{obsd} is virtually independent of the concentration of the barium salt because within the investigated range of concentrations $K_1/C \ll K_2$. Substituting the values of K_1 and K_2 derived in the preceeding section and accepting[4a] $k_- = 55{,}000\ M^{-1}\ sec^{-1}$ at 20°, we obtain

$$k_{obsd} \approx 3.8 \times 10^{-3}\ sec^{-1}$$

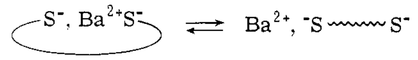
in satisfactory agreement with our observations.

Comparison of the Findings of Francois et al. with Those Reported in This Paper. The results of Francois et al.[10] compare remarkably well with our findings in spite of the great differences in the preparation methods of the barium salts used by both groups. Our method of synthesis of the barium salt of living polystyrene leaves no doubt that the investigated polymers possess only one carbanion per chain. In contrast, the technique used by Francois et al. could yield polymers endowed with two carbanions terminating each chain provided that the initiation arises from electron transfer to monomer followed by the dimerization of the resulting radical ions. It may be questioned whether this initiation mechanism is operative in Francois' system. For example, the barium salt of styrene radical anions formed by the electron transfer from the highly dispersed metal may undergo hydrogen transfer instead of dimerization, viz.

$$(CH_2{:}CHPh)\cdot^-, Ba^{2+}, (CH(Ph){:}CH_2)\cdot \longrightarrow CH_3\cdot C^-H(Ph), Ba^{2+}, C^-(Ph){:}CH_2$$

and the resulting carbanions could propagate then in the usual way yielding barium salt of one-ended living polystyrenes. Our suggestion is spurred by the great similarity of the behavior of our salt and that directly formed from metallic barium. The absorption spectra and the extinction coefficients are identical for both salts. They induce polymerization with virtually the same rate ($-d(\ln S)/dt$), which is independent of the concentration of the barium salt. The results given in Table I indicate that the equivalent conductance is also closely similar for both systems. It is improbable that all these similarities are fortuitous and that the two systems are different.

The structure of the barium salt proposed by Francois et al. is at variance with their conductance data. Their model visualizes the barium cation as being associated with two terminal carbanions of one bifunctional polystyrene chain. The resulting cyclic units are assumed to be combined into large and unreactive aggregates which remain in equilibrium with the "monomeric" species, the latter representing only a small fraction of the barium salt. The polymerization is induced by the monomeric units which may be present in a closed or open form



$$S^-, Ba^{2+}S^- \rightleftharpoons Ba^{2+}, {}^-S \sim\sim\sim S^-$$

but which could not dissociate into free ions as implied in their paper.[10] Although such a model accounts for the reported kinetics of polymerization, it would be difficult to see how it explains the observed conductance. Even if the open form of the cyclic monomers had contributed to conductance, an unlikely assumption, then the latter should remain constant and independent of the salt concentration, i.e., the *equivalent* conductance should decrease like the total salt concentration. This conclusion is not borne out by their results; Λ decreases only by a factor of 4 as the salt concentration decreases by a factor of 100.

In conclusion, our approach furnishes an alternative way to account for the results of Francois, as well as for our own findings, provided that the barium salt prepared by Francois et al., like our salt, is composed of one-ended living polystyrenes. In addition, it rationalizes the conductance data obtained in both studies.

Note Added in Proof. It has been pointed out to us by Francois[13] that their barium polystyryl was obtained not by direct reaction of the monomer with the barium metal but by reacting α-methylstyrene with the metal and subsequently adding styrene to the supposedly dicarbanionic living oligomer of α-methylstyrene. Our interpretation that the barium salt of Francois et al., like ours, is composed of one-ended living polystyrenes is nevertheless sustained and even corroborated by the observation made by Francois et al., that side reactions such as hydride transfer occurring during the reaction of α-methylstyrene on the metal lead to important amounts of monocarbanionic species especially for extended reaction times. Thus they detected by combined gas chromatography mass spectrometry the presence of such species as $C(CH_3)(Ph){:}CH\cdot CH_2\cdot CH(CH_3)(Ph)$ and higher unsaturated oligomers corrsponding to the terminated products of monocarbanionic living oligomers of α-methylstyrene.

Acknowledgment. The support for the equipment and for a fellowship to one of us (B.D.G.) by the Belgian Ministry of Scientific Programing is gratefully acknowledged.

References and Notes

(1) Visiting professor at the University of Leuven.

(2) M. Szwarc, "Carbanions, Living Polymers and Electron-Transfer Processes", Interscience, New York, N.Y., 1968.

(3) (a) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965); (b) H. Hostalka and G. V. Schulz, *Z. Phys. Chem. (Frankfurt am Main)*, **45**, 286 (1965).

(4) (a) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 796 (1967); (b) T. Shimomura, J. Smid, and M. Szwarc, *ibid.*, **89**, 5743 (1967).

(5) M. Van Beylen, M. Fisher, J. Smid, and M. Szwarc, *Macromolecules* **2**, 575 (1969).

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

(7) D. Honnore, J. C. Favier, M. Fontanille, and P. Sigwalt, *Eur. Polym. J.*, **10**, 425 (1974).

(8) G. Kargier, M. Tardi, and P. Turq, *Eur. Polym. J.*, **10**, 809 (1974).

(9) J. Leuridan and M. Van Beylen, Preprints XXIII IUPAC International Symposium on Macromolecules, Vol. 1, Madrid, 1974, p 137.

(10) C. Mathis, L. Lamande-Christmann, and B. Francois, Preprints XXIII IUPAC International Symposium on Macromolecules, Vol. 1, Madrid 1974, p 145; *Makromol. Chem.*, **176**, 931 (1975).

(11) J. C. Favier, M. Fontanille, and P. Sigwalt, *Bull. Soc. Chim. Fr.*, 526 (1971).

(12) C. B. Wooster, *J. Am. Chem. Soc.*, **59**, 377 (1937).

(13) B. Francois, private communication.