$\Delta H_2^{\ddagger} = 0.1$ kcal/mol, $\Delta S_1^{\ddagger} = -3.3$ eu, $\Delta S_2^{\ddagger} = 0.7$ eu; 1-*tert*-butylbutadiene (M_2) $\Delta H_1^{\ddagger} = -1.0$ kcal/mol, $\Delta H_2^{\ddagger} = -0.6$ kcal/mol, $\Delta S_1^{\ddagger} = -3.6$ eu, $\Delta S_2^{\ddagger} = -1.9$ eu.

In the case of the attack of styryl cation, the activation enthalpy of addition of alkyl-1,3-butadiene as well as the activation entropy was greater than that of styrene. Therefore, alkyl-1,3-butadienes are shown to be less reactive than styrene in enthalpy term but more reactive than in entropy one, toward a styryl cation. This fact was also observed in the cationic copolymerization of styrene with phenyl-1,3-butadienes.[4,5,7] In the cases of isoprene and hexadiene, however, the activation parameters of alkyl-1,3-butadiene are shown to be similar to but a little less than those of styrene, toward an alkyl-1,3-butadiene propagating end. Consequently, r_1 decreased considerably and r_2 decreased a little as the temperature was raised. Other investigators have reported that the product of the monomer reactivity ratios was abnormally low in the cationic copolymerization of styrene with isoprene at 0 °C and above.[35-37] The tendency to alternation was not observed in our present systems at −78 °C. In the cases of isoprene and 1,3-hexadiene, however, the product of the monomer reactivity ratios seems to decrease as the temperature is raised.

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Anionic Polymerization of the Barium Salt of One-Ended Living Polystyrene. 2. The Effect of Added Barium Tetraphenylboride

B. De Groof,[1a] W. Mortier,[1a] M. Van Beylen,*[1a] and M. Szwarc[1b]

University of Leuven, Laboratory of Macromolecular and Organic Chemistry,
B-3030 Heverlee, Belgium, and the Department of Chemistry, State University of New York,
College of Environmental Science and Forestry, Syracuse, New York 13210.

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ABSTRACT: Anionic polymerization of barium salt of one-ended living polystyrene (BaS_2) was investigated at ambient temperature in THF in the presence of variable amounts of added barium tetraphenylboride (BaB_2). It was shown that BaB_2 reacts with BaS_2: $BaB_2 + BaS_2 \rightleftarrows 2BaBS$, $K_a = 40$. Ionic dissociation of BaB_2 ($BaB_2 \rightleftarrows BaB^+ + B^-$) in THF was investigated within the temperature range −70 to 20 °C, the results providing the respective Λ_0's and K_{BaB_2}'s. The conductance of $BaS_2 + BaB_2$ in conjunction with the values of the other pertinent equilibria led to $K_b = 3.6 \times 10^{-5}$ for the dissociation, $BaBS \rightleftarrows BaS^+ + B^-$, in THF at 20 °C. This dissociation inhibits the polymerization by suppressing the ionization of BaS_2 forming the propagating S^- ions. The propagation by $(BaS_3)^-$ ions was found to proceed with a rate constant smaller than 100 $M^{-1}\ s^{-1}$. The value of the dissociation constant $BaS_2 \rightleftarrows BaS^+ + S^-$ was reexamined and shown to be 1.1×10^{-10} M rather than 3.7×10^{-10} M reported in the previous study.

In the previous communication[2] we described the kinetics of anionic polymerization of styrene initiated by living polystyrene endowed with one active end and associated with Ba^{2+} counterions. The reaction proceeded at 20 °C in tetrahydrofuran. Conductance data reported in the above paper[2] demonstrated that four distinct species are present in those solutions, namely, $(\sim\!\sim CH_2C^-HPh)_2Ba^{2+}$, $[\sim\!\sim CH_2C^-HPh, Ba^{2+}]^+$, $\sim\!\sim CH_2C^-HPh$, and $[(\sim\!\sim CH_2C^-HPh)_3,Ba^{2+}]^-$, subsequently referred to as BaS_2, $(BaS)^+$, S^-, and $(BaS_3)^-$, respectively.

The reported kinetic data led to the conclusion that the *propagation of this polymerization is due to the free S^- ions;* the contribution of the other species appeared to be negligible. Additional observation strengthened this conclusion. The

Table I
Conductance of BaB_2 in THF

C, M × 10^5	Λ, $cm^2\ \Omega^{-1}\ mol^{-1}$	C, M × 10^5	Λ, $cm^2\ \Omega^{-1}\ mol^{-1}$
	T = 20 °C		
11.20	22.2	1.58	39.8
5.24	27.1	0.75	47.2
4.87	35.6(?)	0.45	51.8
3.50	32.1	0.33	55.4
3.20	32.0	0.21	55.2
1.60	39.1		
	T = 0 °C		
11.43	18.15	1.61	32.6
5.35	22.2	0.76	38.9
4.98	28.5(?)	0.46	41.6
3.38	27.6	0.35	46.0
3.27	25.9	0.21	46.0
1.63	31.66		
	T = −20 °C		
11.70	13.6	1.65	23.2
5.47	16.8	0.78	28.4
5.09	18.2(?)	0.47	30.5
3.67	18.9	0.36	32.0
3.34	18.7	0.22	34.3
1.67	23.4		
	T = −40 °C		
11.95	10.0	1.68	16.9
5.60	12.4	0.80	20.4
5.20	12.9(?)	0.48	22.0
3.75	13.8	0.37	25.6
3.42	13.4	0.22	24.95
1.71	17.2		
	T = −60 °C		
12.0	7.0	1.72	11.8
5.72	8.55	0.82	14.1
5.32	8.6(?)	0.49	14.9
3.82	9.7	0.38	17.1
3.49	9.2	0.22	17.7
1.75	12.2		

polymerization was totally inhibited by the addition to the investigated solutions of an equimolar amount of barium tetraphenylboride, BaB_2. As will be shown in a later part of this paper, the following equilibria are established under these conditions

$$BaS_2 + BaB_2 \rightleftarrows 2BaSB, \qquad K_a \qquad (a)$$

$$BaSB \rightleftarrows (BaS)^+ + B^-, \qquad K_b \qquad (b)$$

$$BaS_2 \rightleftarrows (BaS)^+ + S^-, \qquad K_1 \qquad (1)$$

$$2BaS_2 \rightleftarrows (BaS)^+ + (BaS_3)^-, \qquad K_2 \qquad (2)$$

The increase in the concentration of $(BaS)^+$, resulting from equilibria a and b, represses the ionization 1 and 2 and makes the concentrations of S^- and $(BaS_3)^-$ ions negligibly small. Hence, the resulting inhibition of polymerization implies that the propagation by (BaS_2) or $(BaS)^+$ is too slow to be observed.

The propagation in the absence of BaB_2 obeys first-order kinetics and the pseudo-first-order rate constants $k_{obsd} = -d \ln [S]/dt$ appeared to be independent of the concentration of living polystyrene, at least in the studied range of concentrations (see Figure 2 of ref 2). Closer examination of those data suggests that k_{obsd} might increase with the total concentration of living polystyrene, C, because the propagation of triple ions could increase k_{obsd} at higher concentrations of living polymers. However, the calculation, based on the data presently obtained and discussed in a later part of this paper, implies that the rate constant of propagation of $(BaS_3)^-$ ions cannot be greater than 100 $M^{-1}\ s^{-1}$.

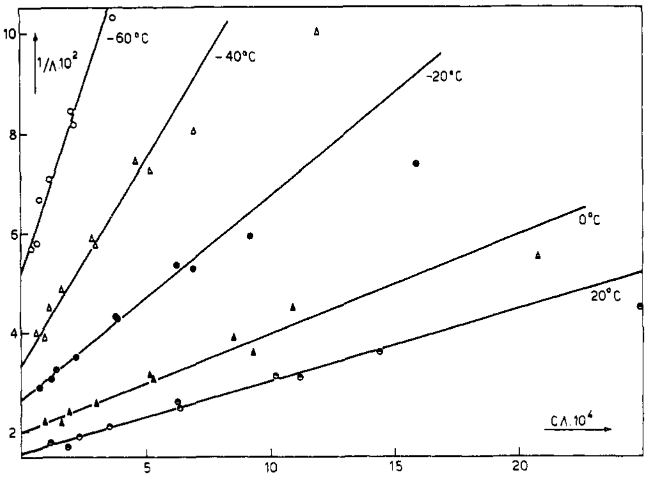

Figure 1. Plot of 1/Λ vs. cΛ for BaB_2 in THF at the specified temperatures. Note the reliability of the intercepts giving the appropriate 1/Λ_0 values.

The scatter of the k_{obsd} values reported in ref 2 (varying from 2.0×10^{-3} to $5 \times 10^{-3}\ s^{-1}$) makes it difficult to ascertain its "true" value, but the present results suggest that its most reliable value is $k_{obsd} = (2.0\text{–}2.5) \times 10^{-3}\ s^{-1}$. This conclusion follows from the kinetics of polymerization of barium polystyrene in the presence of variable concentration of barium tetraphenylboride (BaB_2) reported here.

Preparation of Barium Tetraphenylboride

Barium tetraphenylboride was reported to be prepared by a methathetic reaction, i.e., mixing aqueous solutions of $NaBPh_4$ with $BaCl_2$.[3] We found this method unsatisfactory because neither $Ba(BPh_4)_2$ nor NaCl precipitate under these conditions. Consequently, we prepared barium tetraphenylboride by reacting an equimolar mixture of diphenyl mercury and BPh_3 in THF with barium mirror deposited by the procedure described by Favier et al.[4] The resulting solution of $Ba(BPh_4)_2 = BaB_2$ was filtered and then concentrated by evaporating solvent until a thick slurry is formed. To this benzene was added to extract any unreacted $HgPh_2$ and BPh_3, both compounds being readily soluble in that hydrocarbon. The slurry was then filtered and the resulting precipitate was recrystallized from an acetone–diethyl ether mixture. The white crystals were dried by heating at 50 °C in high vacuum and sealed in evacuated ampules.

The identity of the salt was established by determining Ba^{2+} as $BaSO_4$ and BPh_4^- as $KBPh_4$ in an aqueous solution of a known concentration of that salt.

Conductance Studies of BaB_2 in THF

Conductance of THF solutions of BaB_2 was determined with a Wayne Kerr B221A universal bridge operating at 1592 Hz. The measurements covered concentrations ranging from 1×10^{-4} to 2×10^{-6} M and were performed at temperatures extended from −70 to 20 °C. The results are summarized in Table I and presented in Figure 1 as plots of 1/Λ vs. cΛ. The values of K_{BaB_2} and Λ_0, calculated from the respective lines shown in Figure 1, are given in Table II. The dissociation

$$BaB_2 \rightleftarrows (BaB)^+ + B^-, \qquad K_{BaB_2} \qquad (3)$$

is thermoneutral, the relevant $\Delta S = -22$ eu.

Our value of K_{BaB_2} at 20 °C is twice as low as that previously reported by Nachmanovich et al.[5] although their Λ_0 value agrees well with ours. Nevertheless, the high reproducibility of our data ascertains their reliability. The high degree of

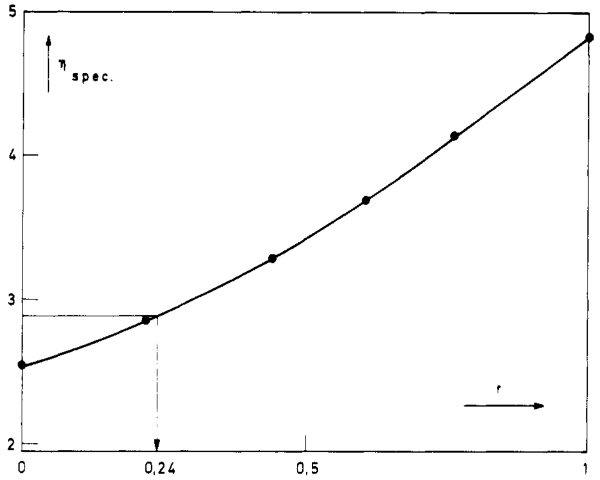

Figure 2. Viscosity of a solution containing BaS_2 and the terminated dead poly-S at various BaS_2/(dead poly-S) proportions but at constant weight concentration of total polystyrene (whether in the form of BaS_2 or dead poly-S). The last point corresponds to a solution of BaS_2 (no poly-S added) while the first results from a solution containing equal weight of dead poly-S. The horizontal line gives the viscosity of the BaS_2 solution after addition of an equimolar amount of BaB_2 and the vertical line gives its composition BaS_2/BaBS = 0.24. BaBS is equivalent to dead poly-S. The average mol wt of poly-S is about 45 000.

dissociation of BaB_2 permits us to accurately determine the pertinent Λ_0 and therefore the dissociation constants of BaB_2 are much more reliable than those of BaS_2 reported in the previous paper.[2] This point needs stressing.

The System BaB_2–BaS_2

Addition of BaB_2 to relatively concentrated THF solutions of BaS_2 leads to the formation of a mixed salt BaSB. Under those conditions the dissociation of either salt into free ions is extremely low and hence the presence of free ions in those solutions may be neglected. Thus the following equilibrium is ultimately established,

$$BaS_2 + BaB_2 \rightleftarrows 2BaSB, \qquad K_a \qquad \text{(a)}$$

The constant K_a was determined by measuring the viscosity of the resulting solution, because the length of the BaS_2 molecule is twice as high as that of BaBS. To increase the sensitivity of this method we used for those studies the BaS_2 salt of about 45 000 molecular weight.

The following procedure was adopted for constructing the calibration curve giving the viscosity of the solution as a function of composition for *a constant total weight concentration of polystyrene* (59 g/L). Required amounts of rigorously dried dead polystyrene, obtained by terminating some of the investigated BaS_2, were added to the solution of living BaS_2 of desired concentration. Thus any desired ratio BaS_2/2(terminated S) could be attained and the viscosity of such solution determined.[7] The results are given in graphic form in Figure 2. The viscosity of the BaS_2 solution of the same concentration was then measured before and after the addition of an equimolar amount of BaB_2. The result is shown in Figure 2 and from the thus determined composition of the mixed solution K_a was found to be 40.

Ionic Dissociation of BaSB

Two modes of dissociation of BaSB should be considered, namely,

$$BaSB \rightleftarrows (BaS)^+ + B^-, \qquad K_b \qquad \text{(b)}$$

and

$$BaSB \rightleftarrows (BaB)^+ + S^-, \qquad K_c \qquad \text{(c)}$$

Table II
$BaB_2 \rightleftarrows (BaB)^+ + B^-$

T, °C	Λ_0 cm^2 Ω^{-1} mol^{-1}	K_{BaB_2}, M × 10^{+5}	$\eta\Lambda_0$ × 10
20	64.4	1.65	3.10
0	51.1	1.92	3.04
−10	44.8	1.47	3.30
−20	38.9	1.61	2.98
−30	33.4	1.59	3.06
−40	28.2	1.60	3.03
−50	23.6	1.60	3.10
−60	19.35	1.76	2.98
−70	15.6	1.81	2.98

Since the addition of an equimolar amount of BaB_2 to BaS_2 totally inhibits the polymerization we have to conclude that $K_b \gg K_c$.[8] The value of K_b was calculated from the conductance data of BaS_2 solutions to which less than equimolar amounts of BaB_2 were added, namely, $[BaS_2]_0 = 5.7 \times 10^{-4}$ M, 5.1×10^{-4} M, and 2.56×10^{-4} M while the corresponding $[BaB_2]_0 = 3.5 \times 10^{-4}$ M, 0.38×10^{-4} M, and 0.19×10^{-4} M, respectively. Under these conditions three simultaneous equilibria are established, namely,

$$BaB_2 + BaS_2 \rightleftarrows 2BaSB, \qquad K_a \qquad \text{(a)}$$

$$BaSB \rightleftarrows (BaS)^+ + B^-, \qquad K_b \qquad \text{(b)}$$

$$BaB_2 \rightleftarrows (BaB)^+ + B^-, \qquad K_{BaB_2} \qquad (3)$$

while the dissociation $BaS_2 \rightleftarrows (BaS)^+ + S^-$ and $2BaS_2 \rightleftarrows (BaS)^+ + (BaS_3)^-$ again may be neglected since they are repressed by the formation of $(BaS)^+$ resulting from the dissociation of BaSB.

The value of K_b was calculated by solving the following set of simultaneous equations,

$$[BaSB]^2/([BaS_2]_0 - \tfrac{1}{2}[BaSB])([BaB_2]_0 - \tfrac{1}{2}[BaSB]) = K_a = 40$$

$$K_b[BaSB] = [(BaS)^+][B^-]$$

$$[(BaB)^+][B^-]/([BaB_2]_0 - \tfrac{1}{2}[BaSB]) = K_{BaB_2} = 1.65 \times 10^{-5}\ \text{M}$$

$$[(BaB)^+] + [(BaS)^+] = [B^-]$$

$$[B^-]\lambda_{0,B^-} + [(BaB)^+]\lambda_{0,BaB^+} + [(BaS)^+]\lambda_{0,BaS^+} = L$$

where L is the conductance of the investigated solution. The following λ_0 values were used, viz., $\lambda_{0,B^-} = 38.9$, $\lambda_{0,BaB^+} = 25.5$, and $\lambda_{0,BaS^+} = 17.5$ all in units cm^2 Ω^{-1} mol^{-1}. The first λ_0 was reported in ref 6, the second was derived from the presently given Λ_{0,BaB_2} (see Table II) in conjunction with λ_{0,B^-}, and the last one was estimated from the approximate diffusion constant of polystyrene of appropriate molecular weight. Thus, the measured L's, viz., 8.4×10^{-3}, 2.1×10^{-3}, and 1.2×10^{-3}, and the respective $[BaS_2]_0$ and $[BaB_2]_0$ give K_b's of 4.4×10^{-5} M, 3.7×10^{-5} M, and 2.8×10^{-5} M. We shall accept $K_b = 3.6 \times 10^{-5}$ M in further discussion.

Kinetics of Polymerization in the Presence of BaB_2

Propagation was found again to be a first-order reaction and the results of ten experiments are collected in Table III. Results of four additional experiments performed in the presence of very small amounts of BaB_2 are given in Table IV. Since the ratio $[BaS_2]_0/[BaB_2]_0$ was large virtually all BaB_2 was converted into BaSB, i.e., $[BaSB] = 2[BaB_2]_0$ and $[BaS_2] = [BaS_2]_0 - [BaB_2]_0$. Concentration of $(BaS)^+ = X$ could therefore by calculated from the relation

$$X^2/(2[BaB_2]_0 - X) = K_b$$

Table III
Propagation of Styrene Polymerization Initiated by BaS_2 in the Presence of BaB_2

Expt	$[BaS_2]_0$, M $\times 10^4$	$[BaB_2]_0$, M $\times 10^4$	k'_{obsd} s^{-1} $\times 10^4$	$X = [(BaS)^+]$, M $\times 10^5$ from equilibrium b
1	3.52	0.408	0.28(?)	3.91
2	1.04	0.121	0.14(?)	1.66
3	0.36	0.042	0.11	0.70
4	5.32	0.390	1.05	3.80
5	1.82	0.134	0.43	1.79
6	0.37	0.027	0.31	0.48
7	6.72	0.177	1.84	2.20
8	6.56	0.173	1.96	2.16
9	1.39	0.037	1.12	0.63
10	0.66	0.017	0.92	0.31

Table IV
Polymerization of BaS_2 in the Presence of Small Amounts of BaB_2

$[BaS_2]_0$, M $\times 10^4$	$[BaB_2]_0$, M $\times 10^6$	k'_{obsd} s^{-1} $\times 10^3$	
		Exptl	Calcd
5.8	2.2	1.1	0.8
4.2	1.6	1.2	0.8
0.71	0.27	1.0	0.7
0.98	0.37	1.0	0.7

neglecting again the dissociation of BaS_2. Nevertheless, it is the latter dissociation that produces the minute concentration of S^- ions that propagate the polymerization.

Before proceeding further, we should determine the upper limit for the propagation constant of the $(BaS_3)^-$ anions, k_{trp}. Propagation was not observed when styrene was added to an equimolar mixture of BaS_2 and BaB_2 ($[BaS_2] = 5 \times 10^{-4}$ M), i.e., $k'_{obsd} < 10^{-6}$ s^{-1}. In such a solution $[BaS_2] = [BaB_2] = 1.2 \times 10^{-4}$ and $[BaSB] = 7.6 \times 10^{-4}$ M, and hence the concentration of $(BaS_3)^-$ ion was 2.3×10^{-9} M (based on the presently determined value of $K_b = 3.6 \times 10^{-5}$ M and the previously reported[2] $K_2 = 2.4 \times 10^{-5}$). Therefore, $k_{trp} < 100$ M^{-1} s^{-1}.

The ratio $[(BaS_3)^-]/[S^-] = K_2[BaS_2]/K_1$ and for the ten experiments listed in Table III this ratio is less than 40 if $K_1 = 3.7 \times 10^{-10}$ and still less than 120 even if K_1 had been 1.1×10^{-10} (it will be seen later why this value of K_1 is considered). Hence, the contribution of $(BaS_3)^-$ ions to the observed propagation could not be greater than 20% at the highest concentration of BaS_2, being still lower for more dilute solutions. We may assume, therefore, that the observed propagation entirely arises from the growth of S^- ions and in this case $[(BaS)^+] = X = k_-K_1[BaS_2]/k'_{obsd}$ with $[BaS_2] = [BaS_2]_0 - [BaB_2]_0$. Alternatively, X could be calculated from the previously deduced relation

$$X^2/(2[BaB_2]_0 - X) = K_b$$

accepting $K_b = 3.6 \times 10^{-5}$ M. Thus calculated X was then plotted in Figure 3 vs. $[BaS_2]/k'_{obsd}$. The experimental points determine then a least-squares straight line through the origin of coordinates with a slope 6.0×10^{-6} s^{-1}. According to the proposed mechanism this slope gives k_-K_1 and since $k_{-1} = 55\,000$ M^{-1} s^{-1}, $K_1 = 1.1 \times 10^{-10}$ M.

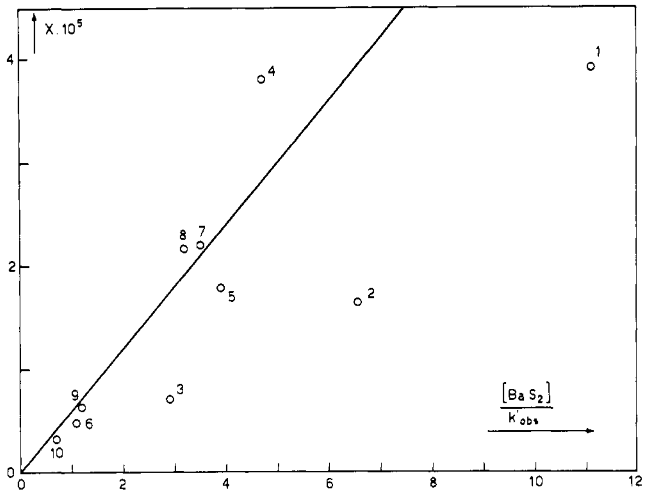

Figure 3. Plot of $X = [(BaS)^+]$ calculated from the relation $X^2/([BaB_2]_0 - X) = 3.6 \times 10^{-5}$ vs. $[BaS_2]/k'_{obsd}$. The experimental points determined a line through the origin with a slope of 6.0×10^{-6} s^{-1}. The first two experiments (No. 1 and 2) are obviously unreliable; nevertheless they were shown in the graph. According to the proposed mechanism, the slope gives k_-K_1.

The presently derived value of K_1 is lower than that obtained from the previously reported[2] conductance data, namely 3.7×10^{-10} M. However, in view of experimental difficulties encountered in conductance studies we consider the latter more reliable. Moreover, there is an additional reason for questioning the validity of $K_1 = 3.7 \times 10^{-10}$, namely its use in calculating X from the relation $k_-K_1[BaS_2]/k'_{obsd}$ gives values *greater* than $[BaSB] = 2[BaB_2]_0$, obviously a physical impossibility.

Finally, accepting k_{obsd} (in the *absence* of BaB_2) as 2×10^{-3} s^{-1} and $K_1 = 1.1 \times 10^{-10}$, we calculate $K_2^{1/2} = k_-K_1/k_{obsd} = 3.0 \times 10^{-3}$ in good agreement with the previously reported[1] value 4.9×10^{-3}. The latter was computed by estimating[2] the relevant $\lambda_0 = 25$ cm^2 Ω^{-1} mol^{-1} while $\lambda_0 = 35$ cm^2 Ω^{-1} mol^{-1} yields $K_2^{1/2} = 3.4 \times 10^{-3}$ in satisfactory agreement with our present calculation.

The treatment outlined above cannot be applied to the results of the four experiments listed in Table IV because the low proportion of BaBS does not permit us to neglect any more the ionization of BaS_2. However, k'_{obsd}'s can be calculated from these results by solving the set of simultaneous equations governing the equilibria b, 1, and 2. These are subject to the additional requirements of electric neutrality

$$[(BaS)^+] = [(BaS_3)^-] + [B^-] + [S^-]$$

and the mass balance $[BaSB] = [BaSB]_0 - [B^-]$, with the simplified approximation $[BaS_2] = [BaS_2]_0$ justified by the $[BaB_2]_0/[BaS_2]_0 \ll 1$. Their solution leads to a third-order equation in terms of the unknown $[S^-]$, namely

$$\begin{aligned}(K_1K_b + K_2K_b[BaS_2]_0)[S^-]^3 + (K_1{}^2[BaS_2]_0 \\ + K_1K_b[BaSB]_0 + K_1K_2[BaS_2]_0{}^2)[S^-]^2 \\ - (K_1{}^2K_b[BaS_2]_0)[S^-] - K_1{}^3[BaS_2]_0{}^2 = 0\end{aligned}$$

Using the values of the equilibrium constants deduced from the previously discussed experiments, i.e., $K_1 = 1.1 \times 10^{-10}$ M, $K_b = 3.6 \times 10^{-5}$ M, and $K_2 = 1.1 \times 10^{-5}$, we find $[S^-]$ and hence calculate $k'_{obsd} = k_-[S^-]$. The calculated values of k'_{obsd} are given in the last column of Table IV and they compare fairly with the experimental k'_{obsd} listed in the preceding column. This agreement provides additional evidence supporting the proposed mechanism.

In conclusion, the proposed mechanism accounts for the observed kinetics, the first two experiments (No. 1 and 2) being apparently unreliable. The results allow us to correct the value of the previously reported dissociation constant K_1, $BaS_2 \rightleftarrows BaS^+ + S^-$, namely $K_1 = 1.1 \times 10^{-10}$ M rather than 3.7×10^{-10} M. Moreover, the present results provide a more accurate estimate for k_{obsd}, namely $(2.0\text{–}2.5) \times 10^{-3}$ s^{-1}, and confirm the previously reported value of K_2.

We may add that an attempt was made to account for the observed kinetics by invoking the reaction

$$\text{BaBS} + \text{S}^- \rightleftarrows (\text{BaBS}_2)^-$$

but the analysis of such a scheme led to unacceptable results and hence to rejection of the contemplated mechanism.

Comparison of the Dissociations $\text{BaB}_2 \rightleftarrows (\text{BaB})^+ + \text{B}^-$ and $\text{BaSB} \rightleftarrows (\text{BaS})^+ + \text{B}^-$.

The former dissociation constant was found to be $K_{\text{BaB}_2} = 1.65 \times 10^{-5}$ M whereas the latter is claimed to be $K_b = 3.6 \times 10^{-5}$ M. The statistical factor of 2 appearing in K_{BaB_2} but not in K_b magnifies this difference even more. It seems that the tight association of S^- ion with Ba^{2+} reduces the attraction of B^- in BaSB, while BaB_2 aggregate probably should be considered as a loose one.

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(7) Note that the molecular weight distribution of any mixture of living and dead polymers used in our studies is the same as that of a corresponding mixture of BaS_2 and BaB_2 of the same specific viscosity. Therefore, the method used in determining K_a is justified for *any* molecular weight distribution.

(8) This inequality follows from the intuitively obvious requirement, namely equilibrium constant $K_{i,ex}$ for $(\text{BaB})^+ + \text{S}^- \rightleftarrows (\text{BaS})^+ + \text{B}^-$ should be much greater than 1. Note that $K_b/K_c = K_{i,ex}$.

Synthesis and Polymerization of Some New Carbazole and Phthalimide Monomers

Harry W. Gibson* and F. C. Bailey

Webster Research Center, Xerox Corporation, Webster, New York 14580.

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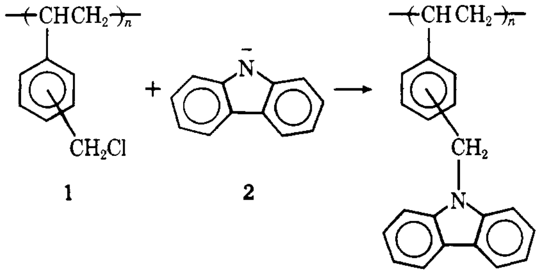
ABSTRACT: *m*- and *p*-(*N*-carbazyl)methylstyrenes and *p*-(*N*-phthalimido)methylstyrene were synthesized by reaction of a mixture of *m*- and *p*-chloromethylstyrene with potassium carbazole and potassium phthalimide, respectively. These polymerize and copolymerize readily with AIBN initiation to medium molecular weights. The resultant polymers are very similar spectrally to the analogous polymers made by chemical modification of poly(vinylbenzyl chloride).

Our interest in chemical modification of polymers led us to apply this method to the synthesis of poly[(*N*-carbazyl)methylstyrene] (**3**) from poly(vinylbenzyl chloride) (**1**) and the anion (**2**) of carbazole.[1] Polymer **1** was a mixture of isomers (60% meta, 40% para according to the manufacturer (Dow Chemical Co.) of the starting monomer) and, therefore, product polymer **3** was also a mixture of isomers inasmuch as the conversion was 100%. A synthesis of the two individual isomers of polymer **3** seemed desirable to ascertain any differences between the two isomers and corroborate the structure of **3**.



1 **2** **3**

This undertaking is reported here.

Discussion

(A) Synthesis of Monomers. A mixture of *m*-chloromethylstyrene (**4**) and the para isomer **5** in 60:40 nominal ratio was available (Dow Chemical Co.). Following the same procedure used for the preparation of polymer **3**,[1] reaction of a mixture of **4** and **5** with potassium carbazole (**2**) led to a mixture of the desired carbazole-containing monomers **6** and **7**. Fractional crystallization of the product mixture from ethanol led to a 29% yield of the less soluble para isomer **7** and a 64% yield of the more soluble meta isomer **6**; the total recovered conversion was therefore 93%. Separation is facile on account of a tenfold difference in the solubilities of the two isomers. The infrared and NMR spectra support the structural assignments.

The ultraviolet spectra of **6** and **7** are very similar to **3** and *N*-ethylcarbazole. Bands below 285 nm do not match in **3** and the monomers, presumably due to the vinyl group in the latter. Below 290 nm the extinction coefficients for **7** are higher than those of **6**.

Reaction of phthalimide anion with the mixture of chloromethylstyrenes (**4** and **5**) by the K_2CO_3/DMF method[1] led to 52% crude yield of solid, from which was isolated *p*-(*N*-phthalimido)methylstyrene (**8**). The lower melting, more soluble meta isomer was not isolated in a pure state. Infrared and NMR spectra are consistent with these assignments.

(B) Polymerization of Vinyl Monomers. Monomers **6**, **7** and **8** were each homopolymerized to polymers **9–11**, respectively, under free-radical conditions (azobisisobutyronitrile (AIBN) initiation) in refluxing benzene. Conversions