Macromolecules 1991, *24*, 2663-2667

Anionic Synthesis of Polysulfide Oligomers from Elemental Sulfur and Methacrylic Esters

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Received May 10, 1990; Revised Manuscript Received September 6, 1990

ABSTRACT: The anionic synthesis of polysulfide oligomers from methacrylic esters (methyl, ethyl, *n*-butyl, *tert*-butyl), elemental sulfur, and sodium was studied in a polar solvent (THF). Kinetic measurements showed that this "one-pot process" can be described by a competition between a slow reaction (initiation) and a fast reaction (deactivation of the anionic species on sulfur) which leads to the establishment of a stationary state in carbanions. The influence of the ester groups as well as the nature of the living species on the initiation, propagation, and deactivation reactions has been analyzed and discussed. In all syntheses, a nucleophilic attack of the carbonyl group by the carbanions was also detected and quantified from the alcohol formed. This secondary reaction is reduced when the steric hindrance of the ester group increases. These data are interpreted by a Bac_2 mechanism. Characterization of the resulting oligomers by GPC and elemental analysis showed that the polysulfide oligomers are mostly macrocycles with a sulfur rank of three to four.

Introduction

Polysulfide polymers are usually prepared by polycondensation between alkali polysulfides and dihalogeno compounds.[1-5] Elemental sulfur has also been used as a reactant in radical or ionic polymerization.[6-8] Recently a new synthesis of polysulfide polymers was developed in our laboratory. This synthesis, based on a carbanion–sulfur reaction,[9] is carried out by mixing the vinylic or dienic monomers in a polar solvent in the presence of sodium and elemental sulfur. The principal reactions involved in this process are initiation of the monomer by electron transfer from the alkali metal to the double bond and dimerization (I), propagation by monomer addition

$$M + Na \xrightarrow{k_i} M^{\bullet -} + Na^+ \qquad (I)$$

$$2M^{\bullet -} \rightarrow {}^-M\text{–}M^-$$

$$(n-2)M + {}^-M\text{–}M^- \xrightarrow{k_p} M_n^{2-} \qquad (II)$$

$$pM_n^{2-} + pS_8 \xrightarrow{k_d} [M_nS_x]_p + pS_{8-x}^{2-} \qquad (III)$$

on the carbanions formed (II), and deactivation of the dianionic species by a nucleophilic attack of sulfur (III). This "one-step process" presents two main advantages as compared with a synthesis in which dianionic oligomers are first prepared and then deactivated on sulfur: absence of organic initiator, which eliminates further purification; fast deactivation of the living species on sulfur, which avoids side reactions due to inherent instability of the carbanion.

By use of this method, polysulfide polymers have been synthesized from styrene, isoprene, and butadiene.[10,11] However, these monomers lead to relatively stable carbanions. A comparable carbanion stability can be obtained in the case of methacrylic esters when drastic conditions[12] are used: very low temperature and the presence of a dissociated salt to suppress free anions. It was then interesting to see if under usual conditions the one-pot process could eliminate side reactions. Another advantage of the methacrylic esters is the possibility of adjusting the physical properties of the polymer by changing the ester group. This paper reports the kinetic study carried out to characterize the reaction scheme and the effects of the ester groups on the different steps of the synthesis.

Experimental Section

Materials. Sulfur (gold label) was obtained from Aldrich Chemical Co. It was simply placed under argon before use.

Methacrylic esters were purified by two distillations over calcium hydride.

The sodium was melted in dry toluene and dispersed in small beads by vigorous stirring under argon at the melting temperature.

THF was distilled on living benzophenone–sodium anions before use.

Polymerization. Under argon, 23 mL of methyl methacrylate (0.2 mol), 5 mL of anisole (internal standard for VPC), and 480 mL of THF were introduced in a glass reactor. After cooling at −60 °C, 26 g of sulfur (0.1 mol) and 4.6 g of sodium (0.2 mol) were added under stirring. After consumption of the monomer, the mixture was poured in acidic water. By addition of ethyl ether a phase separation was obtained. The organic layer was washed several times with water and placed on magnesium sulfate. After filtration, the ethereal solution was concentrated and cooled at −70 °C to precipitate the free sulfur. The polysulfide oligomer was collected after evaporation and drying under vacuum. Analysis: % S, 23.6; % C, 47.0; % O, 23.7; % H, 6.3; % SH, 2.8; $\bar{M}_n = 600$.

Determination of Monomer and Alcohol Contents. Monomer consumption was followed by vapor-phase chromatography, on a Varian 3400 equipped with a capillary column (OV 1701, 50 m). Anisole, which was introduced in the medium, served as an internal standard. The evaluation of the alcohol formed was carried out by adding *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide to the aliquot sample containing the corresponding alcoholate and by injecting the resulting solution in VPC.

Determination of Sodium Content. This was done by titration of the alkaline polysulfide formed during the synthesis. This method is based on the following reaction:

$$Na_2S_x + 2HCl \rightarrow 2NaCl + H_2S + (x-1)/8S_8$$

Characterization of the Polysulfide Oligomers. The sulfur and the thiol contents were determined by elemental analysis. From the sulfur content, the sulfur rank (x) of the polysulfide oligomers ($[M_xS_x]_p$) has been calculated: $x = nM(\%\ S)/32(1 - \%\ S)$. The molecular weight was determined by a GPC apparatus

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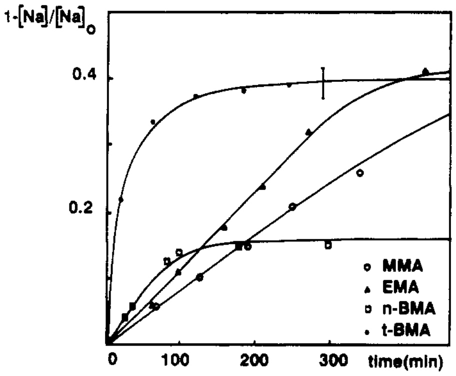

Figure 1. Effect of monomer structure on sodium consumption during the synthesis of polysulfide oligomers in THF at −60 °C. ($[Na]_0 = [M]_0 = 0.4$ mol L^{-1}, $[S_8]_0 = 0.2$ mol L^{-1}.)

Table I
Initiation Rate and Polymerization Rate for Methacrylic Esters at −60 °C, during the Synthesis of Polysulfide Oligomers in THF ($[Na]_0 = [M]_0 = 0.4$ mol L^{-1}, $[S_8]_0 = 0.2$ mol L^{-1})

monomers	$R_i \times 10^5$, mol L^{-1} s^{-1}	$R_M \times 10^5$, mol L^{-1} s^{-1}	$R_p \times 10^5$, mol L^{-1} s^{-1}
MMA	0.5	2.7	2.2
EMA	0.8	2.8	2.0
n-BMA	1.1	13	11.9
t-BMA	7	17	10

equipped with styragel column and calibrated with polymethacrylic ester standards.

Results and Discussion

To compare the different monomers, the same concentrations of reactants were used: $[M] = 0.4$ mol L^{-1}, $[Na] = 0.4$ mol L^{-1}, $[S_8] = 0.2$ mol L^{-1}. Such concentrations allow aliquot sampling with negligible effect on the overall concentration. The study was carried out −60 °C because at this temperature the various reactions take place within 2–4 h.

Initiation Reaction. This reaction was characterized through sodium consumption. The evolution of the sodium concentration vs time is represented in Figure 1. Generally the beginning of the reaction did not correspond to the introduction of the different reactants, especially when sulfur was added at room temperature. This inhibition period was minimized by adding elemental sulfur at low temperature just before sodium introduction. This technique avoids crystallization of S_8 at the sodium surface during the cooling period. For the kinetic studies the initial time ($t = 0$) corresponds to the end of the inhibition period.

From the different plots (Figure 1) it can be observed that the initiation of the methacrylic esters depends on the nature of the ester group. From the initial slopes at the origin, the initiation rates (R_i) were determined (Table I). Thus, *tert*-butyl methacrylate is rapidly initiated as compared with other monomers. The sequence observed is $R_{iMMA} < R_{iEMA} < R_{inBMA} \ll R_{itBMA}$.

Generally the presence of an electron-withdrawing substituent gives the double bond a higher electron affinity. Thus, for a methacrylate monomer, a *tert*-butyl ester group ($\sigma^* = -0.36$), which is a better electron donating group than a methyl one ($\sigma^* = 0.00$), should decrease the polarity of the double bond and consequently lower the electron-transfer reaction. In fact, an opposite behavior is observed, and to explain this phenomenon, it is necessary to take into account the solvating power of tetrahydrofuran. In an electron-transfer reaction the solvation is the driving force of the process.[14] In our case, it means that the solvation energy of the radical ion in the transition state must decrease from the *tert*-butyl methacrylate to the methyl methacrylate.

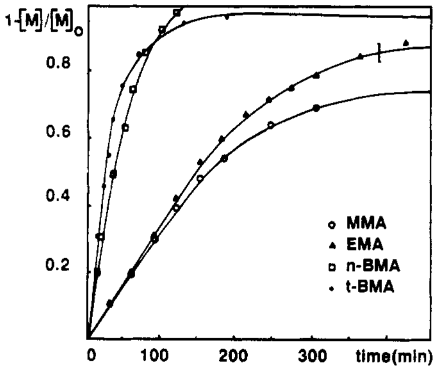

Figure 2. Effect of monomer structure on monomer conversion during the synthesis of polysulfide oligomers in THF at −60 °C. ($[Na]_0 = [M]_0 = 0.4$ mol L^{-1}, $[S_8]_0 = 0.2$ mol L^{-1}.)

Table II
Effect of Monomer Structure on the Ratio k_p/k_d and on the Degree of Polymerization of the Organic Chain Length during the Synthesis of Polysulfide Oligomers in THF at −60 °C ($[Na]_0 = [M]_0 = 0.4$ mol L^{-1}, $[S_8]_0 = 0.2$ mol L^{-1})

		$\overline{DP}_n$	
monomers	$10^2 k_p/k_d$	initial	final
MMA	4.3	11	4.1
EMA	2.4	6.5	4.1
n-BMA	10.5	24	13.3
t-BMA	1.4	4.8	4.8

Propagation Reaction. In Figure 2 the monomer consumption vs time is represented. From this plot, the initial rate of monomer consumption (R_M) was determined. It corresponds to the monomer involved in the initiation reaction and the propagation reaction.

Considering that one atom of sodium consumed leads to the formation of one radical anion, the propagation rate (R_p) was deduced from the following expression:

$$R_p = R_M - R_i$$

In Table II it can be observed that the propagation rate increases from methyl methacrylate to *n*-butyl methacrylate: $R_{pMMA} \simeq R_{pEMA} < R_{ptBMA} < R_{pnBMA}$. In fact, R_p is an apparent rate of propagation because addition of monomer on the active site is limited by deactivation of the carbanion on sulfur.

Considering the k_p values found in the literature for methacrylic monomers[11] and the concentration of carbanions formed at the beginning of the reaction, it is obvious that in the absence of S_8 all the monomer should be consumed in a few minutes. As the reaction time is 2 h, it implies that the deactivation reaction is as fast as the propagation reaction and faster than the initiation reaction: this last reaction constitutes the rate-determining step. Consequently, competition between initiation and deactivation reactions leads to the establishment of a stationary state in carbanions. The conditions required for such a process are fulfilled because the steady-state concentration of carbanions is negligibly small compared to the concentration of the reactants. This is equivalent to stating that the rate of carbanion formation (R_i) and that of carbanion deactivation (R_d) are equal:

$$R_i = R_d \qquad (1)$$

or

$$k_i[\mathrm{Na}][\mathrm{M}] = k_d[\mathrm{M}^-][\mathrm{S}_8] \rightarrow [\mathrm{M}^-] = k_i[\mathrm{Na}][\mathrm{M}]/k_d[\mathrm{S}_8] \quad (2)$$

$$R_p = k_p[\mathrm{M}][\mathrm{M}^-] \quad (3)$$

From (3) and (2)

$$R_p = k_p k_i[\mathrm{Na}][\mathrm{M}]/k_d[\mathrm{S}_8] \quad (4)$$

This expression shows that the variation of R_p can be a result of different values of k_i, k_p, and k_d as the concentration of the reactants was chosen the same for the different kinetics measurements. Consequently, a simple interpretation stemming from the monomer structure cannot be given. However, the variation of the apparent rate of polymerization is accompanied by the change of the organic chain lengths (between two sulfur bridges). The latter, defined by $\overline{\mathrm{DP}}_n$, are directly related to the monomer and sulfur concentrations by the ratio k_p/k_d (relation 5). The variation of the $\overline{\mathrm{DP}}_n$ can thereby be accounted for by the nature of the ester group since only two rate constants are involved. Relation 5 was obtained by considering that the degree of polymerization of the organic chain corresponds to the average number of growth steps undergone by one carbanion (including its formation) before it reacts with elemental sulfur. In other words, it is given by the ratio of the consumption rate of monomer to the rate of deactivation on sulfur. As one chain is formed from two active sites it becomes

$$\begin{aligned}\overline{\mathrm{DP}}_n &= 2R_\mathrm{M}/R_d = 2R_\mathrm{M}/R_i\\ &= 2(R_i + R_p)/R_i\\ &= 2(k_p/k_d)([\mathrm{M}]/[\mathrm{S}_8]) + 2 \quad (5)\end{aligned}$$

The ratio k_p/k_d has been determined from R_p and R_i:

$$R_p/R_i = R_p/R_d = k_p[\mathrm{M}][\mathrm{M}^-]/k_d[\mathrm{M}^-][\mathrm{S}_8] \rightarrow k_p/k_d = R_p[\mathrm{S}_8]/R_i[\mathrm{M}]$$

As elemental sulfur is in large excess as compared to its solubility, $[\mathrm{S}_8]$ corresponds to the concentration of a saturated solution at −60 °C: $[\mathrm{S}_8] = 3.9 \times 10^{-3}$ M. From the data collected in Table II, one can observe the following sequence: $k_p/k_{d(n\mathrm{BMA})} \gg k_p/k_{d(\mathrm{MMA})} > k_d/k_{d(\mathrm{EMA})} > k_p/k_{d(t\mathrm{BMA})}$. These ratios are always lower than 1 ($10^{-2} \rightarrow 10^{-1}$), which indicates that deactivation is faster than propagation. Except for *n*BMA, the differences between MMA, *t*BMA, and EMA are not very large. In fact, if no steric effect is involved, a high reactivity of the carbanion toward monomer implies a high reactivity toward the deactivating agent. These two reactions which have an opposite effect on the propagation cancel the influence of the ester group on the carbanion reactivity. In the case of *n*-butyl methacrylate a particular behavior is observed since $\overline{\mathrm{DP}}_{n0}$ and k_p/k_d are very large compared to those of the three other monomers. This can be the result of a high k_p value or of a lower k_d value. To evaluate separately these two constants, it was necessary to have access to the carbanion concentration in the stationary state. As shown in previous studies,[13] this can be done if $k_\pm$,k_- and K_d are known for the methacrylic esters: all of these constants have not be found in the literature due to the instability of the free anion at −60 °C. Nevertheless, at this temperature, $k_{p\pm}$ of the *n*-butyl methacrylate is close to $k_{p\pm}$ of ethyl methacrylate ($k_{\pm n\mathrm{BMA}} = k_{\pm\mathrm{MMA}}$ = 350 L/mol·s; $k_{\pm\mathrm{EMA}}$ = 235 L/mol·s).[12] As *n*-butyl and ethyl substituents present a Taft parameter σ^* of the same order ($\sigma^*_{n\mathrm{BMA}} = -0.13$; $\sigma^*_{\mathrm{EMA}} = -0.10$), it would be surprising that for free anions 1 order of magnitude would appear between the two propagation constants. Consequently, the difference observed for the ratio k_p/k_d stems probably from steric hindrance between the carbanion, due to the *n*-butyl chain, and the large sulfur molecule. To support this hypothesis, the deactivating agent was changed: sulfur was replaced by *tert*-butyl alcohol. The choice of *tert*-butyl alcohol was made for the following reasons: this compound remains practically unreacted toward sodium at low temperature and the hydrogen of the hydroxyl group is easily accessible to the carbanion.

Table III
Effect of Deactivating Agent on the Organic Chain Length ($[\mathrm{Na}]_0 = [\mathrm{M}]_0$ = 0.4 mol L^{-1}, $[\mathrm{S}_8]_0$ = 0.2 mol L^{-1}, $[t\text{-BuOH}]_0$ = 0.2 mol L^{-1})

	deactivating agent S_8			deactivating agent *t*-BuOH		
monomers	$[\mathrm{Na}]_{\mathrm{cons}}$, mol L^{-1}	$[\mathrm{M}]_{\mathrm{cons}}$, mol L^{-1}	$\overline{\mathrm{DP}}_n$	$[\mathrm{Na}]_{\mathrm{cons}}$, mol L^{-1}	$[\mathrm{M}]_{\mathrm{cons}}$, mol L^{-1}	$\overline{\mathrm{DP}}_n$
MMA	0.14	0.29	4.1	0.12	0.28	4.7
n-BMA	0.06	0.40	13.3	0.20	0.36	3.6

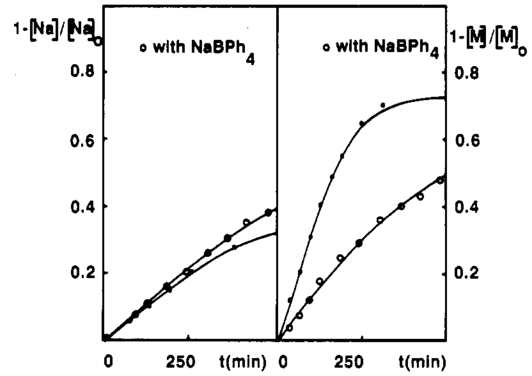

Figure 3. Influence of the nature of active sites on sodium and methyl methacrylate consumptions during the synthesis of polysulfide oligomers in THF at −60 °C. ($[\mathrm{Na}]_0 = [\mathrm{M}]_0$ = 0.4 mol L^{-1}, $[\mathrm{S}_8]_0$ = 0.2 mol L^{-1}.)

For both monomers, the protonated oligomers present a degree of polymerization (Table III) of the same order of magnitude (3.6 → 4.7). In the case of MMA the organic chain length remains practically identical when the deactivating agent is changed (4.7 → 4.1). The large difference observed with *n*BMA (3.6 → 13.3) in the case of S_8 reflects perfectly the role played by the size of the functionalization agent.

Influence of the Nature of the Active Site. As indicated previously the determination of k_p and k_d is not possible since k_p depends on the fraction of free anions and ion pairs present in the medium. To estimate these constants and to show the influence of the nature of the anions on the different steps of the process, a kinetic study was carried out with MMA in the presence of a dissociated salt: NaBPh_4. The addition of NaBPh_4 to a solution containing living poly(methyl methacrylate) suppresses the dissociation to free ions.

From the plot (Figure 3) it is observed that the sodium consumption is not affected by the presence of the dissociated salt. On the contrary, the monomer is consumed less rapidly. This has been quantified, and the data are collected in Table IV.

These results confirm that addition of NaBPh_4 has no influence on the initiation rate, which remains close to 0.5 mol L^{-1} s^{-1} and that the overall rate of monomer consumption decreases sharply. Consequently R_p, $\overline{\mathrm{DP}}_{n0}$, and k_p/k_d decrease in the same way. This suggests the following conclusions:

(1) During the process, different active species are involved, in particular, free ions.

Table IV
Effect of the Nature of the Active Site on the Different Steps of the Polysulfide Oligomer Synthesis ($T = -60$ °C; Solvent THF; $[\mathrm{Na}]_0 = [\mathrm{M}]_0 = 0.4$ mol L^{-1}, $[\mathrm{S_8}]_0 = 0.2$ mol L^{-1}, $[\mathrm{NaBPh_4}] = 2.6 \times 10^{-3}$ mol L^{-1})

additives	$R_i \times 10^5$, mol L^{-1} s^{-1}	$R_M \times 10^5$, mol L^{-1} s^{-1}	$R_p \times 10^5$, mol L^{-1} s^{-1}	$10^2 k_p/k_d$	$\overline{\mathrm{DP}}_{n0}$
no	0.50	2.7	2.2	4.3	11
NaBPh$_4$	0.55	0.9	0.35	0.62	3.5

Table V
Percentage of Alcohol Formed per Carbanion ([ROH]/[Na]) during the Synthesis of Polysulfide Oligomers in THF at −60 °C ($[\mathrm{Na}]_0 = [\mathrm{M}]_0 = 0.4$ mol L^{-1}, $[\mathrm{S_8}]_0 = 0.2$ mol L^{-1})

monomers	$[\mathrm{Na}]_{\mathrm{cons}} \times 10^2$, mol L^{-1}	$[\mathrm{ROH}] \times 10^3$, mol L^{-1}	[ROH]/[Na], %	$\overline{\mathrm{DP}}_n$
MMA	14	18	13	4.0
MMA + NaBPh$_4$	17	13	7.6	3.5
EMA	16.4	13.9	8.5	4.1
n-BMA	6.0	8.4	14	13.3
t-BMA	16	7.3	4.5	4.8

(2) The deactivating constant depends on the active-site nature. When the reaction is done without NaBPh$_4$, the k_p value calculated from the carbanion concentration in the stationary state (4×10^{-8} M) and K_d[15] is close to k_- ($k_p \simeq k_-/4$); on the contrary, in the presence of a common counterion, $k_\pm$ represents the propagation rate constant. Consequently, if k_d is independent of the nature of the active species, the ratio k_p/k_d obtained in the presence of NaBPh$_4$ should decrease by a factor of 10^2 corresponding to the ratio $k_p/k_{p\pm}$. This is not observed, and the small decrease of k_p/k_d shows that k_d is more affected than k_p by the active species involved.

From this experiment it was possible to evaluate $k_{d\pm}$ since $k_{p\pm}$ is known: $k_{p\pm} = 350$ L mol^{-1} s^{-1}. From the ratio k_p/k_d (Table IV), it becomes $k_{d\pm} = 28 \times 10^3$ L mol^{-1} s^{-1}. This value confirms that the reaction of a carbanion on sulfur is fast. The concentration of carbanions in the stationary state was also estimated from the propagation rate:

$$R_p = k_{p\pm}[\mathrm{M}][\mathrm{M}^-] \rightarrow [\mathrm{M}^-] = 4 \times 10^{-8}\ \mathrm{mol\ L^{-1}}$$

This concentration is very low and explains the long reaction time observed.

Secondary Reactions. The most important side reactions occurring during polymerization of methacrylic esters come from a nucleophilic substitution of the ester group by the active species: initiator or MMA carbanion.[16,17] These reactions lead to the formation of alcohol, which is easily quantified by vapor-phase chromatography. This was determined for the different methacrylic esters, and the results are summarized in Table V.

Comparison of the different monomers was done from the ratio [ROH]/[Na], which represents the percent of carbanions leading to secondary reactions. The formation of alcohol increases in the following way: *t*BMA < EMA < MMA < *n*BMA. For the first three monomers the variation can be explained by considering the mechanism involved in the nucleophilic substitution: a Bac$_2$ mechanism.[18] It implies the formation of a tetrahedral intermediate which is difficult to obtain with bulky substituents: this is the case for the *tert*-butyl group which leads to a very low alcohol yield (4.5%). However, in the case of *n*BMA, secondary reactions are more important as is the degree of polymerization of the organic chain length between two sulfur atoms. This implies a greater "lifetime" for the carbanion and leads to a higher probability for the active site to react with an ester function. From the following experiment it was possible to determine whether the side reaction occurs during the initiation step or during the propagation step: the formation of alcohol was quantified (Table VI) during the synthesis of polysulfide polymethyl methacrylate carried out in the presence of NaBPh$_4$.

Table VI
Characteristics of the Polysulfide Polymethacrylic Esters Prepared in THF at −60 °C ($[\mathrm{Na}]_0 = [\mathrm{M}]_0 = 0.4$ mol L^{-1}, $[\mathrm{S_8}]_0 = 0.2$ mol L^{-1})

monomers	$\bar{M}_n$	$\overline{\mathrm{DP}}_n$	% S	x	% SH$_{\mathrm{theo}}$	% SH$_{\mathrm{anal}}$	% cycles
MMA	600	4.1	23.6	3.9	11	2.8	75
EMA	710	4.1	18.3	3.3	9.3	2.6	78
n-BMA	2275	13.3	5.6	3.5	2.9	0.9	69
t-BMA	1270	4.8	14.9	3.7	5.2	1.7	67

When a dissociated salt is present, at −60 °C, the MMA carbanion is stable during the propagation. Consequently, the formation of alcohol ($R = 7.6\%$) in this synthesis shows that the nucleophilic attack of the carbonyl group occurs only during the initiation step. This result has been recently confirmed by characterization of the cyclic compounds issued from an intramolecular cyclization of the dianionic dimers.[19]

Characterization of the Polysulfide Oligomers and Their Functionality. The polysulfide oligomers present a high sulfur content corresponding to a sulfur rank between three and four. This value is usual when the reaction is carried out in the presence of an excess of sulfur as compared to the carbanions formed. In our experiments the ratio $K = [\mathrm{Na}]_{\mathrm{cons}}/[\mathrm{S_8}]$ does not exceed 0.8: our studies on model molecules[20] have shown that for $K < 2$, the sulfur attack predominates and the resulting coupled compounds present a sulfur rank between three and four. However, the molecular weights of the polysulfide oligomers are relatively small in view of the $\overline{\mathrm{DP}}_n$ (of the organic chain): this means that the degree of polycondensation between the dianionic oligomers and sulfur is small. This suggests a fast cyclization which can occur without any condensation step (IV) or after polycondensation steps (V):

$$^-\mathrm{M{-}M_{n-2}M{-}S_8}^- \rightarrow [\mathrm{M}_n\mathrm{S}_x] + \mathrm{S}_y^{\,2-} \qquad \text{(IV)}$$

$$p\,^-\mathrm{M{-}M_{n-2}M{-}S_8}^- \rightarrow {}^-\mathrm{M{-}M_{n-1}{-}S_x{-}[M_n{-}S_x]_{p-2}{-}M_n{-}S_8}^- + (p-1)\mathrm{S}_y^{\,2-} \rightarrow [\mathrm{M}_n\mathrm{S}_x]_p + p\mathrm{S}_y^{\,2-} \qquad \text{(V)}$$

To check this hypothesis, the thiol functionality was determined by elemental analysis and compared to the theoretical thiol content calculated from $\bar{M}_n$ values. From the data collected in Table VI it is concluded that the oligomers are mostly in a cyclic form (70–80%). However, this result provides no information about the two possibilities suggested previously (IV and V). To determine the possible presence of more than one polysulfide bridge, the different polysulfide oligomers were submitted to a reduction reaction. Splitting of the polysulfide bridges was obtained from "nascent hydrogen" (Clemmensen reaction).

In the absence of polycondensation reactions a slight variation in molecular weight with no detectible effect on the polydispersity index should be observed. Data collected in Table VII show that the reduction reaction leads to a net decrease of the molecular weight and polydispersity index. This change is all the more significant because monosulfur bridges cannot be modified by this reduction process. The fact that cyclization occurs after polycondensation steps implies that reaction IV cannot be avoided, especially at the end of the reaction when the concentration of the active species decreases sharply. On

Table VII
Variation of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of Polysulfide Oligomers after Reduction of the Polysulfide Bridges

	before reduction		after reduction	
monomers	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
MMA	600	1.9	375	1.1
EMA	710	2.1	500	1.6
n-BMA	2275	3.7	775	3.1
t-BMA	1270	2.6	790	1.3

the GPC curves of the polysulfide oligomers, a well-defined peak can be observed in a low molecular weight region. Practically nonexistent in the case of *n*-butyl methacrylate, it reaches 12% of the total amount in the case of the ethyl methacrylate. Mass spectroscopy analysis showed that these peaks are made of a mixture of polysulfide cyclic dimers exhibiting one, two, or three sulfur atoms.

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Registry No. (MMA)(S) (copolymer), 132622-21-0; (EMA)(S) (copolymer), 132622-22-1; (*n*-BMA) (copolymer), 132622-23-2; (*t*-BMA) (copolymer), 132622-24-3; MMA, 80-62-6; EMA, 97-63-2; *n*-BMA, 97-88-1; *t*-BMA, 585-07-9; Na, 7440-23-5; *t*-BuOH, 75-65-0; $NaBPh_4$, 143-66-8.