Synthesis of Poly(aliphatic sulfides) by Polycondensation of Sodium Sulfide with Dibromoalkanes in the Presence of Quaternary Onium Salts

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ABSTRACT: A convenient method for the synthesis of poly(aliphatic sulfides) of high molecular weight has been developed. These polymers were prepared readily by the polycondensation of sodium sulfide with dibromoalkanes in the presence of quaternary ammonium or phosphonium salts. The polycondensation was strongly catalyzed by cetyltrimethylammonium chloride or bromide and cetyltributylphosphonium bromide and gave poly(aliphatic sulfides) having inherent viscosities in the range 0.5–0.9 $dL \cdot g^{-1}$. They were highly soluble in concentrated sulfuric acid and chloroform at room temperature, soluble in dichloroacetic acid, *m*-cresol, dichloromethane, and tetrahydrofuran on heating, and practically insoluble in polar aprotic solvents and other common solvents. The melting points of the poly(aliphatic sulfides) were clearly observed by differential scanning calorimetry (DSC). X-ray diffraction patterns of the polymers showed highly crystalline structures.

Introduction

Poly(aliphatic sulfides) are aliphatic polymers with a single sulfur atom in a repeating unit (–R–S–) and have properties quite different from those of their oxygen analogues. They are prepared by four major methods: the polymerization of episulfides, addition of dithiols to diolefins, reaction of dithiols with carbonyl compounds, and reaction of dithiols with dihalides. In spite of this variety of processes, a simple and successful preparative method has not been reported.

Sodium sulfide is an inexpensive raw material for the synthesis of polysulfides. Several workers tried to prepare poly(aliphatic sulfides) from sodium sulfide and dihaloalkanes; however, the polymers obtained were of low molecular weight.[1]

In 1974, Landini and Rolla[2] demonstrated that excellent yields of dialkyl sulfides can be prepared from sodium sulfide and haloalkanes using the phase-transfer-catalysis technique. We also have reported the synthesis of poly(aliphatic sulfides) by the phase-transfer-catalyzed polycondensation of dibromoalkanes with dithiols in aqueous potassium hydroxide.[3] These results prompted us to investigate the synthesis of poly(aliphatic sulfides) using sodium sulfide.

We have found that poly(aliphatic sulfides) of high molecular weight are readily obtained by the polycondensation of sodium sulfide with dibromoalkanes in the presence of quaternary ammonium or phosphonium salts.

Experimental Section

Materials. Reagent grade 1,6-dibromohexane (**4a**), 1,8-dibromooctane (**4b**), and 1,10-dibromodecane (**4c**) were used as received. Cetyltributylphosphonium bromide (CTBPB) was prepared from cetyl bromide and tributylphosphine.[4] It was recrystallized from hexane; mp 53–54 °C (lit.[4] mp 54 °C). Tetrabutylammonium chloride (TBAC), cetyltrimethylammonium chloride (CTMAC), cetyltrimethylammonium bromide (CTMAB), benzyltriethylammonium chloride (BTEAC), and benzyltriphenylphosphonium chloride (BTPPC) were obtained commercially and used as received.

Preparation of a 1 M Aqueous Sodium Sulfide Solution. In a 100-mL volumetric flask was placed $Na_2S \cdot 9H_2O$ (24 g, 0.1 mol) under nitrogen. A 1 M NaOH aqueous solution (1 mL) and distilled water were added with a hypodermic syringe inserted through a serum cap until the flask was filled to the mark.

Model Reaction. Synthesis of Dibenzyl Sulfide (3b). To a mixture of benzyl bromide (0.85 g, 5.0 mmol) and a 1 M Na_2S aqueous solution (2.5 mL) was added 2 mol % of CTBPB as a catalyst. The mixture was stirred vigorously at 80 °C. After 30 min, water (30 mL) and ether (50 mL) were added. The organic layer was separated, washed with water, and dried over calcium chloride. The solvent was evaporated under vacuum; the yield was 0.93 g (87%). Recrystallization from methanol afforded white needles, mp 48–49 °C (lit.[5] mp 49 °C).

Polycondensation. Synthesis of Polysulfide 5b. 1,8-Dibromooctane (**4b**) (1.36 g, 5 mmol) and CTMAC (64 mg, 0.2 mmol) were placed under nitrogen in a 20-mL flask fitted with a serum cap. A 1 M Na_2S aqueous solution (5 mL) was added with a hypodermic syringe inserted through the serum cap. The mixture was stirred vigorously at 100 °C for 24 h. The reaction mixture formed an emulsion as the polymerization proceeded. After cooling, the polymer latex was coagulated by pouring the reaction mixture into rapidly stirred methanol (200 mL). The precipitate was filtered and dried. Then it was dissolved in chloroform and poured again into hexane. The polymer was filtered and dried in vacuo overnight at 40 °C to give 0.66 g (91%) of polysulfide. The inherent viscosity in concentrated sulfuric acid was 0.71 $dL \cdot g^{-1}$, measured at a concentration of 0.5 $g \cdot dL^{-1}$ at 30 °C. Anal. Calcd for $C_8H_{16}S$: C, 66.60; H, 11.18; S, 22.22. Found: C, 66.5; H, 10.3; S, 21.8.

Measurements. The infrared spectra were recorded on a Jasco IRA-1 spectrophotometer and the NMR spectra on a Hitachi R-24B (60 MHz) instrument. Differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DT-30, DT-20B, and TG-20, respectively.

Results and Discussion

Model Reaction. Before attempting the polymer synthesis, we first studied the catalytic effects of various quaternary ammonium or phosphonium salts on the reaction of sodium sulfide (1) with bromoalkanes 2 (eq 1).

$$\underset{1}{Na_2S} + \underset{2}{2RBr} \rightarrow R\text{–}S\text{–}R + 2NaBr \qquad (1)$$

$$\mathbf{a},\ R = (CH_2)_5CH_3$$
$$\mathbf{b},\ R = CH_2C_6H_5$$

Detailed results are listed in Table I. The use of cetyltrimethylammonium chloride (CTMAC) and cetyltributylphosphonium bromide (CTBPB) was particularly effective and dialkyl sulfides **3a** and **3b** were obtained in high yields. In contrast to these catalysts, tetrabutyl-

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Table I
Reaction of Sodium Sulfide (1) with Bromoalkanes 2 in the Presence of Various Catalysts

	reaction conditions[a]			product	
bromoalkane	catalyst	temp, °C	time, min	type	yield, %
2a	none	80	60	3a	4
2a	TBAC	80	60	3a	33
2a	CTMAC	80	60	3a	95
2a	BTEAC	80	60	3a	30
2a	CTBPB	80	60	3a	99
2a	BTPPC	80	60	3a	35
2b	none	20	30	3b	10
2b	TBAC	20	30	3b	10
2b	CTMAC	20	30	3b	78
2b	BTEAC	20	30	3b	23
2b	CTBPB	20	30	3b	70
2b	BTPPC	20	30	3b	18
2b	CTMAC	80	30	3b	89
2b	CTBPB	80	30	3b	87

[a] Reaction was carried out with 2.5 mL of 1 M Na_2S aqueous solution and 5 mmol of the bromoalkane in the presence of the catalyst (2 mol %).

Table II
Polycondensation of Sodium Sulfide (1) with Dibromooctane (4b) in the Presence of Various Catalysts[a]

	polymer	
catalyst	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
none	94	0.08
TBAC	99	0.09
CTMAC	91	0.71
CTBPB	99	0.42
CTMAB	86	0.70
BTEAC	99	0.19
BTPPC	96	0.08

[a] Polycondensation was carried out with 5 mL of 1 M Na_2S aqueous solution and 5 mmol of 4b at 100 °C for 1 day in the presence of the catalyst (4 mol %). [b] Measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ in concentrated sulfuric acid at 30 °C.

ammonium chloride (TBAC), which is effective in the synthesis of polysulfonates,[6] polyether,[7] polyphosphonate,[8] and polysulfides,[3] did not show a pronounced catalytic effect. This may result from the nature of the S^{2-} anion. This divalent anion is more hydrated than phenoxide and thiolate anions, and so it is difficult to transfer from the aqueous phase to the organic phase. Also, TBAC has less lipophilic interaction with the organic phase than CTMAC and CTBPB.

Polymer Synthesis. Polycondensation of sodium sulfide with dibromoalkanes 4 was carried out in the presence or absence of quaternary onium salts under nitrogen without the use of solvents (eq 2). To determine

$$1 + \underset{4}{\text{Br–R–Br}} \rightarrow \underset{5}{(\text{–S–R–})_n} + 2\text{NaBr} \qquad (2)$$

a, R = $(CH_2)_6$
b, R = $(CH_2)_8$
c, R = $(CH_2)_{10}$

the optimum conditions for the polycondensation, the following factors that influence the reaction were studied: structure and amount of catalyst and temperature of the reaction. Table II lists the results of polycondensation between 1,8-dibromooctane (**4b**) and sodium sulfide in the presence of quaternary ammonium salts CTMAC, cetyltrimethylammonium bromide (CTMAB), TBAC, and benzyltriethylammonium chloride (BTEAC) and phosphonium salts CTBPB and benzyltriphenylphosphonium chloride (BTPPC). The polycondensation was carried out with 5 mmol of each monomer in the presence of 4 mol % of the catalyst under nitrogen at 100 °C for 24 h. The presence of CTMAC, CTMAB, or CTBPB significantly affected the attained inherent viscosities of the polymers, whereas no appreciable catalytic effects of TBAC, BTEAC, or BTPPC were observed. These data agreed well with the results of the model reaction and provide a clean choice of catalyst for the synthetic reactions. Thus, the efficient catalysts need to have one long alkyl group, and symmetrical ions and benzyl-containing quaternary salts were ineffective for this polymerization.

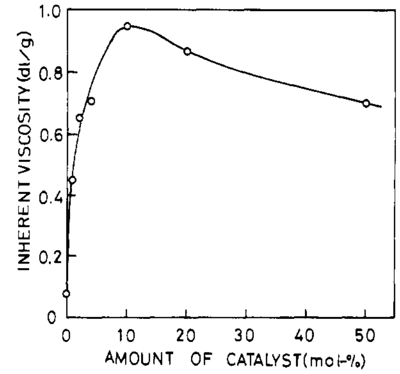

Figure 1. Effect of CTMAC catalyst on inherent viscosity of polysulfide **5b** formed in the polycondensation at 100 °C for 24 h.

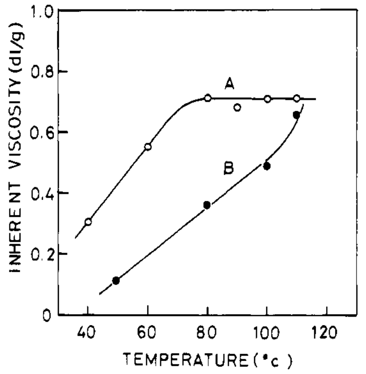

Figure 2. Effect of reaction temperature on inherent viscosity of polysulfide **5b** formed in the polycondensation with various catalysts (4 mol %): (A) CTMAC; (B) CTBPB.

The effect of amount of CTMAC on the polycondensation is shown in Figure 1. The inherent viscosity of the polymer reached its highest value with 10 mol % of the catalyst based on each monomer.

The effect of the reaction temperature on the inherent viscosity of the resulting polymer was examined over the temperature range 40–110 °C in the presence of CTBPB or CTMAC. The results are shown in Figure 2. The inherent viscosity increased with increasing temperature, and the polycondensation catalyzed by CTMAC gave a polymer with a higher molecular weight over the whole temperature range compared with the polycondensation catalyzed by CTBPB. This difference seems to be ascribable to the different state of polycondensation. Below about 90 °C the polycondensation catalyzed by CTBPB proceeded with polymer precipitation, which limits the increase in molecular weight. Above that temperature, the polymer is in a melted state, which then permits the polycondensation in a water–melt two-phase system. Accordingly, CTBPB became soluble in the polymer phase and catalyzed the polycondensation. By contrast, the polycondensation catalyzed by CTMAC proceeded in the

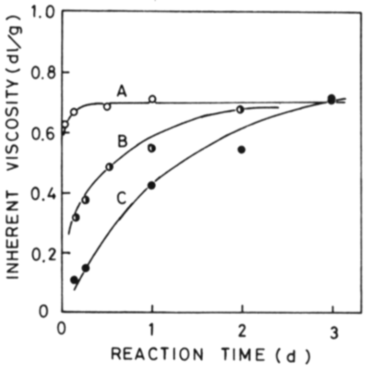

Figure 3. Time dependence of inherent viscosity of the polysulfide **5b** formed in the polycondensation with various catalysts (4 mol %): (A) reaction with CTMAC catalyst at 100 °C; (B) reaction with CTMAC catalyst at 60 °C; (C) reaction with CTBPB catalyst at 100 °C.

Table III
Polycondensation of Sodium Sulfide (1) with Various Dibromoalkanes 4 in the Presence of Catalysts[a]

dibromo-alkane	catalyst	polymer type	polymer yield, %	polymer η_{inh},[b] dL·g^{-1}
4a	CTBPB	**5a**	99	0.68
4a	CTMAC	**5a**	88	0.64
4b	CTBPB	**5b**	99	0.71
4b	CTMAC	**5b**	99	0.70
4c	CTBPB	**5c**	99	0.60
4c	CTMAC	**5c**	99	0.83

[a] Polymerization was carried out with 5 mL of 1 M Na_2S aqueous solution and 5 mmol of **4** at 100 °C for 3 days in the presence of the catalyst (4 mol %). [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C.

emulsion even at a lower temperature than the melting point of the polymer (87 °C). This observation suggests that a substantial fraction of the growing molecules is solubilized by CTMAC which acts as a surfactant. Furthermore, it is well-known that cationic surfactants catalyze the reaction of alkyl halides with anion by micellization. Hence, we suspect CTMAC functions by both emulsification and micellization.

Figure 3 shows the course of the polymerization in terms of inherent viscosity of the resulting polymer. The polymerization proceeded fairly rapidly at 100 °C in the presence of CTMAC and gave polysulfide having an inherent viscosity of 0.62 dL·g^{-1} in 1 h. On the other hand, the polymerization in the presence of CTBPB progressed much more slowly as compared with that in the presence of CTMAC at 60 °C. These results reflect the differences of catalytic effects between CTMAC and CTBPB on the polycondensation.

The results of the polycondensation of sodium sulfide with dibromoalkanes **4a–c** are summarized in Table III. Polysulfides **5a–c** of high molecular weights could be obtained quite readily in the presence of CTMAC or CTBPB.

Polymer Characterization. The polymers were identified as poly(aliphatic sulfides) by comparing their IR spectra with those of models **3a,b**. The IR spectra exhibited characteristic absorptions at 2840–2900 and 1460 cm^{-1} due to CH stretching and CH_2 scissoring modes. The NMR spectra of poly(aliphatic sulfide) **5b** consisted of a multiplet peak at δ 1.4 (12 H) for the methylene protons and a triplet peak at δ 2.44 (4 H) for the methylene adjacent to the sulfide sulfur. Elemental analyses also supported the formation of the expected polymers.

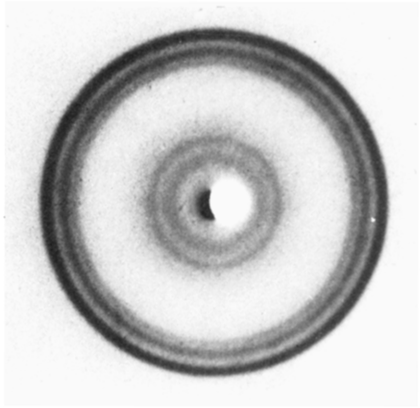

Figure 4. X-ray diffraction pattern of **5b**.

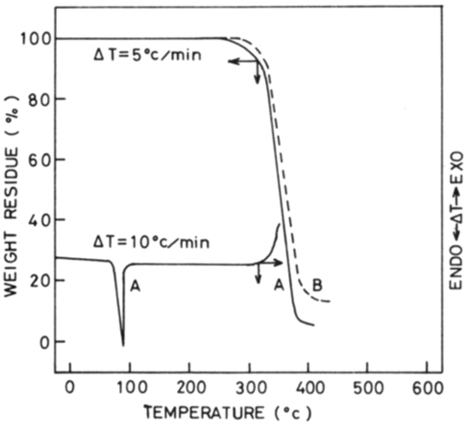

Figure 5. TG and DTA curves of **5b**: (A) in air; (B) in N_2.

Table IV
Thermal Behavior Data of Polysulfides $(-S-R-)_n$

polysulfide	mp,[a] °C	10% wt loss temp,[b] °C in air	10% wt loss temp,[b] °C in N_2
$R = (CH_2)_6$	76	295	300
$R = (CH_2)_8$	87	320	330
$R = (CH_2)_{10}$	93	330	330

[a] Determined by DSC in nitrogen at a heating rate of 20 °C·min^{-1}. [b] Determined by TG at a heating rate of 5 °C·min^{-1}.

The poly(aliphatic sulfides) were white solids. They were readily soluble in concentrated sulfuric acid and chloroform at room temperature and soluble in dichloroacetic acid, *m*-cresol, dichloromethane, and tetrahydrofuran on heating. They were insoluble in polar aprotic solvents and other common organic solvents. All the polymers gave tough films after casting from a chloroform solution or by melt-pressing.

Differential scanning calorimetry (DSC) was performed on these polymers. All the poly(aliphatic sulfides) exhibited well-defined melting transitions. This is correlated to the fact that X-ray diffraction patterns of the polymers obtained with nickel-filtered Cu Kα radiation showed a high degree of crystallinity (Figure 4). Five sharp and well-defined rings are seen for all the polymers. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out at heating rates of 5 and 10 °C·min^{-1}, respectively. Typical thermograms are shown for poly(aliphatic sulfide) **5b** in Figure 5. The DTA curve of **5b** exhibited a sharp endotherm at 89 °C, which is the melting point of **5b**, and a strong exotherm around 310 °C, which correlated well with the TG study showing that the initial weight loss occurred at about this temperature. The data of the thermal behavior are summarized in Table IV.

In summary, we have shown that poly(aliphatic sulfides) with high molecular weights are readily prepared by the polycondensation of sodium sulfide with dibromoalkanes in the presence of quaternary ammonium salts such as CTMAC or CTMAB and phosphonium salts such as CTBPB. Since this preparative method is simple and gives quantitatively polysulfides of high molecular weight, it is generally superior to conventional methods for the synthesis of poly(aliphatic sulfides).

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References and Notes

(1) Sandler, S. R.; Karo, W. "Polymer Syntheses"; Academic Press: New York, 1980; Vol. III, Chapter 3.
(2) Landini, D.; Rolla, F. *Synthesis* **1974**, 565.
(3) Imai, Y.; Kato, A.; Ii, M.; Ueda, M. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 579.
(4) Starks, C. S. *J. Am. Chem. Soc.* **1971**, *93*, 195.
(5) Frost, C. *Justus Liebigs Ann. Chem.* **1875**, *178*, 350.
(6) Imai, Y.; Ueda, M.; Ii, M. *Makromol. Chem.* **1978**, *179*, 2085.
(7) Imai, Y.; Ueda, M.; Ii, M. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 85.
(8) Imai, Y.; Sato, N.; Ueda, M. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 419.

Anionic Polymerization of Isoprene by Oligoisoprenyllithium/Tertiary Polyamine Complexes in Cyclohexane. 2. Proton Magnetic Resonance and Ultraviolet Spectroscopy of Propagating Living Species

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ABSTRACT: The nature of oligoisoprenyllithium complexed with TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) or PMDT (pentamethyldiethylenetriamine) is investigated by proton magnetic resonance and ultraviolet spectroscopy as a function of r = [tertiary polyamine]/[living ends]. ^{1}H NMR shows an upfield shift of both triplets corresponding to the methinic proton in the living unit and a simultaneous trans/cis isomerization of the living ends. The ultraviolet spectra confirm the NMR results and provide information concerning the association of the living species.

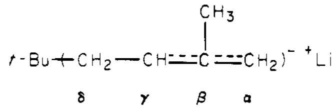
Introduction

The kinetic study of the anionic polymerization of isoprene by the complexes of oligoisoprenyllithium with tertiary polyamines in cyclohexane has been intensively developed in a previous paper.[1] *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) and pentamethyldiethylenetriamine (PMDT) were used as complexing agents. In the present paper the nature of the propagating living species is investigated by proton magnetic resonance and ultraviolet spectroscopy.

The structure[2-12] and the stability[3,13-18] of the propagating living species in the anionic polymerization of dienes (butadiene and isoprene) without tertiary polyamines have been studied in great detail. The purpose of this paper was dictated by the discrepancy existing concerning the mechanism of polymerization in the presence of such complexing agents.[1]

Results

1. Proton Magnetic Resonance of Oligoisoprenyllithium Complexed with TMEDA. An oligoisoprenyllithium of polymerization degree 1.2 is synthesized under vacuum by reaction of *tert*-butyllithium with isoprene in benzene. The living species in solution in C_6D_6 is characterized at room temperature by ^{1}H NMR (100 MHz); its behavior will be roughly the same in cyclohexane. The living oligomer is generally described by the following delocalized structure:[2-12]



$$t\text{-Bu}\!\left(\mathrm{CH_2}-\mathrm{CH}\overset{}{=\!=\!=}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\!=\!=\mathrm{CH_2}\right)^{-}\,{}^{+}\mathrm{Li}$$

The low-field area is most informative. In the absence of TMEDA (r = [TMEDA]/[living ends] = 0) we observe triplets at 4.60 and 4.85 ppm from Me_4Si caused by the γ proton in the cis and the trans forms, respectively, of the living unit (Figure 1). The trans/cis ratio is about 2:1.

Addition of TMEDA to oligoisoprenyllithium induces important changes (Figures 1 and 2): (i) the two triplets shift upfield as r is increased from 0 to 1 and (ii) simultaneously a trans/cis isomerization occurs. Only the cis triplet is observed for r = 0.5; thus the living complexed species has a cis-4,1 configuration.

These results provide information concerning the nature of the propagating species in the polymerization of isoprene by the oligoisoprenyllithium/TMEDA complex in nonpolar solvents. Indeed, the upfield shift demonstrates an increase of electron density on the γ carbon, as shown in polar solvents.[9,11] A parallel increase of 4,3 and 1,2 links must be observed in the polymer; isoprene polymerization in nonpolar solvents and in the absence of TMEDA leads to a predominantly *cis*-4,1-polyisoprene, although the living species has mainly a trans structure.[19]

On the other hand, a complete isomerization for r = 0.5 suggests complexation of all living ends, the oligo-