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Thiylation of Polyelectrophiles with Sulfur in Hydrazine Hydrate–Amine Systems

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Abstract—Thiylation of polyhaloalkanes and Paraform with elemental sulfur activated in hydrazine hydrate–organic amine systems is performed. Monoethanolamine, triethanolamine, and triethylamine were used as amines. The reactions gave thiocols of various structures. The products were characterized by elemental analysis and IR spectroscopy. Reductive cleavage of the synthesized thiocols was performed to obtain di- and polythiols.

Previously we showed that sulfur is easily activated in hydrazine hydrate–alkali (NaOH, KOH) systems to form polydisulfide anions, which allowed such systems to be used for fast and complete dissolution of sulfur [1, 2]. We also found that elemental sulfur is equally effectively activated in hydrazine hydrate–organic amine systems. As the organic amines we tried primary, secondary, and tertiary amines, such as monoethanolamine, morpholine, triethylamine, triethanolamine, as well as pure hydrazine hydrate [3].

Sulfur reacts with hydrazine hydrate (in the absence of bases) with heat release and vigorous evolution of hydrogen sulfide and ammonia, which condense at the outlet of the reactor as ammonium hydrosulfide. The reaction of sulfur with hydrazine hydrate–alkali or hydrazine hydrate–amine systems begins at room temperature and occurs with warming-up of reaction mixture to 60–65°C.

The quantity of dissolved sulfur depends on the nature of the amine and the concentration of the latter in hydrazine hydrate, and reaches 700–1300 g per 1 l of hydrazine hydrate. As the mole fraction of the amine increases from 5 to 50%, the maximum quantity of dissolved sulfur increases by a factor of about 1.5; therewith, primary amines are more active than secondary, and tertiary amines are the least active. The best results were obtained with hydrazine hydrate–alkali and hydrazine hydrate–monoethanolamine systems [4].

We have thoroughly studied thiylation of polyelectrophilic reagent in solutions of sulfur in hydrazine hydrate–alkali systems and developed in the course of this research new synthetic approaches to thiocols of various structures [5]. However, alkalis are hard bases and may induce dehydrohalogenation of alkyl halides; at high concentrations, alkalis can cause corrosion of the reactor material. Therefore, we considered it promising to replace alkalis with amines which are free of the above disadvantages and studied sulfur reactions with polyelectrophilic reagents in hydrazine hydrate–amine systems. As the polyelectrophiles we used dichloromethane, 1,2-dichloroethane, 1-bromo-3-chloropropane, 1,2,3-trichloropropane, β,β'-dichloroethyl ether (Chlorex), and Paraform. We also studied the behavior of mixtures of organochlorine compounds: a fraction containing 78% of 1,2- and 1,3-dichloropropanes and a fraction containing 76% of 1,2,3-trichloropropane. These fractions are epichlorohydrin production wastes whose utilization is an urgent ecological problem [6]. As the amine in most experiments we used monoethanolamine. In addition, for the sake of comparison, the hydrazine hydrate–triethanolamine and hydrazine hydrate–triethylamine systems were tested. The resulting data are shown in Table 1.

The example of dichloromethane and monoethanolamine was used to study the effect of conditions on the synthesis of thiocols in hydrazine hydrate–amine systems. For high yields of poly(methylene polysulfides), dichloromethane should be reacted with sulfur in the hydrazine hydrate medium at a low concentration of monoethanolamine. The $S:HOCH_2CH_2NH_2:N_2H_5OH:CH_2Cl_2$ mole ratio is 8 : 1 : 10 : 4. Therewith, the *x* value in the $–[CH_2S_x]–$ polymer unit is no more than 2.7 (polymer **I**, yield 75%). Decreased fraction of sulfur decreases both the yield of polymers and their sulfur content (polymers **II**, **III**, and **IIIa**). At the

Table 1. Conditions of synthesis and yields of thiocols

Polymer	S, g (g-mol)	Monoethanol-amine, g (mol)	$N_2H_4 \cdot H_2O$, g (mol)	H_2O, ml	CH_2Cl_2, g (mol)	Tempera-ture, °C	Reaction time, h	Yield, g (%)	x (y)
I	8.0 (0.25)	1.8 (0.03)	15.0 (0.3)	–	10.2 (0.12)	36–48	5.0	7.0 (75.3)	2.7
II	6.0 (0.19)	1.8 (0.03)	15.0 (0.3)	–	8.1 (0.095)	35–47	5.0	3.5 (47.7)	2.0
III	4.0 (0.125)	1.8 (0.03)	15.0 (0.3)	–	8.1 (0.095)	35–50	5.0	0.35 (6.3)	1.0
IIIa[a]								0.44 (9.4)	2.5
IV	3.2 (0.1)	6.1 (0.1)	8.1 (0.16)	–	4.2 (0.05)	37–41	4.5	0.7 (15.2)	1.2
V	3.2 (0.1)	6.1 (0.1)	9.0 (0.18)	5.0	4.2 (0.05)	45–65	4.0	0.4 (8.7)	1.0
VI	8.0 (0.25)	1.8 (0.03)	15.0 (0.3)	–	12.4 (0.125)[b]	50–70	2.5	9.7 (90.0)	2.5
VII	6.0 (0.19)	1.8 (0.03)	15.0 (0.3)	–	9.4 (0.095)[b]	65–75	2.5	8.0 (92.5)	2.0
VIII	4.0 (0.125)	1.8 (0.03)	15.0 (0.3)	–	6.2 (0.06)[b]	68–70	2.5	5.1 (90.0)	2.0
IX	6.0 (0.19)	4.5 (0.03)[c]	15.0 (0.3)	–	9.4 (0.095)[b]	65–75	3.0	7.9 (86.9)	2.5
X	4.0 (0.125)	3.0 (0.03)[d]	15.0 (0.3)	–	6.2 (0.062)[b]	65–75	3.0	5.0 (89.4)	2.2
XI	6.0 (0.19)	1.8 (0.03)	15.0 (0.3)	–	9.3 (0.06)[e]	70–85	2.5	7.6 (88.7)	2.0
XII	26.9 (0.84)	12.2 (0.2)	20.0 (0.4)	–	13.8 (0.09)[e]	80	2.0	11.0 (33.0)	4.0
XIII	6.0 (0.19)	1.8 (0.03)	15.0 (0.3)	–	14.8 (0.09)[f]	70–75	6.0	8.7 (87.9)	2.0
XIV	6.0 (0.19)	1.8 (0.03)	15.0 (0.3)	–	10.6 (0.09)[g]	70	6.0	4.2 (42.5)	2.0
XV	6.0 (0.19)	1.8 (0.03)	15.0 (0.3)	–	9.29 (0.063)[h]	75–80	1.5	8.1 (98.0)	2.0
XVI	4.5 (0.14)	1.4 (0.02)	11.3 (0.2)	–	10.1 (0.07)[i]	75–80	2.0	8.2 (83.7)	2.0
XVII	6.4 (0.2)	1.8 (0.03)	15.0 (0.3)	20.0	6.0 (0.2)[j]	65–70	2.0	2.8 (21.9)	1.5 (8.0)
XVIII	6.4 (0.2)	1.8 (0.03)	15.0 (0.3)	20.0	6.0 (0.2)[j]	95	6.0	2.7 (25.1)	2.0 (1.0)
XIX	5.0 (0.156)	1.8 (0.03)	15.0 (0.3)	20.0	9.0 (0.3)[j]	75–80	0.5	3.7 (38.6)	1.5 (2.0)
XX	3.6 (0.11)	6.2 (0.04)[c]	15.0 (0.3)	20.0	6.0 (0.2)[j]	68–75	2.5	2.3 (44.0)	2.0 (1.0)
XXI	2.4 (0.08)	3.0 (0.03)[d]	15.0 (0.3)	20.0	6.0 (0.2)[j]	68–75	2.5	4.5 (30.0)	1.0 (5.0)

[a] Prepared under the same conditions but contains more sulfur. [b] 1,2-Dichloroethane. [c] Triethanolamine. [d] Triethylamine. [e] 1,2,3-Trichloropropane. [f] 1-Bromo-3-chloropeopane. [g] Mixture of 1,2- and 1,3-dichloropropanes. [h] 1,2,3-Trichloropropane fraction. [i] Chlorex. [j] Paraform.

$S:HOCH_2CH_2NH_2:N_2H_5OH:CH_2Cl_2$ mole ratio of 1 : 1 : 1.5 : 0.5, poly(methylene sulfide) **IV** is formed as the major reaction product, but its yield is low (15%). The reaction in water at the same reagent ratio results in exclusive formation of poly(methylene sulfide) **V**, but its yield is even lower (8.7%). The reactions all commenced at room temperature, first occurred with heat release and then heating was required (to 50°C). Thiocols **I** and **II** are rubber-like elastic light green materials. Thiocols **IIIa**, **IV**, and **V** were obtained as light powders. Polymer **III** precipitated as solid green lumps and was ground into powder after treatment.

$$2nS + 5NH_2NH_2 \longrightarrow N_2 + 2(N_2H_5)_2S_n,$$

$$2nS + NH_2NH_2 + 4R_3N \longrightarrow N_2 + 2(R_3NH)_2S_n,$$

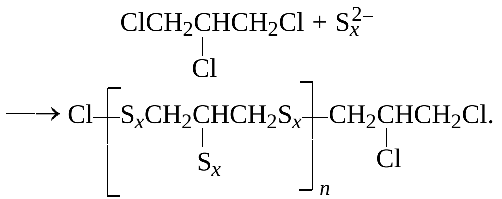
$$CH_2Cl_2 + S_x^{2-} \longrightarrow Cl\!\left[\!-CH_2S_x-\!\right]_n\!CH_2Cl\,.$$

Tiylation of 1,2-dichloroethane with the $S:HOCH_2 \cdot CH_2NH_2:N_2H_5OH$ system (molar ratio 4–8 : 1 : 10) commences at room temperature and occurs vigorously at 65–70°C to form disulfide thiocols **VI**, **VII**, and **VIII** as major products (total yield 92%). The same reaction with monoethanolamine instead of triethanolamine or triethylamine provides polymers **IX** and **X** in a slightly lower yield (87–89%). Polymers **VI**, **VII**, and **IX** precipitated as solid materials. They were washed with water and solvents, dried, and powdered. Polymers **VIII** and **X** precipitated as light powders.

$$ClCH_2CH_2Cl + S_x^{2-} \longrightarrow Cl\!\left[\!-CH_2CH_2S_x-\!\right]_n\!CH_2CH_2Cl.$$

VI–X

1,2,3-Trichloropropane is effectively thiylated at still higher temperatures (75–85°C) to form ether disulfide dendrimer **XI** in high yield (88.7%) ($S:HO \cdot CH_2CH_2NH_2:N_2H_5OH$ 6 : 1 : 10), or tetrasulfide dendrimer **XII** whose yield is no higher than 33% ($S:HOCH_2CH_2NH_2:N_2H_5OH$ 4 : 1 : 2). Polymers **XI** and **XII** are light yellow solid materials that were powdered after treatment and drying.



$$\mathrm{ClCH_2\underset{\substack{|\\ Cl}}{C}HCH_2Cl} + S_x^{2-} \longrightarrow \mathrm{Cl}\!\left[\mathrm{S_xCH_2\underset{\substack{|\\ S_x}}{C}HCH_2S_x}\right]_n \mathrm{CH_2\underset{\substack{|\\ Cl}}{C}HCH_2Cl}.$$

XI, XII, XV

1-Bromo-3-chloropropane is thiylated at 70–75°C to form polymer **XIII** (yield 88%). The polymer was obtained as a light green solid material that was powdered after treatment. Polymer **XIV** was prepared by the reaction of sulfur with the dichloropropane fraction in the hydrazine hydrate–monoethanolamine system and isolated as a light resin-like material that did not change after washing. It should be noted that the yield of polymer **XIV** (42.5%) was lower than that of polymer **XIII**. Polymers **XIII** and **XIV** contain disulfide bridges.

$$\mathrm{Cl(Br)CH_2CH_2CH_2Cl} + S_x^{2-} \longrightarrow \mathrm{Cl(Br)}\!\left[\mathrm{S_xCH_2CH_2CH_2S_x}\right]_n\mathrm{CH_2CH_2CH_2Cl}.$$

XIII, XIV

Polymer **XV** was obtained by treatment with sulfur of the 1,2,3-trichloropropane fraction in the hydrazine hydrate–monoethanolamine system and isolated as a yellow resin-like material. It contained much less sulfur than polymer **XI**, which implies that thiocol **XV** contains hydrocarbon fragments along with disulfide units.

Chlorex reacts with the $\mathrm{S:HOCH_2CH_2NH_2:N_2H_5OH}$ (7 : 1 : 10) thyilating system at 75–85°C to give disulfide polymer **XVI** in high yield (83.7%). The product is a resin-like light yellow material.

$$\mathrm{ClCH_2CH_2OCH_2CH_2Cl} + S_x^{2-} \longrightarrow \mathrm{Cl}\!\left[\mathrm{S_xCH_2CH_2OCH_2CH_2S_x}\right]_n\mathrm{CH_2CH_2OCH_2CH_2Cl}.$$

XVI

Paraform is a less effective bielectrophile in reaction with the $\mathrm{S{-}HOCH_2CH_2NH_2{-}N_2H_5OH}$ system. These reactions fail to commence at room temperature, occur only in aqueous medium, and result in preferential formation of disulfide thiocols with methylene oxide units in the polymeric chain (polymers **XVII**–**XXI**). The product yields are low irrespective of the reagent ratio. Polymers **XVII**–**XIX** were prepared with monoethanolamine as the amine component. With triethanolamine, an almost the same result was obtained, while the reaction with with triethylamine gave a polymer with a low sulfur content, which suggests that the latter polymer contains many methylene oxide and monosulfide units. Polymers **XVII** and **XIX** are light powders, polymer **XVIII** is a resin-like beige solid, and polymer **XX** is a resin-like light green material. Polymer **XXI** precipitates as a white powder. Probably, increased reaction time and temperature favor formation of polysulfide resin-like polymers.

$$\left[\mathrm{CH_2O}\right]_n + S_x^{2-} \longrightarrow \left[\mathrm{CH_2S_x(CH_2O)_y}\right]_n .$$

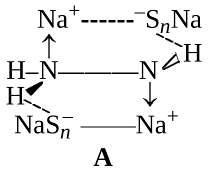
XVII–XXI

All reactions in hydrazine hydrate–amine systems are complete within 2–6 h. The structure of the synthesized polymers was proved by elemental analysis and IR and NMR specrtoscopy. Characteristics of the synthesized thiocols are listed in Table 2.

Thus, in hydrazine hydrate–amine systems sulfur is activated in a different way than in hydrazine hydrate–alkali systems. To prepare a disulfide thiocol in a hydrazine hydrate–alkali system, one should use an equimolar $\mathrm{S:NaOH:N_2H_5OH}$ ratio and perform alkylation with polyelectrophiles in aqueous medium. The corresponding polysulfide polymer can be obtained at equimolar sulfur : alkali : hydrazine hydrate ratios. These reactions always occur at room temperature and are accompanied with heat release [5].

In hydrazine hydrate–amine systems at equimolar reagent ratios in water, sulfur fails to react with dichloroalkanes. The reaction of sulfur with di- and polyhaloalkanes in hydrazine hydrate–amine systems occurs at a 10-fold molar excess of hydrazine hydrate with respect to amine. Sulfur, too, should be used in a 4–8-fold excess with respect to amine, but, irrespective of the quantity of sulfur, the resulting polymers contain mostly disulfide bridges. Paraform only methylenates sulfur solutions in hydrazine hydrate–amine systems heated to 60–90°C, like in hydrazine hydrate–alkali systems. With amine instead of alkali, the yield of polymers is lower.

The observed regularities provide evidence for our previous proposal that sulfur activation in hydrazine hydrate–alkali systems involves formation of a complex reagent [7]. Therewith, the sulfide anions generated from sulfur are stabilized by hydrazine hydrate as 13:10:07complex **A**.



A

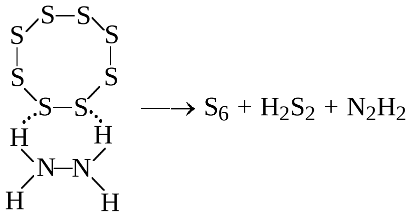
In hydrazine hydrate–amine systems, the cyclic octameric molecule S^8 is cleaved not by OH^- anions,

Table 2. Characteristics of thiocols

Polymer	mp, °C	IR spectrum, cm^{-1}				Found, %			
		$\nu(CH_2)$	$\delta(CH_2$, C–O)	ν(C–S)	ν(S–S)	C	H	Cl	S
I	58–99	3020, 2955, 2898	1480, 1380, 1175	805, 680	490, 470	12.56	2.35	1.05	86.53
II	63–90	3020, 2960, 2895	1480, 1380, 1175	802, 780, 720, 690, 675	480, 460	13.02	1.64	0.97	82.47
III	78–95	2959, 2924, 2895, 2855	1360, 1170, 1405, 1261	777, 760, 731, 702, 660		–	–	4.58	71.78
IIIa	75–97	2951, 2921, 2852	1360, 1170	760, 731, 659, 630	467	–	–	2.48	84.96
IV	104–115	2956, 2921, 2892, 2852	1360, 1170	779, 754, 731, 705, 627	465, 440	19.25	4.48	0.49	72.77
V	91–117	2948, 2892, 2852	1361, 1170	780,759, 731, 702, 669, 627		18.72	4.49	1.87	70.19
VI	92–119	2966, 2916, 2857	1402, 1246, 1185, 1103	725, 670	471, 419	18.55	3.90	1.59	74.53
VII	85–96	2962, 2911	1408, 1246, 1183, 1105	730, 674	489, 471	23.60	4.46	3.25	69.55
VIII	85–134	2901, 2845	1402, 1250 w, 1185, 1101	730, 680	475	24.45	5.15	1.6	71.19
IX	82–98	2947, 2911, 2853	1408, 1247, 1183, 1105	731, 675	472	22.43	3.76	1.39	74.13
X	109–114	2948, 2911, 2851	1408, 1247, 1194, 1182, 1106	732, 675	470, 418	22.40	4.04	1.97	71.86
XI	183–220	2962, 2927, 2865	1500, 1396, 1237, 1209, 1144	868, 824	465, 429, 413	21.29	3.29	3.92	71.21
XII	176–196	2920, 2856 w	1487, 1454, 1397, 1241, 1213, 1149	873, 826, 661, 609	489, 472, 454, 437	11.17	1.92	6.94	80.39
XIII	58–68	2918, 2898, 2858, 2836	1426, 1401, 1338, 1291, 1262, 1239, 1124	834, 770, 667, 649, 613	489, 471, 460, 434	–	–	2.47 5.57[a]	62.68
XIV	110–140	2955, 2920, 2856	1442, 1401, 1368, 1296, 1249, 1165, 1101	886, 822, 736, 660, 627	492, 478, 465, 447, 423	–	–	4.87	68.24
XV	210–230	3045, 2964, 2923, 2868	1492, 1447, 1402, 1334, 1250, 1215, 1145	876, 833, 712, 656	474, 436, 426	–	–	5.98	51.47
XVI	–	2959, 2905, 2860	1420, 1400, 1360, 1297, 1110	740, 670	480	31.29	4.80	8.82	45.42
XVII	180–185	2950, 2889, 2845, 2777, 2711	1471, 1436, 1346, 1292, 1195, 1174	760, 731, 703, 622	489, 470	33.00	6.00	–	29.80
XVIII	145–168	2952, 2902, 2842, 2774, 2718	1470, 1434, 1346, 1280, 1259, 1194, 1173, 1088 w	813, 777, 732, 702	467	26.03	4.92	–	57.06
XIX	176–178	2961, 2922, 2843, 2776, 2714	1469, 1435, 1346, 1290, 1259, 1192, 1089 w	610	458	25.50	4.72	–	48.10
XX	68–101	2954, 2921, 2856	1459, 1405, 1236, 1172, 1079, 1007	813, 668	467	21.76	4.22	–	66.82
XXI	195.5–198	2948, 2924, 2845, 2776, 2714	1469, 1436, 1346, 1291, 1261, 1194, 1090 w	623, 600	436	34.89	6.11	–	15.30

[a] Bromine content.

but directly by hydrazine to form a cyclic transition state like that proposed for sulfur reduction [2].



B

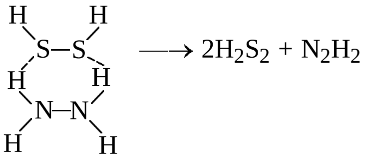
In the absence of amine, sulfane decomposes into hydrogen sulfide and sulfur, and the diimide formed reduces hydrazine to ammonia.

$$N_2H_4 + N_2H_2 \longrightarrow 2NH_3 + N_2.$$

The amine (or excess hydrazine) functions in no other was as to stabilize the sulfane formed.

$$R_3N\text{---}H\text{–}S\text{–}S\text{–}H\text{---}NR_3.$$

Complex **A** in which *n* can be from 1 to 8 or even greater is impossible to form in the absence of alkali. The geometric structure of transition complex **B** predetermines formation of disulfane (H_2S_2) only. The latter can further be reduced to hydrogen sulfide.



Probably, the above reasoning explains the preferential formation of di- and monosulfide fragments in the synthesis of thiocols in hydrazine hydrate–amine systems.

The structure of the synthesized thiocols was confirmed by their reductive cleavage in the hydrazine hydrate–potassium hydroxide system [8, 9]. From polymers **VI** and **VII** we obtained ethane-1,2-dithiol in 60% yield and from polymers **XI** and **XV**, propane-1,2,3-trithiol in ~30% yield.

In whole hydrazine hydrate–amine systems are more potent activators of sulfur. Therewith, the systems are effective at low amine contents, do not corrode metallic reactor surfaces, and feature ecological and practical feasibility. These systems hold promise for production of thiocols from elemental sulfur.

EXPERIMENTAL

The IR spectra of polymers **I**, **II**, and **IX** (in thin films) and polymer **VIII** (in KBr pellets) were measured on a Specord IR-75 spectrometer. The IR spectra of the other polymers were obtained on a Bruker IFS-25 instrument in KBr pellets. The ^1H NMR spectrum of polymer **XVI** was registered on a Bruker DPX-400 spectrometer (400 MHz) in $CDCl_3$ solutions, internal reference HMDS.

The synthesis and reductive cleavage of polymers were performed in a three-necked flack equipped with a stirrer, reflux condenser, thermometer, and dropping funnel.

Preparation of sulfur solutions in $N_2H_4 \cdot H_2O$–amine and $N_2H_4 \cdot H_2O$–amine–water systems. System $N_2H_4 \cdot H_2O$–amine. Hydrazine hydrate and amine were placed into a flask and heated with vigorous stirring to 45°C, after which sulfur powder was added in portions over the course of 1 h. Therewith, the reaction mixture got orange-red and warmed up to 60–65°C. The solution was exposed at this temperature for 1 h and then cooled to room temperature. The reagent ratios used are shown in Table 1.

System $N_2H_4 \cdot H_2O$–amine–water. Hydrazine hydrate, amine, and water were placed into a flask and heated with vigorous stirring to 80–85°C, after which sulfur powder was added in portions over the course of 1 h. The reaction mixture was heated for 1 h at 85–90°C.

Poly(methylene polysulfides). The reactions of polychloroalkanes with sulfur solutions in hydrazine hydrate–amine systems commenced at room temperature and involved heat release. Once all alkylating agent had been added, the reaction mixture was exposed at a specified temperature for some hours (Table 1). Polymers precipitated as powders or resin-like materials. The precipitates were washed with cold water, acetone, and ether, dried first in air and then in a vacuum, washed with hydrogen sulfide to remove unreacted sulfur, dried in a vacuum, and analyzed.

Polymer **XVI** was isolated by extraction with chloroform that was then removed in a vacuum under heating. ^1H NMR spectrum of polymer **XV**, δ, ppm: 2.89 m (CH_2S), 3.08 m (CH_2S_2), 3.15 m (CH_2S_3), 3.62 t (SCH_2CH_2O), 3.74 m (CH_2Cl), 3.8 m (CH_2OCH_2).

Polymers **XVII**–**XXI** were treated with boiling water to remove unreacted Paraform.

Reduction of polymer VII. Potassium hydroxide, 23.5 g, was dissolved in 40 ml of hydrazine hydrate, and 7.54 g of thiocol **VII** was added to the soluton. The mixture was stirred for 2.5 h at 80°C until the polymer has dissolved completely, cooled under argon, and poured into a mixture of ice and 60 ml of conc.

HCl. Ethane-1,2-dithiol was extracted with ether, the extract was dried over $MgSO_4$, the ether was removed, and the product was distilled in a vacuum. Yield 5.6 g (56.8%), bp 56°C (45 mm Hg), n_D^{25} 1.5560 [8].

Reduction of polymer XI. Potassium hydroxide, 5.46 g, was dissolved in 20 ml of hydrazine hydrate, and 3 g of thiocol **XI** was added in portions at 45°C. The mixture was stirred at 80–85°C for 2 h until the thiocol had dissolved completely. After cooling, the reaction mixture was poured into a mixture of ice with 32 ml of conc. HCl. The oily liquid that separated was extracted with ether and methylene chloride and dried with calcium $CaCl_2$. The solvent was removed, and the residue was distilled in a vacuum to obtain 1 g (30%) of propane-1,2,3-trithiol, bp 88–90°C (3 mm Hg) [9].

Polymer XV was reduced in a similar way to obtain 0.6 g (26%) of propane-1,2,3-trithiol.

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