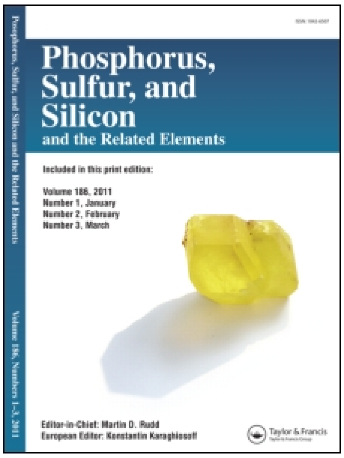

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SOME FEATURES OF THE REDUCTION OF POLY(METHYLENE SULFIDES) AND POLY(METHYLENE POLYSULFIDES)

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SOME FEATURES OF THE REDUCTION OF POLY(METHYLENE SULFIDES) AND POLY(METHYLENE POLYSULFIDES)

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The reductive destruction of poly(methylene sulfides) and poly(methylene polysulfides) in the system hydrazine hydrate – NaOH at 70–115°C involves cleavage of the C-S bond and the formation of sulfide, disulfide and trisulfide anions. Nitrogen and methane are main gaseous products of reduction. The reduction of C-S bonds in these polymers is proven by electrochemical methods.

Keywords: poly(methylene sulfides); poly(methylene polysulfides); hydrazine hydrate; reduction; cyclic voltammetry

INTRODUCTION

Dialkyl sulfides and thioformaldehyde polymers are distinguished for their C-S bond strength ($D = 73$ kcal/mol)[1]. In these compounds the C-S bond cleavage is facilitated by alkylhalides or cyanide bromide through intermediate formation of sulfonium salts[2–4]. The C-S bond can also be broken by alkali metals and zinc[5]. Halogens and sulfur halides cleave this bond in trithiane[6]. Dialkyl disulfides are readily reduced to alkane thiolate anions by alkalis in an aqueous medium or in the system hydrazine hydrate – base[7–9].

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[*] Corresponding Author.

During our systematic search for new sulfur-containing redox polymers[10–12] we have examined some features of C-S and S-S bonds cleavage in poly(methylene sulfides) and poly(methylene polysulfides) in the system hydrazine hydrate – NaOH. The results are briefly discussed in the present paper.

RESULTS AND DISCUSSION

The polymers were prepared by the reaction of paraform or urotropine with sodium sulfide or polysulfide in an aqueous-alcohol medium. Reduction was performed by heating the polymers in a hydrazine hydrate – NaOH solution at 70–115°C with subsequent analysis of the gaseous reaction products and the products of ethylation (with ethyl bromide) of solutions of the decomposed polymers. The reductive destruction of polymers conditions and the yields the products of ethylation are presented in the Table.

When heated in the system hydrazine hydrate – NaOH, poly(methylene sulfides) prepared by reaction of sodium sulfide with paraform decompose completely for 1.5 h to afford sulfide anion (S^{-2}):

$$\left[CH_2S \right]_n \xrightarrow{N_2H_4 \cdot H_2O/NaOH} Na_2S + N_2 + CH_4 + H_2 + NH_3 + O_2 + H_2O \quad (1)$$

The gaseous products of reaction (1) contain nitrogen, methane, hydrogen, oxygen (68, 12.5, 2.5 and 0.95 %, respectively) and ammonia. I-butane and n-butane are present in trace amounts: 0.0001 and 0.00007 %, respectively (GLC). EtBr-assisted ethylation of the liquid products of reaction (1) leads to only diethyl sulfide (yield 61.4%).

In the system hydrazine hydrate – NaOH trithiane is also reduced following equation (1), but much more slowly than poly(methylene sulfide): as little as 18 % of trithiane decomposes for 4.5 h. The products of ethyl bromide ethylation of liquid products of trithiane reduction contain only of diethyl sulfide (yield 10.2%), the rest being 1,1-diethyl hydrazine (58 %) and triethyl hydrazine (8 %) (Table). The latter two compounds are produced upon ethylation of hydrazine. This becomes possible in deficiency of a stronger nucleophile, sodium sulfide.

TABLE Reductive destruction of poly(methylene sulfides) and poly(methylene polysulfides) (polymers conversion 100%)

Run	*Polymer, g (mmol)*	*NaOH, g (mmol)*	*$N_2H_4 \cdot H_2O$, ml*	*EtBr, g (mmol)*	*T, °C (time, h)*	*Yield of reaction products, g*	*Yield ethylation of products, %*		
							Et_2S	*Et_2S_2*	*Et_2S_3*
1	$-[-CH_2S-]-_n$ 1.5 (33)	2.64 (66)	10.0	3.6 (33)	70–100 (1.5)	2.7	61.4	–	–
2	TpHTHaH[a] 1.5 (33)	2.64 (66)	10.0	3.6 (33)	95–115 (4.5)	0.3	10.2[b]	–	–
3	$-[-CH_2S_2-]-_n$ 1.6 (20)	1.6 (40)	6.0	2.2 (20.2)	70–100 (1.5)	2.4	56.5	31.5	–
4	$-[-CH_2S_3-]-_n$ 1.5 (14)	1.1 (27.5)	5.0	1.8 (17)	80–85 (1.0)	2.5	–	83.6	7.5
5	$H_2N\text{-}[CH_2S_2]_5[CH_2S]_{28}CH_2NH_2$ 1.5 (20)	1.6 (40)	6.0	2.2 (20.2)	70–95 (1.5)	1.7	53.7[c]	26.8	–
6	$H_2NCH_2S_2\text{-}[CH_2S]_{11}CH_2NH_2$ 1.34 (18)[d]	1.44 (36)	6.0	2.2 (20.2)	95–108 (1.0)	2.3	58.4	24.2	–
7	$H_2NCH_2S_2\text{-}[CH_2S]_{11}CH_2NH_2$ 0.86 (12)	1.0 (25)	5.0	1.5 (14)	95–110 (2.5)	2.45	73.6	13.8	–

a. Trithiane conversion 18 %.
b. 1,1-diethyl hydrazine (57.8 %) and triethyl hydrazine (8.0 %) are present.
c. MeSEt is present (yield 5.5%).
d. Polymer conversion 95 %.

Poly(methylene disulfide) prepared by the reaction of sodium disulfide with paraform, completely decomposes on heating with the system hydrazine hydrate – NaOH for 1.5 h by equation (2) to form both sodium sulfide and sodium disulfide. Therefore the products of ethylation of the reduced polymer solution contain diethyl sulfide (yield 56.5%) and diethyl disulfide (yield 31.5%,).

$$\left[CH_2S_2 \right]_n \xrightarrow{N_2H_4\cdot H_2O/NaOH} Na_2S + Na_2S_2 + N_2 + CH_4 + H_2 + NH_3 + O_2 + H_2O \quad (2)$$

Poly(methylene trisulfide), prepared by the reaction of sodium trisulfide with paraform, is fastest to reduce (1 h). In this case diethyl disulfide (yield 83.6%) and diethyl trisulfide (yield 7.5%) are the products of ethylation of the destructed polymer. This indicates that sulfur was removed from [CH_2S_3]-units as disulfide and trisulfide anions according to reaction (3):

$$\left[CH_2S_3 \right]_n \xrightarrow{N_2H_4\cdot H_2O/NaOH} Na_2S_2 + Na_2S_3 + N_2 + CH_4 + H_2 + NH_3 + O_2 + H_2O \quad (3)$$

The reduction of poly(methylene polysulfide) for 1.5 h (equation 4) prepared by the reaction of sodium tetrasulfide with urotropine, leads to sodium sulfide and sodium disulfide. The ethylation of the two products gives diethyl sulfide (yield 53.7%) and diethyl disulfide (yield 26.8%). Simultaneously methylethyl sulfide is formed (yield 5.5%).

$$H_2N-\left[CH_2S_2 \right]_5-\left[CH_2S \right]_{28}CH_2NH_2 \xrightarrow{N_2H_4\cdot H_2O/NaOH} \quad (4)$$

$$\longrightarrow Na_2S + Na_2S_2 + N_2 + CH_4 + H_2 + NH_3 + O_2 + H_2O$$

A polymer with a higher nitrogen content, prepared in an analogous manner from urotropine, but in the presence of sodium bicarbonate, is reduced more slowly (2.5 h). In this case the ethylation of the products of polymer reduction also gives mainly diethyl sulfide (yield 73.6%) and diethyl disulfide (yield 13.8%). During 1.5 h the polymer is reduced by 95 %, the rest being sufficiently depleted in sulfur (38 %).

Thus, an interesting feature of the reduction of poly(methylene sulfides) and poly(methylene polysulfides) by the system $N_2H_4 \cdot H_2O$ – NaOH is the unexpectedly ready (compared to dialkyl sulfides and dialkyl disulfides) cleavage of C-S bonds, which leads to the formation of methane, whilst the unreduced di- and trisulfide anions (in case of di- and polysulfide polymers) remain intact.

Under analogous conditions diethyl disulfide gives sodium ethyl thiolate, but not ethane (equation 5):

$$(C_2H_5)_2S_2 \xrightarrow{N_2H_4 \cdot H_2O/NaOH} 2\ C_2H_5SNa + N_2 + H_2 + H_2O \quad (5)$$

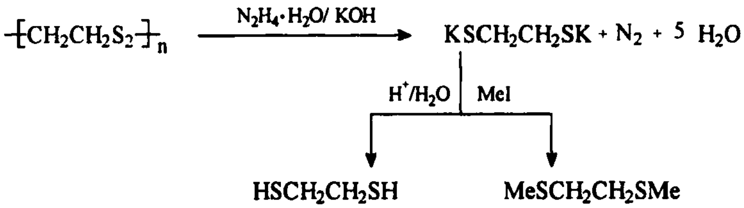
$$2\ C_2H_5SNa + CH_2Cl_2 \longrightarrow C_2H_5SCH_2SC_2H_5$$

Methylene chloride treatment of the reaction mixture results in the expected bis(ethylthio)methane.

It is important that no bis(ethylthio)methane forms on ethylation of the reduced polymers in the system hydrazine hydrate – NaOH. This provides evidence for the fact that the reductive destruction of polymers involves no formation of bis(sodiumthio)methane. As far as bis(ethylthio)methane is concerned, it is reduced only by 18 % in the system hydrazine hydrate – NaOH for over 1.5 h. The reductive destruction of bis(ethylthio)methane is accompanied by cleavage of EtS-CH_2bonds and formation of ethylthio anions, the ethylation of which leads to diethyl sulfide.

Interestingly, the reduction of poly(ethylene disulfides) in the system hydrazine hydrate-KOH and the subsequent methylation of the reaction products give 1,2-bis(methylthio)ethane, whereas the acidification of the reaction mixture leads to the expected 1,2-ethanedithiol; this means that the reduction occurs in a normal fashion without C-S bond cleavage (equation 6)[13].

The redox properties of the synthesized poly(methylene sulfides) and poly(methylene polysulfides) were also examined by electrochemical method of cyclic voltammetry. Cyclic voltammograms are of help in studying the processes of reduction and oxidation of polymers. Cathode peaks



$$-\!\left[CH_2CH_2S_2\right]\!-_n \xrightarrow{N_2H_4\cdot H_2O/\,KOH} KSCH_2CH_2SK + N_2 + 5\,H_2O$$

$$KSCH_2CH_2SK \xrightarrow{H^+/H_2O} HSCH_2CH_2SH \qquad KSCH_2CH_2SK \xrightarrow{MeI} MeSCH_2CH_2SMe$$

(6)

at potentials 2.41, 2.04 and 1.92 V for poly(methylene sulfide) (Fig. 1a), 2.31 and 1.82 V for poly(methylene disulfide) (Fig. 1b), and 2.21, 2.02, 1.84 V for poly(methylene trisulfide) (Fig. 1c) correspond to the reduction of S-S bonds and element sulfur (Fig. 1d), taken as a standard. As expected, the reduction of poly(methylene disulfide) and poly(methylene trisulfide) occurs at higher current amplitudes and with more clearly-expressed reduction peaks compared to those of poly(methylene sulfide). The presence of cathode peaks corresponding to S-S bond reduction on the voltammogram of poly(methylene sulfide) indicates the latter to contain a small amount of polysulfide units, possibly due to admixture of sodium polysulfides in the initial sodium sulfide. The appearance of new reduction peaks in all the three polymers at more negative potentials: 0.68 and 1.22 V, 0.82 and 1.2 V, 0.86 and 1.16 V for poly(methylene sulfide), -di- and -trisulfide, respectively (Fig. 1a,b,c), which are absent in the voltammogram of sulfur, is caused by C-S bond reduction[14] which is in agreement with the results of chemical reduction. The highest peak intensity is observed in poly(methylene sulfide) having, in fact, only C-S bonds (not counting admixed polysulfide units).

In order to evaluate the electric capacity of cathodes we carried out cycling of the obtained polymers (used as active materials) in lithium button cells. The resulting dependencies of discharge capacity change on the cycle order (Fig. 2) show the absence of discharge capacity up in the poly(methylene sulfide)-based cathode (curve 1) and a significant increase in this value in the case of poly(methylene disulfide)- and poly(methylene trisulfide)-based cathodes (curves 2 and 3). For the latter two polymers the electric capacity is stabilized at a level of 160 and 220 mA·h·g^{-1}, respectively, after the forth discharge cycle.

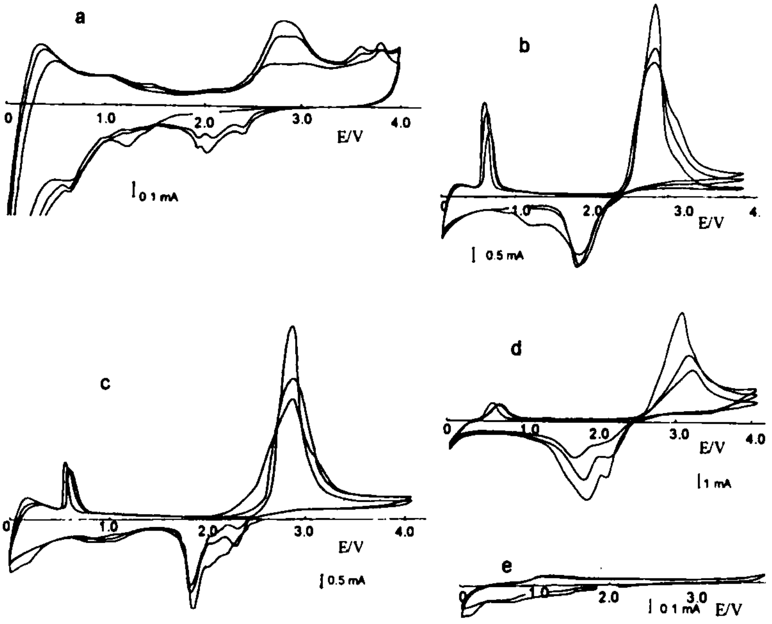


FIGURE 1 Cyclic voltammograms of poly(methylene sulfide) (a), poly(methylene disulfide) (b), poly(methylene trisulfide) (c), element sulfur (d) and cathode without polymer composition (e) (scanning velocity)

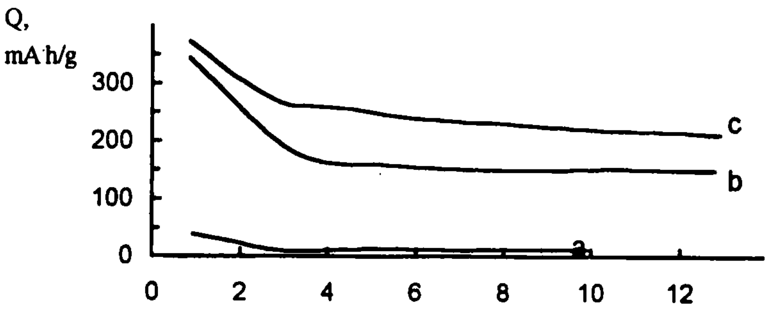
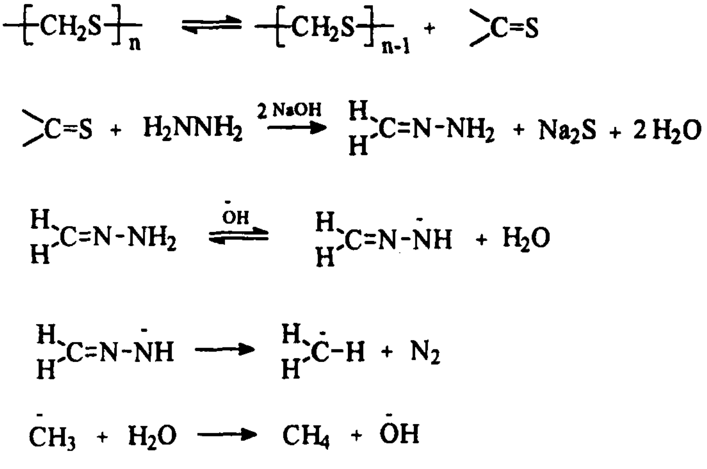


FIGURE 2 Discharge capacity rate (Q) of lithium accumulator cathodes based on poly(methylene sulfide) (a), poly(methylene disulfide) (b) and poly(methylene trisulfide) (c) in the process of cycling (current density)

CONCLUSION

Thus, reductive destruction, that involves selective breakdown of C-S bonds and removal of all sulfide and polysulfide fragments with the formation of methane in the hydrazine hydrate – base system, is prone to only poly(methylene sulfides) and poly(methylene polysulfides), which is undoubtedly caused by some features of the poly(methylene sulfide) and poly(methylene polysulfide) chain.

The reduction of poly(methylene sulfide) (polythioformaldehyde) to methane by the system $H_2NNH_2/NaOH$ probably presents the first example of the Kizhner reaction in the series of thiocarbonyl compounds. The thioformaldehyde, which is reversibly abstracted from poly(methylene sulfides) is unreversibly bonded to formaldehyde hedrasone with formation of an alkali metal sulfide. Further the hydrazonium anion decays to afford methane and nitrogen[15] by a classical scheme (7):



(7)

The above scheme (7) is confirmed by the fact that poly(methylene polysulfides) are also reduced with breakdown of only the C-S bonds (elimination of thioformaldehyde and formation of alkali metal disulfides and trisulfides). Moreover, under analogous conditions poly(ethylene sulfide) is not reduced at all.

The reduction of C-S bonds in poly(methylene sulfide) and poly(methylene polysulfides) is supported by the results of electrochemical study.

EXPERIMENTAL

Analysis of liquid reaction products was carried out by GLC, GLC-MS spectrometry and ^{1}H NMR spectroscopy.

LCM-80MD Chromatograph, liquid phase DC-550 (5 %) and XE-60 on Chromaton N-AW-HMDS, column 2 m × 3 mm, column temperature linear programming from 35 to 230 °C at a rate of 12 °C/min, gas-carrier helium.

LKB-2091 GLC-MS Spectrometer (capillary column, SE 30 phase, column temperature linear programming from 35 to 240 °C at a rate of 8 °C/min), ionization energy 70 eV.

^{1}H NMR Spectra were run on a Jeol FX-90Q (90 MHz) instrument, $CDCl_3$, HMDS.

GLC of gases was performed on a TsVET chromatograph (ionization-flame detector), modified alumo-gel as a solid phase, column 3 m × 3 mm, column temperature 80°C.

Analysis of gases using IR spectroscopy was carried out on a Specord-751R spectrometer.

Synthesis of polymers

Poly(methylene trisulfide) is prepared by fast introduction at 60–70 °C of 1.5 g (50 mmol) of paraform and 4.2 g (50 mmol) of $NaHCO_3$ (buffer) into an Na_2S_3 solution prepared from 3.2 g (0.1 g-at) of sulfur, 12 g (50 mmol) of $Na_2S{\cdot}9H_2O$, 2.5 ml of H_2O and 1 ml of EtOH. The reaction mixture was heated at 80°C for 3 h. Precipitation of the polymer begins immediately after paraform introduction. The reaction mixture decolorizes. The precipitate is separated, washed with water, ethanol and ether and dried to give 3.7 g of a green soft monolithic rubber-like polymer, which becomes hard and abradable to powder on long standing. Yield is 63.7% basing on initial sulfur, m.p. 55–75°C. It was found, %: C 11.2, H 1.6, S 87.2%. IR spectrum of polymer, cm^1: 2944, 2899 (ν CH_2); 1460, 1355 (δ CH_2); 1171, 1000 864, 803 (δ C-H); 773, 758, 728, 691 (ν C-S); 485, 465 (ν S-S).

Poly(methylene disulfide) is prepared by fast introduction at 60–70 °C of 1.5 g (50 mmol) of paraform and 4.2 g (50 mmol) of $NaHCO_3$ (buffer) into an Na_2S_2 solution prepared from 1.6 g (0.05 g-at) of sulfur, 12 g (50 mmol) of $Na_2S{\cdot}9H_2O$. 2.5 ml of H_2O and 1 ml of EtOH. The reaction mixture was heated at 80°C for 3 h. Precipitation of the polymer begins immediately after paraform introduction. The precipitate is separated, washed with water, ethanol and ether and dried to give 2 g of a light-green color hard polymer, which abradable to powder on long standing. Yield is 51.3% basing on initial sulfur, m.p. 70–82°C. It was found, %: C 16.4, H 2.9, S 80.7%. IR spectrum of polymer, cm^1: 2955, 2892 (ν CH_2); 1458, 1361 (δ CH_2); 1170, 1031, 1000 860, 846, 810 (δ C-H); 777, 760, 730, 701 (ν C-S); 488, 467 (ν S-S).

Poly(methylene sulfide) is prepared by fast introduction at 60–70°C of 3 g (100 mmol) of paraform and 8.4 g (100 mmol) of $NaHCO_3$ (buffer) into an Na_2S solution prepared from 24 g (0.1 mole) of $Na_2S{\cdot}9H_2O$, 5 ml of H_2O and 2 ml of EtOH. The reaction mixture was heated at 80°C for 3 h. Precipitation of the polymer begins immediately after paraform introduction. The precipitate is separated, washed with water, ethanol and ether and dried to give 1.5 g of a white powdery polymer. Yield is 32%, m.p. 210–215°C. It was found, %: C 22.5, H 3.8, S 73.3%. IR spectrum of polymer, cm^1: 2955, 2904 (ν CH_2); 1600, 1452, 1366 (δ CH_2); 1173, 1127, 1043, 1006, 880, 851, 840 (δ C-H); 733, 706, 672 (ν C-S).

Polymer (Table, run 5) 14.0 g (100 mmol) of hexamethylenetetramine was added to sodium tetrasulfide solution prepared from 9.6 g (0.3 g-at) sulfur, 24.0 g (100 mmol) $Na_2S{\cdot}9H_2O$, 5 ml H_2O and 2 ml EtOH at 60°C (1 h). The mixture was heated with stirring (100–105°C, 3 h). Polymer began to precipitate in 0.5 h after hexamethylenetetramine addition and under boiling it precipitated in the form of a white powder and the solution became light yellow. Polymer was filtered, washed many times with water, ethanol and dried *in vacuo* to give 10.1 g of powdered product with m.p. 135–148°C. The yield was 42% with respect to starting reagents. It was found, %: C 23.8, H 3.6, S 70.7, N 1.6. Brutto: $C_2H_{3.6}S_{2.2}N_{0.11}$. IR spectrum, cm^{-1} (KBr): 3320 (ν NH_2); 2955, 2905 (ν C-H); 1674 (NH_2); 1417, 1365 (δ CH_2); 1234 (ν C-N); 1173, 1084, 1007, 958 878, (δ C-H); 745, 733, 706, 668 (ν C-S); 470 (ν S-S).

Polymer (Table, run 6) 14.0 g, (100 mmol) of hexamethylenetetramine, 8.4 g (100 mmol) of $NaHCO_3$ (buffer), 40 ml of H_2O were slowly added to hot (40°C) sodium tetrasulfide solution prepared from 4.8 g (0.15 g-at) sulfur, 12.0 g (50 mmol), $Na_2S{\cdot}9H_2O$, 2.5 ml H_2O and 1 ml EtOH. The mixture was heated (95–100°C, 3 h). Polymer precipitated on the flask bottom. Precipitated polymer was filtered, washed with water, ethanol and dried *in vacuo* to give 5.6 g of sticky green product which is not hardened when allowed to stand. The yield was 50% with respect to starting reagents. It was found, %: C 23.0, H 3.4, S 68.6, N 4.8. Brutto: $C_2H_4S_2N_{0.34}$. IR spectrum, cm^{-1} (film): 3323 (ν NH_2); 2961, 2915, 2858 (ν C-H); 1676 (NH_2); 1418, 1383 (δ CH_2); 1332, 1282, 1251 (ν C-N); 1176, 1086, 1007, 959, 921, 869, 805 (δ C-H); 729, 689, 666, 640 (ν C-S); 489, 471 (ν S-S).

Reductive destruction of polymers

Sodium hydroxide was dissolved in hydrazine hydrate with good stirring at 40–45°C in a three-neck flask equipped with a stirrer, a dropping funnel, thermometer and reflux condenser. After addition of polymer the reaction mixture was heated at temperatures indicated in the Table, until complete dissolution of the polymer. This was accompanied by vigorous liberation of gases, which were collected and analyzed. The reaction mixture was cooled to room temperature and ethyl bromide was slowly introduced (in so doing the temperature rose up to 40–42°C). This temperature was maintained for a while until the formation of an organic layer. The organic layer was separated and analyzed. The reaction conditions and the composition of liquid products are presented in the Table. The composition of products is confirmed by mass spectrometry and GLC – comparison with the known samples. IR spectra of gaseous products indicate the presence of saturated hydrocarbons (cm^{-1}): ν3000, δ1295 and δ960.

Analysis of gaseous products of poly(methylene sulfide) reduction

According to GLC data, methane (12.5 %) presents a major component of gaseous hydrocarbons isolated in one of the runs on reduction of poly(methylene sulfide). The amount of i-butane and n-butane is 0.0001 and 0.00007 %, respectively. Ethane, propane and ethylene are absent. Other components of gaseous reaction mixtures are represented by nitrogen (68 %), hydrogen (2.46 %), oxygen (~1.0 %) trapped from the air. GLC-MS spectrometry also showed the presence of ammonia.

Synthesis and reduction of bis(ethylthio)methane

A three-neck flask equipped with a stirrer, a reflux condenser, a thermometer and a dropping funnel was charged with 75 ml of hydrazine hydrate and 12 g (300 mmol) of NaOH, the flask contents was heated upon intensive stirring to 60°C and then 18.3 g (150 mmol) of diethyl disulfide was introduced. The reaction mass was heated at 80–90°C for 2 h, cooled to room temperature and 12.6 g (150 mmol) of methylene chloride was introduced. This was accompanied by a temperature rise to 60°C. This temperature was maintained for 4 h, then the mixture was cooled and the organic layer was separated, washed with water and dried over $CaCl_2$. The solvent was distilled off, the residue distilled in vacuum. This gave 8.3 g of diethyl disulfide and 2.5 g of bis(ethylthio)methane, b.p. 97 °C (50 mm Hg), $n_D^{20} = 1.5145$.[16] Found (%):C 44.93, H 8.12, S 46.95. $C_5H_{12}S_2$. Calculated (%):C 44.12, H 8.82, S 47.06. ^1H NMR spectrum (δ, m. d.): 3.81s ($S\text{-}CH_2\text{-}S$), 2.65k ($S\text{-}CH_2\text{-}C$), 1.25t ($C\text{-}CH_3$). Mass spectrum [m/z (intensity)]: 136 (M^+) 72; 75 (100) ($M\text{-}C_2H_5S$).

In order to reduce bis(ethylthio)methane 0.25 g (6.2 mmol) of NaOH was dissolved in the reaction flask in 2 ml of hydrazine hydrate at 40–45°C. Then 0.42 g (3.1 mmol) of bis(ethylthio)methane was introduced and the reaction mixture was heated at 90–100°C for 1.5 h. After cooling to room temperature 0.5 g (4.6 mmol) of ethyl bromide was introduced. Then the reaction mixture was heated at 40–42°C for 0.5 h, cooled, the organic layer was separated and analyzed by GLC. The composition of the reaction products was as follows: bis(ethylthio)methane 82 %, diethyl sulfide 18 %.

Electrochemical examination

Electrochemical experiments were performed using two-electrode disc cells with an aluminium cathode (1.5 cm^2) coated with carbon and a mixture of polymer, black and polyethylenoxide in a ratio of 50:35:15 ms %, and a lithium anode. A 1M solution of $(CF_3SO_2)_2NLi$ in dimethoxyethane served as an electrolyte. Cyclic voltammograms were fixed on a PI-50–1.1 potentiostate at potential application rate of 1 mV/sec in the 0 – 4 V range and registrated by a two-coordinate PDA-1 recorder.

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