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Preparation and Properties of Polyvinylenepolysulfides Based on Trichloroethene and Sodium Polysulfides

G. F. Prozorova, I. V. Mazyar, V. V. Nosyreva,
S. A. Korzhova, T. I. Vakul'skaya, and B. A. Trofimov

A.E. Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: prozorova@irioch.irk.ru

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Abstract—Interaction of trichloroethene with sodium tetra- and pentasulfide (prepared in turn from sodium sulfide and elemental sulfur) has lead to new family of polyvinylenepolysulfides containing up to 94% of sulfur. The polymers were found highly electrochemically active when applied as active cathode for lithium batteries.

Keywords: polysulfide, electrical conductivity, lithium battery, cathode

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Polysulfide oligomers are promising for development of exciting composite materials [1, 2]. Moreover, compounds with high sulfur contents are redox-active and are therefore efficient as active cathodic component of lithium-sulfur batteries [3–9].

In order to develop new electrochemically active materials, we have recently studied the interaction between 1,2,3-trichloropropane with sodium hydrosulfide; electrochemically active propane-1,2,3-trithiol, 4-thiahepta-1,2,6,7-tetrathiol, and the corresponding oligomers have been prepared [10]. We have developed a procedure to obtain polyenepolysulfides based on the interaction between sodium monoacetylenides with elemental sulfur in liquid ammonia [11]. Following the procedure, we have prepared polyeneoligosulfides (derivatives of ethynedithiols) from acetylene and elemental sulfur [12, 13]. Reaction of tetrachloroethene with sodium polysulfides in DMSO yielded dicarbon polysulfides [14, 15].

In this work we report on preparation and properties of polyvinylenepolysulfides synthesized via interaction of trichloroethene with sodium polysulfides.

The reaction was performed in two stages without isolation of intermediate sodium polysulfides (Na_2S_x, x = 4, 5) generated *in situ* from $Na_2S·9H_2O$ and elemental sulfur under argon (Table 1).

Hydrolysis of sodium ethenethiolates **I** prepared via that reaction led to free ethenethioles II yielding polyvinylenepolysulfides **III–VI** in course of oligomerization (Scheme 1).

Polymers were isolated from the reaction mixture by precipitation with cool water and purified of the unreacted sulfur with boiling benzene. As a result, two

Scheme 1.

$$Na_2S{\bullet}9H_2O + S_8 \xrightarrow[-H_2O]{\text{DMSO-octane}} Na_2S_x$$

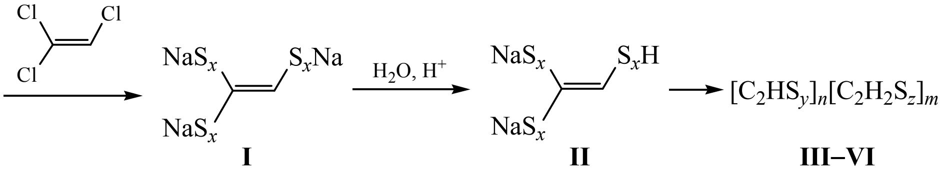


Table 1. Preparation conditions[a], yields, melting points, and elemental composition of polyvinylenepolysulfides **III**–**VI**

Exp. no	Na_2S_x	Time, h	Product	Yield, %	mp, °C	Found, %			Repeating unit	Calculated, %		
						C	H	S		C	H	S
1	Na_2S_4	1.5	**Ia**[b]	35	186–202	16.73	1.17	77.16	20% C_2HS_2 20% C_2HS_3 60% $C_2H_2S_4$	16.46	1.10	78.97
			Ib[c]	28	100–104	10.86	1.15	88.44	48% $C_2H_2S_6$ 52% $C_2H_3S_6$	10.90	1.13	87.31
2	Na_2S_4	2.5	**IIa**[d]	24	176–180	19.64	1.39	78.03	49% $C_2H_2S_3$ 51% $C_2H_2S_3$	19.42	1.23	77.80
			IIb	26	100–102	10.28	1.69	87.89	47% $C_2H_4S_6$ 53% $C_2H_4S_7$	10.10	1.70	87.20
3	Na_2S_5	1.5	**IIIa**[e]	58	106–118	5.91	0.28	91.06	C_2HS_{11}	6.28	0.26	92.22
			IIIb[f]	11	114–122	9.39	1.10	86.89	$C_2H_3S_7$	9.31	1.17	86.99
4	Na_2S_5	2.5	**IVa**[g]	11	124–126	3.54	0.46	93.98	$C_2H_2S_{13}$	3.52	0.37	94.01
			IVb[h]	30	118–122	10.66	1.34	87.63	$C_2H_3S_6$	10.89	1.37	87.20

[a] Trichloroethene to Na_2S_x ratio of 1 : 1.5. Content: [b] Na 2.39%, Cl 1.01%. [c] Cl 0.66%. [d] Na 1.26%, Cl 0.71%. [e] Cl 1.17%. [f] Cl 2.54%. [g] Na 0.43%. [h] Cl 1.31%.

fractions were obtained, containing benzene-insoluble (**IIIa**–**VIa**) and benzene-soluble (**IIIb**–**VIb**) polymers. Yield of the benzene-insoluble fractions decreased with longer reaction run due to hydrolysis and degradation of the polysulfide chain (Table 1). For example, mass of polymer **Va** decreased by 17% after 72 h incubation in aqueous solution of sodium hydroxide (40 wt %).

Polymers **IIIa**–**VIa** were black powders insoluble in water and organic solvents. Their IR spectra contained the absorption bands at 1475–1373 cm^{-1}, assigned to vibrations of the polymer backbone and to stretching of the $C=CS_2$ bond [16–19]. Absorption bands at 1299–1242 and 1213–1178 cm^{-1} were assigned to the C=S bond stretching [20–22], and the bands at 1090–1025 cm^{-1} were due to deformation vibrations of $C=CS_2$ [16, 21]. Weak bands at 730–506 cm^{-1} were assigned to the C–S bond in different surrounding [20, 21] and narrow bands at 470–465 cm^{-1} corresponded to the S–S bond vibration [11, 22, 23]. The bands at 857–816 cm^{-1} were due to deformation vibrations of the C–H bonds [11, 18, 20].

The benzene-soluble polymers **IIIb**–**VIb** were brown or dark-brown powders. Besides the bands typical of the polymers **IIIa**–**VIa**, their IR spectra contained absorption bands at 2950–2850 cm^{-1} assigned to stretching of C–H in the polymer main chain [11, 18, 19]. At the same time, the bands due to vibrations of the $C=CS_2$ and C=S bonds in the spectra of polymers **IIIb**–**VIb** were weaker than those in the spectra of polymers **IIIa**–**VIa** (Table 2).

Basing on the results of elemental analysis and IR spectroscopy, we concluded that besides ethenepolythioles **II**, their tauromeric forms participated in oligomerization, giving rise to irregular structural units **A–D** (Scheme 2).

Scheme 2.

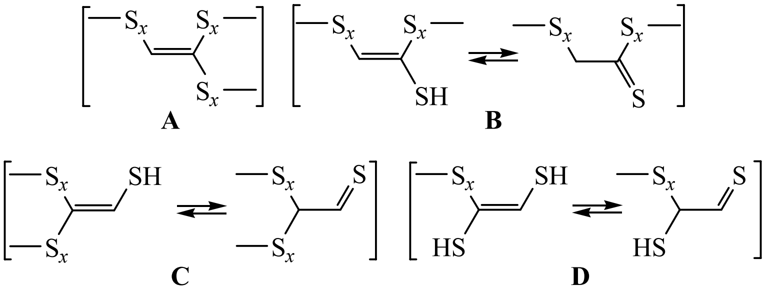


Table 2. Parameters of IR spectra (cm^{-1}) of polyvinylenepolysulfides **III–VI**

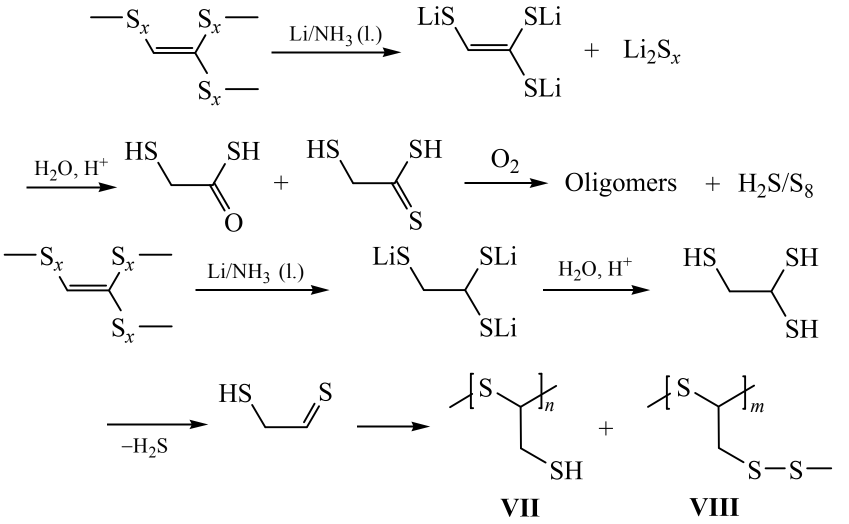
Sample	ν(C–H)	ν(C–C, C=CS$_2$)	ν(C=S)	δ(C=CS$_2$)	δ(C–H)	ν(C–S)	ν(S–S)
IIIa		1474 w, 1417 s	1299 w, 1243 m, 1213 w, 1190 w	1065 s	857 w	621 w, 552 w	469 m
IIIb	2923 w, 2855 w	1457 m, 1376 w	1293 w, 1246 w	1061 m		666 w, 506 w	466 m
IVa		1475 w, 1443 s, 1418 m, 1373 s	1293 m, 1242 m, 1213 w, 1190 w	1067 s, 1045 s, 1029 s	854 w, 816 w	677 m, 550 w	470 w
IVb	2919 s, 2851 s	1463 m, 1443 m, 1376 m	1290 w	1061 w, 1045 w, 1026 w	814 w	730 w, 673 w	467 w
Va		1439 m, 1418 m, 1373 m	1290 m, 1244 m, 1212 m, 1191 w	1067 m, 1025 m	854 w	622 w	468 m
Vb	2950 m, 2920 s, 2851 m	1460 w, 1418 w, 1373 w	1290 w	1024 w	860 w	672 w	461 w
VIa			1266 s, 1244 m, 1178 m	1090 w, 1036 m	840 w	646 m	465 s
VIb	2921 s, 2850 s	1462 m, 1377 w	1270 w	1070 w, 1025 w	840 w	720 w	466 w

Table 3. Conditions of reductive cleavage of polyvinylenepolysulfides **IIIa**–**VIa** with lithium in liquid ammonia and characterization of the products **IX**–**XIV**

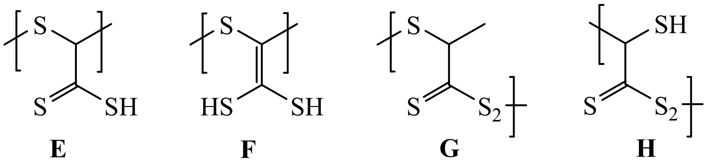
Exp. no.	Initial polymer (1 g)	Li, g (mmol)	Time, h	Product	Yield, %	mp, °C	Found, %			Repeating unit
							C	H	S	
1	**IIIa**[a]	0.14 (20)	2	**IXa**[c]	79	145–160	16.39	0.70	75.77	80% C_2HS_3, 20% $C_2H_2S_5$
				IXb	4	tar	60.24	7.51	31.25	$(C_2H_3)_5S_2$
2	**IIIa**[a]	0.27 (38)	3	**X**[d]	34	>280	19.81	1.60	63.50	50% $C_2H_2S_2$, 50% $C_2H_2S_3$
3	**IVa**[b]	0.35 (50)	2.5	**XIa**	50	220–230	27.06	1.49	69.81	67% C_2HS_2, 33% $C_2H_2S_2$
				XIb	15	88–96	–	–	92.40	C_2S_9
				XIc	4	tar	–	–	–	
4	**Va**[a]	0.14 (20)	2	**XIIIa**	4	tar	79.54	14.00	6.82	$(C_2H_4)_{16}S$
				XIIIb	70	110–120	8.52	1.25	89.72	50% $C_2H_4S_7$, 50% $C_2H_4S_8$
				XIIIc	2	tar	62.00	9.67	32.53	50% $(C_2H_4)_6S_2$, 50% $C_2H_4)_6S_3$
5	**Va**[a]	0.58 (83)	3.5	**XIIa**[e]	31	260–280	23.64	1.43	67.55	50% C_2HS_2, 25% $C_2H_2S_2$, 25% $C_2H_2S_3$
				XIIb	10	108–114	27.78	2.42	68.42	80% $C_2H_2S_2$, 20% C_2H_3S
				XIIc	1	198–206	–	–	–	
				XIId	1	tar	79.50	11.13	1.43	
				XIIe	2		–	–	–	
6	**VIa**[b]	0.78 (110)	3.5	**XIV**	52	108–112	–	–	99.84	S

[a] Polymers **IIIa** and **VIa** were added to solution of lithium in liquid ammonia. [b] Solution of lithium in liquid ammonia was added to polymers **IVa** and **VIa**. Ash content: [c] 3.76%, [d] 10.6%, [e] 6.45%.

Scheme 3.



Scheme 4.



To confirm the structure of the prepared polyvinylenepolysulfides, we performed reductive degradation with lithium in liquid ammonia of the benzene-insoluble fractions **IIIa**–**VIa**. The polymers degradation was carried out in the presence of fair excess of metal lithium with respect to the polymers (Table 3, Scheme 3).

The reaction mixture was successively treated with aqueous solution of ammonium chloride and with 33 wt % aqueous hydrochloric acid. Independently of the starting components ratio, major products of the reductive degradation were black or dark-brown powders insoluble in organic solvents, **IXa**–**XIa** and **XIIa** with the following general formula $(C_2HS_{2-3})_n$ and $(C_2H_2S_{2-5})$ (Table 3). Taking into account the IR spectroscopy and elemental analysis results (Tables 3 and 4), we suggested that the prepared products, along with the above-displayed units, contained the units **E**–**H** (Scheme 4).

Degradation of the starting polymers **IIIa** and **Va** was more complete with higher amount of lithium. In the course of cleavage of polysulfide fragments, yield and content of sulfur in the insoluble polymers decreased twofold. Upon treatment of the reaction mixture with hydrochloric acid (pH ≈ 1–2), additional crosslinking of the polymeric products (Table 3, exp. 1, 3, and 5) occurred simultaneously; melting points of the so formed polymers were high. When the reaction mixture was acidified to pH ≈ 5 only, the major product (70%) was insoluble polymer **XIIIb** with lower melting point (110–120°C), due to its linear structure (Table 3, exp. 4).

Fractionating of the products of degradation of polymer **Va** (insoluble in acidic solution) with hot water and boiling benzene, and analysis of the so obtained fractions pointed at non-uniform composition of the polymer: 32% of the crosslinked structures **XIIa** and **XIIc**, 10% of the degradation product **XIIb** consisting of linear mono- and disulfide oligomers with composition of $(C_2H_2S_2)_4(C_2H_3S)$, and 3% of oligomers **XIId** and **XIIe** in the form of yellow-brown tars containing no sulfur (Table 3, exp. 5).

IR spectra of oligomer products **IXb**, **XIc**, **XIIIc**, and **XIIc**–**XIIe** isolated from acid aqueous solutions via extraction with diethyl ether contained the absorption bands at 2964–2851 cm^{-1} assigned to vibrations of

Table 4. Parameters of IR spectra (cm^{-1}) of polyvinylenepolysulfides **IX**–**XIV**

Sample	ν(C–H)	ν(C=O)	ν(C–C, C=CS$_2$)	ν(C=S)	δ(C=CS$_2$)	δ(C–H)	ν(C–S)	ν(S–S)
IXa			1416 m, 1312 m	1252 m	1062 m	929 w, 857 w	760 w	468 w
IXb	2964 m, 2921 s, 2852 m	1707 m	1463 s, 1377 m			837 w	721 w	465 w
X			1470 m, 1416 m	1221 w	1066 w, 1027 w		768 w, 612 w	467 w
XIa			1442 m, 1403 s	1289 w, 1259 w				467 m
XIb	2964 m, 2921 s, 2853 m	1704 w	1461 w, 1399 w, 1377 w	1291 w, 1243 w, 1192 w, 1130 w		852 w	722 w	467 m
XIc	2964 s, 2920 s, 2851 s	1709 m	1461 m, 1378 w	1293 w, 1137 w	1079 w, 1035 w		721 w	462 w
XIIIa	2920 s, 2850 s		1463 s, 1376 m	1240 w, 1126 w,	1034 w	837 w	720 w	460 w
XIIIb			1442 m, 1403 s	1289 w, 1259 w				467 m
XIIIc	2945 m, 2920s, 2851 m		1457 m, 1376 m	1300 m	1040 w	915 m	715 w	464 w
XIIa			1472 m, 1432 m, 1376 m	1300 m, 1245 w, 1212 w, 1128 w	1030 s	855 w	753 w	463 w
XIIb	2953 m, 2919s, 2855 m		1450 w, 1360 w	1280 w, 1143 w,	1020 w	840 w	722 w	467 w
XIIc	2951 w, 2919 m, 2855 w		1460 s, 1401 s	1285 m, 1247 s, 1214 s, 1190 m	1073 m, 1038 m	945 w, 856 m	756 w, 663 w	
XIId	2955 s, 2920 s, 2850 s		1463 m, 1377 w			840 w	721 w, 618 w	460 w
XIIe	2957 s, 2921 s, 2851 s	1730 w	1457 w	1193 w	1073 w, 1016 w	837 w	723 w, 619 w, 545 w	
XIV			1457 w		1021 w	843 w		468 w

aliphatic CH$_2$ and CH groups along with the band of C=O group stretching at 1730–1704 cm^{-1} pointing at hyd-rolysis of the degradation products (Table 4).

Complete degradation of the initial polymer **VIa** could be performed with the highest excess of lithium. The product **XIV** was obtained in the form of light-brown powder containing 99.84% of sulfur (Table 3, exp. 6).

The prepared polyvinylenepolysulfides revealed noticeable electrical conductivity of 10^{-13}–10^{-16} S/cm and marked paramagnetic properties (10^{15}–10^{18} sp/g) (Table 5). The ESR spectra of samples **IIIa**, **Va**, **Xa**, **XIa**, **XIIa**, and **XIV** contained signals assigned to different paramagnetic centers. In polyvinylenepolysulfides **IIIa** and **Va**, prepared from sodium tetra- and pentasulfide, respectively, 5 types of paramagnetic centers were found. One of them (*g*-factor of 2.0036) was found in all the studied polymers irrespectively of their preparation procedure and further treatment, that was an organic radical. That was in agreement with its concentration decrease down to the lowest in the case of sample **XIV**. Another type of paramagnetic site, giving rise to asymmetric signal with *g*-factor of 2.0097, was assigned to the sulfur-containing radical localized at carbon atom.

In the case of the other three types of paramagnetic centers, significant deviation of *g*-factors from those typical of free electron evidenced about noticeable contribution of spin-orbital interactions; therefore, those species could be assigned to various di- and polysulfide S$_3$- and S$_4$-anion-radicals [24, 25] stabilized by the polymer matrix. Reduction of the polymers with lithium in liquid ammonia and further treatment led either to disappearance of all four types of polysulfide radicals (**Xa** and **XIV**) or to disappearance of three of them accompanied by significant increase of concentration of S_3-anion-radicals (**XIa** and **XIIa**).

The prepared polymers were redox-active. Cyclic voltamperograms (typical example is given in Fig. 1) evidenced about the presence of redox-active polysulfide bonds in the products. Cathodic and anodic polarization curves comprised clearly revealed maxima of multi-stage reduction at 1.9 and 2.4 V as well as single-stage oxidation at 2.5 V, typical of the compounds containing polysulfide units [6–8]. At the first stage, at potential of 2.4 V, higher polysulfides were formed. At the second stage (1.9 V) the soluble polysulfides were reduced to almost insoluble lithium sulfides [26]. General view of cyclic voltamperograms and position of the oxidation-reduction peaks in the case of the polymer products were in agreement with those of elemental sulfur, pointing at similarity of the occurring processes.

Using the prepared polyvinylenepolysulfides as active cathodic material in lithium batteries provided for their prolonged cyclic operation with discharge capacity of 447–880 mA h g^{-1} (Fig. 2). During the first 2–5 cycles, the discharge capacity significantly decreased due to partial irreversible transfer of the active material into the electrolyte in the form of insoluble lithium sulfides and disulfides [27]. Further cyclic operation of the elements revealed stable parameters. The discharge capacity correlated with sulfur content in the samples. Polyvinylenepolysulfide **Va** containing 91.06% of sulfur showed up higher discharge capacity

Table 5. Electrical conductivity (σ) and ESR parameters of polyvinylenepolysulfides **IIIa** and **Va**; and of their reduction products **X**, **XIa**, **XIIa**, and **XIV**

Comp. no.	*S*, %	σ, S/cm	ESR signal		
			g-factor	*N*, sp/g	Δ*H*, mT
IIIa	77.16	1.2×10^{-14}	2.0036	4.5×10^{16}	0.27
			2.0097	5.0×10^{17}	1.0
			2.0230	$\le 10^{15}$	
			2.0280	$\le 10^{15}$	
			2.0340	$\approx 10^{15}$	0.63
Va	91.06	3.5×10^{-15}	2.0036	4.8×10^{16}	0.27
			2.0097	5.9×10^{17}	1.0
			2.0230	$\le 10^{15}$	
			2.0280	$\le 10^{15}$	
			2.0340	$\approx 10^{15}$	0.63
X	63.50	3.2×10^{-13}	2.0036	6.3×10^{18}	0.60
XIa	69.81	3.0×10^{-14}	2.0036	8.0×10^{17}	0.51
			2.0280	4.0×10^{18}	3.6
XIIa	67.55	5.2×10^{-14}	2.0036	1.2×10^{17}	0.6
			2.0280	4.0×10^{18}	3.6
XIV	99.84	1.9×10^{-16}	2.0036	1.2×10^{16}	0.73

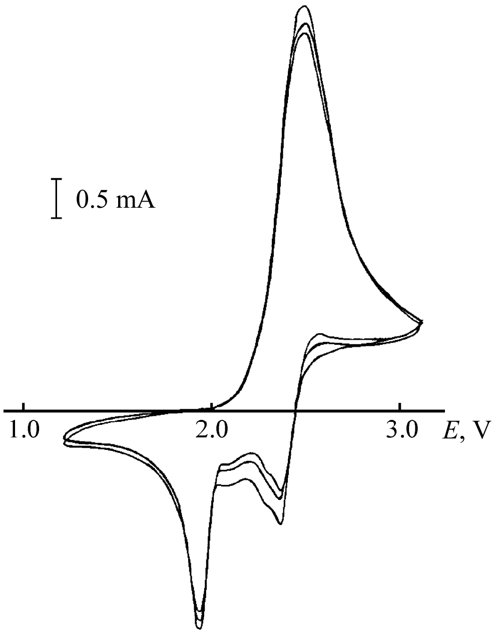


Fig. 1. Cyclic voltamperogram of polyvinylenepolysulfide **Va** (cycles 1–3).

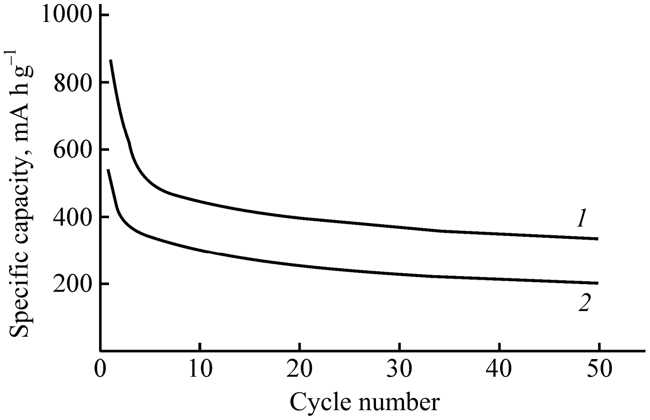


Fig. 2. Change of discharge capacity of cathodes based on polyvinylenepolysulfides **Va** (91.06% S) (*1*) and **XIIa** (67.55% S) (*2*) during cyclic work of the elements.

of the constructed elements as compared with its reduced analog **XIIa** (S 67.55%), confirming the higher content of redox-active S–S bonds in sample **Va**.

To conclude, interaction of trichloroethene with sodium polysulfides yielded sulfur-enriched polyvinylenepolysulfides. The products were high-resistance semiconductors revealing paramagnetic properties and electrochemical activity. These polymers are promising as active cathodic material to be used in lithium batteries, providing for their prolonged efficient cyclic operation.

EXPERIMENTAL

IR spectra (KBr or in microlayer) were recorded with the Bruker Vertex-70 spectrometer. Electrical conductivity was measured with the standard E6-13A teraohmmeter. ESR spectra were registered at room temperature using the SE/X-2547 Radiopan spectrometer (Poland) equipped with the magnetometer and high-frequency measuring device. Concentration of paramagnetic sites was determined following the published procedures [28]. For electrochemical experiments, model button-type lithium elements were used (lithium anode; aluminum cathode covered with carbon, polymer, and polyethylene glycol in the 60 : 35 : 15 weight ratio; highly porous polypropylene Tonen as separator; 1 mol/L solution of CF_3SO_3Li in the 1 : 1 mixture of 1,2-dimethoxyethane and 1,3-dioxolane as electrolyte). Cyclic voltamperograms were recorded using the PI-50-1.1 potentiostat at 1 mV/s in the range of 1.25–3.0 V. Cyclic operation of the elements was performed at constant current (0.25 mA/cm^2, 1.25–2.8 V).

Preparation of polyvinylenepolysulfides III–VI *(general procedure).* A mixture of 5.76 g or 7.68 g (0.18 mol or 0.24 mol) of elemental sulfur and 14.4 g (0.06 mol) of $Na_2S{\cdot}9H_2O$ in DMSO (60 mL) was stirred at 55–60°C during 1.5–2.5 h under argon. 60 mL of octane was added to the mixture, and was then subject to azeotropic distillation with water (Dean–Stark apparatus). The reaction mixture was cooled down to 25–30°C, 5.24 g (0.04 mol) of 1,1,2-trichloroethene was added, and the resulting mixture was stirred at 80–85°C during 1.5–2.5 h under argon. The reaction mixture was cooled down and diluted with cool water (120 mL). The formed precipitate was filtered off, washed with distilled water (pH ≈ 7, till negative reaction for chloride ions), and dried in vacuum to obtain polymer powders: **III** or **IV** (with Na_2S_4) and **V** or **VI** (with Na_2S_5). The powders were washed with boiling benzene (5×10 mL) and dried in vacuum to constant mass to obtain polymers **IIIa–VIa**. After washing the products **III** and **IV** with boiling benzene and cooling down, yellow crystalline powders were obtained (yield of 5% and 7%, respectively; 99.2% and 99.8% of sulfur, respectively). Polymers **IIIb–VIb** were obtained from the benzene extract via the solvent distillation and drying of the residue in vacuum to constant mass (Table 1).

Polyvinylenepolysulfides (IXa, IXb). 1.0 g of polymer **IIIa** was added to solution of 0.14 g (20 mmol) of lithium in 60 mL of liquid ammonia, and the mixture was stirred during 2 h. Major part of ammonia was evaporated off, and the residue was diluted with 40 mL of aqueous solution of NH_4Cl (2.8 wt %) and then with aqueous solution of HCl (33%) (pH ≈ 1–2), the precipitate was filtered off, washed with water (pH ≈ 5, negative for Cl^-), and dried in vacuum to get 0.79 g of polymer **IXa**. The filtrate was extracted with diethyl ether; the extract was dried with Na_2SO_4, ether was eliminated, and the residue was dried in vacuum to get 0.04 g of polymer **IXb** (Table 3, exp. 1).

Polyvinylenepolysulfide (X). 1.0 g of polymer **IIIa** was added to solution of 0.27 g (38 mmol) of lithium in 60 mL of liquid ammonia, and the mixture was stirred during 3 h. Major part of ammonia was evaporated off, and the residue was successively washed with 40 mL of aqueous solution of NH_4Cl (2.8 wt %) and with aqueous solution of HCl (33%) (pH ≈ 1–2); the precipitate was filtered off, washed with water (pH ≈ 5, negative for Cl^-), and dried in vacuum to get 0.34 g of polymer **X** (Table 3, exp. 2).

Polyvinylenepolysulfides (XIa–XIc). Solution of 0.35 g (50 mmol) of lithium in 100 mL of liquid ammonia was added to suspension of 1.0 g of polymer **IVa** in 150 mL liquid ammonia, and the mixture was stirred during 2.5 h. Major part of ammonia was then evaporated off, and the residue was diluted with 40 mL of aqueous solution of NH_4Cl (2.8 wt %) and with aqueous solution of HCl (33%) (pH ≈ 1–2). The precipitate was filtered off, washed with water (pH ≈ 5, negative for Cl^-), with boiling benzene (5×10 mL), and dried in vacuum to get 0.50 g of polymer **XIa**. Benzene was distilled off, and the residue was dried in vacuum to get 0.15 g of product **XIb**. The filtrate obtained after isolation of polymer **XIa** was extracted with diethyl ether; the extract was dried with Na_2SO_4, ether was eliminated, and the residue was dried in vacuum to get 0.04 g of polymer **XIc** (yellow tar). ^{1}H

NMR spectrum ($CDCl_3$), δ, ppm: 0.84 m (3H, Me), 1.24 s (2H, CH_2), 1.42 s (2H, CH_2) (Table 3, exp. 3).

Polyvinylenepolysulfides (XIIIa–XIIIc). 1.0 g of polymer **Va** was added to solution of 0.14 g (20 mmol) of lithium in 60 mL of liquid ammonia, and the mixture was stirred during 2 h. Major part of ammonia was evaporated off, and the residue was diluted with 40 mL of aqueous solution of NH_4Cl (2.8 wt %) and extracted with diethyl ether. The extract was washed with Na_2SO_4, ether was eliminated, and the residue was dried in vacuum to get 0.04 g of polymer **XIIIa** (orange-brown tar). Aqueous solution of HCl (33 wt %) was added to the mixture obtained after isolation of polymer **XIIIa** (pH ~ 5), the formed precipitate was filtered off, washed with water (negative for $Cl^–$), and dried in vacuum to get 0.70 g of polymer **XIIIb**. The filtrate was extracted with diethyl ether; the extract was washed with Na_2SO_4, ether was eliminated, and the residue was dried in vacuum to get 0.02 g of polymer **XIIIc** (brown tar) (Table 3, exp. 4).

Polyvinylenepolysulfides (XIIa–XIIe). 1.0 g of polymer **Va** was added to a solution of 0.58 g (83 mmol) of lithium in 60 mL of liquid ammonia, and the mixture was stirred during 3.5 h. Major part of ammonia was evaporated off, and the residue was diluted with 50 mL of aqueous solution of NH_4Cl (9.4 wt %) and with aqueous solution of HCl (33%) (pH ≈ 1–2). The formed precipitate was filtered off, and washed successively with cold water (pH ≈ 6–7), hot water (80 mL, dark-brown solution), boiling benzene, and then dried in vacuum to get 0.31 g of polymer **XIIa**. From the benzene solution obtained after isolation of polymer **XIIa**, the solvent was distilled off, and the residue was dried in vacuum to get 0.10 g of polymer **XIIb**. The dark-brown aqueous solution (80 mL) was divided into two parts. To the first part (40 mL), aqueous HCl (33 wt %) was added HCl (pH ≈ 1–2). The formed precipitate was filtered off, washed with water (pH ≈ 6–7), and dried in vacuum to get 0.01 g of black polymer **XIIc**. The filtrate was extracted with diethyl ether; the extract was dried with Na_2SO_4, ether was eliminated, and the residue was dried in vacuum to get 0.01 g of polymer **XIId** (yellow tar). The second part of the aqueous solution (40 mL) was extracted with diethyl ether, the extract was dried with Na_2SO_4, ether was eliminated, and the residue was dried in vacuum to get 0.02 g of polymer **XIIe** (brown tar). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 m (3H, Me), 1.24 s (2H, CH_2), 1.67 s (2H, CH_2) (Table 3, exp. 5).

Polyvinylenepolysulfide (XIV). A solution of 0.78 g (110 mmol) of lithium in 100 mL of liquid ammonia was added to a suspension of 1.0 g of polymer **VIa** in 150 mL of liquid ammonia, and the mixture was stirred during 3.5 h. Major part of ammonia was evaporated off, and the residue was successively diluted with 90 mL of aqueous solution of NH_4Cl (2.8 wt %) and with aqueous solution of HCl (33%) (pH ≈ 1–2). The formed precipitate was filtered off, washed with water (pH ≈ 5, negative for $Cl^–$), and dried in vacuum to get 0.52 g of polymer **XIV** (Table 3, exp. 6).

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