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Sulfurization of polymers

6.* Poly(vinylene polysulfide), poly(thienothiophene), and related structures from polyacetylene and elemental sulfur

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Polyacetylene obtained by the dehydrochlorination of polyvinyl chloride in the NaOH—DMSO system undergoes sulfurization with elemental sulfur at 120—300 °C to liberate hydrogen sulfide and to form electroconducting ($0.7 \cdot 10^{-12}$—$5.8 \cdot 10^{-15}$ Sm cm^{-1}) and paramagnetic ($1.5 \cdot 10^{17}$—$1.7 \cdot 10^{19}$ sp g^{-1}, $g = 2.0035$—2.0045, $\Delta H = 0.44$—0.66 mT) dark powders with a metallic luster. Their IR spectra and comparison with the samples of sulfurized polyethylene show that sulfurized polyacetylene contains poly(vinylene polysulfide), poly(thienothiophene), and related structures. The polymers afford the cathode discharge capacity of lithium batteries up to 950 mA h g^{-1} (in the first cycle) and stable cycling at a level of 500—300 mA h g^{-1} (25 cycles).

Key words: polyvinyl chloride, polyacetylene, elemental sulfur, sulfurization, poly(vinylene polysulfide), poly(thienothiophene), paramagnetism, electroconductivity, redox properties.

Polyacetylene (PA) and its derivatives exhibit the semiconducting properties and electrochemical activity and are used, therefore, as active cathodic materials in electrochemical generators.[2—4] At the same time, only restricted data[2] on the application of products of PA interaction with elemental sulfur in lithium batteries and accumulators are available.

It is known[5] that sulfur reacts with alkenes to form thiophene, saturated mercaptanes, sulfides, and polysulfides. The high-temperature (160—365 °C) reaction of polyethylene with elemental sulfur affords poly(thienothiophenes) containing polysulfide chains and exhibiting the electroconductivity, paramagnetism, and redox properties.[6,7]

In this work we report the results of studying the reaction of PA with elemental sulfur and the electrochemical properties of the products obtained.

Results and Discussion

Catalytic polymerization of acetylene[3,8—10] and dehydrochlorination of polyvinyl chloride (PVC)[2,11,12] are the main methods for the synthesis of PA. The first method provides PA as films and, at low catalyst concentrations, as powders. The samples obtained contain admixtures of catalysts, which are difficult to remove completely.[3]

The dehydrochlorination of PVC in the presence of bases is the simplest method for the preparation of powdered PA. However, this method does not allow the synthesis of PA, which corresponds completely to the molecular formula $(CH)_x$. The dehydrochlorination of PVC with sodium or potassium amide in liquid ammonia affords[2,11] polymers, whose particular blocks contain O, N, and Cl atoms.

We dehydrochlorinated a commercial suspension of PVC (molecular weight 90000) in a superbasic NaOH—DMSO system at different molar ratios of the reactants in the 120—125 °C temperature interval (Scheme 1). The reaction conditions and elemental analysis data of the PA samples synthesized are presented in Table 1.

Reactants were mixed immediately (PA-1 and PA-2) or an excess of a base was added by portions during the reaction with 1—2-h intervals at the initial molar PVC : NaOH ratio equal to 1 : 2 (PA-3 and PA-4). The deeper dehydrochlorination of PVC with an increase in the base excess corresponds to an increase in the basicity of the system due to binding of water evolved upon the reaction.[13]

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* For Part 5, see Ref. 1.

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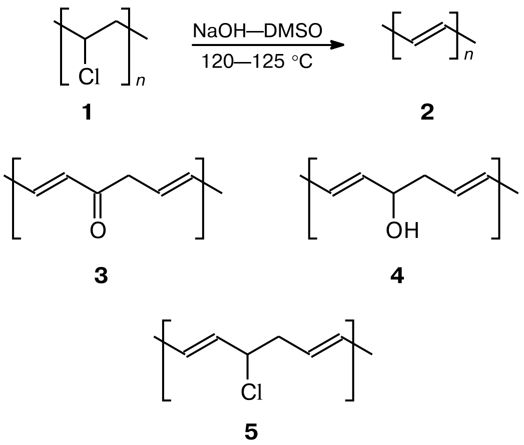
Scheme 1



According to the data of elemental analysis and IR spectroscopy, the dehydrochlorination of PVC **1** is accompanied by the formation of polyenic blocks **2** and also fragments **3** and **4** due to water addition and oxidative processes and, to a less extent, incomplete dehydrochlorination (**5**). In the IR spectra of the obtained PA-1—PA-4 samples the broad band of vibrations at 1636—1655 cm^{-1} corresponds to the polyenic blocks of structures **2** and **3**. Vibrations at 970, 1175, 1400, and 2875—2930 cm^{-1} are attributed to the C—H bonds in the methylene and methine fragments of blocks **3—5**. Absorption bands of the oxygen-containing blocks are observed at 1675—1700 cm^{-1} (for compound **3**), 1048 and 1125 cm^{-1} (C—O bond), and 3428 cm^{-1} (OH group in block **4**). Vibrations of the residual C—Cl bonds are detected at 763 cm^{-1}.

The polymers obtained are dark brown powders, which are insoluble in organic solvents (acetone, DMSO, benzene) and exhibit electroconductivity of ~10^{-15} Sm cm^{-1}. The low electroconductivity values (by three—six orders of magnitude lower than the electroconductivity of classical PA[4]) are caused by fragments **3—5** in the main chain.

The deep sulfurization of the synthesized PA samples (PA-1, PA-2) was carried out by their heating with elemental sulfur in the temperature range from 120 to 300 °C (Table 2). This process resulted in the evolution of hydrogen sulfide, indicating dehydrogenation (Scheme 2). The sulfurization products of the PA samples are black or dark gray powders with a metallic luster and a sulfur content of 57—80% (see Table 2).

The IR spectra of the polymers obtained (pellets with KBr) exhibit very weak absorption bands in the 4000—400 cm^{-1} interval. The absorption bands at 459—468 cm^{-1} are attributed to vibrations of the S—S bonds (including elemental sulfur in residual amounts), and the absorption at 516—598 and 652—734 cm^{-1} is caused by the C—S bonds in structures **6a,b**. Very weak

Table 1. Conditions of PVC dehydrochlorination and elemental analysis data for the PA samples

Sample	PVC : NaOH (mol.)	Reaction time/h	Yield* (%)	Found (%)			Calculated (%)
				C	H	Cl	O
PA-1	1 : 2	5	89.6	66.78	6.75	11.28	15.19
PA-2	1 : 3	5	91.0	65.49	6.34	8.76	19.41
PA-3	1 : 3.7	6	94.7	72.55	6.03	5.63	15.79
PA-4	1 : 5	6	97.4	73.19	6.57	2.79	17.45

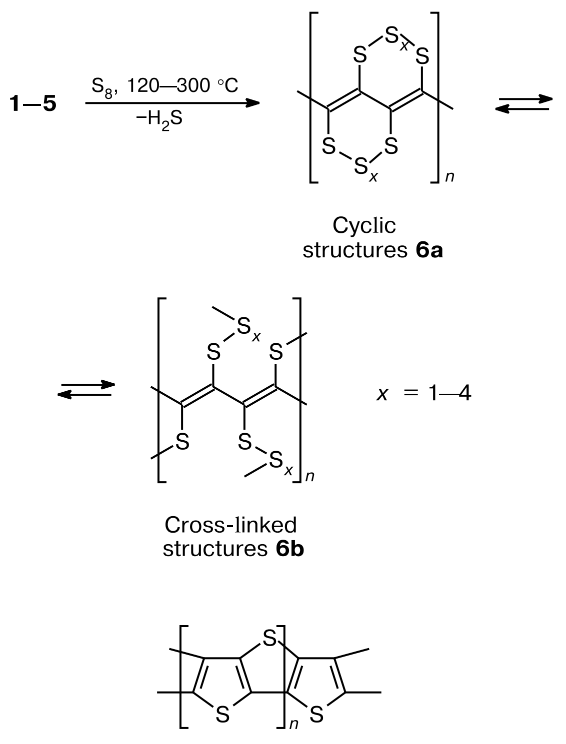
* Degree of PVC dehydrochlorination.

Table 2. Yields and elemental analysis data for the products of PA sulfurization (SPA)

Sample	Initial PA	PA : S (wt.)	*T*/°C	*t*/h	Yield* (%)	Found (%)		
						C	H	S
SPA-1	PA-1	1 : 3	125	2	96	14.00	1.43	75.07
SPA-2	The same	1 : 3	120—260	2.3	62	31.42	3.58	56.98
SPA-3	»	1 : 4	165	3	84	15.49	1.10	78.14
SPA-4	PA-2	1 : 2	160	3	86	23.78	1.17	66.68
SPA-5	The same	1 : 3	160	3	90	15.42	2.12	72.39
SPA-6	»	1 : 4	160	3	91	10.21	1.55	79.94
SPA-7	»	1 : 4	200	3	63	20.29	3.36	69.87
SPA-8	»	1 : 4	300	2.5	71	15.94	3.02	76.59
SPA-9	»	1 : 4	300	0.5	72	10.11	1.90	80.06

* The ratio of the weight to the obtained polymer to the total weight of the initial PA and sulfur.

Scheme 2



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peaks at 1055—1061 and 1420—1570 cm^{-1} can correspond to vibrations of the double bonds in the thienothiophene fragments of **7**. These data coincide with the results described for sulfurized polyethylene,[6] indicating the resemblance of the structures of the polymers obtained. Signals in the 1627—1639 cm^{-1} interval are assigned to vibrations of the double bond of the polyene fragments. The distinctions in the IR spectra of the SPA and sulfurized polyethylene[6] samples are caused by vibrations of the oxygen-containing blocks in the first case. Absorption maxima at 1695—1700 cm^{-1} can be assigned to vibrations of the C=O groups in the C=C—C=O fragment (residual structures **3**). Vibrations of the C=C—OH or C=C—C—OH oxygen-containing fragments are manifested at 1163 and 3430 cm^{-1} (residual structures **4**). Vibrations of the C—H bonds in the methylene groups are observed in the region of 2855—2861 and at 2923 cm^{-1}.

The polymers obtained are paramagnetic and exhibit electroconductivity, whose values correspond to high-ohmic organic semiconductors (Table 3). Signals in their ESR spectra are singlets, which differ from narrow symmetric absorption lines typical of polyacetylenes[14] by a noticeable asymmetry and a greater width between points of the maximum slope. The *g* factors differ from the purely spin value 2.0023 (see Table 3), while for the samples characterized by a high content of paramagnetic sites their values depend more strongly on the contribution of spin-orbital interactions. The concentrations of paramagnetic sites (sp g^{-1}) of the samples studied differ more than by two orders of magnitude (see Table 3).

The highest values of electroconductivity ($0.68 \cdot 10^{-12}$ Sm cm^{-1}) and spin concentration are observed for the SPA-9 polymer with the 80% sulfur content, which was prepared by short-time (30 min) heating with a fourfold (by weight) sulfur excess at 300 °C. In general, the values of electroconductivity and concentration of paramagnetic sites do not correlate with the sulfur content in the sample and, as it should be expected, depend on the composition of the initial PA (see Table 1) and conditions of its sulfurization (see Table 2).

The electrochemical behavior of the sulfurized PA was studied by cyclic voltammetry and in the galvanostatic regime. The cyclic voltammograms of the cathode based on the SPA-2 sulfurized polyacetylene (Fig. 1) are typical of almost all samples studied. The first cycle contains two cathodic maxima and one anodic maximum at 2.20, 1.88, and 2.70 V, respectively. The shape of the cathodic peaks changes with cycling: the peaks become more distinct, their maxima are shifted toward higher potentials, the third peak appears at 2.10 V, and the surface area under the discharge curve decreases significantly compared to the discharge surface area in the first cycle. The

Table 3. Electroconductivity and characteristics of the ESR spectra of the sulfurized PA (SPA) samples

Sample	Content of sulfur (%)	Electroconductivity σ/Sm cm^{-1}	Concentration of spins/sp g^{-1}	*g* Factor	ΔH /mT
SPA-2	57	$1.15 \cdot 10^{-14}$	$0.95 \cdot 10^{19}$	2.0045	0.58
SPA-4	67	$0.66 \cdot 10^{-14}$	$3.50 \cdot 10^{17}$	2.0035	0.56
SPA-7	70	$0.66 \cdot 10^{-15}$	$1.20 \cdot 10^{18}$	2.0042	0.56
SPA-5	72	$2.51 \cdot 10^{-15}$	$0.67 \cdot 10^{18}$	2.0036	0.49
SPA-1	75	$5.80 \cdot 10^{-15}$	$1.50 \cdot 10^{17}$	2.0039	0.66
SPA-8	77	$2.80 \cdot 10^{-14}$	$0.93 \cdot 10^{19}$	2.0044	0.51
SPA-3	78	$3.30 \cdot 10^{-15}$	$2.40 \cdot 10^{17}$	2.0037	0.56
SPA-6	80	$0.81 \cdot 10^{-15}$	$2.60 \cdot 10^{17}$	2.0037	0.56
SPA-9	80	$0.68 \cdot 10^{-12}$	$1.70 \cdot 10^{19}$	2.0045	0.44

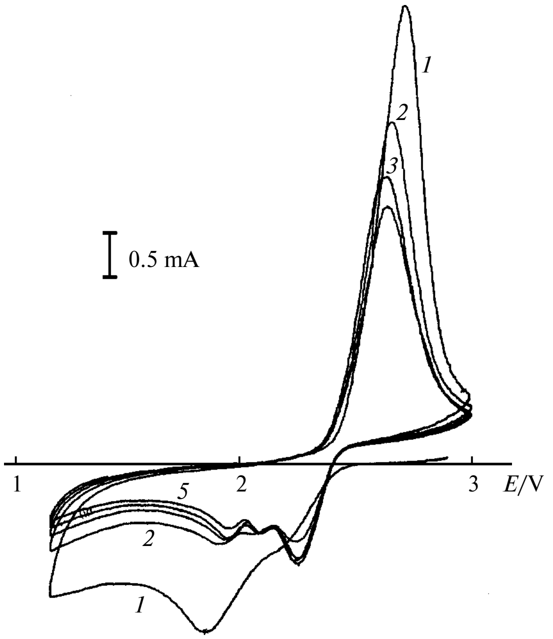
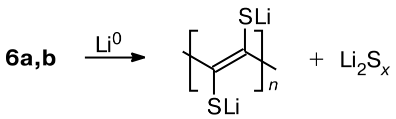


Fig. 1. Cyclic voltammograms of sulfurized PA with the sulfur content 57% (potential sweep 1 mV s^{-1}). Numbers of cycles are designated by figures.

shape of the anodic peaks remains unchanged during cycling but the amplitude of their currents decreases, and the position of the maximum is shifted from 2.70 to 2.64 V. A similar shift of cathodic and anodic maxima indicates an increase in the reversibility of the redox processes occurring in the polymers. A complicated character of the cathodic curve and the corresponding position of its maxima are characteristic of polymers with polysulfide blocks with different structures[6,7] and indicate that the polymer structure contains electrochemically active blocks with the S—S bonds (structures **6a,b**), whose electrochemical reduction is a complicated multistage process (Scheme 3).

Scheme 3



The stages of oxidation of the sulfurized PA are close in potentials and give one maximum similarly to the polysulfide polymers studied previously.[6,7] When the sulfur content increases in the samples studied, the amplitudes of maxima of the cathodic and anodic peaks increase. In addition, for some polymers the character of the cathodic process somewhat changes, namely, the medium peak at 2.10 V disappears.

The results of potentiometric studies (Table 4) correlate well with the results obtained under the galvanostatic conditions (Figs. 2 and 3).

On cycling of the polymeric cathodes in the galvanostatic regime, the capacity (Q) decreases sharply (by 27—40%) at the second discharge cycle compared to the capacity of the first cycle (see Fig. 2). A similar behavior is observed when the polymers are studied by cyclic voltammetry (see Fig. 1), as mentioned above. The discharge capacity of the cathodes in cycle *25* is 47—64% of the capacity of cycle *2* (see Table 4, Fig. 2). The sharp degradation of the characteristics of the cathodes based on sulfurized PA after the first discharge cycle and an insignificant degradation during further cycling are likely a result of the partial transition of the soluble polysulfide fragments from the cathode surface into the electrolyte and the formation of passive films, which partially block the electrode surface.

A correlation of the specific discharge capacitance of the cathodic materials studied to the sulfur content in the sample is mainly observed. As can be seen in Table 4 and Fig. 2, an increase in the sulfur content in the polymer from 57 to 80% increases considerably the capacitance of the cathodes based on these polymers. For example, the discharge capacitance of the cathodes based on the SPA-6 polymer (80% S) exceeds the capacitance

Table 4. Specific discharge capacitance (Q) of the cathodes based on SPA during their cycling (change in the cycle number from *1* to *25*) in lithium batteries

Sample	Q/mA h g^{-1}							
	1	*2*	*3*	*5*	*10*	*15*	*20*	*25*
SPA-2	644	439	400	341	284	254	234	215
SPA-4	937	614	560	505	459	423	391	368
SPA-7	850	554	507	453	340	307	294	260
SPA-5	803	555	464	392	329	299	277	267
SPA-1	645	375	340	297	250	223	215	179
SPA-8	864	514	423	365	348	332	332	315
SPA-3	917	604	536	479	430	388	361	346
SPA-6	946	693	599	490	446	425	418	397
SPA-9	945	565	464	430	380	363	362	363

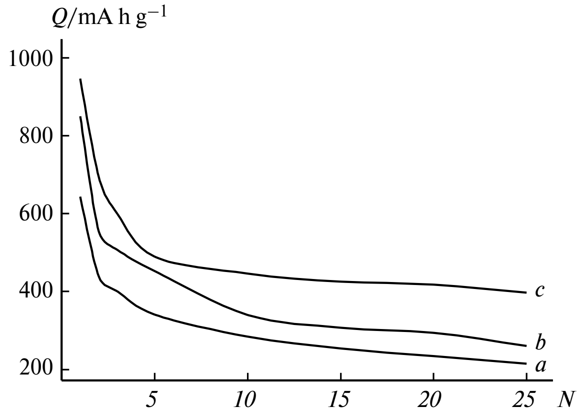


Fig. 2. Change in the discharge capacitance (Q) of the cathodes based on sulfurized PA with the sulfur content 57 (*a*), 70 (*b*), and 80% (*c*) during their cycling in lithium batteries (N is the number of cycles).

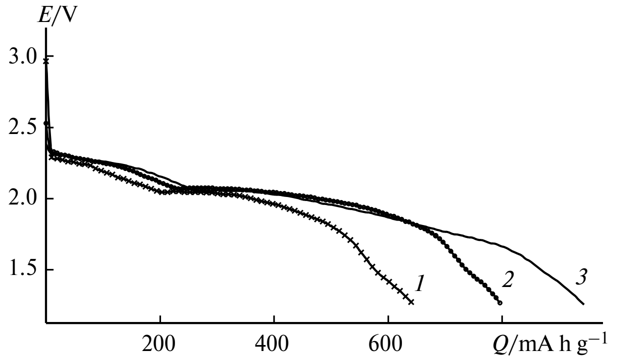


Fig. 3. Characteristics of the cathodes based on sulfurized PA with the sulfur content 57 (*1*), 70 (*2*), and 80% (*3*) in the discharge of the first cycle.

of the cathodes based on the SPA-2 polymer (57% S) by 47, 58, and 85% for cycles *1*, *2*, and *25*, respectively. The cycling of the cathodes based on polymers with a higher sulfur content is more prolonged and stable (see Fig. 2). The exception is the SPA-4 sample (see Table 4) containing 67% sulfur but being highly competitive with the samples containing 80% sulfur (SPA-6 and SPA-9). This can be due to the specific features of the chemical structure of its macromolecules and morphology of the sample. The character of increasing the discharge capacitance with an increase in the sulfur content in the polymers can be monitored in the discharge curves of cycle *1* presented in Fig. 3. Figure 3 demonstrates clearly an increase in the length of both the first and second surface areas for the sample with a higher sulfur content. The potentials (E) of positions of the surface areas in the discharge curves correspond to the potentials of positions of maxima of the cathodic peaks in the cyclic voltammograms (see Fig. 1).

Thus, the deep sulfurization of PA afforded a series of new electrochemically active polymers promising for the development of related high-capacious cathodes for lithium batteries.

Experimental

IR spectra were recorded on a BOMEM M-102 FTIR spectrometer in pellets with KBr in the transmission interval of 4000—400 cm^{-1}.

Electroconductivity of polymers was measured with a VK-2-16 electrometric amplifier and an E6-13A teraohm meter.

Thin-layer two-electrode button-type cells with an aluminum cathode (1.5 cm^2) covered with carbon and a composite of polymer, active carbon, and polyethylene oxide in a ratio of 50 : 35 : 15 (wt.%) were used in electrochemical experiments. Porous polypropylene was used as the separator, and a 1 *M* solution of $(CF_3SO_2)_2NLi$ in 1,2-dimethoxyethane served as the electrolyte. Cyclic voltammograms were obtained at a potential sweep of 1 mV s^{-1} in the 1.25—3.00 V region using a PI-50-1 potentiostat and a PDA two-coordinate recorder. Cells were cycled at a current density of 0.25 mA cm^{-2} in the voltage interval from 1.25 to 3.00 V on a test-measuring desk for chemical current sources.

ESR spectra were recorded on a Radiopan SE/X-2547 spectrometer (Poland). The concentration of paramagnetic sites was calculated using known procedures.[15]

Polyvinyl chloride (S-7059 trade mark, molecular weight 90000) is a commercial product (Joint-Stock Company "Sayanskii Khimprom," Russia).

Dehydrochlorination of PVC (for the preparation of the PA-2 and PA-4 samples). ***A.*** A mixture of PVC (6.26 g, 100 mmol) and NaOH (12.0 g, 300 mmol) in DMSO (100 mL) was stirred for 5 h at 120—125 °C. After cooling the reaction mixture was poured into water (250 mL), and the product that precipitated was washed with water (until Cl$^-$ ions disappeared, test with a 1% solution of $AgNO_3$), acetone, and diethyl ether, and dried *in vacuo*. The product was obtained in 91% yield (3.57 g) as a dark brown friable powder (PA-2, see Table 1).

B. A solution of a mixture of PVC (6.26 g, 100 mmol) and NaOH (8.0 g, 200 mmol) in DMSO (100 mL) was stirred for 1 h at 120—125 °C. Then NaOH (12.0 g, 300 mmol) was additionally added by portions at the same temperature for 5 h. After cooling the reaction mixture was poured into water (300 mL), the product that precipitated was washed with water (until Cl$^-$ ions disappeared, test with a 1% solution of $AgNO_3$), acetone, and ether and dried *in vacuo*. The product was obtained in 97.4% yield (3.33 g) as a dark brown powder (PA-4, see Table 1).

The PA-1 and PA-3 samples were obtained analogously to the PA-2 and PA-4 samples, respectively.

Sulfurization of PA (for the preparation of SPA-2, SPA-6, and SPA-8 samples). ***A.*** PA-1 (0.5 g) was added to melted (120 °C) pulverized sulfur (1.5 g), and the mixture was heated for 2.3 h at 120—260 °C. Hydrogen sulfide (~50 mL) was isolated from the reaction mixture. After cooling a black powder (SPA-2, see Table 2) was obtained in 62% yield (1.24 g).

B. A mixture of PA-2 (0.5 g) and pulverized sulfur (2.0 g) was heated for 3 h at 160 °C. Hydrogen sulfide (~60 mL) was isolated from the reaction mixture. After cooling a black powder (SPA-6, see Table 2) was obtained in 91% yield (2.88 g).

C. A mixture of PA-2 (0.5 g) and pulverized sulfur (2.0 g) was heated for 2.5 h at 300 °C. Hydrogen sulfide (~120 mL) was isolated from the reaction mixture. After cooling a black powder (SPA-8, see Table 2) was obtained in 71% yield (1.8 g).

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