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Sulfurization of polymers
4.* Poly(4,5,6,7-tetrathiono-4,5,6,7-tetrahydrobenzothiophene-2,3-diyl) and related structures based on polystyrene and elemental sulfur

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Polystyrene was exhaustively sulfurized with elemental sulfur at 190—370 °C to liberate hydrogen sulfide and to form black lustrous powders (the sulfur content was up to 67%) possessing conductivity (10^{-7}—10^{-6} S cm^{-1} upon doping with I_2), paramagnetic properties ((3.4—13) $\cdot$ 10^{19} sp g^{-1}, g = 2.0040—2.0046, ΔH = 0.36—0.47 mT), and redox properties. The use of these polymers as active cathode materials in lithium batteries allows their repeated cycling at a specific discharge capacity of up to 330 mA h g^{-1}. The data of elemental analysis and differential scanning calorimetry, the IR and ESR spectra, the conductivities, and the character of electrochemical activity of the polymers synthesized are consistent with poly(4,5,6,7-tetrathiono-4,5,6,7-tetrahydrobenzothiophene-2,3-diyl) and related structures.

Key words: polystyrene, elemental sulfur, sulfurization, fused polybenzothiophenes, conductivity, paramagnetism, electrochemical activity.

As part of our continuing studies on sulfurization of polymers,[1—3] we performed for the first time profound sulfurization of granulated shock-resistant polystyrene (PS) with elemental sulfur. The structure of the resulting polymer is discussed.

The reaction was studied in the temperature range of 190—370 °C at different PS to sulfur molar ratios (from 4 to 16 g-at. of sulfur per elementary unit of PS) to perform either partial or exhaustive sulfurization. It was expected that the reaction would proceed according to Scheme 1.

Sulfurization was performed in a steel reactor equipped with a stirrer and an outlet pipe connected to a gasometer for collection of hydrogen sulfide. The reaction time was varied from 1 to 4 h. The catalytic effects of additives (1.0—10.0 wt.%) of diphenylguanidine (DPG) and 2-mercaptobenzothiazole (MBTA), which are known as vulcanization accelerators, *i.e.*, as catalysts of formation of C—S bonds, were examined. The volume of hydrogen sulfide liberated changed depending on the reaction conditions.

Sulfurization products of PS were obtained as black powders with metallic luster. The products are insoluble in organic solvents. Unconsumed sulfur was washed from the polymers with hot benzene in a Soxlet apparatus. Then sulfurized PS was analyzed for S (selectively, for C and H). For particular samples, the IR spectra (including the photoacoustic spectra) were measured, the conductivity was determined, thermal destruction was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the electrochemical characteristics, paramagnetic properties (ESR spectroscopy), and reduction with lithium in liquid ammonia were examined.

Under the conditions used (Table 1), the reactions of PS with elemental sulfur afforded high-sulfur polymers (the S content was 40—67%) exhibiting semiconducting properties (σ = $2.1 \cdot 10^{-12}$—$2.1 \cdot 10^{-7}$ S cm^{-1}; when doped with I_2, σ = $1.2 \cdot 10^{-7}$—$6.0 \cdot 10^{-6}$ S cm^{-1}).

Exhaustive sulfurization of PS was achieved at 240—370 °C during 2—3 h. In this case, the polymer contained 59.50—66.70% of sulfur (theoretically, 62.50% with respect to molecules **4a**,**b**, see Scheme 1). Repeated sulfurization of the same PS sample (runs *16—18*) led to a decrease in the sulfur content by 4—10%. In the latter case, virtually no elimination of hydrogen sulfide was observed, which confirms that all hydrogen atoms in PS were replaced with sulfur even upon single sulfurization. Partial desulfurization upon repeated heating of sulfurized PS with sulfur is attributable to the tendency of

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* For Part 3, see Ref. 1.

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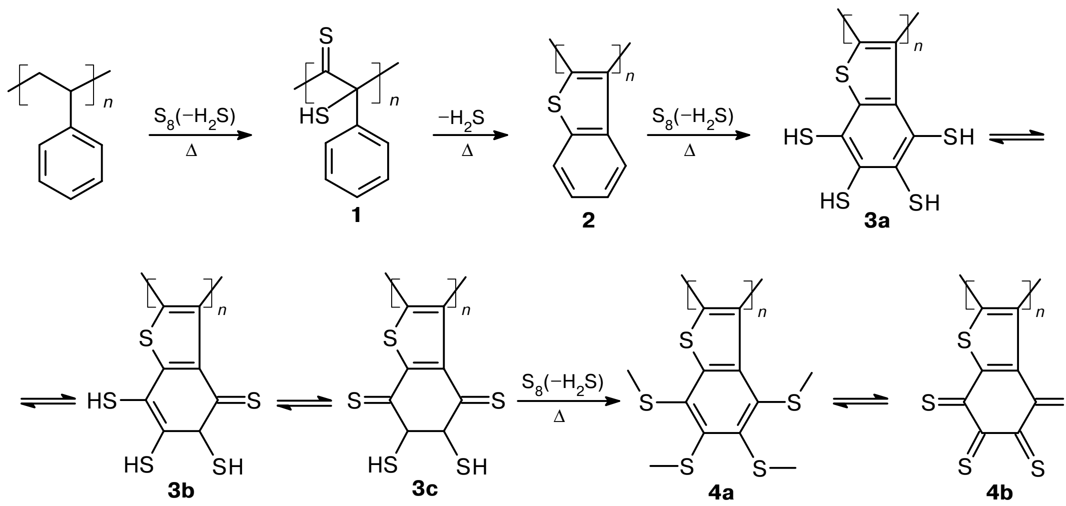
Scheme 1



compound **4a** to eliminate S atoms and to change the $C(sp)^2—S—S—C(sp)^2$ bond system for more stronger $C(sp)^2—S—C(sp)^2$ and $C(sp)^2—C(sp)^2$ bonds to form staircase and parquet multiply fused aromatic blocks.

Diphenylguanidine and mercaptobenzothiazole taken at concentrations of 1 wt.% noticeably promote sulfurization of PS (see Table 1, runs *8*, *9*, and *11—13*) by decreasing the reaction temperature. Thus, DPG allows one to achieve exhaustive sulfurization of PS at 240 °C during 2—3 h (runs *9* and *11*). At 190—210 °C, the reaction was completed in 2—4 h (runs *12* and *13*) in the presence of DPG or in the presence of a mixture of DPG and MBTA (1 : 1).

Apparently, product **1** containing the sulfurized polyethylene chain is formed at the initial stages of the process. Elimination of the hydrogen sulfide molecule from **1** affords polybenzothiophene **2** (see Scheme 1) (it is known[4—7] that the reaction of styrene with sulfur gives rise to phenylthiophene and its homologs). Then the benzene ring is sulfurized to yield (in the ideal case)

Table 1. Results of profound sulfurization of PS with elemental sulfur

Run	PS : S ratio (mol)	T[a] /°C	Time /h	Catalyst (wt.%)	Yield[b] (%)	Found (S) (%)	σ/S cm^{-1}	
							I[c]	II[d]
1[e,f]	1 : 13	350	1.5	No	96.80	62.50	$4.3\cdot10^{-10}$	
2	1 : 4	290	4	No	81.20	39.50	$4.2\cdot10^{-9}$	$1.1\cdot10^{-6}$
3	1 : 8	270	2	No	57.50	53.00	$6.2\cdot10^{-11}$	
4	1 : 16	290	2	No	96.20	65.80	$2.7\cdot10^{-9}$	$6.0\cdot10^{-6}$
5	1 : 16	320	2	No	82.10	66.60	$2.8\cdot10^{-7}$	
6	1 : 12.5	310	3	No	82.10	66.00	$2.1\cdot10^{-7}$	
7	1 : 16	300	3	No	96.50	65.70	$1.1\cdot10^{-12}$	
8	1 : 8	240	2	DPG (1)	47.00	42.10	$3.4\cdot10^{-11}$	$1.2\cdot10^{-7}$
9	1 : 16	240	2	DPG (1)	78.10	66.50	$2.1\cdot10^{-12}$	$4.3\cdot10^{-7}$
10	1 : 16	370	2	MBTA (1)	78.10	66.40		
11	1 : 16	240	3	DPG (1)	98.10	65.90		
12	1 : 16	190	4	DPG,[g] MBTA	84.30	54.70	$3.9\cdot10^{-11}$	
13	1 : 16	210	2	DPG,[g] MBTA	81.20	56.70		
14	1 : 16	300	1	MBTA (1)	~100	59.50		
15	1 : 16	300	1	MBTA (10)	~100	63.30		
16[f,h]		310	2	No		55.90	$8.0\cdot10^{-10}$	$1.4\cdot10^{-7}$
17[f,h]		310	3	No		61.60	$1.7\cdot10^{-9}$	$1.2\cdot10^{-7}$
18[h]		240	2	No		56.60		

[a] Since the process was exothermic, the temperature was controlled with an accuracy of ±10 °C. [b] With respect to exhaustively sulfurized PS. [c] In air. [d] After doping with I_2. [e] Without treatment with hot benzene. [f] Found (%): run *1*, C, 36.00; H, 1.40; run *16*, C, 35.40; H, 0.17; run *17*, C, 37.40; H, 0.65. [g] 0.5 wt.% each. [h] Repeated sulfurization of the products: run *16,* 2.7 g of the product obtained in run *5* and 4.0 g of sulfur; run *17*, 9.7 g of the product obtained in run *6* and 7.0 g of sulfur; run *18*, 1.0 g of the product obtained in run *10* and 3.2 g of sulfur.

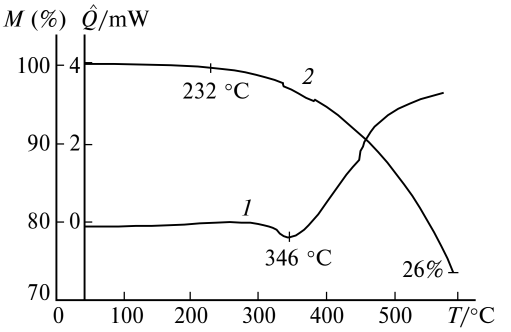
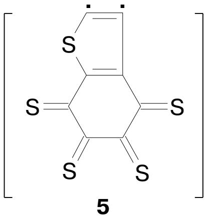


Fig. 1. The DSC (*1*) and TGA (*2*) curves of sulfurized PS (see Table 1, run *17*); *Q* is the thermal flow and *M* is the weight of the sample.

cross-linked or non-cross-linked poly(4,5,6,7-tetrathiono-4,5,6,7-tetrahydrobenzothiophene-2,3-diyl) (**4a** or **4b**, respectively), which is a polymer of hypothetical biradical **5**.



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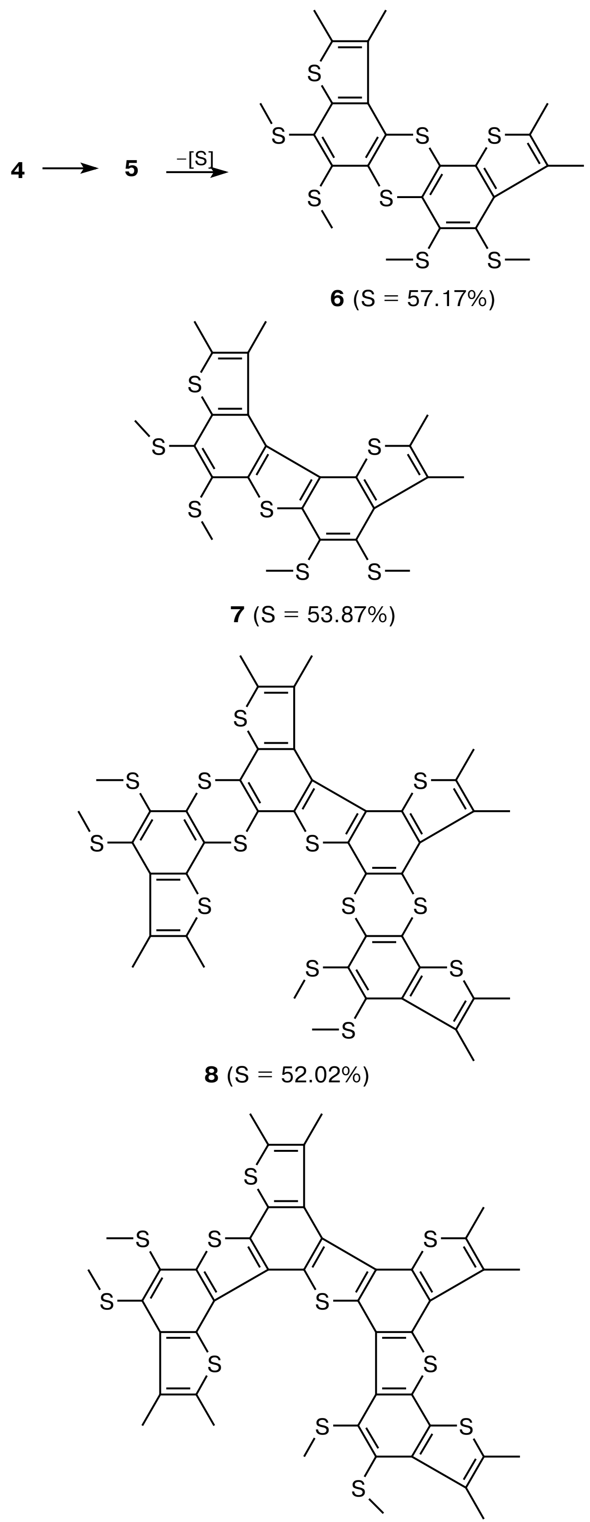
The character of thermal destruction of sulfurized PS is shown in Fig. 1, which presents the DSC and TGA curves for the doubly sulfurized specimen (see Table 1, run *17*). The weak endothermic effect at ~350 °C followed by the exothermic increase in the temperature range of 350—600 °C (curve *1*) is attributable to the initial cleavage of the S—S bonds (the endothermic process) followed by further aromatization due to elimination of S atoms giving rise initially to structures of types **6—9** and then to multiply fused blocks without disulfide bonds (exothermic processes, Scheme 2). Elimination of two S atoms from one elementary unit of polymers **4a**,**b** corresponds to this scheme. This process should be accompanied by the weight loss of 25%, which is almost exactly equal to the weight loss (26%) determined from the TGA curve obtained upon heating of the specimen to ~590 °C at a rate of 10 °C min^{-1}, *i.e.*, during ~1 h. According to the data of TGA analysis, the weight loss started at ~232 °C, whereas this process was not accompanied by the pronounced thermal effect in the DSC curve up to ~300 °C (only a gently ascending slope was observed starting at ~150 °C). Apparently, the energy expended for cleaving the S—S bonds in this temperature range is compensated by the energy released upon formation of a new C—S bond. The results of thermal destruction of exhaustively sulfurized PS are governed by the conditions of the preparation of the sample, *i.e.*, by the ratio between the structural blocks of types **1—4** and **6—9** in the polymer. For example, all thermal effects in the DSC curve of the polymer obtained under conditions of run *16* are more pronounced and are substantially shifted to the higher-temperature region (Fig. 2).

Scheme 2



6 (S = 57.17%)

7 (S = 53.87%)

8 (S = 52.02%)

9 (S = 47.85%)

In mass-spectrometric studies of thermal destruction of sulfurized PS, the formation of volatile products was observed in the temperature range of 250—450 °C (which is in agreement with the DSC and TGA data). The ion chromatogram contains one very broad inseparable peak.

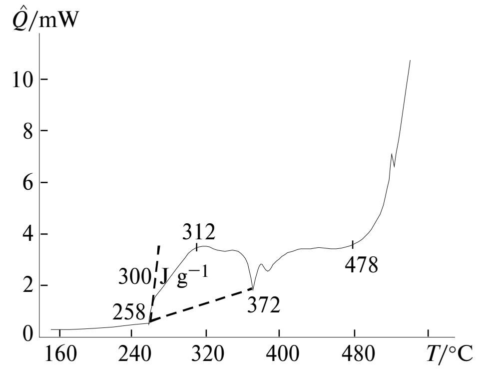
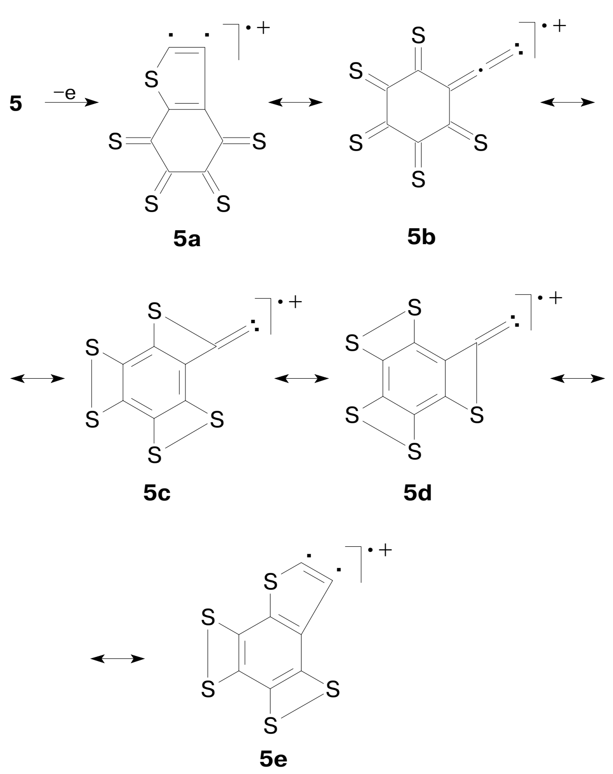


Fig. 2. The DSC curve of sulfurized PS (see Table 1, run *16*). The rate of heating was 10 deg min^{-1}.

Table 2. The m/z values and relative intensities (I) of the peaks of the major fragment ions in the mass spectrum of exhaustively sulfurized PS

Ion	m/z	I (%)
$C_{31}S_{12}$	756	1
$C_{30}S_9$	648	1
$C_{27}S_8$	580	2
$C_{26}S_7$	536	6
$C_{24}S_8$	512	7
$C_{24}S_6$	480	10
$C_{18}S_6$	408	5
$C_{12}S_7$	368	44
$C_{14}S_5$	328	12
C_8S_5	256	100
C_9S_4	236	50

Scheme 3

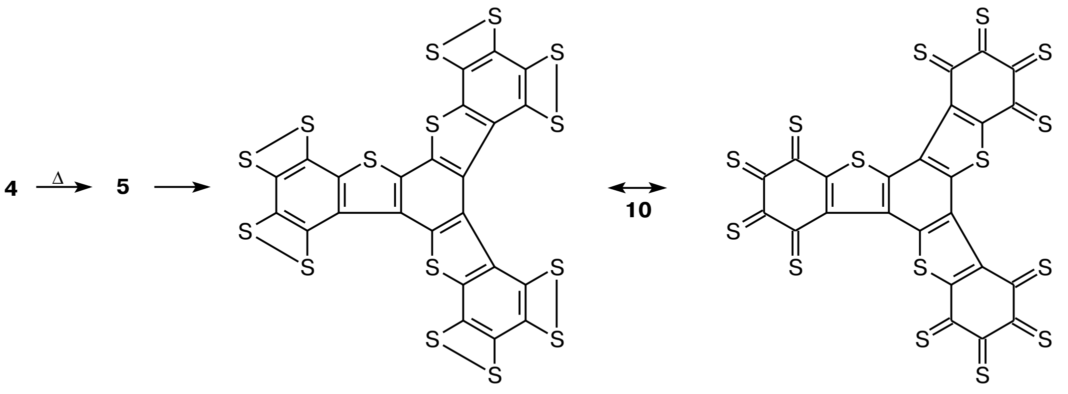


The mass spectra of mixtures of thermal destruction products of the polymer obtained at the beginning and at the close of decomposition are characterized by the presence of ion peaks arising from elimination of molecules and species CS, C_2S, and C_3S (at m/z 44, 56, and 68, respectively) from structural blocks of types **6**—**9** (Table 2). At ~450 °C, the mass spectrum of decomposition products has the most intense peak at m/z 256. This peak cannot be assigned to the ionized $S_8{}^{\cdot +}$ molecule because, according to the data published previously,[8] S_2 molecules prevail at temperatures higher than 500 °C. This mass corresponds exactly to the ionized monomer (C_8S_5), *viz.*, to 4,5,6,7-tetrathiono-4,5,6,7-tetrahydrobenzothiophene-2,3-diyl (**5**), which can be formed as a result of depolymerization of structures **4a,b** (see Scheme 2).

This radical cation (ionized biradical **5a** or vinylidenecarbene **5b**) may be stable due to resonance aromatic stabilization (structures **5c**—**5e**, Scheme 3). A structurally similar radical cation has been observed previously in studies of benzenehexathiolate derivatives.[9,10]

If thermal depolymerization of exhaustively sulfurized PS **4** is actually accompanied by the formation of biradical **5**, the latter can be stabilized as trimeric aromatic structure **10** (Scheme 4), which can be present in the polymer along with other oligomers.

Scheme 4



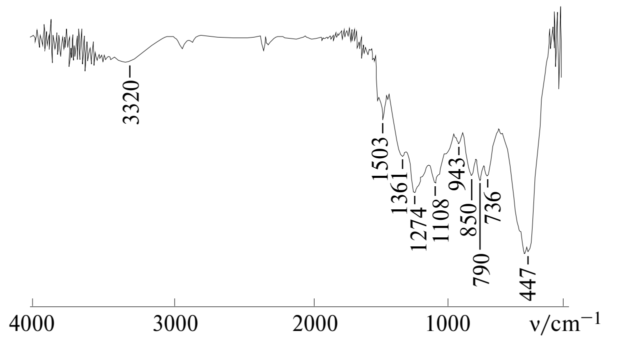


Fig. 3. IR spectrum of doubly sulfurized PS (see Table 1, run *16*).

No diffraction reflections were observed in the X-ray diffraction patterns of the resulting polymers, which indicates that the specimens are X-ray amorphous.

In the IR spectra of the resulting polymers (Fig. 3), an intense broad absorption band with the maximum at 447 cm^{-1}, which belongs to ν(S—S) vibrations, predominates. Apparently, absorption in the region of 1600—1000 cm^{-1} (the maxima at 1503—1361 cm^{-1}) can be assigned to skeletal vibrations[11] of the exhaustively sulfurized benzothiophene core of structure **4a**. The band at 1108 cm^{-1} can be assigned[12] to ν(C=S) vibrations in structures **3b—3c** and **4b**. As has been demonstrated previously,[3] the triplet at 850, 790, and 735 cm^{-1} can be assigned to mixed vibrations of the aromatic C—C and C—S bonds (in the case under consideration, of the bonds in structure **4a**).

The weak triplet in the region of 2900 cm^{-1} (2950, 2920, and 2850 cm^{-1}; ν(C—H) of aliphatic groups) belongs to the residual aliphatic CH_2 and CH groups of PS. The weak broad band in the region of 3400—3000 cm^{-1} with the maximum at 3320 cm^{-1} is assigned to adsorbed moisture.

The photoacoustic IR spectrum of sulfurized PS (Fig. 4) differs substantially from the transmission IR spectrum of the same sample (see Fig. 3) primarily in that the very intense ν(S—S) band at 447 cm^{-1} disappears. The remaining bands of the polyfused benzothiophene structures in the region of 1600—1000 cm^{-1} and the triplet of vibrations of the C—C and C—S aromatic bonds in the region of 900—700 cm^{-1} (see Ref. 3) are retained. The intensity ratio of these bands slightly changes and the bands are shifted to the high-frequency region by 15—25 cm^{-1}.

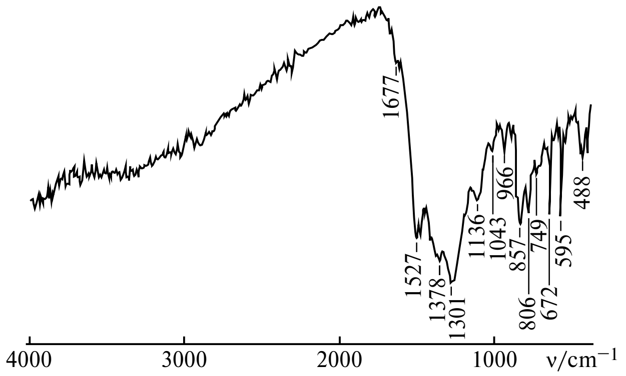


Fig. 4. Photoacoustic IR spectrum of doubly sulfurized PS (see Table 1, run *16*).

It is also important that the photoacoustic IR spectrum differs from the IR spectrum in that the former has two narrow bands at 672 and 595 cm^{-1}, which can be assigned to deformation vibrations of the C—H bonds in the thiophene fragments[11] of the benzothiophene blocks. These bonds can be formed on the surface of microspecies of the polymer due to interaction of active biradical structures of type **5** with atmospheric moisture.

Analysis of microspecies (~50 μm) of the specimen obtained in run *6* by energy dispersive X-ray spectroscopy (EDS) confirmed the high carbon content (68.79—81.26%) and the low sulfur content (18.74—31.21%) in the surface layer of the material (up to 1 μm) with homogeneous distribution of the elements throughout the surface within one species, the C/S ratio (within the above-mentioned limits) in different species being variable.

Therefore, the molecular structure of the surface layer of the microspecies of the polymer differs from that of the species in the bulk. The structure of the former consists primarily of polyfused benzothiophene structures of types **6—9** (see Scheme 2) with substantially reduced contents of S—S and C—S bonds. Apparently, these structures form a thermally stable carbonized layer on the surface of the species, which hinders polycondensation of underlying layers with the cleavage of the S—S and C—S bonds and elimination of elemental sulfur. This suggestion is in agreement with the DSC and TGA data (see Figs. 1 and 2).

The ^{13}C NMR spectrum of a powder of doubly sulfurized PS has a broadened singlet at δ 131 typical of carbon nuclei in condensed aromatic compounds.[13]

All polymers are paramagnetic. As an example, the ESR spectral data for a number of samples with different sulfur contents are given in Table 3. These spectra have

Table 3. Characteristics of the ESR spectra of sulfurized PS

Run[a]	Sulfur content (%)	$C \cdot 10^{19}$ [b] /sp g^{-1}	g Factor	ΔH /mT
3	53.00	6.6	2.0042(6)	0.36
4	65.80	6.5	2.0042(8)	0.38
5	66.60	7.3	2.0041(0)	0.36
6	66.00	9.0	2.0039(3)	0.39
7	65.70	8.1	2.0042(8)	0.42
8	42.10	5.0	2.0044(0)	0.44
12	54.70	3.4	2.0046(9)	0.47
16[c]	55.90	13.0	2.0040(4)	0.46
17	61.60	11.0	2.0041(6)	0.41

[a] See Table 1. [b] *C* is the spin concentration. [c] The spectrum was measured by A. D. Milov.

intense symmetrical narrow singlets with the *g* factors similar to those for the free electron. The above-mentioned characteristics and the high concentration of paramagnetic centers confirm the presence of an extensive system of conjugated bonds in the samples, which is in good agreement with the assumed structures **2—9** (see Schemes 1 and 2).

The redox properties and electrochemical activities of the polymers were examined. One anodic peak at 2.4 V (at 2.5 V for the doubly sulfurized sample) and two pronounced cathodic peaks at 1.98 and 2.38 V (at 1.95 and 2.31 V for the doubly sulfurized sample) are observed in the cyclic voltammograms (Fig. 5), which confirms the presence of redox-active S—S bonds in the polymers. In addition, the cyclic voltammograms have one small pronounced reduction peak at 2.1 V (which is also observed in the voltammogram of elemental sulfur). This peak virtually disappears upon repeated cycling and its presence indicates that soluble reduction products escape from the electrode surface through diffusion. The observed two-step reduction is typical of compounds containing polysulfide blocks.

The specimen of doubly sulfurized PS with the sulfur content of 61.60% possessed the largest discharge capacity (Q = 330 mA h g^{-1}). Judging from the Q value, this specimen corresponds to a greater extent to structure **4a**. The cyclic voltammogram has pronounced oxidation peaks and is very similar to that of elemental sulfur (although the reduction peak at 2.1 V is virtually absent).

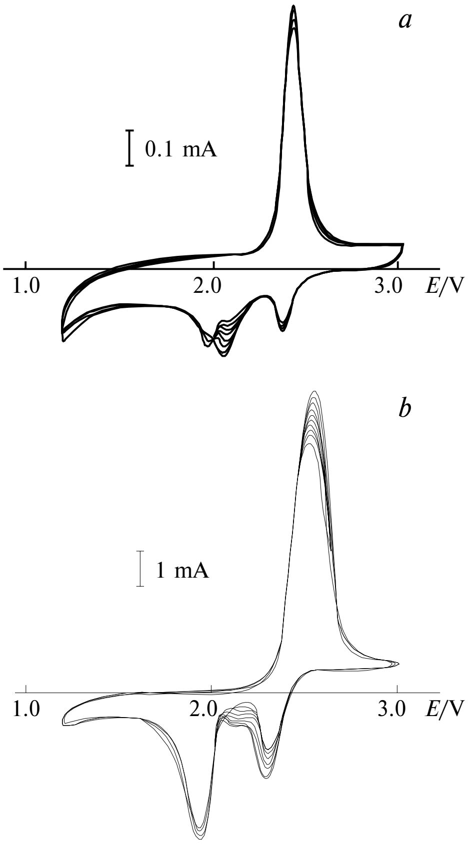


Fig. 5. Cyclic voltammograms of sulfurized PS (see Table 1): *a*, run *6*, cycles 1—10; *b*, run *17*, cycles 5—15 (the rate of the potential scan was 1 mV s^{-1}).

On the whole, the discharge capacities do not correlate with the sulfur content in the specimen, which can be readily explained by the difference in the ratio between structures **1—9**, which changes depending on the conditions of sulfurization. Apparently, structures of types **6—9** (see Scheme 2) consisting of multiply fused benzodithiyne and benzothiophene fragments (S = 50%) should be electrochemically inactive in the voltage range under study.

To estimate the capacities of cathodes with the use of the resulting polymers as active materials, we performed their cycling in lithium button batteries. The dependencies of the discharge capacity on the number of cycles (Fig. 6) are indicative of stable reversibility of the redox process. Apparently, the loss of the capacity after the first cycle is associated with diffusion elimination of polysulfide sulfur atoms from polysulfide fragments. After the second discharge cycle, the capacity of the specimen (run *17*) is consistent with a predominance of structures of type **4** in the polymer, whereas the substantially lower capacity and electrochemical activity of the specimen obtained in run *6* correspond to a greater extent to structures **6—9**.

Chemical reduction of sulfurized PS with lithium in liquid ammonia led to partial desulfurization of PS. Judging from the data of elemental analysis of the reduced products (the S content was 58.50%), stable benzothiophene structures **4—6** primarily persisted in the polymer.

Therefore, PS was sulfurized with an excess of sulfur at temperatures higher than 200 °C with elimination of hydrogen sulfide (at 310—320 °C, the process was completed in 3 h) to form high-sulfur (up to 67%) low-hydrogen conducting polymers.

Diphenylguanidine and 2-mercaptobenzothiazole exert a catalytic action on sulfurization by decreasing its temperature to 190—250 °C.

Based on the data of elemental analysis, the IR, photoacoustic IR, NMR, and ESR spectra, the results of

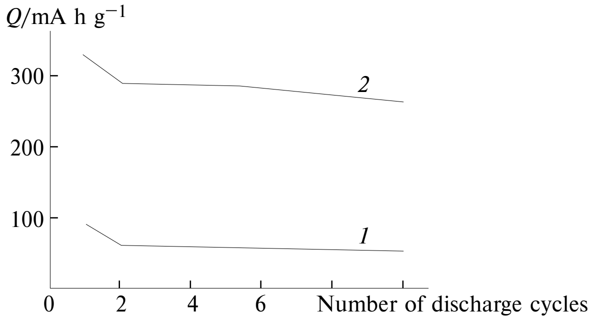


Fig. 6. Change in the discharge capacity (Q) of the cathodes of the lithium battery based on sulfurized PS upon cycling: *1*, run *6*; *2*, run *17* (see Table 1).

mass spectrometry and X-ray diffraction analysis, the DSC-TGA data, the conductivities, the results of chemical reduction, and the character of the electrochemical behavior, the polymers prepared in the present study have primarily cross-linked structures, *viz.*, poly(4,5,6,7-tetrathiono-4,5,6,7-tetrahydrobenzothiophene-2,3-diyl).

Double sulfurization of the same specimen of the polymer or reduction of the polymers with lithium in liquid ammonia led to partial desulfurization and formation of more stable multiply fused staircase and parquet polybenzothiophene structures.

Experimental

Polystyrene (granulated shock-resistant UPS-0803 E, GOST 28250-89) was a commercial product manufactured at the Angarsk Petrochemical Company (Russia). Elemental sulfur (high-purity grade, TU 6-09-2546-77), DPG (reagent grade, TU 6-09-07-897-77), and MBTA (reagent grade, TU 6-09-4012-75) were commercial products and were used without additional purification.

The IR spectra were recorded on an M-102 BOMEM Fourier IR spectrometer in two modes: a) transmission (in CsI pellets) in the frequency range of 4000—240 cm^{-1} (the resolution was 4 cm^{-1})and b) photoacoustic in the frequency range of 4000—400 cm^{-1} (the resolution was 8 cm^{-1}). The photoacoustic IR spectra were recorded with the use of an MTEC Photoacoustics Inc. (USA, model 300) photoacoustic cell. Samples were placed in the photoacoustic cell without pretreatment (without additional grinding or without a filler).

The ^{13}C CP/MAS NMR spectrum was measured on a Bruker DPX 400 spectrometer; the resonance frequency was 100 MHz. Before measurements, the solid sample was ground and placed in a ZrO_2 rotor (the diameter was 7 mm). The magic-angle-spinning technique at a rate of 5 KHz and the pulse cross-polarization mode were used to narrow lines. The duration of the 90-deg pulse was 5 μs, the relaxation delay was 5 s, and the duration of the contact pulse was 5 μs.

The mass spectra were obtained on a Finnigan GCQ mass spectrometer with direct introduction of the sample into the ionization chamber; the source temperature was 200 °C and the energy of ionizing electrons was 70 eV.

The specific dark conductivity was measured with the use of a VK 2-16 electrometric amplifier and an E6-13A teraohmmeter.

The elemental composition (C, H, and S) was determined on an automated Elementar Vario EL analyzer.

The ESR spectra were recorded on Radiopan SE/X-2547 (Poland) and Bruker ESP-300 spectrometers at room temperature, spectrum saturation being not attained. The modulation frequency of the magnetic field was 100 kHz. The modulation amplitude was 0.005—0.01 mT; Mn^{++} in MgO was used as the standard. The scan range of the magnetic field was 10 mT. The numbers of spins in the samples were estimated by comparing the areas of the spectra (determined by double integration) of the samples with the areas of the spectra of the standard $CuCl_2 \cdot 2H_2O$ containing the known number of spins.

Electrochemical experiments were carried out with the use of thin-walled two-electrode disk cells containing a lithium anode and an aluminum cathode (1.5 cm^2) coated with carbon and a mixture of the polymer, an activated carbon, and polyethylene oxide in a ratio of 50 : 35 : 15 wt.%. A 1 *M* solution of $(CF_3SO_2)_2NLi$ in dimethoxyethane was used as the electrolyte. The cyclic voltammograms were recorded on a PI-50-1.1 potentiostat with a rate of the potential scan of 1 mV s^{-1} in the range of 1.25—3.0 V using a two-coordinate PDA-1 recorder.

The polymers were studied by the DSC method on a DSC-2010 instrument (TA-Instrument) and by the TGA method on a TGA-2050 instrument (TA-Instrument).

X-ray diffraction analysis was carried out using a Laue chamber without rotation (Cu radiation) for 3—4 h.

Energy dispersive X-ray analysis was performed on a Kevex Sigma II Noran instrument. The following conditions were used: the voltage was 10 kV, the beam current was 100 pA, and the beam angle was 35°. The errors of the determination were 1.377% and 0.294% for C and S, respectively.

Sulfurization of PS (general procedure). Polystyrene (2.6 g, 25 mmol per elementary unit) and sulfur (10.0 g, 0.31 g-at.) were placed in a steel reactor equipped with a thermometer and a short-paddle stirrer connected to a gasometer. The mixture was heated at 310—320 °C for 3 h. During the first hour, vigorous evolution of hydrogen sulfide occurred with an average rate of ~10 mL min^{-1}. In the course of the reaction, H_2S was collected using a gasometer in a yield of 1800 mL (80 mmol). A black product was obtained in a yield of 8.0 g. The product was powdered and washed with boiling benzene from an excess of sulfur in a Soxlet apparatus for 10—15 h. After drying *in vacuo*, the lustrous black powder was obtained in a yield of 5.3 g (see Table 1, run *6*).

Double sulfurization. Sulfurized PS (9.7 g; see Table 1, run 6) and sulfur (7.0 g) were placed in the reactor described above. The mixture was heated at 310—320 °C for 3 h and H_2S was obtained in a yield of 200 mL (8.9 mmol). The polymer was treated with hot benzene in a Soxlet apparatus for 10 h and dried to a constant weight *in vacuo* to obtain a lustrous black powder in a yield of 8.5 g (87.60%). Found (%): C, 37.40; H, 0.65; S, 61.60 (see Table 1, run *17*).

Catalytic sulfurization. *A*. Polystyrene (1.3 g, 12.5 mol), sulfur (6.4 g, 0.2 g-at.), and DPG (0.08 g) were placed in the steel reactor described above. The mixture was heated with active stirring at 240—250 °C for 2 h (1500 mL of H_2S were collected). The polymer was treated with hot benzene in a Soxlet apparatus for 10 h and dried *in vacuo* to obtain sulfurized PS in a yield of 2.5 g (see Table 1, run *9*).

B. Analogously, sulfurized PS was obtained from PS (1.3 g, 12.5 mol), sulfur (6.4 g, 0.2 g-at.), DPG (0.04 g), and MBTA (0.04 g) (210—220 °C, 2 h, 1000 mL of H_2S were collected) in a yield of 2.6 g (see Table 1, run *13*).

Reduction of sulfurized PS with the Li/NH$_3$ system. Sulfurized PS (1.0 g, S = 66.60%; see Table 1, run *5*) was added to a solution of metallic lithium (0.5 g) in liquid ammonia (150 mL) and the mixture was stirred for 3 h. The ammonia was evaporated and water was added. The polymer was filtered off, washed with water until the reaction became neutral, and then washed successively with ethanol and ether. After drying *in vacuo*, a lustrous black powder was obtained in a yield of 0.7 g (70%). Found (%): C, 32.11; H, 0.90; N, 0.89; S, 58.50; Li, 0.25. The specific conductivity (a pellet, S cm^{-1}) was $3.3 \cdot 10^{-8}$ (in air), $0.8 \cdot 10^{-9}$ (*in vacuo*), and $2.1 \cdot 10^{-7}$ (doped with I_2).

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