Sulfurization of polymers

5.* Poly(6-methyl-5-sulfanylthieno[2,3-*b*]pyridine-4-thione), poly(thieno[2,3-*b*]azepine-4,5(6*H*)-dithione), and related structures from poly(2-methyl-5-vinylpyridine) and elemental sulfur

B. A. Trofimov,[a]★ A. G. Mal´kina,[a] L. V. Sokolyanskaya,[a] V. V. Nosyreva,[a] G. F. Myachina,[a] S. A. Korzhova,[a] I. V. Rodionova,[a] T. I. Vakul´skaya,[a] L. V. Klyba,[a] E. S. Stoyanov,[b] T. A. Skotheim,[c] and Yu. V. Mikhailik[c]

[a]A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 39 60 46. E-mail: bat@irioch.irk.ru
[b]G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
5 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 30 56
[c]Moltech Corporation, 9062 South Rita Road, Tucson, Arizona, USA.
Fax: +1 (520) 799 7501

Poly(2-methyl-5-vinylpyridine) is sulfurized with elemental sulfur at 140—320 °C to release hydrogen sulfide and to give black lustrous powders (sulfur content up to 45%) possessing electric conductivity ($6.4 \cdot 10^{-11}$—$1.6 \cdot 10^{-7}$ S cm^{-1}), paramagnetism (spin concentration $6.2 \cdot 10^{18}$—$5.0 \cdot 10^{19}$ sp g^{-1}, $g = 2.0043$—2.0046, $\Delta H = 0.49$—0.58 mT), and redox and complex-forming properties. Elemental analysis data, IR, ESR, and mass spectra, DSC and TGA data, electric conductivity, electrochemical activity and chemical properties (salt formation and complexation) of the materials synthesized correspond to cross-liked poly(6-methyl-5-sulfanylthieno[2,3-*b*]pyridine-4-thione), poly(thieno[2,3-*b*]azepine-4,5(6*H*)-dithione), and related structures.

Key words: poly(2-methyl-5-vinylpyridine), elemental sulfur, sulfurization, polythienepyridine, polythieneazepine, electric conductivity, paramagnetism, complexation, electrochemical activity.

Polyconjugated sulfur-containing polymers, first of all, polythiophene and its substituted and analogs, are under intense study as organic metals and electroactive materials for accumulators of the new generation.[2] Polyfused structures of the poly(thienothiophene),[2] poly(dithienothiophene),[3] and poly(benzothienoindole)[4] types are considered[2,3] to be especially promising. Redox polymers with thiol, thione, disulfide, and polysulfide groups have already long ago been predominated among active cathodic materials.[2] Therefore, synthesis of new highly sulfurous polymers, which combined in the macromolecule condensed thiophenic and other aromatic heterocyclic fragments and indicated redox-active functions is important.

In the previous reports of this series, we have shown that the direct high-temperature sulfurization with elemental sulfur of common polymers (polyethylene,[5,6] polystyrene,[1] polysiloxanes[7]) opens an unexpectedly simple way to such polymeric materials that cannot so far be obtained by other methods.

In continuation of these studies, in this work we present the data on the deep sulfurization of poly(2-methyl-5-vinylpyridine) (PMVP) and discuss possible routes for the formation of structures and the properties of the obtained polymers.

Experimental

PMVP (AO "Omskkhimprom") with M ≈ 100000 was used. Elemental sulfur (special-pure grade, Technical Standard 6-09-2546-77), $CoCl_2 \cdot 6H_2O$ ("Krasnyi Khimik" Plant, St. Petersburg), $HgCl_2$, $PdCl_2$ (pure grade, Technical Standard 6-09-2025-72), and vinylglycidyl diether of ethylene glycol were commercial products and used as received.

IR spectra were recorded on a BOMEM M-102 IR-Fourier spectrometer using two methods: (a) transmission IR spectra (in pellets with CsI) in the 4000—240 cm^{-1} frequency range with a resolution of 4 cm^{-1}; (b) photoacoustic spectra in the 4000—400 cm^{-1} frequency range with a resolution of 8 cm^{-1}. A photoacoustic cell (MTEC Photoacoustics, Inc. Co., (USA), model 300) was used for recording IR spectra using the second

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method. Samples were placed into the cell without preliminary preparation (additional powdering or using a packing agent).

Mass spectra were obtained on a Finnigan GCQ spectrometer with the direct introduction of the sample into an ionization chamber (30—450 °C, 15 °C min^{-1}).

The specific dark conductivity was measured with a VK 2-16 electrometric amplifier and an E6-13A teraohmmeter (error ±2%). Studied samples were prepared as pellets by molding under a pressure of 300 kg cm^{-2} (to a constant value of electric resistance). Clamping copper electrodes were used in the measuring cell.

Elemental composition (C, H, N, S) was determined on an Elementar Vario EL automated analyzer.

ESR spectra were recorded on a Radiopan SE/X-2547 spectrometer (Poland) equipped with a magnetometer and a high-frequency meter at ~20 °C. The concentration of paramagnetic centers was calculated using known procedures[8] using calibrated DPPH standards.

Polymers were studied by the DSC method on a DSC-2010 instrument (TA-Instrument), and the TGA study was carried out on a TGA-2050 instrument (TA-Instrument).

X-ray diffraction analysis of polymers was conducted on a Dron-3 powder diffractometer (Cu radiation, Ni filter, Si as internal standard (α = 5.4305 Å)).

Sulfurization of PMVP (general procedure exemplified for entry *6*, Table 1). PMVP (1.4 g, 11.8 mmol calculated per elementary unit) and sulfur (6.4 g, 0.2 mol) were placed in a steel reactor equipped with a thermometer and a mixer with short blades and connected with a gasometer. The mixture was heated for 3 h at 320 °C. During the first hour H_2S was vigorously evolved with a mean rate of ~10 mL min^{-1}, and 500 mL (22.3 mmol) of H_2S were collected by the gasometer within the reaction time. A black product (4.5 g) was obtained, powdered, and washed with hot benzene in the Soxhlet apparatus from residual sulfur for 15 h. After drying *in vacuo,* black lustrous power was obtained (1.57 g), the content of S in which (34.38%, see Table 1) corresponds to structures **3—5** with two S atoms in the elementary unit (75% yield).

Table 1. Conditions for sulfurization of PMVP with elemental sulfur

Entry	Ratio S : PMVP (mol)[b]	T[a]/°C	Duration of reaction /h	Yield (%)	Found S (%)
1	49.6	140	7	82 [c]	16.13
2	16.9	170	2	68 [d]	29.10
3	16.9	250	3	60 [d]	31.61
4	16.9	250	4	85 [d]	35.80
5	12.5	320	3	58 [d]	31.05
6	16.9	320	3	75 [d]	34.38
7 [e]	—	310—320	3	91 [f]	44.86

[a] Due of exothermicity of the process, the temperature was monitored with an accuracy of ±10 °C.

[b] Number of S moles per elementary unit of PMVP.

[c] Calculated for structure **2**.

[d] Calculated for structures **3—5**.

[e] Repeated sulfurization: 5.32 g of the product of entry *6* and 10 g of S.

[f] Calculated for the transformation of structures **3**, **4** into structures **9—11**.

The polymer (0.5 g, S content 29.10%, see Table 1, entry *2*) was heated with stirring in 10 mL of 1,2-dimethoxyethane for 8 h at 35—40 °C. The polymer was filtered off, washed with benzene, and dried to obtain 0.41 g of the polymer (S content 22.09%).

The polymer (0.5 g, S content 29.10%, see Table 1, entry *2*) was heated with stirring in 10 mL of vinylglycidyl diether of ethylene glycol for 8 h at 35—40 °C. The polymer was filtered off, washed with benzene, and dried. The polymer with an S content of 18.61% was obtained (0.34 g).

Double sulfurization. Sulfurized PMVP (5.32 g, see Table 1, entry *6*) and elemental sulfur (10 g) were placed into the reactor described above. The mixture was heated for 3 h at 310—320 °C. H_2S (200 mL, 8.9 mmol) was evolved. The non-reacted sulfur was extracted from the polymer with hot benzene in the Soxhlet apparatus for 15 h, dried *in vacuo* to a constant weight, and obtained 5.68 g (91%) of a black lustrous powder. Found (%): C, 44.48; H, 1.89; N, 6.15; S, 44.86 (see Table 1, entry *7*).

Reaction of sulfurized PMVP with HCl. Finely powdered doubly sulfurized PMVP (0.1 g, 0.48 mmol, see Table 1, entry *7*) was added by small portions to 20 mL of a 10% aqueous solution of HCl. The obtained suspension was stirred for 25 h at 20—25 °C, filtered on the Schott funnel, washed with water, 95% EtOH, and Et_2O, and dried *in vacuo*. A black powder (0.106 g, 89.9% calculated per structures **9—11**) was obtained. Found (%): Cl, 18.37; S, 40.69. Calculated (%): Cl, 14.31; S, 38.82 (for structures **9—11**).

Complex formation of sulfurized PMVP with $HgCl_2$. Finely powdered doubly sulfurized PMVP (0.1 g, see Table 1, entry *7*) was added by small portions to a solution of $HgCl_2$ (0.1 g, 0.37 mmol) in 10 mL of H_2O heated to 40 °C. The obtained suspension was stirred at this temperature for 30 h, filtered on the Schott funnel, and washed with water (to the negative reaction for Cl ions), 95% EtOH, and Et_2O. After drying *in vacuo*, a black power (0.13 g) was obtained. Found (%): Hg, 18.00; S, 25.19; Cl is absent.

Complex formation of sulfurized PMVP with $CoCl_2 \cdot 6H_2O$. Finely powdered doubly sulfurized PMVP (0.1 g, see Table 1, entry *7*) was added by small portions to a solution of $CoCl_2 \cdot 6H_2O$ (0.1 g, 0.42 mmol) in 10 mL of H_2O heated to 40 °C. The obtained suspension was stirred at this temperature for 30 h, filtered on the Schott funnel, and washed with water (to the negative reaction for Cl ions), 95% EtOH, and Et_2O. After drying *in vacuo*, a black power (0.08 g) was obtained. Found (%): C, 47.09; H, 1.47; N, 6.20; S, 37.98; Cl is absent.

Complex formation of sulfurized PMVP with $PdCl_2$. Finely powdered doubly sulfurized PMVP (0.2 g, see Table 1, entry *7*) was added by small portions to a solution of $PdCl_2$ (0.25 g, 1.4 mmol) in 10 mL of H_2O heated to 50 °C. The obtained suspension was stirred at this temperature for 25 h, then filtered on the Schott funnel, and washed with water (to the negative reaction for Cl ions), 95% EtOH, and Et_2O. After drying *in vacuo*, a black power (0.17 g) was obtained. Found (%): C, 38.44; H, 1.67; N, 5.79; S, 31.07; Cl is absent.

Results and Discussion

It was assumed that the highly basic and prone to complex formation N atom in PMVP would retain or even enhance these properties in the sulfurized polymer to impart additional valuable properties to it, *e.g.*, the capability of coordinating catalytically active or ecologically dangerous metals, changing its electrochemical and electrophysical properties depending on the pH of the medium, *etc.*

The reaction of PMVP with elemental sulfur was studied in the 140—320 °C temperature range at different ratio of initial reactants (from 12.5 to 49.6 moles of S per elementary PMVP unit). The duration of the reaction was varied from 2 to 7 h (see Table 1). The volume of the evolved H_2S changed depending on the reaction conditions: at 140 °C it was 210 mL (see Table 1, entry *1*), and at 320 °C it was ~500 mL (see Table 1, entries *5* and *6*).

Black powders with metallic luster were obtained (S content 16—45%), possessing the semiconductor properties (specific conductivity $\sigma = 6.4 \cdot 10^{-11}$—$1.6 \cdot 10^{-7}$ S cm^{-1}) (Tables 1 and 2) and insoluble in water and most organic solvents (Et_2O, dioxane, benzene, toluene, MeCN, THF). Some samples (see Table 1, entry *2*) are partially soluble in 1,2-dimethoxyethane and vinylglycidyl diether of ethylene glycol (35—40 °C, 8 h). Upon dissolution the content of S in the solid residue decreases by 7.0 and 10.5%, respectively (for the indicated sample): the fraction containing a greater amount of sulfur are dissolved. The weight loss is also observed (by 18 and 32%, respectively), *i.e.*, some fractionating of the polymer occurs.

For the single sulfurization of PMVP, from 16 to 36% S are incorporated into the polymer, depending on the reaction conditions (see Table 1, entries *1—6*). Deeper sulfurization is achieved by the repeated reaction of S with the already sulfurized sample (see Table 1, entry *7*), which allows one to incorporate up to 45% S into the polymer.

The IR spectra of the polymers obtained (Fig. 1) in a region of 1600—1100 cm^{-1} contain very intense, broad, and weakly resolved band with maxima at 1543, 1487, 1445, 1377, 1339, 1295, 1255, 1184, 1136, 1108, and 1026 cm^{-1}. The high-frequency maxima (1543—1255 cm^{-1}) correspond[9] to vibrations of the skeleton of the poly(thienopyridine) and poly(thienoazepine) structures, and the low-frequency maxima (1184—1026 cm^{-1}) correspond to planar vibrations of C—H [10] in the same structures. In addition, the bands in a region of 1184—1026 cm^{-1} can be attributed[11,12] to stretching vibrations of the C=S bond. Weak diffuse maxima at 645, 618 cm^{-1} belong, according to published data,[9,12] to the C—S bonds with different environments. The narrow peaks at 829, 736, and 678 cm^{-1} are typical of deformational vibrations of the C—H bonds in the heteroaromatic structures.[10]

Table 2. Specific electric conductivity (σ) and characteristics of the ESR spectra of the sulfurized PMVP samples

Content of S (%)	σ /S cm^{-1}	Concentration of spins/sp g^{-1}	*g* Factor	Δ*H* /mT
16.13	$6.4 \cdot 10^{-11}$	$6.2 \cdot 10^{18}$	2.0046(1)	0.49
31.05	$1.7 \cdot 10^{-10}$	$5.0 \cdot 10^{19}$	2.0043(8)	0.56
44.86	$1.6 \cdot 10^{-7}$	$4.5 \cdot 10^{19}$	2.0044(2)	0.58

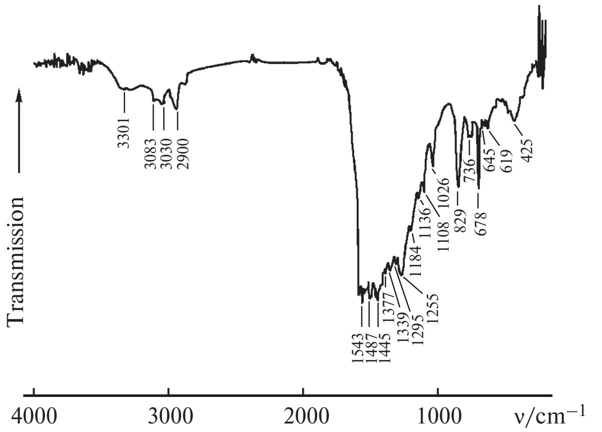


Fig. 1. Transmission IR spectrum of the sulfurized PMVP sample with an S content of 35.80% (for conditions of synthesis, see Table 1, entry *4*).

The weak triplet in a region of 2900 cm^{-1} with frequencies at 2950, 2920, and 2830 cm^{-1} (stretching vibrations of C—H in aliphatic groups) is assigned to the methyl and residual aliphatic CH_2 and CH groups of the main chain of PMVP. The weak broad absorption band at 3301 cm^{-1} belongs, most likely, to the NH groups, and the weak maxima at 3030 and 3083 cm^{-1} are attributed to stretching vibrations of C—H in the heteroaromatic structures.

The photoacoustic IR spectrum of sulfurized PMVP (Fig. 2) differs insignificantly from the IR spectrum of the same sample (see Fig. 1) according to the "transmission"

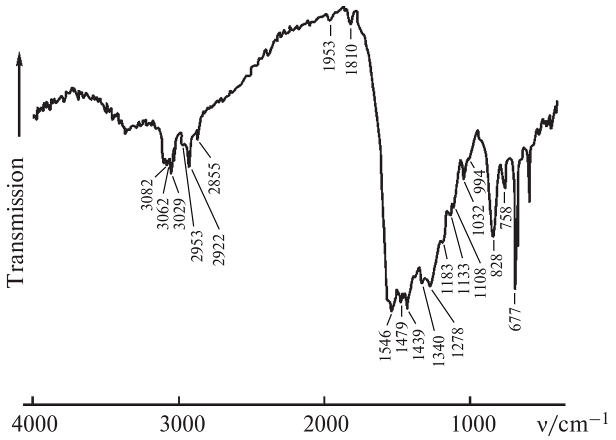
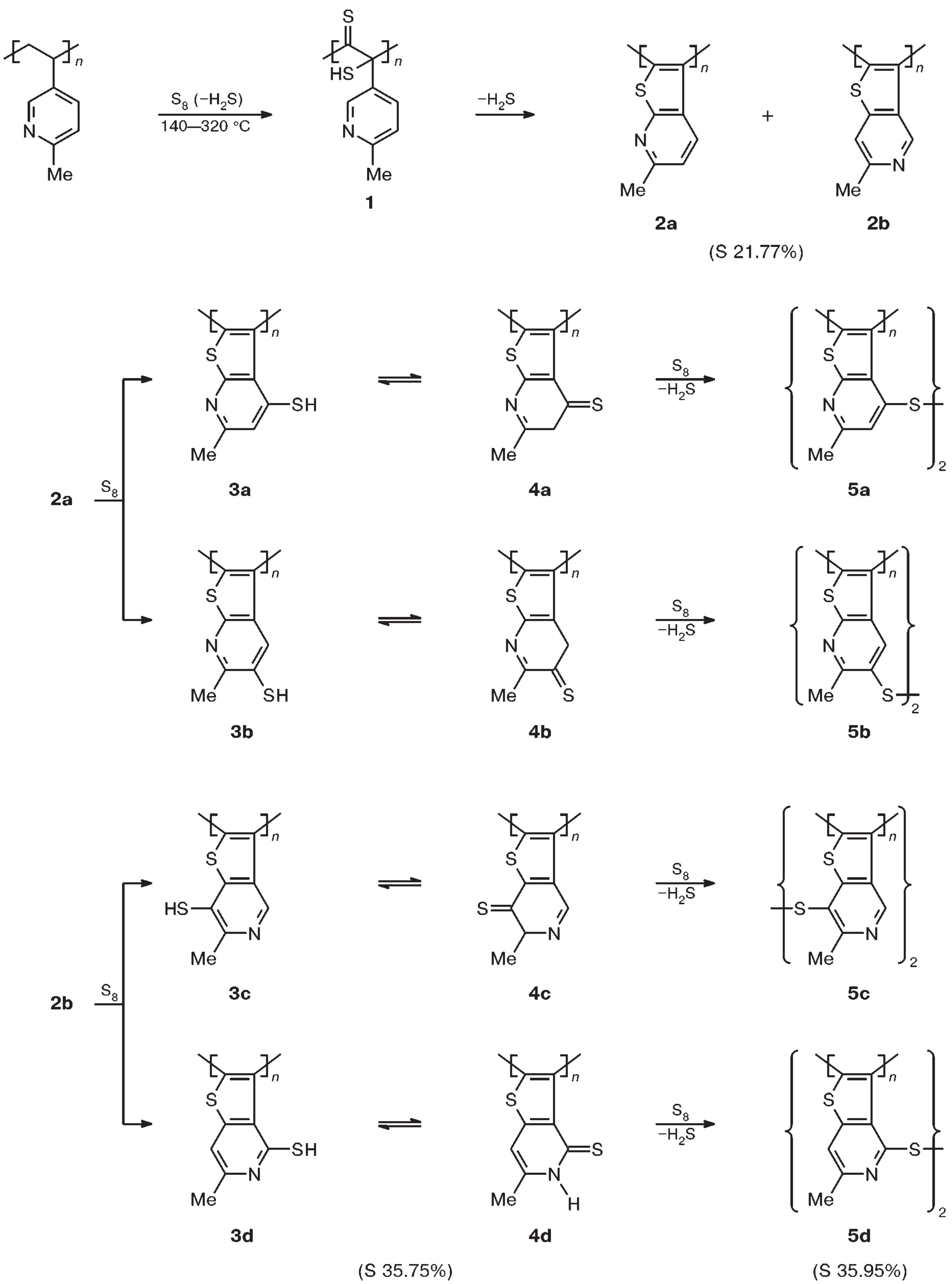


Fig. 2. Photoacoustic IR spectrum of the sulfurized PMVP sample with an S content of 35.80% (for conditions of synthesis, see Table 1, entry *4*).

Scheme 1

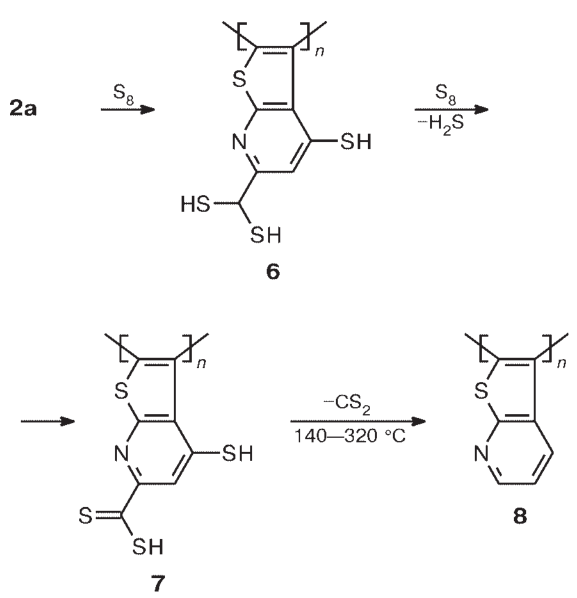

S₈ (−H₂S)
140—320 °C
−H₂S
1
2a
2b
(S 21.77%)
S₈
−H₂S
3a
4a
5a
3b
4b
5b
3c
4c
5c
3d
4d
5d
(S 35.75%)
(S 35.95%)
Me
SH
HS
N
S
n
2

scheme. All maxima in a region of 1600—500 cm^{-1} presumably assigned to the polycondensed thienopyridine and thienoazepine structures remained unchanged, and only the ratio of intensities of the bands changes. A weak broad diffuse absorption corresponding to the SH groups is observed in a region of 2700—2500 cm^{-1}.[13] This resemblance of the IR spectra recorded in different regimes (see Figs. 1 and 2) indicates that the molecular structure of the surface layer of the polymer macroparticle is close to that in the bulk and, most likely, corresponds to the poly(thienopyridinethione) and poly(thienoazepinethione) blocks and their thiolic tautomers.

Based on the IR spectroscopic data and by analogy with the sulfurization of polyethylene[5] and polystyrene,[1] we can assume (Scheme 1) that the main chain is dehydrogenated to form substituted polysulfanylthione **1**, the subsequent closure of which results in structurally isomeric poly(6-methylthieno[2,3-*b*]pyridine) (**2a**) and/or poly(6-methylthieno[3,2-*c*]pyridine) (**2b**), depending on which of the positions of the pyridine cycle (4, 6, or both) participates in dehydrocondensation. The insertion of the second S atom into polymers **2a**,**b** can involve both the pyridine cycle and Me group. Isomeric thiols **3a—d** and/or their tautomers, *viz.*, thiones **4a—d**, and the corresponding polymeric disulfides, *viz.*, cross-linked polymers **5a—d**, should be formed in the first case.

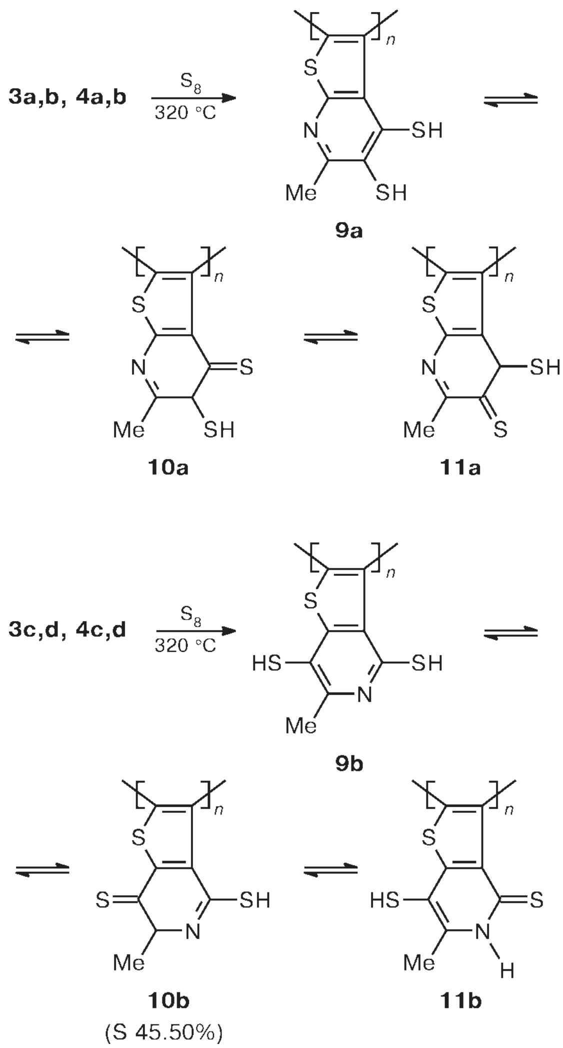
For the possible sulfurization of the Me group of polymers **1—5**, which occurs in parallel, one can expect the formation of *gem*-dithiols **6**, dithiocarboxylic acids **7**, and products of their dedithiocarboxylation **8** (Scheme 2, exemplified for polymer **2a**). The latter, in turn, can undergo further sulfurization at the pyridine cycle.

Scheme 2



The elemental composition of sulfurized PMVP (see Table 1) indicates the single sulfurization of the polymer with the introduction of mainly two S atoms, which corresponds to structures **1**, **3—5**. And only the repeated sulfurization of the already sulfurized sample allows the third S atom to be incorporated into the polymer (see Table 1, entry 7). It occurs, most likely, as shown in Scheme 3, for structural isomers of the polymers with two sulfur atoms (**3** and **4**).

Scheme 3



Dithiols **9a**,**b** and their thionic tautomers **10a**,**b**, **11a**,**b** exist, most likely, in the oxidized (disulfide) forms. The IR spectra (see above) contain bands of all structural elements of these tautomers, including the absorption of the C=S and NH groups.

The character of thermotransformations of the obtained polymers is illustrated by Figs. 3 and 4. The DSC curves of the samples corresponding to structures

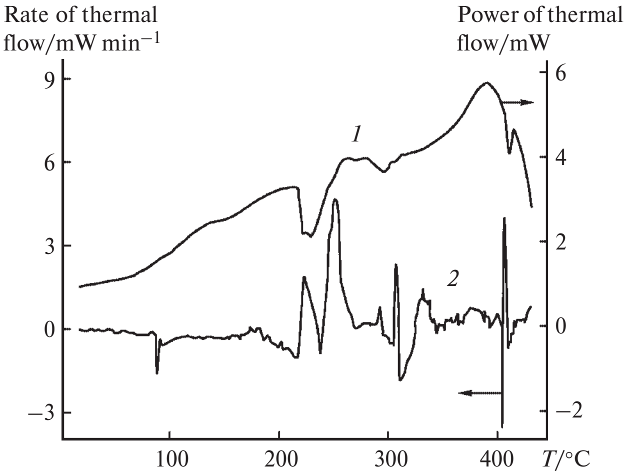


Fig. 3. DSC curves for the sulfurized PMVP samples with an S content of 31.05% (for conditions of synthesis, see Table 1, entry *5*) (*1*) and 34.38% (for conditions of synthesis, see Table 1, entry *6*) (*2*).

3—5 (S content 31—34%) in a temperature region of 200—550 °C exhibit complicated sets of endo- and exothermic peaks with different shapes and intensities (see Fig. 3), which confirm that the compounds involved in further processes of bond cleavage and formation are polyfunctional. Figure 4 combines the DSC and TGA curves for the doubly sulfurized sample (see Table 1, entry *7*). The weak exothermic effect at ~350 °C and its further rise at 370—600 °C (see Fig. 4, curve *2*) correspond to further aromatization and the formation of more condensed blocks containing no disulfide bonds (exothermic processes).

When the sample is heated to ~590 °C with a velocity of 10 °C min^{-1} (achieved in ~1 h), the TGA curve detects the weight loss (24%), which corresponds to the cleavage of one S atom and the Me group per elementary polymeric unit. The main weight loss falls on an interval of 290—590 °C (19%), although the pronounced heat release begins in the DSC curve only at ~400 °C. Evidently, below this temperature, the energy expensed for the cleavage of the S—S and C—S bond is compensated by that evolved upon the formation of the new C—C bond during the formation of the polyfused aromatic systems.

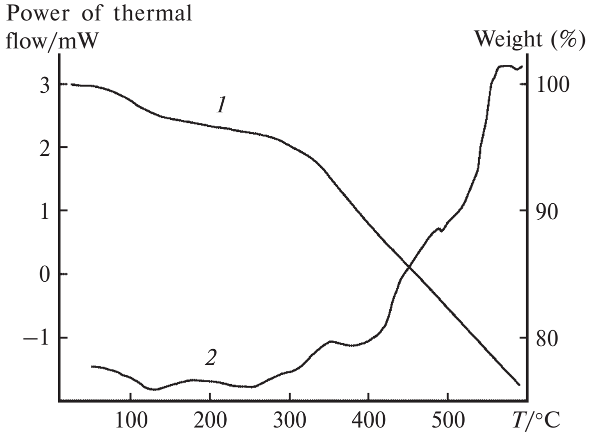


Fig. 4. TGA (*1*) and DSC (*2*) curves for doubly sulfurized PMVP with an S content of 44.86% (for conditions of synthesis, see Table 1, entry *7*).

The mass spectrometric study of doubly sulfurized PMVP showed the formation of volatiles in an interval of 250—450 °C, which agrees with the DSC and TGA data. The time plot of the total ion current in an interval of mass numbers of 21—672 represents a complicated set of weakly separated peaks. The mass spectra of mixtures of the thermodestruction products of the polymer obtained at the beginning and at the end of decomposition are characterized by the peaks of ions with *m/z* 107, 165, and 179 formed due to the elimination of the S, CS, CH_2S, C_2H_2S, and S_2 molecules and particles with *m/z* 32, 44, 46, 58, and 64, respectively, from structures **9—11** and their oxidized (disulfide) forms. The peak with *m/z* 209, to which thienoazepine radical cationic structures **12** and **13** can correspond (Scheme 4; only some of possible isomeric and resonance forms are shown), possesses the highest intensity in the mass spectrum of the decomposition products at ~450 °C.

The possibility of formation of multicentered S—S bonds in polyconjugated carbon-sulfur polymers has recently been confirmed in Hoffmann′s theoretical studies.[14,15]

Predomination of the radical cation with *m/z* 209 in the destruction products of doubly sulfurized PMVP allows one to assign it to the monomeric polymeric unit. It follows from this that the Me group is mainly incorporated into the modified macromolecule rather than undergoes "burning" as it is shown in Scheme 2.

The formation and fragmentation of the ion with *m/z* 209 does not either contradict the presence in the polymers of the thienopyridinic structures fused with the 1,2-dithiolane cycle (as, *e.g.*, in structure **14**), which can be formed according to Scheme 5.

Diffraction reflections are not observed in the powder X-ray patterns,* which indicates that the samples are X-ray amorphous.

The values of paramagnetism and electroconductivity of the obtained polymers (see Table 2) correspond to those for organic semiconductors and confirm that they contain the developed system of conjugated bonds. Signals in the ESR spectra are symmetric singlets with *g* factors close to that of a free electron (2.0043—2.0046) and the width between points of the maximum slope equal to 0.49—0.58 mT.

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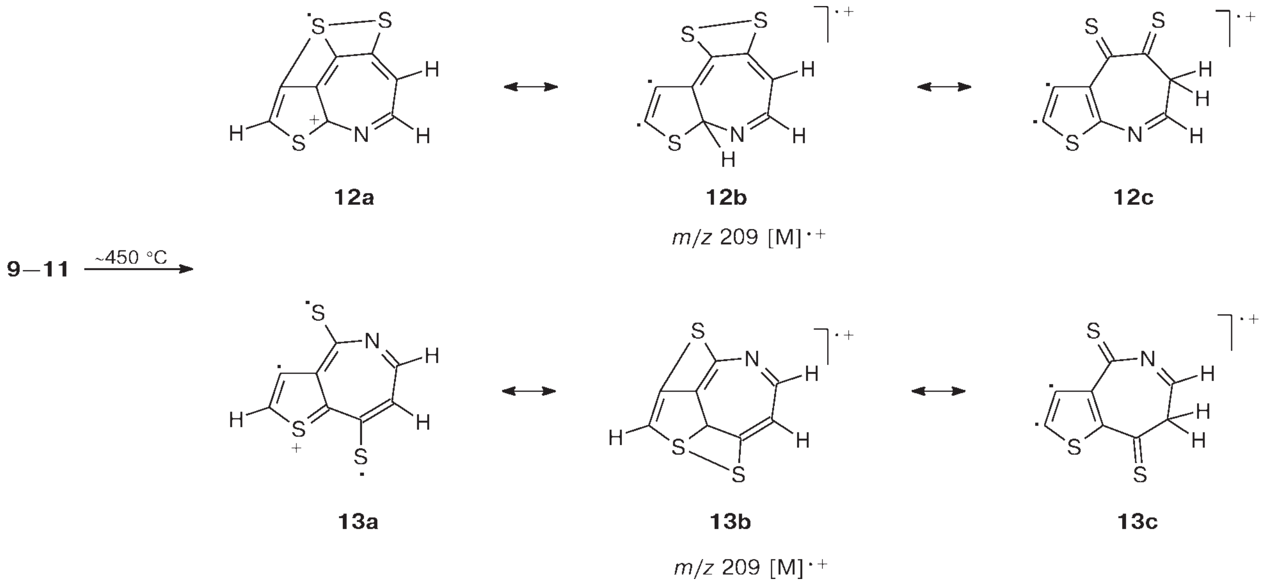
Scheme 4



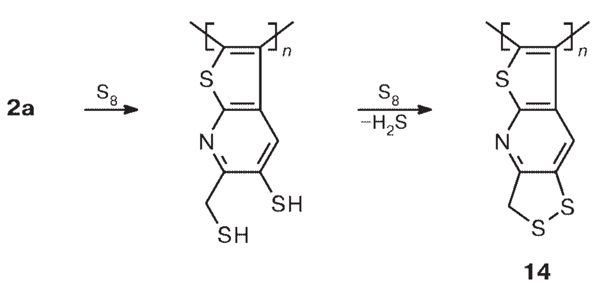
When the S content in the sample increases from 16 to 31% (see Table 2), the specific conductivity increases by 2.6 times, and the concentration of paramagnetic centers increases by an order of magnitude. These facts can indicate both the single nature of unpaired electrons and charge carriers and the strong electronic interaction of the S atoms with the conjugated system, which corresponds to the considered structures. The substantial increase in the electroconductivity (to $1.6 \cdot 10^{-7}$ S cm^{-1}) at the virtually same concentration of spins in the sample with a higher content of S (44.86%) is due, most likely, by a greater ordering of the supramolecular structure of this polymer favoring an increase in the mobility of charge carriers.

The electrochemical behavior of the polymers in model Li accumulators confirms the presence of redox-active groups (thiol, thione, and disulfide) in them. According to the cyclic voltammograms (Fig. 5), the polymers undergo complicated multistage reduction with characteristic peaks at potentials of 2.36, 2.12, and 1.92 V followed by their oxidation at 2.62 V. This redox behavior is characteristic of polymers with the S—H, C=S, and S—S bonds[1,5,6] and agrees with the presence of thiolic, thionic, disulfide, and polysulfide structures of types **5** and **12** in the obtained materials (the results of studying the electrochemical properties of the obtained polymers in Li accumulators will be presented in detail elsewhere).

The ability of doubly sulfurized PMVP (S content 44.86%, 310—320 °C, 3 h, see Table 1, entry *7*) to form salts with HCl and complexes with the $CoCl_2 \cdot 6H_2O$, $HgCl_2$, and $PdCl_2$ salts was studied.

From an aqueous solution of HCl the polymer binds somewhat greater amount of chlorine (18.37%) than that corresponding to the disulfide forms of structures **9—11**

Scheme 5



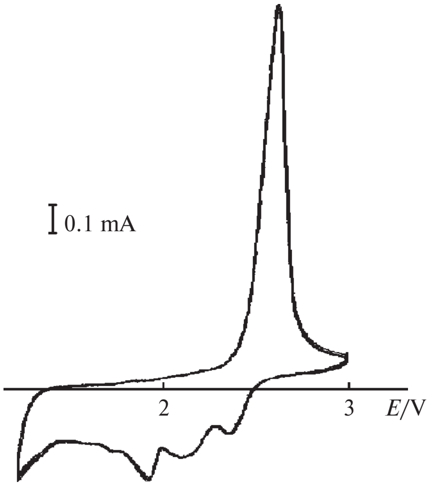


Fig. 5. Cyclic voltammetry of doubly sulfurized PMVP with an S content of 44.86% (for conditions of synthesis, see Table 1, entry *7*).

Table 3. Results of X-ray diffraction analysis of the crystalline phase of the product obtained by the reaction of doubly sulfurized PMVP (content of S 44.86%, see Table 1, entry *7*) with $PdCl_2$

Product		Palladium		
d/Å [a]	I/I_0 [b]	d/Å [a]	I/I_0 [b]	hkl [c]
2.247	100	2.246	100	111
1.943	30	1.945	42	200
1.375	15	1.376	25	220
1.1727	15	1.1730	24	311
1.1230	5	1.1232	8	222

[a] Interplanar distances.
[b] Relative intensity.
[c] Reflection indices.

(14.31%), which can be explained by the presence of elementary units with a lower molecular weight (**2—5**, **8**).

Chlorine is absent in the reaction products with metal chlorides (it is likely, mercaptides are formed in the case of the Co and Hg salts due to the SH groups present in the polymer); Pd in the complex is zero-valence, which corresponds to the expected reduction of the Pd^{2+} cation by the mercapto groups in structures **3**, **6**, **9—11**.

The diffraction pattern of the product obtained by the reaction of doubly sulfurized PMVP (S content 44.86%, 310—320 °C, 3 h, see Table 1, entry *7*) with $PdCl_2$ exhibit intense diffraction lines indicating that the sample contains Pd in the metallic form (Table 3). In addition, the halo characteristic of X-ray amorphous substances is observed.

The data body of elemental analysis, IR, photoacoustic IR, ESR, and mass spectroscopies, X-ray diffraction analysis, DSC—TGA, electroconductivity, results of chemical reduction, and the character of the electrochemical and chemical behavior shows that sulfurized PMVP mainly represents the cross-linked polymer consisting of blocks of poly(6-methyl-5-sulfanylthieno[2,3-*b*]pyridine-4-thione), poly(6-methyl-7-sulfanylthieno[3,2-*c*]pyridine-4-thione), poly(thieno[2,3-*b*]azepine-4,5(6*H*)-dithione), poly(thieno[3,2-*c*]azepine-4,8(7*H*)-dithione), and related structures.

Thus, the results of the complex study of sulfurized PMVP indicate the possibility to synthesize related paramagnetic, current-conducting, and electrochemically active materials capable of complex forming with catalytically active metals, whose properties can be varied changing experimental conditions.

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