# Sulfurization of polymers
## 3.* Paramagnetic and redox properties of sulfurized polyethylene

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Polyethylene exhaustively sulfurized with elemental sulfur shows paramagnetic (spin concentration $2.7-9.7 \cdot 10^{19}$ sp g$^{-1}$, $g = 2.0041-2.0045$, $\Delta H = 0.53-0.62$ mT) and redox properties, which was demonstrated by both voltammetric and chemical methods (sodium reduction in liquid ammonia). The high concentration of unpaired electrons, the character of the electrochemical activity, and the chemical properties are in agreement with the presence in the polymers of polyconjugated ladder polythiophene and parquet polynaphthothienothiophene structures along with polyene-polysulfide blocks. The use of the polymers under consideration as an active cathode material in lithium batteries enables their repeated cycling with a specific charge capacitance of 150—340 mA h g$^{-1}$.

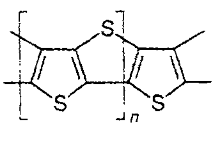
**Key words:** polyethylene, sulfur, sulfurization, fused polythienothiophenes, polynaphthotienothiophenes, polyene-polysulfides, paramagnetism, redox properties, specific capacitance.

Deep sulfurization of polymers with elemental sulfur accompanied by their dehydrogenation and aromatization, and incorporation of sulfur into the polymeric chain followed by the formation of fused polythiophene and polynaphthothiophene structures provides the most direct and simplest approach to synthesis of fundamentally new polymeric materials with properties significant in practice.

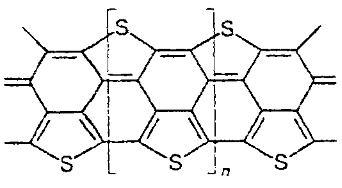
Surprisingly, this simple possibility has not yet been studied systematically. The majority of publications on the interaction of sulfur with polymers, including the widely studied rubber vulcanization, report on the modification of a polymeric material with a rather minor amount of sulfur (except ebonites), which adds to saturated regions of the polymeric chain.[2]

In our opinion, products of deeper sulfurization of polymers, in particular, polyethylene (PE), should gain fundamentally new properties: electroconductivity, paramagnetism, electroactivity, chemi- and thermostability, capability of complexation, *etc.*, and hence, provide additional challenges for development of new materials.

In our previous report,[1] we described the exhaustive thermal and thermocatalytic sulfurization of PE with elemental sulfur occurring, according to the data of complex studies of the obtained sulfurized polymers, with the formation of fused ladder polythienothiophene (**1**) and parquet polynaphthothienothiophene (**2**) semiconducting structures.

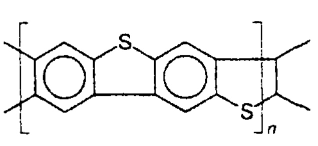


**1**



**2**

It is known that the structurally similar ladder polynaphthothiophene **3** obtained by the reaction of polyphenylenesulfide with sulfur dioxide[3] is also electroconducting.



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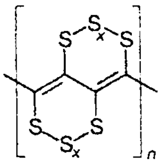

**4**

During deep PE sulfurization, structures **1** and **2** are preceded by polysulfide blocks of the **4** type, which remain in the final product along with polymeric sulfur in amounts determined by the conditions of the process and treatment of the reaction mixture. Blocks **1**, **2**, and **4** should impart paramagnetic and redox properties to the sulfurized PE.

In this report, we discuss the results of ESR and voltammetric studies of the sulfurized PE described in

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**Table 1.** Parameters of ESR spectra of different samples of sulfurized PE

| Content of S (%) | Concentration of spins/sp $g^{-1}$ | $g$ (±0.0004) | $\Delta H$ /mT |
|---|---|---|---|
| 63.98 [a] | $2.2 \cdot 10^{19}$ | 2.0041 | 0.60 |
| 42.65 [b] | $6.7 \cdot 10^{19}$ | 2.0041 | 0.62 |
| 47.27 [c] | $8.6 \cdot 10^{19}$ | 2.0045 | 0.53 |
| 47.85 [d] | $9.7 \cdot 10^{19}$ | 2.0045 | 0.57 |

[a] Prepared by the double sulfurization of granulated LDPE (320 °C, 2 h and 300—320 °C, 4 h).

[b] Prepared by the double sulfurization of granulated LDPE (340 °C, 2 h and 300—320 °C, 4 h).

[c] Prepared by the single sulfurization of granulated LDPE (290—300 °C, 4 h).[1]

[d] Prepared by the double sulfurization of granulated LDPE (300—310 °C, 3 h and 300—320 °C, 4 h).

the previous report.[1] As expected, all polymers are paramagnetic. The ESR characteristics of four samples with different concentrations of sulfur* are presented in Table 1.

The ESR signals of the samples under study are intense symmetric narrow singlets with $g$-factors close to that of a free electron. The characteristics indicated and the high concentration of paramagnetic centers confirm that the samples contain a developed system of conjugated bonds, which agrees well with the proposed structures **1**, **2**, and **4**.

The redox properties and electrochemical activity of the synthesized polymers and the possibility of using them as an active cathodic material in lithium accumulators were studied by cyclic voltammetry and investigation of the discharge characteristics of cathodes containing 50% sulfurized PE. One anodic peak at 2.4 V and two cathodic peaks at 2.4 and 1.9 V are observed in the cyclic voltammograms (Fig. 1), which confirms that the polymers contain redox active blocks **4** with S—S bonds and indicates a complex process of electrochemical reduction.

The presence of two cathodic peaks indicates the two-stage reduction of the polymers. The values of reduction potentials (2.4 and 1.9 V) are characteristic of compounds containing polysulfide blocks. Lithium-thiolate derivatives and inorganic polysulfide $Li_2S_x$ that formed are oxidized at 2.4 V to give one peak. The specific capacitance of the discharge—charge processes correlates with the sulfur content in the polymers. The highest values of the discharge and charge capacitances (Table 2) were found for the sample with a S content of 79.91%. A substantial increase in the charge and discharge capacitances of the samples is observed on going from the lithium triflate-based electrolyte to the electrolyte containing lithium bis(trifluoromethanesulfonyl)amide.

**Table 2.** Specific capacitance ($Q$) of cathodes of a lithium accumulator containing 50% sulfurized PE

| Content of S (%) | Electrolyte (1 mol $L^{-1}$) | Q/mA h $g^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | Discharge[a] | | | Charge[a] | | |
| | | I | II | III | I | II | III |
| 79.91 [b] | $CF_3SO_3Li$ | 242 | 193 | 180 | 269 | 235 | 206 |
| 79.91 [b] | $(CF_3SO_2)_2NLi$ | 339 | 304 | 284 | 342 | 326 | 303 |
| 63.98 | $CF_3SO_3Li$ | 194 | 163 | 157 | 225 | 199 | 188 |
| 63.98 | $(CF_3SO_2)_2NLi$ | 240 | 234 | 230 | 330 | 310 | 295 |
| 49.60 [b] | $CF_3SO_3Li$ | 48 | 47 | 46 | 50 | 47 | 47 |
| 49.60 [b] | $(CF_3SO_2)_2NLi$ | 109 | 97 | 90 | 97 | 92 | 87 |

[a] After one (I), two (II), and three (III) cycles. [b] See Ref. 1.

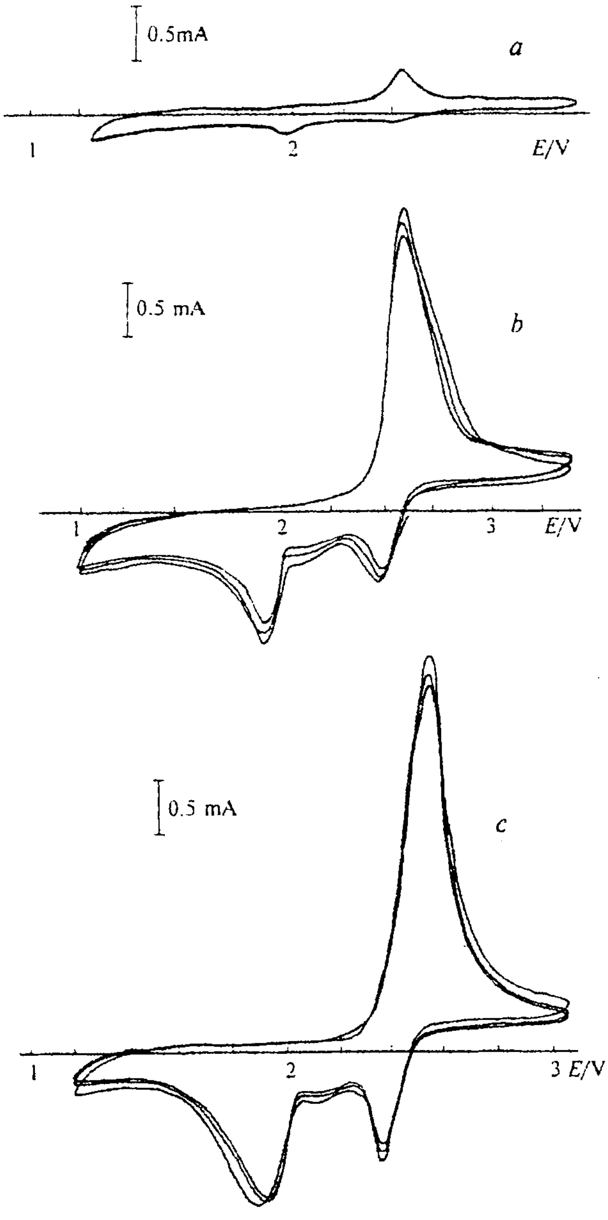

**Fig. 1.** Cyclic voltammograms of sulfurized PE with different concentrations of S: 49.6% (*a*), 64.0% (*b*), and 79.9% (*c*).

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The fact that the redox peaks characteristic of the polysulfide S—S$_x$ chain are retained in the voltammograms of the polymers containing 49.6% S (see Fig. 1) additionally confirms that they contain residual polyene-polysulfide blocks **4** along with the main ladder (**1**) and parquet (**2**) polyfused structures. According to the data in Table 2, in these polymers 10—20% sulfur still remain in the electrochemically active polysulfide form (blocks **4**). Polyene-polysulfides of the **4** type have previously been synthesized by us by the spontaneous polymerization of ethynyl bis(polysulfides) and HS$_x$C≡CS$_y$H and patented as efficient cathodic materials for lithium batteries.[4]

The discharge characteristics of cathodes based on the prepared products indicate their capability of multiple cycling: the decrease in the discharge capacitance at the twentieth cycle is at most 25% of the capacitance of the first discharge cycle (Fig. 2).

As a whole, the position of oxidation and reduction peaks differs slightly from those for sulfur. This was observed for polymers with polysulfide blocks with different structures and, most likely, is their fundamental property. At the same time, other characteristics of cyclic voltammetry (ratio of peak heights, capacitances calculated from oxidation and reduction currents) can differ. Taking into account the aforesaid, the electrochemical behavior of the polymer with polysulfide blocks is determined by its two basically different parts. The first part is polysulfide blocks that give oxidation and reduction peaks close in position to those of sulfur and slightly dependent on the polymer structure. The second part represents the fragments remaining on the cathode (organic or heteroorganic thiolates) that transform the cathodic matrix in a specific way, accelerating or retarding intermediate stages of the redox process. It can be controlled to achieve its maximum reversibility and rate, most likely, by searching for the optimum structure and combination of two indicated parts of the electroactive organosulfur polymer.

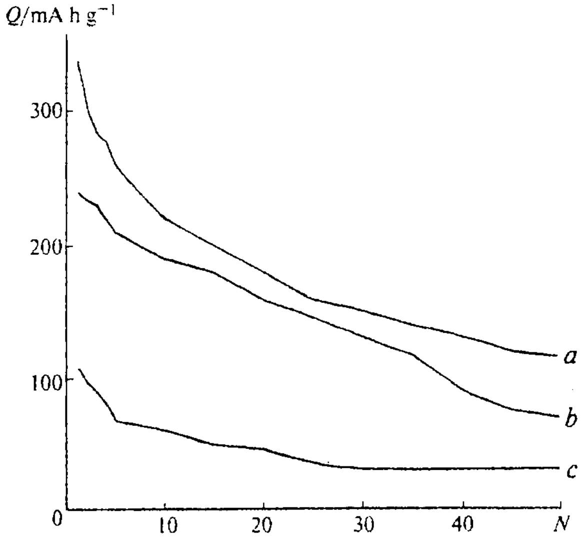
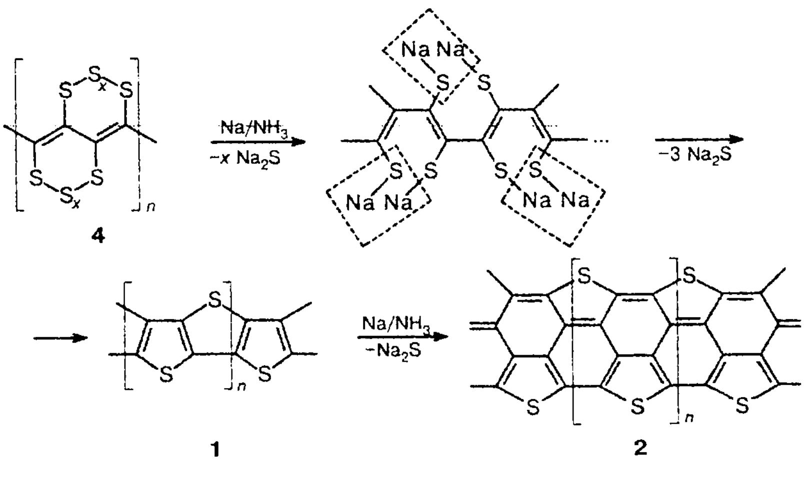


**Fig. 2.** Change in the discharge capacitance ($Q$) of cathodes based on sulfurized PE with different concentrations of S: 79.91% (*a*), 63.98% (*b*), and 49.60% (*c*) during their cycling in the (CF$_3$SO$_2$)$_2$NLi-based electrolyte ($N$ is the number of cycles).

Chemical reduction of the sulfurized PE by sodium in liquid ammonia results in its partial desulfurization. Based on the data of elemental analysis of the reduced products (content of S 42—45%), we conclude that the most stable polynaphthothienothiophene structures **2**, which are probably formed mainly from polyene-polysulfide blocks **4** and preceding less stable primary products of PE sulfurization through intermediate polythienothiophenes **1**, remain unchanged. The real reduction products are, most likely, hybrid polyfused systems containing both structures **4** and **2**.

Sulfurized PE loses a considerable portion of sulfur (for example, from 79.91 to 41.71%) also under the action of sodium amide in liquid ammonia, evidently, due to the nucleophilic cleavage of the S—S bonds

**Scheme 1**



followed by aromatization (Scheme 1), including during hydrolysis of intermediate products (upon treatment with water).

Thus, the data of ESR spectroscopy and the character of the electrochemical and chemical behavior of the product of exhaustive sulfurization of polyethylene are consistent with structures containing polythiene-polysulfide, polythienothiophene, and polynaphthothienothiophene blocks. Reduction of sulfurized polyethylene by the $Na/NH_3$ system or its treatment with sodium amide in liquid ammonia results in its partial desulfurization and formation of more stable and uniform materials consisting of polythienothiophene and polynaphthothienothiophene blocks. The polymers obtained represent a new group of paramagnetic and electrochemically active materials.

## Experimental

ESR spectra were recorded on Radiopan SE/X-2547 (Poland) and Bruker ESP-300 spectrometers at –20 °C in the absence of spectral saturation. The frequency of the magnetic field modulation was 100 kHz, and the modulation amplitude was 0.005—0.01 mT. $Mn^{2+}$ in MgO was used as an external standard. The range of the magnetic field scan was 10 mT. The number of spins in samples was estimated by comparison of the surface areas of the spectra (obtained by double integration) of the samples under study with those of the spectra of the $CuCl_2 \cdot 2H_2O$ standard containing the known number of spins.

Thin-layer two-electrode cells with an electrode surface area of 1.5 cm$^2$ were used in electrochemical experiments. The application of a thin-layer cell has two advantages. First, soluble polysulfides formed during the polymer reduction do not penetrate into the electrolyte bulk by a great distance. Since the thickness of the separator between the cathode and anode is equal to 25 μm, the concentration of polysulfides inside the thin-layer cell remains unchanged during the experiment. Second, in the range of current densities of 0.5—2.0 mA cm$^{-2}$ the polarization of the lithium electrode and ohmic drops in the separator were 20—30 mV, and, hence, no reference electrode was needed.

The thin-layer cell was designed as follows: working and lithium electrodes separated by a separator and wetted with an electrolyte were placed in a standard body of a button-type element, and the system was pressurized. The working electrode (cathode) represented an aluminum disk covered with carbon and a mixture of sulfurized PE, active carbon, and polyethyleneoxide in a ratio of 50 : 35 : 15 (wt.%). The auxiliary electrode (anode) represented a lithium disk 100 μm thick. A 1 *M* solution of $CF_3SO_3Li$ or $(CF_3SO_2)_2NLi$ in 1,2-dimethoxyethane was used as the electrolyte. Cyclic voltammetric curves were measured on a PI-50-1.1 potentiostat with a rate of potential feeding of 1 mV s$^{-1}$ and detected by a PDA-1 two-coordinate recorder. The values of specific capacitance were obtained upon discharge of the elements by a direct current of 0.5 mA cm$^{-2}$ to a voltage of 1.25 V.

**Reduction of sulfurized by the $Na/NH_3$ system.** Sulfurized PE (1.10 g, content of S 71.14%)[1] was added to a solution of metallic Na (0.60 g) in liquid $NH_3$ (50 mL), and the mixture was stirred for 2 h. Ammonia was evaporated, water was added, and the polymer was filtered off and washed with water to a neutral reaction and then with 96% EtOH and diethyl ether. After drying *in vacuo*, we obtained a black powder with metallic luster (0.63 g, 57%). Found (%): C, 49.98; H, 3.61; S, 43.30. $C_8S_2$ (elementary unit of structure **2**). Calculated (%): C, 60.00; S, 40.00. Elemental analysis of the samples showed the absence of nitrogen in the analyzed probes. Probably, the products contained a minor amount of oxygen due to the partial oxidation of the sulfurized polymer with air oxygen. Specific electroconductivity (pellet, $\sigma$/S cm$^{-1}$): $4.9 \cdot 10^{-12}$ (in air) and $1.5 \cdot 10^{-12}$ (*in vacuo*, ~$10^{-3}$ Torr).

**Desulfurization of sulfurized PE by the $NaNH_2/NH_3$ system.** Sulfurized PE (1.10 g, content of S 79.91%)[1] was added to a suspension of sodium amide obtained from sodium metal (0.6 g) in liquid $NH_3$ (50 mL) in the presence of a catalytic amount of $FeCl_3$, and the mixture was stirred for 2 h. After evaporation of ammonia, the product was decomposed with water, and the polymer was filtered off and washed with water to a neutral reaction and then with ethanol and diethyl ether. After drying *in vacuo*, we obtained a black lustrous product (0.60 g, 54.5%). Found (%): C, 50.33; H, 4.83; S, 41.79. Specific electroconductivity (pellet, $\sigma$/S cm$^{-1}$): $2.2 \cdot 10^{-11}$ (in air) and $6.1 \cdot 10^{-11}$ (*in vacuo*, ~$10^{-3}$ Torr).

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