Sulfurization of polymers

2.* Polythienothiophene and related structures from polyethylene and elemental sulfur

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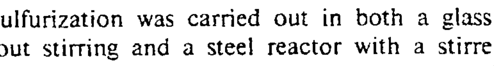
Polyethylene is exhaustively sulfurized by elemental sulfur at 160—365 °C to release hydrogen sulfide and form black lustrous powders (sulfur content ~80%) that possess electric conductivity (10^{-6}—10^{-8} S cm^{-1} when doped with I_2). Elemental analysis data, IR spectra, X-ray patterns, DSC—TGA, derivatographic data, electric conductivity, and mass spectrometric characteristics of the polymers synthesized suggest the presence of fused polythienothiophene and polynaphthothienothiophene blocks in the polymers.

Key words: polyethylene, elemental sulfur, sulfurization, catalysis; fused polythienothiophene, polynaphthothienothiophene, electric conductivity, IR spectra.

The reactions of elemental sulfur with low-molecular alkanes have been studied in detail.[2—11] Sulfurization proceeds with the formation of thiols,[3] sulfides,[4] and polysulfides[4] further decomposing into unsaturated compounds and hydrogen sulfide, unsaturated sulfurous heterocycles, and carbon disulfide. These reactions are of interest for industry and a foundation for synthesis of hydrogen sulfide,[3,5] carbon sulfide,[6,7] thiophene,[8,9] and homologs. For example, the reaction of elemental sulfur with paraffins is successfully used for the preparation of hydrogen sulfide[3,5] in both laboratory practice and pilot installations.

Meanwhile, data on the reaction of elemental sulfur with polyethylene (PE) are scarce.[12—15] Heating of PE with sulfur in the 200—250 °C temperature range has been reported[14] to be accompanied by the addition of sulfur to the polymer, evolution of hydrogen sulfide, an increase in the unsaturation degree, the appearance of cross-linking bonds between polymeric chains, and the formation of an insoluble fraction. It has been assumed that this is also accompanied by other changes, for example, cyclic structures are formed.[14] As the authors of Refs. 12 and 13 assert, the limiting amount of sulfur added to PE is independent of the reaction temperature and amounts to 31—37% of its initial content in the mixture (2—10%), which corresponds to sulfurization of PE by 0.6—3.7% only.

Processes of deep oxidative dehydrogenation of polymers with sulfur excess with the simultaneous insertion of its atoms into the aromatized polymeric framework are still outside the scope of specialists in the area of chemistry of both organic sulfur compounds and polymers. In this work, we present the first result of our studies of the deep sulfurization of PE with elemental sulfur. We used PE of two types: granulated high-pressure PE with a low density (LDPE), as well as the related household film, and granulated low-pressure PE with a high density (HDPE). The reaction was studied in the 160—365 °C temperature interval and at an unchanged S/PE ratio equal to 2 moles of sulfur per mole of CH_2 groups (or 4.57 : 1.00, w/w) calculating per exhaustive sulfurization by the equation



$$\left[CH_2 \right]_n + 1/4\ S_8 \longrightarrow \left[\underset{\overset{\|}{S}}{C} \right]_n + H_2S. \qquad (1)$$

Sulfurization was carried out in both a glass flask without stirring and a steel reactor with a stirrer and outlet tubes connected with a gasometer or a bottle filled with an aqueous solution of NaOH for the determination of the amount of hydrogen sulfide evolved. The duration of the reaction was varied from 0.5 to 6 h. The catalytic effects of additives of 2-mercaptobenzothiazole (MBTA), diphenylguanidine (DPG), ZnO,

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* For Part 1, see Ref. 1.

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Table 1. Results of deep PE sulfurization with elemental sulfur (ratio of reagents: 2 moles of sulfur per mole of CH_2 groups)[a]

Entry	Temperature, T/°C	Duration of reaction, t/h	Catalyst ([Cat] (wt.%))	Yield (%)	Found S (%)	Specific electroconductivity, σ/S cm^{-1}	
						in vacuo[b]	in air
1[c,d]	190—200	3.0	—	90	79.91	$4.4 \cdot 10^{-14}$	$1.1 \cdot 10^{-13}$
2[c,d]	350—360	2.0	—	90	71.14	$3.6 \cdot 10^{-10}$	$3.5 \cdot 10^{-10}$
3[e]	290—300	4.0	—	49	47.27	$2.2 \cdot 10^{-9}$	$2.3 \cdot 10^{-9}$
4[c,e]	350—360	2.0	—	86	70.41	$1.4 \cdot 10^{-12}$	$1.6 \cdot 10^{-12}$
5[c,e]	350—365	6.0	—	88	51.35	$1.4 \cdot 10^{-10}$	$1.4 \cdot 10^{-10}$
6[c,f]	350—360	4.0	—	55	61.90	$1.1 \cdot 10^{-12}$	$1.2 \cdot 10^{-12}$
7[g,h]	290—300	3.0	—	46	49.60	$2.0 \cdot 10^{-9}$	$2.0 \cdot 10^{-9}$
8[h]	290—300	3.0	—	—	49.71	$6.9 \cdot 10^{-9}$	$6.9 \cdot 10^{-9}$
9[e]	230—250	2.5	MBTA	54	47.00	$1.1 \cdot 10^{-12}$	$1.2 \cdot 10^{-12}$
10[e,g]	250—300	1.0	MBTA	58	48.00	—	—
11[e]	200—210	4.0	DPG	55	49.00	$6.1 \cdot 10^{-13}$	$6.6 \cdot 10^{-13}$
12[e]	200—210	4.0	MBTA (0.5) + DPG (0.5)	61	53.00	$1.9 \cdot 10^{-12}$	$2.1 \cdot 10^{-12}$
13[e]	250—260	0.5	MBTA (0.5) + DPG (0.5)	53	43.00	$2.2 \cdot 10^{-10}$	$4.2 \cdot 10^{-10}$
14[e]	160—170	5.0	MBTA (0.5) + DPG (0.5)	10	20.00	$1.4 \cdot 10^{-12}$	$2.0 \cdot 10^{-12}$
15[c,e]	250—300	4.0	ZnO	60	34.00	$4.2 \cdot 10^{-11}$	$4.5 \cdot 10^{-11}$
16[e]	200—210	5.0	$CoCl_2 \cdot 6H_2O$	29	39.46	$1.0 \cdot 10^{-12}$	$1.1 \cdot 10^{-12}$
17[e]	200—210	2.0	$VO_2S_2 \cdot H_2O$	49	35.00	$3.9 \cdot 10^{-11}$	$4.4 \cdot 10^{-11}$

[a] Entries *1*, *2*, *4*, and *5* were carried out in a glass flask without stirring; entries *3*, *7*—*17* were carried out in a steel reactor with intense stirring.

[b] At 10^{-3} Torr.

[c] Experiments without treatment with hot benzene.

[d] LDPE films.

[e] Granulated LDPE.

[f] Granulated HDPE.

[g] The electroconductivity of the product was determined when doped with I_2: $4.9 \cdot 10^{-6}$ S cm^{-1} and entry *10*, $2.0 \cdot 10^{-7}$ S cm^{-1}. Doping with I_2 was performed by the diffusion method in the gas phase at ~20 °C to saturation, *i.e.*, achievement of a maximum stable value of electroconductivity that was checked each 10 min during the first hour and then each 60 min. The maximum duration of doping was 48 h.

[h] Repeated sulfurization of the products: entry *7*, 6.14 g of the product of entry *3* and 10 g of sulfur; entry *8*, 5.8 g of the product of entry *7* and 3 g of sulfur.

$CoCl_2 \cdot 6H_2O$, and $VO_2S_2 \cdot H_2O$[*] (1.0 wt.%; for ZnO, 10 wt.%) were tested. The amount of evolved hydrogen sulfide changed under different reaction conditions within 4—94% of the theoretical value according to Eq. (1). The reaction is exothermic, but since we used small loads (mainly, 1.4 and 6.4 g of S), no special measures for heat removal were taken. However, this prevented thermostatting; therefore, we could maintained the reaction temperature only with an accuracy of ±5 °C.

The sulfurization products are black powders with a metallic luster, insoluble in either solvents. They were washed with hot benzene in a Soxhlet apparatus from unreacted sulfur and analyzed for the determination of S, C, and H (in some cases, without washing). For some samples, we recorded IR spectra (including photoacoustic (PA) IR spectra) and X-ray patterns, determined the electron conductivity, and studied thermooxidative destruction by differential scanning calorimetry (DSC) and derivatography.

The typical experimental results are presented in Table 1. It can be seen that, under the studied conditions, PE and elemental sulfur afford highly sulfurous materials (content of S 20—80%) that possess mainly semiconducting properties (specific electroconductivity σ = $4.4 \cdot 10^{-14}$—$2.0 \cdot 10^{-9}$ S cm^{-1}; when doped with iodine, $2.0 \cdot 10^{-7}$—$4.9 \cdot 10^{-6}$ S cm^{-1}).

As should be expected, the reactivities of various types of PE with respect to elemental sulfur differ. The LDPE film is almost exhaustively sulfurized at 190—200 °C for 3 h (see Table 1, entry *1*) to evolve an almost stoichiometric amount of hydrogen sulfide (hereinafter, by Eq. (1)). At 350—360 °C, the time of exhaustive (until hydrogen sulfide ceases to evolve) sulfurization decreases to 2 h (entry *2*), although the sulfur content in the product somewhat decreases.

Granulated LDPE is less reactive: at 290—300 °C its sulfurization proceeds by 47.27% for 4 h (see Table 1, entry *3*), but at 350—360 °C it reacts with sulfur with approximately the same rate as the film and forms a polymer with the same composition (entry *4*). However, based on the higher (by 2 orders of magnitude) electroconductivity, it differs in structure from the material obtained from the film. A more prolonged heating (6 h) at 350—365 °C results in a sharper decrease in the sulfur content in the sample (from 70.41 to 51.35%)

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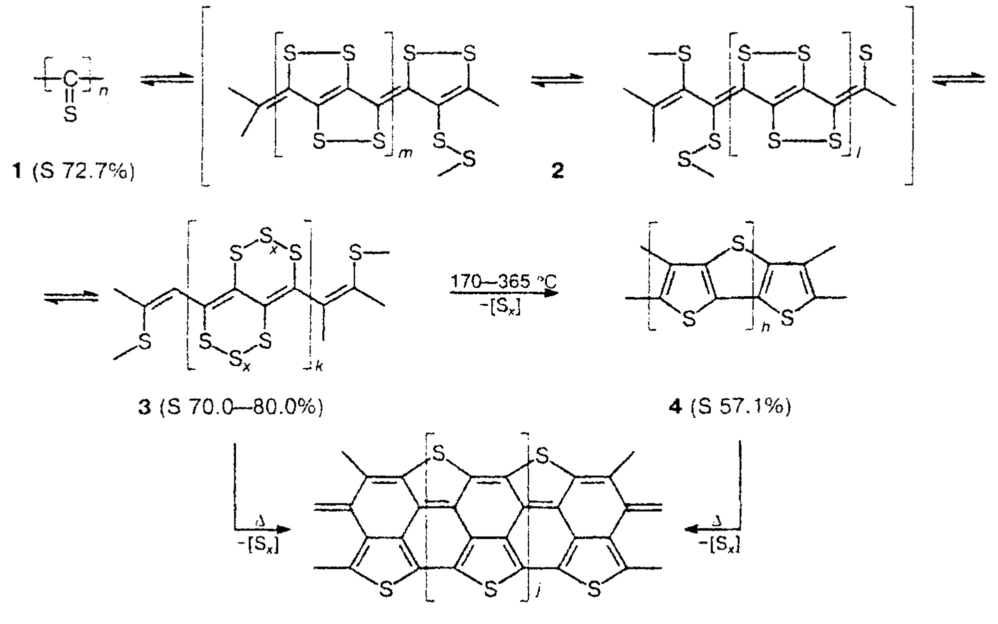
Scheme 1[*]



5 (S 40.0%)

(entry *5*). HDPE is still less reactive (entry *6*): its complete sulfurization (to the content of S of 61.90%) ceases at 350—360 °C within 4 h.

In all cases at temperature higher than 290 °C, the sulfurization of PE occurs most likely with the simultaneous destruction of its macromolecules.[16]

Multiple sulfurizarion of the same PE sample (see Table 1, entries *3*, *7*, and *8*) virtually does not change its composition (content of S 47.27—49.71%), although after triple sulfurization its electroconductivity increases by 0.5 orders of magnitude as compared with that observed for the doubly sulfurized sample (entries *7* and *8*), which indicates intensification and ordering of polyconjugation in the polymer. The evolution of hydrogen sulfide due to the cleavage of the residual C—H bonds by subsequent sulfurization is insignificant, and for the third treatment of the product with sulfur, it amounts to only several percentage of the initial amount. This corresponds to the absence of hydrogen in the triply sulfurized sample.

Standard accelerators of vulcanization (MBTA, DPG) in a concentration of 1 wt.% noticeably facilitate the PE sulfurization (see Table 1, entries *9*—*14*), decreasing the temperature and duration of the reaction. For example, MBTA additives allow the exhaustive sulfurization of granulated LDPE to be performed at 230—250 °C for 2.5 h (entry *9*). At somewhat higher temperature (250—300 °C), the time of exhaustive sulfurization reduces to 1 h (entry *10*). The introduction of DPG and its mixture with MBTA (1 : 1) makes the conditions of sulfurization still milder for the same PE sample: at 200—210 °C, the reaction ceases within 4 h, providing the same stable sulfurization level (content of S 47.0—53.0%). In the presence of the catalytic MBTA—DPG system (1 : 1, 1 wt.%), noticeable evolution of hydrogen sulfide during the interaction of PE with sulfur begins already at 160—170 °C and in 5 h gives a material containing 20.0% S (entry *14*). These results reject the present consensus that the reaction of saturated polymers with sulfur virtually does not occur at temperatures below 210 °C.[13]

Zinc oxide (also being a standard accelerator of vulcanization) even in a concentration of 10 wt.% exerts no catalytic effect on the process (see Table 1, entry *15*). At the same time, the catalytic effects of cobalt dichloride and vanadyl disulfide are evident (entries *16* and *17*).

To obtain polymers with a uniform composition by the reaction of PE with elemental sulfur, the problem of homogenization of a viscous reaction mixture arises. This problem can be solved by the application of a steel reactor with an efficient blade stirrer. Uniform mixing of the reagents (PE and sulfur) can also be achieved by their pre-dissolution in boiling xylene followed by the removal of the solvent.

Based on the composition and properties, we may conclude that the obtained products contain blocks of polymeric carbon polysulfide (**1**), its polyene-polysulfide tautomeric forms (**2**, **3**), including those cross-linked by di- and polysulfide bonds, polyfused thieno[3,2-*b*]thiophene (**4**), related polyfused naphthothienothiophene structures (**5**), and elemental sulfur, most likely, mainly polymeric (Scheme 1). All other

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[*] The sulfur content calculated for each structure is presented in parentheses.

properties of sulfurized PE are consistent with this scheme.

At the first stages of the process and comparatively low temperatures (~200 °C), polyene-polysulfide blocks **2** and **3** with a high sulfur content (~70%, see Table 1) are likely formed from polythione blocks **1** (see Scheme 1). They further undergo desulfurization to form more stable polyfused ladder polythienothiophene structures **4** and parquet polynaphthothienothiophene forms **5**. As shown by the experiments on multiple sulfurization (see above), the elemental composition of the most stable products corresponds to a combination of structures **4** and **5** in a ratio of 1 : 1.

Desulfurization of the polyene-polysulfide blocks also occurs when we attempt to fractionate highly sulfurous products with hot benzene in a Soxhlet apparatus (10—15 h). For example, a similar treatment results in a decrease in the sulfur content in the polymer obtained in entry *2* (see Table 1) from 71.14 to 42.30%. After benzene was removed, a brown crystalline product was isolated, which mainly contained sulfur (99.0%, m.p. 116—118 °C) with a minor admixture of oligomers **2** and **3**.

Derivatographic analysis* (Fig. 1) of the typical sample of doubly sulfurized PE (content of S 49.6%, see Table 1, entry *7*) shows that the thermooxidative destruction of the polymer starts at ~350 °C, occurs with a low rate in one stage, and ceases with the complete decomposition of the product at a temperature higher than 670 °C. This behavior is characteristic of polymers with a system of conjugated bonds and fused polyaromatic compounds. The smooth decomposition without inflections in the thermogravimetric pattern in the region of elevated temperatures indicates that the bonds are equalized by energy. Sulfur atoms do not form volatile products in some narrow temperature interval as is observed for the decomposition of polymers with lateral groups in the chain; they remain in the fused carbon-like framework (structures **4** and **5**). This character of decomposition is typical of polymers with a very low content of hydrogen atoms. The weak exothermic peak in the DTA curve at 205 °C can be a result of the evolution of volatile products due to residual hydrogen atoms and ejection of sulfur atoms from the residual di- and polysulfide fragments followed by their oxidation.

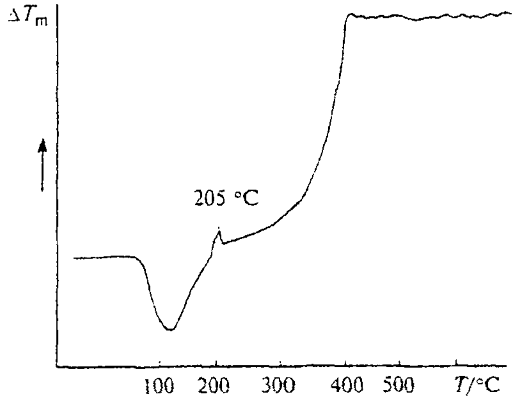

Fig. 1. DTA curve of doubly sulfurized LDPE (content of S 49.6%, see Table 1, entry *7*).

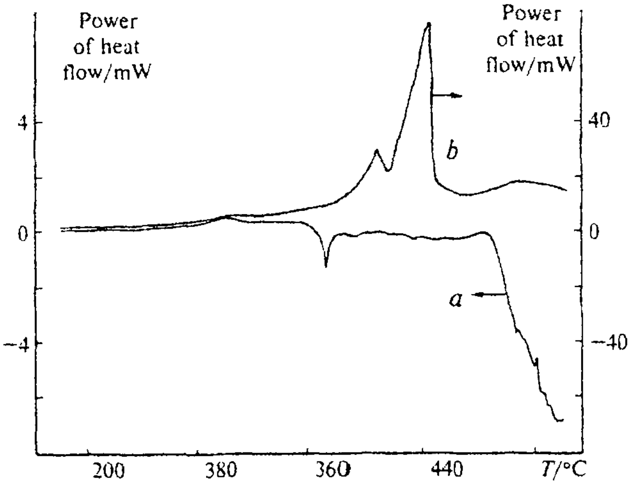

Fig. 2. DSC curves of samples of doubly sulfurized LDPE with different concentrations of S: *a*, 49.6% (conditions of synthesis: 290—300 °C, 3 h; see Table 1, entry *7*): and *b*, 63.98% (conditions of synthesis: 320 °C, 2 h and 300—320 °C, 4 h).

The DSC curve of the same sample (Fig. 2, curve *a*) demonstrates that the polymer is uniform and stable up to ~480 °C (only the weak endothermic peak is detected, which corresponds, most likely, to the cleavage of the residual C—H and S—S bonds). At the same time, the sample with an elevated content of sulfur (63.98%, double sulfurization of granulated LDPE — 320 °C, 2 h and 300—320 °C, 4 h) gives two exothermic peaks (at 407 and 443 °C; see Fig. 2, curve *b*) corresponding to the expected rearrangement of polyene-polysulfide blocks **2** and **3** into fused polythienothiophene and polynaphthothienothiophene structures **4** and **5**, respectively.

The unusual (for polymers with a high sulfur content) thermostability of polythienothiophene and polynaphthothienothiophene structures **4** and **5** is additionally illustrated in Fig. 3 by the DSC and TGA curves for the sample of doubly sulfurized granulated LDPE (content of S 49.6%, obtained by repeated sulfurization of the sample with a S content of 47.27% at 290—300 °C, 3 h; see Table 1, entry *7*). The slope of the DSC curve without pronounced thermal effects and a smooth exothermic rise at 500 °C corresponds to the same smooth run of the TGA curve, indicating that at ~560 °C (this temperature is achieved within approximately 1 h) the sample loses only ~15% weight.

The mass spectrum of the thermodestruction products (40—450 °C) of the sample of doubly sulfurized PE

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* The authors thank V. N. Salaurov (Irkutsk Institute of Chemistry, SB RAS) for recording and interpretation of the derivatograms.

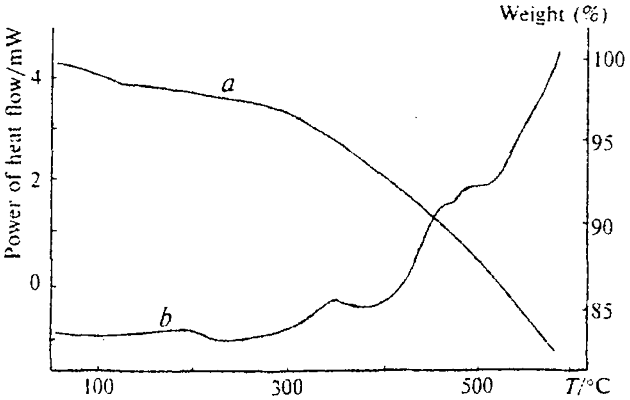

Fig. 3. TGA (*a*) and DSC (*b*) curves of samples of doubly sulfurized granulated LDPE (content of S 49.6%, see Table 1, entry 7).

(content of S 49.6%) contains the peak with *m/z* 64 attributed to sulfur (S_2).

The X-ray patterns* of the polymers exhibit weak terminal reflections and point reflexes from the single crystal. However, their weakness indicates that the samples are mainly X-ray amorphous. X-ray phase analysis of the samples containing >60% sulfur shows the presence of orthorhombic sulfur. This also agrees with the structural-composition heterogeneity of the materials (see Scheme 1).

The IR spectra of the polymers obtained (pellets with CsI) exhibit only very weak peaks in the 4000—400 cm^{-1} range (in the 1600—400 cm^{-1} range, they appear against the background of continuous absorption), which impede their assignment and identification of the fragments (Fig. 4). The number, relative intensity, and position of these peaks change under different conditions of PE sulfurization. The absorption maxima in the region of 940—740 cm^{-1} are most pronounced. According to the published data,[17] they can be attributed to out-of-plane deformation vibrations of residual C—H bonds in polynuclear aromatic compounds; in this case, in surrounding fragments of polythienothiophenes **4** and polynaphthothienothiophenes **5**.

Another group of relatively intense bands lies in the region of 1620—1030 cm^{-1} (for example, 1620, 1505, 1385, 1210, 1145, 1116, and 1027 cm^{-1} for the sample with a S content of 63.98% obtained as shown previously, and 1590, 1507, 1403, 1211, 1167, 1149, and 1034 cm^{-1} for a sample with a S content of 42.65% obtained by double sulfurization of LDPE for 2 h at 340 °C and for 4 h at 300—320 °C. The high-intensity bands (1600—1400 cm^{-1}) are most likely attributed to vibrations of the framework of polyfused thienothiophene and naphthothienothiophene structures **4** and **5**, and the low-intensity bands (1300—1000 cm^{-1}) can be assigned to planar vibrations of the terminal C—H bonds.[17—19]

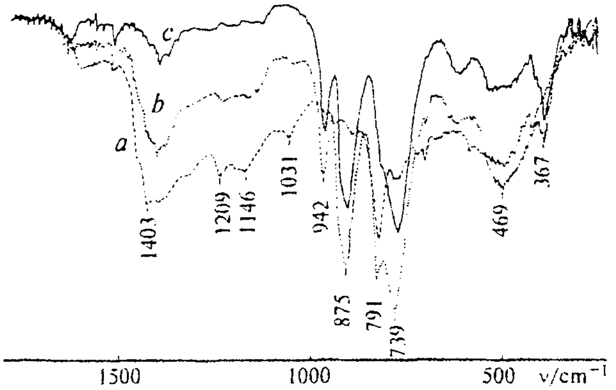

Fig. 4. Transmission IR spectra (*a*, *b*) of samples of doubly sulfurized granulated LDPE with different concentrations of S: *a*, 42.65% (conditions of synthesis: 340 °C, 2 h and 300—320 °C, 4 h); *b*, 63.98% (conditions of synthesis: 320 °C, 2 h and 300—320 °C, 4 h): and *c*, difference of spectra (*b* − *a*)×0.526.

The spectra of all samples exhibit weak peaks in the region of 600—370 cm^{-1} (for example, 594, 474, 397, and 366 cm^{-1} for the sample with a S content of 63.98% and 581, 465 cm^{-1} for the sample with a S content of 42.65%). According to the published data,[18] this adsorption can be assigned to the C—S bonds in polyfused thiophene and naphthothienothiophene structures **4** and **5**.

The weak absorption in the 3060—3030 cm^{-1} region (stretching vibrations of C—H of aromatic and heteroaromatic systems) corresponds to the residual C—H bonds of the polythienothiophene (**4**) and polynaphthothienothiophene (**5**) blocks. The weak triplet with frequencies of 2950, 2920, and 2850 cm^{-1} (deformation vibrations of aliphatic C—H groups) is attributed to the insufficiently sulfurized aliphatic CH_2 groups of PE. The weak diffuse band in the 3450—3300 cm^{-1} region belongs to the adsorbed moisture.

It is noteworthy that the IR spectra of the doubly sulfurized PE samples exhibit a tendency to reducing the bands, more pronounced, predominant maxima and greater resolution of the spectrum as a whole.

It is of interest that the PA-IR spectra of different samples of sulfurized PE containing absorption bands of the near-surface fragments (Fig. 5) are nearly identical. This indicates the homogeneity of the structure of surface layers of microparticles of the polymers, which corresponds to the heterophase dynamics of sulfurization (formation of the solid phase from the PE/S_x melt with simultaneous evolution of H_2S). Naturally, the surface layer of microparticles of the products is formed, in this case, of thermodynamically more stable and chemically more perfect structures, *i.e.*, it should be most homogeneous. In fact, the PA-IR spectra (see Fig. 5) contains no absorption of the aliphatic C—H bonds in the 2900±50 cm^{-1} region, and the peaks attributed to the C—H bonds of the aromatic fragments (3060 and 3030 cm^{-1}) appear at the noise level, which agrees with

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* The authors thank A. I. Kashaev (Irkutsk State Pedagogical University) for X-ray structural analysis and E. V. Moroz (Institute of Catalysis, SB RAS) for X-ray phase analysis.

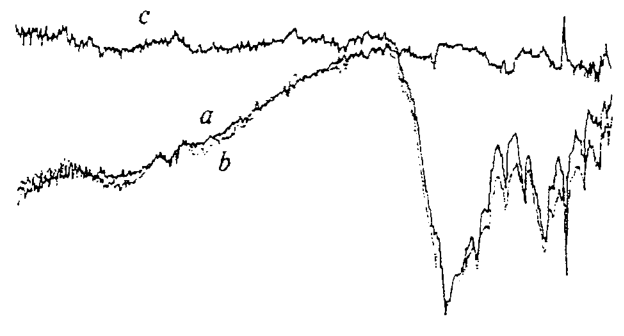

Fig. 5. Photoacoustic IR spectra (*a*, *b*) of samples of doubly sulfurized granulated LDPE with different concentrations of S: *a*, 42.65% (conditions of synthesis: 340 °C, 2 h and 300—320 °C, 4 h); *b*, 63.98% (conditions of synthesis: 320 °C, 2 h and 300—320 °C, 4 h); and *c*, difference of spectra (*b* − *a*).

the expected greater extent of sulfurization of surface layers.

The difference between the PA-IR spectra of the samples with different sulfur concentrations (42.65 and 63.98%) represents one very narrow band at 674 cm^{-1} and a very weak band at 1042 cm^{-1}, and all other absorption bands are virtually compensated (see Fig. 5, *c*). Therefore, despite the different extents of sulfurization of the samples, their near-surface molecular fragments are very close in composition and structure.

The obtained results can be summarized as follows.

Polyethylene is sulfurized with a sulfur excess at temperatures higher than 200 °C to evolve hydrogen sulfide and form highly sulfurous (up to 80%) low-hydrogen electroconducting polymers.

2-Mercaptobenzothiazole, phenylguanidine, cobalt chloride, and vanadyl disulfide exert a catalytic effect on sulfurization by decreasing its temperature (to 160—170 °C) and duration.

According to the data of elemental analysis, IR spectroscopy and mass spectrometry, DSC and derivatography, and characteristics of electroconductivity, the materials obtained contain polyene-polysulfide, ladder polythienothiophene, and parquet polynaphthothienothiophene blocks along with bound polymeric and free orthorhombic sulfur. The ratio of these structures and components depends on the condi~~tions of preparation and methods of treatment of the~~ material.

Temperature increase (250—370 °C), an increase in the reaction duration, and multiple sulfurization of the same sample result in partial desulfurization and formation of more stable and uniform materials formed of the polythienothiophene and polynaphthothienothiophene fragments.

Experimental

IR spectra were recorded on a BOMEM M-102 IR-Fourier spectrometer by two methods: (a) IR transmission spectra (in CsI) in the 4000—240 cm^{-1} frequency region with a resolution of 4 cm^{-1}; and (b) PA-IR spectra in the 4000—400 cm^{-1} frequency region with a resolution of 8 cm^{-1}. A photoacoustic cell (model 300, MTEC Photoacoustics, Inc., USA) was used for recording PA-IR spectra. Samples were placed in the PA cell without preliminary preparation (additional powdering or using a feeder).

Mass spectra were obtained on a Finnigan GCQ spectrometer with direct introduction of the sample into the ionization chamber.

Specific dark electroconductivity was measured by a VK 2-16 electrometric amplifier and an E6-13A teraohmmeter.

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

Oxidative thermographic patterns were obtained on a θ derivatograph (MOM, Hungary), the weight of the sample being 50 mg, DTA sensitivity 1/5, and heating rate 10 deg min^{-1}.

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

High- and low-pressure polyethylene samples (LDPE and HDPE) are commercial products available from the Angarsk Petrochemical Co. (ANKhK). Elemental sulfur (special purity grade, technical conditions 6-09-2546-77), 2-mercaptobenzothiazole (Erevan Plant of Chemical Reagents), diphenylguanidine (Angarsk Plant of Chemical Reagents), cobalt chloride ($CoCl_2 \cdot 6H_2O$) (Plant "Krasnyi Khimik," St. Petersburg), zinc oxide (OAO "Gorkinskii Khimicheskii Zavod") were commercial reagents and used as received.

Vanadyl disulfide ($VO_2S_2 \cdot H_2O$) was prepared by the following procedure*. $Na_2S \cdot 9H_2O$ (19.20 g, 0.08 mol) and elemental sulfur (10.3 g, 0.04 mol) were placed in a glass beaker and heated above the melting temperature for 30 min (to dissolution of sulfur). Then the sodium polysulfide (Na_2S_5) that formed was cooled, water (200 mL) was added, and traces of unreacted sulfur were filtered off. $VOSO_4 \cdot 3H_2O$ (13.0 g, 0.06 mol) was dissolved in water (400 mL) in another beaker. Both solutions were cooled to 3—5 °C, and $VOSO_4$ was rapidly added to a solution of Na_2S_5 with intense stirring to the beginning of frothing (about 40 mL of $VOSO_4$ remained). The finely dispersed blackish-brown precipitate that formed was filtered off on a Schott funnel first without vacuum and then using a water-aspirator pump, washed with water (100 mL) and MeOH (50 mL), and dried *in vacuo*. Free sulfur was washed off with hot benzene in a Soxhlet apparatus. Then the obtained black powder was ground with elemental sulfur in a ratio of 1 : 1 (w/w). The mixture was heated at 150—200 °C in a closed glass flask to complete blackening, cooled to ~20 °C, stirred in a mortar, washed from elemental sulfur with hot benzene in a Soxhlet apparatus, and dried *in vacuo* (3 Torr, 90 °C). $VO_2S_2 \cdot H_2O$ (13.0 g) was obtained. Found (%): H, 1.33; S, 37.38; V, 31.43. $H_2O_3S_2V$. Calculated (%): H, 1.22; S, 38.85; V, 30.86.

Sulfurization of PE (general procedures). *A.* A mixture of finely cut LDPE film (1.4 g, 0.05 mol with respect to elemental CH_2CH_2 unit) and sulfur (6.4 g, 0.2 mol) was heated in a glass flask for 3 h at 190—200 °C. The homogeneous melt rapidly (after 30 min) became blackish-brown and then black, and intense evolution of hydrogen sulfide started with a mean rate of ~10 mL min^{-1}; the exothermic effect was observed: after the achievement of 100—150 °C, the mixture was self-heated to ~200 °C, the rate of hydrogen sulfide evolution reached a maximum and then began to decrease gradually, and the vis-

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* Developed by A. M. Vasil'tsov (Irkutsk Institute of Chemistry, SB RAS).

cosity of the reaction mixture increased rapidly (from glycerol-like to honey-like). At the end of the reaction, the product gained the consistency and visual appearance of melted bitumen. H_2S (1900—2000 mL) was gathered in a gasometer during the reaction. After cooling of the reaction mixture, we obtained 4.0 g of a black friable product with metallic luster that could hardly be powdered (see Table 1, entry *1*).

B. A mixture of finely cut LDPE film (1.4 g, 0.05 mol) and sulfur (6.4 g, 0.2 mol) was homogenized in xylene (50 mL) with boiling and heated for 6 h with stirring (the reagents were completely dissolved in 2 h). After cooling the reaction mixture, the precipitate that formed (a homogeneous light-yellow powder — a mixture of PE and sulfur) was filtered off, dried *in vacuo*, placed in a glass flask, and heated for 4 h at 240—250 °C. H_2S (~1000 mL) was gathered in a gasometer during this time. The solid mass that formed was powdered and washed off with boiling benzene in a Soxhlet apparatus from sulfur excess during 10—15 h. After drying *in vacuo*, we obtained 3.0 g of a black lustrous powder. Found (%): S, 49.21.

C. Granulated LDPE (4.2 g, 0.15 mol) and sulfur (19.2 g, 0.6 mol) were placed in a steel reactor provided with a thermometer and stirrer with short blades and attached to a gasometer, and the mixture was heated for 4 h at 290—300 °C. About 4000 mL of H_2S evolved from the reaction mixture. The obtained solid mass (13.5 g) was powdered and washed with hot benzene in a Soxhlet apparatus from residual sulfur and oligomers for 15 h. After drying *in vacuo*, we obtained 6.5 g of a black powder with metallic luster (see Table 1, entry *3*).

D. LDPE (1.4 g, 0.05 mol) and finely powdered sulfur (6.4 g, 0.2 mol) were heated in a glass flask to 350 °C for 1 h. Heating was continued for 4 h more at 350—360 °C, and ~400 mL of H_2S were evolved. After the treatment described above, we obtained 2.40 g of the polymer (see Table 1, entry *6*).

Multiple sulfurization. ***A.*** Sulfurized PE (6.14 g) with a S content of 47.27% and sulfur (10.0 g) were placed in a steel reactor. The mixture was heated for 3 h at 300—310 °C to evolve 300 mL of H_2S. After the polymer was treated with hot benzene in a Soxhlet apparatus for 10 h and dried *in vacuo* to constant weight, we obtained a black lustrous powder (5.8 g). Found (%): C, 48.47; H, 1.38; S, 49.57 (see Table 1, entry *7*).

B. Doubly sulfurized PE (5.8 g, content of S 49.57%) and sulfur (4.0 g) were placed in a steel reactor. The mixture was heated for 3 h at 300 °C. No evolution of hydrogen sulfide was observed. After treatment similar to that described above, we obtained 5.65 g of a black product with metallic luster (see Table 1, entry *8*).

Catalytic sulfurization. ***A.*** Granulated LDPE (1.4 g, 0.05 mol), sulfur (6.4 g, 0.2 mol), and MBTA (0.08 g) were placed in a steel reactor. The mixture was heated for 2.5 h at 230—250 °C with vigorous stirring (1700 mL of H_2S was collected). After the polymer was treated with hot benzene in a Soxhlet apparatus for 10 h and dried *in vacuo*, we obtained 2.4 g of sulfurized PE (see Table 1, entry *9*).

B. Sulfurized PE (2.43 g) was obtained similarly (see Table 1, entry *11*) from the same PE (1.4 g, 0.05 mol), sulfur (6.4 g, 0.2 mol), and DPG (0.08 g) (210 °C, 4 h, 1750 mL of H_2S were collected).

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