Homopolycondensation of 1-halogenopropane-2-thiones

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Homopolycondensation of 1-halogenopropane-2-thiones was studied; the polymers obtained were structurally characterized by ESR, UV, and IR spectroscopy, elemental analysis, and electrochemical methods. Their molecular masses, dark conductivities, and photoconductivities were determined. The capability for film formation on various substrates was investigated. These polymers were found to be new organic metals (Hal = I), semiconductors (Hal = Cl and Br), and photoconductors (Hal = Cl, Br).

Key words: 1-halogenopropane-2-thiones, homopolycondensation, polyconjugated polymers, sulfur-containing polymers, paramagnetism, electric conductivity, photoconductivity.

Propane-2-thione (Me—C(=S)—Me) polymerizes spontaneously at 20 °C to give linear polymers $[-\mathrm{CMe_2-S-}]_n$ with molecular masses ranging from 2000 to 14000.[1,2]

We synthesized for the first time 1-halogenopropane-2-thiones ($\mathrm{Me-C(=S)-CH_2-X}$, X = F, Cl, Br, and I).[3–5] Red 1-chloro-, 1-bromo-, and 1-iodopropane-2-thiones decolorize at 20 °C within five minutes after preparation. Then, they turn brown and black, and a corresponding hydrogen halide is evolved. This fact motivated us to investigate the processes involved, determine the structures of the reaction products, and find out possible ways of their practical uses.

The homopolycondensation of 1-chloro- and 1-bromopropane-2-thiones was carried out in $CHCl_3$ in an atmosphere of N_2 for 72 and 62 h, respectively, while the homopolycondensation of 1-iodopropane-2-thione was conducted in acetone for 24 h. Cessation of evolution of the corresponding hydrogen halide indicated that the reactions went to completion. 1-Fluoropropane-2-thione remained unchanged even upon heating to 80 °C for 1 day. This indicates that the rate of homopolycondensation of 1-halogenopropane-2-thiones decreases as the carbon—halogen bond energy increases and the atomic number of X decreases: *E*(C—I) << *E*(C—Br) < *E*(C—Cl) < *E*(C—F).

The resulting polymers are dark brown (X = Cl) or black powders (X = Br and I) soluble in $CHCl_3$, Me_2CO, and DMF and insoluble in water. On various substrates (quartz, glass, and aluminum), they form high-quality metal-lustrous black films.

Table 1 summarizes data from elemental analysis, melting points, yields, and molecular masses (determined by the isopiestic method) for polymers **1—3** (see below).

The UV spectra of polymers **1—3** in chloroform exhibit bands with λ_{max} 416—500 nm (visible region) corresponding to an $n\rightarrow\pi^*$ transition localized on the thiocarbonyl fragment.[6] The band of the thiocarbonyl group for a solution in HCl exhibits a hypsochromic shift, which allows it to be assigned to an electron transition involving nonbonding orbitals. A characteristic absorption with maxima from 238 to 300 nm is due to $n\rightarrow\pi^*$ and $n\rightarrow\sigma^*$ transitions in the $\mathrm{CH_2{=}CH-S-}$ group.

IR spectroscopic data (Table 2) correlate well with the electron absorption spectra of polymers **1—3**. A

Table 1. Homopolycondensation products of 1-halogenopropane-2-thiones **1—3**

Polymer	X	T_{decomp} /°C	Yield (%)	C (Found / Calculated, %)	H	S	X	Molecular formula	M_n Found / Calculated	$\frac{m}{n}$
1	Cl	109—113	63	44.19	5.94	38.67	11.19	$C_{69}H_{98}S_{23}Cl_6$	1800	17
				44.16	5.23	39.25	11.36		1875	4
2	Br	156—158	72	43.43	5.14	35.91	12.11	$C_{48}H_{66}S_{16}Br_2$	1400	14
				43.84	5.02	38.96	12.18		1314	0
3	I	90—92	80	40.12	5.00	36.88	21.29	$C_{39}H_{54}S_{13}I_2$	1200	11
				39.26	4.53	34.90	21.31		1192	0

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Table 2. IR spectroscopic data for polymers **1—3**

Polymer	ν/cm^{-1}				
	Me	S—CH$_2$	C=C	C=S	C—X
1	2960 2870	2690 2730	1640	1220	750
2	2960 2870	2690 2730	1640	1220	720
3	2960 2730	2690 2730	1640	1220	600

band at 1220 cm^{-1} indicates the presence of a thione group in the polymers.[7]

The results of electrochemical analysis of polymers **1—3**, obtained with a dropping mercury electrode in acetonitrile against 0.05 *M* Bu_4NClO_4, attest that the polymers contain a C=S thiocarbonyl group and/or an —SH group formed upon its enthiolization. The polarogram of polymer **2** shows one anodic (−0.17 V, 8.8 μA mL mg^{-1}) and two cathodic waves (−0.97 V, 8.3 μA mL mg^{-1} and −2.01 V, 5.0 μA mL mg^{-1}). The potential range of the anodic half-wave and the shape of the cyclic voltammetric curve suggest the formation of mercury thiolate.[8] Cathodic processes seem to be due to the reduction of the thiocarbonyl group bonded through a methylene bridge to a conjugated macrochain system.

Polymers **1—3** are paramagnetic. Their ESR spectra exhibit somewhat asymmetric singlets at *g* factors close to the *g* factor of a free electron (*g* = 2.00232). The singlet width, ΔH_{max}, varies from 0.8 to 1.4 mT and corresponds to a concentration of lone electrons on the order of 10^{17} spin g^{-1}. The concentration of paramagnetic centers (*N*/spin g^{-1}) and the signal width (ΔH_{max}/mT) increase in accordance with the atomic number of the halogen (Table 3). The parameters of these ESR signals are characteristic of polyconjugated systems, and their paramagnetism can be explained by polar states occurring in a polymer system.[9]

The experimental data presented in Tables 1—4 allow us to assign the following structures to polymers **1—3** and propose a plausible scheme for their formation (Scheme 1).

Apparently, the chain termination results from addition of hydrogen halide to the terminal double bond. The system of n→π conjugation in polymer **1** is partially interrupted by (—S—CX(Me)—CH$_2$—) groups, which is suggested by its less deep color as compared to analogs **2** and **3**. The arrangement of these fragments still remains unknown. For X = Br and I, hydrogen halide does not add to internal double bonds, probably, because of steric hindrances (bulky X$^-$ anions) and easy elimination of HBr and HI from possible adducts.

Table 3. ESR spectral parameters for polymers **1—3**

Polymer	$N\cdot10^{-17}$ /spin g^{-1}	ΔH_{max} /mT	*g*
1	0.93	0.82	2.0062
2	1.00	0.80	2.0069
3	1.60	1.42	2.0060

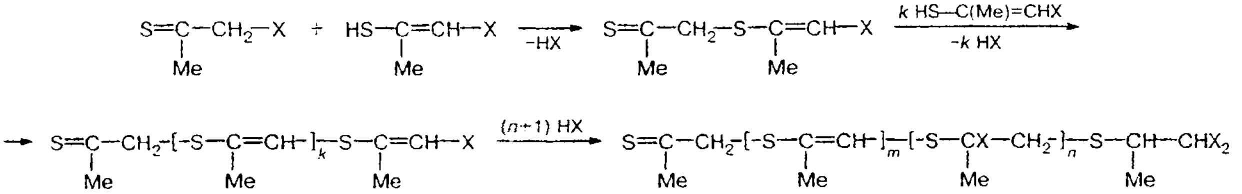
Results obtained in measuring electrical and photoconductivity of polymers **1—3** (see Table 4), as well as ESR data, attest to a developed system of conjugation and allow them to be considered as organic semiconductors (**1** and **2**) and organic metals (**3**).

An important feature of organic semiconductors is their photoconductivity or enhanced electrical conductivity when exposed to light (see Table 4). The dark conductivities of polymers **1** and **2** are on the order of 10^{-14} S cm^{-1} and increase by a factor of 11 to 12 when polymer films are exposed to monochromatic light. The maximum photoconductivity is noted in the visible region (λ_{max} = 450—460 nm), which corresponds to maxima in the UV absorption spectra. This suggests a uniform character of excitation of the photoconductor in the range of strong absorption.

The electrical conductivity of polymer **3** is higher by six orders of magnitude than that of analogs **1** and **2**. Presumably, this can be explained by a considerable mass content of the halogen in polymer **3** (21%) and a large mass of the iodine atom, which makes the C—I bond highly polarizable. Higher concentration of paramagnetic centers ($N = 1.6\cdot10^{17}$ spin g^{-1}) also corresponds to higher conductivity of polymer **3** ($\sigma = 2.6\cdot10^{-8}$ S cm^{-1}). This seems to indicate a close relation between its electrical and magnetic properties. When stored for one year, polymers **1—3** retain their conductivity values in air and *in vacuo* (*e.g.*, for polymer **1**: $\sigma = 2.1\cdot10^{-14}$ and $1.8\cdot10^{-14}$ S cm^{-1} (in air) and $\sigma = 1.0\cdot10^{-14}$ and $0.8\cdot10^{-14}$ S cm^{-1} (*in vacuo*), respectively).

Hence, synthesized polymers **1—3** possess a film-forming ability, paramagnetism, electrical conductivity, and photoconductivity. This suggests their possible application in the development of active materials for electrophotographic layers and solar energy converters.

Scheme 1



X = Cl (*m* = 17, *n* = 4); X = Br (*m* = 14, *n* = 0); X = I (*m* = 11, *n* = 0) **1—3**

Table 4. Electrical conductivity (σ) and photoconductivity (I) of polymers **1—3**

Polymer	$\sigma \cdot 10^{14}$/S cm^{-1}		I_p/I_d (relative units)	λ_{max} /nm
	in air	*in vacuo*		
1	2.1	1.0	12	460
2	6.5	4.1	11	450
3	$2.6 \cdot 10^6$	$1.2 \cdot 10^6$	—	—

Experimental

The UV spectra of compounds **1—3** were recorded in $CHCl_3$ on a Specord UV-VIS spectrometer in 0.1—1.0-cm cells. IR spectra were recorded on a Specord IR-75 spectrometer in KBr pellets (triple grinding and pressing were necessary to obtain high-quality spectra), Vaseline oil, and a solution in chloroform in 0.025—0.1-cm cells. Measurement scale 50/100 cm^{-1}, recording time 11 min. The ESR spectra of solid samples were recorded at 20 °C on a Radiopan SE/X-2547 spectrometer equipped with a magnetometer and a microwave frequency meter.

The molecular masses of polymers were determined by the isopiestic micromethod[10,11] in chloroform with polyethylene glycol (molecular mass 1000) as a standard.

The conductivities of polymers were measured using the known procedure.[12] Their photoconduction was studied following exposure of polymer layers to light of a DKSSh-1000 xenon lamp passed through a DMP-4 monochromator.

1-Bromopropane-2-thione.[3] 1-Bromopropan-2-one (10.0 g, 0.073 mol) was saturated with HCl at −10 °C. A flow of H_2S was then passed at −70 °C for 3 h. The reaction mixture was purged with N_2 at −40 °C to remove HCl and H_2S. The residual crimson-red liquid contained virtually pure 1-bromopropane-2-thione (10.94 g, 98%). The compound begins to decompose at 18 °C. At −40 °C, it can be kept for several weeks in a sealed tube. ^{1}H NMR (−40 °C, $CDCl_3$), δ: 2.01 (s, 3 H, Me); 3.88 (s, 2 H, CH_2).

1-Chloropropane-2-thione was obtained in a similar way from 1-chloropropan-2-one (9.0 g, 0.097 mol) in the form of a rose-red liquid.[3] Yield 9.76 g (93%), T_{decomp} = 15 °C. ^{1}H NMR (−50 °C, $CDCl_3$), δ: 1.89 (s, 3 H, Me); 3.84 (s, 2 H, CH_2).

1-Fluoropropane-2-thione was obtained in a similar way from 1-fluoropropan-2-one (10.0 g, 0.131 mol).[4] Yield 13.0 g (96%). ^{1}H NMR ($CDCl_3$), δ: 2.37 (s, 3 H, Me); 3.88 (d, 2 H, CH_2, J = 47.6 Hz). ^{19}F NMR, δ: −202 (t). ^{13}C NMR, δ: 30.90 (Me); 92.53 (d, CH_2, J = 187 Hz); 261.64 (C=S).

1-Iodopropane-2-thione was obtained from 1-bromopropane-2-thione (12.0 g, 0.065 mol) by an exchange reaction with NaI in anhydrous acetone.[5] Yield 16.06 g (96%). ^{1}H NMR (−50 °C, $CDCl_3$), δ: 2.33 (s, 3 H, Me); 4.59 (s, 2 H, CH_2).

Homopolycondensation of 1-chloropropane-2-thione. A solution of 1-chloropropane-2-thione (9.76 g, 0.09 mol) in 30 mL of anhydrous chloroform was purged with N_2 and kept at 20 °C for 72 h until evolution of HCl vapors ceased. The resulting black mass was poured into a Petri dish and allowed to solidify for two months. The bright black film that formed was ground and dissolved in 50 mL of chloroform. The solution was filtered and hexane (100 mL) was added. The precipitate that formed was isolated and dried *in vacuo* (5 Torr) to give polymer **1** (4.44 g) in the form of dark brown powder.

Homopolycondensation of 1-bromopropane-2-thione was carried out as described above. 1-Bromopropane-2-thione (10.94 g) gave polymer **2** (4.5 g) as lustrous black powder (see Tables 1—4).

Homopolycondensation of 1-iodopropane-2-thione was carried out as described above. 1-Iodopropane-2-thione (18 g) in 30 mL of anhydrous acetone gave polymer **3** (6.64 g) as lustrous black powder (see Tables 1—4).

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