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LETTERS TO THE EDITOR

Homopolycondensation of 1,3-Dibromopropane-2-thione

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Earlier we have found a high propensity of 1-bromopropane-2-thione to homopolycondensation at 20°C with the formation of linear soluble in organic solvents polymers of molecular mass 1400 [1]. The solutions of these polymers form black glittering coatings showing high adhesion to different supports (quartz, glass, aluminum), paramagnetism, electroconductivity ($\sigma = 6.5\times10^{-14}$ Sm cm^{-1}) and photoconductivity (λ_{max} = 450 nm).

The data obtained allowed to suggest that introduction of the second halogen atom to the α-position of 1-bromopropane-2-thione would lead to the formation of polymers of larger molecular mass and better electroconductivity. To prove this assumption we studied homopolycondensation of 1,3-dibromopropane-2-thione (DBPT) [2].

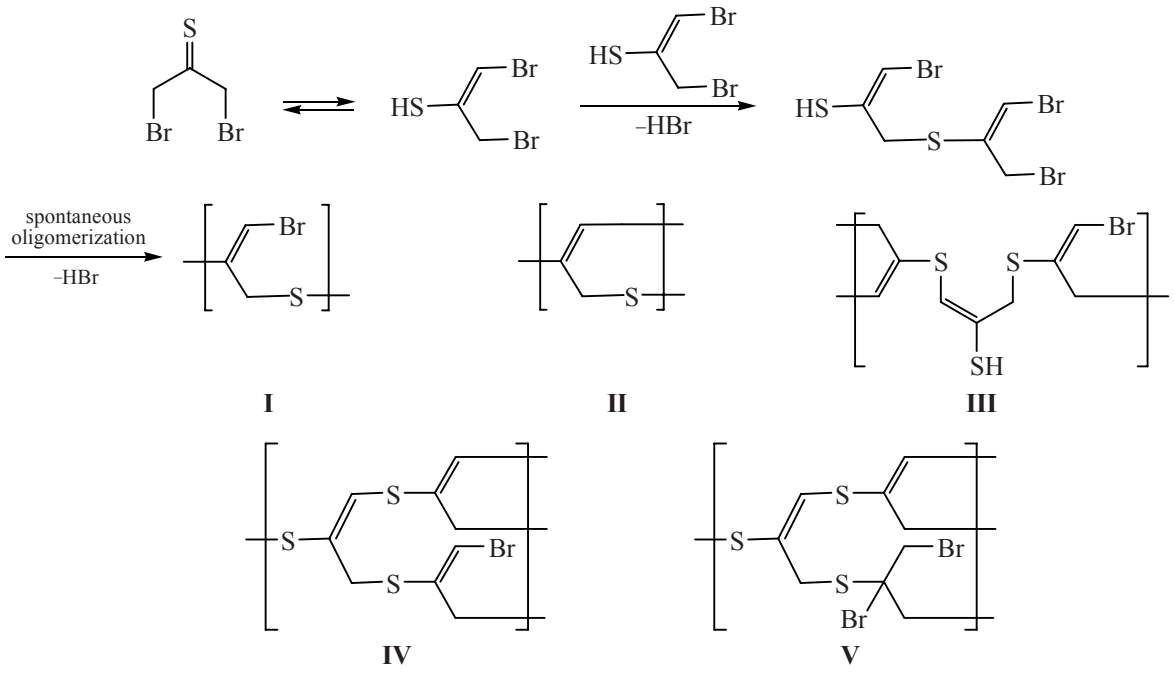
It was established as a result that homopolycondensation of DBPT at 20°C in chloroform in a flow of an inert gas proceeded with the formation of high-melting polymers insoluble in conventional organic solvents.

To determine the composition of the low-molecular fraction of the polymer formed, after 10 days from its chloroform solution an oligomer with molecular mass 580 (mp 50–53°C) was precipitated by hexane. The compound corresponds to empirical formula $C_{18}H_{24}S_6Br_2$. In its IR spectrum wide absorption bands in the range of 1374–1434 cm^{-1} are observed typical for oligomer polyenepolysulfide structures [3–5]. Absorption bands at 1028–1095 cm^{-1} can be assigned to bending vibrations of the C=C–S bonds [4]. Weak wide maxima at 876–844, 730–742, 691, 525–547 cm^{-1} correspond to the stretching vibrations of the C–S bonds of various fragments of oligomer and to C–H bending vibrations. Stretching vibrations of methylene groups are observed at 2918 and 2853 cm^{-1} [5]. In addition, in the spectrum of the oligomer absorption bands at 601 and 2484 cm^{-1} appear which can be assigned to C–Br and S–H bond vibrations [5].

NMR monitoring of the process of homopolycondensation of DBPT in $CDCl_3$ has shown that its first step is enthiolization of the starting thione because in the ^{1}H and ^{13}C NMR spectra appear the signals at 2.47 s (H, SH); 3.92 s (2H, CH_2Br); 5.69 s (H, C=CHBr); 29.46 (*C*H_2Br); 119.86 (C=*C*HBr); 141.16 (C=*C*SH) ppm. The growth of macromolecules, apparently, occurs due to the reaction of bromine atoms with hydrogen atoms of mercapto groups, followed by evolution of HBr and formation of polymer insoluble in organic solvents. All this is indicative of the presence of structural fragments **I–V** in the polymer.

Photochemical homopolycondensation (λ = 254 nm) of DBPT in CCl_4 proceeds much faster than the dark reaction (1 h) and according to the data of IR, ^{1}H and ^{13}C NMR spectroscopy leads to the same polymer. However, the content of bromine in it is slightly increased due to UV initiated addition of HBr to double bonds of the polymer. In the IR spectrum of the photochemically synthesized polymer intense absorption bands of the C–Br bonds at 609 cm^{-1} and maxima of methylene fragments at 1168–1224 cm^{-1} appear that is characteristic of compounds containing the CH_2Br group [5].

Investigation of electroconductivity of the polymers prepared by the two routes showed them to be high-



omic organic semiconductors having electroconductivity of 10^{-9}–10^{-7} Sm cm^{-1}, which was seven orders of magnitude higher than that of polymer prepared by homopolycondensation of 1-bromopropane-2-thione [1].

Dark homopolycondensation of DBPT. Through the solution of 1.6 g of DBPT in 10 ml of dry chloroform at 20°C the flow of argon was passed during 64 h to remove the evolved HBr. The obtained brown solution was poured into a Petri dish and was left standing for 2 months at room temperature in the air. Black film formed was ground to powder, washed with ether, and dried in a vacuum; 0.8 g of black high-melting powder (temp.decomp. >350°C) was obtained, insoluble in conventional solvents. IR spectrum, ν, cm^{-1}: 2916-2851 (C–H), 1628–1655 (C=C), 1024–1096 (C=C–S), 848–841, 741 (C–S), 615 (C–Br), 2484 (S–H) (v.w.). Found, %: C 36.10; H 3.76; S 31.22; Br 28.04. $C_9H_9S_3Br$ (fragment **IV**). Calculated, %: C 36.86; H 3.07; S 32.76; Br 27.30.

Photochemical homopolycondensation of DBPT. The solution of 1.6 g of DBPT in 10 ml of CCl_4 was irradiated with UV-light (λ = 254 nm) in the flow of argon at room temperature for 1 h until precipitation of an insoluble fraction. The obtained brown suspension was poured into a Petri dish and allowed to stay for 20 days in the air. Black film formed was ground to powder, washed with ether, and dried in vacuum; 0.9 g of black powder (temperature decomp. 210–214°C) was obtained, insoluble in conventional organic solvents. IR spectrum, ν, cm^{-1}: 2925–2852 (C–H); 1035–1078 (C=C–S); 1605 (C=C); 883–849, 711 (C–S); 609 (C–Br); 1168–1224 (CH_2Br). Found, %: C 34.19; H 3.39; S 29.36; Br 32.46. $C_9H_{10}S_3Br_2$ (fragment **V**). Calculated, %: C 28.87; H 2.67; S 25.66; Br 42.78.

IR spectra were recorded on a Bruker IFS 25 instrument in KBr. ^1H and ^{13}C NMR spectra were registered on a Bruker DPX-400 instrument (400 MHz for ^1H and 100 MHz for ^{13}C) in $CDCl_3$, CCl_4. Molecular mass of oligomer was determined by isopiestic micromethod in methanol [6]. Specific electroconductivity was measured by the use of electrometric amplifier BK2-16 and teraommeter E6-13A. The purity of the products obtained was checked by TLC on Silufol UV-254 plates with chloroform as an eluent.

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