POLYMERIZATION OF 3-(ORGANYL-o-CARBORANYL)-1,2-EPITHIOPROPANES

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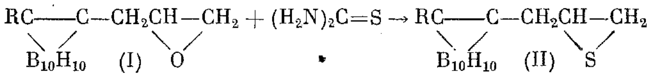
It is known that aliphatic polysulfides are insoluble compounds with a low heat stability. For example, the crystalline polyethylene sulfide, obtained by the polymerization of thiirane [ethylene sulfide], begins to decompose even at 150°C [1]. At the same time, carborane-containing polysulfides, obtained by the polycondensation of dilithiumcarborane with dichlorosulfenylcarboranes, are heat stable up to 300° [2]. Consequently, it seemed of interest to obtain and study the possibility of polymerizing carboranyl-substituted thiiranes in order to obtain polymerization polysulfides with a high solubility and heat resistance.

For this we developed a convenient method for the preparation of 3-(organyl-o-carboranyl)-1,2-epithiopropanes by reacting thiourea with the appropriate α-epoxides in alcohol medium.

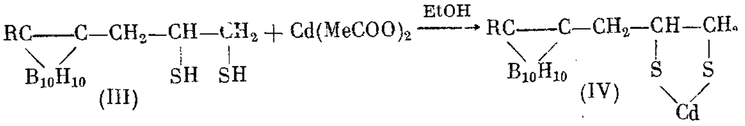


$R = Ph$ (a), *i*-Pr (b)

The given reaction permits obtaining carboranylthiiranes in 90-95% yield.

The IR spectra of (IIa, b) have absorption bands in the vicinity of 650, 690, 3000, 1450, 1110, and 2600 cm^{-1}, which are characteristic for the C—S bonds and CH_2 groups of the thiirane ring and carboranyl group. The PMR spectra have signals from the protons of the CH_2 group attached to the carborane with δ 2.25 ppm, and of the CH and CH_2 groups of the thiirane ring with δ 2.9 and 2.6 ppm (centers of multiplets), with a 2:1:2 ratio of the integral intensities.

To initiate the ionic polymerization of the carboranylthiiranes we used BF_3 etherate, and also the cyclic Cd carboranylthiolates (IV), which were specially synthesized from carboranyldithiols (III) and cadmium acetate. The (IV) compounds are white crystals that melt at about 240° and are soluble in benzene, ether, and other organic solvents.



$R = Ph$ (a), *i*-Pr (b)

The polymerization of the carboranylthiiranes was run either as block or in solution at temperatures ranging from —20 to 140°. Here the products with the highest molecular weight were obtained by the anionic polymerization of the carboranylthiiranes, initiated by the cyclic cadmium carboranylthiolates (IV). Using (IVa) as the initiator, higher molecular-weight products are obtained in solution at 60° than when synthesis is in bulk at 140° (250,000 and 49,000, respectively). The cationic polymerization of the carboranylthiiranes using BF_3 etherate proceeds even at —20°, but leads to polymers with a lower molecular weight (17,000).

The obtained products are white powders that are soluble in acetone and benzene, but are insoluble in alcohol, ether, CCl_4, and other organic solvents. The IR spectra of the polymers have absorption bands in the vicinity of 660-690, 740-760, 2930, 2855, 1340, 2600, 1580, 3040-3070, and 3090 cm^{-1}, which are, respectively, characteristic for the C—S bond, the CH_2 group, the carborane nucleus, and the aromatic rings. Apparently, the obtained polymers are poly(R-o-carboranyl) sulfides with the following formula:

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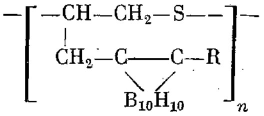

R = Ph, *i*-Pr; *n* = 60—970.

Based on the x-ray structure analysis data, the polycarboranyl sulfides are amorphous substances that, based on the thermomechanical curves, soften at 50-120°. Based on the dynamic thermogravimetric analysis (DTGA) data, the polymers have a higher thermooxidative stability than the starting carboranylthiiranes: a 5% weight loss is observed at 250-300° for the polymers and at 190° for the carboranylthiiranes. Up to 400° the weight losses for all of the poly(R-o-carboranyl) sulfides are 60-65%, while with further increase in the temperature some increase in the weight of the samples is observed clear up to 800°, which is probably caused by oxidation of the carborane nuclei.

EXPERIMENTAL

The GLC analysis of the monomers was run on a Tsvet-4 chromatograph at 220°, using a 2 m × 3 mm column packed with SKTFT-50 deposited on Chromatone N-AW-HMDC and helium as the carrier gas at a flow rate of 60 ml/min. The IR spectra were taken on a UR-20 spectrometer, the PMR spectra were taken in $CDCl_3$ solution on a Bruker WR-200SY spectrometer, and the x-ray spectra were taken on a Dron-1 instrument. The thermogravimetric analysis was run on a Q 1500 D derivatograph in the air at a rate of 5 deg/min. The molecular weights of the polymers were determined by the light-scattering method in benzene solution. The viscosity of the polymers was measured in benzene at 20° (0.1 g of polymer/10 ml of solvent).

3-(R-o-Carboranyl)-1,2-epithiopropanes (IIa, b). To a solution of 2.76 g (10 mmoles) of 3-(phenyl-o-carboranyl)-1,2-epoxypropane (Ia) [3] in 15 ml of MeOH was added 1.6 g (20 mmoles) of thiourea and the reaction mixture was stirred until the starting oxirane disappeared (GLC). The MeOH was evaporated in vacuo, and the residue was diluted with water and extracted with ether. The ether extract was dried over $MgSO_4$ and evaporated. The residue was recrystallized from hexane to give 2.77 g (95%) of (IIa), mp 87-88° (cf. [3]).

In a similar manner, from 2.4 g (10 mmoles) of 3-(isopropyl-o-carboranyl)-1,2-epoxypropane (Ib) and 1.6 g (20 mmoles) of thiourea we obtained 2.47 g (96%) of (IIb), mp 40-42° (cf. [3]).

3-(R-o-Carboranyl)-1,2-dimercaptopropanecadmium (IVa, b). To a solution of 1.63 g (5 mmoles) of carborane dithiol (IIIa) [4] in 10 ml of EtOH was added a solution of 1.33 g (5 mmoles) of $Cd(MeCOO)_2 \cdot 2H_2O$ in 30 ml of EtOH. The reaction mixture was stirred for 1 h, and the obtained precipitate was filtered and dried in vacuo to give 1.38 g (91%) of (IVa), mp 238-239°. Found: S 15.00%. $C_{11}H_{20}B_{10}CdS_2$. Calculated: S 14.67%. Infrared spectrum (ν, cm^{-1}): 2600 (CBH), 1590 and 3050, 3070 (C_6H_5), 740 and 770 (SC).

In a similar manner, from 1.46 g (5 mmoles) of dithiol (IIIb) and 1.33 g (5 mmoles) of $Cd(MeCOO)_2 \cdot 2H_2O$ we obtained 1.84 g (92%) of (IVb), mp 240-241°. Found: C 23.70; H 5.96; B 27.00%. $C_8H_{22}B_{10}CdS_2$. Calculated: C 23.85; H 5.50; B 26.83%. Infrared spectrum (ν, cm^{-1}): 660, 730 (CS), 1340 and 2830, 2950 (CH_2), 1145-1180 and 1370-1390 ($i-C_3H_7$), 2600 (CBH).

Polymerization of 3-(Organyl-o-carboranyl)-1,2-epithiopropanes Using Cadmium Mercaptides (IV). To a solution of 2.92 g (10 mmoles) of (IIa) in 10 ml of abs. benzene was added 0.044 g (0.1 mmole) of (IVa). The reaction mixture was stirred for 10 h at 60°, and then it was cooled and filtered. The filtrate was washed with 10 ml of 0.1 N HCl solution and dried over $MgSO_4$. Then the benzene layer was filtered from the $MgSO_4$ and poured into 20 ml of EtOH. The obtained white polymer powder was dried, purified by reprecipitation from benzene solution with EtOH, and dried in vacuo to constant weight. We obtained 2.8 g (95%) of the carborane polymer which, based on the thermomechanical curve, softened at 105-110°. Mol. wt. 254,000, η 0.31. Found: C 45.64; H 7.06; B 37.28; S 10.20%. Calculated for the starting monomer: C 45.17; H 6.89; B 36.96; S 10.96%. Infrared spectrum (ν, cm^{-1}): 740, 760 (CS), 1570, 3040-3070-3090 (C_6H_5), 2600 (CBH). DTGA: 5% weight loss at 300°.

To 2.92 g (10 mmoles) of (IIa) was added 0.044 g (0.1 mmole) of (IVa) and the reaction mixture was stirred for 6 h at 140°, after which it was cooled to 20°, dissolved in benzene, and filtered. The polymer was isolated by the above-described method. We obtained 2.32 g (80%) of a polymer which, based on the thermomechanical analysis data, softened at 80-85°. Mol. wt. 49,000, η 0.21. Found: C 45.70; H 7.08; B 37.00; S 10.15%.

In a similar manner, from 2.58 g (10 mmoles) of (IIb) and 0.044 g (0.1 mmole) of (IVb) we obtained 2.08 g (81%) of a polymer with softening point 55°, η 0.18. Found: C 37.60; H 8.60; B 41.50; S 12.01%. Calculated for the polymer: C 37.18; H 8.58; B 41.83; S 12.40%. DTGA: 5% wt. loss at 250°.

Polymerization of 3-(Phenyl-o-carboranyl)-1,2-epithiopropane Using BF_3 Etherate. To a solution of 2.92 g (10 mmoles) of (IIa) in 15 ml of CH_2Cl_2 at −20° was added 0.044 g (0.3 mmole) of freshly distilled BF_3 etherate. The reaction mixture was kept in a sealed ampul for 24 h at 20°, after which the ampul was opened and the polymer was poured into EtOH. The obtained white polymer powder was dried and purified by reprecipitation from benzene solution with EtOH. We obtained 2.66 g (91%) of a polymer which, based on the thermomechanical curves, softened at 115-125°. Mol. wt. 17,000, η 0.18. Found: C 45.50; H 6.90; B 37.02; S 10.92%. $C_{11}H_{20}B_{10}S$. Calculated: C 45.17; H 6.89; B 39.96; S 10.96%. DTGA: 5% wt. loss at 260°.

CONCLUSIONS

A study was made of the ionic polymerization of some 3-(organyl-o-carboranyl)-1,2-epithiopropanes in bulk and in solution, which was initiated either by BF_3 etherate or some specially synthesized cyclic cadmium carboranylthiolates. The obtained polysulfides are soluble, heat resistant up to 250-300°, and have molecular weights ranging up to 250,000.

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MASS SPECTRA OF ELECTRON IMPACT OF METHYL- AND ACETYLCYCLOPROPYLTHIOPHENES

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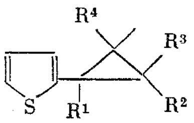
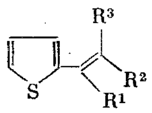
As a continuation of our studies on the mass spectrometry of compounds with small rings (see [1] and papers cited there) in the present paper we studied the mass spectra of the electron impact (EI) of cyclopropylthiophene, its methyl and acetyl derivatives (I)-(VI), and also of some vinylthiophenes (VII)-(IX).



(I)—(VI)



(VII)—(IX)

$R^1 = R^2 = R^3 = R^4 = H$ (I); $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$ (II); $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$ (III)*; $R^1 = R^4 = H$, $R^2 = R^3 = CH_3$ (IV); $R^1 = CH_3$, $R^2 = COCH_3$, $R_3 = R^4 = H$ (V)*; $R^1 = H$, $R^2 = R^3 = CH_3$, $R^4 = COCH_3$ (VI)*; $R^1 = CH_3$, $R^2 = R^3 = H$ (VII); $R^1 = R^3 = H$, $R^2 = CH_3$ (VIII)*; $R^1 = H$, $R^2 = R^3 = CH_3$ (IX).

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*Mixture of trans and cis isomers.

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