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A Novel Functionalized Polysulfides. Preparation of Polysulfides Containing Spiroorthocarbonate Moiety in the Main Chain

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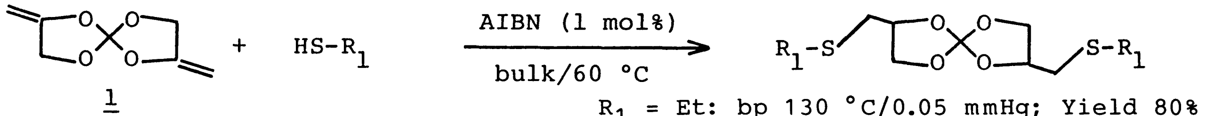
Preparation of polysulfides containing spiroorthocarbonate structure in the main chain by the radical polyaddition of unsaturated spiroorthocarbonate, 2,7-dimethylene-1,4,6,9-tetra-oxa-spiro[4.4]nonane, with dithiols is described.

It has been reported that the cationic ring-opening transfer polymerization of spiroorthocarbonates is carried out to obtain the corresponding poly(ether-carbonate) and undergoes no shrinkage on polymerization.[1-5] Further, the radical ring-opening isomeric polymerization of unsaturated spiroorthocarbonates has been described.[6,7]

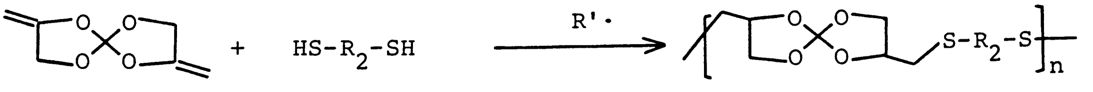
In this communication, we wish to report the polyaddition of an unsaturated spiroorthocarbonate [2,7-dimethylene-1,4,6,9-tetraoxaspiro[4.4]nonane (1)], which undertakes only vinyl polymerization with dithiols.

At first, the model reactions of 1 and monothiols in the presence of a radical initiator (AIBN) was carried out at 60 °C for 24 h to obtain the corresponding compounds in good yields, respectively.



R_1 = Et: bp 130 °C/0.05 mmHg; Yield 80%
R_1 = Ph: mp 43-45 °C; Yield 92%

Next, the polyaddition of 1 with dithiols was carried out in a sealed tube in the presence of a radical initiator, azobisisobutyronitrile (1 mol%), at 60 °C for 24 h. The results are summarized in Table 1. The obtained polymers were isolated by pouring the reaction mixture to hexane. These polymers were soluble in N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chloroform, and 1,2-dichloroethane (EDC) but insoluble in ether, tetrahydrofuran (THF) and acetone.



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P-1: R_2 = $\text{(CH}_2\text{)}_2$ P-2: R_2 = $\text{(CH}_2\text{)}_3$
P-3: R_2 = $\text{(CH}_2\text{)}_4$ P-4: R_2 = $\text{(CH}_2\text{)}_6$

The structure of the obtained polymers were confirmed by IR spectra and ^{1}HNMR spectra. The IR spectra showed the absorption bands between 1300 cm^{-1} and 950 cm^{-1} attributable to spiroorthocarbonate structure, but no C=O absorption band resulting from the ring-opening transfer polymerization of 1 was observed. The ^{1}HNMR spectra of each polymer showed the chemical shifts based on the polymer structure proposed above. The typical spectral data of polysulfide (P-1) are ; IR(neat)cm^{-1}: 2957, 2903, 1477, 1423, 1327, 1213(br s), 1060(br s), 1022(br s), 987, 839, 783; ^{1}HNMR($CDCl_3$) δppm: 4.7-4.2 (4H, m), 4.0-3.8(2H, m), 3.0-2.5(4H, m), 2.68(4H, t, J=6.8 Hz), 1.87(2H, tt, J=7.0, 7.0 Hz).

The obtained polysulfides functionalized with spiroorthocarbonate moiety are expected as polymeric cross-linking agents and polymer composites which undergo no shrinkage on cross-linking or polymerization.

Table 1. Polyaddition of 1 and Dithiols[a)]

Run	Dithiol	Yield / %[b)]	$\overline{Mn}$[c)]	$\overline{Mw}/\overline{Mn}$
1	$HS\text{(CH}_2\text{)}_2SH$	68.1	4000	2.65
2	$HS\text{(CH}_2\text{)}_3SH$	96.3	11400	5.18
3	$HS\text{(CH}_2\text{)}_4SH$	95.1	5800	4.60
4	$HS\text{(CH}_2\text{)}_6SH$	97.0	11100	3.05

a) 1/dithiol = 1 mol/1 mol, at 60 °C for 24 h. with AIBN(1 mol%) in bulk.
b) Insoluble polymer in hexane.
c) Based on polystyrene by GPC.

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