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LETTERS TO THE EDITOR

Reaction of 4,4'-Dithiobis(2,6-di-*tert*-butylphenol) with Sulfur Containing Its Polymeric Modification

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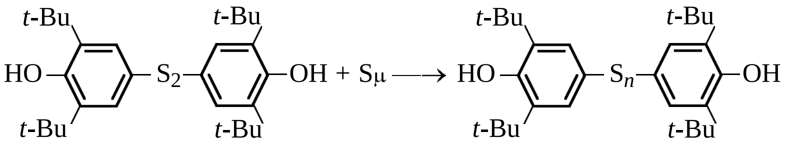
Bis(hydroxyaryl) polysulfides exhibit diverse valuable properties. They are applied as adhesives, antioxidants, additives to adhesion compositions, etc. Moreover, high polysulfides can act as curing agents in rubber mixtures.

Sterically hindered (2,6-disubstituted) phenols in the presence of catalytic amounts of a base (NaOH) do not react with sulfur. At the same time, with stoichiometric amounts of a base (NaOH), 2,6-dimethyl- or 2,6-diphenylphenols react with sulfur at 170°C to give the corresponding bisphenyl sulfide. In the presence of stoichiometric amounts of KOH at a lower temperature (80°C), 2,6-disubstituted phenols and sulfur react, yielding bisphenyl polysulfides [1]. Earlier, using 4,4'-polythiobis(2,6-di-*tert*-butylphenol) (**II**) as an example, we showed that the polysulfide chain in 4,4'-dithiobis(2,6-di-*tert*-butylphenol) (**I**) can be elongated up to 14 sulfur atoms by reacting compound **I** with sulfur in melt.

To find out if polymeric sulfur can favor elongation of the polysulfide chain, we studied the reaction of compound **I** with a sulfur containing ~50% of its polymeric modification (S_μ) by the following scheme:



n = 1–11.

First a melt was prepared, containing up to 50% of polymeric sulfur (S_μ), in cyclooctasulfur at 190–200°C for 1.5–2 h, and then the melt was heated with disulfide **I** at the **I**-to-sulfur weight ratio 0.6 : 1 at 185–190°C for 1 h. Quenching in a 0.3% aqueous solution of polyvinyl alcohol (5–10°C) gave light yellow granules that hardened in air within some days.

The resulting 4,4'-polythiobis(2,6-di-*tert*-butylphenol) had a uniform polysulfide composition, on average, by 5% for S_3–S_8. The fraction of the highest polysulfide S_{11} in this mixture was 1.76%. The residual sulfur was 56 to 66%. No polymeric sulfur was found.

The fact that the reaction of compound **I** with S_μ gives polysulfides with a lower content of sulfur atoms in the highest polysulfides than the reaction with S_8 can be explained by a longer S–S bond (2.07–2.08 Å) in polymeric sulfur compared with a shorter (2.04 Å) and thus stronger S–S bond in cyclooctasulfur [2].

Thus, the example of the synthesis of 4,4'-polythiobis(2,6-di-*tert*-butylphenol) (**II**) showed that the sulfur containing up to 50% of its polymeric modification (S_μ) is more reactive than S_8, which results in formation of a polysulfide chain with up to 11 sulfur atoms and in complete depolymerization of S_μ.

Reaction of 4,4'-dithiobis(2,6-di-*tert*-butylphenol) (I) with 50% polymeric sulfur in melt. Compound **I**, 12.5 g, was added to 20 g of sulfur preheated for 2 h at 190°C, and the mixture was heated at 185–190°C for 1 h. The melt was quenched in a 0.3% aqueous solution of polyvinyl alcohol with a temperature of 5–10°C to obtain soft light yellow granules that hardened in air on handling. The conversion of compound **I** was 95%.

Analysis of the polysulfides was performed by HPLC on a Perkin–Elmer-1022LC PLUS chromatograph with a UV detector with diode array (230 nm); column 30 × 3 mm, phase C_{18} (5 μm); mobile phase acetonitrile–methanol, 9 : 1 (by volume), flow rate 2 ml/min.

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