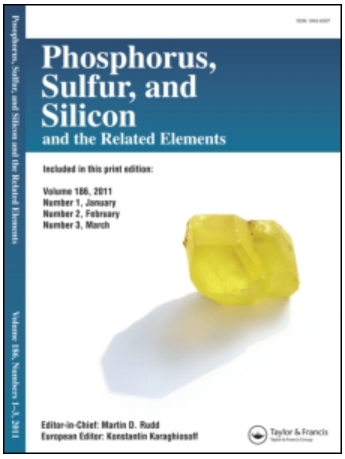

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Cyclic Arylene Sulfide Macromolecules: Synthesis, Structure and Properties.

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Synthesis, X-ray structure, ring-opening polymerization macrocyclic phenylene sulfides and their role in chemistry and technology of polyarylene sulfides are discussed.

INTRODUCTION

Investigation of cyclic aromatic oligomers was initiated several years ago to determine whether aromatic macrocycles might be useful as polymerizable monomers for the preparation of high molecular weight thermoplastics. So, Brunelle[1] has developed the process for preparation of bisphenol A cyclic oligomeric carbonates and industrial polycarbonate on their base. Macrocyclic phenylene sulfides (MPS) were first detected by mass-spectrometry in the low-molecular weight polycondensation products of 1,4-dichlorobenzene with sodium sulfide[2] and have received little attention[3,4]

RESULTS AND DISCUSSION

From the low-molecular weight products of this reaction we have separated a number of MPS containing 3-8 phenylene sulfide units[5]. Structure of cyclotris- and tetra-1,3-phenylene sulfides[6-8], cyclotetra- and penta-1,4-phenylene sulfides[9,10], cyclohexa-, hepta- and octa-1,4-phenylene sulfides[11,12] and cyclotris (4,4'-benzophenone sulfide)[13] were confirmed by X-ray diffraction analysis. The diversity of observed conformations of these macrocycles of the general formula $\underline{\text{c-}(C_6H_4\text{-}S)_n\text{-c}}$, when n > 5, indicates that there are no noticeable steric strains connected with the high flexibility of the sulfide linkages and favors macrocyclization processes. The ratio of linear polymer and MPS can vary by polymerization conditions. The relative role of macrocyclization in the synthesis of poly(arylene sulfides) is so great, that under certain conditions macrocyclization predominates over linear polycondensation and the yield of the

individual macrocycles reaches 73%[14]. It has been founded that tendency to macrocyclization in the polycondensation of dihaloarenes with Na_2S depends on such factors as: 1) isomerism of aromatic moieties and their number; 2) presence of other "bridges"; 3) synthesis conditions. Polymerisability of macrocycles in different conditions (nucleophilic attack, high temperature, mechanical deformation etc.) is also studied. The equilibrium macrocyclization-polymerization in chemical, thermo- and mechanochemical destruction processes of aromatic polymers has been ascertained[15,16]. It was discussed there is dependence between aromatic polymers stability to certain kinds of destruction and relative stability of macrocycles formed: with increasing of the latter the destruction degree grows.

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