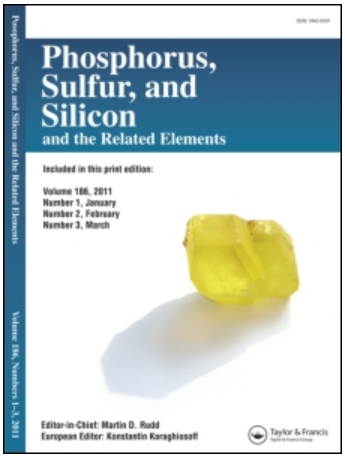

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Elemental Sulfur as Monomer in Syntheses of Poly (Arylene Sulfides)

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ELEMENTAL SULFUR AS MONOMER IN SYNTHESES OF POLY (ARYLENE SULFIDES).

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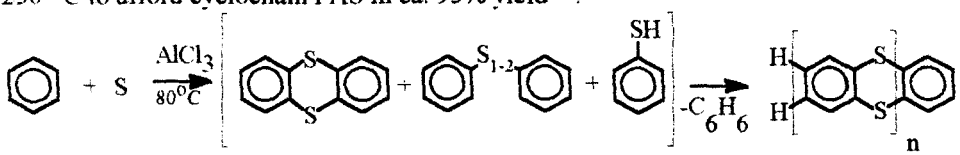
Abstract Direct polycondensation of elemental sulfur with benzene, naphthalene, binuclear aromatic hydrocarbons as well as substituted benzenes and their mixtures has been investigated. The mechanism of polycondensation, structure and properties of poly(arylene sulfides) formed has been studied.

INTRODUCTION

Sulfur is one of the most widespread elements in nature whose world production continues to grow. Therefore the application of sulfur in the chemistry of industrial classes of polymers is rather perspective. At present only one method is used for obtaining industrial poly(arylene sulfides) (PAS) - polycondensation of sodium sulfide with dihaloaromatic compounds. But direct interaction of elemental sulfur with aromatics is one of the most accessible methods for the syntheses of PAS.

UNACTIVATED AROMATIC COMPOUNDS

To obtain the polymeric products, the reaction of benzene and sulfur in the presence of $AlCl_3$ was first conducted under the conditions of Friedel-Crafts condensation with boiling benzene, following by distilling off the unreacted excessive benzene, at 175-250 ^0C to afford cyclochain PAS in ca. 95% yield [1] :



The structure of these polymers is supported by chemical analysis, preparative liquid chromatography and mass-spectrometry. Contrary to benzene, reaction of binuclear arenes (biphenyl, diphenylamine, etc.) with sulfur and $AlCl_3$ occurs through the intermediate formation and subsequent polymerization of cyclic sulfides

(dibenzothiophene, phenothiazine) and leads to soluble amorphous PAS containing mainly 1,2- substituted phenylene fragments in the chain .

It was found, that the polymer chains growth in the course of polycondensation of naphthalene with sulfur in the presence of $AlCl_3$ occurs by two competitive reactions, i. s. : polysulfidation and dehydropolycondensation of naphthylene under the action of $AlCl_3$. The second process is predominating and in polymer one atom of sulfur corresponds to more than one naphthalene fragment [2].

SUBSTITUTED AROMATIC HYDROCARBONS

Aniline in the absence of catalysts undergoes bulk polycondensation with sulfur at 180-220 ^{0}C to form polymeric products in high yield[3] .

The resulting amorphous polymer of molecular weight of 2-9 * 10^3 softens at 60-90^{0}C. In order to obtain available and useful polymers with a controlled content at the reactive amino- and oxygroups we have recently developed copolymers of sulfur with aniline / phenol mixtures.

All these reactions seem to be very simple and available. But there is an ecological problem; evolving of hydrogen sulfide during of polycondensation. To avoid this, we have suggested to oxidize hydrogen sulfide into sulfur directly in the reaction block by addition of co-monomers, namely arylnitro compounds. Nitro groups are reduced by hydrogen sulfide into amino groups (conversion up to 83%) and sulfur is returned in polycondensation. Metal oxides affect the polycondensation of aniline and sulfur. Some oxides (Pb, Cd, Zn) bind hydrogen sulfide evolved directly in the reaction block to give stable fine dispersed sulfides that also serve as useful fillers and stabilisators of polymers in the composite materials. This is, probably, the first example of the chemical polycondensative filling when a side-product of polycondesation is converted into a filler of polymers.

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