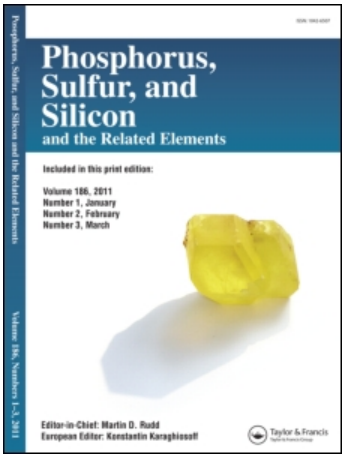

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Polysulfoximine: A Novel Sulfur-Based Polymer for High Performance Engineering Plastics

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First polysulfoximine was synthesized and characterized. 4-Phenoxybenzenesulfonimidoyl chloride was prepared by the reaction of 4-phenoxybenzenesulfinyl chloride with anhydrous chloramine T. Acid-catalyzed polycondensation of the sulfonimidoyl chloride with 10% of anhydrous ferric chloride in nitrobenzene at 120 °C for 48 h afforded 80% yield of polysulfoximine having tosyl group at the nitrogen atom (NTs derivative). The spectral characteristics of the NTs derivative suggested occurrence of the regioselective polycondensation. The NTs derivative was treated with conc. sulfuric acid followed by neutralization with sodium hydroxide to give corresponding "free" polysulfoximine having hydrogen atom at the nitrogen atom (NH derivative) in 80% conversion. Benzylated derivative (NBz derivative) was obtained by benzylation of the NH derivative with benzyl chloride. Thermal properties of these polysulfoximines were examined.

INTRODUCTION

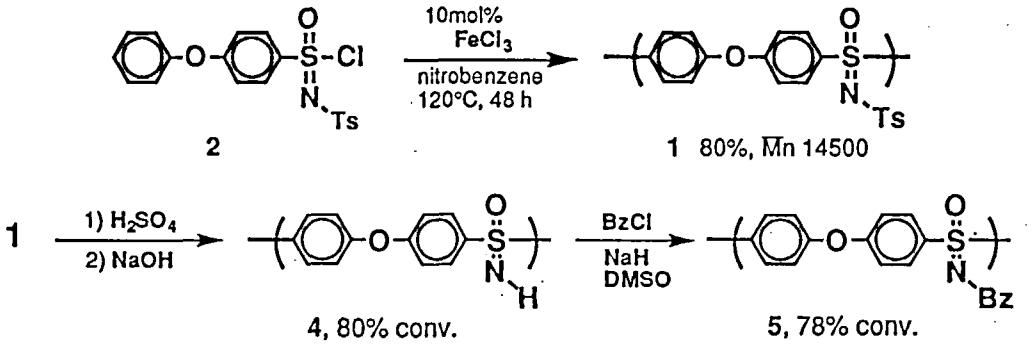
Sulfur-containing polymers such as polysulfone and poly(*p*-phenylene sulfide) as high performance engineering plastics involve sulfide and sulfone groups as major functional groups of their backbones. Although many organic sulfur-based functional groups are known,[1] there has been no polymer having sulfoximine function in the main chain. Sulfoximine[2] is a well known sulfur-containing compound showing sulfone-like properties. The chemical and physical properties of "polysulfoximine" are of particular interest due to the rigid and unsymmetrical structure. Recently, we have first prepared a polysulfoximine by a self polycondensation via a catalytic Friedel-Crafts reaction.[3] This paper discloses the synthesis, reaction, and characterization of polysulfoximine (**1**) and its derivatives (**4** & **5**).

RESULTS AND DISCUSSION

4-Phenoxybenzenesulfonimidoyl chloride (**2**) was obtained in 76 % yield, by the reaction of 4-phenoxybenzenesulfinyl chloride (**3**) with anhydrous chloramine T.[5] **3** was derived from diphenyl ether via a four step reaction sequence (62% overall yield).

A mixture of 2 and 10 mol% of anhydrous ferric chloride ($FeCl_3$) in nitrobenzene (0.5 M) was heated at 120°C for 48 h under a Friedel-Carfts condition[4] (Scheme 1). Polymeric product (80% yield) isolated as methanol-insoluble fraction was determined as polysulfoximine **1** by the IR, NMR, and gel permeation chromatography (GPC).

Scheme 1



The polymerization of **2** occurred through the successive regioselective condensative addition by the $FeCl_3$-catalyzed self Friedel-Crafts condensation. When the polymer **1** was treated with conc. sulfuric acid, the corresponding polymer containing the "free" sulfoximine moiety (**4**, NH derivative) was obtained. *N*-Benzylation of the NH derivative (**4**, containing 27% NTs unit) with excess amount of benzyl chloride in the presence of sodium hydride was performed. The product polymer (**5**, NBz derivative) obtained in 78% conversion was confirmed to have *N*-benzyl sulfoximine unit.

Glass transition temperature and thermogravimetric analyses of the polymers revealed that the thermal stability of **4** seems to be comparable to that of poly(ether-sulfone) (Tg 220°C; Td_{20} 550°C).

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