Synthesis of nitro-substituted aromatic polysulfide from bis(4-chloro-3-nitrophenyl) sulfone and sodium sulfide by activated nucleophilic displacement polymerization

Pradip Kumar Dutta
Department of Applied Chemistry, Shri G.S. Institute of Technology & Science, Indore 452 003, India
Received 4 March 1999; accepted 19 August 1999

Nitro-substituted polysulfide sulfone has been synthesized by the displacement polymerization between bis(4-chloro-3-nitro phenyl) sulfone and anhydrous sodium sulfide in N-methyl-2-pyrrolidone at 200°C. The polymer is soluble in aprotic solvents and was characterized by elemental analysis, IR and 1H-NMR spectroscopies and viscometry.

A variety of techniques have been used for the preparation of aromatic polysulfides possessing good thermal and oxidative stability. Most of the practical synthesis involve the class of aromatic nucleophilic substitution reaction. Imai et al. reported aromatic nucleophilic substitution polymerizations using activated aromatic dichlorides leading to the formation of polyarylamines, polyethers and polysulfides. Recently, aromatic polysulfides with high molecular weights prepared/synthesized by the reaction between activated aromatic dihalides and S-silylated dithiol have been reported by a group of Japanese workers. Aromatic polysulfide by the reaction between activated dichloride and anhydrous sodium sulfides (Na2S) is not reported elsewhere. In this communication, a successful synthesis and characterization of novel aromatic polysulfide through nucleophilic chlorodisplacement reaction with an AA type monomer, bis(4-chloro-3-nitrophenyl) sulfone (BCNPS) which is doubly activated by sulfone and nitro groups, is reported.

Experimental Procedure

Materials—Bis(4-chloro-3-nitrophenyl) sulfone (BCNPS) was prepared according to the reported procedure by the nitration of bis(4-chlorophenyl) sulfone. Na2S, 9H2O was dehydrated following the reported procedure. N-methyl-2-pyrrolidone (NMP) was distilled under vacuum and stored over 4Å molecular sieves.

Measurements—Elemental analysis for carbon, hydrogen and nitrogen was done by a Heraeus Carbo Erba 1108 elemental analyzer and the elemental sulfur and chlorine were analyzed by the Schöninger combustion flask method. IR spectrum was recorded with KBr pellets using a Perkin Elmer Model 837 spectrophotometer. 1H-NMR spectrum was recorded with a Varian EM 360, 60 MHz spectrometer using dimethyl sulfoxide (DMSO) -d6 as solvent and tetramethyl silane (TMS) as an internal standard.

Polymerization—An equimolecular mixture containing 5×10⁻³ mole (1.885 g) of bis(4-chloro-3-nitrophenyl) sulfone (BCNPS) and 5×10⁻³ mole (0.39 g) anhydrous Na2S in 50 ml NMP was charged in a 3-necked flask, equipped with a water condenser, a stirrer and a nitrogen inlet tube. The reaction was carried out at 200°C for 10h. After cooling to room temperature the mixture was neutralized with glacial acetic acid and poured into a water-methanol (50:50, w/v) mixture. The brown solid was collected by suction filtration and washed with hot water and finally with hot acetone to remove unreacted BCNPS.

Results and Discussion

The aromatic nucleophilic displacement reaction of activated aromatic halides (I) with (trimethyl silylthio) benzene (II) has been reported by Imai et al.11.
It is, therefore, expected that a similar nucleophilic displacement reaction may occur between S²⁻ ion, a strong nucleophile and an activated aromatic halide. The reaction between BCNPS and Na₂S is carried out in NMP at 200°C for 10 h may be represented as follows:

![Scheme - II](image)

The results are given in Table 1. The polymerization reactions of aromatic polysulfides are generally carried out in NMP due to its relatively higher boiling point and better thermal stability than those of similar other aprotic solvents. NMP, in this way, facilitates the nucleophilic displacement reaction through its dipolar aprotic properties and functions as a catalytic reactant in transforming Na₂S into a soluble nucleophile. The nucleophile attacks the BCNPS and thus forms a Meisenheimer type complex in a transition state (T.S.). Finally, the T.S. passes through the formation of a polymer.

Characterization—The chemical structure of the polymer was established on the basis of elemental analysis, IR and ¹H-NMR spectroscopies.

The elemental analysis of the polymer, dimer and trimer is shown in Table 2. The elemental per cent deviates from calculated value of dimer and trimer as DP increases. The experimental result of elemental analysis is in good agreement only with proposed structure of the polymer.

The IR spectrum of the polymer (spectrum not shown) shows peaks at 1340 cm⁻¹, 1440-1500 cm⁻¹ and 1180 cm⁻¹. This result agrees well with the stretching vibration of sulfone groups, C-N stretching and sulfide linkages respectively of the polymer.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>Time</th>
<th>Yield</th>
<th>η*_{inh}</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>200</td>
<td>10</td>
<td>78</td>
<td>0.18</td>
</tr>
</tbody>
</table>

*0.5% solution (w/v) in DMF

The structure of the repeat unit of the polymer was also confirmed by ¹H-NMR spectroscopy (Fig.1). The ¹H-NMR spectrum of the polymer shows three different types of aromatic protons (Table 3). The inherent viscosity value indicates that the molecular weight is low whereas nitro-substituted polysulfide sulfone obtained by Imai et al. from BCNPS and methylated dithiophenol was of higher molecular weight. This may be attributed to the close reaction centre of the structural unit of the polymer and thus hindrance. Moreover, the absence of peaks corresponding to nitro-substituted chlorophenyl end groups show that the reaction is quantitative. The polymer is soluble in polar aprotic solvents like NMP, DMSO, hexamethyl phosphoramide (HMPA).

<table>
<thead>
<tr>
<th>Protons ortho to sulfone group (P₁)</th>
<th>Protons ortho to sulfone (P₂)</th>
<th>Protons around well as ortho to nitro (P₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 - 8.3</td>
<td>7.5 - 7.8</td>
<td>6.9 - 7.1</td>
</tr>
</tbody>
</table>

Acknowledgement

The author appreciates the use of analytical facilities for elemental analysis, IR and ¹H-NMR spectroscopies and preparative studies of the polymer of RSIC at CDRI, Lucknow and Prof. S. Maiti's Laboratory at IIT, Kharagpur respectively. The author also thanks Dr. P.C. Sharma, Director and Dr. J.K. Agrawal, Head of Chemistry of this Institute for permission to publish this paper.
DUTTA: SYNTHESIS OF NITRO-SUBSTITUTED AROMATIC POLYSULFIDE

References