Halogenated polyethersulfone sulfides

A. M. Kharaev*, R. Ch. Bazheva, and A. S. Borodulin

Abstract. This paper presents the results of a study of random copolyethersulfone sulfides based on 4,4'-dichlorodiphenylsulfone, 1,1'-dichloro-2,2'-di(4-hydroxyphenyl)ethylene, and sodium sulfide. The synthesis of copolyethersulfone sulfides with different ratios of polyethersulfone and polyphenylenesulfone sulfide units was carried out by high-temperature polycondensation by the reaction of nucleophilic substitution in N,N-dimethylacetamide medium and using potassium carbonate as an alkaline agent. The effect of the solvent used on the yield and reduced viscosity of polyethersulfone sulfides was studied. It has been shown that polymers with high reduced viscosity can be obtained in N,N-dimethylacetamide and N,N-dimethylformamide. The growth dynamics of the reduced viscosity of polyethersulfone sulfides was also studied depending on the ratio of sulfone and sulfide groups. The solubility of these polymers in various solvents has been studied.

1 Introduction

Progress in modern technology is impossible without polymeric materials and highly efficient technologies for their production. It is essential that the role of polymeric materials and their competitive ability in relation to other materials are continuously increasing. Such materials must be heat-resistant withstanding long-term operation at temperatures up to 2500°C and short-term exposure at temperatures up to 4000°C. Such materials include the so-called superstructural materials, in particular, polysulfones, polyethersulfones, polyetherketones, polyphenylene sulfides, numerous studies of which are aimed at the development of new and improvement of known structural polymers [1-8].

Currently, polyphenylene sulfide (PPS) is produced and widely used in the world, which is a polymer in which benzene rings alternate with a sulfur atom in the macrochain. It is a heat-resistant, durable, flame-retardant polymer. However, PPS does not melt at a temperature of about 300°C, it is not soluble in any of the known organic solvents, which creates certain difficulties in its processing. It is not possible to obtain a high molecular weight polymer; to increase the molecular weight, it is heated in an oxygen atmosphere. In this case, crystallization occurs, the degree of crystallinity reaches 50%. In addition, this polymer is very expensive.
Polysulfones based on bisphenol A and 4,4'-dichlorodiphenylsulfone are a structural amorphous material with increased heat resistance, good electrical and mechanical properties. It can work for a long time at temperatures up to 160°C, and for a short time it withstands heating up to 200°C. Withstands cooling down to minus 100°C. Soluble in amide solvents and chlorinated hydrocarbons [9-16].

Often it is not possible to obtain a polymer that would combine all the necessary qualities, therefore, composite polymer materials are usually obtained, or chemical modification is carried out at the stage of polymer synthesis by combining various monomers in the synthesis of copolymers. In copolymers and block copolymers, it is possible to combine the positive qualities of two or more classes of polymers and obtain a material with a special set of properties and characteristics.

At present, studies in the field of obtaining poly(arylene sulfide sulfones) as promising heat-resistant structural thermoplastics with high chemical resistance and good processability by injection molding have aroused some interest. In this characteristic, polyarylene sulfide sulfones are superior to polysulfones [17-26].

An analysis of the literature data showed that the study of the synthesis of copolymers of arylene ether sulfone sulfones to obtain polymers with improved technological and operational characteristics is relevant and promising, since it will allow creating their competitive industrial production based on available starting compounds and built on the basis of the existing production of polysulfones.

This paper presents the results of a study of random copolyethersulfone sulfides based on 4,4'-dichlorodiphenylsulfone, 1,1'-dichloro-2,2-di(4-hydroxyphenyl)ethylene, and sodium sulfide.

2 Experimental

The experimental section details the synthesis of the copolymer. The reaction process involves charging specified amounts of each component into a reaction flask equipped with a mechanical stirrer, a thermometer, a capillary for supplying an inert gas, and a distillation system. The flask is heated to 165°C with a continuous supply of an inert gas and stirring. DMAA distillation is stopped when the distillation vapor temperature equals the boiling point of DMAA, and heating is continued for 5-10 hours until the required value of the reduced viscosity is reached.

Then, 100 ml of DMAA are added to the reaction mass, stirred until homogenized, cooled to 90°C, and a solution of 4.5 g of oxalic acid in 50 ml of DMAA is added. After adding oxalic acid, inorganic salts are separated by filtration on a Buchner funnel. The resulting filtrate is poured in a thin stream into a fivefold volume of distilled water with vigorous stirring. The precipitated polymer is filtered off, washed repeatedly with distilled water, and dried at 100–120°C for 24 h.

1,1'-dichloro-2,2-di(4-hydroxyphenyl)ethylene were purified by recrystallization from aqueous alcohol (water:alcohol = 5:2). After recrystallization, they had melting points equal to 213 ºС.

The study of the crystallinity of polymers was carried out on a DRON-6.0 X-ray diffractometer on copper K-radiation with a wavelength of 1.54051Å. The survey was carried out in the range of angles q-7–45 ° with a given step of 1 ° per minute with an accuracy of measuring diffraction angles of 0.030 degrees.
3 Results and discussions

The synthesis of copolyethersulfone sulfides with different ratios of polyethersulfone and polyphenylenesulfone sulfide units was carried out by high-temperature polycondensation by the reaction of nucleophilic substitution in N,N-dimethylacetamide (DMMA) medium and using potassium carbonate as an alkaline agent at the boiling point of DMMA (165-167°C) according to the general scheme shown at fig. 1.

Fig. 1. The general scheme for synthesis of copolyethersulfone sulfides.

The study of the dependence of the influence of the solvent used showed that polymers with a high reduced viscosity are obtained in N,N-dimethylacetamide, N,N-dimethylformamide, somewhat worse in dimethyl sulfoxide (Fig. 1).

Subsequently, DMAA was used as a solvent for the synthesis of PESS.

The growth dynamics of the reduced viscosity of PESS was also studied depending on the ratio of sulfonic and sulfide groups (Fig. 2).

Fig. 1. Change in the reduced viscosity of PESS-50 over time in various solvents: ■ DMSO, ▲ DMF, ● DMMA where: PESS-polyethersulfone sulfide, where the ratio of 1,1-dichloro-2,2-di(4-hydroxyphenyl)ethylene and sodium sulfide is 50:50 % mol.
As studies have shown, this method of preparation allows obtaining with a higher molecular weight when sulfonic groups predominate in PEES, which is logical, since such PEES have better solubility in DMMA. However, PESS with high viscosity are obtained with high contents of sulfide groups.

All synthesized PESS, according to X-ray diffraction analysis, are amorphous. It is known that information about the solubility of the polymer is important when choosing processing methods, especially when it comes to processing through solutions. In addition, it is necessary to know the resistance of the polymer to the action of various solvents.

Table 1. Solubility of PESS depending on the composition

<table>
<thead>
<tr>
<th>The content of sulfonic groups, % mol./ Solvent</th>
<th>0</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>100</th>
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<tbody>
<tr>
<td>Chloromethane</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>SW</td>
<td>IS</td>
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<tr>
<td>1,2-Dichloromethane</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<td>Methylbenzene</td>
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<tr>
<td>Chlorobenzene</td>
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<td>N,N-dimethylacetamide</td>
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<td>N,N-dimethylformamide</td>
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<td>Dimethyl sulfoxide</td>
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<td>N-methylpyrrolidone</td>
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where: S - dissolves, SW - swells, SH - dissolves when heated, IS - does not dissolve

4 Conclusion
References
Physica Polyphenylene I

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random copoly (arylene ether C 4,4'-dihydroxybiphenyl: Synthesis and propertien (2,2 bis(4-mercaptophenyl)propane II Eur. Polym. J.,

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