Halogenated polyethersulfone sulfides

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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 - withstand long-term operation at temperatures up to 250^0 C and short-term exposure at temperatures up to 400^0 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, PSF does not melt at a temperature of about 300^0 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.

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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

A 250 ml four-necked flask equipped with a mechanical stirrer, a thermometer, a capillary for supplying an inert gas, a system for distilling water (a Wurtz nozzle, a straight condenser, an allonge, a receiver) charge 43.936 g (0.153 mol) of 4,4-dichlorodiphenylsulfone, 17.121 g (0.075 mol) of 1,1-dichloro-2,2-di(4-hydroxyphenyl)ethylene, 18.010 g (0.075 mol) of sodium sulfide, 27 g (0.195 mol) of potassium carbonate and 150 ml of DMAA.

The reaction flask is placed in an oil bath and the reaction mass is heated to 165°C with a continuous supply of an inert gas and with stirring. The distillation of DMAA is stopped when the distillation vapor temperature is equal to 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 ºC.

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 1.54051A. 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 (165-167^0 C) according to the general scheme shown at fig. 1.

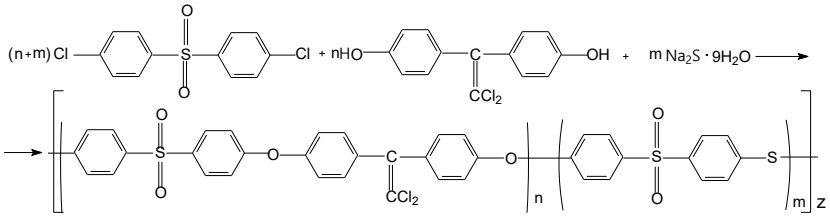

Fig. 1. The general scheme for synthesis of copolyethersulfone sulfides

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).

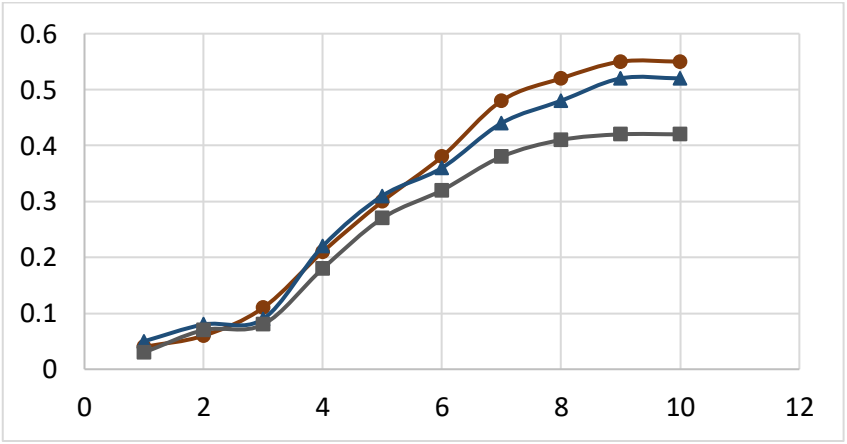

Fig. 1. Change in the reduced viscosity of PESS-50 over time in various solvents: ■- DMSO, ▲ - DMF, ●- DMMA where: PESS - polyethersulfone sulfide, where the ratio of 1,1-dichloro-2,2-di(4-hydroxyphenyl)ethylene and sodium sulfide is 50:50 % mol.

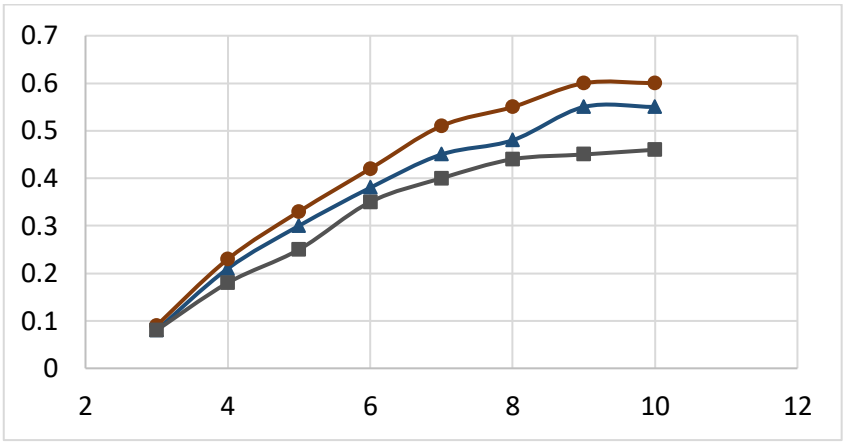

Fig. 2. Change in the reduced viscosity of PESS over time depending on the composition: ■- PESS-70, ▲ - PESS-50, ●- PESS-30

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.

The table 1 shows the solubility of PESS depending on the composition

Table 1. Solubility of PESS depending on the composition

The content of sulfonic groups, % mol./ Solvent	**0**	**10**	**30**	**50**	**70**	**90**	**100**
Chloromethane	S	S	S	S	S	SW	IS
1,2-Dichloromethane	S	S	S	S	S	SW	IS
Methylbenzene	S	S	S	S	S	SW	IS
Chlorobenzene	S	S	SH	SH	SW	SW	IS
N,N-dimethylacetamide	S	S	S	S	S	S	S
N,N-dimethylformamide	S	S	S	S	S	S	S
Dimethyl sulfoxide	S	S	S	S	S	SW	SW
N-methylpyrrolidone	S	S	S	S	S	S	S

where: S - dissolves, SW – swells, SH - dissolves when heated, IS - does not dissolve

4 Conclusion

The results of theoretical and experimental study of methods for obtaining polyethersulfone sulfides showed that these polymers with high reduced viscosity and practical yields are obtained by high-temperature polycondensation in aprtic dipolar solvents, such as N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide. The kinetics of the synthesis of these polymers was studied. Polyethersulfone sulfides with different ratios of starting components have been synthesized. The solubility of these polymers has been

studied. So, PESS with a content of sulfide sulfone units up to 70 mol.% is readily soluble in solvents such as 1,2-dichloroethane, chloroform, dichloromethane, N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone. The solubility of these PESS is comparable to the solubility of polysulfone. The solubility of PESS with a content of sulfide sulfone groups of 90 mol.% and more close to polyphenylene sulfide.

The presence of two chlorine atoms in the monomer unit makes it possible to obtain polymers with high fire resistance, the presence of a double bond makes it possible to carry out post-polycondensation at certain temperatures, as well as the possibility of cross-linking the polymer at the site of double bond opening. This leads to an increase in many operational properties - heat resistance, heat resistance, mechanical characteristics.

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