Aromatic polyethersulphones with improved performance characteristics

R Ch Bazheva 1, A.M. Kharaev1, A S Borodulin and A N Kalinnikov2

1Kabardino-Balkaria State University named after Kh.M. Berbekov, Nalchik, Chernyshevsky street, 173, Russian
2Moscow State Technical University named after N.E. Bauman, Moscow, 2nd Bauman, 5/3, Russian

Abstract. Synthesized modified aromatic polyethersulfones containing dichloroethylene and arylate groups in the main chain. The kinetics of the synthesis of polyethersulfones by the method of acceptor-catalytic polycondensation was studied. It is shown that the property of the obtained polymers depends on the ratio of the starting monomers. It is shown that the property of the obtained polymers depends on the ratio of the starting monomers. The presence of two chlorine atoms in the initial monomer in combination with an unsaturated bond provides the polyethersulfones based on it with high fire resistance and good physical and chemical properties, including frost resistance.

Keywords: oligosulfone, polyethersulfone, bisphenol A, 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene, dichloroethylene group, acceptor-catalytic polycondensation.

1. Introduction
The rapid development of technology requires the creation of new polymers with a predetermined set of valuable properties and working under the influence of various external conditions. One of these polymers are aromatic polysulfones and polyethersulfones, which have a range of valuable performance properties. At the same time, the cost and energy costs of their synthesis are relatively low [1-9]. However, polysulfones are not without drawbacks, one of which is a partial or complete loss of performance at low temperatures, that is, limited frost resistance. Frost resistance of polymers is the ability of materials to maintain their performance properties at low (negative) temperatures.

The problem of frost resistance is relevant for almost all areas of application of polymeric materials: household, construction and utilities, in the transport sectors (automotive, shipbuilding, space and aviation industries). The chemical structure, as well as the physical state of the polymer material, can significantly affect the frost resistance of materials. The possibility of using polymer materials well proven in a temperate climate in the North is a topical issue in modern materials science.

The main ways to increase the frost resistance of amorphous polymers is plasticization by low molecular weight and polymer plasticizers, and crystalline ones by copolymerization and modification, that is, by changing the properties of polymers by chemically reacting them with low molecular weight modifiers [8-15].
The purpose of this work is to produce polyethersulfones (PES) with a long-term operation temperature of 2000°C and higher, with high fire resistance and frost resistance, and are resistant to UV radiation.
Numerous studies have shown that polymers containing dichloroethylene groups, in addition to fire resistance, have high mechanical and thermal properties [16-21].

2. Experimental
X-ray diffraction studies were carried out on powder samples using a DRON-6 diffractometer in copper K-radiation with a graphite monochromator on a diffracted beam.
The IR spectra of the materials were measured on a SPECTRUM TWO FTIR spectrometer with a computer control system at a frequency domain of 400-5000 cm⁻¹.
Mechanical properties were investigated under uniaxial tension conditions on a GT-2000 testing machine at a temperature of 20°C, a relative stretching rate of 0.017 s⁻¹ and various strain rates.
Phase transitions were studied on a Perkin Elmer DSK 4000 differential scanning calorimeter at a heating rate of 5 deg / min in air.
The thermal stability of the samples was studied by the method of thermogravimetric analysis using a Perkin Elmer TGA 4000 derivatograph in an atmosphere of air at a heating rate of 5 degrees min⁻¹ from 30 to 700°C.
Ubbelohde viscometer was used to determine the intrinsic viscosity. Solutions with relative viscosity = 1.1 were diluted for subsequent measurements of viscosity in such a way that the intervals of the obtained concentrations were approximately the same, and the η of the most diluted solution should not be less than 1.1. These limits of measurement specific viscosity η = 1.1-1.5 correspond to concentrations of polymer solutions for which the dependence of [η] on the velocity gradient of fluid outflow from the capillary is not observed and with dilution there is no deviation from the linear dependence of ηsp / C or ln ηrel. / C from S.

3. Results and discussions
Modified polyethersulfones synthesized according to the following scheme:
Oligosulfone was synthesized by high temperature polycondensation in dimethyl sulfoxide [8, 14]. Polymers were synthesized by acceptor-catalytic polycondensation in 1,2-dichloroethane. The ratio of bisphenols varied from 0 to 100 molar percent. The amount of oligosulfone with a degree of polycondensation of n = 10 (OASO-10D) was taken constant and amounted to 10 wt.% Of the total number of bisphenols.

The structure of the obtained copolyesters was confirmed by IR spectroscopy, an X-ray phase analysis was carried out, and polydispersity was studied.

Poyesters were obtained with high viscosity indices (0.90-1.25 dl/g) and quantitative yield. The structure of the obtained copolyesters is confirmed by IR spectroscopy and elemental analysis. The presence on the spectra of the corresponding absorption bands and the absence of bands for hydroxyl groups confirms the preparation of polymers of this structure. The IR spectra of the polymers contain absorption bands corresponding to: ester bonds (1200-1250, 1735, 1740 cm⁻¹); the isopropylidene group in the remainder of bisphenol A (1290-1365, 1385, 1415-1465, 2930-2980 cm⁻¹), the group >C=CCl₂ (980 cm⁻¹), sulfonyl groups of oligosulfones (560-570, 1150-1170, 1290, 1300, 1320 cm⁻¹), which indicates the formation of polymers of a given structure. X-ray diffraction analysis of film samples of polymers obtained by irrigation from solution showed that they have an amorphous structure. The studies were carried out using a DRON-6 diffractometer in the step scan mode with a wavelength of 1.54051 Å.

The study of the polydispersity of the copolymers showed that the coagulation threshold of polyesters based on bisphenol 1,1-dichloro-2,2-di(4-hydroxyphenyl)ethylene and bisphenol A increases with an increase in the content of the chlorine-containing component, due to the polarity of >C=CCl₂-groups, and, therefore, the better solubility of these polymers.

The presence on the differential curves of turbidimetric titration of copolymers of one maximum confirms the formation of copolymers, rather than a mixture of homopolymers (Fig. 1). The polydispersity of the copolymers was determined by turbidimetric titration on a FEC 56M photocalorimeter. As solvent, 1,2-dichloroethane was used, and precipitant was isopropyl alcohol.

On differential titration curves constructed from integral ones by graphic differentiation, there is only one maximum.

**Fig.1.** Integral and differential curves of turbidimetric titration of polyethersulfones based on equimolar amounts of starting monomers

This method is based on measuring the optical density of a medium using a photoelectrocolorimeter and is a very convenient and fast method for distinguishing homopolymers and their mixtures from copolymers of various structures (regular and irregular structures, block and familiar copolymers). In addition, the solubility of the polymers can be judged by the deposition curves.

All obtained copolymers are readily soluble in a number of organic solvents: dichloroethane, tetrachloroethane, tetrahydrofuran, chloroform, methylene chloride, etc. The molecular weight of the copolyesters is in the range of 40,000-70000.
The results of thermomechanical tests of the synthesized copolymers based on bisphenol A bisphenol 1,1-dichloro-2,2-di(4-hydroxyphenyl) ethylene showed that the latter have relatively low thermomechanical properties. Depending on the ratio of the starting bisphenols in the BSP series, the glass transition temperature changes only by 100 °C. With an increase in the proportion of bisphenol 1,1-dichloro-2,2-di(4-hydroxyphenyl) ethylene, the pour point changes from 250 °C to 350 °C (table 1).

In polymers where the content of sulfonic O = S = O groups prevails over ester arylate –C(O)–O– groups, the heat resistance is higher. The increase in heat resistance in this case is due to the fact that polycondensation aromatic polymers are characterized by the occurrence of branching and crosslinking processes in the region of relatively low degradation temperatures (250-400 °C), which ultimately leads to the formation of a three-dimensional structure and a change in the operational characteristics of the polymers.

| 2,2 bis-(4,4'-oxyphenyl)propane, % | 1,1-dichloro-2,2-di(4-hydroxyphenyl) ethylene, % | η, dl/g | Tg, °C | σt, MPa | εt, % | A, kJ/m² | Izod (notched) |
|----------------------------------|-----------------------------------------------|--------|--------|----------|-------|---------|----------------|
| 100                              | 0                                             | 1.20   | 207    | 93       | 14    | 8.0     |                |
| 75                               | 25                                            | 1.25   | 210    | 97       | 20    | 8.5     |                |
| 50                               | 50                                            | 1.06   | 212    | 124      | 25    | 8.5     |                |
| 25                               | 75                                            | 1.02   | 215    | 113      | 20    | 9.0     |                |
| 0                                | 100                                           | 0.95   | 217    | 87       | 15    | 9.5     |                |

4. Conclusion

The possibility of obtaining high molecular weight polyethersulfones of block structure using various polycondensation methods: high temperature and acceptor-catalytic was studied. By the methods of IR spectroscopy, elemental, X-ray phase analysis, the formation of polymers of a given structure is proved. Among copolymers, the highest values of the deformation-strength characteristics are exhibited by a copolymer based on equimolar amounts of the starting bisphenols. A further increase in the content of this does not lead to an increase in tensile strength (σ) and elongation (ε), which is most likely associated with a decrease in the reduced viscosity, and, consequently, the molecular weight of these polymers. Studies have shown that synthesized after exposure for 48 hours at a temperature of 50 °C, retain their basic physical and mechanical characteristics. The complex of physico-chemical characteristics allows us to recommend these polyethersulfones as fire-resistant, heat- and frost-resistant structural and film materials.

Acknowledgement

The reported study was funded by RFBR according to the research project № 18-29-18063.

References

[1] Borodulin A S, Kalinnikov A N, Bazheva R C, Kharaev A M and Beshtoev B Z 2018. Receipt and investigation of performance characteristics of super constructions polyesters. International Journal of Mechanical Engineering and Technology (IJMET) 9-13 1117–1127, Article ID: IJMET_09_13_117.

[2] Borodulin A S, Kalinnikov A N, Bazheva R C and Beshtoev B Z 2018. Synthesis and properties of Aromatic Polyethersulfones. International Journal of Mechanical Engineering and Technology (IJMET) 13 1109–1116, Article ID: IJMET_09_13_116.

[3] Kharaev A M, Mikitaev A K, Bazheva R Ch, Khashulatova Z S, Kharaeva R A, Chumachenko T N and Istepanov M I 2008. Modified aromatic copolyesters. International Polymer Science and Technology, 12 17–20. ISSN: 0544-2901.
[4] Mikitaev A K, Rusanov A L, Koumykov R M 2013. The novel polynaphthylimides of improved solubility on the basis of derivatives from chloral and dichlordiphenyltrichlorethane /Characterization and Development of Novel Materials Research Compendium/. 186-192.

[5] Ozden S, Kharaev A M and Bazheva R C 2009 Synthesis and Modification of Aromatic Polyesters With Chloroacetil 3,5-dibromo-p-hydroxybenzoic Acid. J. of Applied Polymer Science, 111-4 1755–1762. DOI: https://doi.org/10.1002/app.29147.

[6] Baranov A B, Peksimov O Ye, Prudskova T N, Andreyeva T I, Yemel'yanov I D and Shembel N L 2016, Study of the technological characteristics of materials based on polysulfone. Thin chemical technologies, 11-5 87–90

[7] Zenitova L A and Shteynberg Ye M 2012, Polysulfone as a functional polymer material and its production. International Research Journal, 6-6 23–28. DOI: 10.18454/IRJ.2227-6017.

[8] Kumykov R M and Vologirov A K 2018. New aromatic dinitro-derivatives of chloral as monomers for the synthesis of polyesters and polyheteroarylenes // News of higher educational institutions. Series: Chemistry and Chemical Technology. 61-20 4-14.

[9] Patent № 2382756 (RF). Kharaev A M, Bazheva R Ch, Kharaeva R A, Khasbulatova Z I and Istepanov M.I. Chlorine-containing aromatic oligoethers. Publ. 02.27.2010. Bul 6.

[10] Kharaev A M, Shao A Kh, Bazheva R Ch 2013. The synthesis and stabilization of polymers. Monograph /Saarbrücken/. – 300 p.

[11] Kharaev A M, Bazheva R C and Chayka A A 2006 Aromatic block-copolymers as prospective heat resistant constructive materials: Polymers, Polymer Blends, Polymer Composites and Filled Polymers: Synthesis, Properties and Applications 115-120.

[12] Barokova E B, Bazheva R Ch and Haraev A M 2010 Oligosulphones on the basis of 1,1-Dichlor-2,2-di(4-oxyphenyl)-ethylene and 4,4'-dichlorodiphenyl-sulphone obtained by high-temperature polycondensation. //J. of the Tribological Association. 16-2 284-287.

[13] Kharaev A M, Bazheva R C and Barokova E B 2008 Fireproof aromatic block copolymer resin on the basis of 1,1-dichlor-2,2 di(n-oxyphenyl) ethylene. Modern Tendencies in Organic and Bioorganic Chemistry: Today and Tomorrow (New York). 219-222.

[14] Barokova E B, Haraev A M, Bazheva R C and Haraeva R A 2010 Oligosulifons on the basis of 1,1-dichlor-2,2-di(4-oxyphenyl)ethylene and 4,4’-dichlorodiphenylsulfolone obtained by high temperature polycondensation. Handbook of Condensed Phase Chemistry. 233-236.

[15] Nelyub V A 2016 A study of the microstructure of dressed glass fibers, Polymer Science - Series D 9 96-100

[16] Nelyub V A 2015 Determination of adhesion interaction between carbon fiber and epoxy binder, Polymer Science - Series D 8-1 6-8.

[17] Nelyub V A, Borodulin A S, Kobets L P and Malysheva G V 2016 Capillary hydrodynamic of oligomer binder, Polymer Science – Series D 9-3 322-325

[18] Nelyub V A, Borodulin A S, Kobets L P and Malysheva G V 2016 A study of structure formation in a binder depending on the surface microrelief of carbon fiber, Polymer Science – Series D 9-3 286-289.

[19] Borodulin A S and Kalinnikov A N, Bazheva R C 2018 Receipt and investigation of performance characteristics of super constructions polyesters, International Journal of Mechanical Engineering and Technology 9-13 1117-1127.

[20] Borodulin A S, Kalinnikov A N and Bazheva R C 2018 Synthesis and properties of aromatic polyethersulfofones, IJMET 9 1109–1116.

[21] Borodulin A S, Kalinnikov A N and Kharaev A M 2018 New Polymeric Binders for the Production of Composit, Materials today:proceedings 11 1107–1111.