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AROMATIC COPOLYETHER ETHER KETONES DERIVED FROM HYDROQUINONE

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Data are given on aromatic copolyether ether ketones obtained from aromatic diols, namely, hydroquinone and diphenylolpropane (Bisphenol A). The copolyethers were synthesized by high-temperature copolycondensation of the corresponding diols with 4,4'-difluorobenzophenol. The dependence of the rheological and thermochemical properties of the polymer samples on the mole ratio of the diphenols was studied for a broad range of monomer concentrations. Enhanced heat resistance along with decreased intrinsic viscosity and glassy point temperature were found for copolyether ether ketones with a greater content of hydroquinone.

Aromatic copolyether ether ketones (ACPEEK) are used as engineering plastics and have found many industrial applications. The development of new and improved methods for the production of copolyether ether ketones [1-3] will further research on these materials. The interest in this area is attributed to the great and not yet fully discovered potential of the structure of copolyarylene ethers. The realization of these possibilities undoubtedly would lead to the development of construction polymers and derived composite materials with excellent useful properties for many important industrial technologies.

Polymer substances considerably differing in their important useful properties may be obtained by regulating the molecular design of the copolyethers through change in the chemical structure of the starting monomers and the order of their bonding with each other.

Crystallizable copolyethers may sometimes be synthesized by this approach [4]. This property is important for additive technologies, in particular, for 3D printing. We should also note that the use of a mixture of monomers with different structure (for example, diphenols and activated aromatic arylene dihalides) in some cases permits optimization and simplification of the synthesis of aromatic copolyethers itself in comparison with the methods of preparing the related homopolymers [5].

Hence, in the present work, we studied the preparation of ACPEEK from hydroquinone, diphenylolpropane (Bisphenol A), and 4,4'-difluorobenzophenone. The preparation of the copolyarylene ether ketones was carried out by high-temperature polycondensation through a mechanism of nucleophilic substitution upon the simultaneous introduction of all the reagents as shown in Schemes (1) and (2) (see Insert).

Potassium diphenolates of hydroquinone and diphenylolpropane are formed initially (1) followed by reaction (2) of these intermediates with 4,4'-difluorobenzophenone. The syntheses of the copolyethers were carried out with hydroquinone/diphenylolpropane mole ratios from 0.1:0.9 to 0.9:0.1. The nucleophilic replacement of the fluorine atoms in the aryl dihalides proceeded through the formation of a Meisenheimer complex (Scheme (3), Insert). The negative charge of the ring is stabilized by transferring an electron to the electron-withdrawing group.

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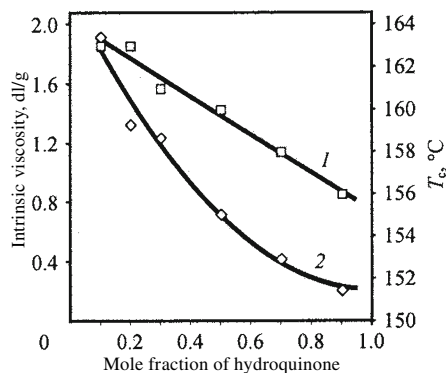


Fig. 1.

Fig. 1. Dependence of the intrinsic viscosity (1) and glassy point temperature (2) of the copolyether ketones on the hydroquinone content

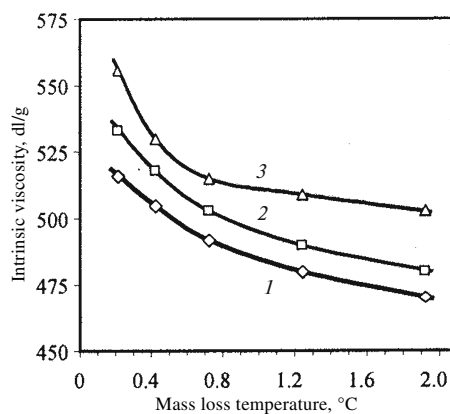


Fig. 2.

Fig. 2. Dependence of the temperature of the loss of mass of the copolyether ether ketones on the intrinsic viscosity with hydroquinone content 2% (1), 5% (2), and 10% (3).

The intrinsic viscosity was measured for 0.5% solutions of ACPEEK in 2,2-dichloroethanoic acid. The thermal properties of these copolymers were studied by differential scanning calorimetry on a Perkin Elmer DSC 4000 instrument and by thermogravimetric analysis on a Perkin Elmer TGA 4000 instrument at a heating rate of 5°C/min in the air. Prior to testing, the samples were dried in a vacuum dry box in several steps at different temperatures in the range from 90° to 150°C.

Our results indicated that the intrinsic viscosity and glassy point temperature decrease with increasing hydroquinone content in the system under our conditions for the polycondensation, while the heat resistance of the copolymers increases (Figs. 1 and 2).

At first glance, this experimental result is not in accord with previous findings indicating that some aromatic diols do not permit the preparation of polyethers with high solution viscosity due to the presence of bulky groups displaying a shielding effect.

The observed stable reduction in the intrinsic viscosity of the ASPEEK with increasing molar concentration of hydroquinone is apparently related to some tendency of this dihydroxy compound to undergo oxidation with its transformation to the quinoid form (Eq. (4), Insert).

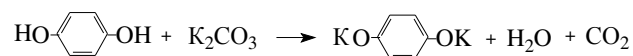
The conversion of the diol to the quinoid form leads to a breakdown in the equimolarity of the monomers and, as a consequence, a decrease in the intrinsic viscosity of the aromatic copolyether ether ketones, which was observed in our work.

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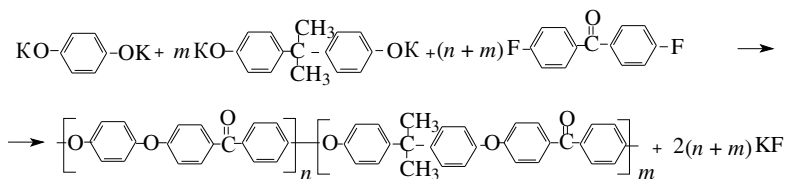
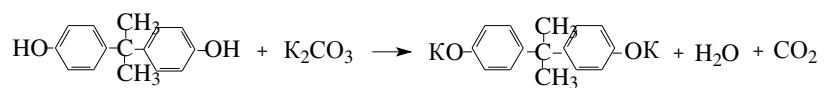
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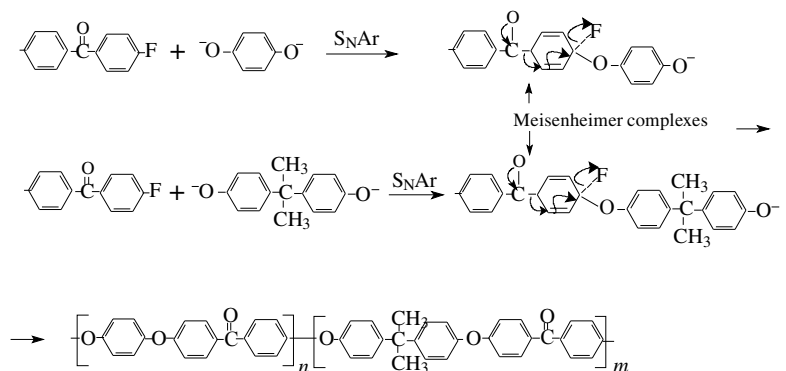
Appendix



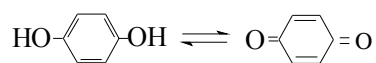
(1)



(2)



(3)



(4)