

Synthesis and Properties of Soluble Aromatic Polyetheretherketones

Kharaev Arsen Mukhamedovich¹, Bazheva Rima Chamalovna², Borodulin Aleksey Sergeevich³, Salamov Ali Khasmagometovich⁴

¹Doctor of Chemistry, professor, Kabardino-Balkarian State University, Nalchik, Kabardino-Balkaria, Russia.

²Doctor of Chemistry, professor, Kabardino-Balkarian State University, Nalchik, Kabardino-Balkaria, Russia.

³PhD in Engineering, associate professor, Kabardino-Balkarian State University, Nalchik, Kabardino-Balkaria, Russia.

⁴PhD in Pedagogics, professor, Kabardino-Balkarian State University, Nalchik, Kabardino-Balkaria, Russia.

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ABSTRACT

In order to obtain soluble and relatively inexpensive polyaryletheretherketone by high-temperature polycondensation different oligo ketones based on 4,4'-dichlorobenzophenone have been obtained. Polyaryletheretherketones characterized by solubility in organic solvents and complex operational characteristics have been obtained by acceptor-catalytic polycondensation.

Key words: high-temperature polycondensation, oligo ketone,

acceptor-catalytic polycondensation, polyaryletheretherketone, heat resistance, tensile strength, fire resistance.

Correspondence:

Kharaev Arsen Mukhamedovich

Doctor of Chemistry, Professor, Kabardino – Balkarian State University, Nalchik, Kabardino – Balkaria, Russia

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INTRODUCTION

Aromatic polyetheretherketones are promising polymer systems, which have gained wide application in almost all branches of technology. It is a relatively new class of polymers, the study of which began not so long ago. Aromatic polyetheretherketones have high physical and mechanical characteristics due to the presence in their main chains of phenylene groups providing a high degree of crystallinity of these polymers [1-5]. Polyetheretherketones are obtained by high-temperature polycondensation using 4,4'-difluorobenzophenone at 300-34000°C during 6-12 hours. The obtained polymer is not soluble, and the use of expensive digalogenide increases its price by an order of magnitude in comparison with well-known structural polymers. A large amount of polyetheretherketones based on various monomers and methods of their production are known [6-15].

The purpose of this work was to obtain soluble polyetheretherketones under sufficiently mild conditions with the replacement of 4,4'-difluorobenzophenone with cheaper and more affordable digalogenide, namely 4,4'-dichlorobenzophenone, which will significantly reduce the cost of final products.

Both high-temperature polycondensation and acceptor-catalytic polycondensation were used at different stages of synthesis to achieve the goal.

At the first stage of synthesis on the basis of diphenylolpropane (or 4,4'-dioxyphthalophenone) and 4,4'-dichlorobenzophenone in the medium of dimethyl sulfoxide oligo ketones of different composition and degree of condensation were obtained. Depending on the ratio of the initial monomers oligo ketones with the degree of condensation n=1, 5, 10 and 20 were obtained. Oligo ketones have the following structure.

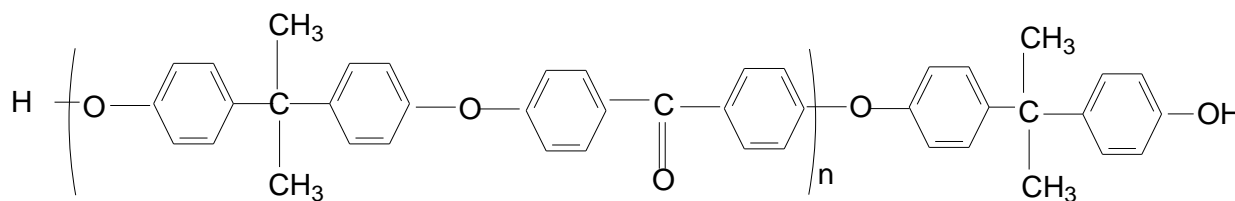


Figure 1: OK-1-20A

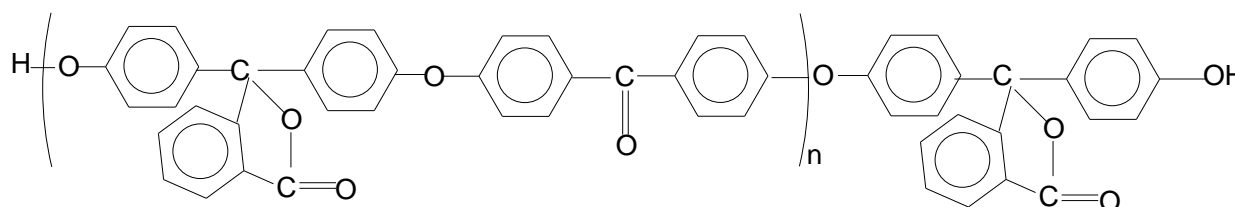


Figure 2: OK-1-20B

Properties of synthesized oligo ketones are given in Table 1.

Table 1: Properties of aromatic oligo ketones

Oligo ketones	Degree of condensation	Output, %	Softening point, °C	Calculated molecular weight	Content of OH-groups, %	
					Calculated	Found
OK-1A	1	94	125-126	634	5,41	5,35
OK-5A	5	94	143-144	2260	1,55	1,60
OK-10A	10	95	156-158	4293	0,84	0,80
OK-20A	20	95	163-166	8358	0,46	0,45
OK-1B	1	94	192-193	814	4,22	4,27
OK-5B	5	95	206-207	2800	1,26	1,25
OK-10B	10	96	223-225	5283	0,69	0,70
OK-20B	20	96	247-250	10248	0,38	0,35

In order to obtain polyetheretherketones with quantitative yield and high molecular weight, the synthesis regularities of aromatic polyetheretherketones based on oligo ketone with $n=1$ acceptor-catalytic polycondensation were studied (Figs. 1, 2). As a result of the conducted studies, as it follows from Fig. 1. 1 and 2, optimal conditions for the synthesis of polyetheretherketone based on oligo ketone OK-1A and dichloroanhydride

1,1-dichloro-2,2-di(p-carboxyphenyl)ethylene (CA) have been determined: solvent - dichloroethane; concentration of initial monomers 0,2 mol/l; synthesis temperature 15-200°C (288-293K); synthesis duration 1 hour ($3,6 \times 10^3$); amount of triethylamine - double excess in relation to oligoketone.

For investigation of some characteristics with observance of the established regularities for oligomer OK-1A polyetheretherketones of different composition and structure

were obtained. Synthesis of polyetheretherketones on the basis of obtained oligo ketones of different degree of condensation was carried out by acceptor-catalytic polycondensation in dichloroethane medium for 1 hour using triethylamine as acceptor-catalyst. Dichloroanhydride 1,1-dichloro-2,2(n-carboxyphenyl)ethylene (CA) was used as an acid component. The polymers were obtained with a quantitative yield and high rates of reduced viscosity. The values of reduced viscosity of 0.5% solution of polymers in dichloroethane are 0.80 - 1.00 dl/g. Higher values of reduced viscosity are characteristic of polymers based on short oligo ketones, which indicates high activity of the latter. The obtained polyetheretherketones have the following structure.

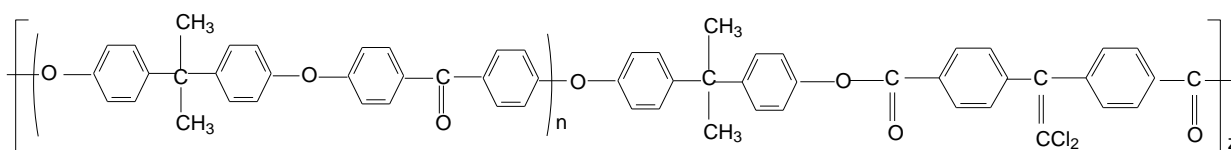


Figure 3: Polyetheretherketone - A

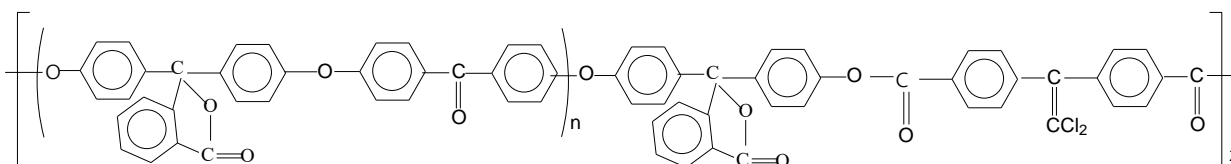


Figure 4: Polyetheretherketone - B

The structure of the synthesized polyetheretherketone is confirmed by elemental analysis, infrared spectroscopy and turbidimetric titration data.

The study of polydispersibility of the obtained polymers showed that the coagulation threshold of polyether ether ketones based on two rows of oligo ketones and dichloroanhydride 1,1-dichlor-2,2-di(p-carboxyphenyl)ethylene decreases with increasing solubility of block-polyetherketones. Thus, it can be concluded that polyetheretherketones based on short oligo ketones should have better solubility at relatively equal molecular weight values. This is due to their lower packing density.

Comparison of two series of polyetheretherketones indicates higher solubility of polyetheretherketone based on OK-B of oligo ketones, which is explained by their structure, i.e. lower

packing density due to the content of volumetric carding groups as compared to polyetheretherketone based on OK-A.

All polyetheretherketones obtained are soluble in dichloroethane, chloroform, tetrachloroethane and insoluble in alcohols, acetone, tetrahydrofuran, dimethylformamide, and others.

The molecular masses of synthesized polyetheretherketones, measured by sedimentation in an ultracentrifuge by the method of approximation to dissolution, are in the range of 40 - 50 thousand. The highest values of molecular mass are typical for polyetherketones based on short oligo ketones. As the length of the initial OKs grows, the molecular weight drops markedly.

The study of thermomechanical properties shows that the values of glass transition temperatures and polyetheretherketones flow depend on the content of flexible simple ester bonds in the chain. Moreover, the share of simple ester bonds in the chain increases with the length (degree of condensation) of the original oligo ketone, which

provides a decrease in the glass transition and flow temperatures of polymers. It is established that the second row of polyetheretherketones is characterized by higher glass transition and flow temperatures, which is due to the introduction of volumetric cardo groupings in the polymer structure (Table 2).

Table 2: Properties of polyetheretherketones

Oligo keton-based polyetheretherketones	Glass transition temperature, K	Stream temperature, K	Tensile strength, MPa	Coefficient of elongation, %
OK-1A	473	516	72,5	14,5
OK-5A	464	509	74,5	13,6
OK-10A	455	495	78,7	11,2
OK-20A	448	483	82,7	8,1
OK-1B	494	523	77,6	18,9
OK-5B	489	517	79,8	16,8
OK-10B	476	510	82,1	15,0
OK-20B	470	498	88,5	9,2

It follows from Table 2 that the obtained polyetheretherketones combine high values of tensile strength with good plasticity. In the ranges of polyetheretherketones with increasing length of initial oligo ketones there is some increase of tensile strength that can be explained by increasing density of chain packing in polyetheretherketones based on longer oligo ketones. This assumption is indirectly confirmed by the drop in the relative elongation of polyetheretherketones samples for both ranges. In ranges of polyetheretherketones with increasing length of initial oligomers a significant increase in thermal resistance is observed (Table 3). The similar character of change of the

given characteristic can be explained by the fact that on the one hand, in these polyetheretherketone ranges the saturation of polymer chain with thermally stable simple ether bonds is observed, on the other hand, the share of low-stable ester bond, introduced into structures by residues of dichloroanhydride 1,1-dichloro-2,2-di(p-carboxyphenyl) ethylene decreases sharply. Besides, with increasing degree of polycondensation of initial oligo ketones packing density of polyetheretherketones considerably increases. Obviously, these three factors contribute to such a natural growth of heat resistance of polyetheretherketones in these ranges.

Table 3: Thermal and fire resistance of polyetheretherketones

No.	Initial oligo keton	Thermal resistance, K			Oxygen index , %
		2%	10%	50%	
1	OK-1A	640	704	832	35,5
2	OK-5A	645	711	830	32,0
3	OK-10A	649	737	840	31,0
4	OK-20A	661	785	856	30,0
5	OK-1B	648	750	836	36,5
6	OK-5B	650	749	837	34,0
7	OK-10B	652	754	840	33,5
8	OK-20B	660	761	851	32,0

In case of thermal destruction of polyetheretherketones, along with decomposition reactions, structuring processes are intensive and this feature is related to the presence of a grouping of polymers in the structure of these polymers

>C=CCl_2 , which is capable of stitching to the double bond opening, which leads to slowdown of the destruction

process. Taking into account all received direct and indirect confirmations of thermal structuring of polyetheretherketones it is possible to assume that structuring process goes on a place of a double bond by the following scheme:

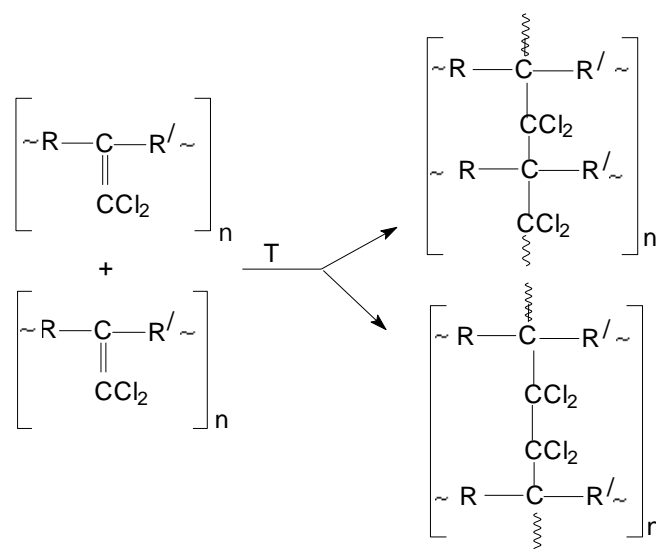


Figure 5

CONCLUSION

The values of the oxygen index of synthesized polyether ether ketones given in Table 3 characterize them as polymers with increased fire resistance, i.e., they do not burn in the air atmosphere. Polyetheretherketones in contact with the flame (or combustion) is charred on the surface, and the resulting coal layer appears to act as a barrier to the transfer of heat from the flame to the polymer, which slows down the release of gaseous pyrolysis products.

Analysis of the obtained results shows that in polyetheretherketone ranges with increasing degree of polycondensation of initial oligo ketones, i.e. with decreasing content of chlorine-containing component (ChA), the oxygen index decreases. Thus, polyetheretherketone at OK-1A does not burn but only charshes, while polyetheretherketone based on longer oligoketones OK-10A and OK-20A burn but does not support combustion. During combustion, these polymers do not form ignition droplets, i.e. polyetheretherketones are not secondary ignition sources.

Thus, using oligo ketones of different composition and structure on the basis of bisphenols and relatively inexpensive and accessible digalogenide 4,4'-dichlorobenzophenone, under sufficiently mild conditions soluble polyetheretherketones with high performance characteristics are obtained.

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Drawings for article A.M. Kharaev

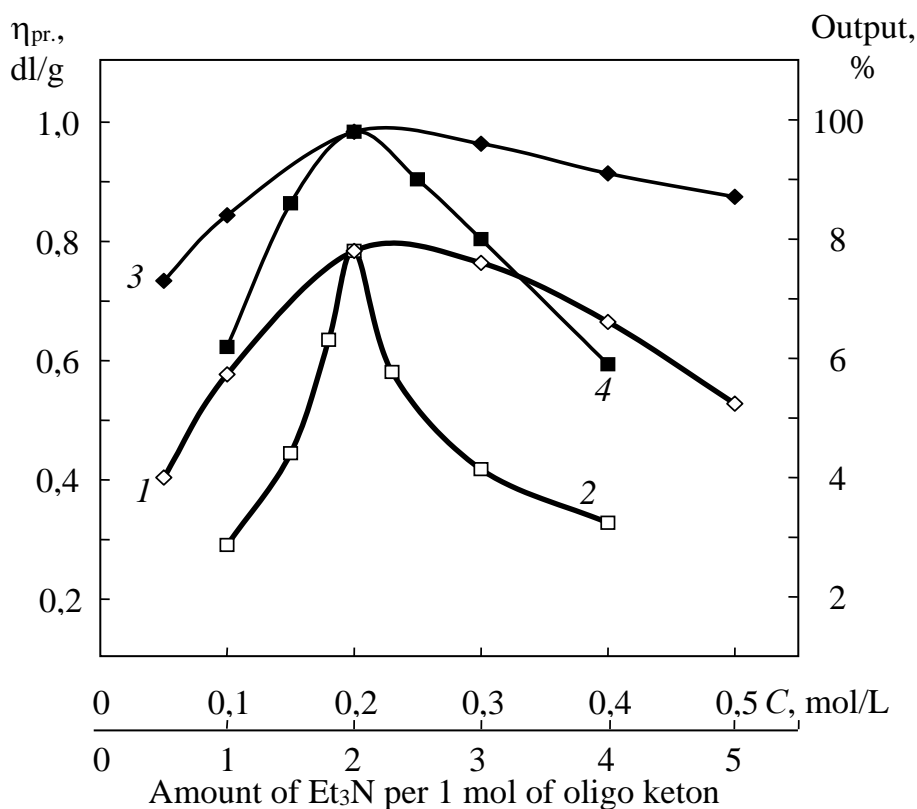


Fig. 1: Dependence of reduced viscosity (1,2) and output (3,4) of polyetheretherketones from concentration of monomers (1, 3) and amount of triethylamine in relation to 1 mol of oligo ketones (2, 4)

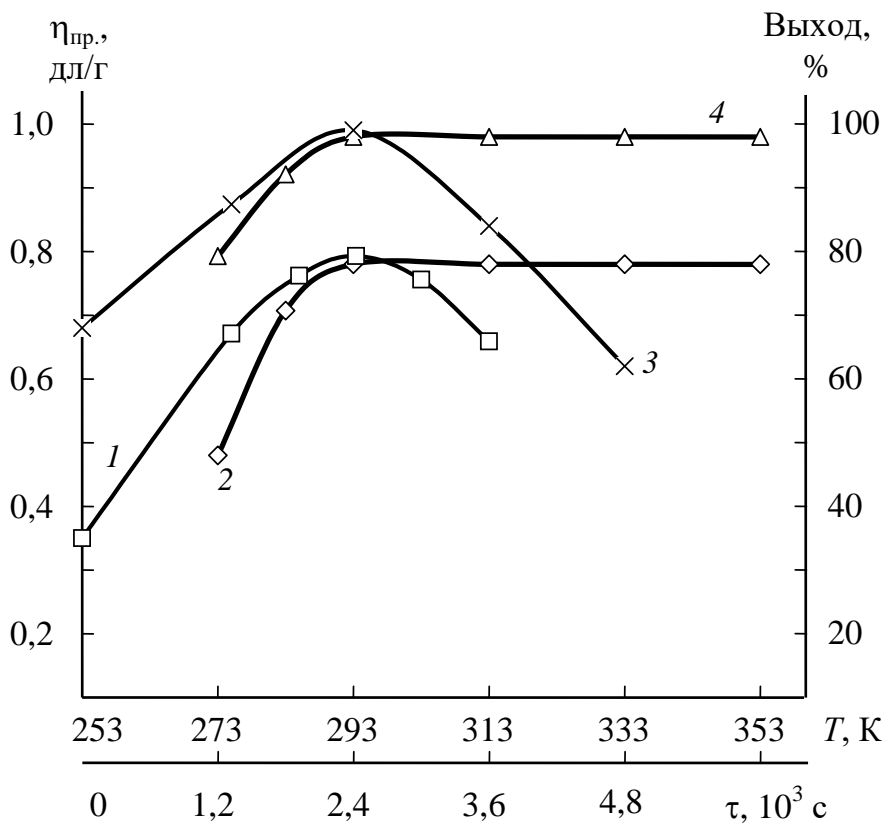


Fig. 2: Dependence of reduced viscosity (1, 2) and output (3, 4) of polyetheretherketones from temperature (1, 3) and synthesis time (2, 4)

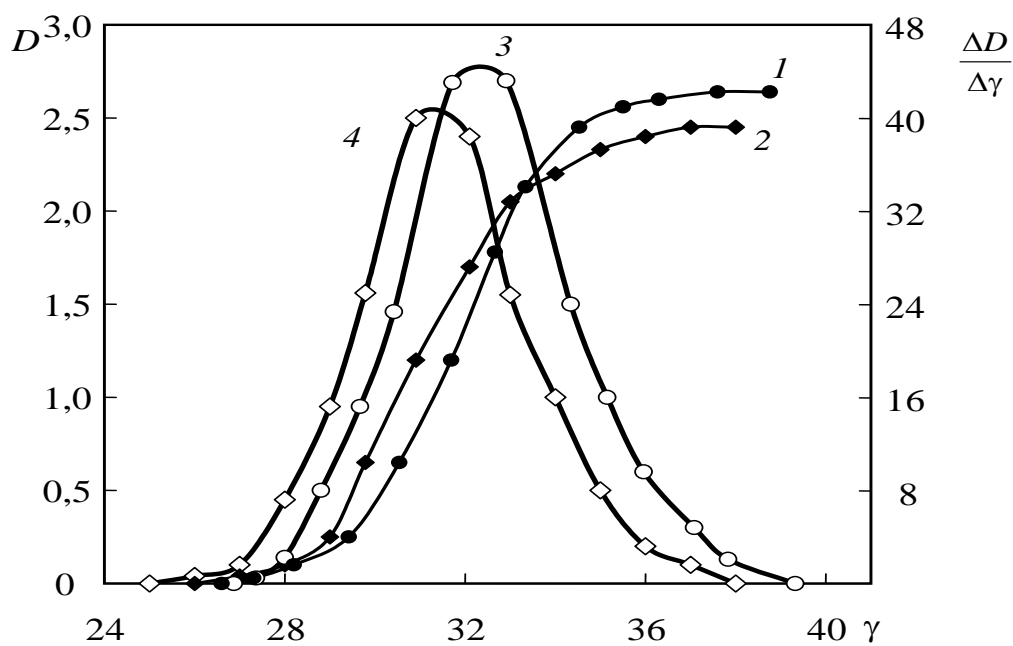


Fig.3a: Turbidimetric titration curves of polyetheretherketones (1, 2 - integral and 3, 4 - differential MMR curves):
1, 3 - OK-1A; 2, 4 - OK-20A

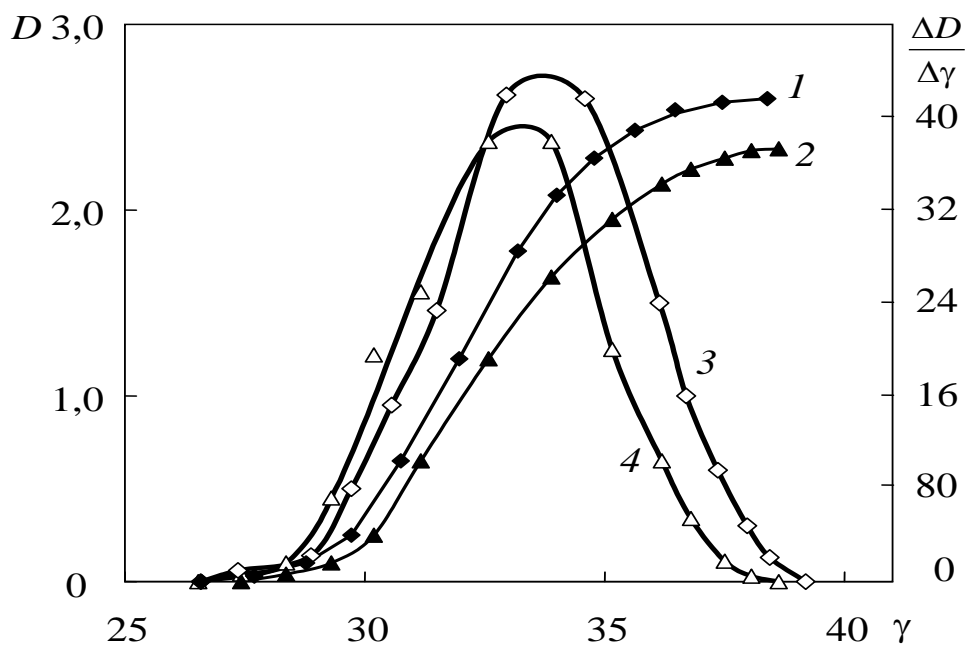


Fig.3b: Turbidimetric titration curves of polyetheretherketones
 (1, 2 - integral and 3, 4 - differential MMR curves):
 1, 3 - KA-1B; 2, 4 - KA-20B)