Synthesis and Properties of Soluble Aromatic PolyetheretherKetones

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ABSTRACT
In order to obtain soluble and relatively inexpensive polyaryletheretherketone by high-temperature polycondensation different oligo ketones based on 4,4ʹ-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.

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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 4,4ʹ-difluorobenzophenone at 300-3400°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 4,4ʹ-difluorobenzophenone with cheaper and more affordable digalogenide, namely 4,4ʹ-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 4,4ʹ-dioxyphthalophenone) and 4,4ʹ-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.

Properties of synthesized oligo ketones are given in Table 1.

![Figure 1](image1.png)

**Figure 1**: OK-1-20A

![Figure 2](image2.png)

**Figure 2**: OK-1-20B

Table 1: Properties of aromatic oligo ketones

<table>
<thead>
<tr>
<th>n</th>
<th>Properties</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td></td>
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<tr>
<td>5</td>
<td></td>
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<tr>
<td>10</td>
<td></td>
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<tr>
<td>20</td>
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</table>
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\(^4\)) ; 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

```
\[
\text{Structure of polyetheretherketone A}
\]
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**Figure 4:** Polyetheretherketone – B

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\[
\text{Structure of polyetheretherketone B}
\]
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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 polyetherketones based on two rows of oligo ketones and dichloroanhydride 1,1-dichloro-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 polyetheretherketones 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

<table>
<thead>
<tr>
<th>Oligo ketone-based polyetheretherketones</th>
<th>Glass transition temperature, K</th>
<th>Stream temperature, K</th>
<th>Tensile strength, MPa</th>
<th>Coefficient of elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>OK-1A</td>
<td>473</td>
<td>516</td>
<td>72,5</td>
<td>14,5</td>
</tr>
<tr>
<td>OK-5A</td>
<td>464</td>
<td>509</td>
<td>74,5</td>
<td>13,6</td>
</tr>
<tr>
<td>OK-10A</td>
<td>455</td>
<td>495</td>
<td>78,7</td>
<td>11,2</td>
</tr>
<tr>
<td>OK-20A</td>
<td>448</td>
<td>483</td>
<td>82,7</td>
<td>8.1</td>
</tr>
<tr>
<td>OK-1B</td>
<td>494</td>
<td>523</td>
<td>77,6</td>
<td>16,9</td>
</tr>
<tr>
<td>OK-5B</td>
<td>489</td>
<td>517</td>
<td>79,8</td>
<td>16,8</td>
</tr>
<tr>
<td>OK-10B</td>
<td>476</td>
<td>510</td>
<td>82,1</td>
<td>15,0</td>
</tr>
<tr>
<td>OK-20B</td>
<td>470</td>
<td>498</td>
<td>88,5</td>
<td>9.2</td>
</tr>
</tbody>
</table>

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 polyetheretherketones 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

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial oligo keton</th>
<th>Thermal resistance, K</th>
<th>Oxygen index, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2%</td>
<td>10%</td>
</tr>
<tr>
<td>1</td>
<td>OK-1A</td>
<td>640</td>
<td>704</td>
</tr>
<tr>
<td>2</td>
<td>OK-5A</td>
<td>645</td>
<td>711</td>
</tr>
<tr>
<td>3</td>
<td>OK-10A</td>
<td>649</td>
<td>737</td>
</tr>
<tr>
<td>4</td>
<td>OK-20A</td>
<td>661</td>
<td>785</td>
</tr>
<tr>
<td>5</td>
<td>OK-1B</td>
<td>648</td>
<td>750</td>
</tr>
<tr>
<td>6</td>
<td>OK-5B</td>
<td>650</td>
<td>749</td>
</tr>
<tr>
<td>7</td>
<td>OK-10B</td>
<td>652</td>
<td>754</td>
</tr>
<tr>
<td>8</td>
<td>OK-20B</td>
<td>660</td>
<td>761</td>
</tr>
</tbody>
</table>

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 \( \overset{\text{C=C}}{\text{C=CCl₂}} \), 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:
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 chars, 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 4,4ˈ-dichlorobenzophenone, under sufficiently mild conditions soluble polyetheretherketones with high performance characteristics are obtained.

REFERENCES

Drawings for article A.M. Kharayev

**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)