

# Synthesis of *Block* Copolyetherether Ketones and Investigations of Their Properties

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**ABSTRACT:** Using oligoketones with different degrees of condensation ( $n = 1, 10, 20$ ), dichlorides of isophthalic and terephthalic acids and 2,2-bis[4-hydroxyphenyl]-propane *block*-copolyetherether ketones (BCPEEKs) were synthesized by means of acceptor–catalytic polycondensation. Their properties were also investigated. It was shown that BCPEEK possesses good solubility, high molecular weight, and is characterized by high thermal and mechanical properties. The correlation between some properties of the polyethers and the degree of condensation of oligoketones was also investigated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 485–490, 2002

**Key words:** poly(etherether ketone); oligoketone; step polymerization; molecular mass; thermal stability

## INTRODUCTION

In recent years there has been a great deal of work on the synthesis of poly(etherether ketones) (PEEKs) and investigations of their mechanical and thermal properties. PEEKs possess good physical and chemical properties.<sup>1–4</sup> They are largely used as construction materials and coating elements of electric transmission wires, which may be under operation for long periods of time at temperatures up to 200°C. Although the cost of PEEK is 5–20 times higher than that of the ordinary polymers used as construction materials, the excellent properties of PEEKs guarantee wide use in all branches of the economy.<sup>5</sup>

Poly(ether ketones) (PEKs) based on different oligoketone phenolphthaleines (OKPP) with different degrees of condensation were investigated in our laboratory and the results reported.<sup>6,7</sup> Similarly, poly(etherether ketones) (PEEK) were syn-

thesized from OKs of 2,2-bis[4-hydroxyphenyl]-propane (bisphenol A) containing hydroxyl end groups and equimolar mixtures of dichlorides of isophthalic and terephthalic acids; their properties were also reported in the literature.<sup>8</sup>

As a continuation of this research, in the present study different OKs were reacted with bisphenol A and a *block-co*(PEEK) (BCPEEK) was obtained by the polycondensation method. The tensile, thermal, and dielectric properties of the new copolymer were investigated.

## EXPERIMENTAL

### Materials and Processing

This study investigated the properties of PEEKs, which were synthesized from OKs of bisphenol A containing hydroxyl end groups and an equimolar mixture of dichlorides of isophthalic and terephthalic acids. The chemically pure bisphenol A was obtained from Mitsui Co. Ltd. The dichlorides of phthalic acids were obtained from Gosniichlor-

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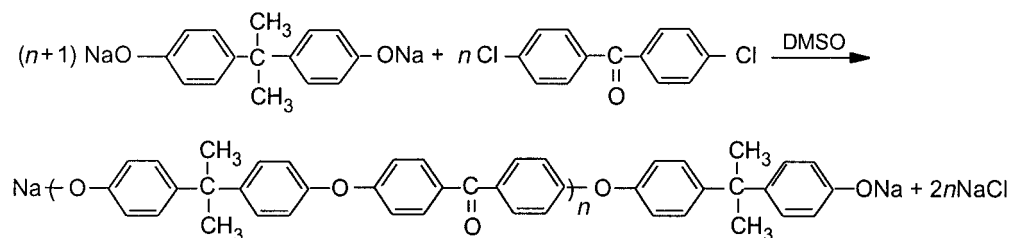
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proekt. The OKs with different degrees of condensation (OK-1D, OK-10D, OK-20D for condensation degrees of 1, 10, and 20, respectively) were synthesized by means of the interaction of a salt of diphenylpropane with 4,4'-dichlorodiphenylketone in anhydrous dimethylsulfoxide (DMSO) according to analogous techniques for the production of oligosulfones.<sup>7</sup>

Initially, 4,4'-dichlorodiphenylketone was obtained from 4,4'-dichlorodiphenyltrichloromethylmethane (DDT) in two steps: in the first stage 1,1-

dichloro-2,2-di-(4-chlorophenyl)ethene was synthesized from DDT by means of dehydrochloration; in the second stage this product was reacted with chromic anhydride in glacial acetic acid, and 4,4'-dichlorodiphenylketone with a melting temperature of 146°C was obtained. The process was described by Yanota et al.<sup>9</sup>

The disodium salt of bisphenol A was reacted with 4,4'-dichlorodiphenylketone in the DMSO solvent. The products obtained were light-brown colored powders.

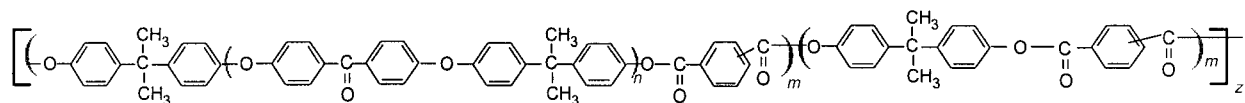


The OKs were then cleaned in distilled water until no chloride ions were left. Some of the properties of these OKs are given in the literature.<sup>8</sup>

Then the BCPEEKs based on OKs indicated above and bisphenol A were obtained by acceptor-catalytic polycondensation in dichloroethane for 1 h at 20°C. An equimolar (1:1) quantity of OKs and bisphenol A was used. The dichlorides of

isophthalic and terephthalic acids were used in a molecular ratio of 1:1. The resulting material was poured into isopropyl alcohol and the copolymer was filtered. Finally it was cleaned in distilled water.

Triethylamine was employed as the proton acceptor catalyst. The resultant BCPEEKs had the following structure:



## Test Methods

### Viscosity Measurements

The viscosity measurements were made according to GOST 10028-81 (Russian State Standards) using an Ubbelohde viscometer with a diameter of 0.56 mm. The experiments were conducted at room temperature (20°C), and the concentration of polymer in the solution was 0.5 g/dL. Dichloroethane was used as a solvent.

### Molecular Structure and Weight Measurement Tests

The properties of the BCPEEKs were investigated by various methods. Their molecular structure was identified by a Perkin-Elmer 283 IR

spectrometer. The copolymer is dissolved in dichloroethane and the solution is poured into a 100-mm diameter plate. After the solvent is evaporated the copolymer is heated under a vacuum to 100°C and kept at this temperature until the weight changes stabilized. Then the IR measurements were performed.

The molecular weight of the linear BCPEEKs was measured by the sedimentation method on a 317 V-MOM ultracentrifuge. In the equilibrium approaching method that was used the cell is rotated at a relatively low speed until an equilibrium is attained, whereby the centrifugal forces balance the tendency of the molecules to diffuse back against the developed concentration gradient. Measurements are made of the equilibrium concentration profiles for a series of solutions

with different initial polymer concentrations so that the results can be extrapolated to  $c = 0$ , where  $c$  is zero concentration.<sup>10</sup>

### Mechanical Tests

The measurement of the mechanical properties of the BCPEEKs was carried out according to GOST 17-316-71 (Russian State Standards) by using film specimens ( $100 \times 10 \times 0.1$  mm) on a tensile testing machine (MRS-500) with a constant deformation rate of 40 mm/min at 20°C. The film test specimens were obtained by pouring the polymeric solution onto a surface and letting the dichloroethane evaporate. Then the resultant polymeric sheet was put into an SPT-200 oven under a vacuum at 100°C for 2 h and dried.

### Thermomechanical and Other Property Tests

Thermomechanical analyses of the polymers was conducted under room (atmospheric) conditions. The tests were carried out on a Pribor thermomechanical analyzer. The temperature was increased at the rate of 4°C/min and the load was maintained to give a constant stress value of 0.05 MPa. The thickness and width of the test specimens were 0.1 and 8 mm, respectively, and the distance between the clamps was 80 mm. A thermal chamber with a diameter of 30 mm and length of 150 mm was employed. The temperature gradient of the thermal chamber was 2°C along the length and 0.1°C along the diameter. The deformation of the specimen was measured by a strain gauge. The temperature and deformation were recorded on an  $x$ - $y$  recorder.

Thermogravimetric analysis of the specimens was carried out by a MOM derivatograph. The temperature was increased at the rate of 5°C/min in air.

Investigation of the polydispersity of the block copolymers was conducted by the turbidimetric titration method on a FEC-56M device. The principle of titration is that the diluted polymeric solution will become turbid if a nonsolvent is added and will have a different optical density from the original solution. The turbidity increases with the amount of the nonsolvent until the polymeric solution forms a stable suspension. The resulting optical density and corresponding nonsolvent volume are related to the dispersity of the polymer. In the present work dichloroethane and isopropanol were used as the solvent and nonsolvent, respectively. The polymer solution had a concentration of 0.05 g/m<sup>3</sup>.

The fire resistivity of the polymers was evaluated by the oxygen index method. The dielectric properties of the polymer were investigated by the dielectric weight loss method on a Kumetre VM-560 Tesla machine at a frequency of  $10^6$  Hz and with a temperature interval of 20–300°C.

The crystallinity of the copolymer was measured by means of X-ray diffraction Analyses on a DRON-3 instrument. The diffraction graphs were obtained by a CUPRUM analyzer using Cu radiation with a wavelength of 1.5405 Å.

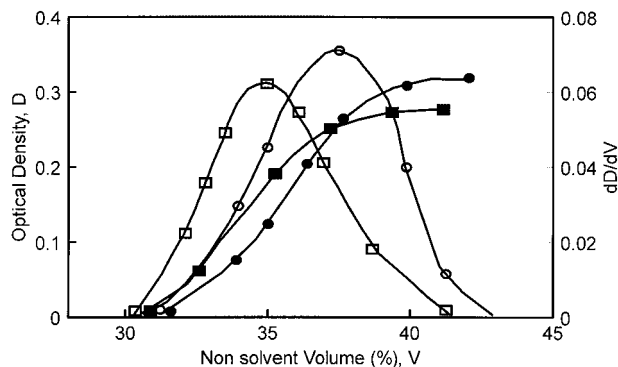
## RESULTS AND DISCUSSION

### Molecular Structure and Molecular Weight Measurement Tests

The data obtained from the elemental analysis, IR spectroscopy and turbidimetric titration were used to confirm the given chemical structure of the polymers. The molecular mass of BCPEEK was in the interval of 100.000–230.000 g/mols. The highest molecular weights were obtained from the OKs with a polycondensation degree of 1. As the lengths of the initial OKs grew, the molecular masses of BCPEEKs decreased substantially. These results agree with the literature about PEEKs.<sup>8</sup>

The IR spectra results showed that the resultant bands of absorption peaks correspond to different bonds and groups. The presence of absorption bands that corresponds to ether bonds, ( $920$ – $940$  cm<sup>-1</sup>), ester bonds ( $1000$ – $1300$  cm<sup>-1</sup>), isopropylidene groups ( $1350$ – $1360$ ,  $1385$ ,  $2875$ ,  $2970$  cm<sup>-1</sup>), and diarylketone groups ( $1600$ – $1675$  cm<sup>-1</sup>); the ester carbonyl stretching frequency was recorded as  $1735$  and  $1745$  cm<sup>-1</sup>. The absence of hydroxyl groups ( $3600$  cm<sup>-1</sup>) points to the fact that the polycondensation of the copolymers and dichlorides of isophthalic and terephthalic acids were completed and their properties were manifested.

The results of the turbidimetric titration confirmed the structure of the above-mentioned copolymers (see Fig. 1). The differential curves for each copolymer show only a single maximum, which means that the reactants of the copolymers are statistically mixed. On the other hand, the differential maximums change as a function of the condensation rate of OK. This means that the resulting formation is a block copolymer and not a mixture of homopolymers.

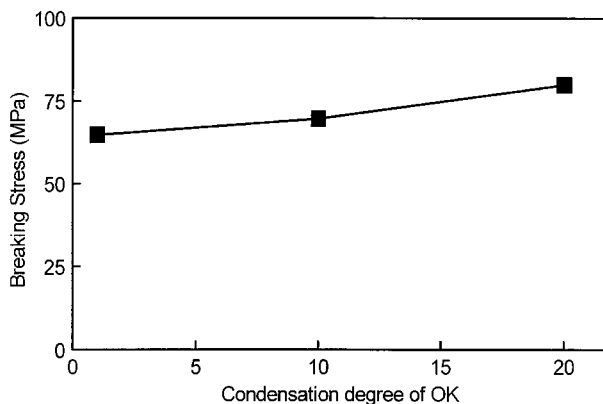


**Figure 1** The dimetric titration curves of BCPEEKs as (■, ●) integral curves and (□, ○) differential curves from the molecular mass distribution tests for BCPEEKs obtained from (●, ○) OK-1D and (■, □) OK-20D.

To further investigate the composition of the BCPEEKs, quantitative elemental analysis was carried out in a special laboratory of the Institute of Electromagnetic Compounds of the Academy of Science. The specimens were burned and the products were separately analyzed. The results showed that the difference between the theoretically calculated and the experimentally measured atomic mass of the elements such as C, H, and O was not larger than 0.15%. The BCPEEKs are characterized by a high viscosity (Table I). As the condensation rate of the initial OKs increased, the inherent viscosity decreased.

All of the results of the IR spectrometry, turbidimetric analyses, elemental mass analyses, and viscometric results testify to the fact that the resultant material is BCPEEK.

The coagulation threshold of the BCPEEKs obtained from the short OKs is in the regions of the larger nonsolvent volume (Fig. 1). Probably the increase in the initial length of the OKs leads to the increase of poly(etherether)'s packing density



**Figure 2** The dependence of the breaking stress of BCPEEKs on the degree of polycondensation of OKs.

and thus the coagulation threshold moves to the left, where the volume of the nonsolvent is less (Fig. 1). The introduction of bisphenol A seems to have improved the solubility of BCPEEKs.

### Mechanical Properties

The BCPEEKs demonstrated high tensile strength values combined with high ductility. Figure 2 shows that the breaking stress of PEEKs increased with the increase of the condensation degree of the initial OKs (from 65 to 85 MPa) while the ductility decreased (Fig. 3). Such a change in the breaking strengths may serve as a confirmation of the above assumption that the packing density in the chains of BCPEEKs varies, depending on the formation process.

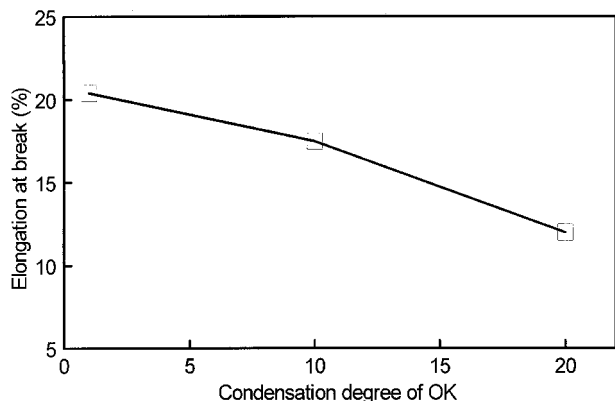
### Thermomechanical Properties

The thermomechanical tests showed that the newly synthesized BCPEEKs were characterized with comparatively low values for the glass-transition temperature ( $T_g$ ); (Fig. 4) and melt temper-

**Table I** Properties of BCPEEKs

BCPEEKs Obtained from	Mass of Stabilizer (%)	$\eta^a$ (m <sup>3</sup> /kg)	Thermal Stability (°C)		
			2% Mass Loss	10% Mass Loss	50% Mass Loss
OK-1D	98.8	0.30	390	480	572
OK-10D	98.5	0.25	402	488	580
OK-20D	98.0	0.14	410	510	600

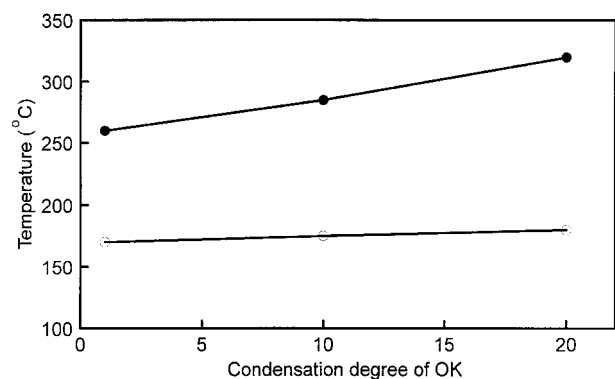
<sup>a</sup>The inherent viscosity.



**Figure 3** The dependence of the elongation at break of BCPEEKs on the degree of polycondensation of OKs.

ature ( $T_m$ ). This fact may be explained by the presence of a large number of simple flexible etheral bonds in their main chains. On the other hand, it should be noted that some increase in the  $T_g$  and  $T_m$  (Fig. 4) with the increase of the lengths of the initial OK is due to the fact that the saturation of the polymeric chain by flexible simple etheral bonds is accompanied by the increased density of the chain packing. This in turn causes a decrease in the mobility of the macromolecules.

It should be noted that the lower values of these thermodynamical characteristics in the series of BCPEEKs with lower condensation degrees is related to the fact that, although the polymeric chain is saturated with flexible simple bonds, the packing density of the main chain increases. This density increase causes a decrease in the macromolecular mobility. The growth of the ordering decreases the macromolecule mobility and the loss of mobility causes the rise of the



**Figure 4** The dependence of the (○) glass-transition and (●) melt temperature of BCPEEKs on the degree of polycondensation of OKs.

**Table II** Dependence of Properties of BCPEEKs on Temperature

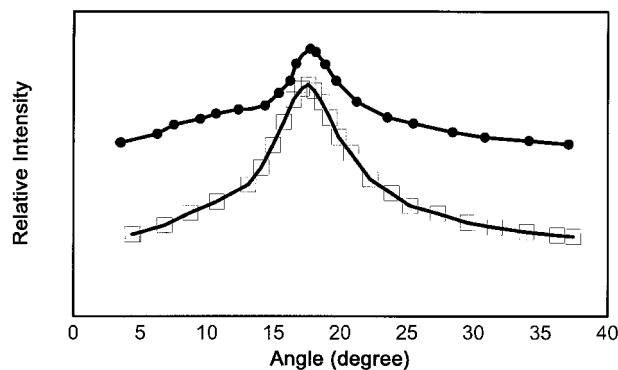
BCPEEKs Obtained from	Temperature (°C)	Dielectric Loss	$\tan \delta \times 10^2$
OK-1D	20	3.81	0.13
	100	3.80	0.14
	200	4.05	0.07
	300	4.88	3.33
OK-10D	20	3.63	0.23
	100	3.60	0.27
	200	3.90	0.21
	300	4.85	4.01
OK-20D	20	3.71	0.46
	100	3.80	0.40
	200	4.04	0.32
	300	4.20	4.13

$T_g$  and  $T_m$  of the BCPEEKs with higher condensation rates of the initial OKs (longer oligomers).

The data obtained from the thermogravimetric analysis showed that (Table I) the BCPEEKs possess high indices of thermal resistance (i.e., they start to lose weight at high temperatures). It should be noticed that for all synthesized polymers the 2% loss of their mass took place at around 400°C or higher. The comparison of the results shows that as the condensation rate of the initial oligomers increases, the thermal stability of BCPEEKs (obtained from OKs and bisphenol A) also increases steadily. The higher thermal resistance shown by the BCPEEK obtained from long OKs may be attributed to the higher content of stable simple etheral bonds and compact packing. This phenomenon can be explained in this way: as the molecular chains of the polymer were saturated by thermally stable ether bonds, the effect of the thermally unstable ester bonds (introduced by the remainders of the dichlorides of phthalic acids) falls abruptly. Besides, the density of the BCPEEK pack grows considerably with the increase of the length of the initial oligomers. All these effects enhance the thermal stability of BCPEEK.

The dielectric constant and the  $\tan \delta$  of the dielectric loss angle for the three synthesized BCPEEKs (with three different OKs) are presented in Table II. For the glassy state, the values of the dielectric permeability were between 3.63 and 3.81 and the  $\tan \delta$  values of the dielectric loss were in the range of  $(0.13\text{--}0.46) \times 10^{-2}$ . The resultant BCPEEKs do not contain strongly polar





**Figure 5** The relationship between the X-ray diffraction and the angle for (●) OK-1D and (□) OK-20D.

groups and substituents that could considerably influence the dielectric characteristics of the polymers. Probably this is the reason for the relatively low and similar values of the BCPEEK indices. As it is known,<sup>8</sup> under similar conditions the lower values of the dielectric characteristics correspond to the more compact packing of the polymers. This higher packing may also be responsible for the observed decrease in the  $\tan \delta$  (see Table II) of the BCPEEKs with longer OKs. The small differences in these dielectric characteristics may be attributed to the different molecular packings of the polymers, and the lower values of the dielectric characteristics correspond to the more compact packing of the copolymers.

The dielectric properties strongly depend on the temperature. As the BCPEEKs are subjected to different temperature environments, the change in the dielectric properties is also expected. It is clear that as the temperature approaches the  $T_g$ , the frozen molecular chains start to mobilize and recover their orientations. Although the molecular movements may occur along the main polymeric chain segment, the side groups may also mobilize and tend to reorient around the main chains. All these behaviors may account for the increased dielectric loss values of BCPEEKs at higher temperatures (see Table II).

The X-ray diffraction results (Fig. 5) reveal the amorphous nature of the synthesized copolymer.

## CONCLUSION

The BCPEEKs were obtained from OKs with different condensation degrees and dichlorides of

isophthalic and terephthalic acids of bisphenol A. The mechanical and thermal properties were investigated. As the condensation degree of the monomers increased, so did the density, thermal stability, and tensile strength. Low dielectric loss properties were obtained for BCPEEKs. Because of the high thermal, electrical, and mechanical characteristics of the BCPEEKs, they are suggested for the use of thermally stable construction and sheet materials.

The increase in the breaking strength and thermal properties of BCPEEKs with the initial length of OKs indicates in all cases that the experimental procedures (within the error limits) give reliable results. Although the titration method may be susceptible to errors, it is clear that the overall titration results indicate the uniform composition of the polymer.

The results agree with the literature in which PEEKs obtained from bisphenol A and 4,4'-dichlorodiphenylketone<sup>7</sup> and PEKs obtained from OKPPs<sup>8</sup> with different degrees of condensation and dichloranhydrides of isophthalic and terephthalic acids showed improved thermal and mechanical behaviors with an increased degree of condensation.

## REFERENCES

1. Shaov, A. H.; Charaev, A. M.; Mikitaev, A. K.; Kardanov, A. V.; Hasbulatova, Z. S. *Plast Massy* 1990, 11, 14. [in Russian].
2. Shav, A. H.; Charaev, A. M.; Mikitaev, A. K. *Plast Massy* 1990, 12, 35. [in Russian].
3. Thorsen, K. A. *SMEA* 1989, 2, 14.
4. Seymour, R. B. *Rev Plast Mod* 1989, 40, 120.
5. Golemme, G.; Drioli, A.; Lufan, F. *Vysokomolek Soed* 1994, 36, 1946.
6. Mikitaev, A. K.; Shustov, G. B.; Charaev, A. M.; Korshak, V. V.; Kunizhev, B. I.; Dorofeev, V. T. *Vysokomol Soed A* 1984, 26, 75.
7. Ozden, S.; Charaev, A. M.; Shaov, A. H.; Shustov, G. B. *J Appl Polym Sci* 1998, 68, 1013.
8. Ozden, S.; Charaev, A. M.; Shaov, A. H. *J Mater Sci* 1999, 34, 2741.
9. Yanota, H.; Malov, E.; Moskvichev, Y. A.; Mironov, G. S. *J Org Himia* 1985, 21, 365.
10. Young, R. J.; Powell, P. A. *Introduction to Polymers*, 2nd ed.; Chapman & Hall; London, 1997; p 202.