

The Synthesis of Block Copolyetherketones Based on 4,4'-Dichlorodiphenylketone, Phenolphthaleine, and Bisphenol A and Investigation of Their Properties

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ABSTRACT: Block structured polyethers based on phenolphthaleine, 4,4'-dichlorodiphenylketone, and bisphenol A with different degrees of condensation ($n = 1, 5, 10,$ and 20) were synthesized by means of acceptor-catalytic polycondensation. Equimolar quantities of chloranhydrides of iso- and terephthalic acids were used. Higher molecular masses were obtained from longer oligoketones with higher condensation

degrees. Better molecular packing, increased thermal and mechanical properties were obtained with higher condensation degrees of oligoketones. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2459–2465, 2008

Key words: polyetherketones; polycondensation; thermal properties and mechanical properties

INTRODUCTION

The aromatic polyethers have an important place among the high molecular polycondensed polymers because of their combined high thermal stability, high tensile strength, and chemical resistivity to aggressive media. The polyethers may combine various properties of different polymeric materials. There has been a large extent of work on polyethers and their combinations with other materials. Yang et al.¹ have investigated the thermal and mechanical properties of polyethersulfone/poly(phenylene) sulfide blends. They have shown that, the impact strength was improved by the blending with poly(phenylene) sulfide while the high strength of the polyether was maintained. Another work² indicated that the fracture toughness of the polyether sulfone is increased by blending with thermotropic crystal polymers.

Schuur et al.³ synthesized block copolyether based on poly(propylene oxide) and terephthalates. High molecular weight poly(propylene oxide) block copolymers were obtained following a 2 h the reaction at 250°C under vacuum. Higher temperatures (280°C) and longer times resulted in lower inherent viscosities, probably due to degradation of the polyether. Karger-Kocsis and Gryshchuk⁴ modified bisphenol-A and novolac-based vinyl ester resins by a polyisocyanate.

Polyetheretherketones (PEEK) also have an important place in industry. They are good engineering materials possessing high physical and chemical properties.⁵ They are largely used as construction materials and coating element of the electric transmission wires which may be under operation for a long times up to 200°C and higher temperatures. Although the cost of PEEK is much higher than that of the ordinary polymers used as construction materials, the excellent properties of PEEKs guarantees a wide use in all branches of the economy.^{6–8}

PEEKs are used as sleeveings on the electrical harnesses in their large aircraft engines.⁹ They can be machined and honed to very tight tolerances, providing a perfect fit on the shaft¹⁰ and used as a sanitary insulator because of excellent mechanical strength and its ability to withstand the high temperatures and pressures encountered in the food, pharmaceutical, pulp and paper, and chemical industries.¹¹

The PEEKs are readily used with other polymeric and metallic elements to compose high-performance engineering copolymers and composites. Extrand et al.¹² injected carbon fiber poly(etheretherketone) (CF PEEK) into a mold containing one-half of a poly(ether imide) (PEI). They found that, these PEI/CF PEEK composites retained much of their strength and dimensional integrity at temperatures as high as 200°C. They suggested found adhesion between the PEI and CF PEEK.

Mercer et al.¹³ synthesized aromatic poly(etherketone)s with cyano, oxadiazole, and pyridazine moieties. The resultant films of the aromatic polyether

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TABLE I
Elemental Analysis Results of BCPEEKs

Oligoketons	Degree of condensation	Yield	Softening temperature, T_s ($^{\circ}\text{C}$)	Molecular mass (calculated)	% Content of OH-groups	
					Calculated	Measured
OK-1D	1	98.0	196–200	814.85	4.17	4.20
OK-5D	5	98.5	210–215	2800.94	1.21	1.20
OK-10D	10	99.0	237–244	5283.75	0.64	0.65
OK-20D	20	99.0	255–260	10,248.77	0.33	0.30

ketones displayed good thermal stability and flexibility. Lakshmi et al.¹⁴ sulfonated a commercially available PEEK in powder form in concentrated sulfuric acid different reaction conditions.

Goyala et al.¹⁵ obtained dense and homogeneous high-performance PEEK matrix composites incorporating Al_2O_3 up to 50 wt %. They observed improvement in the thermal stability of the composites due to strong interaction or interfacial bonding between the PEEK matrix and the Al_2O_3 particles. In another work, Goyala et al.¹⁶ have prepared the dense new high-performance PEEK matrix composites incorporating aluminum nitride (AlN) up to 50 wt % by solution blending followed by hot pressing. They observed increased thermal stability, char yield Vickers hardness, crystallinity, melting point, and hot crystallization temperature. They attributed these improvements to the good interfacial adhesion between AlN particles and polymer matrix.

Zhang et al.¹⁷ prepared a series of block copolymers composed of PEEK and poly(ether ether ketone) (PEEKK) components were prepared from their corresponding oligomers via a nucleophilic aromatic substitution reaction and their copolymers showed good tensile properties.

Rath et al.¹⁸ obtained flexible composite of PEEK and liquid crystalline polymer (LCP) in presence of polyphosphazene by blending. They observed an increase in the elongation as well as enhanced modulus and strength good adhesion between the matrix and dispersed phase upon addition of polyphosphazene to ketone based polymer (PEEK) with LCP.

There has been a wide range of research going at our laboratory for a long time. We have synthesized and evaluated the properties of different new polyethers. Polyetherketones (PEK) based on different oligoketone-phenolphthaleins and 4,4'-dichlorodiphenylketone with different condensation degrees was reported.¹⁹ Similarly, PEEK were synthesized from oligoketones of 2,2-bis[4-hydroxyphenyl]-propane (bisphenol A) and 4,4'-dichlorodiphenylketone.²⁰ A new unsaturated block copolyether was obtained from a monomer described as 1,1-dichloro-2,2-di(4-oxophenyl)ethylene, polysulphone, and bisphenol A (or phenolphthaleine).²¹ The resultant unsaturated block copolyethers were characterized with high mechanical

and thermal properties. The impact strength results of the copolyethers were compared with some of the industrial polymers reported in the literature.²² The new materials differed from the conventional polymers, especially, by their high impact strength properties. Different oligoketones were reacted with bisphenol A and a block copolyetheretherketone was obtained by the polycondensation method.²³

As a continuation of the research, oligomers of 4,4'-dichlorodiphenylketone and phenolphthaleine were reacted with bisphenol-A and a new block copolyether was synthesized and its mechanical and thermal properties were investigated.

EXPERIMENTAL PROCEDURE

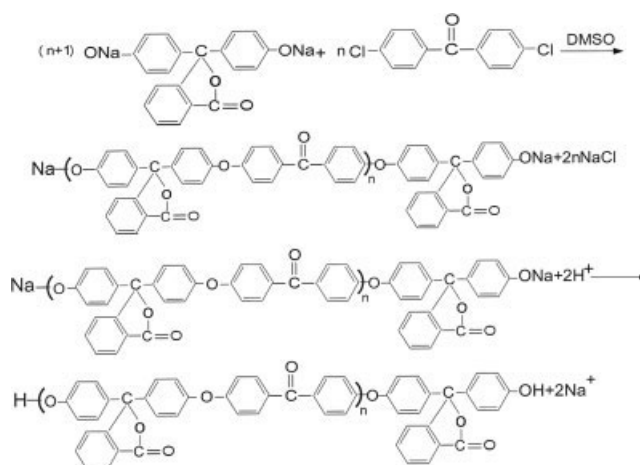
Material and processing

In this work, a new copolyethers based on phenolphthaleine, 4,4'-dichlorodiphenylketone, and bisphenol-A were synthesized. Initially, oligoketones with different condensation degrees (OK-1D, OK-10D, OK-20D for condensation degree $n = 1$, $n = 10$, and $n = 20$, respectively) were synthesized by reacting phenolphthaleine with 4,4'-dichlorodiphenylketone in anhydrous dimethylsulfoxide (DMSO). Later the oligoketones were precipitated in acidic water and dried at 100°C . The resultant powdered oligoketones had a brownish color.

The reactions for oligoketones were as follows:

To confirm the identity of the resultant product, a quantitative elemental analyses and IR spectroscopy analyses of oligoketones were conducted. The atomic mass measurements were performed in a special laboratory of the Institute of Electromagnetic Compounds Academy of Science. The calculated and measured atomic masses of the elements were compared (see Table I). The other properties of oligoketones were also supplied in the same table.

The IR-spectra results of oligoketones showed that the resultant bands of absorption peaks correspond to different bonds and groups. The presence of absorption bands corresponding to ether bonds, (1135 cm^{-1}) lactone group ($1710\text{--}1760\text{ cm}^{-1}$), and C=O groups ($1600\text{--}1675\text{ cm}^{-1}$) point to the fact that the resultant material is the above oligomer.

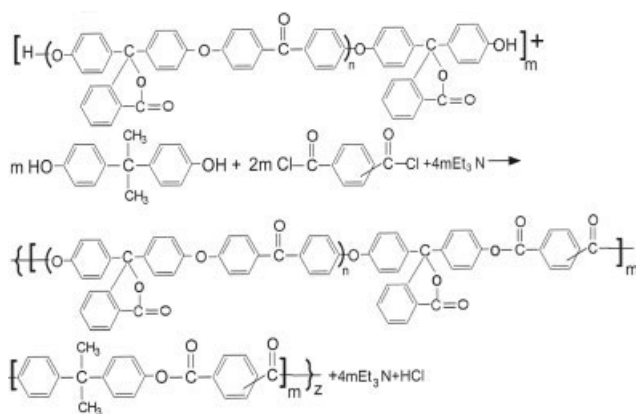


Scheme 1 The synthesis of oligoketones.

Block copolyetheretherketones (BCPEEKs) based on the synthesized oligoketones and bisphenol A were obtained by acceptor-catalytical polycondensation. Fresh-distilled dichloroanhydrides of isophthalic and terephthalic acids were used as acidic components in 1 : 1 ratio. Polycondensation was carried in a dichloroethane medium with triethylamine as acceptor-catalyzer. The initial monomer concentration was 0.2 mol/L, the polymerization temperature was 15–20°C. The polymerization lasted for 1 h. The quantity of triethylamine was the double of the dioxyl compositions. The synthesis was conducted as the according to the following scheme (Schemes 1 and 2).

After polymerization was completed, the low molecular products of reaction were washed off from the BCPEEKs and the product was dried in vacuum at 100°C.

To confirm the identity of the resultant product, a quantitative elemental analyses and IR spectroscopy analyses were conducted (see Fig. 1). The atomic mass measurements were performed in a special laboratory of the Institute of Electromagnetic Com-



Scheme 2 The polymerization of BCPEEKs.

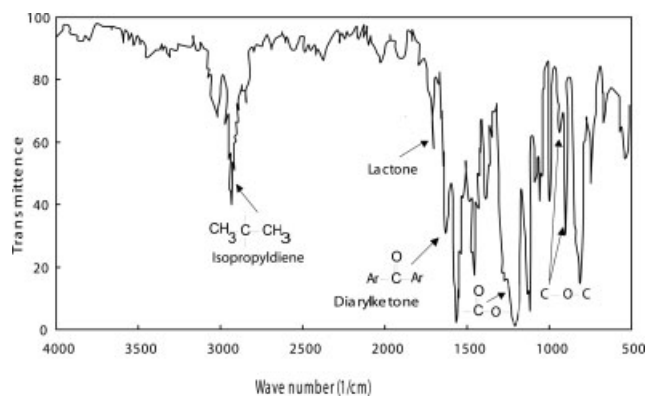


Figure 1 The IR spectrum of BCPEEK based on OK-5D.

pounds Academy of Science. The calculated and measured atomic masses of the elements were presented in table.

Test methods

IR measurements and elemental analyses

The molecular structure of benzoic acid and the new copolyester was identified by a “Perkin–Elmer 283” in 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 vacuum up to 100°C and kept at this temperature, and then the IR measurements were performed. A quantitative element analyses experiment was carried out. The specimens were burnt and the products were separately analyzed.

Viscosity measurements

The viscosity measurements were made according to GOST 10,028-81 (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 density of the solution was 0.5 g/dL. Dichloroethane was used as a solvent.

Molecular structure and weight measurement tests

The molecular weight of block copolyethers was measured by sedimentation method on an ultracentrifugal 317 V-MOM (made in Hungary) machine by equilibrium approaching method. In this method, the cell is rotated at a relatively low speed (5000–10,000 rpm) until equilibrium is attained whereby the centrifugal forces balance the tendency of the molecules to diffuse back against concentration gradient developed. Measurements were made of the

equilibrium concentration profiles for series of solutions with different initial polymer concentrations so that the results can be extrapolated to $c = 0$, where c is zero concentration.²⁴

Mechanical tests

The measurement of the mechanical properties of block copolyethers was carried out according to GOST (Russian State Standards) 17-316-71 by using film specimens ($100 \times 10 \times 0.1$ mm) on a tensile test 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 to a surface and letting the gaseous material to evaporate.

Thermomechanical and other tests

Amorphous polymers can exist in three physical conditions. These are glassy, rubbery (highly elastic), and viscous-flow regions. The polymer test specimens are subjected to a constant stress and the temperature is slowly increased. The deformation of the polymer is measured as a function of temperature. In the displacement-temperature diagram the phase changes are clearly marked. The glass transition temperature is taken as a temperature where the polymer changes from glassy state to a rubbery state and the softening temperature is the temperature at which the material becomes viscous.

Thermomechanical analyses of the polymers were conducted in the room (atmospheric) conditions. The tests were carried out on a Pribor thermo mechanical analyser. The temperature was increased at the rate of 4°C/min and the load was kept to give a constant stress value of 0.05 MPa. The thickness and the width of the test specimens were 0.1 and 8 mm, while the distance between the clamps was 80 mm. A thermal camera with a diameter of 30 mm and length of 150 mm were employed. The temperature gradient of the thermal camera 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 analyses of the BCPEEKs were carried out on a "MOM" derivatograph (made in Hungary) under a temperature increase rate of 5°C/min in atmosphere.

The investigation of the polydispersity of the block copolymers were conducted by turbidimetric titration method on a FEC-56M device. The principle of titration is that the diluted polymeric solution will turbid if a precipitator is added and will have a different optical density from the original solution. The turbidity increases with the amount of the precipita-

tor until the polymeric solution forms a stable suspension. The resultant optical density and corresponding precipitator volume are related to the dispersity of the polymer. Dichloroethane and isopropyl alcohol were used as solvent and precipitator, respectively. Concentration of the solution was 0.05 kg/m³.

The fire resistivity of the polymers was evaluated by the oxygen index method. The oxygen index test carried out on film samples (strips) fixed vertically in the cylindrical chamber through which passes a laminar stream of a mixture of nitrogen with oxygen. Tests are carried out at various ratios of a gas mixture until the optimum burning the sample is reached. The sample is set on fire from the top end with the help of a gas torch that is then withdrawn.

Dielectric properties of the polymer were investigated by dielectric weight losing method on a Kumetre VM-560 Tesla machine at a frequency of 10⁶ Hz and at a temperature interval of 20–300°C.

Chemical resistivity of BCPEEKs was investigated in diluted and concentrated solutions of acids (H₂SO₄) and alkalis (NaOH). The specimens were kept in an aggressive condition at 200°C for 15 days.

DISCUSSION OF THE RESULTS

The IR-spectra results showed that the resultant bands of absorption peaks correspond to different bonds and groups (see Fig. 1). The presence of absorption bands which corresponds to ether bonds, (920–940, 1135 cm⁻¹), ester bonds (1000–1300 cm⁻¹), diarylketone groups (1600–1675 cm⁻¹), lactone group (1710–1760 cm⁻¹), and isopropylidene groups (1350–1360, 1385, 2875, 2970 cm⁻¹) points to the fact that the polycondensation of the copolymers and dichloroanhydrides of isophthalic and terephthalic acids are complete and the resultant product has the expected polyether structure.

To further confirm the structure of the BCPEEKs, an element analysis was carried out similar to the oligoketones. The results showed that the theoretically measured and experimentally obtained atomic masses of H, C and O did not differ more than 0.2% (see Table II).

The resultant intrinsic viscosities of BCPEEKs are quite high (see Table III). This fact also conform the structure obtained.

The turbidimetric titration results confirmed the expected structure BCPEEKs (see Fig. 2). The differential curves for the copolymers show only a single maximum which means that the reactants of the copolymers are statistically mixed. On the other hand, the differential maximums changes as a function of condensation rate of oligoketone. This means that the resultant formation is a block-copolymer and not a mixture of homopolymers.

TABLE II
The Properties of the Aromatic Oligoiketons

BCPEEKs based on oligoiketons	Degree of condensation	Calculated (%)			Measured (%)		
		C	H	O	C	H	O
OK-1D	1	77.41	4.18	18.41	77.13	4.1	18.17
OK-10D	10	79.28	4.09	16.63	79.06	4.05	16.50
OK-20D	20	79.53	4.07	16.39	79.43	4	16.31

The coagulation threshold of the BCPEEKs obtained from the short oligoiketons is in the regions of the higher sediment volume (see Fig. 2). The degree of condensation of initial oligoiketons influences extremely the density of macromolecular packing. Probably, the increase in the initial length of oligoiketons increased the packing density of the polyethers and thus the coagulation threshold moved to the left, where the volume of the sediment (precipitator) is low (see Fig. 2).

The remains of 4,4'-dioxidiphenyl-2,2-propane positively increases the solubility of BCPEEKs in organic solvents. Similar results are obtained with a different block copolyether.¹⁶

Figure 3 shows that the BCPEEKs have high breaking stress combined with high ductility. As the condensation degree of the initial oligoiketons increased from 1 to 20, the breaking stress of BCPEEKs increased from 77.1 to 85.3 MPa. On the other hand, the ductility decreased from 22.5 to 15%. For the same range of condensation degrees (see Fig. 4). These results confirmed that the BCPEEKs became stronger and harder with the longer oligoiketons.

It is important to remember that intrinsic viscosity of BCPEEKs prepared with OK-1D and BCPEEKs prepared with OK-20D were 0.28 and 0.10, respectively. This means that the molar mass of BCPEEKs with shorter oligoiketons (prepared with OK-1D) are much larger than that of BCPEEKs based on longer oligoiketons (prepared with OK-20D). It can be concluded that the growth of the initial OK length was accompanied by an increase in breaking strength. This result may be attributed to the fact that, as the initial length of oligomers increased, the entanglement of the branches also increased. Therefore, the flow of the molecules under tensile forces was re-

stricted and the breaking strength of increased. The decrease of elongation at break with longer OK lengths also confirms this explanation. Probably better packing is also responsible for the enhanced breaking stress behavior.

The BCPEEKs possess high thermal stability. Table III shows that the BCPEEKs lost 2% of their mass at around 400°C or higher temperatures. The length of the initial oligomers had a positive effect on the thermal stability of BCPEEKs. The higher thermal resistance of BCPEEKs obtained from longer oligoiketons may be attributed to the higher content of stable ether bonds. These ether bonds may reduce the effects of thermally unstable ester bonds introduced by the remainders of dichlorides of phthalic acids. Compact packaging is also responsible for the higher thermal stability.

The thermomechanical tests have shown that the newly synthesized BCPEEKs were characterized with comparatively high values of the glass transition temperature (T_g) and softening temperature (T_s) (see Table III). Both T_g and T_s increased with the initial length of the oligoiketons. This is due to the fact that, the saturation of the polymeric chain by flexible simple ethereal bonds is accompanied by the increased density of the chain packing. This, in turn, causes a decrease in the mobility of the macromolecules. The growth of the packaging retards the macromolecules mobility and causes an increase in T_g and T_s .

When the new BCPEEKs were synthesized at our laboratory, one of the aims was to investigate the possibilities of BCPEEKs to employ as insulating materials. 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 IV. At room temperature conditions when the BCPEEKs

TABLE III
Some Thermal Properties of BCPEEKs

Oligoiketons	Yield (%)	Intrinsic viscosity, η (dL/g)	Glass transition temperature, T_g (°C)	Softening temperature T_s (°C)	Thermal stability (°C)		
					2% Mass loss	10% Mass loss	50% Mass loss
OK-1D	98.0	2.8	195	300	397	467	567
OK-5D	98.5	1.7	200	302	400	472	574
OK-10D	99.0	1.5	207	307	407	495	587
OK-20D	99.0	1	220	320	412	500	594

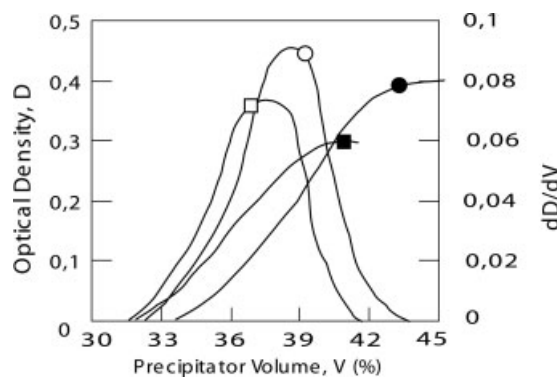


Figure 2 The dimetric titration curves of block copolyetheretherketones (■, ●—integral curves and □, ○—differential curves of molecular mass distribution tests) for: (●, ○) BCPEEK obtained from OK-1D and (■, □) BCPEEK obtained from OK-20D.

are in a glassy state, the values of dielectric permeability were between 3.8 and 4.07 and the $\tan \delta$ of the dielectric loss were in the range of $(0.37\text{--}0.57) \times 10^{-2}$.

Under similar conditions, the lower values of dielectric characteristics correspond to a more compact packing of the polymers. This higher packing may also be responsible for the observed decrease in $\tan \delta$ and dielectric constant (see Table IV) of the BCPEEKs with longer oligoketones. As the dielectric properties strongly depend on the temperature, the BCPEEKs are subjected to different temperature environments and their properties are measured. Both the dielectric constant and $\tan \delta$ loss increased with temperature. As the temperature approaches T_g , the frozen molecular chains start to mobilize and recover their orientations. While the molecular movements takes place along the main polymeric chain segment, the side groups may also mobilize and tend to reorient around the main chains. All these behaviors may be accounted for the increased dielectric loss values of BCPEEKs at higher temperatures (see Table IV).

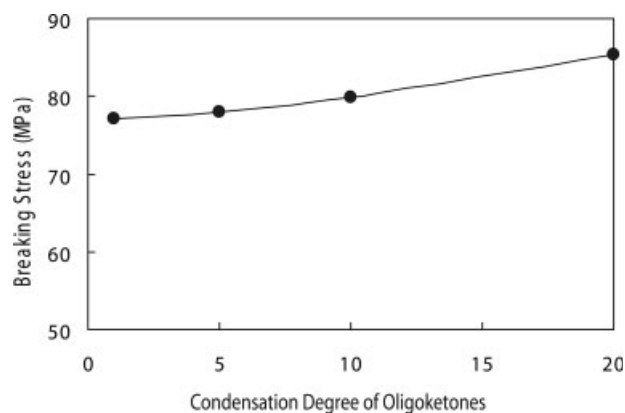


Figure 3 Breaking stress of block copolyetheretherketones versus condensation degree of oligoketones.

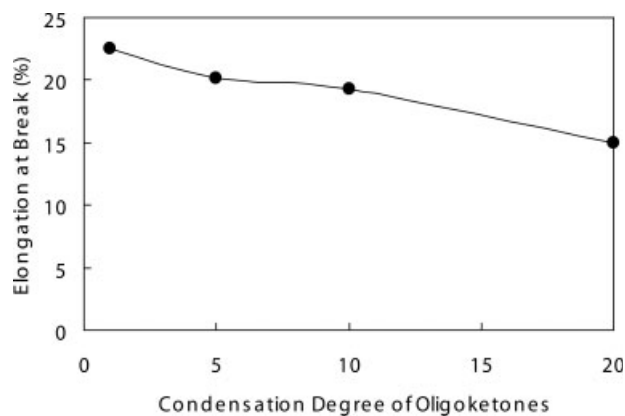


Figure 4 Elongation at break of block copolyetheretherketones versus condensation degree of oligoketones.

To investigation chemical stability of BCPEEKs, all the specimens were subjected to diluted and concentrated solutions of H_2SO_4 and HCl for 15 days. The new polymers were stable and showed no signs of destruction in these acids. On the other hand, all the BCPEEKs subjected to NaOH started to degrade after 4 days. Especially the BCPEEK based on OK-1D was very susceptible to NaOH and completely degraded after 34 days.

The fire resistance of the synthesized BCPEEKs was investigated by the limiting oxygen index method (LOI). LOI was between 32.0 and 32.5% for all materials. It means that the present polyethers did not burn in the atmosphere and are self-extinguishing and hard-burning polymers.

The molecular mass of BCPEEK was in the interval of 180,000–200,000 g/mol. The highest molecular weights were obtained from the oligoketones with a polycondensation degree of 1. As the lengths of the initial oligoketones grew, the molecular masses of BCPEEKs decreased substantially.

TABLE IV
Dependence of Dielectric and $\tan \delta$ Loss Characteristics of BCPEEK on Temperature

Oligoketone	Test		
	Temperature, T ($^{\circ}\text{C}$)	Dielectric constant, ϵ'	$\tan \delta$ loss $\tan \delta (\times 10^2)$
OK-1D	20	4.07	0.40
	100	4.15	0.40
	200	4.40	0.57
	300	4.60	2.03
OK-10D	20	4.05	0.57
	100	4.0	0.5
	200	4.05	0.47
	300	4.13	2.22
OK-20D	20	3.80	0.37
	100	3.70	0.36
	200	3.85	0.30
	300	4.10	0.97

CONCLUSIONS

BCPEEKs were obtained from phenolphthaleine and 4,4'-dichlorodiphenylketone, bisphenol A, and chloranhydrides of isophthalic and terephthalic acids with different condensation degrees. The initial length of the oligoketones increased with the condensation degree. BCPEEKs obtained from longer oligoketones had higher thermal stability and tensile strength. Low dielectric loss properties were obtained for BCPEEKs. Because of high thermal, electrical, and mechanical characteristics of the BCPEEKs, they are suggested for the use of thermally stable constructional insulators and sheet materials.

The increase in breaking strength and thermal stability of BCPEEKs with the initial length of oligoketones in all cases indicates to the fact that the molecular structure was strongly influenced by the polymerization degree.

References

1. Yang, Y.; Binyao, L.; Zhang, Y.; Zhuang, G. *J Appl Polym Sci* 1995, 55, 633.
2. Yang, Y.; Yin, J.; Li, B.; Zhuang, G.; Li, G. *J Appl Polym Sci* 1995, 52, 1365.
3. Schuur, M. V. D.; Feijen, J.; Gaymans, R. J. *Polymer* 2005, 46, 327.
4. Karger-Kocsis, J.; Gryshchuk, O. *J Appl Polym Sci* 2006, 100, 4012.
5. Shaov, A. H.; Charayev, A. M.; Mikitaev, A. K.; Kardanov, A. V.; Hasbulatova, Z. S. *Plastich Massy* 1990, 11, 14 (in Russian).
6. Thorsen, K. A. *SMEA* 1989, 2, 14.
7. Seymour, R. B. *Rev Plast Mod* 1989, 40, 120.
8. Golemme, G.; Drioli, A.; Lufuran, F.; *Vysokomolekul Soed* 1994, 36 (in Russian).
9. Ashley, S. *Mech Eng* 1997, 119, 30.
10. Hope, M. *Plast Eng* 2000, 56, 8.
11. Hope, M. *Plast Eng* 2001, 57, 9.
12. Extrand, C. W.; Bhatt, S.; Monson, L. *J Mater Sci* 2001, 36, 4603.
13. Mercer, F. W.; McKenzie, M. T.; Merlino, G.; Fone, M. M. *J Appl Polym Sci* 2003, 56, 1397.
14. Lakshmi, R. T.; Muthu, S.; Choudhary, V.; Varma, I. K. *J Mater Sci* 2005, 40, 629.
15. Goyala, R. K.; Negi, Y. S.; Tiwari, A. N. *J Appl Polym Sci* 2006, 100, 4623.
16. Goyala, R. K.; Negia, Y. S.; Tiwarib, A. N. *Eur Polym J* 2005, 41, 2034.
17. Zhang, Y. H.; Liu, Q. H.; Niu, Y. M.; Zhang, S. L.; Wang, D.; Jiang, Z. H. *J Appl Polym Sci* 2005, 97, 1652.
18. Rath, T.; Kumar, S.; Mahaling, R. N.; Mukherjee, M.; Das, C. K.; Pandey, K. N.; Saxena, A. K. *J Appl Polym Sci* 2007, 104, 3758.
19. Ozden, S.; Charaev, A. M.; Shaov, A. H.; Shustov, G. B. *J Appl Polym Sci* 1998, 68, 1013.
20. Ozden, S.; Charaev, A. M.; Shaov, A. H. *J Mater Sci* 1999, 34, 2741.
21. Ozden, S.; Charaev, A. M.; Shaov, A. H. *J Mater Sci* 2001, 36, 4479.
22. Akay, M.; Ozden, S. *J Mater Sci* 1995, 30, 3358.
23. Ozden, S.; Charaev, A. M.; Shaov, A. H. *J Appl Polym Sci* 2002, 85, 485.
24. Young, R. J. *Introduction to Polymers*, 2nd ed.; Chapman and Hall: London, 1997; p 202.