

Synthesis and Assessment of the Properties of Polyetherketones (PEK) Based on Olygoketonephenolphthaleines (OKPP)–Polyester Block Copolymers

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Received 12 December 1996; accepted 4 September 1997

ABSTRACT: Different polyetherketones (PEK) based on olygoketonephenolphthaleines (OKPP) with different condensation degrees and dichloranhydrides of isophthalic and terephthalic acids were obtained by means of an acceptor-catalytic polycondensation. The correlation between the composition of the initial olygoketones and the properties of the resultant polyetherketones was established. Some of the physico-chemical properties of PEK were also investigated. It was shown that as the initial length of OKPP increased the yield strength, heat stability, the glass transition temperature and melt temperature increased. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1013–1017, 1998

Key words: polyetherketone; olygoketonephenolphthaleine; olygoketone; step polymerization; molecular mass

INTRODUCTION

Aromatic PEK possesses high physico-chemical properties. This is due to the presence of phenylene groups in its main chain, which prompts a high degree of crystallinity of the polymer.¹ PEK is a semicrystalline polymer of whose heat resistance depends on the glass transition temperature (affected by its amorphinity) and melting temperature (affected by its crystallinity). This resistance increases as the mobility of the macromolecules decreases.² Although PEK is not soluble in typical solvents, it is solved in concentrated nitrogen acids.³ PEK shows high wear resistance and exhibits satisfactory electrical properties for a wide range of temperatures and frequencies. It is easily processed by pressing, casting under

pressure, and is capable of reprocessing.⁴ The fracture behavior of PEK and the dependence of its yield strength on temperature were investigated by Han et al.⁵

PEK is used mainly as construction and electrical-coating material for long times to stand up to 200°C or even higher temperatures. The cost of PEK is 10–20 times higher than that of the ordinary polymers used in constructions such as polycarbonate and polyamide.⁶ However, the superior properties of PEK assure its wide use in all branches of the economy.⁷

The synthesis of the PEK is carried by means of alkylation according to the Friedel–Crafts' reaction or by the reaction of nucleophylic substitution of activated dihalogen-containing aromatic compounds and biphenolates of alkalic metals.^{8,9} PEK is usually obtained by the polycondensation method at high temperature. The resultant PEK possesses low indices of molecular mass and weak solubility in organic solvents. These disadvan-

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tages can be easily eliminated if the polymerisation is based on some olygoketones obtained by means of an acceptor-catalytic polycondensation method. Although the introduction ester linkages into the main chain increases the crystallinity and consequently the solubility, the aromatic branches tends to delay the crystallisation and increase the solubility.

Benzophenone derivatives that are dihaloid substituted in the 4,4^I form are monomers with promising futures. Because this type of monomers is impossible to obtain from benzophenone by direct haloidizing, they are synthesised from benzene derivatives, *n*-haloid benzoin acids, diphenylmethane, 4-4^I-dichlordiphenyltrichlormethylmethane (DDT), and its 4,4^I haloid-substituted elements, etc.¹⁰

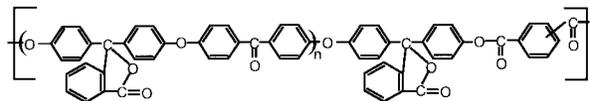
EXPERIMENTAL

4,4^I Dichlordiphenylketone (4,4^I-DCDPK) is the monomer that exhibits the best prospect among dihaloid-substituted benzophenone derivatives for the production of PEK, because it is easily produced and reacted.

4,4^I-DCDPK was obtained from DDT in two stages. First, 2×10^{-2} kg of DDT in 400 mL of water-ethanol mixture was reacted with 1.24×10^{-2} kg of caustic potassium solved in 16×10^{-5} m³ of water. The reactants were kept at 78°C for 14.4×10^3 s and then the mixture was poured into water. At the end of this process, 1,1-dichlor-2,2^I-di-(4-chlorphenyl)ethane was obtained. The resultant product had a melting temperature of 89°C. At the second stage, 1×10^{-2} kg of 1,1-dichlor-2,2^I-di-(4-chlorphenyl)ethane, 5×10^{-2} kg of chromic anhydride and 3×10^{-4} m³ of ice wingard acid were placed into a flask fitted with a reverse cooler. The mixture was stirred for 14.4×10^3 s in a water bath at 70–80°C. Then it was poured into cold water and 4,4^I-dichlordiphenylketone was obtained. After recrystallization, the product showed a melting temperature of 146°C.¹¹ Then, the block-structured PEK based on 4,4^I-dichlordiphenylketone and phenolphthaleine was obtained by a technique similar to the production of olygosulphone.¹² Olygoketonephenolphthaleines (OKPP) were synthesized with different degrees of condensation $n = 1, 5, 10,$ and 20 (see Table I).

Fresh-distilled dichloranhydrides of isophthalic and terephthalic acids were used as acidic components in 1 : 1 ratio. Polycondensation was carried in a dichlorethane medium with tri-

ethylamine as acceptor-catalyzer. The resultant PEK had the following structure:



The techniques of IR spectroscopy and elemental analysis were used to confirm the structure of olygoketones (OK) and the resultant PEKs. Investigation of the polydispersity of the block copolymers were conducted by turbidimetric titration method on a FEC-56M device.

The test specimens used for the determination of the physico-chemical properties of PEKs were obtained from casted film specimens.

Thermogravimetric analysis of polyethers were made at a "MOM" derivatograph with a heating rate of 5°C/min under atmospheric conditions. Thermomechanical properties of the polymers were determined in the air with a temperature increase rate of 4°C/min and a constant stress of 0.05 MPa on a Pribor thermal-mechanical analyzer. The molecular weights were measured by sedimentation method on an ultracentrifugal MOM (type 317 V) machine using the equilibrium approaching method.

The measurement of the mechanical properties of PEKs was carried out using sheet specimens ($100 \times 10 \times 0.1$ mm³) on a tensile test machine MRS-500 with a constant deformation rate of 40 mm/min at 20°C.

The fire resistivity of the polymers was evaluated by the oxygen index method. The viscosity measurements were obtained by classical viscometric method using an Ubbelohde-type viscometer.

Dielectric properties of the PEKs were obtained by means of dielectrical loss technique. The investigations were made on the Kumetre VM-560 "TESLA" machine under a frequency of 1 MH in the temperature range of 20–300°C. Chemical stability was also investigated in an aggressive media for 12.96×10^5 s at 20°C.

RESULTS AND DISCUSSIONS

The data obtained from the elemental analysis, IR spectroscopy, and turbidimetric titration were used to confirm the given chemical structure the polymers. The IR spectra results showed that the resultant bands of absorption peaks correspond to different bonds and groups, including diaryl-

Table I Properties of Olygoketons

Olygoketons	Degree of Condensation	Softening Temperature, T_{soft} (°C)	Molecular Mass (Calculated)	% Content of OH-Groups	
				Calculated	Measured
OK-1F	1	196–200	814.85	4.17	4.20
OK-5F	5	210–215	2800.94	1.21	1.20
OK-10F	10	237–244	5283.75	0.64	0.65
OK-20F	20	255–260	10248.77	0.33	0.30

ketone group ($1675\text{--}600\text{ cm}^{-1}$). The bands did not show absorptions, which characterizes the hydroxyl group of olygoketones. This result is in accordance with the expected structure formation of PEK. The presence of one maximum of the turbidimetrical titration curves points to the statistically mixed polyetherketone formations (see Fig. 1).

The synthesized PEKs are characterized by high softening temperature and viscosity indices (see Tables I and II).

Although they are soluble in chlorated organic solvents, no significant difference in their solubility was observed among the different grades of the synthesized PEKs. The coagulation threshold of the PEKs obtained from the short olygoketones was, as expected, in the regions of the higher precipitators' volume (see Fig. 1). However, it should be remembered that the high molecular mass of PEKs based on the short olygoketones do not improve their solubility. Therefore, it may be suggested that, under comparatively equal values of the molecular masses, the PEKs based on short

olygoketones are characterised by considerably better solubilities.

The measured molecular weights of PEKs are in the range of 60,000–240,000 of carbon units. The highest values of the molecular weights are characteristic of PEKs obtained from short olygoketones. As the initial length of OK chains increased, the molecular mass of PEKs significantly decreased.

The results of the thermomechanical tests have shown that polyetherketones possess comparatively low glass transition temperature (T_{gl}) and flow temperature (T_{fl}). This may be explained by the presence of the great amount of simple flexible ethereal bonds in their chains. On the other hand, it should be noted that some increase in T_{gl} and T_{fl} (see Fig. 2) with the increase of the lengths of initial OK 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.

As it is known¹² PEK is a semicrystalline copolymer and its thermomechanical properties strongly depend on the structure of their orderings. The increase of the latter decreases the mobility of the macromolecules, which leads to the increase of T_{gl} and T_{fl} .

The glassy state the PEKs were characterized by the low values of dielectric loss factor (see Table 2). This fact was due to the absence of polar groups and substituents that could considerably influence the dielectric properties of the polymers. This may explain the comparatively similar values of these indices for all PEKs. As it is known, under similar conditions, the lower values of dielectric characteristics correspond to the more compact packing of the polymers. This higher packing may also be responsible for the observed decrease in $t_g \delta$ (see Table II) of the PEKs with longer olygoketones.

The resultant PEKs did not burn in the atmo-

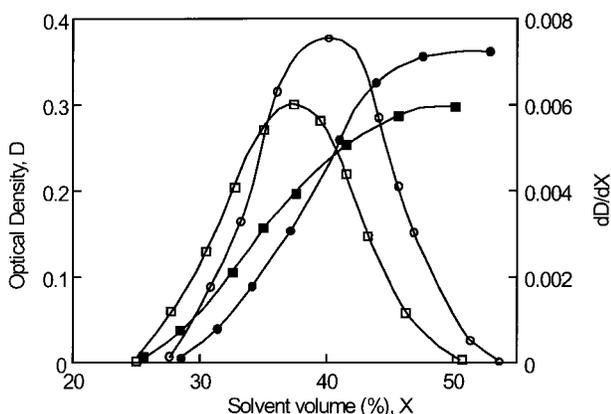


Figure 1 Turbidimetrical titration results of polyetherketones: (■, ●) integral and (□, ○) differential curves for molecular mass distribution of polyetherketones obtained from (○, ●) OK-1F and (□, ■) OK-20F.

Table II The Properties of Polyetherketones

Polyetherketones Obtained from	Intrinsic Viscosity η (m ³ /kg)	Molecular Weight (in Thousands of Carbon Units)	Oxygen Index %	Dielectric Loss ϵ'	$t_g\delta$ 10 ³
OK-1F	0.25	240	31	3.43	0.4
OK-5F	0.18	150	31.5	3.46	0.45
OK-10F	0.14	80	31.5	3.25	0.35
OK-20F	0.12	60	32	3.06	0.27

sphere, and the fire stability of the block polyetherketones did not show significant differences. Nevertheless, in spite of the absence of any anti-pirenes in the PEKs, the values of oxygen index were found to be around 31–32%.

PEKs were stable against to the diluted acids and to the concentrated hydrogen chloridic acids. The results of the viscosity tests of the specimens which had been kept in an acidic media did not show any significant difference. It meant that the acids did not cause any harm to the polymer.

The synthesized polymers showed high breaking strength combined with good ductility (see Fig. 3). All tested specimens demonstrated ductile failure. The growth of the initial OK length was accompanied by an increase in breaking strength. It 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 restricted and the breaking strength of PEKs increased. The decrease of elongation at break with longer OK lengths also confirms this explanation.

The investigation of the thermal properties

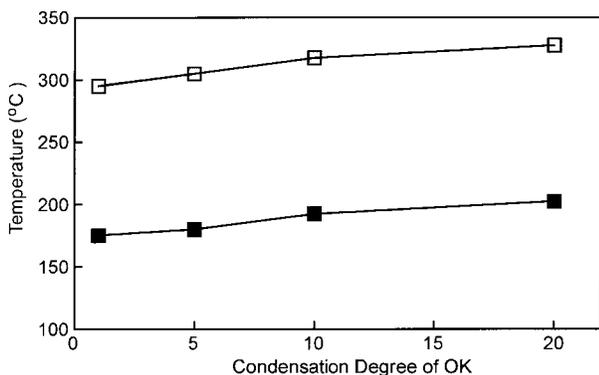


Figure 2 Dependencies of the glass transition (■) and flow temperatures (□) of polyetherketones on the degree of condensation of oligoetherketones.

shows that the PEKs possess high thermal stability (see Table III). The comparison of the test results demonstrated that a considerable rise in the thermal properties of the PEKs was obtained as the initial length of OK increased. This phenomenon may be explained in the following way: while the polymeric chain is saturated by the thermally stable simple etheral bonds, at the same time, the amount of nonstable complex etheral bonds introduced in the structure of the polymers by the rest of dicloranhydrides of phthalic acids falls abruptly. Besides, the density of packing in PEKs increases considerably with the increase of the initial OK lengths. The thermal stability of the PEKs may be attributed to these three factors.

The comparison of the thermal characteristics of the PEKs with polyethers that have similar structures, namely polyethersulfones obtained from phenolphthaleinic oligoarylenesulfonoxides (OASO) with the same degree of condensations,¹³ has shown that the differences in 10% mass loss are around 80–100°C. The temperature for 2% mass loss for all PEKs is around of 397°C or higher. This temperature value is high enough,

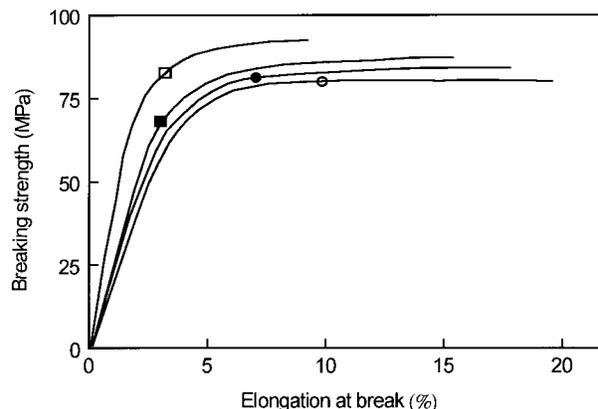


Figure 3 Breaking strength vs. elongation of polyetherketones obtained from: (○) OK-1F, (◆) OK-5F, (■) OK-10F, and (□) OK-20F oligoetherketones.

Table III Thermal Stability of Different Polyetherketones

Polyethers Obtained from	Thermal Stability (°C)		
	2% (Mass Loss)	10% (Mass Loss)	50% (Mass Loss)
OK-1F ^a	397	497	587
OK-5F ^a	407	500	590
OK-10F ^a	409	507	587
OK-20F ^a	417	517	600
OASO-10F ^a	332	402	507
OASO-20F ^b	342	407	512
OASO-10F ^c	387	427	512
OASO-20F ^c	392	437	517

^a Polyetherketones.

^b Polyethersulfones obtained from OASO-10F of phenolphthaleinic oligoarylenesulfonoxides (OASO) and dichloranhydride of terephthalic acid.

^c Polyethersulfones on the base of phenolphthaleinic OASO and dichloranhydride of 1,1-dichloro-2,2-di-(4-carboxyphenyl)ethylene.

and it exceeds the temperature range at which the thermally stable polymeric materials are widely used.

CONCLUSION

Polyetherketones (PEK) obtained from oligoketonephenolphthaleines (OKPP) with different condensation degrees and dichloranhydrides of isophthalic and terephthalic acids were processed and their mechanical and thermal properties were investigated. Their softening temperatures are high, and their stability against heat and environmental effects are excellent. The thermal stability and tensile strength of the copolymers increased with longer oligoketones. High thermal and mechanical characteristics of the PEKs enable us to presuppose that these polymers may be widely used as thermally stable constructional and sheet materials. The initial length of the oligoketones, the content of oligoketones in the molecular chain, and their molecular weights affected most of the mechanical and thermal properties.

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