

The synthesis of polyetheretherketones and investigations of their properties

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Using hydroxyl-containing olygoketones with different condensation degrees and dichloranhydrides of isophthalic and terephthalic acids, polyetheretherketones (PEEK) were synthesized by means of acceptor-catalytic polycondensation, and their properties were investigated. It was shown that PEEK possesses a better solubility, a higher molecular weight and is characterized by high thermal and mechanical properties. The correlation between some properties of polyethers and the degree of condensation of olygoketones was also investigated. © 1999 Kluwer Academic Publishers

1. Introduction

Recently, in the literature, a great deal of attention has been paid to the synthesis and properties of polyetheretherketones (PEEK) possessing high physical and chemical properties [1]. They are largely used as construction materials and coating elements of electric transmission wires which may be under operation for long times at up to 200°C and higher temperatures. 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 guarantees a wide use in all branches of the economy [2–4].

2. Experimental procedure

2.1. Materials and processing

In the present paper, the properties of PEEKs which were synthesized from olygoketones (OK) of 4,4'-dioxiphenyl-2,2-propane containing hydroxyl end groups and an equimolar mixture of dichloranhydrides of isophthalic and terephthalic acids, were investigated. Olygoketones with different condensation degrees were synthesized by means of an alchalic salt of diphenylolpropane interacting with 4,4'-dichlordiphenylketone in anhydrous dimethylsulphoxide according to the tech-

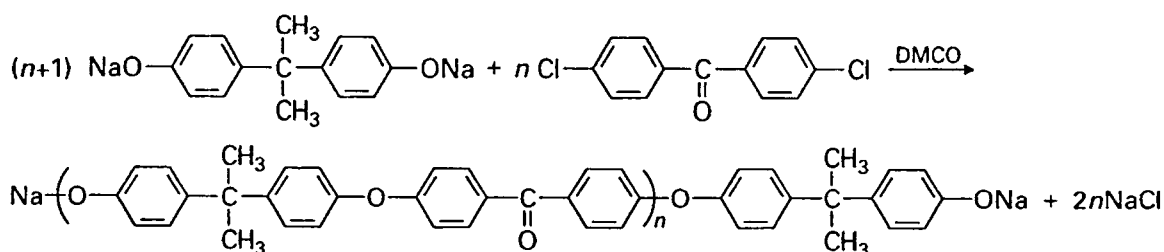
niques analogous to those of the production of olygosulphones [5] (scheme 1) where $n = 1, 5, 10$ and 20.

Some properties of the olygoketones are given in Table I. Initially, 4,4'-dichlordiphenylketone was obtained from 4,4'-dichlordiphenyltrichlormethylmethane (DDT) in two steps: in the first stage, 1,1-dichlor-2,2-di-(4-chlorphenyl)ethane was synthesized from DDT by means of dehydrochloration in the second stage this product was reacted with chromium anhydride in icy winegarn acid and 4,4'-dichlordiphenylketone with a melt temperature of 146°C was obtained. The process has been described by Yanota *et al.* [6]. Then PEEK was obtained by the technique of acceptor-catalytic polycondensation in dichlorethane for 1 h at 20°C. Triethylamine was used as an acceptor-catalyser. The resultant PEEKs have the following structure (scheme 2) where $n = 1, 5, 10$ and 20.

2.2. Test methods

2.2.1. 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 and

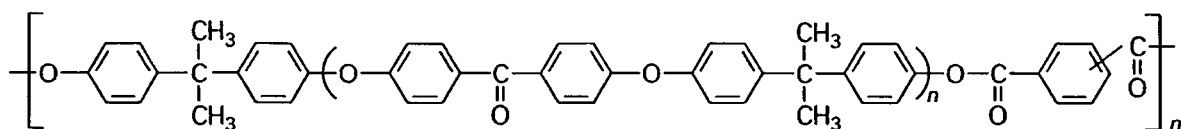


Scheme 1

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TABLE I The properties of olygoketones

Olygoketones	Condensation degree	Softening temperature (°C)	Molecular weight (in carbon units)	OH-group content (%)	
				Calculated	Measured
OK-1D	1	129–132	634.78	5.36	5.3
OK-3D	5	147–152	2260.72	1.5	1.55
OK-10D	10	160–165	4293.17	0.79	0.75
OK-20D	20	167–175	8358.43	0.41	0.4



Scheme 2

the density of the solution was 0.5 g dl⁻¹. Dichlorethane was used as a solvent.

2.2.2. Mechanical tests

As PEEKs are widely used as polymeric construction materials, the mechanical properties of film PEEK specimens (100 mm × 10 mm × 0.1 mm) were tested (GOST 17-316-71) on a MRS-500 model rupture tensile test machine with a constant strain rate of 40 mm min⁻¹ at 20 °C. The film test specimens were obtained by pouring the polymeric solution on to a surface and allowing the gaseous material to evaporate.

2.2.3. Molecular structure, thermomechanical and other tests

The PEEK structures were confirmed from the data of elemental analysis and infrared spectroscopy. The molecular masses of the PEEKs were measured by sedimentation in an ultracentrifuge “MOM” (type 317 B) through the balance approach technique.

Thermo-gravimetric analysis of the PEEK was performed on the derivatograph “MOM” under a temperature increase rate of 5 °C min⁻¹ in the atmosphere. (MOM is the abbreviation of the Hungarian company that manufactured the derivatograph).

Investigation of the polydispersity of the block copolymers was conducted by the turbidimetric titration method on an FEC-56M device. The principle of titration is that the diluted polymeric solution will become 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 precipitator until the polymeric solution forms a stable suspension. The resultant optical density and corresponding precipitator volume are related to the dispersity of the polymer. In the present work, dichloroethane and isopropanol were used as solvent and precipitator, respectively.

The investigation of the thermodynamical properties of the film specimens was carried out on a Pribor thermomechanical analyser. The temperature was increased at the rate of 4 °C min⁻¹ 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 mm and 8 mm, respectively, while the distance between the clamps was 80 mm. A thermal camera with a diameter of 30 mm and length of 150 mm was 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 using a strain gauge. The temperature and deformation were recorded on a x-y recorder.

The tests of the dielectric properties were carried out at a set with a Kumetre VM-560 Tesla machine at a frequency of 10⁶ Hz. The values of dielectric permeability and tan δ of the dielectric loss angle were found for all specimens over the temperature range 20–300 °C.

3. Results and discussion

3.1. Mechanical properties

The PEEKs demonstrated high tensile strength values combined with high ductility. If, during the processing of PEEKs, the condensation degrees of the initial olygoketones are increased, then their breaking strengths

TABLE II Some properties of polyetheretherketones

PEEKs obtained from	η^a (m ³ kg ⁻¹)	Molecular weight (in thousands units)	T_g (°C)	T_m (°C)	σ_{break} (MPa)	ε (%)	Mass loss temp. (°C)		
							$T_{2\%}$	$T_{10\%}$	$T_{50\%}$
OK-1D	0.24	250	150	240	75	15	397	460	590
OK-5D	0.19	160	152	250	77	14	407	467	587
OK-10D	0.16	100	157	272	80	13	407	492	597
OK-1D	0.13	60	160	290	85	8	417	540	613

^aIntrinsic viscosity.

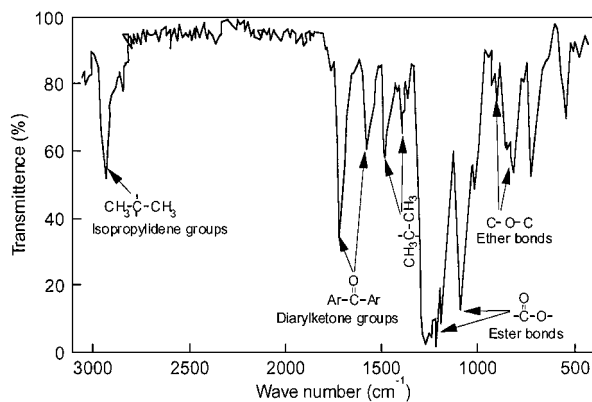


Figure 1 The IR spectrum results of PEEK.

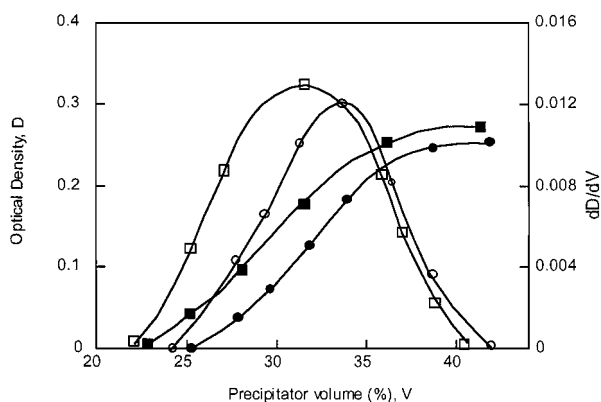


Figure 2 The dimetric titration curves of polyetheretherketones (■, ●) integral curves, (□, ○) differential curves of molecular mass distribution tests for (●, ○) PEEK obtained from OK-1D, and (■, □) PEEK obtained from OK-20D.

(75–85 MPa) also show an increase with a decrease in ductility (see Table II). Such a change in the breaking strengths may serve as confirmation of the above assumption that the packing density in the macrochains of PEEKs varies with the formation process. The PEEK polymers, except that obtained from OK-1D, exhibited ductile failure.

3.2. Molecular structure

The presence of the absorption bands (see Fig. 1) which correspond to simple ether bonds ($920\text{--}940\text{ cm}^{-1}$), ester bonds ($1000\text{--}1300\text{ cm}^{-1}$), isopropylidene groups ($1350\text{--}1360$, 1385 , 2875 , 2970 cm^{-1}), diarylketone group ($1600\text{--}1675\text{ cm}^{-1}$) and the absence of the absorption bands of hydroxyl groups in the infrared spectra points to the fact that polycondensation of olygoketones and dichloranhydrides of isophthalic and terephthalic acids were thoroughly completed and their properties were manifested in the resultant product.

PEEKs are characterized by a high viscosity. The results of turbidimetric titration also confirmed the structure of the above mentioned polymers. This fact was documented by the presence of only one maximum in the differential curves (see Fig. 2) which means that the reactants of the polymer were statistically mixed. Among the different PEEK samples, no significant difference was observed in their solubility. According to the results obtained, it may be asserted that, under equal

values of molecular weight, the PEEKs obtained from olygoketones with lower condensation degrees will be characterized by better solubility (see Fig. 2).

All the PEEKs obtained were well dissolved by a number of organic solvents (dichloroethane, chloroform, tetrachlorethane) and characterized by low polydispersity. The molecular weights of PEEKs were found to be in the interval $60\text{--}250,000$ carbon units. The highest molecular weight values of the PEEKs were obtained from the olygoketones with polycondensation degrees of 1 and 5. As the lengths of the initial olygoketones grew, the molecular masses of PEEKs decreased substantially.

3.3. Thermomechanical properties

The thermomechanical tests have shown that the PEEK samples possess comparatively low values of the glass transition temperature, T_g , (see Table II) and melt temperature, T_m . This fact is probably due to the presence of a great number of simple flexible etheral bonds in their macrochains.

It should be noted that lower values of these thermodynamical characteristics in the series of PEEKs with lower condensation degrees is related to the fact that during the course of the polymeric chain saturation with flexible simple bonds, a growth of the packing density of the macrochain is observed. This density increase causes a decrease in the macromolecular mobility. PEEKs are semi-crystalline polymers and their thermodynamical properties are strongly dependent on the degree of ordering in their structures [7]. The growth of the ordering decreases the macromolecules mobility and the loss of mobility causes a rise in T_g and T_m of the PEEKs.

The data obtained from thermo-gravimetric analysis have shown that (see Table II) the PEEKs 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 in mass took place at around 400°C or higher temperatures. The higher thermal resistance shown by the PEEK obtained from long olygoketones may be attributed to the higher content of stable simple etheral bonds and compact packing.

The investigated PEEKs are self-damped polymeric materials and their oxygen indices are at the level of 31%, 32%.

3.4. Dielectric properties

For the glassy state, the values of dielectric permeability and $\tan \delta$ of the dielectric loss were equal to $2.8\text{--}2$ and $0.003\text{--}0.0035$, respectively, and they were not effected by the condensation degree of the initial olygoketones.

The resultant structure of PEEK (given at the end of Section 2) shows that PEEKs do not contain strongly polar groups and substituents which could influence considerably the dielectric characteristics of the polymers. This may explain the low values of the PEEKs indices. Some differences in these values are also the result of the structural peculiarities of PEEKs. It may be asserted that under similar conditions, the lower values of the dielectric characteristics correspond to the

TABLE III The dependence of weight variations of PEEK on the exposure time in an aggressive environment

PEEK	Exposure time (h)	Weight variations (%)				
		Diluted acid		Conc. acid	Diluted alkali	
		10%	30%		10%	50%
OK-1D	24	0.34	0.24	0.67	0.91	0.34
	48	0.98	0.9	1.68	2.64	-0.60
	96	1.61	1.76	2.71	2.69	-1.97
	384	1.69	1.34	2.88	-0.13	-10.13
OK-5D	24	0.29	0.27	0.7	0.8	0.3
	48	0.64	0.83	1.55	2.33	-0.87
	96	1.37	1.55	2.47	2.47	-2.16
	384	1.4	1.43	2.6	0.34	-9.91
OK-10D	24	0.3	0.17	0.58	0.81	0.24
	48	0.55	0.77	1.5	0.94	-0.79
	96	1.26	1.31	2.13	2.13	-1.81
	384	1.29	1.3	2.21	1.07	-7.64
OK-20D	24	0.11	0.15	0.33	0.62	0.12
	48	0.38	0.4	1.21	1.55	-0.54
	96	0.64	0.98	1.69	1.71	-0.97
	384	0.69	1.09	1.71	1.56	-6.33

more compact packing of the polymers. In the range 20–200 °C, the PEEKs showed stable dielectric characteristic values.

PEEKs are also distinguished by good chemical resistance to the diluted acids and to the concentrated hydrogen chloridic acids. They are less resistant to concentrated alkali and the PEEKs obtained from OK-1D and OK-5D are similar. This may be caused by the chemically non-stable complex-ethereal bonds which are present in macrochains of the PEEKs (see Table III). The failure of the PEEKs based on short olygoketones saturated with such bonds faster than those of the PEEKs based on OK-10D and OK-20D, also supports this argument. Low packing density of PEEKs based on short olygoketones explains enhanced polymer failure.

4. Conclusion

Polyetheretherketones obtained from olygoketones with different condensation degrees and dichloranhydrides of isophthalic and terephthalic acids and their mechanical and thermal properties were investigated. Their softening temperatures are high and their stability against heat and environmental effects are excellent. As the condensation degree of the monomers increases, so does the density, thermal stability and tensile strength. PEEKs with high condensation degrees have good resistance to diluted and concentrated acids. The lower dielectric loss properties were obtained for PEEKs. Because of high thermal, electrical and mechanical characteristics of the PEEKs, they are suggested for the use of thermally stable constructional and sheet materials.

The increase in breaking strength and thermal properties of PEEKs with the initial length of olygoketones in all cases, indicates 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 results of the titration results indicate the uniform mixture of the polymer. Therefore it is also reliable.

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