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Publisher's version / Version de l'éditeur:

Journal of Polymer Science: Part A: Polymer Chemistry, 40, 20, pp. 3449-3454, 2002

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Synthesis and Characterization of Soluble Copoly(ether ketone)s Containing Double Bonds

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Received 14 June 2002; accepted 25 July 2002

ABSTRACT: A series of copoly(ether ketone)s containing double bonds along the polymer chains were synthesized from the condensation polymerization of hydroquinone with 4,4'-difluorobenzophenone and 4,5-bis(4-fluorobenzoyl)-1-methylcyclohexene in sulfolane containing anhydrous potassium carbonate. The presence of methylcyclohexene in the polymer chains resulted in an improvement in the solubility of poly(ether ketone)s in organic solvents such as chloroform, chlorobenzene, and sulfolane. As a result, the conditions for synthesizing these polymers were much milder than those for poly(ether ether ketone). The new copoly(ether ketone)s also showed good tensile properties and reasonable thermal stability. New polyethers containing pyrazine units were obtained from the cyclization reaction of these copoly(ether ketone)s with hydrazine. The hydrazine cycloderivatives led to an increase in the glass-transition temperatures and a decrease in solubility in organic solvents. © 2002 Government of Canada. Exclusive worldwide publication rights in the article have been transferred to Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 3449–3454, 2002

Keywords: poly(ether ketone)s; double bond; cyclization reaction; poly(ether ether ketone) (PEEK); polycondensation

INTRODUCTION

Copoly(ether ketone)s (PEKs) are a category of important high-performance engineering plastics known for their excellent thermooxidative, mechanical, electrical, and chemical resistance properties.^{1–7} These characteristics permit PEKs to be used as insulation, as matrix resins for composite materials, and in electronics applications. Within this category of high-performance plastics, the best known PEK is poly(ether ether ketone) (PEEK), which was developed by ICI Co.⁸ It is a

semicrystalline polymer with a glass-transition temperature (T_g) of 144 °C and a melting temperature (T_m) of 335 °C. The high crystallinity makes PEEK insoluble in most organic solvents. Primarily because of the polymer's insolubility, the synthetic reaction conditions for PEEK are rather rigorous. High molecular weight, semicrystalline PEEK is generally prepared in diphenylsulfone at elevated temperatures very close to its boiling point. In addition, it is difficult to process this type of thermally stable polymer material. To improve the synthetic reaction conditions and processability, the synthesis of soluble, amorphous PEKs has been investigated over the past decade. Numerous groups have been incorporated into polymers in an effort to find new PEKs signifi-

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 40, 3449–3454 (2002)
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Scheme 1. Synthetic scheme for polymerizing PEKs.

cantly more soluble in organic solvents than PEEK and other known PEKs.^{9–15} For example, PEKs synthesized with monomers having bulky groups or asymmetric structures such as 2,2',3,3',5,5'-hexaphenyl-4,4'-diphenol¹⁶ or 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one^{6,9} have improved solubility in chloroform, *N,N*-dimethylacetamide (DMAc), and *N*-methylpyrrolidone (NMP). Polymerization reactions could then be performed in dipolar aprotic solvents such as DMAc, dimethyl sulfoxide (DMSO), and sulfolane and lowered to temperatures of 180–220 °C. The purification of PEKs, particularly the removal of inorganic salts that could cause PEK creep behavior at elevated temperatures, becomes more manageable. Recently, other applications have also been sought for PEKs, such as membrane materials and polymeric reagents. Consequently, there is increased interest in the development of functional or reactive PEKs.^{17–21} Here we report the synthesis of a series of reactive PEKs containing PEEK units consisting of hydroquinone (HQ), 4,4'-difluorobenzophenone (DFK), and 4,5-bis(4-fluorobenzoyl)-1-methylcyclohexene (DFKK) by solution condensation polymerization under mild reaction conditions. These PEKs are further converted into cyclized product via ring-closing reactions with hydrazine. Both polymers before and after cyclization contain double bonds in their molecular chains.

EXPERIMENTAL

Materials

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. Fluorobenzene was dried with

CaCl₂ before use. Sulfolane was distilled under reduced pressure. DFK was recrystallized from ethanol. DFKK was synthesized according to the procedure for 4,5-bis(4-fluorobenzoyl)-cyclohexene reported by Singh and Hay,¹⁶ except that 2-methyl-1,3-butadiene was used instead of 1,3-butadiene in the Diels–Alder reaction.^{20,21}

General Procedure for the Synthesis of the PEKs

As depicted in Scheme 1, the PEKs synthesized with various compositions are denoted PEK (DFK/DFKK). The synthesis of PEK (20/80) is used as a typical example. To a three-necked flask equipped with a magnetic stirrer, a Dean–Stark trap, a condenser, and a nitrogen inlet, DFK (0.3419 g, 1.6 mmol), DFKK (2.1784 g, 6.4 mmol), HQ (0.8809 g, 8 mmol), and potassium carbonate (1.5480 g, 11.2 mmol) were added. Then, 19.3 mL of sulfolane and 40 mL of toluene were charged into the reaction flask under a nitrogen atmosphere. The reaction mixture was heated to 120 °C. Upon dehydration and the removal of toluene, the reaction temperature was increased to 180 °C. After a period of 3–6 h, when the solution viscosity had obviously increased, the mixture was cooled to 100 °C. The resultant reaction mixture was diluted fivefold with chloroform, and the viscous solution was left to stand to precipitate inorganic salts and then coagulate in ethanol. After the recovery and drying of the product, PEK was redissolved in chloroform and coagulated in ethanol. The yellowish, fibrous PEK was heated in water and dried in a vacuum oven at 100 °C for 24 h.

Cyclization

A three-necked flask equipped with a thermometer, a Dean–Stark trap, a condenser, and a mag-

Table 1. Properties of the PEKs

Entry	Unit	DFK/DFKK Feed Ratio (mol/mol)					
		PEK (50/50)	PEK (40/60)	PEK (30/70)	PEK (20/80)	PEK (10/90)	PEK (0/100)
Reaction time	h	3.0	3.0	3.0	3.0	6.0	4.5
$[\eta]^a$	dL/g	2.0	2.1	2.5	2.2	2.7	2.4
Tensile Strength	MPa	42.6	50.0	64.5	51.5	58.2	57.0
Elongation at rupture	%	10.0	8.14	67.8	9.10	11.9	30.2
T_g	°C	168	182	184	189	192	196
T_m	°C	321	316	335	325	320	—
5% weight-loss temperature	°C	355	375	365	374	353	357

^a Measured at 25 °C in CHCl₃.

netic stirrer was charged with 2 g of PEK, 20 mL of sulfolane, and 10 mL of toluene. The resulting mixture was heated to and maintained at 100 °C. Ten milliliters of 50% hydrazine hydrate in water was added dropwise, followed by an 8-h reaction time. The cyclized polymer product appeared as a precipitate. Toluene was then removed under reduced pressure, and the mixture was poured into water, filtered, and heated in water several times. The brown polymer was dried in a vacuum oven at 100 °C for 24 h, and cyclized copoly(ether ketone) (CPEK) was produced.

Instrumentation

Inherent viscosity data were obtained with an Ubbelohde dilution viscometer for chloroform solutions of the polymers with a concentration of 0.5 g/dL at 25 °C. T_g and T_m were measured with a DuPont 200 differential scanning calorimetry (DSC) instrument at a heating rate of 10 °C/min. Five percent weight-loss temperatures were determined on a PerkinElmer TG/DTA instrument at a heating rate of 10 °C/min. Tensile tests were performed on a Shimadzu tensile tester (model AG-2000) at a strain rate of 10 mm/min. IR spectra were recorded on a Nicolet 5DX Fourier transform infrared (FTIR) spectrometer. Wide-angle X-ray diffraction (WAXD) patterns were obtained on a Rint2000 wide-angle goniometer with Cu K α radiation.

RESULTS AND DISCUSSION

Synthesis of the New PEKs

The synthesis of the PEKs was conducted according to the procedure shown in Scheme 1. For a homo-

geneous reaction mixture and a high polymer molecular weight to be obtained, a high-boiling-point solvent, sulfolane, was used. In the nucleophilic displacement polymerization reaction, the solid composition, that is, the weight percentage of DFK, DFKK, HQ, and K₂CO₃, was maintained at 20 wt %, and any water present or generated during the bisphenoxide formation was removed as an azeotrope with toluene. The reaction was gradually heated to 120 °C. Upon completion of bisphenoxide formation and dehydration, it was heated to and maintained at 180 °C to effect the displacement reaction. Table 1 lists the intrinsic viscosities of the new PEKs. Both the homogenous polymer and copolymers synthesized exhibit very high intrinsic viscosities. However, the synthetic conditions for these PEKs are much milder than those for PEEK. In addition, the higher the feed ratio is of DFK to DFKK, the shorter the reaction time is that is needed for a high intrinsic viscosity. This may occur because of the higher reactivity of DFK compared with that of DFKK. The separation of two electron-withdrawing carbonyl groups by 1-methylcyclohexene in DFKK results in a slight decrease in the electrophilic ability of the carbon atom attached to the F atom. In addition, the double bonds in the polymer chain may cause some crosslinking. As a result, the viscosities of these DFK/DFKK PEKs are higher than those of other known PEKs. For polymers with a feed ratio of DFK to DFKK higher than 60/40, high-viscosity polymers could not be obtained under the described conditions. HQ-rich segments may crystallize and precipitate before the formation of a high molecular weight polymer.

Properties of the New PEKs

The tensile properties of the PEKs are tabulated in Table 1. All the PEKs have good mechanical

Figure 1. WAXD spectra of PEKs.

strength. For the homopolymer and copolymers, the tensile strength varies from 42 to 64.5 MPa, and no big difference is observed.

The thermal properties of the PEKs are also listed in Table 1. It is apparent that T_g 's of these PEKs increase with the DFKK content and are higher than that of commercial PEEK (144 °C). The introduction of the rigid DFKK moiety into the backbone leads to an increase in polymer chain stiffness, as shown by T_g . All the PEKs obtained, except the homopolymer, show a crystalline melting point in the DSC spectra. The asymmetric DFKK makes the homopolymer chain twisted and prevents it from orderly stacking. T_m 's, however, do not change regularly according to the DFKK contents. T_m 's of the new PEKs are about 316–335 °C, very close to that of commercial PEEK (335 °C). It is believed that the crystallinity of the PEKs arise mainly from

the —O—Ph—O—Ph—CO—Ph-rich (PEEK) segments. The amorphous nature of the homopolymer and the crystallinity of the copolymers have been proved by the WAXD method (Fig. 1). It shows that there is only one diffuse reflection peak for homopoly(ether ketone). However, all PEKs show several obvious sharp peaks. These diffraction peaks bear an analogy to those of commercial PEEK. The thermogravimetric data listed in Table 1 indicate that these PEKs are less thermally stable than PEEK, the 5% weight-loss temperature of which is greater than 500 °C. Presumably this is due to the presence of thermally unstable methylcyclohexene units.

The solubility of the new PEKs was examined in various solvents at room temperature with a concentration of 1% (w/v). Compared with commercial PEEK, which is insoluble in all organic solvents, the PEKs show high solubility in many organic solvents. PEKs with DFK/DFKK ratios of 0/100 to 50/50 were soluble in chlorinated solvents such as chloroform, chlorobenzene, and tetrachloroethane. The polymers were also soluble in tetrahydrofuran (THF) and pyridine as well as a range of polar aprotic solvents such as sulfolane, dimethylformamide (DMF), NMP, and DMAc, but they were insoluble in DMSO. The incorporation of asymmetric DFKK units into poly(ether ketone) main chains improves the solubility of PEKs. All PEKs could be cast into flexible and tough films. For this reason, new PEKs could possibly be used in applications other than those of PEEK, such as membranes for gas separation. In addition, the double bonds of the methylcyclohexene structure serve as reactive sites along the polymer chain, which can be converted easily into various other functional groups. For

Scheme 2. Cyclization of PEK with hydrazine for the production of CPEK.

Table 2. Thermal Properties of the CPEKs

Property	Unit	PEK (0/100)	PEK (10/90)	PEK (20/80)	PEK (30/70)	PEK (40/60)	PEK (50/50)
T_g	°C	233	224	211	213	219	187
5% weight-loss temperature	°C	322	302	350	347	312	277

example, carboxyl, aminoaniline, halide, and sulfonic acid could be attached onto the polymer chain via a general organic reaction with the double bonds. The derivatives of new PEKs could potentially be used as polymer reagents, polymer supports, and polymer catalysts.

Cyclization Reaction and Its Product

Two carbonyls on the third and fourth positions of methylcyclohexene react with hydrazine to form a pyrazine structure. The cyclization reaction (Scheme 2) was conducted in a sulfolane/chlorobenzene (2/1) mixture at 100 °C. Hydrazine hydrate was added dropwise. After hydrazine was added completely, the reaction was kept at 100 °C for 8 h. The products of the cyclization reactions were characterized by FTIR spectroscopy. The IR spectrum of PEK (0/100) shows strong characteristic PEK absorptions at 1675 (C=O) and 1233 cm^{-1} (C—O). However, a weak carbonyl group absorption (1675 cm^{-1}) of the corresponding cyclization product (CPEK 0/100) can be observed in the IR spectrum.

The thermal properties and solubilities of cyclized polymers differ from those of corresponding PEKs. T_g 's of the cyclized product (Table 2) are 20–30 °C higher than those of PEKs. This is caused by the conversion of two rotatable carbonyl groups into one stable pyrazine unit, which makes the polymer backbone more rigid. However, the 5% weight-loss temperatures of CPEKs are somewhat lower than those of the corresponding PEKs. The decrease in the 5% weight-loss temperatures is possibly due to the loss of hydrazine absorbed on the polymer samples. Although PEKs have excellent solubility in most organic solvents, CPEKs are less soluble than PEKs in many kinds of organic solvents examined. The CPEKs with feed ratios of DFK/DFKK in the range of 0/100 to 50/50 were primarily soluble in the polar aprotic solvents DMSO, DMAc, DMF, and NMP but not in sulfolane. The CPEKs were soluble in tetrachloroethane but insoluble in chloroform, chlorobenzene, pyridine, and THF. This was believed to be due to the change in the polar-

ity and regularity of the polymer chain after the carbonyl groups were converted into less polar and more regular pyrazine units after the cyclization reaction.

CONCLUSIONS

In this study, a series of new PEKs were prepared under mild polymerization reaction conditions by the incorporation of the asymmetric reactive monomer DFKK. These modified PEEKs exhibited very good organic solubility, good tensile properties, and reasonable thermal stability. The cyclization reaction of the new PEKs with hydrazine gave polymers containing pyrazine units, which increased T_g values of the polymers by as much as 20–30 °C and reduced their solubility in organic solvents.

The authors express their sincere gratitude to the National Natural Science Foundation of China for its financial support (20104001).

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