Preparation and Characterization of Soluble Copoly(aryl ether ketone)s Containing Hindering Structures

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ABSTRACT: New copoly(aryl ether ketone)s have been synthesized by polycondensation of 2,2′,3,3′,6,6′-hexaphenyl-4,4′-diphenol, 2,2′-*p*-hydroxyphenyl-*iso*-propane, and 4,4′-difluorobenzophenone. The technology of ^{13}C-NMR was used to determine contents of the two bisphenols in the copolymers. Chain structure was characterized by illustrating average block length (L_A, L_C) in terms of portion of the triads (AKA, CKC, AKC). The obtained copoly(aryl ether ketone)s have the properties of excellent solubility, high heat-resistance, good tensile strength, and good selectivity for gas permeability. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 20–24, 2000

Key words: polycondensation; copoly(aryl ether ketone); chain structure; property; solubility

INTRODUCTION

Poly(aryl ether ketone)s constitute a family of high-performance engineering plastics.[1-3] Typically, poly(ether ether ketone) (PEEK) has been widely used in both commercial and aerospace industries because of its excellent resistance to heat and radiation, and its good mechanical properties.[1] However, PEEK has a high melting point of 336°C and a high crystallinity, thereby making the synthesis and processing difficult. Further application of PEEK, such as membrane for gas separation, is limited. Therefore, some efforts have been made on synthesizing soluble, easily processed poly(aryl ether ketone) that maintains reasonable heat resistance and mechanical properties.[4,5] Some approaches, such as attaching appropriate side groups onto the main chain, have been successful in improving the solubility.[6-8] Nevertheless, side groups usually make the backbone rigid and difficult to rotate. Therefore, the mechanical properties of these poly(aryl ether ketone)s are usually poor. Hay et al.[6] have synthesized soluble homopoly(aryl ether ketone) (HPAE) from 2,2′,3,3′,6,6′-hexaphenyl-4,4′-diphenol (HPDP) and 4,4′-difluorobenzophenone (DFK); the glass transition temperature (T_g) of the polymer is 265°C and the polymer has good solubility in many kinds of organic solvents. However, it cannot be used for its brittleness.

In this study, we have synthesized a series of soluble copoly(aryl ether ketone)s by condensation of 2,2′-*p*-hydroxyphenyl-*iso*-propane (BPA), HPDP, and DFK. These new copolymers are of short block lengths. The results of characterization show that the copolymers have excellent solubility in some organic solvents, high heat resistance, good tensile strength, and good selectivity for gas permeability.

EXPERIMENTAL

Materials

The preparation of HPDP followed the procedure described by Hay.[9] The DFK (Jilin University,

Table I Intrinsic Viscosity of New Polymers

Entry	Unit	HPDP/BPA Feed Ratio (mol/mol)			
		100 : 0	71.4 : 25.9	48.8 : 51.2	23.9 : 76.1
Reaction time	(h)	6	6	4	4
$[\eta]^a$ of polymer	(dL/g)	0.606	0.642	0.668	0.818

a Measured at 25°C in $CHCl_3$.

Jilin, China) was recrystallized from ethanol. Sulfolane (Jinzhou Chem. Fact., Liaoning, China) was purified by stirring with NaOH for 1 day and distilling in vacuum. BPA, Na_2CO_3, K_2CO_3, and other reagents were purchased from commercial products and used as received.

Condensation

In a typical example, to a 100-mL flask were added 4 g (6.23 mmol) HPDP, 1.4913 g (6.54 mmol) BPA, 2.7839 g (99%, 12.77 mmol) DFK, 1.4498 g (13.67 mmol) Na_2CO_3, 0.1881 g (1.36 mmol) K_2CO_3, 9 mL sulfolane, and 20 mL chlorobenzene. After the reaction system was flushed with nitrogen, the solution was stirred at 140°C for 1 h, then 210°C for 4–6 h under nitrogen atmosphere. After that, the solution was poured into a larger amount of ethanol. The precipitate formed was filtered, washed with ethanol, and dried at 150°C in vacuum for several days.

Characterization

Intrinsic viscosity ($[\eta]$) measurements were performed in $CHCl_3$ at 25°C using a Cannon-Ubbelohde viscometer. ^{13}C-NMR spectra were recorded on a Varian 90 MHz spectrometer (model JEOL-FX-90Q) in dimethylsulfoxide-d_6 (DMSO-d_6). Thermogravimetric analysis and determination of T_g were made on a Perkin-Elmer DSC-7X and a TGA module (in an air atmosphere) with a heating rate of 10°C/min. Tensile test was performed on a Shimadzu tensile tester (model AG-2000) at a strain rate of 10 mm/min. Gas permeation behavior was estimated on a Yanaco gas permeability measuring system (K-315-N01).

RESULTS AND DISCUSSION

Intrinsic Viscosity

Hay et al.[6] synthesized HPAE in N-methylpyrrolidone (NMP) at 180°C. For a polymer having a

$[\eta]$ of 0.46, reaction time of 72 h was necessary. In this study, sulfolane was used as the solvent and the reaction was performed at 210–220°C. It can be seen from Table I that a reaction time of 6 h is long enough for obtaining the same polymer having a $[\eta]$ of 0.606. Reaction time is greatly shortened. Table I also lists the intrinsic viscosity of copoly(aryl ether ketone)s synthesized via Scheme I. An increase in viscosity is seen with the decrease in the ratio of HPDP/BPA. Less hindering effect of BPA makes it more reactive than HPDP. The viscosity demonstrates that the polycondensation yields polymers having molecular weights high enough for usual applications.
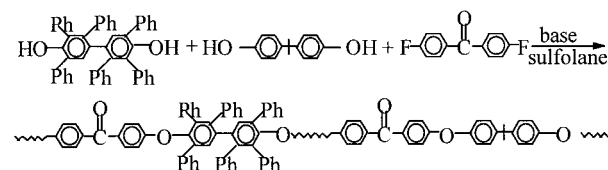
Scheme I

Structure of Copolymers

In a copolycondensation, it is necessary to know whether the product is actually a copolymer or a

Table II Sequence Distribution in Copolymers with Various Ratios

Statistical Parameter	HPDP/BPA Feed Ratio (mol/mol)		
	74.1 : 25.9	48.8 : 51.2	23.9 : 76.1
C_{AKA}	0.638	0.278	0.106
C_{AKC}	0.247	0.401	0.263
C_{CKC}	0.115	0.321	0.631
C_A/C_C	76.2 : 23.8	47.9 : 52.1	23.8 : 76.2
L_A	6.17	2.39	1.81
L_C	1.93	2.60	5.79
K_m	0.680	0.803	0.725

Table III   Thermal Properties of New Polymers

Property	Unit	HPDP/BPA Feed Ratio (mol/mol)			
		100 : 0	74.1 : 25.9	48.8 : 51.2	23.9 : 76.1
$[\eta]$	(dL/g)	0.606	0.642	0.668	0.818
T_g	(°C)	265	215	201	187
5% weight loss temperature	(°C)	>500	>500	>500	>500

mixture of homopolymers and the degree of randomness in the copolymer chains. Polycondensation of HPDP, BPA, and DFK yields copoly(aryl ether ketone) whose chain structure contains three possible linkages as in Scheme II.

Scheme II
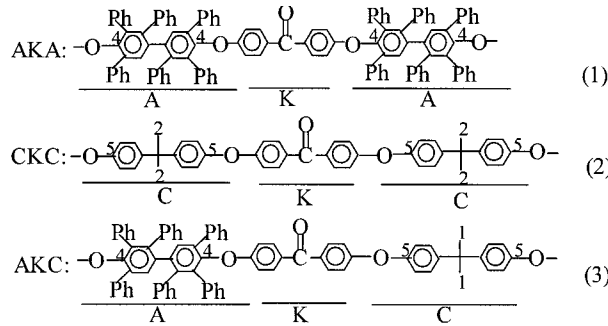
AKA as well as CKC are called homolinkages and AKC is called heterolinkage. Their proportion in the copolymer can be represented by C_{AKA}, C_{CKC}, and C_{AKC}, respectively. According to references 10–12, molar fractions of two bisphenols, HPDP (C_A) and HPA (C_C), can be obtained via the following expression:

$$C_A = C_{AKA} + C_{AKC}/2; \quad C_C = C_{CKC} + C_{AKC}/2 \quad (1)$$

The number-average sequence lengths of an AKA unit (L_A) and a CKC unit (L_C) are given by:

$$L_A = 2C_A/C_{AKC}; \quad L_C = 2C_C/C_{AKC} \quad (2)$$

The degree of randomness is defined by:

$$K_m = 1/L_A + 1/L_C \quad (3)$$

When $K_m = 1$, AKA and CKC take a random distribution. If $K_m < 1$, these units tend to cluster in blocks of each units, and finally $K_m = 0$ in a homopolymer mixture, whereas if $K_m > 1$, the sequence length becomes shorter, and $K_m = 2$ in an alternative copolymer.

C_{AKA}, C_{AKC}, and C_{CKC} can be obtained from the intensities of the three kinds of signals in the ^{1}H-NMR or ^{13}C-NMR spectra.[10–12] In this report, ^{13}C-NMR spectra of the obtained polymers are measured.

The existence of AKC linkage in copolymer makes the chemical surrounding its C atom different than that in homopolymer. For example, the signal of methyl carbon (C_1) in AKC linkage appears at 22.6 ppm and at this chemical shift in the ^{13}C-NMR spectrum of homopolymer, no peak appears. This means that the copolycondensation produces a copolymer but not a mixture of homopolymers. The intensity of this peak represents the amount of heterolinkage. Correspond-

Table IV   Tensile Properties of Copolymers

Property	Unit	HPDP/BPA Feed Ratio (mol/mol)			
		100 : 0	74.1 : 25.9	48.8 : 51.2	23.9 : 76.1
$[\eta]$	(dL/g)	0.606	0.642	0.668	0.818
Tensile strength	(Mpa)	15.3	85.5	73.1	51.6
Elongation at rapture	(%)	5.08	9.65	66.7	36.8

Table V   Solubility of New Polymers

	HPDP/BPA Feed Ratio (mol/mol)			
Solvent	100 : 0	74.1 : 25.9	48.8 : 51.2	23.9 : 76.1
Chloroform	++	++	++	++
1,2-Dichloroethane	++	++	++	++
Chlorobenzene	++	++	++	++
Toluene	++	++	++	++
N-Methyl-2-pyrrolidone	+	+	+	+
N,N-Dimethylacetamide	+	+	+	+
Sulfolane	+	+	+	+

+, Soluble on heating; ++, soluble at room temperature.

ingly, the chemical shift of methyl carbon (C_2) in CKC linkage, which appears in spectra of both homopolymer and copolymer, is 31.1 ppm. Its intensity represents the amount of CKC linkage. The ratio of these two intensities equals to C_{AKC}/C_{CKC}. Meanwhile, chemical shifts at 152.2 ppm and 149.9 ppm are attributed to C_3 and C_4, respectively. Corresponding change in chemical shift due to AKC linkage is not detected. The ratio of the intensities of these two peaks equals to C_A/C_C. Calculated with Eqs. (1–3), the statistical data obtained are summarized in Table II. It shows that for all feed ratios examined, the values of K_m are less then and approach to 1, whereas L_A and L_C are short. So, copoly(aryl ether ketone)s can be recognized to have a short block distribution.

Properties

Table III lists T_g and data from thermogravimetric analysis of the homo- and copolymers. Copolymers from various ratios of HPDP/BPA show only a single T_g. This coincides with its short block length. T_g increases with decreasing amount of BPA incorporated. T_gs of new poly(aryl ether ketone)s are higher than that of PEEK (144°C). Thermal decomposition temperatures of the homo- and copolymers are generally higher than 500°C. All of the new polymers exhibit good heat resistance.

Having a great number of hindering side groups in the molecule, HPDP lowers the tensile strength of the homopolymer (Table IV). In copolymers, improvement of tensile properties is observed with the incorporation of less hindered BPA. For the homopolymer, brittle fracture takes place in the course of tensile test, whereas incorporation of BPA increases toughness of copolymers.

No great difference in solubility between copolymers from various HPDP/BPA ratios is observed. All the polymers are easily dissolved in a few kinds of organic solvents (Table V). This makes possible the use of the new polymers in more new fields than PEEK, such as membrane for gas separation. Because the homopolymer,

Table VI   Permeabilities and Selectivities of Copolyetherketones

			HPDP/BPA Feed Ratio (mol/mol)		
Property	Unit		74.1 : 25.9	48.8 : 51.2	23.9 : 76.1
Permeability	Barrer	CO_2	10.0	5.13	4.49
		O_2	1.35	1.04	0.75
		N_2	0.439	0.220	0.107
Selectivity	25°C	P_{O2}/P_{N2}	3.09	4.73	7.01
		P_{CO2}/P_{N2}	22.8	23.3	42.0
	60°C	P_{O2}/P_{N2}	2.42	3.91	4.54
		P_{CO2}/P_{N2}	14.5	14.2	19.5

HPAE, has a lower tensile strength, good membrane is not obtained. Study results on permeability of gas of copolymers are summarized in Table VI. Permeability coefficients for all gases tested become lower with the increase in the amount of incorporated BPA. The selectivity for permeation (P_{O2}/P_{N2} and P_{CO2}/P_{N2}) becomes higher correspondingly. In general, copolymers have good permeability at room temperature and 60°C. For instance, P_{O2}/P_{N2} and P_{CO2}/P_{N2} are 42 and 7, respectively, at room temperature for copolymer from HPDP/BPA of 23.9 : 76.1. They are 50% and 26% higher than the values of commercial polysulphone (PSF) membrane.

CONCLUSIONS

A series of new copoly(aryl ether ketone)s containing hindering structures were successfully synthesized from HPDP, BPA, and DFK. Chain structures of copoly(aryl ether ketone)s are of short block distribution. Copolymers have good tensile strength and high heat resistance. New polymers are easily dissolved in a few organic solvents such as chloroform, toluene, chloroben-zene, and sulfolane. Copolymers have good permeability of gases at room temperature and 60°C.

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