

Effects of Molecular Weight on Selected Physical Properties of Polyaromatic Ether-Ketones

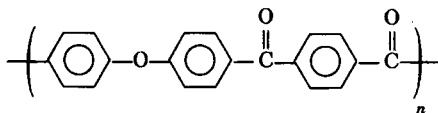
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Synopsis

Polyaromatic ether-ketones with various inherent viscosities were prepared and their thermal properties and stress-strain relationships were studied. It was found that the polymer should have an inherent viscosity greater than 0.8 in order to give flexible films, but there was no difference in thermal and stress-strain properties among polymers with viscosities greater than 0.8. Values of 110 MPa and 13% are considered to be the standard values of tensile strength and elongation, respectively, for these polyaromatic ether-ketones. The crosslinking effects on these properties were also studied, using polymers containing 1 and 5 mol % of crosslinkable biphenylene units, but no significant changes in the properties due to crosslinking were observed.

INTRODUCTION

Polyaromatic ether-ketones (I) obtained by the reaction of diphenyl



ether and iso- or terephthaloyl dichloride with anhydrous aluminum chloride, are known to have excellent thermal and chemical stabilities.¹ However, the inherent viscosity of polymer obtained is greatly affected by the polymerization conditions, and it is difficult to obtain high viscosity polymers unless extreme care is taken regarding the purity of the reagents. In order to obtain high molecular weight polymers, Swedo and Marvel² synthesized polymers containing biphenylene units which lead to crosslinked materials on heating at temperatures over 300°C. Later Sutter, Schmutz, and Marvel³ studied this cross linking behavior using various isomers of biphenylene carboxylic acid in order to see if there was any difference in curing ability between the isomers.

It is of interest to know what magnitude of mechanical strength these polyaromatic ether-ketones possess and how mechanical strength depends on the molecular weight and/or crosslink density. Therefore, the thermal behav-

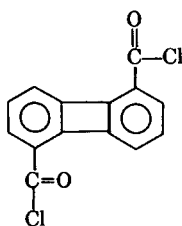
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iors and mechanical strengths of polymers having different inherent viscosities were determined, and the effect of crosslinking was studied using polymers containing different amounts of biphenylene units. The results are reported in this paper.

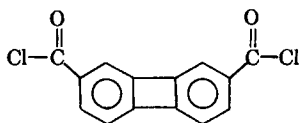
EXPERIMENTAL

Materials

Isophthaloyl and terephthaloyl dichlorides used were supplied by the Aldrich Chemical Co., and were purified by recrystallization from *n*-hexane before use. Biphenylene-1,5-dicarboxylic acid chloride (II) was synthesized by the method described by Newman and Logue,⁴ and biphenylene-2,6-dicarboxylic acid chloride (III) was prepared by the oxidation of 2,6-diacetyl biphenylene



(II)



(III)

as reported previously.³ Diphenyl ether, supplied by the J. T. Baker Chemical Co., was distilled under reduced pressure before use. Anhydrous aluminum chloride supplied by the Aldrich Chemical Co. was used without further purification. 1,2-Dichloroethane supplied by Fisher Scientific Products and the Aldrich Chemical Co. was used as solvent after distilling from phosphorus pentoxide.

Polymerization

The polymerization was carried out by the method previously reported.³ A typical polymerization procedure is described below and the others are summarized in Table I. When 1,2-dichloroethane supplied by Fisher Scientific Products was used as a solvent for the polymerization, polymers with higher inherent viscosity were produced than when 1,2-dichloroethane supplied by Aldrich Chemical Company was used as a solvent, even though both were purified by exactly the same method; i.e., reflux over and distillation from phosphorus pentoxide immediately before use. The polymers were purified by heating in 20% hydrochloric acid for 1 h followed by refluxing in 88% formic acid, and then washing thoroughly with water and methanol.

TABLE I
 Polymerization Conditions^a

Run	Diphenyl ether (mol)	Dichloride (mol) ^b	Dichloroethane (mL) ^c	Aluminum trichloride (g) ^d	Polymerization time (h)	Yield (%)	η_{inh}
P-1	0.25	0.25 (i)	1250 ^A	80 (20)	64	70	0.20
P-6	0.25	0.25 (i)	1500 ^A	80 (90)	48	80	0.33
P-2	0.25	0.25 (i)	1000 ^A	80 (30)	48	90	0.72
P-3	0.25	0.25 (i)	1250 ^A	80 (20)	48	100	0.88
P-4	0.25	0.25 (i)	1400 ^F	80 (120)	90	100	0.94
P-8	0.25	0.25 (i)	1500 ^F	83 (30)	36	96	1.08
P-9	0.20	0.20 (i)	1200 ^F	69 (30)	40	100	1.28
PT-1	0.20	0.14 (i) 0.06 (t)	1200 ^F	70 (30)	50	100	1.16
PT-2	0.25	0.125 (i) 0.125 (t)	1500 ^F	80 (2880)	55	96	0.91
PC-1	0.20	0.198 (i) 0.002 (b)	1200 ^F	70 (30)	40	100	1.08
PC-2	0.20	0.198 (i) 0.002 (b)	1500 ^F	70 (60)	50	100	1.10
PC-3	0.25	0.2375 (i) 0.0125 (b)	1800 ^F	80 (60)	50	95	0.79

^aThe polymerization system was cooled to 3–5°C when the first portion of aluminum chloride was added. After a few hours, the temperature was raised to room temperature (22–23°C).

^b(i): isophthalic dichloride, (t): terephthalic dichloride, (b) biphenylene dicarboxylic acid dichloride.

^cA = supplied by Aldrich Chemical Company; F = supplied by Fisher Scientific Products.

^dThe numbers in () are the periods (mins) during which aluminum trichloride was added continuously in small amounts or in portions with time intervals.

General Polymerization Procedure

42.55 g (0.25 mol of diphenyl ether and 50.76 g (0.25 mol) of isophthaloyl dichloride were dissolved in 1250 mL of 1,2-dichloroethane in a 2 l, three-necked flask equipped with a mechanical stirrer and a dry nitrogen inlet. The mixture was cooled to 2–3°C with an ice bath, and 80 g of anhydrous aluminum chloride suspended in 100 mL of dichloroethane were slowly added. The temperature of the system rose to 7°C. After 3 h the ice bath was removed, and the mixture was stirred for 45 h at room temperature. A red solid precipitated which was filtered, washed with hydrochloric acid, methanol, and water, and made into powder in a blender with methanol. The yield was 75 g (100%).

Measurements

The inherent viscosity was determined in sulfuric acid at 30°C for a concentration of 0.5 g/100 mL. Polymer films with a thickness of 0.2–0.3 mm were prepared by heating the polymer powders using a hot plate placed in a press with a compressing pressure of approximately 10 kg/cm². The pale brown to dark brown transparent films thus obtained were cut into a dumbbell shape (ASTM No. 0638-820A) and their mechanical properties were measured using an Instron Model 1125 Universal Testing Machine, with an elongation velocity of 50 mm/min. The results shown in Table III are those of an

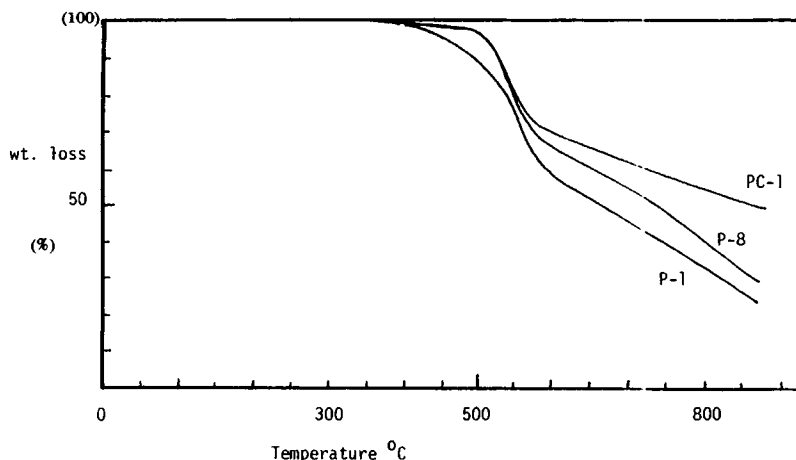


Fig. 1. Thermogravimetric analysis curves for polyaromatic ether-ketones.

average of two or more samples. The thermogravimetric analysis was carried out on powder samples using a DuPont thermoanalyzer Model 951 with a heating rate of 25°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The polyaromatic ether-ketones (I) lose 1–3% of their weight when heated in a hot air circulating oven at 310°C for a few days.³ When the polymer powders were compressed into films at temperatures above 350°C over a period of a few hours, gas bubbles were formed in the films. These bubbles were also observed when samples were heated at lower temperatures such as 330°C for a period of more than 24 h. In order to check the thermal decomposition behavior of these polymers, thermal gravimetric analysis was carried out and the typical weight loss curves are shown in Figure 1. The results are summarized in Table II. As can be seen from these results, the polyaromatic ether-ketones decompose rapidly at temperatures above 500°C, giving black porous solids. The polymers having lower molecular weights (P-1

TABLE II
Thermogravimetric Analysis for Polyaromatic Ether-Ketones

Sample number	η_{inh}	Temp (°C) for wt loss		Wt loss (%) at		
		0.5%	1%	500°C	600°C	850°C
P-1	0.20	350	380	13	42	73
P-6	0.33	350	380	18	45	72
P-2	0.72	425	460	2.5	32	62
P-3	0.88	430	460	4	36	55
P-4	0.94	430	465	1	26	55
P-8	1.08	380	440	3	35	66
P-9	1.28	420	475	2.5	35	66
PC-1 ^a	1.08	380	420	3	30	43

^a Contains 1 mol % 1,5-biphenylene units.

TABLE III
Relationships between Inherent Viscosity and Stress-Strain Properties

Sample no.	η_{inh}	Temp ($^{\circ}$ C) ^a	Tensile strength (MPa)	Elongation at break (%)
P-4	0.94	325	119.5	13.8
P-4	0.94	350	108.9	13.8
P-11	0.81	328	116.8	13.1
P-11	0.81	330	116.9	15.1
P-11	0.81	338	110.3	13.8
P-11	0.81	360	108.9	14.3
P-8	1.08	345	103.5	13.1
P-8	1.08	350	99.5	13.5
P-8	1.08	360	112.1	13.2
P-9	1.28	340	106.8	13.6
P-9	1.28	348	87.3	13.4
P-9	1.28	352	105.4	13.1
PT-1 ^b	1.16	330	107.6	13.5
PT-2 ^c	0.91	330	92.6	13.8

^aTemperature of the hot plate; heating duration is 1 h, then cooled slowly by disconnecting the power.

^b30% terephthalic unit.

^c50% terephthalic unit. The others are of 100% isophthalic unit.

and P-6) decompose more rapidly than the others, but there is no significant difference in thermal decomposition behavior when the viscosity exceeds 0.8.

The films of polymers having inherent viscosities less than 0.8 are brittle and break on bending, and therefore they could not be cut into dumbbell specimens. Those with viscosities higher than 0.9 are flexible and can be folded without breaking. This is analogous to previous results obtained on sulfonated polyaromatic ether-ketones, which give strong, flexible films when cast from DMF solution provided inherent viscosity before sulfonation was 1.1 or greater.⁵ Table III shows the results of stress-strain measurements for polymer films having different inherent viscosities. Clearly, there are no significant differences in tensile strengths or elongation at break among the polymers, indicating that approximately 110 MPa can be thought of as the typical value of the tensile strength of polyaromatic ether-ketones of type I, provided inherent viscosity is > 0.8 . There was little effect of heating temperature on the film strength. Table IV shows the relationships between the curing conditions and tensile properties of the polymers containing biphenylene units. Some of the polymer films of Table IV were partially insoluble (PC-1 and PC-2) and one was mostly insoluble (PC-3) in concentrated sulfuric acid, showing that the crosslinking took place under these curing conditions. However, the tensile strength did not increase as a result of this crosslinking, being more or less the same as those of uncured polymers (Table III). The inferior strengths of PC-1 and PC-2 films heated at 318 $^{\circ}$ C for 24 h might be due to decomposition during curing. The elongation at break remained the same as that for type I polymers, and 13% seems to be the standard value for these flexible polyaromatic ether-ketone films. The films heated for longer periods at higher temperatures were more brittle, and it was difficult to obtain dumbbell specimens due to cracking or gas bubbles in the films.

TABLE IV
Relationships Between Curing Conditions and Stress-Strain Properties
of Polymers Containing Crosslinkable Biphenylene Units

Sample no.	Biphenylene		η_{inh}	Temperature (° C)	Time ^a (h)	Tensile strength (MPa)	Elongation at break (%)
	Type	mol %					
PC-1	1,5-	1	1.08	318	24	82.9	12.5
PC-2	1,5-	1	1.10	318	24	86.0	13.8
PC-2	1,5-	1	1.10	325	1	120.3	13.1
PC-2	1,5-	1	1.10	355	1	88.8	13.5
PC-2	1,5-	1	1.10	355	2	98.5	13.1
PC-2	1,5-	1	1.10	360	0.5	118.5	13.1
PC-3	2,6-	5	0.79	313	24	117.1	13.1
PC-3	2,6-	5	0.79	320	1	95.9	13.1
PC-3	2,6-	5	0.79	320	2	85.3	13.1

^aThe period during which the temperature indicated was maintained does not include the pre- and post-heating periods.

From the results of this work it can be said that polyaromatic ether-ketones give films with a tensile strength of ~ 110 MPa and an elongation at break of 13% by pressing the polymer powder at 300–350 °C. Crosslinking using biphenylene units did not improve the tensile properties. However, more detailed studies on crosslinkable polyaromatic ether-ketones are in progress at present.

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References

1. W. H. Bonner, U.S. Pat. 3,065,205 (1962); I. Goodman and J. E. McIntyre, U.S. Pat. 3,385,825 (1967); B. M. Marks, U.S. Pat. 3,441,538 (1967); R. J. Angelo, Ger. Offen. 2,1218,734 (1971).
2. R. J. Swedo and C. S. Marvel, *J. Polym. Sci., Polym. Lett. Ed.*, **15**, 688 (1977).
3. A. Sutter, P. Schmutz, and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 609 (1982).
4. M. S. Newman and M. W. Logue, *J. Org. Chem.*, **36**(10), 1398 (1971).
5. T. Ogawa and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 4 (1985).

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