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POLY(ARYLENE ETHER)S CONTAINING 1,5- DIBENZOYLNAPHTHALENE UNITS

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ABSTRACT

High molecular weight, soluble poly(arylene ether)s containing 1,5-dibenzoylnaphthalene units were synthesized based on the difluoro-substituted monomer derived from naphthalene and 4-fluorobenzoyl chloride by a Friedel-Crafts reaction. The glass transition temperatures of the polymers range from 199 to 259°C. The 5% weight loss for these polymers by thermogravimetric analysis are all above 500°C in nitrogen and 480°C in air.

INTRODUCTION

Aromatic poly(ether ketone)s (PAKs) are an important class of high performance polymers displaying excellent thermal and chemical stability and good mechanical properties. Since the commercialization of poly(ether ether ketone) (PEEK) by ICI a number of new PAKs have been synthesized in an effort to improve overall properties [1], [2]. Much effort has been expended in the development of new PAKs with high glass transition temperature (T_g) because PEEK has a relatively low T_g of 145°C. Synthesis of high performance polymers containing naphthalene units has received attention recently because of its rigid symmetrical

structure which gives enhanced thermal stability to the polymers. In the PAK synthesis area, some new PAKs containing naphthalene units have been synthesized and the structure-property relationship have been studied. Hergenrother synthesized PAKs containing 2,6-substitution on the naphthalene unit. These PAKs possess higher T_g s but lower solubilities in organic solvents [3]. Wang synthesized PAKs containing the unsymmetrical benzonaphthone [4],[5] and 1,8-dibenzoylnaphthalene [6] units, which have high T_g s and improved solubility. Endo reported PAKs containing the 2,6-dimethyl-1,5-naphthalene unit, which have higher T_g s but decreased thermooxidative stability [7], [8]. In this work, methyl substituents play an important role both in the enhancement of T_g and in the decreased thermal stability. Bottino synthesized PAKs and poly(ether sulfone)s containing 2,6- and 1,5-naphthalene units with methyl substituted biphenyl-4,4'-diols [9]. The polymers showed high T_g s, but decreased thermooxidative stability.

In order to expand the study on the effects of the substitution pattern on properties, we have synthesized PAKs containing 1,5-dibenzoylnaphthalene units which do not contain any aliphatic substituents.

EXPERIMENTAL

General Methods

Melting points were recorded on a Fisher-Johns melting point apparatus. Inherent viscosity data was obtained using 1, 1', 2, 2'-tetrachloroethane (TCE) solutions at a concentration of 0.5 g/dL in a calibrated 1 Å (176) Ubbelohde dilution viscometer at 25°C. A Waters 150 μ -styragel HT Linear 10 μ m column was used to determine apparent molecular weights by gel permeation chromatography using polystyrene standards with CHCl_3 as a solvent. Glass transition temperatures (T_g s) were measured using a Seiko 220 DSC instrument at a heating rate of 20°C/min under nitrogen atmosphere. The T_g was taken as the midpoint of the change in slope of the baseline. All values reported are from the second run unless otherwise noted. TGA measurements were obtained using a Seiko 220 TG/DTA instrument. The 5% weight loss points were recorded using a heating rate of 20°C/min under atmospheres of nitrogen and air. All polymer samples were dried under a nitrogen atmosphere at the T_g (as determined by DSC) for 1 hour before performing TGA measurements. Young's moduli were recorded using a Seiko TMA/SS120. The polymer films used for these measurements were prepared as follows: 200 mg of polymer was dissolved in 3 mL of TCE. The films were cast from TCE solutions

onto glass plates using circular glass molds, 1 inch in diameter. The solvent was allowed to evaporate and the films were dried at 100°C for 24 hours in a forced air oven. Elemental analysis were performed by Galbraith Laboratories, Knoxville, TN.

Materials

4-Fluorobenzoyl chloride (Lancaster), naphthalene, aluminum trichloride (Omega), methanol (ACP), toluene (A&C Chemicals) were used as received. N,N-Dimethylacetamide (DMAc), N-methylpyrrolidinone (NMP) (Aldrich) were distilled over phosphorus pentoxide before use.

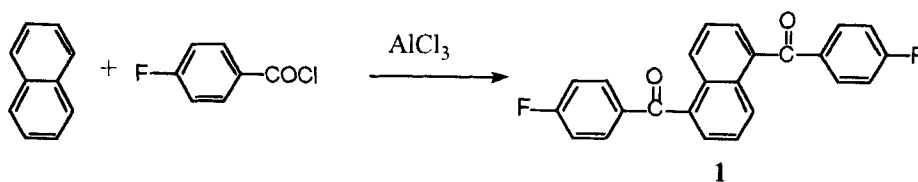
Monomer Synthesis

1,5-Bis(4-fluorobenzoyl)naphthalene

In a flame-dried 500 mL three-neck flask equipped with a thermometer and calcium chloride drying tube and a mechanical stirrer, was placed 37.64 g (0.25 mole) of 4-fluorobenzoyl chloride. 53.34 g (0.40 mole) of anhydrous aluminum chloride was added slowly and then the temperature was raised to 70°C. To the yellow slurry, was added 12.82 g (0.10 mole) of naphthalene portion wise with care, at 60-65°C. The reaction mixture turned into a reddish black viscous liquid. It was stirred at 70°C for 18 hours. Then, the reaction mixture was slowly added to water to form tan yellow chunks which were washed thoroughly until acid free and filtered. Recrystallization from toluene gave 24.92 g (67.0 %) of tan yellow plates. ¹H-NMR (270MHz, DMSO-d₆) 7.36-7.47 (m, 4H), 7.64-7.72 (m, 4H), 7.86-7.93 (m, 4H), 8.09 (d-d, J₂=7.64, J₃=1.73, 2H); m.p. 216-8°C; MS (EI, 250°C) 372.14 (M⁺, 100), 277.07 (42.0), 249.08 (90.9); Anal. calc'd for C₂₄H₁₄F₂O₂: C, 77.41; H, 3.79; F, 10.20; O, 8.59; found: C, 77.56 ;H, 3.79

Polymer Synthesis

Polymerization reactions were typically carried out in a 50 mL, three-necked flask equipped with a stir bar, a Dean-Stark trap fitted with a condenser, and a nitrogen inlet. The following is a typical procedure. A flask was charged with **3** (0.558 g; 1.50 mmol), BPA (0.342 g; 1.50 mmol), potassium carbonate (0.230 g; 1.65 mol), NMP (4.5 mL), and toluene (10 mL). The reaction mixture was heated to a gentle reflux (135°C) and this temperature was maintained for 2 hours to ensure complete dehydration. The reaction temperature was increased to 190°C by removing the toluene from the Dean-Stark trap. The reaction was discontinued when the solution viscosity increased dramatically. The solution was diluted with 5



Scheme I

mL of DMAc and coagulated into 300 mL of methanol containing several drops of glacial acetic acid. The recovered polymer was dissolved in CHCl₃ and filtered hot through a thin pad of Celite. The CHCl₃ solution was concentrated and the polymer was coagulated in methanol (250 mL). The solid polymer was recovered by filtration and dried *in vacuo* for 24 hours.

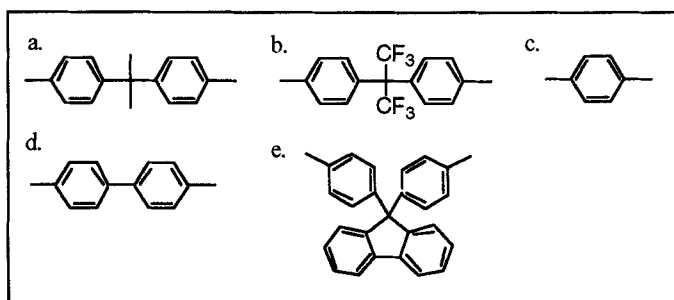
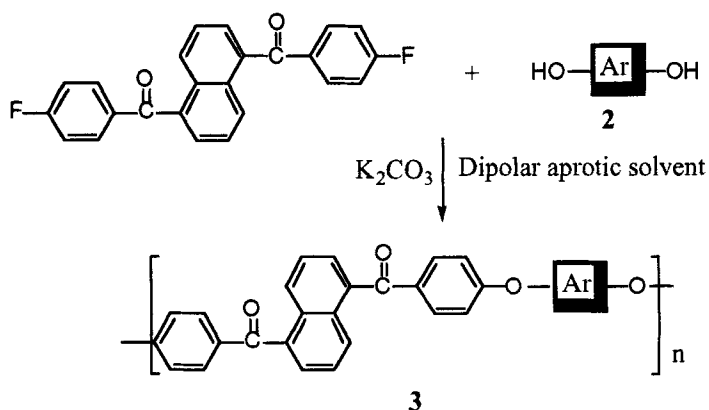
DISCUSSION

Monomer Synthesis

Friedel-Crafts reaction of naphthalene with 4-fluorobenzoyl chloride in the presence of a Lewis acid such as aluminum trichloride in solvents such as nitrobenzene gave only monoacylation under all conditions used. 1,5-Bis(4-fluorobenzoyl)naphthalene, was synthesized by Friedel-Crafts acylation of naphthalene with a slight excess of 4-fluorobenzoyl chloride in the absence of solvent at 80°C in 68% yield (Scheme I).

Polymer Synthesis

Polymerization reactions were carried out in a dipolar aprotic solvent using a stoichiometric ratio of monomers in the presence of excess potassium carbonate at a concentration of 25 wt % (Scheme II). The water, formed by deprotonation of the phenols, was removed by azeotropic distillation with toluene at 130°C during the early stages of reaction. High molecular weight polymers with inherent viscosities of 0.69-0.88 were prepared from bisphenols **2b**, **2c**, **2d** in NMP at 190°C for 18 hours (Table I). In the case of **2a** and **2e**, somewhat lower molecular weight polymers formed in NMP. It is reported that fluoride anion cleaved ether links in the synthesis of amorphous poly(ether ketone)s over prolonged reaction times [10]. To avoid this, polymerization was carried out in DMAc at 160°C and high molecular



Scheme II

weight polymer was obtained. GPC data for the polymers which are soluble in CHCl_3 are shown in Table I. Their M_w s compared to polystyrene standards are over 100,000, indicating formation of high molecular weight polymer. The polydispersity values are within the range expected for condensation polymers.

Polymer Solubilities

The solubility of the resulting polymers is shown in Table IV. Polymers which have flexible chains such as **3a**, **3b** are soluble in CHCl_3 at room temperature. As the chain rigidity increases, the solubility decreased; **3d** is soluble in TCE, **3c** is soluble in dipolar aprotic solvents.

Thermal Properties

The polymers were investigated with respect to their thermal properties by DSC and TGA. The results are summarized in Table II and illustrated in Figure 2.

TABLE I. Polymerization of **1** with Biphenols

Polymer	Solvent	Yield (%)	η_{inh}^a	M_n^b	M_w	M_w/M_n
3a	DMAc	92	0.45	55500	121000	2.2
3b	NMP	87	0.69	68200	150000	2.2
3c	NMP	93	0.86	-	-	-
3d	NMP	97	0.88	-	-	-
3e	NMP	91	0.37	27000	88000	3.3
3e	DMAc	89	0.51	64100	137000	2.1

^a η_{inh} was measured at a concentration of 0.5 g/dL in NMP at 25°C.

^bMolecular weight was determined by GPC in CHCl₃ based on polystyrene standards.

TABLE II. Thermal Properties of Polymers **3a-e**

3a	199	523	450
3b	208	516	507
3c	207"	506	456
3d	213	521	512
3e	259	535	467

a) T_g determined by DSC at heating rate 20°C/min under N₂ (160 mL/min), the values reported are from the second scan.

b) Report for 5% weight loss at heating rate 20°C/min under air or N₂ (flow rate 200 mL/min).

c) T_m at 288°C after annealing at 220°C for 1 hour.

The results demonstrate the general excellent thermal stability of these poly(arylene ether)s. The 5 % weight losses in nitrogen were around 500-520°C with no weight losses up to 400°C. In air, these temperatures are up to 30°C lower. Thermal transitions were investigated by DSC in the temperature range from 100°C to 400°C. With increasing chain stiffness the detection of the glass transition by DSC became more difficult as shown for **3b**, **3d** in Figure 1. The most flexible polymer with a BPA unit in the main chain showed the lowest T_g, 199°C. Polymer **3e** which contains the bulky fluorene group showed the highest T_g, 259°C. Polymers **3a**, **3b**, **3d**, appeared to be amorphous since none of them show any crystalline behavior even after extensive annealing above the T_g. Polymer **3c** showed a melting endothermic peak at 288°C after annealing 10°C above T_g for 1 hour.

TABLE III. Solubility of Polymers 3a-e

Polymer					
	m-cresol	TCE	CHCl ₃	NMP	THF
3a	+	+	+	+	+/-
3b	+	+	+	+	-
3c	+	+	+/-	+	-
3d	+	+	+/-	+	-
3e	+	+	+	+	-

a) Solubility: +, soluble at room temperature; +/-, partially soluble; -, insoluble.

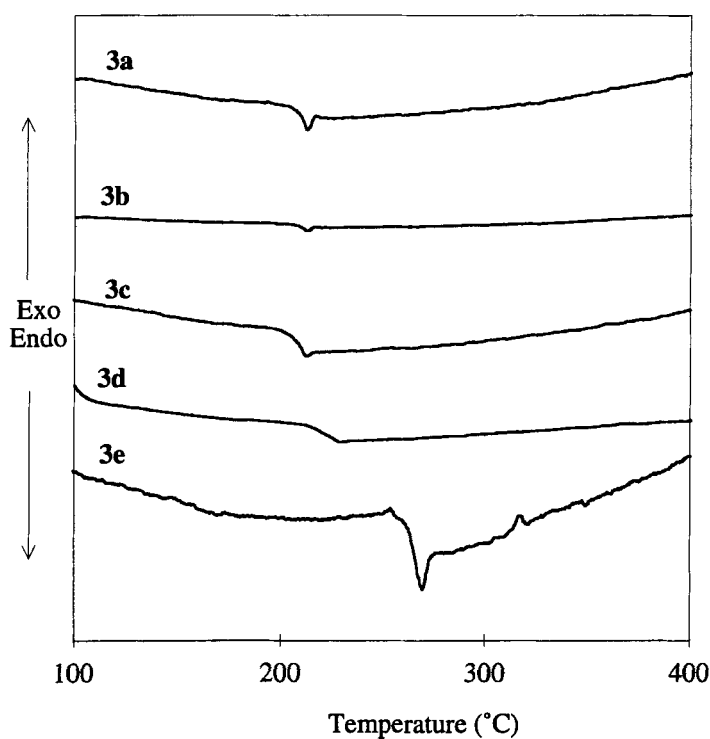


Figure 1. DSC Traces of Polymers 3a-e.

Mechanical Properties

The solvent cast thin films of the polymers were clear, creasable, and tough. Young's moduli were measured by TMA in the tensile stress-strain mode (Table II). They maintained dimensional integrity from room temperature to close to their

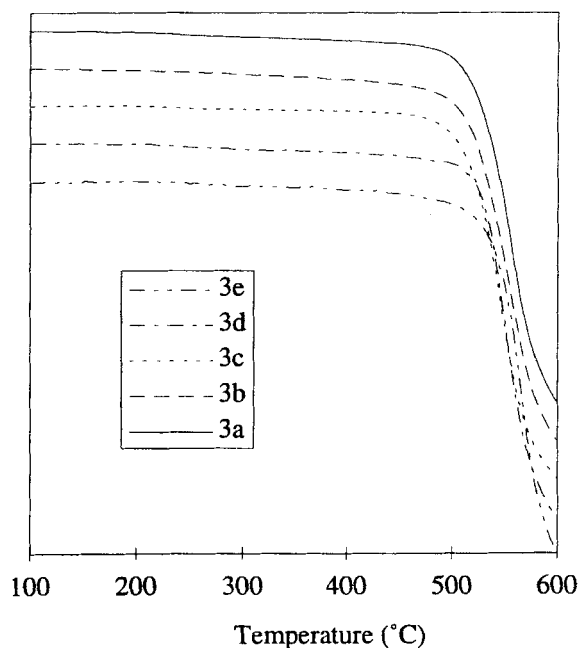


Figure 2. TGA Traces of Polymers **3a-e**.

T_g (Figure 2). The T_g s as determined by TMA agreed with those determined by DSC. The Young's moduli from TMA/SS were in the range 0.92-2.18 Gpa between 25-190°C. These values are typical for engineering thermoplastics such as poly(sulfone)s and poly(ether imide)s.

Comparison with Other Naphthalene Containing PAKs

The comparison of the thermal properties of naphthalene-containing PAKs is shown in Table IV. T_g s of poly(ethylene naphthalene dicarboxylate)s decrease in the order 2,6-, 1,5-, 1,4- [11], i.e. the T_g s increase with increasing linearity of the polymer chains. T_g of PAKs containing dibenzoylbiphenyl moieties also increases with increasing linearity of the dibenzoylbiphenyl unit except for the 2,2'-substituted PAK [11] in which there is sterically restricted motion in the biphenyl unit caused by the 2,2'-substitution. In dibenzoyl naphthalene containing PAKs' the T_g s decrease in the order 2,3-, 1,5-, 2,6-. In this case the T_g s decreased with increasing linearity of the naphthalene unit because of steric interactions, i.e. peri-interactions with 1,5- and ortho-substitution in the 2, 3-disubstituted case, which inhibits the chain motion. This agreed with the 5% weight loss data from TGA ($T_{d5\%}$) and the

TABLE IV. Mechanical Properties of Polymers 3a-e

Polymer	Young's Modulus (GPa)		Tan δ ($^{\circ}$ C)
	20 $^{\circ}$ C	200 $^{\circ}$ C	
3a	1.78	0.92	183
3b	1.99	1.21	200
3c	2.18	1.33	194
3d	2.03	1.22	192
3e	1.87	1.14	248

TABLE V. Comparison of Properties of PAKs Containing Naphthalene Units

T _g	215	185	238	199	
T _{d5%}	475	522	457	501	
Solubility	CHCl ₃	NMP	CHCl ₃	CHCl ₃	
Reference	[5]	[2]	[6]		

solubility for naphthalene-containing PAKs. The order of T_{d5%} is 2,6-, 1,5-, 2,3- and solubility decreases in order of 2,6-, 1,5-, 2,3-. Compared with PAKs with 1,5-dibenzoyl-4,8-dimethyl units, they showed lower T_g, higher thermostability and less solubility. Methyl substitution causes "crowding" with the adjacent groups which hinders the motions of the polymer chains, hence increases the chain stiffness and

causes T_g to increase. Methyl substitution also decreases crystallinity and increases solubility. However, because of the aliphatic groups, thermooxidative stability is greatly reduced.

CONCLUSIONS

A series of novel poly(arylene ether ketone)s have been synthesized. The polymers were amorphous, except for the polymer from hydroquinone which showed semicrystalline behavior. The T_g s are in the range 199-252°C, and they exhibit 5% weight losses around 500°C in nitrogen, and 480°C in air, by TGA. Many of these polymers are soluble in common organic solvents such as CHCl_3 . The mechanical properties are typical of high performance engineering thermoplastics (modulus = 1.78-2.18 GPa) and the properties are maintained up T_g .

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