# **Polyaramides Containing Sulfone Ether Units**

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Aromatic polyamides with aryl ether or aryl sulfone links have increased chain flexibility and lower glass transition temperatures than those of crystalline polyaramides without these groups. Aromatic polyamides containing both aryl sulfone and aryl ether links between amide groups, that have been obtained by polymerization of 4,4'-[sulfonylbis(pphenyleneoxy)]dianiline with isophthaloyl or terephthaloyl chlorides, for example, are amorphous.<sup>2</sup> These polyaramides have glass transition temperatures of 230 and 260 °C, respectively, and show excellent mechanical properties. Polyaramides of this general structure are of interest since they offer the possibility of facile processability, especially by melt techniques; in addition, they should possess the superior thermal stability displayed by the crystalline polyaramides.<sup>3</sup>

# **Results and Discussion**

The synthesis of 4,4'-[sulfonylbis(p-phenyleneoxy)]dibenzoic acid (4) was accomplished by reaction of the potassium salt of methyl p-oxybenzoate (1) and 4,4'-dichlorodiphenyl sulfone (2) followed by hydrolysis of the resulting diester. Diacid 3 was converted to the diacid chloride (5) with thionyl chloride.

The polycondensation reaction of the diacid chloride (5) with various aromatic diamines (6) in *N*-methylpyrrolidone containing propylene oxide as an acid acceptor<sup>4,5</sup> afforded a series of polyaramides (7).



In the reaction of 5 with 4,4'-diaminodiphenyl ether (6d), various acid acceptors (Table I) were added. Propylene oxide afforded the highest molecular weight polymer as measured by inherent viscosity.

Table IPolycondensation Reaction of Diacid Chloride (5) with4,4'-Diaminodiphenyl Ether (6d)<sup>a</sup>

Solvent (25 mL)	Acid acceptor	$\eta_{\mathrm{inh}}{}^{b}$
NMP	Propylene oxide (1.5 mL)	1.96
	CaO (0.190 g)	1.48
	$Et_3N(2 mL)$	1.19
DMAC		0.80
	CaO (0.190 g)	0.83
HMPA		1.18
	$Et_3N$ (2 mL)	1.25

 $^a$  Monomer concentration 0.26 M (9.7 wt %). Initial reaction temperature -30 °C.  $^b$  In DMF at 25 °C.

Table II Polyamides 7a-g from Diacid Chloride (5) and Aromatic Diamines 6a-g

Polyamida		Solubility <sup>c</sup>		$T_{g}^{d}$			
7	$\eta_{\mathrm{inh}}{}^a$	NMP	sol	DSC	TMA	$T_{\rm m}$	
а	1.18 <sup>b</sup>	s	i	260 <i>°</i>	280 <i>°</i>	450 <i>f</i>	
b	0.97	vs	vs	245	255		
с	$1.19^{b}$	s	i			g	
d	1.96	vs	s	260	250	-	
					255		
е	0.71	vs	vs	250	255		
					260		
f	0.78	vs	s				
g	1.55	vs	S	260 e		375	

<sup>a</sup> DMF at 25 °C. <sup>b</sup> 96% H<sub>2</sub>SO<sub>4</sub> at 25 °C. <sup>c</sup> vs = very soluble; s = difficulty soluble; i = insoluble. <sup>d</sup> Obtained on a Du Pont 990 thermal analyzer with a differential scanning calorimeter and a 943 thermomechanical analyzer. <sup>e</sup>  $T_g$  observed only after heating the sample above  $T_m$  and quenching in liquid nitrogen. <sup>f</sup>  $T_c$  = 310 °C. <sup>g</sup> Unable to observe  $T_g$  due to partial crystallinity.  $T_m$  is above  $T_d$  (430 °C).

Polyamides 7a-g (Table II), obtained by reaction in NMP in the presence of propylene oxide, were completely soluble in sulfuric acid, DMF, and NMP, but only the polymers with more flexible chains were soluble in *m*-cresol. The polyamides were largely amorphous with glass transition temperatures near 250 °C, typical of polyaromatics containing *p*-phenylene ether and sulfone links. Polyamides prepared from the more rigid diamines, **6a,c,g**, were partially crystalline.

#### **Experimental Section**

**Materials.** The amide solvents, N-methylpyrrolidone, dimethylacetamide, and hexamethylphosphoric triamide, <sup>6</sup> were freshly distilled under reduced pressure from phosphorous pentoxide before use. Of the amine monomers, both m- and p-phenylenediamine were purified by distillation under reduced pressure while the remainder were recrystallized under a nitrogen atmosphere: 4,4'-diaminodiphenyl ether, benzidine, 1,5-diaminonaphthalene, and 4,4'-diaminodiphenyl sulfone from ethanol. 4,4'-Diaminodiphenylmethane was recrystallized from benzene.

4,4'-Dichlorodiphenyl Sulfone. To 56 g (0.50 mol) of chlorobenzene at 0 °C was slowly added with stirring 116 g (1.00 mol) of chlorosulfonic acid. The solution obtained was left overnight at room temperature. The 56 g (0.50 mol) of C<sub>6</sub>H<sub>5</sub>Cl was added, and the mixture was heated very slowly to 140–150 °C for 4–5 h, during which time the evolution of hydrogen chloride was evident. No aluminum chloride was added.<sup>7</sup> The cooled solution was poured into ice water (~2 L) to precipitate the crude product. This slurry was heated with stirring to 65–70 °C (2–3 h), in order to destroy the unreacted sulfonyl chloride. After cooling to room temperature, the white precipitate was filtered, washed with water, and dried. Recrystallization from ethanol afforded 48.6 g (34%) of pure 4,4'-dichlorodiphenyl sulfone, mp 147–148 °C.<sup>7</sup>

Table III Elemental Analy (%) of Polyamida 7

Elemental Analyses (76) of Folyamide 7							
Polymer 7		С	Н	N			
	Calcd	68.31	3.94	4.97			
а	Found	67.88	4.16	5.01			
	Calcd	68.31	3.94	4.97			
b	Found	66.81	3.98	4.99			
	Calcd	71.46	4.10	4.38			
с	Found	69.30	3.99	4.65			
	Calcd	69.71	4.00	4.27			
d	Found	69.87	4.53	4.14			
	Calcd	71.76	4.32	4.29			
е	Found	70.08	4.57	3.80			
-	Calcd	64.94	3.72	3.98			
f	Found	63.42	3.86	4.17			
	Calcd	71.14	3.87	4.48			
g	Found	69.05	3.84	4.42			

4,4'-[Sulfonylbis(p-phenyleneoxy)]dibenzoic Acid (4). To 30 mL of dry methanol was added under nitrogen 2.15 g (0.05 mol + 10% excess) of potassium metal and with stirring 8.4 g (0.05 mol + 10% excess) of methyl p-hydroxybenzoate.8 The methanol was removed under reduced pressure with heating at 30-40 °C. To the resulting potassium salt was added 7.15 g (0.025 mol) of 4,4'-dichlorodiphenyl sulfone, 1 g of potassium fluoride, and 20 mL of dry NMP.

The mixture was heated at 175-185 °C under nitrogen with stirring for 6 h. After cooling, 50 mL of 10% aqueous sodium hydroxide was added and the mixture was then heated at 100 °C with stirring, 2-3 h. After cooling, the volume of the mixture was diluted to 1 L with water and 10% sulfuric acid was slowly added, with stirring, to pH 2. The white precipitate of crude acid was filtered, washed with distilled water 3-4 times, and dried. Recrystallization from glacial acetic acid afforded 4.3 g (36%) of pure acid 4, mp 306-308 °C.

Anal. Calcd for C<sub>26</sub>H<sub>18</sub>SO<sub>8</sub>: C, 63.66; H, 3.69. Found: C, 63.31; H, 3.74.

4,4'-[Sulfonylbis(p-phenyleneoxy)]dibenzoyl Chloride (5). A mixture of 40 mL of thionyl chloride and 4.9 g (0.01 mol) of diacid (4) was heated to the reflux temperature for 2 h, after which time 3-4drops of DMF was added. The heating was continued another 2 h and then was left overnight at room temperature. The thionyl chloride was removed under reduced pressure at 40-50 °C. The dry crude product (5) was recrystallized from dry benzene to yield 4.7 g (89%) of monomer, mp 183-185 °C.

Polymerization Reactions. Polymer 7e from 4.4'-[Sulfonylbis(p-phenyleneoxy)]dibenzoyl Chloride (5) and 4,4'-Diaminodiphenyl Ether (6d). The polymerization flask was charged under nitrogen with 0.666 g (0.0033 mol) of 6d and 20 mL of dry NMP. After cooling the solution to 0 °C, 1.5 mL of propylene oxide was added. The mixture was then cooled to -25 to -30 °C and with vigorous stirring 1.757 g (0.0033 mol) of dichloride (5) was added; 5 mL of dry NMP was used to wash the dichloride addition funnel. The solution was stirred at this temperature for 1 h and then for 4 h at room temperature. The solution obtained was slowly poured into a large volume of methanol (300 mL) with vigorous stirring. The white polymer was collected by filtration, washed well with methanol (3-4 times), and dried.

The polycondensation reactions of dichloride (5) with other aromatic diamines (6) were carried out in NMP/propylene oxide, under the same conditions. The elemental analyses are given in Table III.

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## **Temperature Dependence of Positron Lifetimes in** Linear Polyethylene

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When positrons enter a condensed molecular medium, they rapidly lose almost all of their energy by collisions with molecules. After a further, somewhat longer, period annihilation may take place directly between the "free" positrons and electrons bound to molecules or through a bound state of positron-electron pair, called positronium (Ps). The characteristics of the annihilation process, such as energies, momenta, and time of emission, depend almost entirely on the initial state of the positron and molecule medium. Thus, observation of positron decay in a medium provides useful information concerning electronic, atomic, molecular, and crystal properties of the medium.

The measurement of positron annihilation lifetime has been used to study many properties of polymers.<sup>2-15</sup> The lifetime spectrum of positrons annihilating in a polymer normally consists of at least two lifetime components, a short lifetime component with a meanlife  $\tau_1$  of about 0.3–0.4 ns and a longlifetime component with a meanlife  $\tau_2$  of about 1–3 ns. The  $\tau_1$  component has a complex origin, such as due to self-annihilation of p-Ps, direct annihilation of free positrons, and conversion and chemical qenching of o-Ps. The  $\tau_2$  component is attributed to the pick-off annihilation of o-Ps in amorphous regions, including defects in the crystalline lattice, of the polymer.

The pick-off annihilation rate of o-Ps in a molecular substance not only depends on the "free volume" of the samples but also on the interaction between o-Ps and the surrounding molecules.10,11,22

Therefore, a plot of the annihilation rate of the long-lifetime component ( $\lambda_2 = 1/\tau_2$ ) against temperature should generally resemble that of density against temperature. Indeed, this kind of general trend has been found for several polymers including polyethylene.<sup>10</sup> However, only a few data appeared for polyethylene in the temperature range below 300 K. It has also been found that the positron annihilation rate  $\lambda_2$ , in polystyrene,<sup>2</sup> polyisobutylene,<sup>3</sup> and Nylon 6,<sup>4</sup> all show a marked change at or near the glass transition temperature  $T_g$ reported by other conventional methods.

The glass transition temperature of polyethylene is still a subject of widespread and growing controversy as indicated in a recent review by Boyer<sup>16</sup> and by the work of Davis and Eby.<sup>17</sup> This situation exists, as stated by Davis and Eby,<sup>17</sup> because the experimental techniques which can be used to identify glass transitions in wholly amorphous polymers yield less clear results in highly crystalline polymers. In parallel with our measurements on positronium, annihilation of free positrons is sensitive to the presence of defects in crystalline solids.18

In this note, we report briefly the changes of positron lifetimes in linear polyethylene in a temperature range from 80 to 300 K and show that this technique is useful for detecting transitions in amorphous regions dispersed relatively sparse