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Poly(aryl ether ketone) (PAEK) Block and Chain-Extended Copolymers. 2. Preparation and Characterization of Chain-Extended PAEK Copolymers and Poly(ether ketone ketone)/Poly(ether ether ketone) Block Copolymers

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ABSTRACT: A series of chain-extended poly(aryl ether ketones) (PAEKs) and poly(ether ketone ketone)/poly(ether ether ketone) (PEKK/PEEK) block copolymers have been prepared via the nucleophilic polycondensation and evaluated. The former were prepared by reacting a bisphenol, such as hydroquinone, with a series of difunctional PAEK oligomers, while the latter were prepared by reacting those same oligomers with a bisphenol, such as hydroquinone, and an activated dihalo compound, such as 4,4′-difluorobenzophenone. The chain-extended copolymers show good mechanical and thermal properties which can be varied by varying the particular bisphenol used and/or the oligomer molecular weight. The PEKK/PEEK block copolymers also have overall attractive properties; an in-depth evaluation of one particular polymer showed properties comparable to those of commercial poly(aryl ether ketones).

Introduction

Poly(aryl ether ketones) (PAEK's) are a family of semicrystalline, insoluble, high-temperature, high-performance engineering thermoplastics. They display an excellent combination of physical, thermal, and mechanical properties and solvent-resistance characteristics. Selected poly(aryl ether ketones) and their thermal transitions are listed in Table I.[1]

Poly(aryl ether ketones) can be prepared via one of two routes, the nucleophilic or the electrophilic polycondensation. These routes are illustrated in Schemes I and II.

Both the free acids and the corresponding acid chlorides were used to prepare high molecular weight polymers.

The electrophilic preparation of well-characterized functional PAEK oligomers having a high degree of difunctionality was described in the first paper of this series.[12] The base-catalyzed polycondensation of these oligomers with bisphenols yielded novel chain-extended PAEK's; reaction with both bisphenols and dihaloaromatic compounds led to hitherto undescribed PEKK/PEEK block copolymers. The two classes of materials are thus prepared by a unique combination of the nucleophilic and electrophilic methods. Their preparation and characterization are the subject of this report.

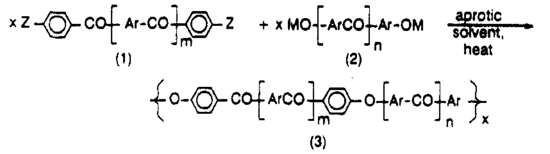
Results and Discussion

Two types of polymer systems were investigated, chain-extended oligomers and block copolymers. The polymerization processes utilized in this study are shown in Schemes III and IV.

The reactions were performed in diphenyl sulfone at elevated temperatures (about 300–320 °C). The polymers were isolated by cooling and grinding the solidified reaction mixtures, followed by extraction with boiling acetone and deionized water. The final materials were dried under house vacuum (~28 Torr) at 100 °C prior to evaluation.

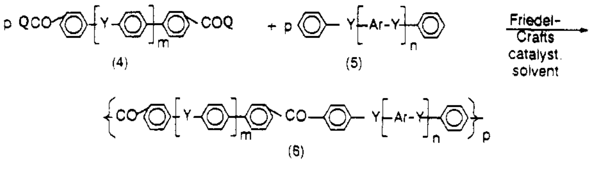
A number of base systems were used. These included mixtures of sodium carbonate with potassium carbonate,[3] sodium carbonate with potassium fluoride,[13] and sodium carbonate with salts of organic acids such as potassium acetate, for example.[14,15] Increased reaction rates were observed with these latter systems.

Scheme I
Nucleophilic Polycondensation[2-7]



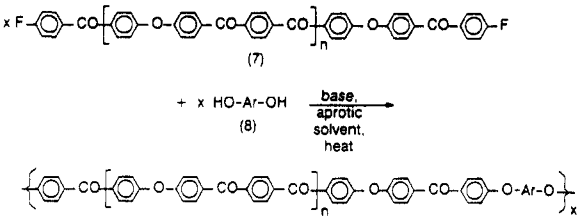
Z = halogen, NO_2 or $OSO_2C_6H_5$; M = alkali metal or $Si(CH_3)_3$; m, n = 0 or 1.

Scheme II
Electrophilic Polycondensation[8-11]



Q = F, Cl, OH; Y = chemical bond, O; m, n = 0 or 1.

Scheme III
Preparation of Chain-Extended Copolymers



(9), chain-extended copolymer

In our initial experiments some of the polymerization reactions yielded soluble thermoplastic polymers; others resulted in gelation of the reaction mixtures and gave insoluble polymers which did not flow at 400 °C. Still others yielded products which exhibited very high melt viscosities at 400 °C. It was discovered that this behavior was related to the degree of alkylation of the oligomers used. As indicated in our previous paper,[12] the oligomers are preferably prepared via the aluminum chloride catalyzed reaction of diphenyl ether with terephthaloyl chloride and *p*-fluorobenzoyl chloride in 1,2-dichloroethane solvent. Depending on the reaction conditions, oligomers with various degrees of alkylation are obtained. The extent of alkylation is best determined via multistage

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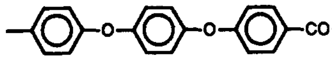
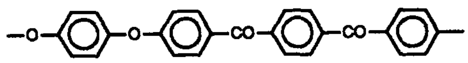
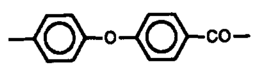
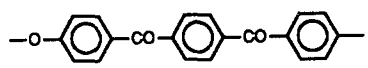
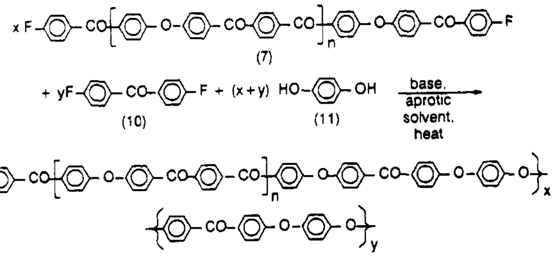
Table I
Selected Poly(aryl ether ketones)

structure	code	T_g (°C)	T_m (°C)
	PEEK	141	335
	PEEKK	155	365
	PEK	155	365
	PEKK	165–175	385

Scheme IV
Preparation of Block Copolymers

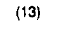


(12), PEKK/PEEK block copolymer

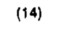
pyrolysis gas chromatography/mass spectrometry (MPY-GC/MS).[12] The technique consists of preheating the sample under helium to a high enough temperature (150–200 °C) to vaporize all of the volatile components but still below the pyrolysis temperature of the PAEK oligomer. Residual solvents are thus removed, and the possibility of undesirable gas-phase reactions during pyrolysis is eliminated. The devolatilized sample is then pyrolyzed (700 °C); the volatile components are separated via gas chromatography and analyzed by mass spectrometry. Since in all cases investigated toluene corresponded to the largest alkylated peak in the pyrogram, the degree of alkylation was expressed in peak height of toluene per milligram of sample.

It was found that the higher the degree of alkylation of the oligomer, the more likely it was that it will yield a gelled reaction mixture. It is believed that the reason for this behavior is first of all the fact that alkylation is accompanied by the formation of pending unsaturated groups and of reactive chlorinated byproducts,[12] in addition, the alkyl groups are in themselves inherently unstable at high temperatures. Hence, cross-linking takes place under the high-temperature conditions of the polymerization reaction. We were unable to establish a quantitative correlation between alkylation and gelation. However, our experimentation suggests that oligomers with alkylation levels (peak height of toluene per milligram of sample) lower than about 15 should be used in order to make polymers with acceptable properties.

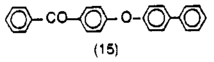
The reactions depicted in Schemes III and IV are expected to be accompanied by transetherification processes, leading to partial scrambling of the block structure. In order to determine the extent of transetherification, model compounds 13–16 were prepared and reacted as described below.



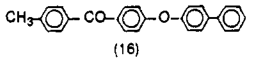
(13)



(14)

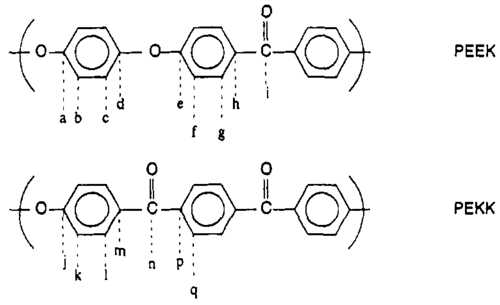


(15)



(16)

In the competitive reaction equimolar amounts of compounds 13 and 14 and *p*-phenylphenol were heated to 300 °C in diphenyl sulfone for 30 min in the presence of potassium carbonate. The ratio of compounds **16**:**15** in the resulting mixture was determined by gas chromatography to be 3:1. Since compound **13** has two equally reactive sites (on either side of the ether oxygen atom), the ratio of the rates of fluorine displacement to transetherification is 6:1. Hence, it is believed that the copolymers prepared herein are true block copolymers with only marginal randomization. In fact, the above kinetic data are in agreement with ^{13}C NMR analysis of the block copolymers. Chemical shifts for the two blocks (EEK = ether ether ketone and EKK = ether ketone ketone) were determined for the corresponding high molecular weight homopolymers and are shown. The difference in chemical shifts for equivalent positions on each polymer is quite surprising; hence, the degree of scrambling can be determined with a reasonable degree of accuracy.



carbon atom	chemical shift (ppm)	carbon atom	chemical shift (ppm)
a	152.1	i	199.2
b	123.6	j	166.4
c	123.6	k	120.0
d	152.1	l	131.9
e	170.4	m	124.0
f	123.9	n	202.9
g	139.8	p	135.4
h	118.3	q	140.4

Representative chain-extended copolymers (Scheme III) and their properties are summarized in Table II.

The data of Table II indicate that the chain-extended copolymers show an attractive combination of properties. Their mechanical characteristics are good. They are semicrystalline thermoplastics having single glass transition temperatures that are a function of both the proper choice of *n* and of the extending bisphenol. It appears that the two "blocks", i.e., the oligomer and the extending bisphenol, are of too low molecular weight to yield a phase-separated amorphous region. Thus, the two blocks are thermodynamically compatible in the amorphous phase at these molecular weights. The behavior is clearly illustrated by the modulus/temperature curve of polymer no. 4 (Table II) shown in Figure 1. The latter polymer (*n* = 2: bisphenol-S as the extending bisphenol) displays a T_g of 180 °C. Yet it is remarkable that the melting point

Table II
Chain-Extended Copolymers and Their Properties[a]

				tensile		elongation				
no.	oligomer 7, n	bisphenol	RV[b] (dL/g)	modulus (psi × 10^{-3})	strength (psi)	yield (%)	break (%)	pendulum impact (ft·lb/in.^{3})[c]	T_g (°C)	T_m (°C)
1	1	hydroquinone	1.5	316	15 300	7.5	15.5	61	155	365
2	2	hydroquinone	1.75	397	14 600	7.3	11.2	57	160	370
3	2	4,4′-biphenol	1.17	358	13 700	7.5	6–15.5	24–71	170	334
4	2	4,4′-bisphenol-S	1.18–1.55	355	14 800	7.7	60	66	172–180	318–338

[a] Data on compression-molded films. [b] Reduced viscosity in concentrated H_2SO_4 (25 °C, 1 g/100 mL). [c] Test developed in-house, similar to the Charpy impact test for measuring unnotched toughness; see the Experimental Section.

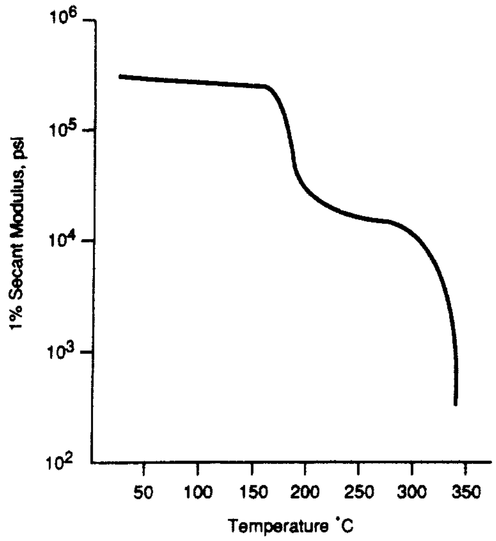


Figure 1. Modulus/temperature curve of polymer no. 4 (Table II).

Table III
PEKK/PEEK Block Copolymers and Their Properties

	copolymer			
property	no. 5[a]	no. 6[b]	no. 7[b]	no. 8[b]
PEKK oligomer				
n	2	2	2	20
mol %	5	11	33	20
RV[c] (dL/g)	1.2–1.5	1.76	1.19	1.19
HDT, 264 psi (°C)	160–170			
T_m (°C)		344	359	
tensile strength (psi)	14 900	12 900	14 900	14 200
tensile modulus (psi × 10^{-3})	633	334[d]	397	377[d]
elongation at yield (%)		6	5.7	7.0
elongation at break (%)	11	39	15	12.5
flexural strength (psi)	22 500			
flexural modulus (psi × 10^{-3})	542			
pendulum impact (ft·lb/in.^{3})[e]		131	63	103
tensile impact (ft·lb/in.^{2})	40			
notched Izod (ft·lb/in.)	2.2			
unnotched Izod (ft·lb/in.)	18			

[a] On parts that were injection molded into a mold heated at 150 °C followed by annealing for 30 min prior to testing. [b] On compression-molded films. [c] Reduced viscosity in concentrated H_2SO_4 (25 °C, 1 g/100 mL). [d] 1% secant, not tensile, modulus. [e] Test developed in-house, similar to the Charpy method (see the Experimental Section).

Table IV
Mechanical Properties of 40% Glass-Reinforced Poly(aryl ether ketones)

	material	
property	polymer no. 5	Victrex PEEK 380G
tensile strength (psi)	28 900	24 900
elongation (%)	2.1	2.0
tensile modulus (psi × 10^{-3})	2170	1680
flexural strength (psi)	41 600	38 500
flexural modulus (psi × 10^{-3})	1890	1770
notched Izod impact (ft·lb/in.)	2.3	2.2
unnotched Izod impact (ft·lb/in.)	18	
tensile impact (ft·lb/in.^{2})	89	86

of this material is just about the same as that of commercial poly(ether ether ketone) (PEEK) which has a much lower T_g (T_g = 141 °C, T_m = 335 °C[16]). These findings are important. Since there is an abrupt decrease in stiffness at the T_g, poly(aryl ether ketones) with higher transition temperatures are of high interest for many applications, especially advanced composites. However, previous attempts to obtain PAEK's with high T_g's led to materials with inordinately high melting points, requiring impractically high temperatures for melt fabrication. For example, the condensation of 4,4′-difluorobenzophenone with 4,4′-biphenol gave a polymer[4] having a T_g of about 170 °C and a T_m of 416 °C.

Our studies of the chain-extended copolymers were cursory, and no in-depth evaluation of the materials was performed. Our investigations have shown, however, that the chain-extension approach is a versatile synthetic method for the preparation of tailor-made semicrystalline poly(aryl ether ketone) products.

The block copolymers prepared via the route shown in Scheme IV display attractive properties that are comparable to those of commercially available poly(aryl ether ketones). Representative block copolymers and their properties are listed in Table III.

Of the materials listed in Table III, copolymer no. 5 and its glass fiber reinforced composite were submitted to an in-depth evaluation. Mechanical properties of the 40% glass-reinforced material are presented in Table IV. For comparative purposes the corresponding data for 40% glass-reinforced Victrex PEEK 380G are also shown.

It is remarkable that the mechanical properties of glass-filled polymer no. 5 are practically independent of the melt flow (i.e., molecular weight) of the base resin, as measured within the range of 6–38 g/10 min at 400 °C under a load of 1 P (44 psi). Over the same range, however, the melt viscosity of the composite decreases by an order of magnitude. The finding is of great practical importance because compositions possessing at the same time good mechanical properties and good melt fabricability (due to their low melt viscosities) are at hand.

The variations of the flexural modulus as a function of temperature for both the neat and the 40% by weight glass-filled polymer no. 5 (Table III) are shown in Figure 2. Fabrication temperatures of the materials are listed in Table V. For comparison purposes, the corresponding temperatures for a number of other commercial and semicommercial poly(aryl ether ketones) are also included in the table.

Clearly, the fabrication temperatures required for polymer no. 5 (Table III) are rather moderate in comparison with those needed for the fabrication of other poly(aryl ether ketones).

Other data of interest obtained on polymer no. 5 and its 40% glass fiber composite are given in Table VI.

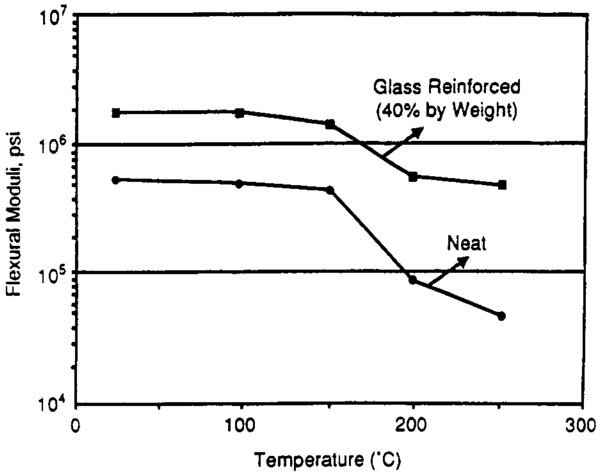


Figure 2. Polymer no. 5 (Table III): Variation of flexural modulus as a function of temperature.

Table V
Fabrication Temperatures of Poly(aryl ether ketones)

product (company)	fabrication temp (°C) material	mold
polymer no. 5	340–380 (neat)	150–190
Table III	360–400 (glass reinforced)	150–190
Victrex PEEK (ICI, Ltd.)	350–380 (neat)	150–180
	370–400 (glass reinforced)	150–180
Victrex PEK (ICI, Ltd.)	≥400	180–190
Ultrapek (BASF, A.G.)	390–420	180–210
Hostatec (Hoechst, A.G.)	380–420	>150

Table VI
Miscellaneous Properties of Polymer No. 5 (Table III)

property	test method	neat	40% glass filled
heat deflection temp (°C), 264 psi	ASTM D-648	160	326
flammability	UL 94	V-0 (31 mil)	V-0 (31 mil)
specific gravity	ASTM D-792	1.30	1.55
water absorption (%), 24 h	ASTM D-570	0.1	0.05
dielectric strength ($^1/_8$ in. V/mil)	ASTM D-149	355	420
dielectric constant at 10^3 Hz	ASTM D-150	3.28	4.01
dissipation factor at 10^3 Hz	ASTM D-150	3.30	3.00

Crystalline polymers are known to display good stress-crack and solvent-resistance characteristics. Hence, a similar behavior was expected of the highly crystalline poly(aryl ether ketone) block copolymers that were prepared in the course of this investigation. Such is indeed the case. Thus, polymer no. 5 and its 40% glass fiber composite are stable at room temperature toward almost all organic and inorganic liquids. Concentrated sulfuric acid and certain strongly oxidizing media (e.g., fuming nitric acid) are exceptions. Resistance to various environments is excellent at elevated temperatures as well. Pertinent data are shown in Tables VII and VIII.

In closing, it should be mentioned that polymer no. 5 possesses satisfactory resistance to ionizing (γ) radiation, a property found also with other poly(aryl ether ketones). Data are shown in Table IX.

Table VII
Chemical Resistance of Polymer No. 5 (Table III)

environment	temp (°C)	retention of tensile strength (%) 7 days	3 mos	retention of elongation (%) 7 days	3 mos
acetone	60	90	86	129	93
isopropyl alcohol	100	98	90	143	129
jet fuel A	130	98	100	136	57
Skydrol LD-4	130	93	96	86	107
deionized water	130	97	94	136	57
28% ammonium hydroxide	60	89	86	139	129
30% sodium hydroxide	130	96	96	107	86
20% hydrochloric acid	130	97	77	107	20
37% sulfuric acid	130	97	98	129	79
85% phosphoric acid	130	90	99	86	129

Table VIII
Chemical Resistance of 40% Glass Fiber Reinforced Polymer No. 5 (Table III)

environment	temp (°C)	retention of tensile strength (%) 7 days	3 mos	retention of elongation (%) 7 days	3 mos
acetone	60	90	89	95	100
isopropyl alcohol	100	91	90	84	105
jet fuel A	130	90	87	95	84
Skydrol LD-4	130	94	91	100	95
deionized water	130	70	66	79	63
28% ammonium hydroxide	60	71	61	79	74
30% sodium hydroxide	130	80	65	84	89
20% hydrochloric acid	130	64	46	79	84
37% sulfuric acid	130	72	134	68	84
85% phosphoric acid	130	89	84	89	84
brake fluid DOT 3	130	97		90	
ethyl acetate	100	100		100	
transmission fluid	130	100		95	
1,1,1-trichloroethane	100	100		100	
methylene chloride	60	98		100	

Table IX
Radiation Exposure Study of Polymer No. 5 (Table III) (Retention of Tensile Strength vs Control)

exposure to ionizing γ radiation [source: cobalt-60 (Mrad)]	polymer no. 5 neat (%)	40% glass reinforced (%)
2	100	101
20	99	100
100	97	98
150	102	100
1000	97	97

Conclusions

Several chain-extended poly(aryl ether ketones) are PEKK/PEEK block copolymers were prepared and evaluated. The chain-extended copolymers display good mechanical properties. They are crystalline thermoplastics with glass transition temperatures that can be varied by the proper choice of the oligomer molecular weight and the nature of the extending bisphenol. The chain-extension approach is believed to be a valuable synthetic tool for the preparation of poly(aryl ether ketone)-based materials with a unique combination of properties.

The PEKK/PEEK block copolymers were synthesized by condensing the oligomers with 4,4′-difluorobenzophenone and hydroquinone. In-depth evaluation of polymer no. 5 (Table III) revealed that it possesses excellent properties that are comparable to or better than the properties of commercially available poly(aryl ether ketones).

The instant chain-extended and block copolymers are but one example of a practically infinite variety of new polymer systems that can be derived from our oligomers.[12] Among other classes of products that were prepared and evaluated by us are the very interesting poly(aryl ether ketone)/poly(aryl ether sulfone) block copolymers. They will be the subject of a forthcoming paper.

Experimental Section

Mechanical property data were obtained using two types of specimens, the first being 0.02-in.-thick strips from compression-molded plaques and the other being 0.125-in.-thick injection-molded ASTM specimens. The compression-molded samples were tested for strength and modulus in a manner similar to ASTM specification D-638, the difference being that no extensiometer was used and that the elongation was determined from crosshead travel. The pendulum impact was measured on compression-molded strips; it is an internally developed test analogous to the Charpy impact test for measuring unnotched toughness. It is performed as follows. A steel pendulum is used, cylindrical in shape with a diameter of 0.83 in. and weighing 1.562 lb; the striking piece, mounted almost at the top of the pendulum, is a cylinder 0.3 in. in diameter; film specimens, 4 in. long, 0.125 in. wide, and about 1–30 mil thick, are clamped between the jaws of the tester so that the jaws are spaced 1 in. apart; the 0.125 in. width of the film is mounted vertically, the pendulum is raised to a constant height to deliver 1.13 ft·lb at the specimen; when the pendulum is released, the cylindrical striking piece hits the specimen with its flat end, breaks the film, and travels to a measured height beyond; the difference in the recovery height (i.e., the difference in the potential energy of the pendulum at the maximum point of the upswing) represents the energy absorbed by the specimen during the rupture; the impact strength, expressed in ft·lb/in.^{3} is obtained by dividing the pendulum energy loss by the volume of the specimen.

Melt flows for the polymers were determined using a Tinius–Olsen Extrusion Plastometer melt flow apparatus; the procedure was similar to that of ASTM D-1238. The melt mass flow rate (grams per 10 min) was recorded after a dwell time of 10 min in the unit to ensure temperature equilibration. The temperature was 400 °C and the applied pressure 44 psi (1 P). Nominal die dimensions were 0.8 cm length × 0.2 cm inside diameter.

1. **Preparation of Oligomer 7 (n = 2).** A 500-mL, four-neck, round-bottomed flask equipped with a mechanical stirrer (Teflon blade), nitrogen inlet, thermometer, solids addition funnel, and gas outlet to a NaOH scrubber was purged with dry nitrogen and charged with 190 mL (240 g) of 1,2-dichloroethane, 21.25 g (0.1340 mol) of 4-fluorobenzoyl chloride, 34.04 g (0.200 mol) of diphenyl ether, and 27.20 g (0.1340 mol) of terephthaloyl chloride. The addition funnel was charged with 75.04 g (0.5628 mol) of aluminum chloride. The solution was cooled to <5 °C (ice water bath), and aluminum chloride was added at a rate such that the reaction temperature did not rise above 5 °C. The reaction mixture was stirred with cooling for 6 h, *during which time it became homogeneous*. The viscous reaction mixture was pumped slowly using nitrogen pressure through a $^3/_8$-in. polyethylene cannula into a 2-L, three-neck, round-bottomed flask (equipped with a heating mantle, mechanical stirrer, Claisen head, thermometer, Dean–Stark trap, and condenser) containing 400 mL of water at 85 °C. Dichloroethane was removed by distillation during the transfer. Once the transfer was complete, the slurry was heated to 95 °C, held there for 15 min to remove traces of dichloroethane, and allowed to cool to 45 °C. The crude product was recovered by vacuum filtration, rinsed on the filter with methanol, then with deionized water until the rinsings were neutral, and then again with methanol, and allowed to dry in air.

The product was then added to a solution of 9 mL of concentrated HCl in 155 mL of methanol, and the resulting slurry was heated at reflux for 90 min with stirring. The product was recovered by vacuum filtration, rinsed with deionized water until the rinsings were neutral and then rinsed with methanol, and allowed to dry in air. The air-dried product was heated overnight under house vacuum (~28 Torr) at 100 °C to give 63.8 g (94%) of the oligomer. Anal. Calcd for $C_{66}H_{40}O_9F_2$: C, 78.10; H, 3.97; O, 14.19; F, 3.74. Found: C, 78.06; H, 4.07; O, 14.08; F, 3.76.

2. **Polymerization of Oligomer 7 (*n* = 2) with 4,4′-Bisphenol-S [Bis(4-hydroxyphenyl) Sulfone].** A 250-mL, four-neck flask equipped with a mechanical stirrer (stainless steel blade), nitrogen inlet, thermometer, Claisen adapter, addition funnel, Dean–Stark trap, condenser, and heating mantles (upper and lower) was purged with nitrogen and charged with 18.85 g (0.018 mol) of the oligomer, 4.50 g (0.018 mol) of 4,4′-bisphenol-S, 1.19 g (0.018 mol) of sodium carbonate, 0.089 g (0.0015 mol) of potassium fluoride, and 70 g of diphenyl sulfone. Xylene (20 mL) was charged in the addition funnel; the mixture was heated, and the xylene was added to it when it began to liquefy, at which time stirring was started. Simultaneously, about 7 mL of fresh xylene was placed in the Dean–Stark trap. When the temperature reached about 175 °C, distillation of xylene (with continuous recycling) took place. The xylene was drained dropwise from the trap, and the temperature was gradually increased to 300 °C. At 265–275 °C, all of the xylene was removed from the Dean–Stark trap. The reaction mixture was kept at 300 °C for 75 min. It was then poured into an aluminum pan. After cooling and solidification, the reaction mass was broken up and ground to a powder. The powder was extracted with refluxing acetone (two times, 700 mL; 1.5 h each time), refluxing deionized water (two times, 700 mL; 1.5 h each time), and refluxing acetone (700 mL; 1.5 h). The final product was recovered by vacuum filtration, washed with acetone, and allowed to air dry, followed by heating under house vacuum (~28 Torr) at 100 °C for 3 days. The reduced viscosity of the polymer (measured in concentrated H_2SO_4 at 25 °C; 1 g/100 mL) was 1.18 dL/g.

3. **Preparation of Polymer No. 5 (Table III). General Procedure.** A 250-mL, round-bottomed Pyrex flask equipped with nitrogen inlet, temperature probe, Claisen adapter, addition funnel, Dean–Stark trap, condenser, heating mantles (upper and lower), and mechanical stirrer was charged with oligomer 7 (*n* = 2; 0.00300 mol, calculated from the fluorine content; i.e., enough material to contain 0.00600 mol of fluorine), 4,4′-difluorobenzophenone (12.44 g, 0.0570 mol), hydroquinone (6.61 g, 0.0600 mol), sodium carbonate (6.36 g, 0.0600 mol), potassium fluoride (0.296 g, 0.00509 mol), and diphenyl sulfone (60 g). The flow of nitrogen through the reactor was begun, and the mixture was heated until it began to liquefy. At this point 25 mL of xylene was added *via* the addition funnel, the Dean–Stark trap was filled with xylene, and stirring was started. The reaction mixture was heated to 200 °C. Xylene was removed from the system as necessary to increase the temperature of the reaction mixture, but enough was kept in the system to maintain a steady reflux rate.

The mixture was maintained at 200 °C for 30 min, and then the temperature was increased to 250 °C, again removing xylene from the system as necessary. After 30 min at 250 °C, the temperature was increased to 300 °C. At about 270 °C, all the xylene was drained from the Dean–Stark trap. The mixture was kept at 300 °C until viscous and then terminated by the addition of lithium chloride (0.432 g, 0.0102 mol), 1,4-bis(4-fluorobenzoyl)benzene (0.387 g, 0.00120 mol), and diphenyl sulfone (2 g). Fifteen minutes after termination, the reaction mixture was poured into an aluminum pan, allowed to cool, broken up, and ground to a powder. The crude product was extracted twice with 700 mL of refluxing acetone, twice with 700 mL of boiling water, and once again with 700 mL of refluxing acetone (each extraction 1.5 h) to give the final product, which was heated at 100 °C under house vacuum to constant weight.

4. **Preparation of Polymer No. 7 (Table III). General Procedure.** The apparatus described for the previous polymerization was charged with oligomer 7 (*n* = 2; 0.0132 mol, calculated from the fluorine content), 4,4′-difluorobenzophenone (5.85 g, 0.0268 mol), hydroquinone (4.40 g, 0.0400 mol), sodium carbonate (4.24 g, 0.0400 mol), potassium fluoride (0.198 g, 0.00341 mol), and diphenyl sulfone (66 g). The polymerization procedure was the same as that described above, except that the 30-min hold at 250 °C was omitted. The product was worked up in a manner similar to that described above.

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