Poly(aryl ether ketone) Block and Chain-Extended Copolymers. 3. Preparation and Characterization of Poly(ether ketone ketone)/Poly(ether sulfone) Block Copolymers

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ABSTRACT: Poly(ether ketone ketone)/poly(ether sulfone) (PEKK/PES) block copolymers have been prepared by the nucleophilic polycondensation of difluoro-terminated PEKK oligomers with 4,4′-bisphenol-S and 4,4′-difluorodiphenyl sulfone. The condensations were conducted in diphenyl sulfone at 300 °C with base/promoter systems such as sodium carbonate/potassium fluoride or calcium carbonate/potassium acetate. Mechanical properties were similar to those of PES, with tensile strength and modulus increasing at higher PEKK levels (near 80 wt %); materials comprising these high PEKK levels were crystalline as molded with melting points >300 °C. At 65 wt % PEKK, crystallinity could only be induced by annealing. The polymers had a single T_g which decreased as the PEKK content increased. Stress-crack resistance of the copolymers improved to ketone-containing solvents, improved modestly to aromatic solvents, and did not improve to chlorinated aromatics.

Introduction

Poly(aryl ether sulfones) are an important class of engineering thermoplastics.[1,2] They display a unique combination of toughness, excellent high-temperature and oxidative resistance, good electrical properties, and outstanding hydrolytic stability. They are generally amorphous transparent materials with high T_g values. Representative poly(aryl ether sulfones) and their thermal transitions are listed in Table I.

A shortcoming of these materials is their relatively low chemical, solvent, and stress-crack resistance, although they are highly resistant to attack by acids and bases.

Poly(aryl ether ketones)[3] are opaque, semicrystalline, tough thermoplastics having excellent high-temperature, hydrolytic, chemical, solvent, and stress-crack resistance. Representative members of this class of polymers and their thermal transitions are shown in Table II.[4]

Drawbacks of poly(aryl ether ketones) include their high cost and relatively low glass transition temperatures. In advanced composite applications it is desirable to utilize poly(aryl ether ketone) materials with higher glass transition temperatures.

Poly(aryl ether ketone)/poly(aryl ether sulfone) block copolymers are expected to combine the toughness, high T_g values, and the other attractive features of poly(aryl ether sulfones) with the excellent chemical, solvent, and stress-crack resistance of the poly(aryl ether ketones). Block copolymers of this type have been described.[5-12] The method most widely used for the preparation of these copolymers[7-11] consists of first preparing the more soluble poly(aryl ether sulfone) block by the polycondensation of an aromatic dihalo sulfone with a bisphenol in, e.g., *N*-methylpyrrolidone/K_2CO_3 or dimethyl sulfoxide/NaOH, followed by further reaction of this block with poly(aryl ether ketone) forming ingredients to give the final block copolymer. The block copolymers were also synthesized via a bulk process using trimethylsilylated diphenols, activated difluoroaromatic compounds, and cesium fluoride catalyst.[12]

A new class of functional poly(aryl ether ketone) oligomers was described in the first paper of this series.[13] These oligomers were prepared by the aluminum chloride catalyzed polycondensation of diphenyl ether with terephthaloyl chloride and *p*-fluorobenzoyl chloride and were shown to possess a high degree of difunctionality. Further reaction of the difluoro-terminated oligomers with poly(aryl ether sulfone) forming reactants yields block copolymers. The latter materials, made by a unique combination of the electrophilic and nucleophilic methods, are structurally different from the products that were heretofore described. On the basis of previous results,[14] they are believed to be block copolymers with at best only marginal randomization. Note also that the use of well-characterized aryl ether ketone oligomers as the starting building blocks is expected to yield copolymers with a much better defined microstructure, and, hence, to allow for a more rigorous structure-property correlation of this very interesting class of products.

The preparation and characterization of PEKK/PES block copolymers are described in this report.

Results and Discussion

The block copolymers were prepared via the process depicted in Scheme I. All of the reactions were performed in diphenyl sulfone at 300 °C, in the presence of a base/promoter system. The various systems that were utilized and the results obtained with these systems are listed in Table III. As can be seen, sodium carbonate/potassium fluoride[15] and calcium carbonate/potassium acetate[16] gave the best results. For comparison purposes, PES was also prepared under these conditions.

Mechanical properties and glass transition temperatures of the block copolymers were determined on films that were compression molded at 660-750 °F. The data are listed in Table IV. Properties obtained on the prepared PES samples are shown for comparison. All materials except polymer no. 7 were amorphous as molded and gave transparent films. Copolymer no. 7 yielded a crystalline, translucent film.

The data of Table IV show that the copolymers have properties that are generally comparable to those of PES. Interestingly, a rather sharp increase in the modulus and tensile strength is observed with polymer no. 7 due probably to the contribution of the crystalline phase. All materials displayed one glass transition temperature indicative of the absence of phase separation in the amorphous region of the copolymers. It is believed that the lengths of the respective blocks, which may be additionally decreased by some transetherification ac-

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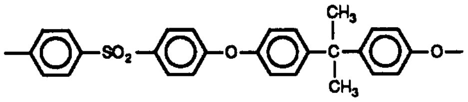
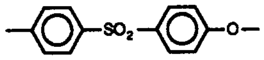
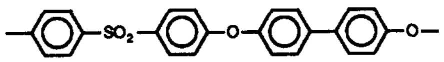
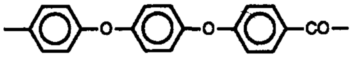
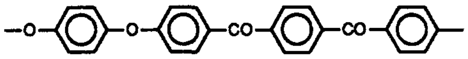
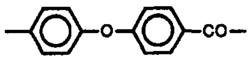
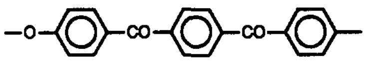
Table I
Selected Poly(aryl ether sulfones)

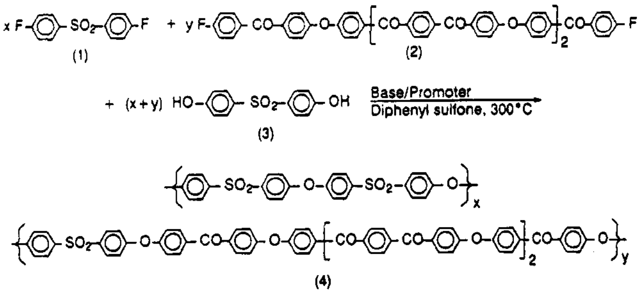
structure	name	T_g[a] (°C)
	UDEL polysulfone (UDEL PSF)	190
	Victrex poly(ether sulfone) (Victrex PES)	220
	RADEL polyphenylsulfone	220

[a] Measured in our laboratories.

Table II
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 I
Preparation of PEKK/PES Block Copolymers



companying the polymerization, are insufficient to cause such phase separation.

As noted before, polymer nos. 1–6 were amorphous as molded. Polymer no. 7 (80 wt % PEKK) was crystalline. Annealing (30 min at 250 °C) resulted in the development of crystallinity in material no. 6 (65 wt % of PEKK), and it became translucent. The other films remained essentially amorphous (transparent) upon annealing. Table V summarizes the T_g and T_m data of the copolymers. T_g and T_m values for poly(ether sulfone) and for PEKK are also included.

Variation of the glass transition temperature as a function of PEKK content is shown in Figure 1.

Polymer nos. 1–3 and 6 were submitted to stress–crack resistance testing. The tests were performed as follows: the polymer sample was compression molded into a 20-mil plaque; strips, $^1/_8$ in. wide, were cut from the films; a strip was wrapped with a cotton patch saturated with a given solvent. In order to prevent evaporation of the solvent, this was then wrapped with aluminum foil. The strip was then placed in the jaws of the Instron apparatus (2-in. gage length), and the tensile strength was measured at a rate of 0.02 in./min, at room temperature. The higher the tensile strength, the better the stress–crack resistance of the polymer. Results are shown in Table VI.

Some of the observed effects (e.g., of annealing in the case of polymer no. 3) are difficult to explain. There is no doubt, however, that, as far as ketone-containing solvents are concerned, the incorporation of PEKK into PES results in a significant improvement of stress–crack resistance. The effect, as expected, is particularly pronounced in the case of the annealed polymer no. 6. Additional studies have shown that, contrary to expectations, results were rather disappointing with other solvents. Thus, in the case of toluene, there was practically no change in the tensile strength in going from PES up to and including polymer no. 3. There was, however, a significant improvement with the annealed polymer no. 6 (4600 psi for PES versus 6200 psi for annealed polymer no. 6). Limited testing was performed with chlorobenzene. A slight decrease in the tensile strength was actually observed in going from PES (3500 psi) to polymer no. 3 (2700 psi). We are unable to provide an explanation of this behavior at this time.

Conclusions

The nucleophilic polycondensations of difluoro-terminated oligomeric PEKK (oligomer 2) with 4,4′-bisphenol-S and 4,4′-difluorodiphenyl sulfone yielded PEKK/PES block copolymers. The reactions were performed in diphenyl sulfone, at 300 °C; several base/promoter systems were used. Best results were obtained with the sodium carbonate/potassium fluoride and calcium carbonate/potassium acetate systems.

The block copolymers displayed good mechanical properties, generally comparable to those of PES; higher tensile strengths and moduli were obtained at increased PEKK contents (about 80 wt %). The copolymers were amorphous at PEKK contents below 65 wt %. At 65 wt % of PEKK, crystallinity could be induced via annealing (30 min at 250 °C). The material containing 80 wt % of PEKK was crystalline as molded. Melting points of the two crystalline products were greater than 300 °C. All of the copolymers displayed a single T_g which decreased with increasing amounts of PEKK.

Stress–crack resistance studies indicated that the copolymers had significantly improved resistance to ketone-containing solvents. Improvement was modest with

Table III
Preparation of PEKK/PES Block Copolymers

oligomer 2 (mol %)	PEKK (wt %)	base/promoter (mol %)[a]	procedure[b] polymzn	procedure[b] workup	time at 300 °C (min)	RV[c] (dL/g)
0	0	Na_2CO_3/KF (100/8.5)	B	B	35	1.12
0	0	Na_2CO_3/KF (100/8.5)	B	A	85	1.07
0	0	$CaCO_3$/KOAc (100/10)	A	A	35	1.58
5	10	Na_2CO_3/KF (100/8.5)	A	A	60	1.17
5	10	$CaCO_3$/KOAc (100/10)	B	D	20	1.12
5	10	$CaCO_3$/KOAc (100/10)	A	A	50	1.62
10	19	Na_2CO_3/KF (100/8.5)	A	A	45	1.23
10	19	Na_2CO_3/NaOAc (100/5.0)	A	A	185	0.75
10	19	$CaCO_3$/KOAc (100/10)	B	D	35	1.43
10	19	$CaCO_3$/KOAc (100/10)	A	A	45	1.88
20	33	Na_2CO_3/KF (100/8.5)	A	A	50	1.22
20	33	Na_2CO_3 (100)	B	A	265	0.83
20	33	Na_2CO_3/NaOAc (100/10)	B	B	90	1.15
20	33	Na_2CO_3/NaOAc/KF (100/10/0.5)	B	B	120	0.58
20	33	Na_2CO_3/NaOBz (100/2.0)	B	B	180	0.59
20	33	Na_2CO_3/NaOBz (100/5.0)	B	B	120	0.33
20	33	$CaCO_3$/KOAc (100/10)	B	A	30	1.83
30	43	$CaCO_3$/KOAc (100/10)	B	A	60	1.64
40	52	$CaCO_3$/KOAc (100/10)	B	A	75	1.51
60	65	$CaCO_3$/KOAc (100/10)	B	A	75	1.52
100[d]	80	Na_2CO_3/KF (100/8.5)	C	C	75	1.18
100[d]	80	Na_2CO_3/KF (100/8.5)	C	C	50	1.12

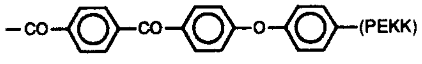
[a] Mole percent relative to 4,4′-bisphenol-S. [b] Details of polymerization and work-up procedures are given in the Experimental Section. [c] Reduced viscosity in concentrated H_2SO_4 at 25 °C (1 g/100 mL). [d] 4,4′-Bisphenol-S chain-extended oligomer 2.

Table IV
Properties of the Block Copolymers

	material PES	1	2	3	4	5	6	7
PEKK (wt %)	0	10	19	33	43	52	65	80
RV (dL/g)[a]	1.58	1.12	1.03	1.15	1.64	1.51	1.52	1.12
T_g (°C)	235[c]	222	216	206	197	192	182	172
tensile modulus ($\times 10^{-3}$ psi)	224	279	278	266	263	273	272	355
tensile strength (psi)	11 400	11 200	11 200	10 700	11 600	11 500	11 400	14 800
elongation (%)								
yield				7.7	7.8	6.8	7.6	
break	7.2	6.7	6.3	8.8	15.0	32.0	14.0	60.0
pendulum impact (ft·lb/in.^{3})[b]	71	34	35	54	109	113	111	43
molding temp (°F)	660	750	660	750	750	750	750	750

[a] Reduced viscosity in concentrated H_2SO_4 at 25 °C (1 g/100 mL). [b] Test developed in-house, similar to the Charpy method.[14] [c] Value obtained on the sample prepared in the course of this study.

Table V
Glass Transition (T_g) and Melting Point (T_m) Data

polymer	T_g (°C)	T_m (°C)	remarks
poly(ether sulfone) (PES; 0 wt % PEKK)	235		
polymer no. 1 (10 wt % PEKK)	222		
polymer no. 2 (19 wt % PEKK)	216		
polymer no. 3 (33 wt % PEKK)	206		
polymer no. 4 (43 wt % PEKK)	197		
polymer no. 5 (52 wt % PEKK)	192		
polymer no. 6 (65 wt % PEKK)	182	309	amorphous as molded; developed crystallinity on annealing for 30 min at 250 °C
polymer no. 7 (80 wt % PEKK)	172	318	crystalline as molded
	165–175	385	crystalline as molded

aromatic hydrocarbons, and there was no improvement in the case of chlorinated aromatics.

Experimental Section

Mechanical property data were obtained using 0.02-in-thick strips from compression-molded plaques. These 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 as described in a previous paper.[14]

1. Polymerizations. Polymerization Procedure A. 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 the appropriate reagents (amounts listed below). Xylene (20 mL) was charged in the addition funnel. Once charged, the mixture was heated. The xylene was added when the mixture began to liquefy and stirring was begun. Simultaneously, about 7 mL of xylene was placed in the Dean–Stark trap. When the temperature reached about 175 °C, distillation of xylene began. The temperature was increased to 200 °C, draining xylene

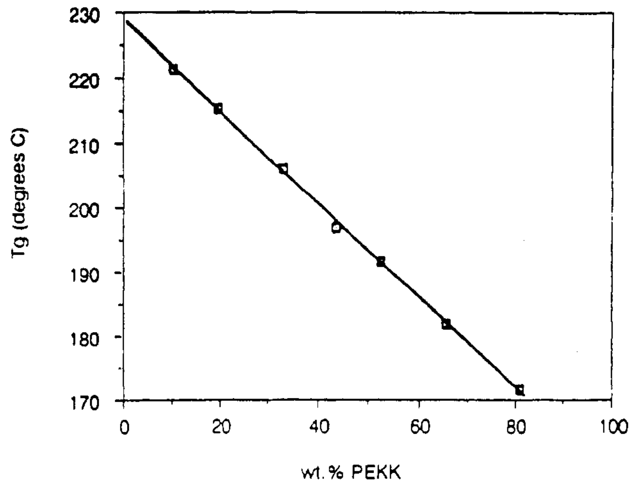


Figure 1. Glass transition temperature of the block copolymers versus their PEKK content.

Table VI
Stress–Crack Resistance Data

polymer	tensile strength at 0.02 in./min in psi PES	1	2	3	3	6
(wt %) PEKK	0	10	19	33	33	65
annealed?[a]	no	no	no	no	yes	yes
acetone	300	1000	1000	1700	1300	5200
butanone	100	1100	900	2100	1000	4800

[a] 30 min at 250 °C.

dropwise from the trap as necessary. The mixture was maintained at 200 °C for 30 min, with addition of some xylene (if necessary) to maintain a steady reflux. The mixture was then heated to 250 °C, draining xylene dropwise from the trap as necessary to increase the temperature. The mixture was maintained at 250 °C for 30 min, with addition of some xylene (if necessary) to maintain a steady reflux. The mixture was then heated to 300 °C. At 265–275 °C, all of the xylene was removed from the Dean–Stark trap. The mixture was maintained at 300 °C until it became viscous and was then poured into an aluminum pan. After cooling and solidification, the reaction mass was crushed and ground to a powder.

Polymerization Procedure B. This polymerization procedure was performed in the same manner as procedure A, except that the hold at 250 °C was omitted.

Polymerization Procedure C. This polymerization procedure was performed in the same manner as procedure A, except that both the holds at 200 and 250 °C were omitted.

2. Workup. Work-up Procedure A. The ground reaction mixture was extracted with a 1:1 mixture by volume of methanol/acetone at reflux (700 mL, 1.5 h), methanol at reflux (two times, 700 mL, 1.5 h each time), 5% by weight of aqueous HCl at reflux (700 mL, 1.5 h), deionized water at reflux (two times, 700 mL, 1.5 h each time), and a 1:1 mixture by volume of methanol/acetone at reflux (700 mL, 1.5 h). The final product was recovered by vacuum filtration, washed with a 1:1 mixture by volume of methanol/acetone, allowed to air dry, and then heated in vacuo at 100 °C for 3 days.

Work-up Procedure B. The ground reaction mixture was extracted with methanol at reflux (three times, 700 mL, 1.5 h each time), deionized water at reflux (two times, 700 mL, 1.5 h each time), and a 1:1 mixture by volume of methanol/acetone at reflux (700 mL, 1.5 h). The final product was recovered by vacuum filtration, washed with a 1:1 mixture by volume of methanol/acetone, allowed to air dry, and then heated in vacuo at 100 °C for 3 days.

Work-up Procedure C. The ground reaction mixture was extracted with acetone at reflux (two times, 700 mL, 1.5 h each time), deionized water at reflux (two times, 700 mL, 1.5 h each time), and acetone at reflux (700 mL, 1.5 h). The final product was recovered by vacuum filtration, washed with acetone, allowed to air dry, and then heated in vacuo at 100 °C for 3 days.

Work-up Procedure D. This work-up procedure was performed in the same manner as work-up procedure B, except that 5% by weight of aqueous HCl was substituted for deionized water in the first aqueous extraction.

3. Specific Examples. Additional details regarding the polymers listed in Table IV are given below.

Polymer no. 1 (5 mol % oligomer **2**; 10 wt % PEKK). The amounts used were 2.11 g (0.002 mol) of oligomer **2**, 9.66 g (0.038 mol) of 4,4′-difluorodiphenyl sulfone, 10.01 g (0.04) mol) of 4,4′-bisphenol-S, 4.00 g (0.04 mol) of calcium carbonate, 0.393 g (0.004 mol) of potassium acetate, and 61 g of diphenyl sulfone. The polymerization was performed according to procedure B. The workup was performed according to procedure B. The reaction time at 300 °C was 20 min.

Polymer no. 2 (10 mol % oligomer **2**; 19 wt % PEKK). The amounts used were 4.22 g (0.004 mol) of oligomer **2**, 9.15 g (0.036 mol) of 4,4′-difluorodiphenyl sulfone, 10.01 g (0.04 mol) of 4,4′-bisphenol-S, 4.00 g (0.04 mol) of calcium carbonate, 0.393 g (0.004 mol) of potassium acetate, and 65 g of diphenyl sulfone. The polymerization and work-up procedures were B and D, respectively. The reaction time at 300 °C was 60 min.

Polymer no. 3 (20 mol % oligomer **2**; 33 wt % PEKK). The amounts used were 7.04 g (0.006 67 mol) of oligomer **2**, 6.78 g (0.0267 mol) of 4,4′-difluorodiphenyl sulfone, 8.34 g (0.0333 mol) of 4,4′-bisphenol-S, 3.53 g (0.0333 mol) of sodium carbonate, 0.273 g (0.003 33 mol) of sodium acetate, and 62 g of diphenyl sulfone. The polymerization and work-up procedures were B and B, respectively. The reaction time at 300 °C was 90 min.

Polymer no. 4 (30 mol % oligomer **2**; 43 wt % PEKK). The amounts used were 9.50 g (0.009 03 mol) of oligomer **2**, 5.34 g (0.0210 mol) of 4,4′-difluorodiphenyl sulfone, 7.51 g (0.0300 mol) of 4,4′-bisphenol-S, 3.00 g (0.0300 mol) of calcium carbonate, 0.29 g (0.0030 mol) of potassium acetate, and 63 g of diphenyl sulfone. The polymerization and work-up procedures were B and A, respectively. The reaction time at 300 °C was 60 min.

Polymer no. 5 (40 mol % oligomer **2**; 52 wt % PEKK). The amounts used were 10.76 g (0.0102 mol) of oligomer **2**, 3.89 g (0.0153 mol) of 4,4′-difluorodiphenyl sulfone, 6.38 g (0.0255 mol) of 4,4′-bisphenol-S, 2.55 g (0.0255 mol) of calcium carbonate, 0.25 g (0.0025 mol) of potassium acetate, and 60 g of diphenyl sulfone. The polymerization and work-up procedures were B and A, respectively. The reaction time at 300 °C was 75 min.

Polymer no. 6 (60 mol % oligomer **2**; 65 wt % PEKK). The amounts used were 13.40 g (0.0127 mol) of oligomer **2**, 2.15 g (0.008 46 mol) of 4,4′-difluorodiphenyl sulfone, 5.30 g (0.0212 mol) of 4,4′-bisphenol-S, 2.12 g (0.0212 mol) of calcium carbonate, 0.21 g (0.0021 mol) of potassium acetate, and 60 g of diphenyl sulfone. The polymerization and work-up procedures were B and A, respectively. The reaction time at 300 °C was 70 min.

Polymer no. 7 (100 mol % oligomer **2**; 80 wt % PEKK). The amounts used were 18.85 g (0.0180 mol) of oligomer **2**, 4.50 g (0.0180 mol) of 4,4′-bisphenol-S, 1.91 g (0.0180 mol) of sodium carbonate, 0.089 g (0.0015 mol) of potassium fluoride, and 70 g of diphenyl sulfone. The polymerization and work-up procedures were C and C, respectively. The reaction time at 300 °C was 50 min.

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