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Synthesis and Characterization of Poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene) and Related Polymers

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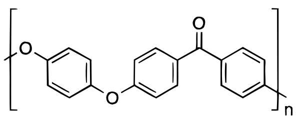
ABSTRACT: The title composition, isoPEK, was prepared from 4-fluoro-3′-hydroxybenzophenone in *N*-methylcaprolactam at 225 °C. Cyclomer formation interfered with polymerization at lower temperatures in alternative solvents and dominated in dilute solutions. The 50/50 to 70/30 copolymers of PEK and isoPEK were prepared using 4-fluoro-4′-hydroxybenzophenone. An analogous composition, poly(oxy-1,3-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) or isoPEKEK, was prepared from 4,4′-difluorobenzophenone and 3,4′-dihydroxybenzophenone using similar conditions. Thermal crystallization of the copolymers was successful, but isoPEK and isoPEKEK were only capable of solvent-induced crystallization. The semicrystalline materials were studied by thermal analysis and X-ray diffraction. The copolymers melted at 264−307 °C and possessed random microstructures with isomorphic crystallization of the PEK and isoPEK repeat units. IsoPEK and isoPEKEK melted, respectively, at the low temperatures of 180 and 193 °C. IsoPEK crystallized with both Form 1 and Form 2 unit cells, while isoPEKEK and the copolymers crystallized with the Form 1 unit cell. IsoPEK was also prepared by ring-opening polymerization of its cyclomers in the melt using cesium fluoride as catalyst. The 3,4′ catenation of the isoPEK repeat unit and the related monomers was used to rationalize the unique chemistry and properties of these polymers.

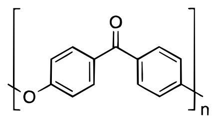
Introduction

Poly(arylene ether ketone)s are thermoplastic engineering polymers possessing an excellent balance of mechanical properties and flexible processing with thermooxidative and chemical resistance.[1] The most utilized compositions employ *p*-phenylene units to impart semicrystallinity with high melting points. The well-known poly(ether ether ketone), PEEK, retains melt processibility because the consecutive ether linkages provide flexibility, while poly(ether ketone), PEK, possesses an excessively high melting point. The alternative poly(ether ketone ketone)s, PEKK, possess lower melting points, despite the rigidity imparted by the consecutive ketone linkages, because *m*-phenylene units are incorporated into their copolymers.[2] Both PEEK and PEKK are used as matrix resins in high-performance composites.



PEEK

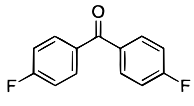
T_g 144 °C T_m 343 °C



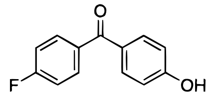
PEK

T_g 154 °C T_m 366 °C

A principal issue for the preparation of poly(arylene ether ketone)s is the harshness of the conditions. PEEK and PEK, as well as many other compositions, are polymerized by nucleophilic aromatic substitution (S$_N$Ar) of fluoro-substituted benzophenones with aromatic diols in the presence of inorganic bases,[3] which proceeds through the formation of Meisenheimer complexes due to activation by the carbonyls (Scheme 1). PEEK is prepared from the AA/BB comonomer system of hydroquinone and 4,4′-difluorobenzophenone (DFB), while PEK can be prepared from either the AA/BB system of 4,4′-dihydroxybenzophenone and DFB, or the AB monomer 4-fluoro-4′-hydroxybenzophenone (FHB). These semicrystalline polymers require high temperatures to maintain solubility in diphenyl sulfone[4] or benzophenone,[5] but more moderate conditions suffice for amorphous compositions.[6] Alternatively, PEKK is polymerized from mixtures of terephthaloyl and isophthaloyl chlorides with diphenyl ether by Friedel−Crafts acylation, although linear polymer requires stoichiometric aluminum chloride in both stages of a two-stage process.[7]

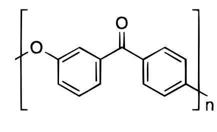


DFB

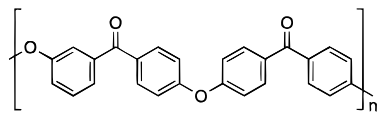


FHB

The solubility and stability of poly(arylene ether ketone)s in strong acids led to the attempted construction of molecular composites using rigid-rod polymers. Although phase separation prevented true molecular dispersions, amorphous matrix resins are hypothesized to prevent such behavior. An amorphous poly(arylene ether ketone) reported by Evers and co-workers to show promise for this application is poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene).[8] Although the trivial name mPEK was used for this composition, it is known as isoPEK in our laboratory because it is the simplest isomer of PEK that possesses a well-ordered microstructure of alternating *m*- and *p*-phenylene rings. A companion composition, poly(oxy-1,3-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), reported herein is known as isoPEKEK.



isoPEK



isoPEKEK

IsoPEK was originally prepared from 3-phenoxybenzoic acid following the procedure of Ueda and Sato;[9]

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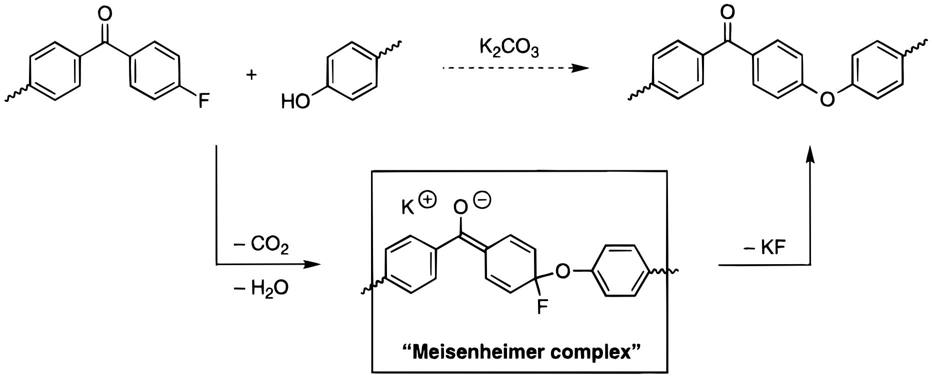
Scheme 1. Mechanism of S$_N$Ar Polymerization



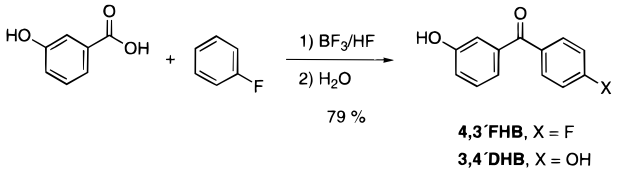
PEK was also prepared by Evers and co-workers from 4-phenoxybenzoic acid for comparison. These benzoic acids are activated for polymerization via Friedel–Crafts acylation in a medium of methanesulfonic acid and phosphorus pentoxide. High molecular weights were only observed for isoPEK, based on solution viscosity, although Ueda and Sato reported a higher value for isoPEK. Although the ^{13}C nuclear magnetic resonance (NMR) spectrum of isoPEK[10] showed that *para* acylation dominated the polymerization, low levels of *ortho* acylation below the detection limit are always a possibility with Friedel–Crafts chemistry.

Evers and co-workers induced crystallinity in isoPEK by slowly cooling a melt to room temperature. Differential scanning calorimetry (DSC) showed a modest melting endotherm (T_m) at 304 °C with an enthalpy of fusion (H_f) of 26.5 J/g. X-ray diffraction confirmed that isoPEK had the same unit cell as PEK. A solvent-induced endotherm at the glass transition temperature (T_g) of 132 °C was due to a solvent adduct. The mechanical properties of amorphous samples were promising but fell short of the best matrix resins due to the development of microvoids during mold shrinkage. These difficulties might be overcome by crystallinity or by a polymerization method that gives higher molecular weights and eliminates the possibility for microstructural defects.

The S$_N$Ar polymerization of isoPEK was investigated for the potential of higher molecular weights using a monomer that ensures a regular microstructure with strict alternation of *meta* and *para* catenation. This approach led to the preparation of copolymers with PEK and that of isoPEKEK as well. Our results are quite revealing as to the unique chemistry and properties of these polymers and will be reported herein and in a subsequent publication.

Results

Monomer Synthesis. The S$_N$Ar polymerization of isoPEK requires 4-fluoro-3′-hydroxybenzophenone (4,3′FHB), while isoPEKEK can be prepared from DFB and 3,4′-dihydroxybenzophenone (3,4′DHB). 4,3′FHB was prepared following the method of Irwin for 3,4′DHB.[11] The Friedel–Crafts acylation of fluorobenzene with *m*-hydroxybenzoic acid is activated by the strong acid medium of BF$_3$/HF despite the lower reactivity of carboxylic acids.



4,3′FHB, X = F
3,4′DHB, X = OH

Table 1. NMR Chemical Shifts for Selected Nuclei of *p*-Fluorobenzophenones

compd	^{1}H (CDCl$_3$) *ortho* H	^{13}C (CDCl$_3$) *para* C	^{19}F (DMSO-d_6) *para* F
4,3′FHB	7.85	165.53	−106.47
DFB	7.82	165.27	−106.01
FHB	7.80	165.24	−107.60

Monomer Reactivity. The reactivity of fluoro-substituted monomers in S$_N$Ar polymerizations can be probed using NMR spectroscopy by correlating their chemical shifts with electron density.[12] Theoretical studies verify the correlation of electron density with reactivity and with ^{13}C and ^{19}F NMR chemical shifts.[13] Table 1 shows the chemical shifts for the relevant ^{1}H, ^{13}C, and ^{19}F nuclei of benzophenone monomers. The downfield chemical shifts for the nuclei of 4,3′FHB indicate that it should display high reactivity. The ^{19}F NMR chemical shift for DFB shows that its difluoro nuclei are more electrophilic than that of 4,3′FHB, but the *para*-carbon and *ortho*-hydrogen chemical shifts indicate that this does not translate as effectively to their nuclei. Since ^{19}F NMR is the most sensitive probe of S$_N$Ar reactivity, the initial rates of polymerization with DFB may be greater than those with 4,3′FHB. However, polymerizations employing DFB slow with conversion and approach the rates of those using FHB, as *para*-oxy bond formation in both results in the same end group.[3]

Polymerization of IsoPEK. The S$_N$Ar polymerizations of isoPEK from 4,3′FHB in common dipolar aprotic solvents are displayed in Table 2. The polymerizations were monitored in their early phases by the consumption of solid potassium carbonate and the intensity of the yellow-orange color for the potassium phenolate end groups. The completion of polymerization was judged by the increase in solution viscosity, the precipitation of potassium fluoride, and the discharge of color, which typically required only a few hours. The polymerizations were initially worked up by coagulating in water and washing with methanol.

Although high molecular weights were attained, the polymerizations were plagued by the formation of cyclomers. This was first evident by gel permeation chromatography (GPC), which showed bimodal distributions with substantial low molecular weight fractions; the GPC conditions were originally developed for PEEK,[14] and the reported molecular weights and integrations are uncorrected. For example, the polymer from *N*-methylpyrrolidone (NMP) and toluene at 200 °C (item 3) contained 37% low molecular weight fraction, which was shown by fast atom bombardment mass spectrometry (FAB MS) to consist of cyclomers from dimer to octamer

Table 2. S_NAr Polymerization of IsoPEK in Common Dipolar Solvents

					η_{inh} (dL/g)		GPC (cyclomer integral)			
item	solvent	concn (%)	temp (°C)	yield (%)	initial	final[a]	M_n	M_w	M_{peak}	(%)
1	DMSO/toluene	14	170−190	83.4	0.98		2 260	31 800	52 300	40
2	sulfolane/toluene	14	170−200	70.7	1.07		3 730	22 600	22 600	15
3	NMP/toluene	14	170−200	98.0	2.51	2.80	1 990	84 100	107 000	37
4	NMP	14	200	87.8	1.47	1.85	2 950	51 600	66 500	29
5	NMP	20	190−220	88.4		2.33	8 000	74 900	76 400	9
6	NMP	20	220	80.5[b]		2.40	12 700	57 100	56 200	0
7	NMP	20	160[c]	85.2[b]		2.30	8 150	57 900	55 800	0

[a] After acetone extraction. [b] Coagulated in acetone; washed with acetone and water. [c] 24 h.

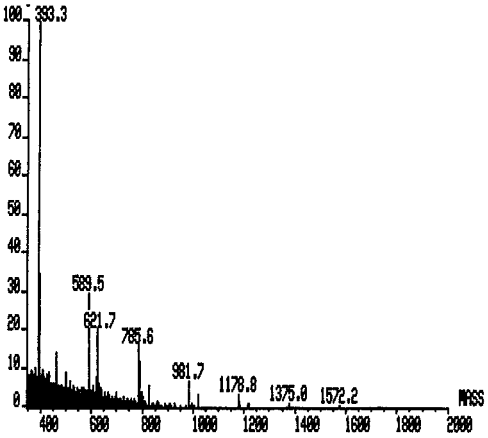


Figure 1. FAB mass spectrum of residual cyclomers in a sample of isoPEK (Table 2, item 3). The peak at *m/z* 621.7 was due to a matrix-generated ion.

(Figure 1). Integration of the high polymer fractions showed the same peak molecular weights (M_{peak}) as the full chromatographs, and the polydispersities (M_w/M_n) of the former were close to the most probable distribution. Simple washing of the isolated polymers with acetone removed some of the cyclomers and increased their inherent viscosities (η_{inh}).

Formation of the cyclomers was reduced, but not eliminated, by increasing the concentrations of the polymerizations. This was mainly achieved by eliminating the toluene used to remove water as an azeotrope. Some aprotic solvents used in S_NAr polymerizations can displace water at high temperatures without the aid of azeotropes, especially when the resulting polymer is hydrophobic, and NMP did not require toluene to obtain high molecular weights. Fewer cyclomers were observed with NMP at 220 °C (item 5), but coagulation of the polymer preparations in acetone reduced the cyclomers to levels undetectable by FAB MS (item 6). Solvent degradation made the completion of polymerization difficult to judge and the isolated polymers were discolored. Polymerization at 160 °C was slower, but the resulting polymer was not discolored, and it was free of cyclomers after coagulation in acetone.

Table 3. S_NAr Polymerization of IsoPEK in NMC at 225 °C for 4 h

				GPC		
item	concn (%)	yield (%)	η_{inh} (dL/g)	M_n	M_w	M_w/M_n
1	20[a]		1.10	13 300	31 000	2.33
2	20	85.2	1.15	11 400	33 200	2.90
3	25	92.9	1.15	9 710	40 300	4.15
4	30	90.3	1.27	11 600	39 700	3.42

[a] Immersed in preheated bath.

N-Methylcaprolactam (NMC) is a good solvent for the S_NAr polymerization of poly(arylene ether ketone)s at moderate temperatures using azeotrope-forming cosolvents.[15] IsoPEK was successfully polymerized from 4,3′FHB in neat NMC at 225 °C at several concentrations (Table 3). Although solvent degradation was avoided with NMC, the completion of polymerization was judged solely on solution viscosity because the yellow color only faded as the solutions were cooled to room temperature; 4 h of reaction time was sufficient to reach an apparent viscosity plateau. Good yields of high molecular weight polymers containing no cyclomers were obtained after coagulation in acetone and washing with water. The molecular weight distributions of the polymers from NMC were narrower than those from Table 2, and the polydispersities occasionally approached the most probable distribution. The observed thermal properties (Table 4) were comparable to those previously reported for amorphous isoPEK, but no melting endotherms were induced by slow cooling to below T_g before the second heating cycles.

Characterization of IsoPEK Cyclomers. The isoPEK cyclomers were initially assigned by FAB MS using the polymers from Table 2; Figure 1 shows a representative example. Samples of the cyclomers were also isolated from the polymers by extraction with methanol or acetone. The cyclomer mixtures were soluble in acetone, but only the cyclic dimer showed limited solubility in methanol. Consequently, the polymerization mixtures were thereafter coagulated in acetone to ensure isolation of cyclomer-free polymers.

Authentic cyclomer samples were easily prepared in more dilute solutions than those of polymerization. At

Table 4. Thermal Properties of Selected Polymers

		DSC [°C (J/g)]			TGA (10 wt %) (°C)	
polymer	source	T_g	T_m (H_f)	T_c (H_f)	air	N_2
isoPEK	Table 2, item 6	132			460	430
isoPEK	DMAc crystallized	131	180 (26)		490	490
isoPEKEK	Table 5, item 1	147				
isoPEKEK	CH_2Cl_2 crystallized	145	193 (33)		525	525
50/50 PEK/isoPEK	Table 5, item 2[a]	142	264 (20)		445	460
60/40 PEK/isoPEK	Table 5, item 5	146	279 (23)		480	525
65/35 PEK/isoPEK	Table 5, item 6	147	296 (20)	225 (19)	525	525
70/30 PEK/isoPEK	Table 5, item 7	150	307 (17)	215 (15)	460	495

[a] Melted and annealed at 210 °C.

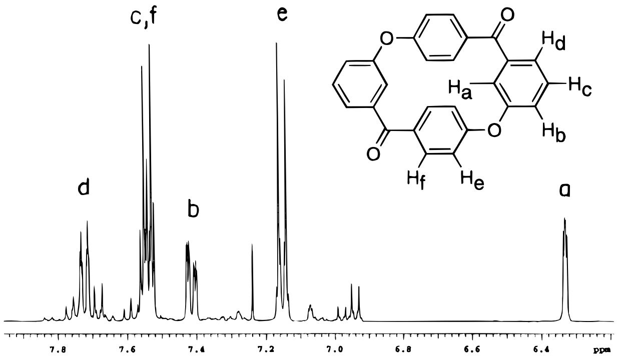


Figure 2. ^{1}H NMR spectrum of the isoPEK cyclomers prepared in DMSO. The major peaks are assigned to the structure of the cyclic dimer.

a 2% concentration in dimethyl sulfoxide (DMSO) at 170 °C, a crude yield of 45% was obtained, and the material was purified by filtering a dichloromethane solution through silica gel. FAB MS showed a mixture of cyclic dimer, trimer, and tetramer with a large majority of the dimer. The ^{1}H NMR spectrum also showed a preponderance of cyclic dimer (Figure 2). The upfield resonance at δ 6.3 supports the structure of cyclic dimer because the assigned hydrogens, which are *ortho* to both substituents of the *m*-oxybenzoyl groups, lie in the shielding cones of both *p*-phenylene rings. DSC showed a T_g of 84 °C and three T_m at 166, 207, and 235 °C (Figure 3).

The preparation of cyclomers at a 2% concentration in NMP at 150 °C gave a higher yield of 60% after purification. FAB MS showed a mixture of cyclomers from dimer up to heptamer. The ^{1}H NMR spectrum confirmed that it was a more complex mixture than the product from DMSO, although the relative intensities again indicated a preponderance of cyclic dimer. DSC showed this mixture to be amorphous with a T_g of 101 °C.

Both cyclomer mixtures displayed η_{inh} less than 0.1 dL/g. GPC showed only low molecular weight material, although these conditions are not calibrated for isoPEK cyclomers. Indeed, both cyclomer samples gave peak molecular weights for cyclic dimer that were about one-half of the calculated value of FW 392. Further refinements of the synthetic conditions using dilute solutions of DMSO, NMP, and dimethylacetamide (DMAc) gave no improvement.

Ring-Opening Polymerization of IsoPEK Cyclomers. The ring-opening polymerization of isoPEK cyclomers was investigated due to the value of such an approach in advanced composite applications. The recent development of this chemistry is well known, but useful examples of poly(arylene ether ketone)s have not been forthcoming for a variety of reasons.[16] The syntheses of their cyclomers are difficult, except for various systems with little utility in advanced composites or those with complex monomer syntheses. Additionally, the ring-opening polymerizations, which are initiated using nucleophilic catalysts such as cesium fluoride or the potassium salt of 4-hydroxybenzophenone, suffer due to the high melting temperatures of either the cyclomers or the resulting polymers. The isoPEK cyclomer/polymer system could represent a useful compromise between polymer properties and ease of processing via ring-opening polymerization.

A cyclomer mixture that contained a majority of dimer according to ^{1}H NMR, and up to heptamer according to FAB MS, was successfully polymerized in the melt at 240−260 °C using 2 mol % cesium fluoride[16] as the nucleophilic catalyst. Chain growth was indicated by the increase in η_{inh} from 0.08 to 0.93 dL/g. GPC confirmed that high molecular weight polymer was obtained with M_w of 22 900, but the low value for M_n of 2080 was affected by the presence of 11% residual cyclomers. The ^{1}H NMR spectrum showed both polymer and cyclic dimer, with the characteristic resonance at δ 6.3 for the latter, and FAB MS revealed that indeed only cyclic dimer remained after polymerization. Judging from the GPC and ^{1}H NMR, at least some cyclic dimer is converted to polymer under these conditions.

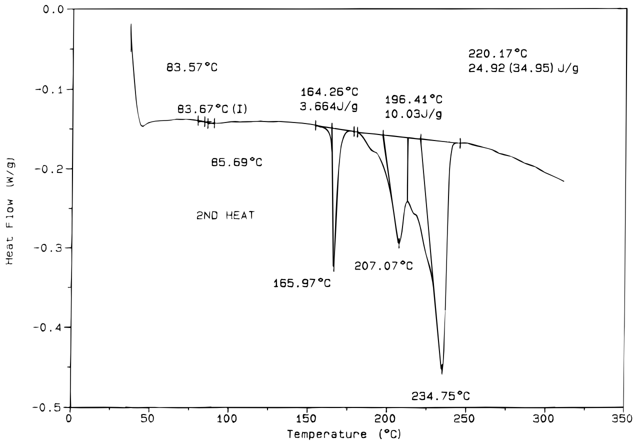


Figure 3. DSC thermogram of the isoPEK cyclomers prepared in DMSO.

IsoPEKEK Polymerization. IsoPEKEK was prepared from 3,4′DHB and DFB in NMC at 225 °C (Table 5). The yellow color from the potassium phenolate end groups did not discharge until the viscous solution was cooled to room temperature after 7 h. GPC showed high molecular weight polymer and no evidence of cyclomers. The T_g was higher than that of isoPEK and slightly higher than that of PEEK, but the isolated polymer was amorphous (Table 4). The ^{13}C NMR spectrum was consistent with the structure of isoPEKEK, although it showed apparent doublets for three quaternary carbons whose chemical shifts are consistent with either ether or ketone substituents.

Crystallization of IsoPEK and IsoPEKEK. The respective regular and semiregular microstructures of isoPEK and isoPEKEK were not sufficient to enable their thermal crystallization even after annealing at temperatures below their melting points. However, it was possible to induce crystallization by treatment of each with a suitable solvent. IsoPEK showed variable solubility in DMAc, with good solutions being used to wet spin weak fibers, but the occasional insolubility was found to be due to solvent-induced crystallization of the polymer. In retrospect, the only apparent uncontrolled variable was the moisture content.

An insoluble sample of isoPEK was extracted with methanol at reflux to remove DMAc and then with toluene and 2-butanone to extract low molecular weight materials that interfered with X-ray diffraction analysis. DSC showed a T_m at the low temperature of 180 °C on the first heating cycle (Figure 4), but only a T_g of 131 °C on the second cycle (Table 4). The X-ray diffraction pattern confirmed that the sample was semicrystalline and indicated a mixture of the Form 1 and Form 2 unit cells, as is seen for cold-crystallized 50/50 PEKK (Figure 5).[2] The Form 1 unit cell is seen for PEEK, PEK, and melt-crystallized PEKK, while Form 2 is seen for PEKK crystallized by treatment of amorphous samples with

Table 5. S_NAr Polymerization of IsoPEKEK and PEK/IsoPEK Copolymers in NMC at 225 °C

item	copolymer ratio	concn (%)	time (h)	yield (%)	η_{inh} (dL/g)	GPC M_n	M_w	M_w/M_n
1	isoPEKEK	25	7	90.1	2.02	23 600	76 300	3.24
2	50/50[a]	16	21	99.2	1.72	13 100	40 600	3.11
3	50/50	20	4	93.9	1.45	12 300	39 500	3.21
4	60/40	20	9	94.6	1.03	8 700	30 600	3.51
5	60/40	24	6	91.3	1.29	15 800	43 600	2.76
6	65/35	24	4	93.5	1.09	12 600	31 400	2.50
7	70/30	24	9	93.9	1.24	10 900	29 100	2.67

[a] 200 °C in NMP.

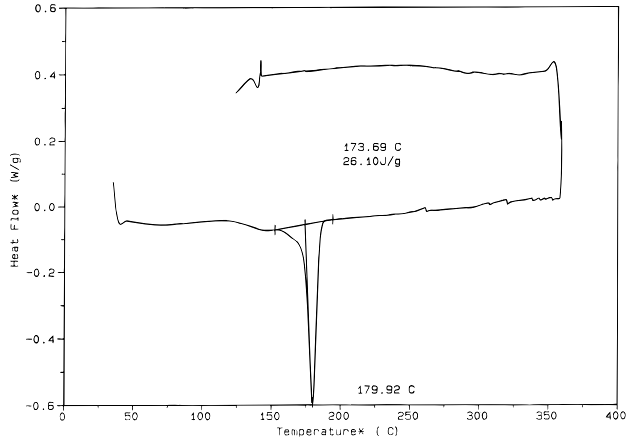


Figure 4. DSC thermogram of semicrystalline isoPEK.

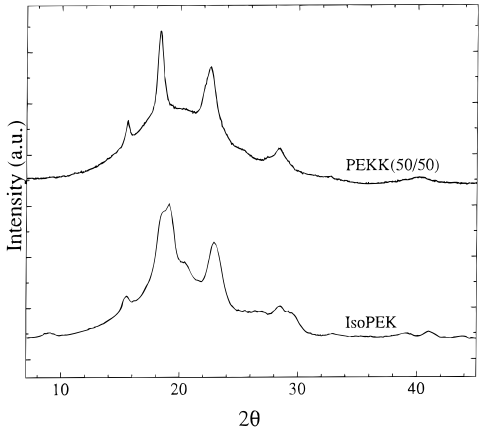


Figure 5. X-ray diffraction patterns for semicrystalline isoPEK and cold-crystallized 50/50 PEKK.

dichloromethane. Irreproducible endotherms above 300 °C were occasionally observed for isoPEK in our work, but the associated samples never gave X-ray diffraction patterns.

IsoPEK is soluble in chloroform and 1,1,2,2-tetrachloroethane (TCE) and slightly soluble in dichloromethane at reflux, in which solid samples are dispersed into fine powders. However, the powders showed no crystallinity by DSC or X-ray diffraction. IsoPEKEK was fully soluble in dichloromethane at reflux, but the solution gelled upon standing at room temperature. The gel was coagulated in methanol to give semicrystalline isoPEKEK powder. DSC showed a low T_m of 193 °C on the first heating cycle (Figure 6), but only a T_g of 145 °C on the second cycle (Table 4). TGA showed that the semicrystalline polymer had good thermal stability under both air and N_2 (Table 4). The X-ray diffraction pattern indicated a Form 1 unit cell (Figure 7).

PEK/IsoPEK Copolymers. Since the X-ray diffraction patterns of isoPEK and isoPEKEK indicated the same unit cell as PEK, the copolymers of isoPEK and PEK were expected to show isomorphic crystallization. The low melting point for isoPEK also suggested the potential for an ideal composition possessing a $T_g \geq 150$ °C and $T_m \leq 300$ °C, which would provide a good balance of processing and product properties. The PEK/isoPEK copolymers were prepared in NMC at 225 °C (Table 5). The conditions were more critical for the copolymers with higher PEK contents because of the lower reactivity of FHB versus 4,3′FHB, and high molecular weights were most easily obtained at concentrations greater than 20%.

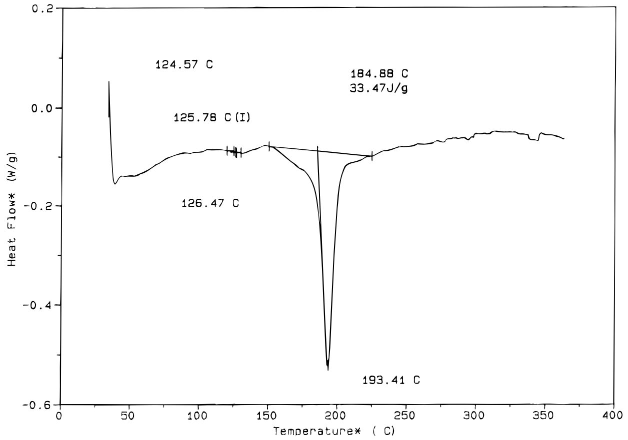


Figure 6. DSC thermogram of semicrystalline isoPEKEK.

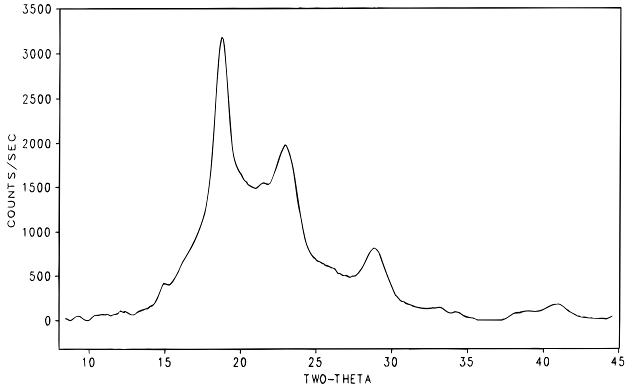


Figure 7. X-ray diffraction pattern for semicrystalline isoPEKEK.

DSC thermal analysis of the copolymers showed progression in T_g and T_m with increasing PEK content (Table 4). The values for the 65/35 and 70/30 copolymers are from the second heating cycle, and crystallization exotherms (T_c) were observed on their cooling cycle and the second heating cycle. The melting endotherms for 60/40 and 50/50 copolymers are from the first heating cycles because they do not show T_c; the T_g are from the second cycle. The values for the 50/50 copolymer are from an annealed sample because the as-

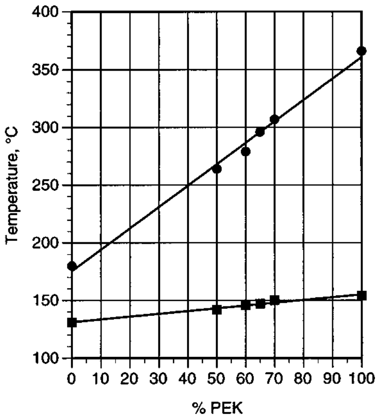


Figure 8. Linear dependence of T_g (squares) and T_m (circles) for isoPEK, PEK, and the PEK/isoPEK copolymers vs their compositions.

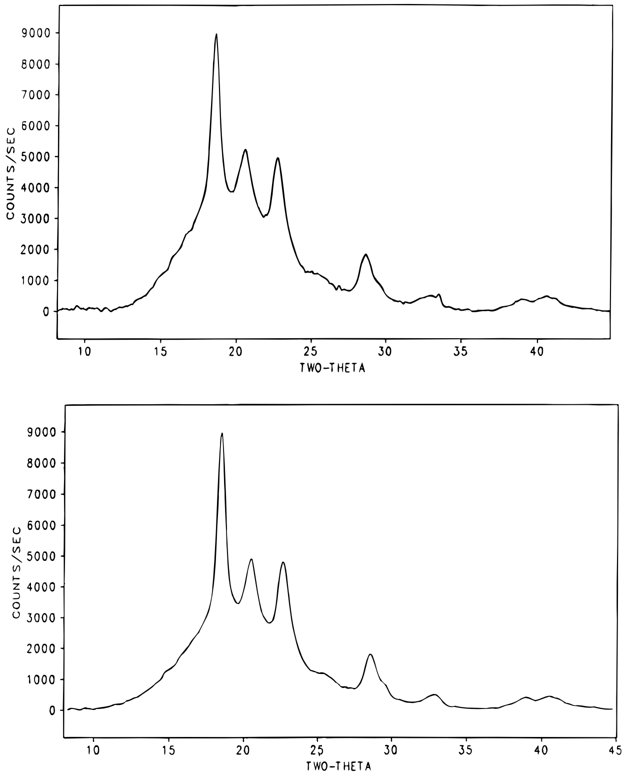


Figure 9. X-ray diffraction patterns for semicrystalline 60/40 (top) and 65/35 (bottom) PEK/isoPEK copolymers annealed at 210 °C.

isolated copolymers show very broad endotherms. Figure 8 shows the linear dependence of T_g and T_m versus the PEK content of the copolymers using the values of the homopolymers to anchor the lines. This indicates that the copolymers possess random microstructures with isomorphic crystallization.

The 60/40 and 65/35 copolymers were examined by X-ray diffraction using films pressed at 320 °C and annealed at 210 °C to give thermal-induced crystallinity. The diffraction patterns showed that both were semicrystalline with Form 1 unit cells (Figure 9). DSC showed that the single melting endotherms of the original samples had separated into multiple endotherms, with the most endothermic peaks of the latter roughly corresponding to those of the former (Figure 10). Also, the average of each set of endotherms appears to qualitatively coalesce to the T_m of 264 °C seen for the single endotherm of the annealed 50/50 copolymer.

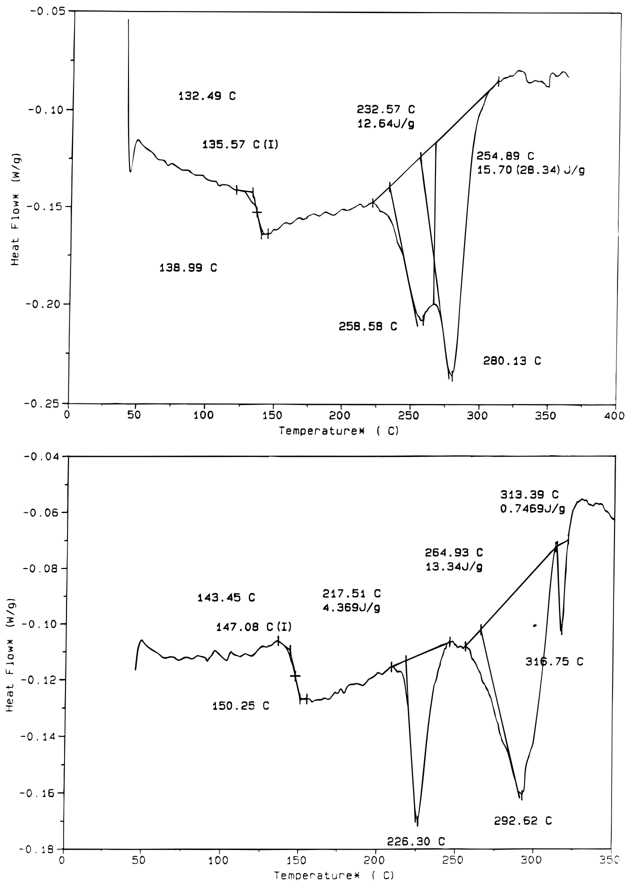
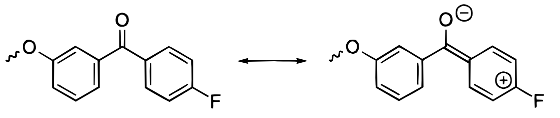


Figure 10. DSC thermograms of semicrystalline 60/40 (top) and 65/35 (bottom) PEK/isoPEK copolymers annealed at 210 °C.

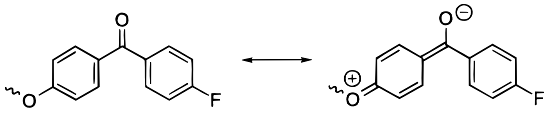
Multiple melting endotherms were previously observed for melt-crystallized PEKK with a Form 1 unit cell.[2]

Discussion

The NMR study of monomer electron densities agrees with the results of the S_NAr polymerizations of isoPEK and the PEK/isoPEK copolymers in that the 3,4′ catenation of 4,3′FHB renders it more reactive than FHB. According to electron resonance theory, the *para*-fluoro groups of the monomeric anion or polymeric end group are activated for *ipso* substitution by conjugation with

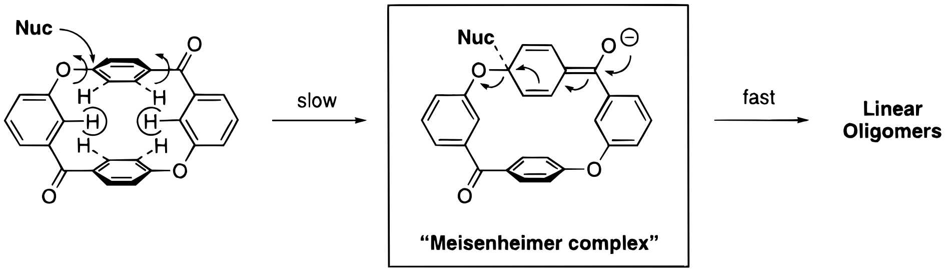


the carbonyl group. The electrophilicity of the *para*-fluoro group in FHB is compromised by the conjugation between the carbonyl group and the *para*-oxy phenolate



anion, or the bond derived during polymerization. The *para*-oxy anion will deactivate the carbonyl more than the *para*-oxy bond, due to its higher charge density, so its nucleophilicity will be reduced as well. However, the

Scheme 2. Ring Opening of IsoPEK Cyclic Dimer



meta-oxy groups derived from 4,3′FHB cannot enter conjugation with the carbonyl group, which will increase the electrophilicity of its *para*-fluoro group and the nucleophilicity of its phenolate anion. Such "bridge effects" are well known for the S_NAr polymerizations of poly(arylene ether sulfone)s, where the chloro-sulfone analog of 4,3′FHB demonstrated a rate enhancement factor of 60 over the same analog of FHB.[17,18]

The nucleophilicities of the phenolate anion end groups derived from 3,4′DHB should be affected by conjugation in a similar fashion. The *meta*-oxy anion should be more nucleophilic than the *para*-oxy anion, although the latter should be less than the *para*-oxy anion end group from FHB. Coupled with the electrophilicity of DFB, the polymerization of isoPEKEK from 3,4′DHB and DFB should show a high initial rate that slows with conversion as the *meta*-oxy anion is consumed preferentially, and DFB is converted to a less reactive *para*-fluoro end group. Indeed, the polymerization of isoPEKEK gave very high molecular weight, although it did take longer than those of isoPEK and the PEK/isoPEK copolymers to reach a viscosity plateau.

Although 3,4′ catenation imparts high reactivity to 4,3′FHB and the isoPEK end groups, it also provides more degrees of freedom for their conformational isomers. Together, they allow cyclization of the linear oligomers to compete effectively with chain extension for enthalpic reasons. Cyclomer formation plagues the reaction in less than concentrated solutions and dominates with only simple dilution. However, it can be overcome by copolymerization with 4,4′-catenated FHB and in the homopolymerization of isoPEKEK from 3,4′DHB and DFB.

The polymerizations of isoPEK at higher temperatures, or for a longer time at a milder temperature, gave lower levels of cyclomers, which shows that they are kinetic rather than thermodynamic products. Although an increase in temperature reduces the rate of cyclomer formation for entropic reasons, it must also accelerate the equilibration of the linear and cyclic oligomers via transetherification. The transetherification of PEK is catalyzed by potassium carbonate at >250 °C in diphenyl sulfone,[19] but the higher reactivity associated with the isoPEK repeat unit, coupled with the more polar natures of NMP and NMC, may enable transetherification at lower temperatures. In addition, our conditions employed a slight excess of potassium carbonate, which could serve as catalyst. Moreover, the ring-opening polymerization of arylene ether cyclomers, which proceeds by transetherification, is catalyzed by nucleophiles like cesium fluoride or the potassium salt of 4-hydroxybenzophenone,[16] and our conditions have both potassium fluoride and potassium phenolate end groups to serve this function.

Although transetherification during solution polymerization was not explicitly shown, the persistent yellow color of the NMC solutions at 225 °C, which is due to unreacted potassium phenolate end groups, supports its role as well. It is also significant that the color faded upon cooling to room temperature because phenolate end groups were not observed in the prior PEK work. This suggests a recombination of the phenolate end groups with the other end group species responsible for transetherification; our results point to the *p*-fluorobenzoyl end group. At lower temperatures, the yellow color completely discharges at the completion of polymerization, and cyclomers are quite prevalent unless long reaction times are used, so transetherification is presumably much slower under these conditions.

The ring-opening polymerization of isoPEK cyclomer mixtures in the melt confirms the existence of transetherification. The required temperature was not much higher than that for polymerization in NMP or NMC, even though the conditions were certainly less polar. The residue of cyclic dimer suggests that its rate of ring-opening polymerization is slower than those of higher cyclomers. Although this is probably a kinetic steric effect, one cannot strictly rule out a thermodynamic mixture. The structure of cyclic dimer must retard the rate of the nucleophilic attack by either fluoride catalyst or phenolate end groups that leads to the formation of the intermediate Meisenheimer complexes (Scheme 2). The steric interaction between the relevant hydrogens of the *m*- and *p*-phenylene rings forces the latter to rotate out of conjugation with the ketone functions, which should slow the formation of the Meisenheimer complexes. Thus the 3,4′ catenation of the isoPEK repeat unit favors the formation of cyclomers in dilute solution yet still permits their ring-opening polymerization to high molecular weight polymer in the melt. Further work will be needed to exploit the potential of this chemistry.

Although the strict alternation of *meta* and *para* catenation in isoPEK is enforced by its AB monomer, 4,3′FHB, this does not result in the desired thermal-induced crystallinity. The reasons for its absence and for the difference in the previously reported melting point and that observed here for solvent-induced crystallinity are not clear with the available data. The Form 1 unit cell implied by Evers and co-workers may have the higher melting point, while the mixed crystallinity of the Form 1 and Form 2 unit cells may lead to the lower temperature, although the linear dependence in T_m for the isomorphic PEK/isoPEK system shown in Figure 8 supports the lower melting point for isoPEK. S_NAr polymerization ensures a regular microstructure, while the Friedel−Crafts acylation previously employed for isoPEK can give structural isomers. The amorphous polymer of Ueda and Sato was of higher molecular weight than that crystallized by Evers and co-workers, but only the former polymer was explicitly shown to possess a regular microstructure. Since the polymers prepared here have even higher molecular weights, it is possible that this reduces their rate of crystallization to an undetectable level.

The analogous AA/BB polymer, isoPEKEK, was prepared to increase the *para* content in a semiregular way, but thermal-induced crystallinity was still not observed. While this homopolymer might be considered to be a 50/50 copolymer of isoPEK and PEK, isoPEKEK differs from the 50/50 PEK/isoPEK copolymer because it has strict alternation of the isoPEK and PEK repeat units, while the copolymer has a random distribution. However, isoPEKEK does not have a regular distribution of *meta* and *para* catenation due to the head−tail isomerism introduced by 3,4′DHB. Although the two phenolate end groups from 3,4′DHB are not equivalent in reactivity, a preference for head-to-head/tail-to-tail or head-to-tail order was not expected because this requires a long-range bridge effect through an entire repeat unit. Indeed, a small bridge effect is seen in the ^{13}C NMR spectrum of isoPEKEK, which showed apparent doublets for three quaternary carbons bearing either ketone or ether substituents that are due to chemical shift differences in the head−tail isomers.

The differences in the microstructures of isoPEKEK and the 50/50 copolymer are readily apparent from their thermal properties. While possessing a similar T_g, the T_m of isoPEKEK is 70 °C lower than that of the 50/50 copolymer, nor can isoPEKEK be crystallized thermally. This is due to the absence of blocks of the PEK repeat unit, and the disorder introduced by the head−tail isomers. Moreover, the thermal properties of both isoPEKEK and isoPEK are unusual compared to those of typical poly(arylene ether ketone)s. For example, their value for T_g (K)/T_m (K) of 0.90 is unusually high compared to typical values of 0.65−0.71. So *meta* catenation has a more profound effect on the crystallization of poly(arylene ether ketone)s when distributed in a semiregular fashion along the polymer chain.

The linear dependence of T_g and T_m for the PEK/isoPEK copolymers indicates that they have random microstructures. The difference in the reactivities for FHB and 4,3′FHB may affect the rates of polymerization for the copolymers, but their microstructures probably randomize by transetherification. The 65/35 PEK/isoPEK copolymer has nearly ideal thermal properties for typical applications.

Conclusion

The 3,4′ catenation of the isoPEK repeat unit and related monomers provides high reactivity and unique versatility to this monomer/polymer system. High molecular weight isoPEK that is free of cyclomers can be prepared by S_NAr polymerization of 4,3′FHB in NMC at 225 °C and coagulation in acetone. Under the same conditions, isoPEKEK homopolymer and PEK/isoPEK copolymers are easily prepared with no evidence of cyclomer formation. IsoPEK and isoPEKEK are amorphous as isolated from S_NAr polymerization and cannot be thermally crystallized, but solvent-induced crystallization shows that these compositions have low melting points for poly(arylene ether ketone)s. This makes them suitable for applications that are unusual for poly(arylene ether ketone)s, such as adhesives or films, although nucleating agents might be needed to exploit their crystallization behavior. The PEK/isoPEK copolymers can be thermally crystallized and have a good balance of thermal properties for both processing and typical applications. Mixtures of isoPEK cyclomers are easily prepared in moderate yields in dilute solutions, and after their purification, can be converted to high molecular weight polymer by ring-opening polymerization. This indicates promise for their *in situ* polymerization to matrix resin during the fabrication of composite parts.

Experimental Section

General Procedures. All starting materials, anhydrous solvents, powdered K_2CO_3 (325 mesh), and *N*-methylcaprolactam (NMC) were supplied by Aldrich Chemical Co. NMC was purified by vacuum distillation. 4-Fluoro-4′-hydroxybenzophenone (FHB) and 4,4′-difluorobenzophenone (DFB) were recrystallized, respectively, from 2-butanone/cyclohexane and ethanol/cyclohexane. Pure 3,4′-dihydroxybenzophenone (3,4′DHB) was provided by Irwin.[11]

A Varian Unity 400 spectrometer was operated at 399.952 MHz for ^{1}H NMR and 100.57 MHz for ^{13}C NMR with tetramethylsilane as internal reference and at 376.289 MHz for ^{19}F NMR with $CFCl_3$ as internal reference. Routine ^{13}C NMR used acquisition-gated Waltz-16 ^{1}H decoupling with adequate delay times to ensure quantitative spectral integrations, and the carbon multiplicities were determined using the APT pulse sequence. A VG ZAB-E double-focusing mass spectrometer was operated in the FAB MS mode using Xe ionization and *m*-nitrobenzyl alcohol as matrix; the samples were prepared using 1,1,2,2-tetrachloroethane. The η_{inh} were measured in methanesulfonic acid at a concentration of 0.5 g/dL at 30 °C. DuPont 2100 and 2200 thermal analyzers were used at 10 °C/min for TGA under air and nitrogen and for DSC under nitrogen; the latter results are reported for the second heating cycle unless noted otherwise. X-ray diffraction scans were collected in the symmetrical transmission mode using an automated Philips diffractometer (curved crystal monochromator, 1° divergence and receiving slits, sample rotating) and Cu Kα radiation; the data were collected in a fixed time mode with a step size of 0.05° 2θ and run from 4 to 65° 2θ. A Waters 150C chromatograph was used for GPC following the method originally developed for PEEK.[14]

Synthesis of 4-Fluoro-3′-hydroxybenzophenone. Fluorobenzene (95 mL, 1.0 mol) and 138 g of *m*-hydroxybenzoic acid (1.00 mol) were charged to a Hastelloy C autoclave. The sealed autoclave was cooled, evacuated, and then charged with 500 g of HF and 136 g of BF_3 (2.00 mol). The autoclave was shaken at room temperature for 6 h under 30 psig of BF_3 with periodic repressurization until uptake had ceased. The BF_3 and HF were vented from the autoclave, and the residue was rinsed onto ice with methanol. The acidic slurry was neutralized to pH 7 using 50% aqueous sodium hydroxide. The product was collected by vacuum filtration, washed with water, and dried to give 171.1 g of red-brown solid for a 79.2% crude yield. The product was sublimed at 130 °C and 0.5 Torr to give a light yellow solid, recrystallized from 550 mL of toluene, and dried to give 133.3 g of white solid for a 61.6% yield; mp 99−99.5 °C (lit. 105,[20] 102 °C[21]). ^{1}H NMR (TCE-d_2): δ 7.115 (1H, ddd, $J = 8.0, 2.8, 1.2$ Hz), 7.165 (2H, dddd, $J = 8.8, 2.8, 2.0$ Hz, $J_{HF} = 8.4$ Hz), 7.274 (1H, ddd, $J = 7.6, 1.2, 1.2$ Hz), 7.308 (1H, dd, $J = 2.8, 1.2$ Hz), 7.364 (1H, dd, $J = 8.0, 7.6$ Hz), 7.835 (2H, dddd, $J = 8.8, 2.8, 2.0$ Hz, $J_{HF} = 5.2$ Hz). ^{1}H NMR ($CDCl_3$): δ 7.110 (1H, ddd, $J = 8.0, 2.8, 1.2$ Hz), 7.148 (2H, dddd, $J = 9.2, 3.2, 2.4$ Hz, $J_{HF} = 8.4$ Hz), 7.257 (1H, ddd, $J = 7.6, 1.6, 1.2$ Hz), 7.338 (1H, dd, $J = 8.0, 7.6$ Hz), 7.357 (1H, dd, $J = 2.8, 1.6$ Hz), 7.848 (2H, dddd, $J = 9.2, 2.8, 2.4$ Hz, $J_{HF} = 5.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 115.5 (2CH, d, $J_{CF} = 21.9$ Hz), 116.5 (CH), 120.3 (CH), 122.4 (CH), 129.6 (CH), 132.9 (2CH, d, $J_{CF} = 9.2$ Hz), 133.2 (C), 138.3 (C), 156.2 (C), 165.5 (C, d, $J_{CF} = 254.6$ Hz), 196.4 (C). ^{19}F NMR (DMSO-d_6): δ −106.5 (tt, $J_{HF} = 8.3$ and 5.5 Hz). Anal. Calcd for $C_{13}H_9FO_2$: C, 72.22; H, 4.20. Found: C, 72.33; H, 4.12.

Synthesis of IsoPEK in NMP/Toluene. 4,3′FHB (4.32 g, 20.0 mmol), 1.45 g of potassium carbonate (10.5 mmol), 50 mL of toluene, and 25 mL of NMP were charged to a 100 mL round-bottom flask equipped with a one-piece Claisen distillation apparatus and mechanical stirrer. After purging with argon, the yellow solution was heated to 170 °C with an oil bath, where it evolved gas with the consumption of potassium carbonate. The toluene/water azeotrope distilled at a head temperature of 106 °C, which continued for 100 min. The dark yellow solution was then heated to 200 °C to drive off residual toluene. Over the next 4 h, the solution lightened in color with the separation of a white precipitate to ultimately give a viscous brownish-green mixture. The solution was cooled, acidified with 2 mL of acetic acid, and coagulated in water in a blender to give a fibrous mass. The polymer was collected by vacuum filtration, washed several times with water, extracted with 150 mL of methanol at reflux for 4 h, collected by vacuum filtration, and washed with methanol. The off-white polymer was dried in a 50 °C vacuum oven under a nitrogen purge to give 3.84 g for a 98.0% yield. The η_{inh} was 2.51 dL/g. A sample was washed with acetone, and the η_{inh} increased to 2.80 dL/g. FAB MS: *m/z* 393.3, 589.5, 785.6, 981.7, 1178.8, 1375.0, 1572.2; calcd (M + H for cyclic $(C_{13}H_8O_2)_n$): 393.1 (dimer), 589.2 (trimer), 785.2 (tetramer), 982.0 (pentamer), 1178.2 (hexamer), 1374.4 (heptamer), 1570.7 (octamer).

Synthesis of IsoPEK in NMC. 4,3′FHB (4.32 g, 20.0 mmol), 1.45 g of potassium carbonate (10.5 mmol), and 9 mL of NMC were charged to a 50 mL round-bottom flask equipped with a Claisen adapter, a mechanical stirrer, and a gas inlet. After purging with nitrogen, the yellow solution was heated to 225 °C with an oil bath. Over a 4 h period, it darkened in color and evolved gas during the consumption of potassium carbonate. Then the color partly faded and the viscosity increased slightly with the separation of a white precipitate. The solution increased in viscosity and the color discharged to off-white as it cooled to room temperature. The polymer was coagulated in 250 mL of acetone in a blender, collected by vacuum filtration, and washed with acetone. It was washed with water in the blender to extract the inorganic residues, collected by vacuum filtration, and washed with water. The off-white polymer was dried in a 100 °C vacuum oven under a nitrogen purge to give 3.54 g for a 90.3% yield. The η_{inh} was 1.27 dL/g. ^{1}H NMR (TCE-d_2): δ 7.09 (2H, d, $J = 8.6$ Hz), 7.32 (1H, d, $J = 7.6$ Hz), 7.52 (1H, bs), 7.52 (1H, dd, $J = 7.6, 7.6$ Hz), 7.57 (1H, d, $J = 7.6$ Hz), 7.84 (2H, d, $J = 8.6$ Hz). ^{1}H NMR ($CDCl_3$): δ 7.059 (2H, *AA′*XX′, $J = 8.8, 2.8, 2.0$ Hz), 7.288 (1H, ddd, $J = 7.6, 1.8, 1.2$ Hz), 7.494 (1H, dd, $J = 8.0, 7.6$ Hz), 7.504 (1H, dd, $J = 1.6, 0.8$), 7.569 (1H, ddd, $J = 7.6, 1.2, 1.2$ Hz), 7.829 (2H, AA′*XX′*, $J = 8.8, 2.8, 2.0$ Hz). ^{13}C NMR ($CDCl_3$): δ 117.4 (2CH), 120.8 (CH), 123.6 (CH), 125.8 (CH), 129.9 (CH), 131.8 (C), 132.4 (2CH), 139.8 (C), 155.5 (C), 161.0 (C), 194.0 (C).[10]

Synthesis of IsoPEKEK. 3,4′DHB (2.142 g, 10.0 mmol), 2.182 g of DFB (10.0 mmol), and 12 mL of NMC were charged to a 50 mL round-bottom flask equipped with a three-neck adapter, a mechanical stirrer, a gas inlet, and a gas outlet connected to a bubbler. The vessel was purged with nitrogen, and then 1.45 g of potassium carbonate (10.5 mmol) was added under nitrogen. The flask was heated to 225 °C with an oil bath under a slow nitrogen purge. The clear solution became yellow at >200 °C and then orange after 30 min, with the consumption of potassium carbonate and separation of a white precipitate. After a total of 7 h, the solution was diminished in color to light yellow and was very viscous. The solution became extremely viscous as it cooled to room temperature, and the color discharged to off-white. The polymer was coagulated in 250 mL of acetone with 1 mL of acetic acid in a blender, collected by vacuum filtration, and washed with acetone. It was washed with water in the blender to extract the inorganic residues, collected by vacuum filtration, and washed with water. The white polymer was extracted with water, then methanol, at reflux to remove any residues and dried in a 70 °C vacuum oven under a nitrogen purge to give 3.53 g for a 90.1% yield. The η_{inh} was 2.02 dL/g. ^{1}H NMR (TCE-d_2): δ 7.11 (2H, dd, $J = 8.4, 3.6$ Hz), 7.17 (4H, m), 7.34 (1H, d, $J = 7.6$ Hz), 7.53 (2H, m), 7.59 (1H, d, $J = 7.6$ Hz), 7.84 (4H, m), 7.88 (2H, d, $J = 7.2$ Hz). ^{13}C NMR (TCE-d_2): δ 117.6 (2CH), 118.5 (2CH), 118.7 (2CH), 120.7 (CH), 123.7 (CH), 125.8 (CH), 130.1 (CH), 132.3 (4CH), 132.4 (2C), 132.5 (2CH), 133.1 (0.5C), 133.2 (0.5C), 139.5 (C), 155.6 (C), 159.3 (0.5C), 159.4 (0.5C), 160.0 (C), 160.5 (0.5C), 160.6 (0.5C), 193.9 (C), 194.2 (C).

Synthesis of 65/35 PEK/IsoPEK Copolymer. FHB (2.81 g, 13.0 mmol), 1.51 g of 4,3′FHB (7.00 mmol), 1.45 g of potassium carbonate (10.5 mmol), and 12.5 mL of NMC were charged to a 50 mL round-bottom flask equipped with a three-neck adapter, a mechanical stirrer, a gas inlet, and a gas outlet connected to a bubbler. The vessel was purged with nitrogen, and then the yellow solution was heated to 225 °C with an oil bath under a slow nitrogen purge. The solution became orange as it evolved gas, consumed potassium carbonate, and formed a fine white precipitate. After 3.7 h, the solution was very viscous and orange-brown. The solution became extremely viscous as it cooled to room temperature, and the color discharged to an off-white. The polymer was coagulated in 200 mL of acetone with 8 mL of acetic acid in a blender, collected by vacuum filtration, and washed with acetone. It was washed with water in the blender to extract the inorganic residues, collected by vacuum filtration, and washed with water. The off-white polymer was dried in a 70 °C vacuum oven under a nitrogen purge to give 3.67 g for a 93.5% yield. The η_{inh} was 1.09 dL/g.

Synthesis of IsoPEK Cyclomers in DMSO. 4,3′FHB (4.32 g, 20.0 mmol), 1.45 g of potassium carbonate (10.5 mmol), and 200 mL of DMSO were charged to a 300 mL round-bottom flask equipped with a large oval magnetic stirring bar, a condenser, and a gas inlet. The vessel was purged with argon, and then the yellow solution was heated to 170 °C with an oil bath. The solution darkened with the consumption of potassium carbonate. After several hours, a white precipitate had separated from the dark solution. After 2 days, the mixture was cooled and poured into water to give a suspension. Dark solids were collected by vacuum filtration, and the filtrate was extracted with dichloromethane to leave a clear aqueous phase. The organic phase was evaporated to give dark solids. The solids were combined by dissolving them in acetone, filtering the solution, and evaporating to give 1.77 g for a 45.1% yield. A sample was dissolved in dichloromethane, filtered through silica gel with additional solvent, and evaporated to give an off-white solid. The η_{inh} was 0.06 dL/g. ^{1}H NMR ($CDCl_3$; major peaks for cyclic dimer): δ 6.331 (2H, dd, $J = 2.8, 1.6$ Hz), 7.153 (4H, *AA′*XX′, $J = 8.8, 2.4, 2.0$ Hz), 7.414 (2H, ddd, $J = 8.0, 2.8, 1.0$ Hz), 7.541 (4H, AA′*XX′*, $J = 8.8, 2.4, 2.0$ Hz), 7.542 (2H, dd, $J = 8.0, 7.6$ Hz), 7.723 (2H, ddd, $J = 7.6, 1.6, 1.0$ Hz). ^{1}H NMR (TCE-d_2; major peaks for cyclic dimer): δ 6.320 (2H, dd, $J = 2.4, 1.6$ Hz), 7.184 (4H, *AA′*XX′, $J = 8.4, 2.4, 2.0$ Hz), 7.461 (2H, ddd, $J = 8.0, 2.4, 1.2$ Hz), 7.549 (4H, AA′*XX′*, $J = 8.4, 2.4, 2.0$ Hz), 7.584 (2H, dd, $J = 8.0, 7.6$ Hz), 7.725 (2H, ddd, $J = 7.6, 1.6, 1.2$ Hz). ^{13}C NMR (TCE-d_2; major peaks for cyclic dimer): δ 118.3 (2CH), 121.2 (4CH), 122.20 (2CH), 122.24 (2CH), 130.7 (2CH), 131.2 (4CH), 135.1 (C), 138.6 (2C), 157.4 (2C), 157.9 (2C), 195.9 (2C). FAB MS: *m/z* 393.4, 589.5, 785.7; calcd (M + H for cyclic $(C_{13}H_8O_2)_n$): 393.1 (dimer), 589.2 (trimer), 785.2 (tetramer).

Ring-Opening Polymerization of IsoPEK Cyclomers. Cesium fluoride (6 mg, 0.04 mmol) was dispersed in 400 mg of cyclomer mixture (2.0 mequiv of repeat unit) with 20 mL of methanol in a glass polymer tube. The solvent was evaporated under vacuum, and then the tube was immersed in a 200 °C metal alloy bath for 2 min before venting to nitrogen. The heat was increased to 240 °C for 1 h, and then to 260 °C for 1 h. The initial melt was orange, but it darkened to brown as it increased substantially in melt viscosity. The tube was cooled to room temperature and shattered to isolate the tough polymer with an η_{inh} of 0.93 dL/g. The ^{1}H NMR (TCE-d_2) spectrum showed isoPEK polymer and the resonance for cyclic dimer at δ 6.3. FAB MS: *m/z* 393.2; calcd (M + H for cyclic dimer, $(C_{13}H_8O_2)_2$): 393.1.

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