Synthesis, Characterization, and Ring-Opening Polymerization of the Cyclic Oligomers of Poly(Oxy-1,3-phenylenecarbonyl-1,4-phenylene)

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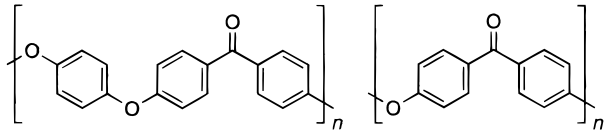
ABSTRACT: The cyclic oligomers (cyclomers) of the title composition were prepared from 4-fluoro-3′-hydroxybenzophenone by nucleophilic aromatic substitution. Cyclomers prepared in dimethyl sulfoxide and toluene at 150−160 °C using pseudo-high dilution contained a high fraction of cyclic dimer, which was isolated by vacuum sublimation. Cyclomers prepared in *o*-dichlorobenzene at 180 °C using catalytic 18-crown-6 were suitable for polymerization. High-performance liquid chromatography was used to quantify the mixtures. The ring-opening polymerization of the cyclic dimer was studied using nucleophilic initiators. The conversions and relative molecular weight distributions were measured using gel permeation chromatography. Absolute molecular weights were estimated on the basis of laser light-scattering measurements using cyclomer-free polymer samples. Cesium fluoride and alkali-metal carbonates gave incomplete conversion of the cyclic dimer to very high molecular weight polymers. Potassium and cesium 4-benzoylphenolate gave essentially complete conversion and their stoichiometry controlled the molecular weights. The amorphous polymers possessed T_g = 132 °C and M_w = 60 000−180 000. The initiators are differentiated by the competition between the chain extension of the linear species generated by initiation and propagation of the ring-opening polymerization. The reactivity of the cyclomers was correlated with their ^{1}H and ^{13}C NMR chemical shifts. The cyclic dimer is less reactive than the higher cyclomers due to its structure. X-ray crystallography showed that the *p*-phenylene rings of the cyclic dimer are partially rotated out of conjugation with the carbonyls due to steric interactions with the *m*-phenylene rings. The steric and electronic effects, and the chemistry of the cyclomers in general, are due to the 3,4′-catenation of the repeat unit.

Introduction

Poly(arylene ether ketone)s are thermoplastic engineering polymers with applications in molding and extrusion resins, coatings, and advanced composites.[1,2] These applications are based on their excellent balance of physical properties with thermo-oxidative and chemical resistance. The best-known compositions, poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK), are



PEEK **PEK**

T_g 144 °C T_m 335 °C T_g 154 °C T_m 367 °C

polymerized at high temperature[3] through nucleophilic aromatic substitution (S_NAr).[4] PEEK is more widely used than PEK due to its lower melting point, but its melt processing is still challenging, especially in the fabrication of advanced composites.

For advanced composites, thermoplastics require multiple steps to ensure impregnation of the reinforcing fibers and consolidation to low-void parts. Thermosets have distinct advantages in composite fabrication, although a final curing step is required to develop the toughened cross-linked network. Since thermoplastic composites are usually tougher than thermoset composites, thermoset-style processing of thermoplastics could have benefits for their composites. The ring-opening polymerization of macrocyclic oligomers (cyclomers) has received much scientific attention[5] and provides a solution to this technological dilemma, as well as a route to high-temperature adhesives. The low viscosity of cyclomer melts improves fiber wetting and impregnation during fabrication, and the absence of volatile byproducts during polymerization aids in their consolidation.

The synthesis and ring-opening polymerization of arylene ether cyclomers, especially those of poly(arylene ether ketone)s and poly(arylene ether sulfone)s, are largely based on S_NAr chemistry. In general, arylene ether ketone cyclomers have been more difficult to prepare, except for certain mixed aliphatic/aromatic and ortho-catenated compositions, and their polymerizations require rather high temperatures due to the high melting points of the cyclomers and the final polymers. All-aromatic biarylene ether ketone and sulfone cyclomers were first prepared in low yield using an intramolecular nickel-promoted cyclization of bis(4-chlorobenzoyl) derivatives, but their S_NAr-mediated ring-opening polymerizations were demonstrated using cesium fluoride (CsF) or potassium 4-benzoylphenolate (KOPhBz) as nucleophilic initiators.[6] Partially aromatic systems containing bent aliphatic units, especially spirobisindanes, showed a higher propensity for cyclomer formation, but their ring-opening polymerizations required excessively high temperatures.[7] In addition, these polymerizations are reported elsewhere to proceed to only partial conversion.[8]

The cyclomer chemistry of poly(ether sulfone) and other simple aromatic polyethers was facile under S_NAr conditions, while that of PEK and similar compositions was exceedingly difficult.[9] Indeed, the cyclomers of PEEK were prepared from the bisphenol (2:1) and difluoro (1:2) adducts of hydroquinone and 4,4′-difluorobenzophenone in a two-step process, although the

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Table 1. Synthesis of IsoPEK Cyclomers from 4,3′-FHB and K_2CO_3 in DMSO/Toluene Using Pseudo-High Dilution

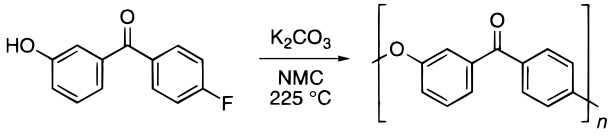
			yield (%)		
item	temp (°C)	time[a] (h)	crude	cyclic dimer	HPLC cyclomers: % (total %)
1	160	0/8	96.1		dimer−nonamer: 37.9, 22.4, 15.8, 8.7, 4.8, 3.5, 2.1, 0.4 (95.6)
2	160	8/4	93.1	60.2	dimer−hexamer: 81.9, 9.0, 4.4, 1.6, 1.1 (99.0)
3	150	12/4	91.1		dimer−hexamer: 57.9, 19.6, 6.0, 3.6, 2.5 (89.6)
4	150[b]	4/4	87.8	46.0	dimer−heptamer: 66.1, 18.3, 9.2, 3.3, 0.9, 1.8 (99.6)

[a] 4,3′-FHB addition (0.1 M final concentration)/reflux. [b] 1 mol % 18-crown-6.

latter was actually prepared by Friedel−Crafts chemistry.[10] The ring-opening polymerization of PEEK cyclomers was straightforward using a phenolate initiator at 340 °C, but cesium fluoride led to an insoluble polymer.

An elegant solution for poly(arylene ether ketone)s employed the 1,2-dibenzoylbenzene unit to promote cyclomer formation, yet permit ring-opening polymerization to high-molecular-weight polymers.[8,11] Both aliphatic/aromatic and all-aromatic ether ketone cyclomers were easily prepared and converted into novel phthalazine and isoquinoline derivatives.[12] However, their ring-opening polymerizations did not always proceed to completion even at high temperatures. In addition, branching side reactions associated with the 1,2-dibenzoylbenzene unit lead to polymers with broad molecular weight distributions and insoluble fractions.

An all-aromatic composition from a simple monomer that displays efficient cyclomer synthesis, controlled molecular weight growth in polymerization with low-residual cyclomers, and useful thermal properties remains a worthwhile goal. As recently reported,[13] 4-fluoro-3′-hydroxybenzophenone (4,3′-FHB) polymerizes in



4,3′FHB **isoPEK**

N-methylcaprolactam (NMC) to poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene), isoPEK, of high molecular weight under milder S_NAr conditions than many other poly(ether ketone)s. IsoPEK prepared at lower temperatures in dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP) was contaminated by high levels of cyclomers. IsoPEK displays a glass transition temperature (T_g) of 132 °C, an unusually low melt-transition temperature (T_m) of 180 °C for its solvent-induced crystallinity, and thermal stability up to 490 °C. The isoPEK repeat unit has also been prepared by Friedel−Crafts acylation using 3-phenoxybenzoic acid,[14] which allowed its application to graft copolymers of articulated polybenzobisthiazole for molecular composites.[15]

Authentic mixtures of the isoPEK cyclomers were also prepared by dilution of the polymerization conditions to 0.1 M. Cyclomers containing the highest fraction of the cyclic dimer were obtained with DMSO rather than NMP as solvent. Ring-opening polymerization of the cyclomers using CsF as the catalyst provided a soluble polymer containing residual cyclic dimer. This manuscript details the recently reported[16] advances in the synthesis, characterization, and ring-opening polymerization of isoPEK cyclomers. Although limited to a single composition possessing modest thermal properties, these results are useful in understanding some of the important factors in the synthesis and ring-opening polymerization of cyclomers.

Results and Discussion

Synthesis of IsoPEK Cyclomers. Cyclic Dimer. White sublimates were observed during the ring-opening polymerizations of cyclomer mixtures discussed in the Introduction. These sublimates were later shown to be cyclic dimer using ^1H nuclear magnetic resonance (NMR) spectroscopy. This indicated a convenient way to isolate the cyclic dimer from the crude mixtures for polymerization studies. Although DMSO is superior to NMP for cyclomer synthesis, the process required optimization to obtain the highest fraction of cyclic dimer. Dimethylacetamide gave poor results at 0.1 M, which is not surprising considering the degradation reactions of this solvent under S_NAr conditions.[9,12]

The fraction of cyclic dimer in the crude products from DMSO was maximized using pseudo-high dilution[17] (Table 1). Toluene was added to remove water as an azeotrope because hydrolysis of the *p*-fluorobenzoyl end groups gives bisphenol adducts that can only give chain extension rather than cyclization. The reactions were performed at as high a temperature as possible without leading to gross solvent degradation. The reaction times were chosen after considering that polymerizations under similar, more concentrated conditions required at least 4 h to reach completion as indicated by their increase in solution viscosity. Although the slow rate of reaction limits the effectiveness of the pseudo-high dilution technique, increasing the temperature and decreasing the concentration should at least favor unimolecular cyclization over bimolecular chain extension by increasing the reaction rate toward diffusion control.

Crude cyclomers were isolated by evaporating the solvents, dissolving the residues in toluene, and performing aqueous extractions. The emulsions that formed due to insoluble materials were broken by filtration through a filter aid, which accounts for the less than quantitative crude yields. According to ^1H NMR, the insoluble materials were mixtures of linear and cyclic oligomers. The drop in crude yield with total reaction time suggests equilibration to insoluble linear oligomers. The ^1H NMR spectra of the crude cyclomers showed a majority of cyclic dimer in all cases. The distributions were quantified using high-performance liquid chromatography (HPLC) as discussed below.

The cyclic dimer was isolated from the crude mixtures by vacuum sublimation. Good mass balances were only obtained with the mixtures containing the highest fractions of cyclic dimer because the residues became black tars during sublimation. Indeed, the ^1H NMR spectra of the tars showed residual cyclic dimer in several cases. The sublimates were recrystallized from tetrahydrofuran (THF) and ether to give analytically pure cyclic dimer. Figure 1 shows the X-ray crystal

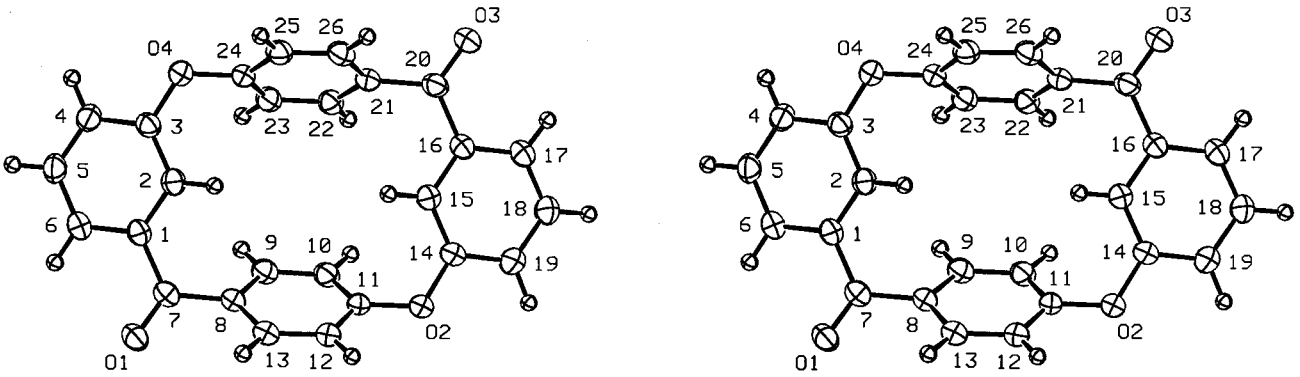


Figure 1. ORTEP stereodrawing of the X-ray crystal structure of isoPEK cyclic dimer. The thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level; those of the hydrogen atoms are artificial. Selected bond distances with estimated standard deviations of 0.002 Å: O1−C7, 1.225; O2−C11, 1.383; O2−O14, 1.387; O3−C20, 1.226; O4−C3, 1.384; O4−C24, 1.390 Å. Selected bond angles with estimated standard deviations of 0.01°: C11−O2−C14, 118.0; C3−O4−C24, 117.2; C1−C7−C8, 117.7; C16−C20−C21, 118.1°. Selected dihedral angles with estimated standard deviations of 0.01°: O1−C7−C8−C13, 43.77; O3−C20−C21−C26, 56.08°.

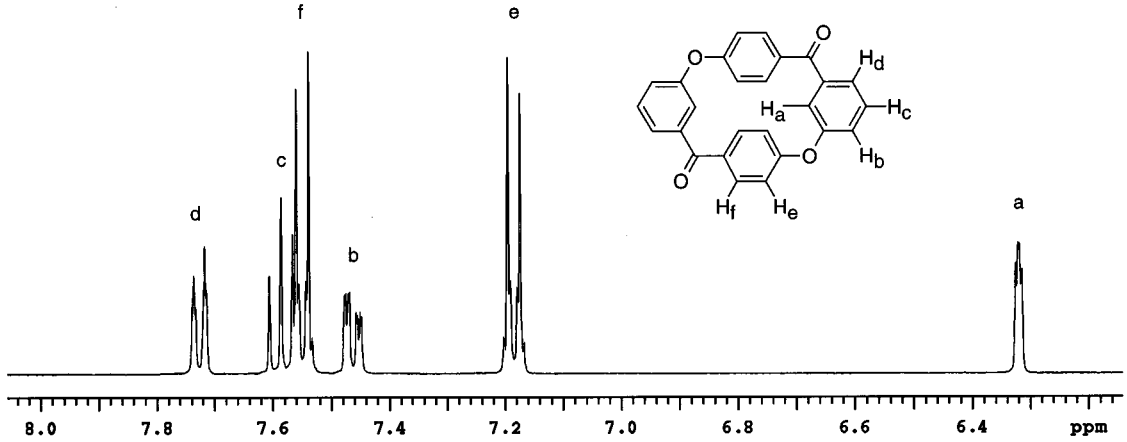


Figure 2. ^{1}H NMR spectrum of isoPEK cyclic dimer in TCE-d_2.

Table 2. Synthesis of IsoPEK Cyclomers from 4,3′-FHB in ODCB at 180 °C with K_2CO_3 and Catalytic 18-Crown-6

item	18-C-6 (mol %)	concn (M)	time (h)	yield (%)	η_{inh} (dL/g)	HPLC cyclomers: % (total %)	GPC M_n	GPC M_w	GPC M_z
1	5.0	0.1	28	86.5	0.19	dimer−nonamer: 4.4, 6.2, 7.3, 9.1, 3.9, 2.5, 22.0, 15.9 (71.3)	807	2740	12800
2	5.0	0.08[a]	28	31.4	0.23	linear dimer−nonamer: 1.1, 6.2, 40.2, 26.1, 14.1, 5.9, 3.2, 1.0 (97.8)			
3	5.0	0.1	33.5	97.9	0.20	dimer−decamer: 15.0, 20.1, 19.5, 13.7, 10.1, 8.3, 6.4, 3.5 1.6 (98.2)	547	1070	3170
4	5.0	0.08	29.5	94.9	0.14	dimer−decamer: 17.6, 21.7, 20.6, 13.5, 8.9, 5.9, 4.7, 3.0, 1.5 (97.4)	521	901	2300
5		0.08	90	85.7	0.18	linear dimer−decamer: 3.6, 22.3, 23.5, 16.8, 11.1, 2.3, 3.6, 1.4, (84.6)[b]			
6	10.0	0.08	21	94.9	0.13	dimer−decamer: 14.9, 20.4, 19.9, 13.6, 9.5, 6.6, 5.3, 5.0, 2.6 (97.8)			

[a] Chlorobenzene at 130 °C. [b] HPLC (25 h); linear dimer−decamer: 6.9, 39.9, 29.3, 13.1, 5.1, 2.0, 1.3, 0.3, 0.2 (98.1 %).

structure obtained for cyclic dimer. The dihedral angles between the carbonyls and the *p*-phenylene rings are 43.8 and 56.1°, while those between the planes of the *m*- and *p*-phenylene rings are 36.3 and 119.5°. The ^{1}H NMR spectrum (Figure 2) shows a distinctive upfield chemical shift for the hydrogens ortho to both the carbonyl and oxy groups, which is due to their residence in the shielding cones of the *p*-phenylene rings. Differential scanning calorimetry (DSC) and HPLC also testify to the purity of the cyclic dimer.

The benefit of pseudo-high dilution was partly realized in obtaining a high fraction of cyclic dimer with DMSO at 160 °C using an addition time of 8 versus 0 h (item 2 vs item 1). A lower fraction of cyclic dimer was obtained at a lower temperature with a longer addition time (item 3). This suggests either that cyclization is less competitive with chain extension at lower temperatures or that the cyclic and linear oligomers equilibrate by transetherification. In item 4, the addition time was reduced, but catalytic 18-crown-6 (18-C-6) was added to increase the solvation of the potassium cation, which should accelerate the rate of cyclization. The cyclic dimer fraction was higher relative to item 4, but it was still lower than that obtained at a higher temperature in item 2.

Cyclomer Mixtures. Since cyclomer mixtures are more practical than a purified cyclic dimer, a synthesis of the pure mixtures was developed as well (Table 2). Thermally stable aromatic solvents, such as chlorobenzene and *o*-dichlorobenzene (ODCB), were employed under dilute conditions (0.08−0.1 M) because they are capable of removing water from the reactions as azeotropes. 18-Crown-6 was used to catalyze the S_NAr reaction of the ionic intermediates in these low-polarity solvents. The reactions were monitored by their color changes, which were not masked by solvent degrada-

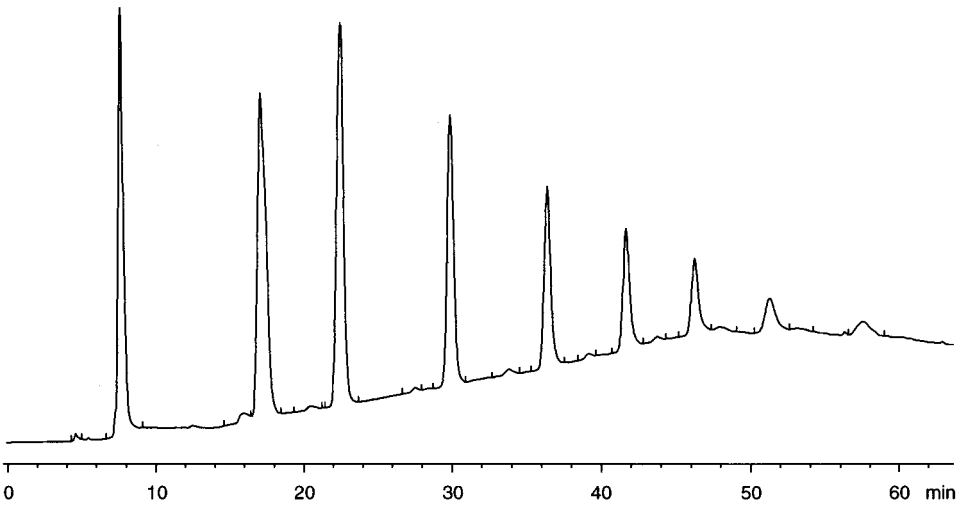


Figure 3. HPLC trace of an isoPEK cyclomer mixture (Table 2, item 4) using a Freon 113/THF solvent gradient modified with 0.05% aqueous ammonium hydroxide. The linear oligomers are resolved as the minor peaks.

tion. The solutions built to an intense orange-yellow as water evolved from the reaction of K_2CO_3 with 4,3′-FHB. Conversion of the linear oligomers to cyclomers was indicated by the complete discharge of color to an off-white mixture containing a suspension of precipitated potassium fluoride.

The main variable in Table 2 was the manner in which the azeotrope was removed from the reaction: inverse Dean−Stark trap, distillation, or reflux with a nitrogen sweep. With either solvent, the separation of water from the azeotrope in the inverse Dean−Stark trap was not rapid enough to prevent its return to the reaction. With ODCB (item 1), HPLC showed that the product contained linear oligomers, and cyclic octamer and nonamer constituted the largest fraction of the cyclomers. In addition, the high value for M_z from gel permeation chromatography (GPC) indicated that the sample contained polymer as well. With chlorobenzene and inverse Dean−Stark trap (item 2), the color never discharged and the product consisted solely of linear oligomers according to FAB MS. The low yield was due to the loss of soluble material during methanol extraction. This probably consisted of the linear dimer and trimer, which were present in much lower amounts than the higher oligomers.

Distillation of the azeotrope from the reaction mixture under a slow nitrogen sweep provided cyclomers containing a low level of residual linear oligomers (item 3). The ^{1}H NMR spectrum of these cyclomers was quite different from that of the linear oligomers (see Supporting Information). Reflux of the reaction mixture with a rapid nitrogen sweep successfully removed water from the azeotrope, as judged from its dissipation from the condensate in the reflux ring, and the resulting cyclomers also contained low levels of linear oligomers (item 4). The low values for M_z indicated the absence of polymer in both items 3 and 4.

The catalytic effect of 18-crown-6 was examined using the reflux method. The reaction was exceedingly slow without 18-crown-6 and the product consisted mainly of linear oligomers; HPLC analysis during the reaction also showed very little conversion to cyclomers. The reaction time was decreased slightly by doubling the 18-crown-6, but there was little change in the cyclomer distribution. The cyclomers that were synthesized in ODCB using 18-crown-6 as catalyst under conditions of distillation or reflux with nitrogen sweep were deemed suitable for ring-opening polymerizations. In comparison to mixtures prepared in NMP or DMSO without pseudo-high dilution, the distributions of these cyclomers were shifted to the higher members, which imparted slightly higher inherent viscosities (η_{inh}).

HPLC Analysis. HPLC was used to quantify the cyclomers and to determine their purity. The cyclomers were dissolved in *N*,*N*-dimethylformamide (DMF) and diluted with 80% THF to avoid degradation of the column packing. The cyclomers and linear oligomers analyzed in this manuscript were soluble under these conditions, but an authentic polymer gave precipitate upon dilution. The UV/visible diode array detector was set at 275 nm on the basis of the spectrum of a representative sample. The cyclomers were not retained by reverse-phase octadecyl columns using THF and precipitated in more polar mobile phases.

Normal-phase conditions were developed using a cyano-functionalized silica column with a 7-μm particle size and 300-Å pore size. Freon 113 gave high retention of the cyclomers, so THF was used to finish the chromatograph. Excellent resolution was obtained using a solvent gradient of Freon 113 to 80:20 Freon 113/THF, but some of the cyclomers eluted as doublets, typically the cyclic trimer and tetramer. No difference was found in the chromatographs of a representative sample using the detector at 275 nm or the full wavelength array.

Mobile-phase modifiers were examined for enhanced column performance. Acetic acid increased the number of peaks that eluted as doublets. Aqueous ammonium hydroxide at 0.05% collapsed the doublets and sharpened the resolution, but the column was slow to re-equilibrate to starting conditions. Ammonium hydroxide at 0.1% partly compensated for the slow re-equilibration, but gave uniform chromatograms with re-injection of the same sample. This indicated that the doublets could be integrated together. The linear oligomers (Table 2, item 2) confirmed that the doublets were not due to poor resolution versus the cyclomers because they eluted with different retention times. In addition, samples containing both cyclomers and linear oligomers were resolved sufficiently for their individual integration (Figure 3). Authentic samples of the cyclic dimer and cyclic tetramer confirmed the identity of their peaks as well. The retention times varied between analyses due to difficulties in duplicating the solvent gradient and the amount of the mobile-phase modifier.

Table 3. Ring-Opening Polymerization of IsoPEK Cyclic Dimer with Alkali-Metal Fluorides and Carbonates

						GPC (conversion)			
item	catalyst (equiv %)	18-C-6 (equiv %)	temp (°C)	time (h)	η_{inh} (dL/g)	M_n	M_w	M_w/M_n	(%)
1	CsF (2.0)		260	5	0.36	14 000	249 000	17.7	28
2	CsF (2.0)		275	2.5	1.18	34 200	161 000	4.69	39
3	CsF (5.0)		275	2	0.57	25 400	80 500	3.16	26
4	CsF (2.0)	2.0	275	3.5	0.59	29 700	73 600	2.48	26
5	CsF (5.0)	5.0	275	1.5	0.76	23 400	70 200	3.00	37
6	K_2CO_3 (2.0)		275	3	0.56	31 200	88 300	2.83	25
7	K_2CO_3 (3.2)		275	2.2	1.02	36 900	115 000	3.11	47
8	K_2CO_3 (2.0)	2.0	275	0.75	2.20	49 600	207 000	4.17	74
9	K_2CO_3 (2.0)	2.0	260	0.75	1.17	46 700	167 000	3.57	38
10	K_2CO_3 (3.2)	3.2	275	0.5	2.51	39 600	374 000	9.45	86
11	Cs_2CO_3 (3.2)		275	1.5	gel	21 000	2 080 000	98.7	97
12	Cs_2CO_3 (3.2)		275	0.75	0.78	31 200	81 500	2.62	36

Table 4. Ring-Opening Polymerization of IsoPEK Cyclic Dimer at 275 °C with Alkali Metal Phenolates

						GPC (conversion)			
item	initiator (equiv %)	18-C-6 (equiv %)	time (h)	η_{inh} (dL/g)	M_n calcd[a]	M_n (corrected)[b]	M_w (corrected)[b]	M_w/M_n	(%)
1	KOPhBz (2.0)		1	0.38	9800	4780 (20 000)	9590 (40 000)	2.01	72
2	KOPhBz (2.0)		1.5	0.35	9800	5230 (22 000)	12 600 (53 000)	2.40	84
3	KOPhBz (2.0)	2.0	1.5	0.46	9800	5660 (24 000)	15 000 (63 000)	2.64	98
4	KOPhBz (1.0)	1.0	2	0.82	19 600	9250 (39 000)	24 000 (100 000)	2.60	98
5	KOPhBz (0.5)	0.5	1.5	1.19	39 200	12 600 (53 000)	38 900 (160 000)	3.10	98
6	CsOPhBz (1.0)		4	0.92	19 600	9000 (38 000)	33 600 (140 000)	3.73	97
7	CsOPhBz (0.5)	0.5	2	1.29	39 200	12 900 (54 000)	43 800 (180 000)	3.39	98

[a] M_n = FW 196 ÷ equiv phenolate initiator. [b] M (corrected) = 4.2M (observed).

Ring-Opening Polymerization. Cyclic Dimer. The ring-opening polymerization was investigated using the sort of nucleophilic initiators that participate in transetherification by the S_NAr mechanism: alkali-metal fluorides, carbonates, and phenolates. The cyclic dimer was studied first due to its homogeneous composition and purity. The stoichiometries of the initiators were based on the isoPEK repeat unit (FW 196). The polymerization temperature was chosen to avoid the sublimation of the cyclic dimer, and polymer degradation was only apparent with long reaction times or the most aggressive initiators. 18-Crown-6 was used as a co-initiator with the alkali-metal salts to aid their dispersion in the melts and to increase their nucleophilicity.

The conversions of the cyclic dimer and the molecular weight distributions were measured using a GPC method that had been originally developed for PEEK,[18] but which was recalibrated at the low molecular weights using model compounds. The conversions were determined from the uncorrected integration of the full chromatograms, in which the residual cyclic dimer appeared as a narrow peak near its FW 392. The polymer molecular weights were obtained by excluding the cyclic dimer from the integrations. Polymers with high polydispersities (M_w/M_n) showed multimodal distributions, which normally indicate branching.

CsF was examined first (Table 3) because it is a superior initiator for poly(ether sulfone)s and poly(ether ketone)s.[6,8,9] The melts became quite viscous during polymerization, but upon cooling they often separated into glassy and opaque regions. Although the polymers possessed very high molecular weights, the conversions of the cyclic dimer never exceeded 40%. 18-Crown-6 had little effect on these polymerizations, and the amount of initiator did not correlate with the conversions or the molecular weights.

The alkali-metal carbonates behaved like CsF rather than alkali-metal phenolate salts (Table 3). The carbonates were expected to cleave the cyclic dimer to generate phenolate end groups capable of initiating ring-opening polymerization,[19] and some gas evolution was observed early in the polymerizations. Instead, K_2CO_3 gave low conversions to very high molecular weight polymers. The addition of 18-crown-6 led to higher conversions, but the polymers possessed multimodal distributions indicative of branching. Polymerization at a lower temperature of 260 °C with K_2CO_3/18-crown-6 gave no evidence of branching (item 9), but with a loss of conversion as well. Cesium carbonate was intermediate in reactivity, but gave a gelled polymer in item 11.

Alkali-metal phenolates initiate ring-opening polymerizations of arylene ether cyclomers, and potassium 4-benzoylphenolate (KOPhBz) is reported[6] to be quite effective. In our hands, the potassium and cesium salts (MOPhBz, M = K, Cs) were effective initiators for high conversions of the cyclic dimer to high-molecular-weight polymers (Table 4). There was little difference in reactivity between CsOPhBz and KOPhBz. 18-Crown-6 was not necessary to obtain high conversions, but it did reduce the reaction time. Tough polymers were only obtained using 0.5% phenolate initiator, which must allow the molecular weights to rise above chain entanglement threshold.

Figure 4 compares the GPC traces for representative polymers obtained from the cyclic dimer using CsF and CsOPhBz initiation to show the differences in their conversions. The observed molecular weights of Table 4 did not correlate with the stoichiometries of the initiators, as shown by comparison of the calculated and observed values for M_n. The GPC calibration was checked using two samples of cyclomer-free isoPEK synthesized in NMC solution. Table 5 shows the absolute M_w values and molecular parameters obtained from the Zimm plots (see Supporting Information) generated by laser light-scattering (LS) measurements.[20] The second viral coefficient, A_2, for item 1 indicates that 2-chlorophenol was a fair solvent for this sample. The Zimm plot for item 2 showed curvature at each concentration, which often suggests a broad mo-

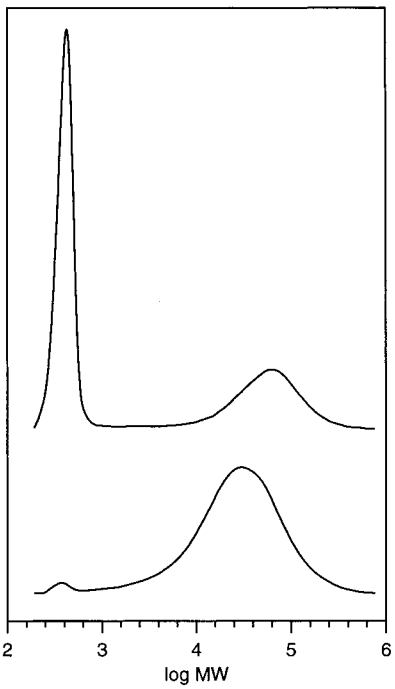


Figure 4. GPC traces of isoPEK polymers produced by ring-opening polymerization of the cyclic dimer using CsF (top; Table 3, item 5) and CsOPhBz (bottom; Table 4, item 7). The polymers contained, respectively, 63 and 2% residual cyclic dimer.

lecular weight distribution for the polymer. Indeed, the value of M_w/M_n was broader for item 2 than for item 1 and the slightly negative value of A_2 for item 2 indicated a poorer quality solution.

The values of $M_{w,LS}/M_{w,GPC}$ in Table 5 show that GPC underestimated the true isoPEK molecular weights. IsoPEK possesses greater conformational freedom than PEEK, which increases its solubility and reduces its hydrodynamic volume for a given molecular weight. Consequently, the average value of 4.2 for $M_{w,LS}/M_{w,GPC}$ from Table 5 was used as a multiplier to estimate the correct molecular weights from the GPC values. Since the GPC method was not re-calibrated, both the observed and corrected values are shown in the tables.

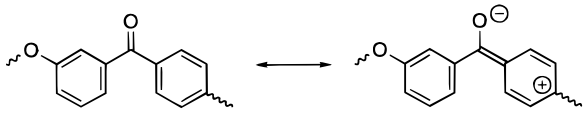
The corrected molecular weights indicate that the stoichiometries of the phenolate initiators controlled the polymerizations in an unexpected way. The corrected values of M_n were about twice the calculated values, so the phenolate initiators apparently "cap" both ends of the polymer chains. As shown in Scheme 3, the initial polymer **I** can equilibrate to the bis(4-oxybenzophenone) end-capped polymer **II** through transetherification because the 4-oxybenzophenone end groups are activated for *ipso* substitution by the 3-phenolate end groups. Judging from the polymerizations with intermediate conversions, this equilibrium is reached before complete conversion so that additional time is needed to equilibrate the polymer with the remaining cyclic dimer. At the lowest initiator level of 0.5%, the molecular weights start to fall off toward those for polymers containing a single 4-oxybenzophenone end group.

Cyclomer Mixtures. The ring-opening polymerizations of the cyclomer mixtures were initiated using CsF and the phenolate initiators with 18-crown-6 (Table 6). The cyclomers gave higher conversions with CsF than did those with cyclic dimer, but the molecular weights were lower. CsOPhBz was superior to KOPhBz in providing higher conversions to higher molecular weight polymers in less time. According to the calculated and corrected values of M_n, KOPhBz gives polymers containing a single 4-oxybenzophenone end group, while 0.5% CsOPhBz controlled the molecular weights in the intermediate manner observed with the cyclic dimer.

Residual cyclic dimer was seen by GPC in every item of Table 6 except for the first item using CsF. With only 51% conversion, the first item possessed a broad bimodal distribution with residual cyclomers displaying peak values near those for the cyclic dimer and cyclic trimer (FW 589). At low conversions, higher cyclomers should remain unreacted because the cyclic dimer is not the major fraction of the original mixtures. The rate of ring opening for the cyclic dimer must not be much less than those for the higher cyclomers because the polymerization times for the mixtures are not that different from those of the pure cyclic dimer.

The cyclomers gave polymers with lower η_{inh} than those from the cyclic dimer using 0.5% phenolate initiator. Judging from GPC, this was mainly due to narrower molecular weight distributions, although the M_n values were somewhat lower as well. The slightly lower molecular weights obtained with the cyclomers might be due to residual linear oligomers, since the latter would cap the polymer chains. It should be possible to obtain purer cyclomers by extracting the phenolate-terminated linear oligomers with aqueous base during workup. Indeed, these species could have been responsible for the emulsions that formed under these conditions.

Implications of the IsoPEK Repeat Unit. The cyclomer chemistry of 4,3′-FHB and the isoPEK repeat unit is unique compared to typical 4,4′-catenated systems due to the reactivity and conformational freedom provided by 3,4′-catenation. Their cyclomers are both readily synthesized and converted by ring-opening polymerization to high-molecular-weight polymers. In terms of their reactivity in S_NAr chemistry, the *m*-oxy and carbonyl groups cannot stabilize each other through electron resonance, but the para-substituted carbons are activated for *ipso* substitution through resonance with



the unstabilized carbonyl. Consequently, the nucleophilicity of the *m*-phenolate anion end groups and the electrophilicity of the *p*-fluorobenzoyl end groups are not compromised by electron resonance because the carbonyls are not capable of "bridging"[21] the 3,4′-substituents. This promotes the unimolecular cyclization of the linear oligomers versus their bimolecular chain extension for the same reasons discussed above.

The electron resonance arguments also apply to the reactivity of the cyclomers in ring-opening polymerization, except that the *p*-fluoro substituent is replaced by a *m*-oxy group of the isoPEK repeat unit. The electrophilicity of S_NAr-active compounds can be estimated using NMR as a probe of electron density.[22] Table 7 shows the relevant ^1H and ^{13}C NMR chemical shifts for the benzophenones used in this work. In ^1H NMR, the *o*-hydrogens are diagnostic due to their proximity to the carbonyl deshielding zone, while with ^{13}C NMR, it is the *p*-carbon that undergoes *ipso* substitution. The spectra were obtained in tetrachloroethane-d_2 (TCE-d_2)

Table 5. Comparison of Molecular Parameters from Laser Light-Scattering (LS) and GPC Measurements of Cyclomer-Free IsoPEK Polymers in 2-Chlorophenol

	LS			GPC			
item	$M_w \times 10^{-5}$ (g/mol)	R_g (nm)	$A_2 \times 10^4$ ((cm^3 mol)/g^2)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	$M_{w,LS}/M_{w,GPC}$
1	1.40(±0.08)	24.7	4.05	14 500	31 300	2.16	4.47
2	1.60(±0.10)	31.9	−2.56	9710	40 300	4.15	3.97

Table 6. Ring-Opening Polymerization of IsoPEK Cyclomer Mixtures at 275 °C

						GPC (conversion)			
item	initiator (equiv %)	18-C-6 (equiv %)	time (h)	η_{inh} (dL/g)	M_n calcd[a]	M_n corrected[b]	M_w corrected[b]	M_w/M_n	(%)
1	CsF (2.0)		2	0.48		19 000 (80 000)	52 200 (220 000)	2.75	51
2	KOPhBz (0.5)	0.5	2	0.65	39 200	9230 (39 000)	172 000 (720 000)	18.62	95
3	KOPhBz (0.7)	0.5	3.5	0.58	28 000	7670 (32 000)	15 200 (64 000)	1.98	94
4	CsOPhBz (0.5)	0.5	1.5	0.80	39 200	12 400 (52 000)	28 400 (120 000)	2.29	96
5	CsOPhBz (0.5)	0.5	2	0.69	39 200	11 200 (47 000)	27 900 (120 000)	2.50	97

[a] M_n = FW 196 ÷ equiv phenolate initiator. [b] M (corrected) = 4.2M (observed).

Table 7. NMR Chemical Shifts of Selected Nuclei from the *p*-Phenylene Rings of 3,4′-Disubstituted Benzophenones Involved in IsoPEK Cyclomer Chemistry

	ortho ^{1}H		*para* ^{13}C	
benzophenone	$CDCl_3$	TCE-d_2	$CDCl_3$	TCE-d_2
4,3′-FHB	7.85	7.84	165.5	165.3
isoPEK polymer	7.83	7.85	161.0	160.9
cyclic hexamer		7.82		161.0
cyclic tetramer		7.79		161.2
cyclic trimer		7.71		161.3
cyclic dimer	7.55	7.55	158.0	157.9

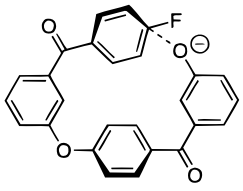
because the semi-pure cyclomer samples obtained by the fractionation of cyclomer mixtures had low solubility in $CDCl_3$. The assignments for the cyclic trimer and hexamer mixture were made by comparing their spectrum to those of cyclic dimer, cyclic tetramer, and cyclomer mixtures containing sufficient amounts of the cyclic trimer to distinguish its distinctive chemical shifts (see Supporting Information).

The ^{1}H chemical shift for isoPEK suggests that the electrophilicity of the *p*-phenylene ring is not seriously compromised by replacing the *p*-fluoro substituent with the isoPEK repeat unit, yet the ^{13}C chemical shift indicates that the *p*-carbon is less electrophilic. When considering the S_NAr mechanism, this suggests that the rate of formation for the Meisenheimer complex from the isoPEK repeat unit is retarded versus 4,3′-FHB. The chemical shifts for the cyclic dimer indicate that it is substantially less electrophilic than the isoPEK polymer or the higher cyclomers. Its structure (see Figure 1) certainly should reduce the electron resonance between the carbonyl and the *p*-phenylene rings. The *o*-hydrogens of the higher cyclomers move progressively to higher chemical shifts as they increase in ring size and approach the chemical shift of the isoPEK polymer. This suggests that equilibration of the molecular weight distributions by transetherification is competitive with ring-opening polymerization and that the cyclic dimer polymerizes slower than the higher cyclomers.

As an AB monomer, 4,3′-FHB imparts AB character to its linear oligomers during cyclomer synthesis, so that each is capable of cyclization. AA and BB monomer systems will generate a mixture of linear oligomers with AA−AA, AA−BB, and BB−BB end groups. The AA−BB oligomers are capable of cyclization, but the AA−AA and BB−BB oligomers must react with each other, or an appropriate monomer, before they can form cyclomers. Although AB monomers have been previously employed,[9] AA and BB monomer systems are more common in arylene ether cyclomers. IsoPEK cyclomers have a statistical disadvantage in ring-opening polymerization due to their 3,4′-catenation. Compared to simple 4,4′-catenated cyclomers, only one-half of the isoPEK ether bonds are activated for *ipso* substitution, although some more complicated systems also suffer from similar statistical disadvantages.

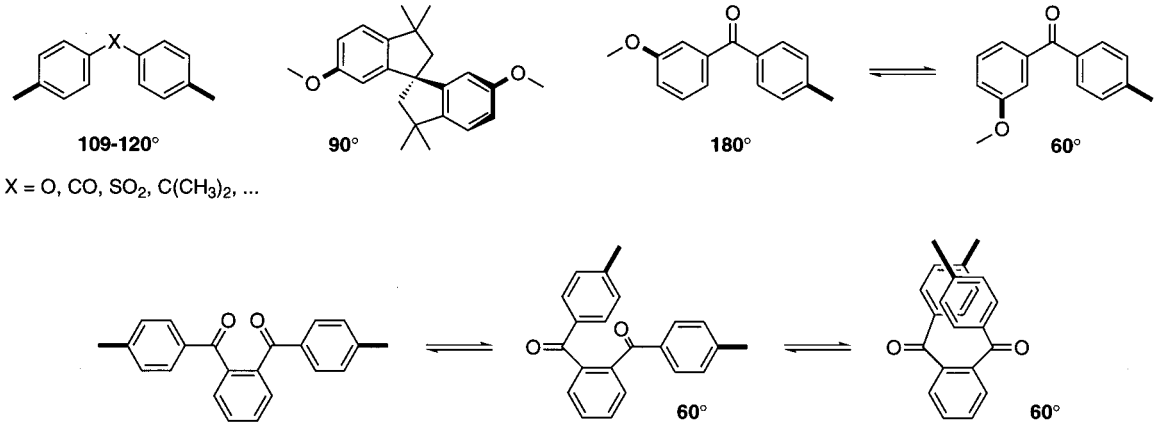
The 3,4′-catenation of the isoPEK repeat unit imparts sufficient molecular flexibility for efficient cyclization without precluding chain extension. Most arylene ether cyclomers are prepared from para-substituted monomers, such as bisphenol A and 4,4′-disubstituted benzophenones, diphenyl sulfones, xanthones, or dibenzofurans, with fixed catenation angles of about 109−120° (Scheme 1). The spirobisindane diol enhances cyclization by closing down the catenation angle to almost 90°. The rigidity of both systems leads to low yields of cyclomers with high melting points, and their ring-opening polymerizations were complicated by degradation. In contrast, the facile synthesis of cyclomers containing 1,2-dibenzoylbenzene arylene ethers, and their poor conversion to polymer, are probably due to the statistical effect of multiple conformations containing catenation angles of about 60°.

IsoPEK possesses two conformations with catenation angles near 60 and 180° (Scheme 1). The 60° conformation promotes the cyclization of the linear oligomers by increasing the collision frequency of the end groups. The cyclic dimer is especially favored because the linear dimer can perfectly situate the end groups for the formation of the intermediate Meisenheimer complex.

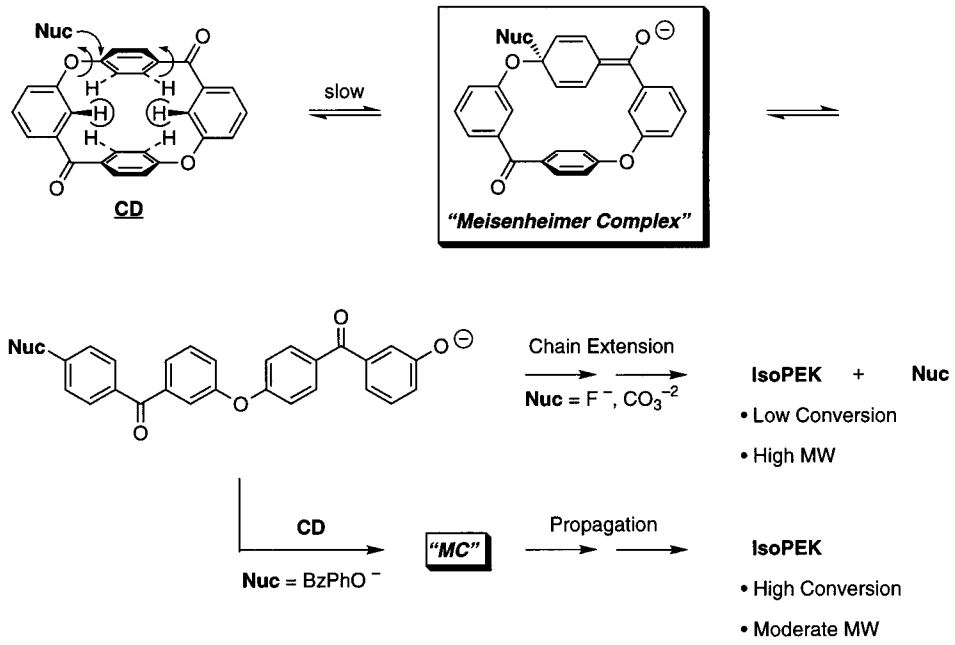


However, the 180° conformation is readily accessible, so that a high polymer can be formed by ring opening or chain extension. Indeed, the random-coiled polymer must be more thermodynamically stable than the higher cyclomers because only residual cyclic dimer is observed, except in one case of intermediate conversion. Moreover, the melting points of isoPEK cyclomers and polymer are lowered, so that degradation and side reactions are largely avoided during ring-opening polymerization. In general, catenation angles of less than

Scheme 1. Conformations and Catenation Angles of 4,4′-Disubstituted, Spirobisindane, and 1,2-Dibenzoylbenzene Arylene Ethers Compared to 3,4′-Catenated IsoPEK



Scheme 2. Mechanistic Differences in the Ring-Opening Polymerization of IsoPEK Cyclic Dimer Dependent on the Nucleophilic Initiator



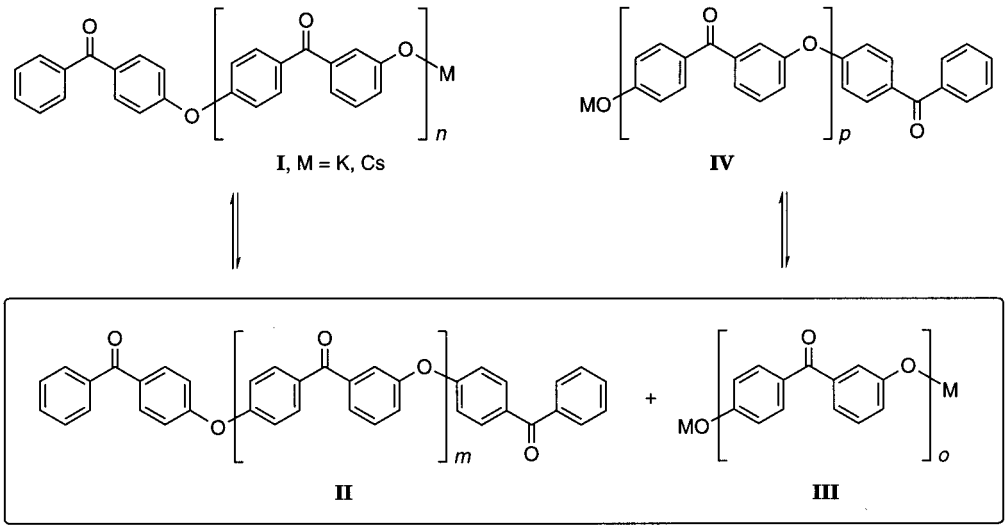
109° promote the cyclization of linear oligomers and shift the equilibrium away from chain extension unless conformations with catenation angles of greater than 120° are competitively populated.

Mechanism of the Ring-Opening Polymerization. The nucleophilic initiators can be divided into two classes based on their behavior in the ring-opening polymerizations of cyclic dimer. The structure of cyclic dimer (see Figure 1) forces its *p*-phenylene rings to rotate partially out of conjugation with the carbonyl. As shown in Scheme 2, the formation of the Meisenheimer complex from a cyclic dimer requires the *p*-phenylene ring to rotate into conjugation, where it will experience steric hindrance. This should retard the rate of *ipso* attack on the cyclic dimer versus the higher cyclomers, which agrees with the conclusions from the NMR study. Indeed, the cyclic dimer was the only unconverted species in all but one of the cyclomer polymerizations, although the amounts may reflect the equilibrium level.

CsF and the carbonates give low conversions of the cyclic dimer to very high molecular weight polymers because *ipso* substitution generates linear dimers that undergo chain extension instead of propagating the ring-opening polymerization (Scheme 2). Chain extension is preferred because the fluoride and carbonate anions are excellent leaving groups and the *ipso* substitution is reversible. The phenolates give almost quantitative conversions to moderate molecular weight polymers because the 4-oxybenzophenone end groups that they generate are inferior leaving groups. Consequently, the *m*-phenolate end groups can propagate the ring-opening polymerization without competition from chain extension (Scheme 2).

The corrected GPC data suggests that bis(4-oxybenzophenone) end-capped polymer **II** is generated unless using less than 1% phenolate initiator (Scheme 3). This implies that the phenolate end groups reside in undetected low-molecular-weight species **III**. Their fate remains open to speculation, but such ionic species may undergo phase separation from the polymer. At less than 1% phenolate initiator, M_n deviates from the expected values. This may indicate the partial formation of polymer **IV**, which should be more stable than **I** due to the electron resonance of the 4-phenolate end group. As seen in Table 4, the molecular weight distributions are closest to the most probable distribu-

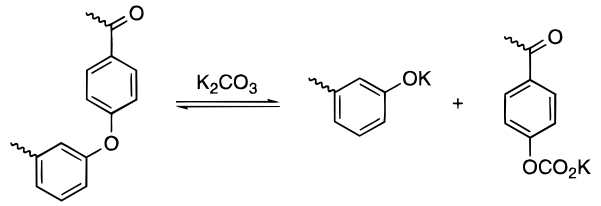
Scheme 3. Transetherification of IsoPEK Containing the 4-Oxybenzophenone End Group



tion ($M_w/M_n \approx 2$) at intermediate conversions of the cyclic dimer. As the cyclic dimer drops in concentration, transetherification of the polymer chains becomes competitive with ring-opening polymerization. At this point, further conversion of the cyclic dimer occurs at the expense of the molecular weight distribution.

The cyclomer mixtures are less susceptible than the cyclic dimer to broadening of the molecular weight distribution. This is probably due to the higher rates of ring-opening for the higher cyclomers, which minimize the end capping of the polymer until late in their conversion. In both cases, there is no indication that the molecular weights will equilibrate to the most probable distribution by transetherification. Indeed, broadened distributions are observed, even multimodal distributions on occasion, which are most likely the result of uncharacterized degradative side reactions. Phenolate initiators incapable of *ipso* substitution may alleviate the broadening by avoiding end capping of the polymer. However, the bis(4-oxybenzophenone) end-capped polymers are higher in molecular weight than the single end-capped polymers and should possess greater long-term thermal stability.

The chemistry of the carbonates was surprising because they were expected to behave like phenolate initiators by cleaving the cyclomer rings to generate phenolate end groups. K_2CO_3 induces transetherification in PEK linear oligomers and 18-crown-6 catalyzes the reaction, although no phenolate end groups were found in the final polymers due to the absence of decarboxylation.[19] Our results also indicate that *ipso* substitution by the carbonate anion is reversible and that the carbonate end groups do not undergo decarboxylation.



Experimental Section

General Procedures. 4-Fluoro-3′-hydroxybenzophenone (4,3′-FHB) was prepared according to the published procedure.[13] Powdered K_2CO_3 (325 mesh) was supplied by the Aldrich Chemical Co. The NMR spectra were obtained using deuterated solvents on a Varian Unity 400 spectrometer at 399.952 MHz for ^1H (tetramethylsilane reference), 100.57 MHz for ^{13}C (tetramethylsilane reference via solvent), and 376.289 MHz for ^{19}F ($CFCl_3$ reference). Routine ^{13}C NMR used acquisition-gated Waltz-16 ^1H 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} values were measured using 0.5 g/dL solutions in methanesulfonic acid at 30 °C. DSC and TGA were performed at 10 °C/min using a DuPont 2100 thermal analyzer. The DSC results are reported for the second scan unless noted otherwise.

Chromatography. GPC analyses were performed according to the method developed for PEEK[18] using a Waters 150C liquid chromatograph equipped with two Shodex columns from Showa Denko (AD-80 M/S) in series and a mobile phase of a 50:50 solution of phenol and 1,2,4-trichlorobenzene at 115 °C. The low-molecular-weight region of the chromatogram was calibrated using diphenyl ether and bis-1,4-(4-phenoxybenzoyl)benzene. HPLC analyses were performed on a Hewlett-Packard 1090M liquid chromatograph equipped with a J&W Scientific 4.6 × 250 mm cyano column with 7-μm particle size and 300-Å pore size (171−0641). The UV/visible diode array detector was set at 275 nm. A flow rate of 0.7−0.75 mL/min was used with HPLC-grade solvents modified with 0, 0.05, or 0.1% aqueous ammonium hydroxide. The mobile-phase program consisted of a solvent gradient of Freon 113 to 80:20 Freon 113/THF over 40 min followed by a 30-min hold.

Laser Light-Scattering Measurements of Absolute Molecular Weights. Cyclomer-free isoPEK samples were dissolved in 2-chlorophenol at 135 °C for 2 h at concentrations of 0.5−6 g/L, cooled to room temperature, and filtered through 0.45-μm PTFE membrane filters. The solutions were visibly stable several weeks after the measurements. A refractive index increment, d*n*/d*C*, of 0.117 cm^3/g was determined at room temperature using a C. N. Wood differential refractometer with a 488-nm blue filter. The light-scattering measurements were taken at 23 °C using a Brookhaven Instrument Model BI200SM goniometer with a Lexel 4-W argon ion laser operating at a wavelength of 488 nm and a power of 200 mW. The instrument was calibrated for absolute intensity measurements using benzene.

IsoPEK Cyclic Dimer. A 2-L three-neck RBF equipped with a mechanical stirrer, Dean−Stark trap with reflux condenser and gas inlet, and septum adapter was charged with 6.98 g of K_2CO_3 (50.5 mmol), 200 mL of toluene, and 700 mL

of DMSO. The contents were purged with nitrogen and heated to a reflux to give a pot temperature of 155−160 °C. A solution of 21.62 g of 4,3′-FHB (100.0 mmol) in 100 mL of DMSO was added over an 8-h period using a syringe pump. After addition, the reflux was continued for 4 h. The solvents were evaporated by vacuum distillation and the residue was dissolved in toluene. The solution was extracted with dilute hydrochloric acid and then dilute aqueous sodium carbonate. The emulsion that formed was broken by vacuum filtration through a filter aid. The organic phase was dried with magnesium sulfate and evaporated to give 15.43 g of a light-yellow solid. ^{1}H NMR showed a mixture of cyclomers containing a majority of cyclic dimer. The filter aid and the aqueous phase were extracted with dichloromethane, dried, and evaporated to give 2.82 g of an off-white solid. ^{1}H NMR showed a mixture of cyclomers and linear oligomers. The samples were combined for a 93.0% yield. The η_{inh} was 0.09 dL/g. HPLC: 8.7 (dimer, 81.9), 17.0 and 17.6 (trimer, 9.0), 22.5 (tetramer, 4.4), 29.7 (pentamer, 1.6), 36.2 min (hexamer, 1.1%).

The mixture (17.87 g) was sublimed at 240 °C and 0.25 Torr to give 12.23 g of the cyclic dimer, which was recrystallized from 75 mL hot THF by adding 125 mL of ether and cooling in an ice bath. The first crop was filtered and washed with cold ether. A second crop was obtained by evaporating the solvents and recrystallizing the residue from 10 mL of THF with 20 mL of ether as above. The white solids were combined and dried in a 100 °C vacuum oven to give 11.56 g. The yield of pure cyclic dimer was 60.2%. HPLC: 10.0 min (100%, UV λ_{max} 300, 256, 230 nm). DSC: mp 247.2 °C (99.80%). ^{1}H NMR ($CDCl_3$): δ 6.355 (dd, J = 2.8, 1.6 Hz, 2H), 7.168 (AA′XX′, J = 8.8, 2.4, 2.0 Hz, 4H), 7.422 (ddd, J = 8.0, 2.8, 1.0 Hz, 2H), 7.543 (dd, J = 8.0, 7.6 Hz, 2H), 7.550 (AA′XX′, J = 8.8, 2.4, 2.0 Hz, 4H); 7.720 (ddd, J = 7.6, 1.6, 1.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 118.4 (2CH), 121.1 (4CH), 122.0 (2CH), 122.2 (2CH), 130.6 (2CH), 131.1 (4CH), 135.3 (2C), 138.8 (2C), 157.4 (2C), 158.0 (2C), 195.7 (2C). ^{1}H NMR (TCE-d_2): δ 6.320 (dd, J = 2.4, 1.6 Hz, 2H), 7.185 (AA′XX′, J = 8.6, 2.4, 2.0 Hz, 4H), 7.463 (ddd, J = 8.2, 2.4, 0.8 Hz, 2H), 7.550 (AA′XX′, J = 8.6, 2.4, 2.0 Hz, 4H); 7.586 (dd, J = 8.2, 7.6 Hz, 2H), 7.727 (ddd, J = 7.6, 1.6, 0.8 Hz, 2H). ^{13}C NMR (TCE-d_2): δ 118.3 (2CH), 121.2 (4CH), 122.20 (2CH), 122.24 (2CH), 130.7 (2CH), 131.1 (4CH), 135.2 (2C), 138.7 (2C), 157.4 (2C), 157.9 (2C), 195.9 (2C). FAB MS m/z: 393.3, 785.2. Calcd (M + H for cyclic $(C_{13}H_8O_2)_n$): 393.1 (dimer), 785.2 (tetramer).

X-ray Crystal Structure of IsoPEK Cyclic Dimer. A sublimate of cyclic dimer was dissolved in THF at reflux to give a dilute solution, which was diluted further with ether and allowed to set for several days. The fine crystals that formed were collected by vacuum filtration, washed with ether, and dried in a 60 °C vacuum oven. A platelike crystal with approximations of 0.12 × 0.35 × 0.37 mm was mounted on a Rigaku RU300 diffractometer equipped with graphite-monochromatized MoKα radiation (λ = 0.71069 Å). With the crystal cooled to −118 °C, 30 frames of diffraction data were collected: oscillation range = 6°/frame, exposure = 8.0 min/frame, box sum integration, 2393 reflections measured, and 2.7 < 2θ < 48.4°. From the positions of the diffraction spots, the following triclinic unit cell parameters were refined: a = 9.291(1), b = 13.371(2), c = 8.813(1) Å, α = 95.04(1), β = 117.69(1), γ = 98.16(1)°. From an analysis of the intensity data, it was determined that there were 1977 unique reflections with $I > 3\sigma(I)$. The structure was solved by direct methods in space group *P1*. The refinement and analysis of the structure were carried out using a package of local programs.[23] In the full-matrix, least-squares refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weights, w, assigned as $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. All the non-hydrogen atoms were refined with anisotropic displacement parameters: hydrogen atoms were refined with isotropic displacement parameters. The refinement of 335 parameters (data/parameter ratio of 5.9) converged at R = 0.034 and R_w = 0.036. The largest peak in the final difference Fourier map had a magnitude of 0.12 e Å^{-3}.

IsoPEK Linear Oligomers. A 500-mL three-neck RBF equipped with a mechanical stirrer, gas inlet, and Dean−Stark trap with reflux condenser and gas outlet was charged with 4.32 g of 4,3′-FHB (20.0 mmol), 1.40 g of K_2CO_3 (10.1 mmol), 0.26 g of 18-crown-6 (1.0 mmol), and 250 mL of chlorobenzene. The contents were purged with nitrogen and heated to a reflux. The yellow mixture gave a cloudy distillate, which was drained (12 mL) after 5 h. Another 12 mL of cloudy distillate was drained from the trap the following day. After a total of 28 h, the yellow mixture was cooled to room temperature. The solution was extracted with dilute hydrochloric acid and three times with water, dried with K_2CO_3, and evaporated. The residue was extracted with methanol at reflux, filtered, and dried under vacuum to give 1.23 g of white solid. The η_{inh} was 0.23 dL/g. The ^{1}H NMR (TCE-d_2) spectrum displayed a complex mixture different from that of cyclomer mixtures (see Supporting Information). FAB MS m/z: 413.3, 515.3, 609.3, 805.4, 1001.5, 1197.3, 1393.4, 1590.4, 1785.5. Calcd (M + H for linear $H(C_{13}H_8O_2)_nF$): 413.1 (dimer), 515.1 (trimer − C_6H_5-OH), 609.2 (trimer), 805.2 (tetramer), 1001.3 (pentamer), 1197.3 (hexamer), 1393.4 (heptamer), 1589.5 (octamer), 1785.5 (nonamer). HPLC: 14.4 (1.1), 20.4 (6.2), 26.4 (40.2), 32.3 (26.1), 37.6 (14.1), 42.5 (5.9), 46.8 (3.2), 52.1 min (1.0%).

IsoPEK Cyclomers. A 500-mL three-neck RBF equipped with a gas inlet, mechanical stirrer, and simple distillation apparatus was charged with 4.32 g of 4,3′-FHB (20.0 mmol), 1.45 g of K_2CO_3 (10.5 mmol), 0.26 g of 18-crown-6 (1.0 mmol), and 250 mL of ODCB. The contents were purged with nitrogen and heated to a reflux. The ODCB/water azeotrope (50 mL) was distilled from the mixture over a 2-h period. The reaction was maintained at reflux under a slow nitrogen purge. The yellow solution faded in color over 30 h. The off-white mixture was cooled to room temperature after a total of 33.5 h. The mixture was extracted with dilute hydrochloric acid and three times with water to remove the residual color. The solution was dried and evaporated by vacuum distillation. The solids were extracted with cyclohexane at reflux for 3 h to remove residual ODCB, filtered, and dried under vacuum. The white solids weighed 3.84 g for a 97.9% yield. The η_{inh} was 0.20 dL/g. ^{1}H NMR (TCE-d_2) displayed the complex spectrum of a cyclomer mixture (see Supporting Information). FAB MS m/z: 393.2, 589.3, 785.5, 981.5, 1177.5, 1373.1. Calcd (M + H for cyclic $(C_{13}H_8O_2)_n$): 393.1 (dimer), 589.2 (trimer), 785.2 (tetramer), 981.3 (pentamer), 1177.3 (hexamer), 1373.4 (heptamer). HPLC: 8.7 (15.0), 17.1 and 18.1 (20.1), 22.3 and 23.1 (19.5), 29.6 (13.7), 35.8 (10.1), 41.0 (8.3), 45.6 (6.4), 50.4 (3.5), 56.5 min (1.6%).

Potassium and Cesium 4-Benzoylphenolate. Equimolar amounts of the alkali-metal hydroxides and 4-hydroxybenzophenone were dissolved in hot deionized water to give yellow-green solutions. The solutions were cooled to recrystallize excess 4-hydroxybenzophenone, filtered through a filter aid, and evaporated, and the residues were dried under high vacuum to give yellow solids. The potassium salt (KOPhBz) was pulverized in a mortar and pestle to give a fine yellow powder, washed with ether and cyclohexane, and dried at 130 °C in a vacuum oven under nitrogen purge: mp 262−263 °C (dec). The hygroscopic cesium salt (CsOPhBz) was extracted with ether at reflux, which dispersed it into a fine yellow powder, washed with ether and cyclohexane, and dried at 200 °C in a vacuum oven under nitrogen purge: mp 219−220 °C.

General Polymerization Procedure. The ring-opening polymerizations were performed in glass reactors consisting of a microtube equipped with a three-neck adapter, one-piece helical-blade mechanical stirrer, gas inlet, and gas outlet. The reactants were charged to the microtube, purged with nitrogen, and heated to 275 °C after immersing in a metal alloy bath at 200 °C. A slow stirring rate was used to mix the contents and monitor the melt viscosity. The reaction time was determined by doubling the time it took for the polymer melt to begin climbing the stirrer blade. The polymers were isolated for analysis by shattering the reactors.

Ring-Opening Polymerizations of Cyclic Dimer with KOPhBz. A mixture of 980 mg of the cyclic dimer (2.5 mmol), 12 mg of KOPhBz (0.05 mmol), and 13 mg of 18-crown-6 (0.05 mmol) gave a red-brown melt at 275 °C. After 1 h, the polymer was climbing the stirrer blade. After an additional 1 h, it was cooled to room temperature. The dark-brown polymer had an

η_{inh} of 0.82 dL/g. ^{1}H NMR ($CDCl_3$): δ 7.06 (4H, d, J = 8.8 Hz); 7.29 (2H, d, J = 7.6 Hz), 7.49 (2H, dd, J = 7.6, 7.6 Hz), 7.51 (2H, s), 7.57 (2H, d, J = 7.6 Hz), 7.83 (4H, d, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$): δ 117.4 (4CH), 120.8 (2CH), 123.5 (2CH), 125.8 (2CH), 129.9 (2CH), 131.8 (2C), 132.4 (4CH), 139.8 (2C), 155.5 (2C), 161.0 (2C), 193.9 (2C). ^{13}C NMR (TCE-d_2): δ 117.6 (2C), 120.5 (C), 123.2 (C), 125.5 (C), 129.8 (C), 132.2 (3C), 140.0 (C), 155.8 (C), 160.9 (C), 193.6 (C).

Fractionation of IsoPEK Cyclic Tetramer. Insoluble material was observed when a crude cyclomer mixture was dissolved in ethyl acetate. The white solids were filtered off, washed with ethyl acetate, and dried to give 0.20 g. HPLC: 10.5 (2.7% dimer), 24.1 (93.7% tetramer, UV λ_{max} 279, 229 nm), 31.5, 37.9, 43.0, 47.7 min (2.9% pentamer−octamer). FAB MS m/z: 393.3, 785.4. Calcd (M + H for cyclic $(C_{13}H_8O_2)_n$): 393.1 (dimer), 785.2 (tetramer). ^{1}H NMR (TCE-d_2): δ 7.019 (8H, d, J = 8.4 Hz), 7.298 (4H, s), 7.365 (4H, d, J = 8.0 Hz), 7.565 (4H, dd, J = 8.0, 7.6 Hz), 7.662 (4H, d, J = 7.6 Hz), 7.789 (8H, d, J = 8.4 Hz). ^{13}C NMR (TCE-d_2): δ 117.3 (8C), 120.4 (4C), 123.6 (4C), 125.1 (4C), 130.2 (4C), 131.9 (4C), 132.1 (8C), 139.7 (4C), 155.1 (4C), 160.9 (4C), 193.7 (4C). ^{13}C NMR (TCE-d_2): δ 117.3 (8C), 120.4 (4C), 123.6 (4C), 125.1 (4C), 130.2 (4C), 131.9 (4C), 132.1 (8C), 139.7 (4C), 155.1 (4C), 160.9 (4C), 193.7 (4C).

Fractionation of IsoPEK Cyclic Trimer and Hexamer. Insoluble material was observed when a crude cyclomer mixture was dissolved in ethyl acetate. The white solids were filtered off, washed with ethyl acetate, and dried to give 0.36 g. FAB MS m/z: 589.1, 1177.2. Calcd (M + H for cyclic $(C_{13}H_8O_2)_n$): 589.2 (trimer), 1177.3 (hexamer). ^{1}H NMR (TCE-d_2): cyclic trimer δ 6.991 (6H, d, J = 8.8 Hz), 7.112 (3H, s), 7.456 (3H, d, J = 8.0 Hz), 7.625 (3H, dd, J = 8.0, 8.0 Hz), 7.713 (6H, d, J = 8.8 Hz), 7.741 (3H, d, J = 8.0 Hz); cyclic hexamer δ 7.064 (12H, d, J = 8.8 Hz), 7.337 (6H, d, J = 8.0 Hz), 7.442 (6H, s), 7.527 (6H, dd, J = 8.0, 7.6 Hz), 7.593 (6H, d, J = 7.6 Hz), 7.817 (12H, d, J = 8.8 Hz). ^{13}C NMR (TCE-d_2): δ 117.3 (integral = 2), 117.6 (2), 120.4 (2), 123.4 (1), 124.3 (1), 125.0 (1), 125.4 (1), 130.0 (1), 130.8 (1), 131.9 (1), 132.1 (4), 132.2 (1), 139.9 (2), 154.9 (1), 155.6 (1), 161.0 (1), 161.3 (1), 193.6 (1), 194.0 (1).

4-Fluoro-3′-Hydroxybenzophenone. ^{13}C NMR (TCE-d_2): δ 115.1 (2CH, d, J_{CF} = 21.3 Hz), 116.6 (CH), 120.1 (CH), 121.9 (CH), 129.4 (CH), 132.4 (2CH, d, J_{CF} = 9.2 Hz), 133.5 (C), 138.6 (C), 156.1 (C), 165.3 (C, d, J_{CF} = 254.8 Hz), 195.9 (C).

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Supporting Information Available: X-ray crystal structure analysis of cyclic dimer with atomic coordinates, anisotropic thermal parameters for the non-hydrogen atoms, bond distances and angles, intramolecular and intermolecular nonbonding distances, and symmetry operations (5 pages). Zimm plots from the laser light-scattering measurements of cyclomer-free isoPEK samples (2 pages). ^{1}H NMR spectra of cyclic and linear oligomers (4 pages). Ordering information is given on any current masthead page.

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