An Aromatic Polyether in Which Sequence-Randomization Leads to Induction of Crystallinity: X-ray Structure of the Crystalline Phase [$-OArCOArArCOAr-]_n$ (Ar = 1,4-Phenylene)

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Received June 22, 1992; Revised Manuscript Received September 28, 1992

ABSTRACT: High-temperature (330 °C) polycondensation of 4,4′-dihydroxydiphenyl sulfone with 4,4′-bis(4-fluorobenzoyl)biphenyl, using diphenyl sulphone as solvent and sodium carbonate as base, leads to formation of an amorphous polymer (A) in which the monomer-derived subunits [$-OArSO_2Ar-$] ("S") and [OArCOArArCOAr–] ("K") essentially alternate along the polymer chain. In contrast, the polymer (B) formed on replacing part (ca. 10%) of the sodium carbonate by potassium carbonate is partially crystalline, and sequence analysis by ^{13}C NMR indicates that the distribution of S and K units within a chain is now almost entirely random. The crystalline phase of polymer B is identified as [$-OArCOArArCOAr-]_n$, and a structure is proposed for this phase on the basis of X-ray fiber studies, single-crystal X-ray oligomer data, and molecular-modeling/diffraction-simulation techniques.

Introduction

High-performance composite materials have traditionally been based on thermosetting matrix polymers such as the epoxies and bis(maleimides), but in recent years the potential advantages of thermoplastic polymers in this application (increased speed of fabrication and greater toughness) have begun to be realized, notably with the introduction of ICI's PEEK-based carbon-fiber composite APC-2.[1]

During a program to develop higher-performance thermoplastic matrix polymers (in particular we sought an enhancement of glass-transition temperature without loss of crystallinity or processability)[2] we discovered a new type of aromatic polyether,[3] formed by condensation of 4,4′-dihydroxydiphenyl sulfone with 4,4′-bis(4-fluorobenzoyl)biphenyl. The crystallizability of this polymer varied dramatically with changes in polymerization conditions, and we now report that this variability originates in the sequence distribution of [$-OArSO_2Ar-$] ("S") and [–OArCOArArCOAr–] ("K") units within the polymer chain. Somewhat remarkably, maximum crystallinity is achieved when a statistically random sequence of S and K units is present.

Experimental Section

Instrumentation and Analysis. NMR spectra were obtained at 67.8 MHz (for ^{13}C) using a JEOL FX-270 spectrometer. Polymer samples were dissolved in 98% sulfuric acid at about 10% concentration (w/w), and spectra were run with the solutions at 30 °C. The central resonance of external DMSO-d_6 (δ 39.6 ppm) was used as reference. Broad-band proton decoupling was carried out with the irradiating frequency at the center of the proton resonances, and standard spectrometer settings were as follows: pulse width 90° (tip angle); acquisition time 0.5 s; spectral width 16 kHz; spectral delay 0.1 s; line broadening 2.5 Hz; scans accumulated 50 000–100 000; points Fourier transformed 16K.

Differential scanning calorimetry was carried out under nitrogen on a Perkin-Elmer DSC-1B instrument, at a scan rate of 20 °C min^{-1}.

X-ray fiber patterns were obtained with a flat-plate camera using synchrotron radiation (λ = 1.54 Å) at the SERC Daresbury Laboratory.

Single-crystal X-ray data were collected on a Nicolet R3m diffractometer (copper Kα radiation, λ = 1.541 78 Å) using ω-scans. Computations relating to the single-crystal structure were carried out on an Eclipse S140 computer using the SHELXTL program system.[4]

Monomer and Oligomer Synthesis. 4,4′-Bis(4-fluorobenzoyl)biphenyl was prepared in high purity (>99.8% by DSC) by a new route involving nickel-catalyzed coupling[5] of 4-chloro-4′-fluorobenzophenone. The catalyst solution was prepared by stirring a mixture of zinc dust (15 g, 230 mg atom), triphenylphosphine (10.5 g, 40 mmol), tetra-*n*-butylammonium iodide (3.7 g, 10 mmol), and tetrakis(pyridine)nickel(II) chloride (4.5 g, 10 mmol), in dry acetone (150 cm^3) at reflux under nitrogen for 20 min. To the resulting dark red solution was added, dropwise with stirring under nitrogen over 4 h, a solution of 4-chloro-4′-fluorobenzophenone (77.4 g, 330 mmol) in an anhydrous mixture of acetone (300 cm^3) and pyridine (67 cm^3). After refluxing for a further 1 h, the mixture was cooled and the crystallized product was filtered off and washed with acetone until the washings were colorless. Recrystallization from 1,2-dichlorobenzene afforded 53 g (80% yield) of 4,4′-bis(4-fluorobenzoyl)biphenyl, mp 269–270 °C (lit.[6] 263–265 °C).

The six-ring oligomer ArOArCOArArCOArOAr (Ar = phenyl or 1,4-phenylene) was prepared by room-temperature condensation of excess diphenyl ether (1.0 g, 5.9 mmol) with biphenyl-4,4′-dicarboxylic acid (0.48 g, 2.0 mmol) in trifluoromethanesulfonic acid (20 cm^3). After 16 h the orange solution was poured into water, and the resulting suspension was stirred for 1 h. The precipitate was filtered off, washed with water until the washings were acid-free, dried, and recrystallized from dimethylformamide. Slow cooling afforded X-ray-quality single crystals of the desired oligomer (0.88 g, 81% yield), mp 276–278 °C.

Polymerization Studies. Polymerizations were carried out on a 25-mmol scale under nitrogen at around 20 wt % concentration of polymer in diphenyl sulfone (Scheme I). The two monomers and solvent were melted together and stirred at 220 °C before addition of (A) sodium carbonate (102% of theoretical) or (B) a mixture of sodium carbonate (90%) and potassium carbonate (12%). A 2% molar excess of the difluoro monomer

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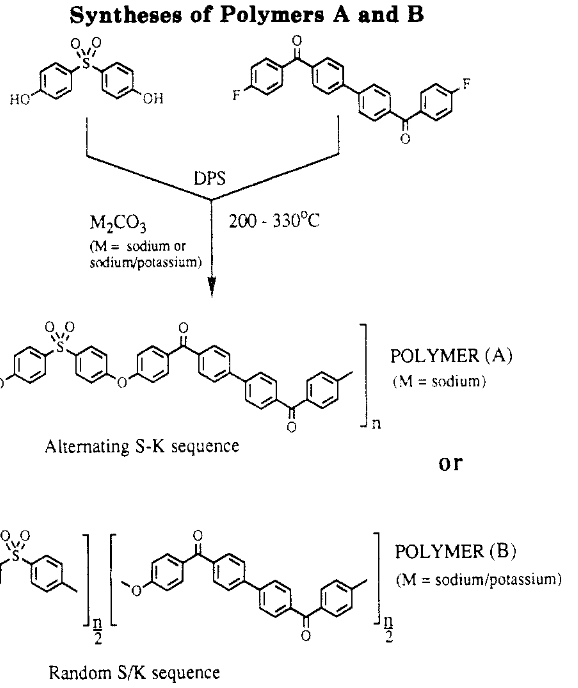
Scheme I
Syntheses of Polymers A and B



was used to control molecular weight. After stirring for 1 h, the reaction temperature was raised to 330 °C over 90 min and held at that temperature for 3 h. On cooling to room temperature, the polymer was isolated by milling the solid reaction mixture and extracting the resulting powder successively with acetone and water to remove diphenyl sulfone and inorganic salts, respectively. A final extraction with methanol at reflux reduced the residual diphenyl sulfone level to below 100 ppm.

Single-Crystal X-ray Structure Determination. Crystal data: $C_{38}H_{26}O_4$, M = 546.6, monoclinic, $P2_1/a$, a = 6.101 (1) Å, b = 7.536 (1) Å, c = 29.389 (5) Å, β = 92.33 (1)°, U = 1350 Å^3, Z = 2 (the molecule is disposed about a center of symmetry), D_c = 1.34 g cm^{-3}, μ(Cu Kα) = 7 cm^{-1}, $F(000)$ = 572.

The structure was solved by direct methods using 1320 independent observed reflections $[|F_o| > 3\sigma(|F_o|)]$. The data were corrected for Lorentz and polarization factors. No absorption correction was applied. Non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealized (C–H = 0.96 Å) and allowed to ride on their parent carbon atoms. Refinement by block-cascade least squares gave an R factor of 0.037, R_w = 0.040 $[w^{-1} = \sigma^2(F) + 0.00038F^2]$. Atomic coordinates, bond lengths and angles, and significant torsional angles are given in Tables II–IV.

Results and Discussion

Polymer A, produced using only sodium carbonate as base, had a reduced viscosity (RV) in 98% sulfuric acid of 0.74 and proved completely amorphous by differential scanning calorimetry (DSC), showing only a glass transition (onset) at 207 °C. In contrast, polymer B, for which a fraction of the base used in the polymerization was present as potassium carbonate, had a significantly higher molecular weight (RV 1.18) and was partially crystalline by DSC. The glass transition at 210 °C was close to that of polymer A, but a broad crystal-melting process was now also observed at about 350 °C (peak temperature), with a heat of fusion ΔH_f of 15 J g^{-1}. Although polymer B crystallized only slowly from the melt, the original level of crystallinity present in the "as made" polymer could be recovered by annealing for several hours at 250–300 °C.

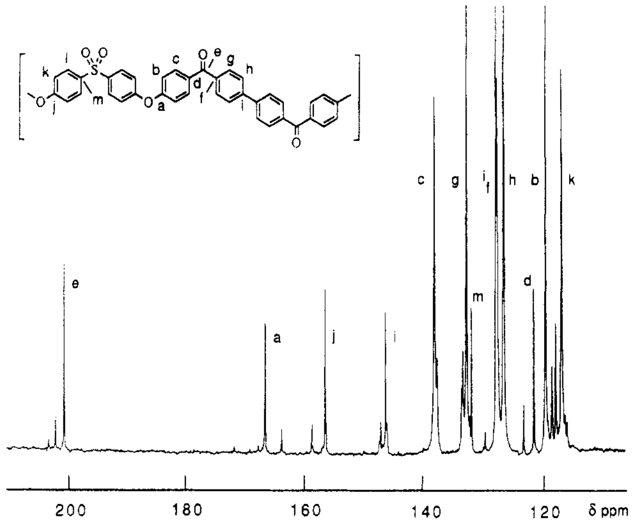


Figure 1. ^{13}C NMR spectrum of polymer A in 98% H_2SO_4.

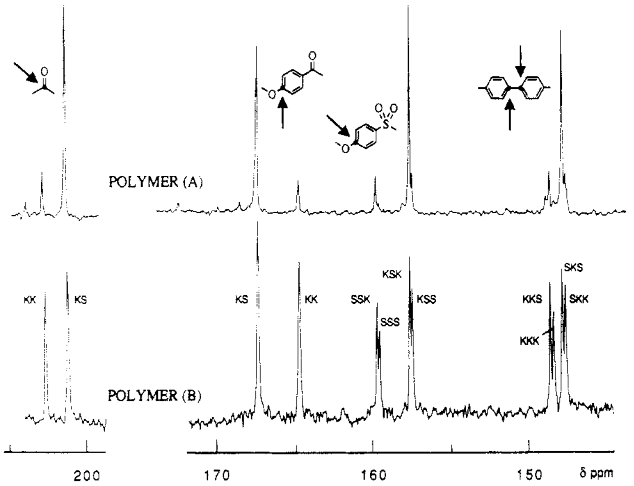


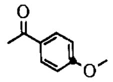
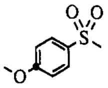
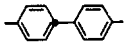
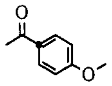
Figure 2. ^{13}C NMR resonances of polymers A and B in the carbonyl and quaternary regions.

Figure 1 shows the ^{13}C NMR spectrum of polymer A, run at 67.8 MHz in 98% sulfuric acid solution (the polymer dissolves without reaction). This spectrum is relatively simple and indicates that the amorphous polymer (A) has a predominantly (though not entirely) alternating structure with the repeat unit [–OArSO$_2$Ar–OArCOArArCOAr–], where Ar = 1,4-phenylene. The assignments of resonances shown in Figure 1 were derived by reference to spectra of known poly(ether sulfones) and model compounds and to empirically calculated chemical shifts.[7]

Previous sequencing studies of aromatic ether sulfone copolymers have shown that chemical shift values can be influenced by substituents as far away as four aromatic rings along the chain.[8] In this type of polymer, resonances from quaternary carbons are known to be very sensitive probes of the monomer sequence distribution, and Figure 2 shows an expansion of the quaternary and carbonyl resonances of polymers A and B. The spectrum of the crystallizable polymer (B) differs considerably from that of the amorphous polymer (A), and the relative intensities of the peaks clearly indicate that the spectrum of B can be assigned on the basis that it is an essentially random copolymer of [–OArSO$_2$Ar–] (S) and [–OArCOArArCOAr–] (K) subunits. Most obviously, Figure 2 shows that polymer B contains approximately *equal* populations of carbonyl groups associated with KS and KK sequences. Full assignments of the carbonyl and ipso carbon resonances are given in Table I.

This transformation from an alternating, $[\text{–S–K–}]_n$ structure (A) to a random $[\text{–S–}]_x[\text{–K–}]_x$ structure (B) must depend on reversible cleavage of the ether linkages in A. Such linkages, being activated by electron-withdrawing groups on both adjacent aromatic rings, are of a type known to be susceptible to transetherification as a result of

Table I
Carbon-13 Chemical Shifts and Sequence Assignments for ipso Carbons in Polymer B

carbon type	chemical shift,[a] ppm	sequence[b]
	202.63	KK
	201.14	KS
	167.56	KS
	164.82	KK
	159.76	SSK
	159.59	SSS
	157.63	KSK
	157.45	KSS
	148.38	KKS
	148.18	KKK
	147.87	SKS
	147.61	SKK
	124.57	KK
	122.90	KS

[a] Referenced to external DMSO-d_6 at 39.6 ppm. [b] For triplet sequences the assigned carbon is in the left-hand ring of the central subunit.

Table II
Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for the Oligomer, with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq}[a]
C(1)	2272 (4)	9067 (3)	1249 (1)	54 (1)
C(2)	1411 (4)	9063 (4)	809 (1)	63 (1)
C(3)	2455 (4)	9952 (4)	470 (1)	65 (1)
C(4)	4355 (4)	10870 (4)	573 (1)	61 (1)
C(5)	5266 (4)	10904 (3)	1013 (1)	52 (1)
C(6)	4181 (3)	9994 (3)	1348 (1)	46 (1)
O(7)	5264 (2)	9967 (2)	1772 (1)	58 (1)
C(8)	4129 (3)	9971 (3)	2172 (1)	42 (1)
C(9)	2119 (3)	10793 (3)	2212 (1)	47 (1)
C(10)	1179 (3)	10812 (3)	2632 (1)	43 (1)
C(11)	2245 (3)	10053 (3)	3011 (1)	36 (1)
C(12)	4285 (3)	9262 (3)	2962 (1)	41 (1)
C(13)	5204 (3)	9206 (3)	2541 (1)	43 (1)
C(14)	1095 (3)	10030 (3)	3449 (1)	41 (1)
O(14)	−911 (2)	10064 (3)	3442 (1)	63 (1)
C(15)	2340 (3)	9962 (3)	3895 (1)	36 (1)
C(16)	1356 (3)	9209 (3)	4267 (1)	41 (1)
C(17)	2391 (3)	9213 (3)	4691 (1)	40 (1)
C(18)	4447 (3)	9995 (3)	4770 (1)	33 (1)
C(19)	5411 (3)	10760 (3)	4396 (1)	39 (1)
C(20)	4399 (3)	10732 (3)	3965 (1)	39 (1)

[a] Equivalent isotropic U defined as one-third of the orthogonalized U_{ij} tensor.

nucleophilic cleavage by the fluoride ion.[9] We suggest that the relatively low solubility of sodium fluoride in dipolar aprotic solvents (presumed to include diphenyl sulfone) inhibits fluoride-catalyzed transetherification, leading to the more or less alternating structure A. When potassium fluoride is present, however, as will be the case in polymerization B, its greater solubility and reduced degree of ion pairing permits extensive fluoride-catalyzed transetherification to occur so that, after 3 h at 330 °C, an essentially random structure is produced.

The structure of the crystalline phase of polymer B was investigated using a combination of wide-angle X-ray fiber diffraction, molecular modeling, diffraction simulation, and single-crystal X-ray oligomer studies. A melt-quenched, amorphous film of polymer B was uniaxially drawn (draw ratio 3:1) at 190 °C and then annealed at constant length for 10 h at 300 °C. The oriented material gave a fiber-type X-ray diffraction pattern, although significant arcing of the reflections does suggest a degree of crystallite disorientation about the draw direction.

The fiber pattern shows distinct similarities to the patterns given by ether ketone homopolymers such as PEEK and PEK[10] and can be indexed in terms of an orthorhombic unit cell with lattice parameters $a = 7.64$ Å and $b = 6.09$ Å. Despite the orthorhombic cell, several [00l] reflections appear on the meridian. These also appear to result from incomplete crystallite orientation and indicate layer lines consistent with a chain axis repeat which is a multiple of about 19 Å. This repeat distance is approximately the length calculated for the subunit K, and a single-crystal X-ray study of the six-ring oligomer [ArOArCOArArCOArOAr] (Ar = phenyl or 1,4-phenylene) confirmed that the "monomer repeat" distance [−OArCOArArCOAr−] is indeed 18.99 Å (Figure 3). Further diffraction and modeling studies (see below) suggest that the observed [00l]'s are in fact even-order reflections of a polymer unit cell which is twice this length; i.e. the polymer c-axis is approximately 38 Å.

The oligomer unit cell is monoclinic, with lattice parameters $a = 6.10$ Å, $b = 7.54$ Å, $c = 29.39$ Å, and $\beta = 92.3°$. The a and b dimensions compare very closely with those found for the polymer at 6.09 and 7.64 Å (transposition of the a and b axes is not significant in this context). The oligomer cell dimensions, together with the relatively small deviation of β from 90° and the 18.99 Å [−OArCOArArCOAr−] repeat distance (Figure 3), all indicate that the oligomer crystal structure provides a sound basis for modeling chain conformation and packing in the crystalline phase of polymer B. Atomic coordinates, bond lengths and angles, and selected torsional angles for the oligomer are given in Tables II–IV.

The biphenyl unit in the oligomer is essentially planar, and this plane is torsionally related to the mean plane of the backbone (containing the ether and carbonyl groups) by about 30°, as are the planes of the other two crystallographically independent aromatic rings. The bond

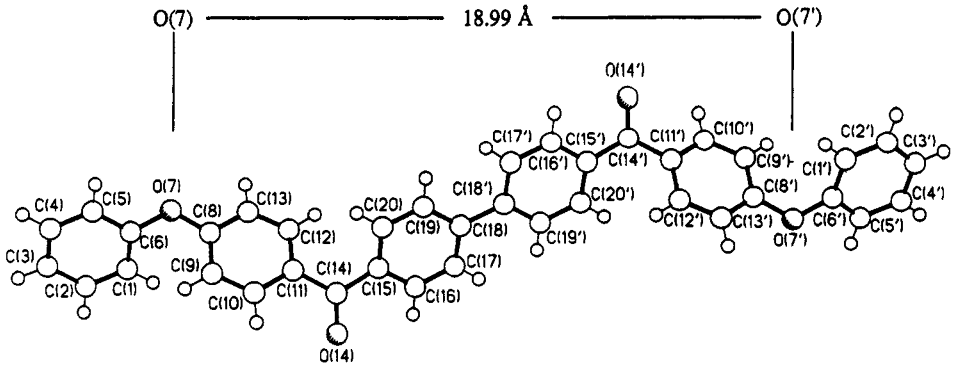


Figure 3. X-ray structure of an oligomeric model for the crystalline phase of polymer B, [−OArCOArArCOAr−]$_n$.

Table III
Bond Lengths (Å) and Angles (deg) for the Oligomer, with Estimated Standard Deviations in Parentheses

C(1)–C(2)	1.374 (3)	C(1)–C(6)	1.379 (3)
C(2)–C(3)	1.378 (3)	C(3)–C(4)	1.373 (4)
C(4)–C(5)	1.380 (3)	C(5)–C(6)	1.376 (3)
C(6)–O(7)	1.386 (2)	O(7)–C(8)	1.390 (2)
C(8)–C(9)	1.383 (3)	C(8)–C(13)	1.371 (3)
C(9)–C(10)	1.382 (3)	C(10)–C(11)	1.390 (3)
C(11)–C(12)	1.393 (3)	C(11)–C(14)	1.491 (3)
C(12)–C(13)	1.378 (3)	C(14)–O(14)	1.223 (2)
C(14)–C(15)	1.489 (3)	C(15)–C(16)	1.390 (3)
C(15)–C(20)	1.392 (3)	C(16)–C(17)	1.374 (3)
C(17)–C(18)	1.397 (3)	C(18)–C(19)	1.394 (3)
C(18)–C(18′)	1.484 (3)	C(19)–C(20)	1.385 (3)
C(2)–C(1)–C(6)	119.1 (2)	C(1)–C(2)–C(3)	120.6 (2)
C(2)–C(3)–C(4)	119.8 (2)	C(3)–C(4)–C(5)	120.3 (2)
C(4)–C(5)–C(6)	119.3 (2)	C(1)–C(6)–C(5)	120.9 (2)
C(1)–C(6)–O(7)	123.4 (2)	C(5)–C(6)–O(7)	115.6 (2)
C(6)–O(7)–C(8)	121.7 (2)	O(7)–C(8)–C(9)	123.1 (2)
O(7)–C(8)–C(13)	115.5 (2)	C(9)–C(8)–C(13)	121.3 (2)
C(8)–C(9)–C(10)	118.8 (2)	C(9)–C(10)–C(11)	120.9 (2)
C(10)–C(11)–C(12)	118.9 (2)	C(10)–C(11)–C(14)	118.4 (2)
C(12)–C(11)–C(14)	122.6 (2)	C(11)–C(12)–C(13)	120.3 (2)
C(8)–C(13)–C(12)	119.8 (2)	C(11)–C(14)–O(14)	119.4 (2)
C(11)–C(14)–C(15)	121.3 (2)	O(14)–C(14)–C(15)	119.3 (2)
C(14)–C(15)–C(16)	119.0 (2)	C(14)–C(15)–C(20)	122.8 (2)
C(16)–C(15)–C(20)	118.0 (2)	C(15)–C(16)–C(17)	121.0 (2)
C(16)–C(17)–C(18)	121.9 (2)	C(17)–C(18)–C(19)	116.6 (2)
C(17)–C(18)–C(18′)	121.7 (2)	C(19)–C(18)–C(18′)	121.7 (2)
C(18)–C(19)–C(20)	121.9 (2)	C(15)–C(20)–C(19)	120.6 (2)

Table IV
Selected Torsional Angles (Those >3° from Zero or 180°, plus Biaryl Torsions) for the Oligomer (deg), with Estimated Standard Deviations in Parentheses

C(2)–C(1)–C(6)–O(7)	–174.9 (2)
C(4)–C(5)–C(6)–O(7)	174.6 (2)
C(1)–C(6)–O(7)–C(8)	–38.6 (3)
C(5)–C(6)–C(8)–C(9)	146.3 (2)
C(6)–O(7)–C(7)–O(9)	–31.2 (3)
C(6)–O(7)–C(8)–C(13)	153.2 (2)
O(7)–C(8)–C(9)–C(10)	–176.3 (2)
O(7)–C(8)–C(13)–C(12)	175.2 (2)
C(9)–C(10)–C(11)–C(14)	–176.8 (2)
C(14)–C(11)–C(12)–C(13)	175.2 (2)
C(10)–C(11)–C(14)–C(15)	–154.4 (2)
C(12)–C(11)–C(14)–O(14)	–150.7 (2)
C(12)–C(11)–C(14)–C(15)	29.1 (3)
C(11)–C(14)–C(15)–C(16)	–153.0 (2)
C(11)–C(14)–C(15)–C(20)	31.7 (3)
O(14)–C(14)–C(15)–C(16)	26.9 (3)
O(14)–C(14)–C(15)–C(20)	–148.5 (2)
C(14)–C(15)–C(16)–C(17)	–176.1 (2)
C(14)–C(15)–C(20)–C(19)	–174.6 (2)
C(17)–C(18)–C(18′)–C(17′)	180
C(17)–C(18)–C(18′)–C(19′)	–0.2 (3)

angles at ether and ketone are 121.7 and 121.3°, respectively. On the basis of these data, a crystal structure for the polymer [–OArCOArArCOAr–]$_n$ (Figure 4) was modeled using the diffraction-simulation packages OSCA and CERIUS.[11]

The chain dimensions and conformation of the proposed polymer structure (Figure 4) are based on those of the oligomer. It is particularly noticeable that the mutual steric influence of adjacent aromatic rings manifests itself in significant (up to 4°) in-plane bending distortions of the *arene* sp^2 bond angles associated with each bridging ether or ketone group. This is in sharp contrast to a number of previous analyses of poly(ether ketone) structures, where the assumption of rigid and idealized arene geometry has led to some unlikely values for ether and ketone bond angles.[12]

Chain packing for the polymer is analogous to that observed for the oligomer and for PEEK.[10] In view of the slight increase in the unit cell dimension perpendicular to the plane of the carbonyl groups (7.54 Å for the oligomer; 7.64 Å for the polymer), the average torsion angle between an aromatic ring plane and the plane containing the carbonyl groups was increased from 30° in the oligomer to 34° in the polymer. A simulated fiber pattern (Figure 5a) based on the structure shown in Figure 4, with an average crystallite misalignment of 10°, certainly agrees quite closely with the nonmeridional X-ray data obtained for polymer B (Figure 5b). Although the experimentally observed meridional reflections *are* reproduced in the simulation, for reasons as yet unclear they are much weaker than in the experimental pattern and are visible only at high simulated intensity. A more detailed and quantitative diffraction-modeling study of this polymer is planned, but the essential structural features reported here seem to be reasonably well established.

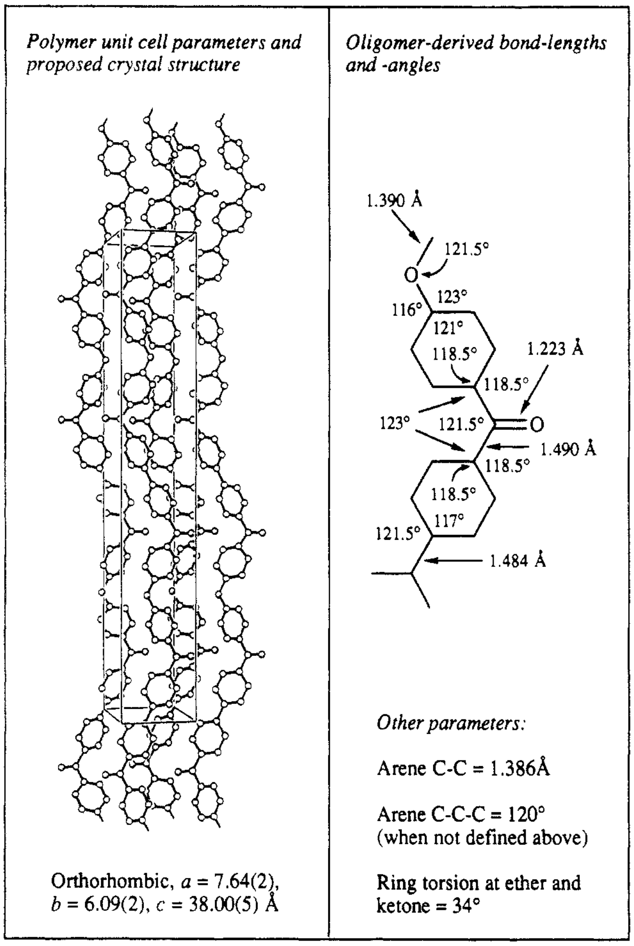
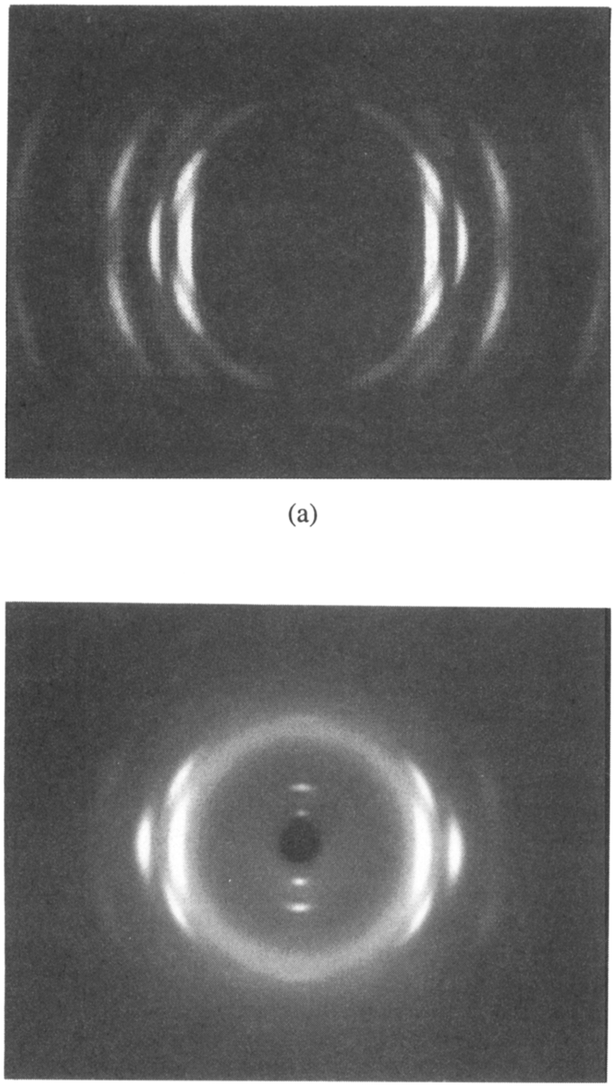


Figure 4. Proposed structure for the crystalline phase of polymer B, [–OArCOArArCOAr–]$_n$ (Ar = 1,4-phenylene).

The presence of the crystalline phase [–OArCOArArCOAr–]$_n$ found in polymer B may be rationalized as follows. In an idealized, statistically random, infinite polymer chain containing equal numbers of S and K subunits, the weight fraction of K units occurring as isolated "singlets" (i.e. in the sequence –S–K–S–) can be shown to be 15.5%. The same weight fraction of K units, 15.5%, is also present in the form of doublets (–S–KK–S–). The weight fraction of triplets is 11.6%, quadruplets 7.7%, pentuplets 4.8%, sextuplets 2.9%, and other, higher multiplets 3.9%. The total weight fraction consisting of "ketone" triplets [–S–KKK–S–] and higher [S–(K)$_n$–S] multiplets is therefore 31%.

Since the regularly alternating polymer A fails to crystallize, it is clear that a lamellar crystallite based on the four-ring subunit [–OArCOArArCOAr–] (K), isolated



(a)

(b)

Figure 5. (a) Simulated X-ray fiber diffraction pattern based on the structure shown in Figure 4. (b) Experimental pattern for polymer B.

within the sequence [S–K–S], is not sufficiently high-melting to constitute a thermally crystallizable unit. In polymer B it is conceivable, though still perhaps unlikely, that crystallization of the eight-ring [–KK–] doublets could occur, but the [–KKK–] triplet constitutes a much more plausibly crystallizable sequence since it contains 12 aromatic rings, six of which are present in the form of biaryl units. A lamellar crystallite made up of such triplet sequences would be ca. 57 Å thick and should have a melting point well in excess of 300 °C (PEEK lamellae melting at 333 °C have been shown by small-angle X-ray scattering to be some 59 Å thick).[13] Lamellae made up of higher multiplets would of course have correspondingly greater thicknesses and melting points.

Thus, assuming all [–KKK–] triplets and higher multiplets can crystallize, a random-sequence polymer of this type contains, in principle, approximately 31 wt % of thermally crystallizable material. In practice, however, aromatic ether ketone homopolymers such as PEEK, which are potentially 100% crystallizable (but have relatively inflexible chains and hence restricted mobility), achieve a maximum crystallinity of only about 40%. The very *highest* crystallinity level expected for polymer B would therefore be 40% of 32%, i.e. around 12%. If the crystallinity achieved in polymer B is in fact closer to 10%, then the observed melting endotherm (15 J g^{-1}) implies a quite reasonable heat of fusion ΔH_f for the crystalline phase [–OArCOArArCOAr–]$_n$ of approximately 150 J g^{-1} (cf. 130 J g^{-1} for the PEEK homopolymer).[10]

The optimum sequence distribution for achieving maximum crystallinity in this type of polymer, without allowing the melt temperature of the crystallites to exceed the polymer decomposition temperature, would seem to be one in which [K] subunits occur only in the form of isolated triplets, i.e. a repeat unit [–SKKK–]. Such a sequence *might* be accessible by polycondensation of $Me_3SiOArSO_2ArOSiMe_3$ with the preformed "trimer" F[ArCOArArCOArO]$_2$ArCOArArCOArF, where continuous removal of fluoride from the system as volatile Me_3SiF[14] should limit the extent of any transetherification.

Acknowledgment. We wish to thank Alan B. Newton for preparing the oriented polymer films used for X-ray diffraction studies.

References and Notes

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