First Structural Analysis of a Naphthalene-Based Poly(ether ketone): Crystal and Molecular Simulation from X-ray Powder Data and Diffraction Modeling

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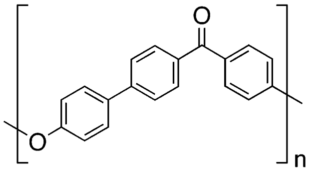
ABSTRACT: Polycondensation of 2,6-dihydroxynaphthalene with 4,4′-bis(4″-fluorobenzoyl)biphenyl affords a novel, semicrystalline poly(ether ketone) with a melting point of 406 °C and glass transition temperature (onset) of 168 °C. Molecular modeling and diffraction-simulation studies of this polymer, coupled with data from the single-crystal structure of an oligomer model, have enabled the crystal and molecular structure of the polymer to be determined from X-ray powder data. This structure—the first for any naphthalene-containing poly(ether ketone)—is fully ordered, in monoclinic space group $P2_1/b$, with two chains per unit cell. Rietveld refinement against the experimental powder data gave a final agreement factor (R_{wp}) of 6.7%.

Introduction

It has recently been shown that structural analysis of semicrystalline aromatic polymers on the basis of X-ray powder and/or fiber data can be greatly simplified by use of oligomer-based, diffraction-modeling techniques.[1,2] This type of approach uses quantitative single-crystal X-ray data from an oligomer analogue, both to construct realistic trial-structures for the polymer in question *and* to parametrize molecular mechanics force-fields so as to accurately reproduce the crystal structure of the oligomer. A high degree of confidence can then be placed on the initial choice of polymer model and also on the validity of subsequent molecular mechanics calculations carried out on this model. Diffraction modeling, especially when interfaced to single-crystal oligomer data, can thus provide a greatly increased understanding of aromatic polymer structure,[3−7] most recently for example enabling the comprehensive structural analysis of a group of very high-melting poly(ether ketone)s based on the 4,4′-biphenylene unit (polymers **1** and **2** and their copolymers, $T_m = 460-470$ °C).[8]

In the present paper, we report the synthesis and structure of a novel semicrystalline poly(ether ketone), **3**, formally derived from polymer **2** by replacing the 4,4′-biphenylenedioxy units with 2,6-dioxynaphthalene residues. This modification leads to a sharply lowered polymer melting point (406 °C), which could thus enable polymer **3** to be processed in the melt rather than necessarily from solution in strong-acid solvents, as for its high-melting analogues **1** and **2**.[8] Despite the lowered melting point, polymer **3** displays a high degree of crystallinity. A number of other naphthalene-based poly(ether ketone)s, some also displaying significant levels of crystallinity, have been described in recent publications,[9−14] but no previous attempt at crystallographic characterization of any such material has been reported. The structure of polymer **3** has now been solved from X-ray powder data, single-crystal oligomer studies and diffraction modeling—the first crystallographic characterization of *any* naphthalene-based aromatic poly(ether ketone).



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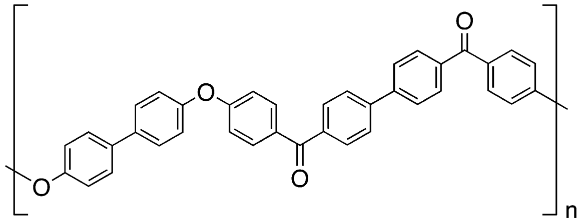

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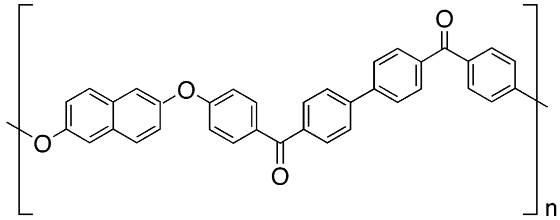

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Experimental Section

Methods and Materials. The monomer 4,4′-bis(4″-fluorobenzoyl)biphenyl was obtained by catalytic coupling of 4-chloro-4′-fluorobenzophenone, as previously described.[15] Other re-

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agents and solvents were obtained from Aldrich and were used as received. Proton and ^{13}C NMR spectra were run on a Bruker 250 MHz spectrometer, and mass spectra (EI/CI) were run on a VG Autospec instrument. Inherent viscosities were measured using a Schott-Geräte CT 150 semi-automated viscometer. Differential scanning calorimetry (DSC) was carried out under nitrogen using a Mettler DSC20 system.

Synthesis of Polymer 3. Polymer **3** was obtained by condensation of 4,4′-bis(4″-fluorobenzoyl)biphenyl (1.342 g, 3.37 mmol) with 2,6-dihydroxynaphthalene (0.529 g, 3.34 mmol) in *N*-cyclohexylpyrrolidone (7.40 g) as solvent, in the presence of anhydrous sodium carbonate (0.360 g, 3.40 mmol). The reaction mixture was stirred under conditions of slow nitrogen purge and heated to 305 °C over about 2 h, and held at this temperature for a further 40 min. The solution was then cooled to room temperature and diluted with methanol (200 mL). The resulting suspension was refluxed for 30 min and the polymer was filtered off, washed with methanol, and dried. It was extracted with boiling water (3 × 200 mL) to remove residual salts and then again with refluxing methanol (200 mL) before filtering and drying under vacuum at 80 °C overnight. The yield of polymer **3** was 1.72 g (98%). Melting point (DSC, 10 °C min^{-1}) was 406 °C, T_g was 168 °C, and the inherent viscosity (η_{inh}) at 0.1% concentration at 25 °C in 98% sulfuric acid was 0.26 dL g^{-1}.

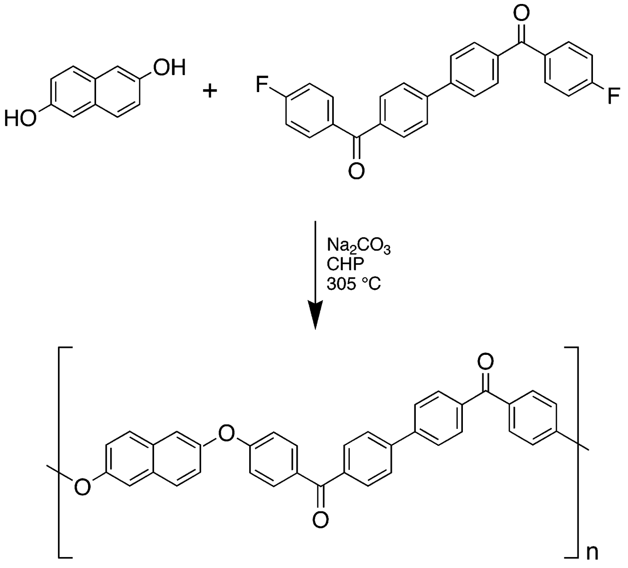
Synthesis of Oligomer 4. A mixture of 4-fluorobenzophenone (4.40 g, 22.0 mmol), 2,6-dihydroxynaphthalene (1.60 g, 10.0 mmol), potassium carbonate (2.76 g, 20.0 mol), DMAc (50 mL), and toluene (20 mL) was heated to reflux under nitrogen, with azeotropic removal of water. After 3 h, the toluene was distilled off and the temperature was raised to 160 °C. After a further 4 h, the reaction mixture was cooled to room temperature and poured into water (200 mL), and the precipitate was filtered off. After washing with water and then methanol, the solid was dried at 80 °C for 3 h and then purified by recrystallization from toluene with charcoal treatment, affording a white crystalline solid (4.52 g, 44% yield), mp 209 °C. ^{1}H NMR (CDCl$_3$/TFA, 250 MHz): δ (ppm) 7.90 (d, $J = 8.8$ Hz, 4H), 7.89 (d, $J = 9.1$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 4H), 7.70 (t, $J = 7.6$ Hz, 2H), 7.56 (m, 2H$_a$ and 4H), 7.37 (dd, $J =$ 8.7 and 2.5 Hz, 2H), 7.15 (d, $J = 8.7$ Hz, 4H); ^{13}C NMR (CDCl$_3$/TFA, 63 MHz): δ (ppm) 200.65, 163.45, 152.89, 137.02, 134.12, 134.03, 132.20, 131.04, 130.86, 130.22, 129.00, 121.86, 117.73, 117.33. MS (CI): calcd for $C_{36}H_{24}O_4$, $m/z = 520.58$; found, 521.

Crystallographic Methods. Single crystals of oligomer **4** were grown by vapor diffusion of diethyl ether into a solution of the oligomer in dichloromethane/trifluoroacetic acid. X-ray data for this compound were measured on a Siemens P4/RA diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) using ω-scans. The structure was solved using the SHELXTL-PC program system. X-ray powder data were obtained using Cu Kα radiation on a Bruker D5000 instrument (Bragg−Brentano geometry) externally calibrated with quartz powder. Computational model-building, diffraction simulation, and crystallographic refinements (from powder data) were carried out using the program systems *Cerius2* (v. 3.5) and *Materials Studio* (v. 1.2), both from Accelrys Inc., San Diego, CA.

Crystal data for oligomer 4: $C_{36}H_{24}O_4$, monoclinic, space group $P2_1/c$, $a = 6.030(2)$ Å, $b = 7.648(1)$ Å, $c = 55.902(8)$ Å, $\beta = 90.30(2)°$, $V = 2577.8(9)$ Å^3, $Z = 4$, $D_c = 1.341$ g cm^{-1}, μ(Cu−Kα) = 6.93 cm^{-1}, $T = 293$ K. Independent reflections measured 4036, $R_1 = 0.0652$, $wR_2 = 0.1444$ for 2138 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$]. CCDC 215582. Full crystallographic details for this structure are available as Supporting Information.

Structure determination for polymer 3: $[C_{36}H_{22}O_4]_n$, $M = (518.54)_n$, monoclinic, space group $P2_1/b$, $a = 7.62(1)$ Å, $b = 6.09(1)$ Å, $c = 26.36(1)$ Å, $\alpha = 93.11(1)°$, $V = 1221(1)$ Å^3, $Z = 2$, $T = 298$ K, $D_c = 1.41$ g cm^{-3}. Powder data collection range, $2\theta = 5.0{-}55.0°$, step size 0.02°, Cu Kα, $\lambda = 1.542$ Å. Peak profile function: pseudo-Voigt, $U = 1.7113$, $V = -0.4912$, $W = 0.0352$. Peak asymmetry correction: Berar-Baldinozzi, P1 = −5.0745, P2 = −0.9240, P3 = 10.4592, P4 = 1.9023 (all parameters as defined in *Materials Studio* v. 1.2). Zero point correction 0.0069°. Polymer crystallite dimensions: $a = 174$, $b = 225$, $c = 100$ Å. Lattice strain: $a = 0.073$, $b = 0.014$, $c =$ 0%. Agreement factors: $R_{wp} = 0.068$, $R_p = 0.138$.

Scheme 1. Synthesis of Polymer 3



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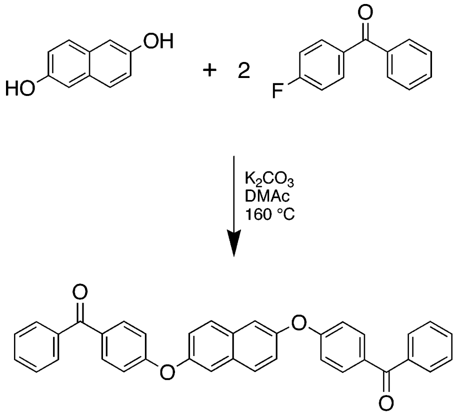
Scheme 2. Synthesis of Oligomer 4



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Results and Discussion

Polymer **3** was synthesized by high-temperature nucleophilic polycondensation of 2,6-dihydroxynaphthalene with 4,4′-bis(4-fluorobenzoyl)biphenyl in *N*-cyclohexylpyrrolidone, as shown in Scheme 1. The product was fully soluble in 98% sulfuric acid, but insoluble in conventional organic solvents. It had a relatively low inherent viscosity (0.26 dL g^{-1}), suggesting that crystallization from solution had occurred before high molar mass could be reached. This material gave a well resolved wide-angle X-ray powder pattern although, as previously noted for polymers **1** and **2**,[8] intense but diffuse low-angle X-ray scattering below $2\theta \approx 4°$ (reflecting the high degree of microporosity generally associated with polymers crystallized from solution)[16] masked any crystalline reflections in this region.

To provide a starting point for the structural analysis of polymer **3**, an oligomeric model compound (**4**) was synthesized by reaction of 2,6-dihydroxynaphthalene with excess 4-fluorobenzophenone (Scheme 2). Single crystals of **4**, suitable for X-ray analysis, were grown from a solution in dichloromethane/trifluoroacetic acid.

The X-ray structure of oligomer **4** revealed a monoclinic unit cell, space group $P2_1/c$, containing four

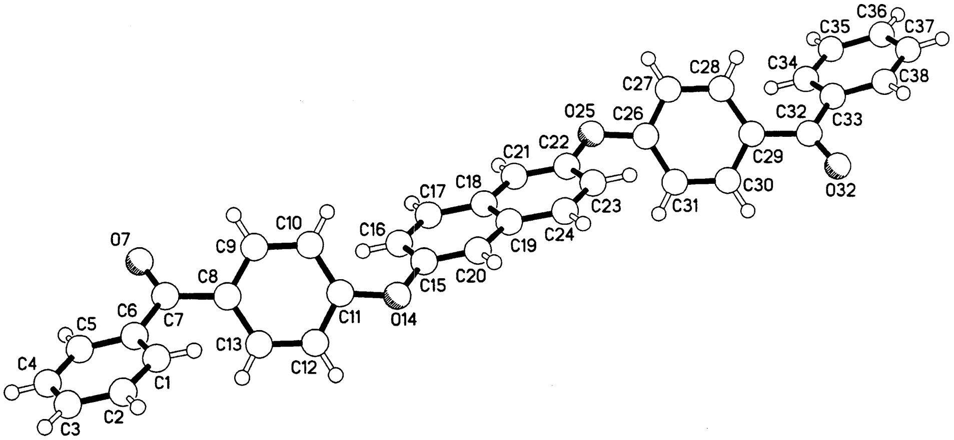

Figure 1. Molecular structure of oligomer **4** from single-crystal X-ray analysis.

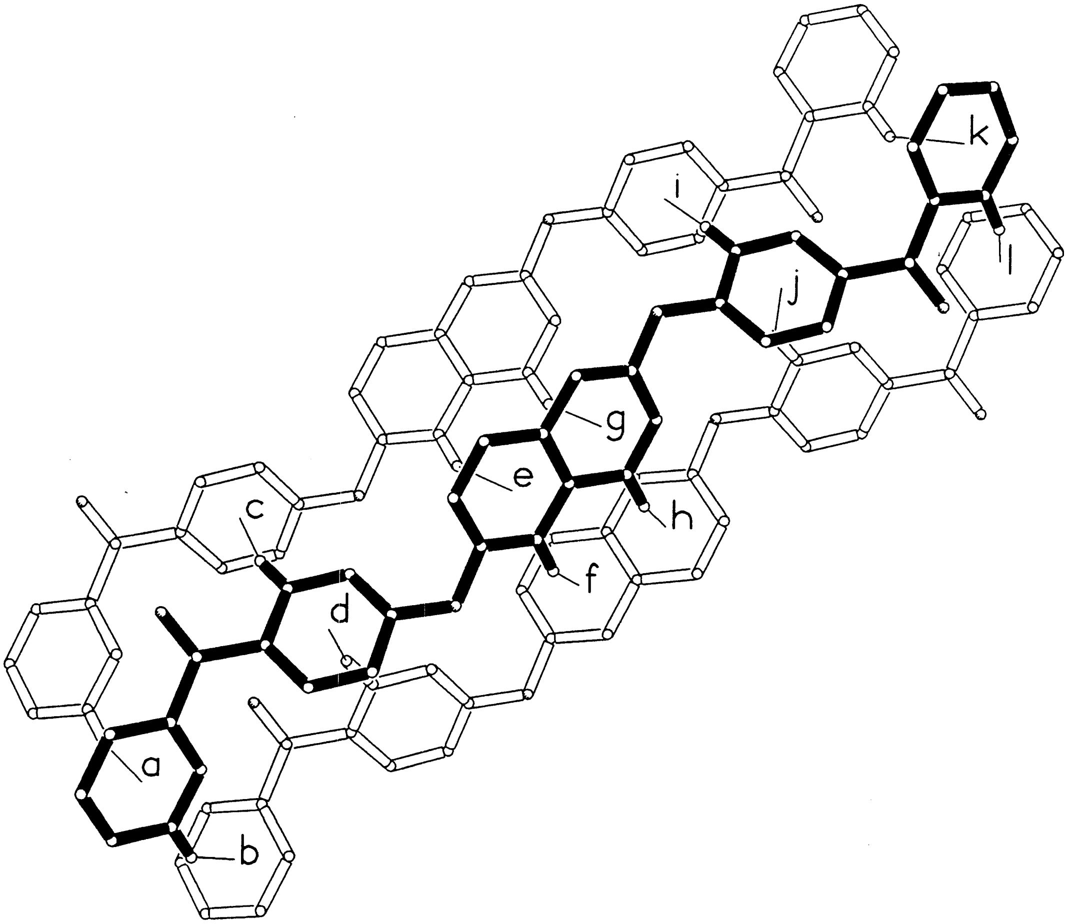

Figure 2. Conformation and packing of laterally adjacent molecules in the crystal structure of oligomer **4**. The H$\cdots\pi_{\mathrm{centroid}}$ contact distances (Å) shown are (a) 3.06, (b) 2.99, (c) 2.86, (d) 2.88, (e) 3.28, (f) 3.27, (g) 2.65, (h) 2.62, (i) 3.01, (j) 2.99, (k) 3.00 and (l) 2.97.

molecules of the oligomer. Although the molecule has potential for crystallographic inversion symmetry, this is not in fact adopted. The oligomer shows a fully extended chain conformation (Figure 1) with bridge-bond angles averaging 122.0° at the carbonyl groups and 120.8° at the ether linkages. Torsion angles between the aromatic rings and the planes of the bridging units average 29(1)° at carbonyl and 31(2)° at ether, with very little torsional asymmetry about the plane of the polymer backbone.

As shown in Figure 2, laterally adjacent oligomer molecules pack "in register" and are related, in symmetry terms, by an *n*-glide. The planes of aromatic ring-systems in adjacent molecules are mutually inclined by 60(2)°, such that hydrogens of one molecule are directed toward the π-systems of its neighbor with H$\cdots\pi_{\mathrm{centroid}}$ separations ranging from 2.62 to 3.28 Å and C$-$H$\cdots\pi_{\mathrm{centroid}}$ angles from 132 to 136°. The interactions between adjacent naphthalene units are noticeably asymmetric, with distances "e" and "f" in Figure 3 being significantly longer than those for "g" and "h". Indeed, the C$-$H$\cdots\pi$ interactions "e" and "f" are too long to even be considered as significant contacts. The predicted *c*-repeat distance for polymer **3**, derived from the structure of oligomer **4** by generating a biphenyl linkage (C$-$C = 1.495 Å) at the terminal carbon C(36), was found to be 26.39 Å.

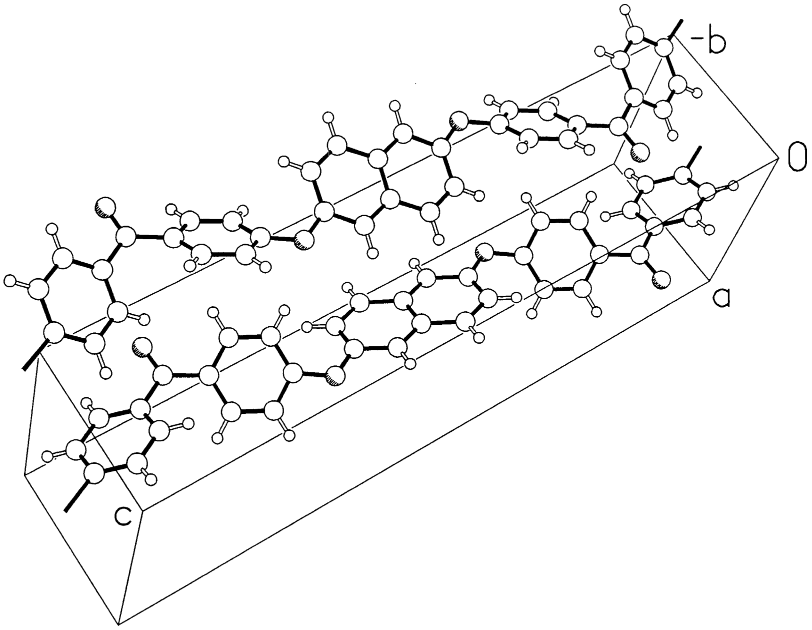

Figure 3. Perspective view of the unit cell of polymer **3**.

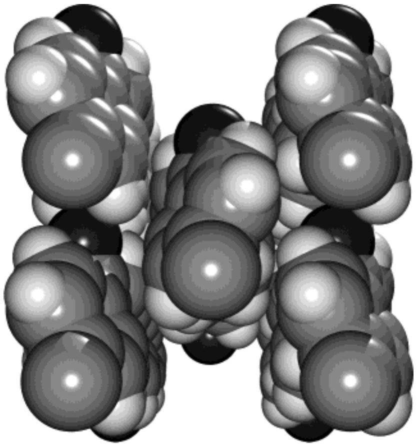

Figure 4. Space filling representation in *c*-projection of polymer **3**.

The information obtained from this single-crystal analysis was used to optimize the Dreiding II molecular mechanics force field in *Cerius2* by redefining optimum bond lengths, bond angles, torsion angles, and Lennard-Jones potentials, such that energy-minimization using the modified force field reproduced not only the molecular geometry and conformation of oligomer **4**, but also its unit cell to a very good degree of accuracy. A preliminary crystal model for polymer **3** was then constructed in a monoclinic unit cell (*a*-axis unique), retaining the oligomer cell parameters *a*, *b*, and β, and assigning the same symmetry relationship between polymer chains as found for laterally adjacent oligomer molecules. By convention the *c* axis was defined parallel to the polymer chain direction and, based on the polymer repeat distance estimated from the structure of oligomer **4**, the unit cell was assigned a provisonal *c*-dimension of 26.4 Å.

Optimization of the polymer unit cell dimensions *a*, *b*, and *c* and (in this setting of the monoclinic crystal system) the cell angle α, with respect to the experimental X-ray powder pattern, followed by energy minimization within the fixed, optimized cell, gave a structure (Figures 3 and 4) in the monoclinic space group $P2_1/b$ with two chains per unit cell. In this space group, crystallographic inversion centers are present at the centers of both the naphthylene and biphenylene residues. For polymers **1** and **2**, a disordered structure involving random positioning of ether and ketone linkages in adjacent chains can occur, as a result of the geometrical near-equivalence of 4,4′-dioxybiphenyl units (O···O = 9.83 Å) and 4,4′-biphenyldicarbonyl residues (O=C···C=O = 10.08 Å).[8] However, in polymer **3** there is no possibility of positional disorder of this type, as the O···O separation in the 2,6-dioxynaphthalene residue, at 7.71 Å, is so very much shorter than the O=C···C=O distance in a 4,4′-biphenyldicarbonyl unit (10.08 Å) that these units are far from being geometrically equivalent.

In the final model for polymer **3** the 2,6-naphthylene residues, like the 4,4′-biphenylene units in polymers **1** and **2**, pack edge-to-face with corresponding residues in neighboring chains, just as was found in the crystal structure of oligomer **4**. In both the oligomer and polymer structures the "offset" linking-geometry associated with the 2,6-substituted naphthalene residues results in a noticeably unsymmetrical interaction between these units, and it seems possible that this feature of the chain-packing is responsible for the observed reduction in the melting point of polymer **3** relative to the analogous biphenyl-based polymers **1** and **2**.[8]

The X-ray powder pattern simulated from this model was generally in very good agreement with the observed data. Rietveld refinement of the model in terms of unit cell parameters, crystallite size and strain, peak asymmetry and temperature factors, with respect to the X-ray powder pattern for polymer **3**, gave unit cell parameters a = 7.62 Å, b = 6.09 Å, c = 26.36 Å, and α = 93.11°. The model was finally reminimized in energy terms within this refined unit cell, leading to an ultimate weighted-profile agreement factor, R_{wp}, of 6.8%. The final simulated and difference powder diffraction patterns for polymer **3** are shown in Figure 5 superimposed on the (background-subtracted) experimental data. Atomic coordinates for the final structure are given in Table 1, and bond lengths and bond angles for the asymmetric unit are shown in Table 2.

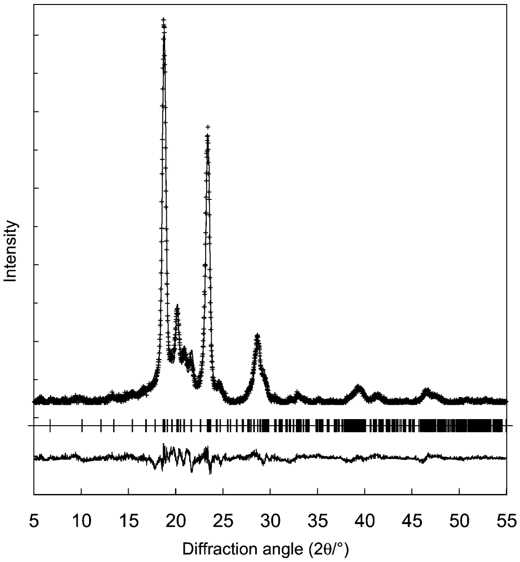

Figure 5. Rietveld difference plot (lower line) for the final model of polymer **3**. Experimental data (background-subtracted) are shown as + marks, calculated data as a solid line, and calculated peak positions as tick marks.

Table 1. Fractional Atomic Coordinates of the Final Model for Polymer 3, in Space Group *P*2$_1$/*b*

name	*x*	*y*	*z*
C1	0.425	0.546	0.385
H1A	0.369	0.468	0.355
C2	0.427	0.453	0.431
H2A	0.373	0.308	0.434
C3	0.500	0.552	0.475
C4	0.573	0.757	0.468
H4A	0.627	0.836	0.497
C5	0.574	0.856	0.422
H5A	0.627	1.002	0.419
C6	0.500	0.750	0.379
C7	0.502	0.860	0.330
O7	0.508	1.061	0.330
C8	0.500	0.731	0.280
C9	0.417	0.822	0.240
H9A	0.362	0.968	0.244
C10	0.412	0.708	0.193
H10A	0.351	0.771	0.164
C11	0.493	0.505	0.186
C12	0.576	0.414	0.227
H12A	0.632	0.269	0.222
C13	0.581	0.528	0.274
H13A	0.642	0.465	0.302
O14	0.490	0.375	0.141
C15	0.508	0.465	0.094
C16	0.586	0.665	0.085
H16A	0.631	0.758	0.114
C17	0.600	0.733	0.036
H17A	0.654	0.875	0.030
C18	0.539	0.600	−0.004
C19	0.444	0.333	0.054
H19A	0.386	0.193	0.060

Table 2. Bond Lengths and Bond Angles for the Asymmetric Unit of Polymer 3

C(1)−C(6)	1.384	C(10)−C(11)	1.386
C(1)−C(2)	1.384	C(11)−C(12)	1.385
C(2)−C(3)	1.388	C(11)−O(14)	1.389
C(3)−C(4)	1.388	C(12)−C(13)	1.385
C(3)−C(3)#1	1.490	O(14)−C(15)	1.389
C(4)−C(5)	1.385	C(15)−C(16)	1.386
C(5)−C(6)	1.384	C(15)−C(19)	1.390
C(6)−C(7)	1.490	C(16)−C(17)	1.385
C(7)−O(7)	1.224	C(17)−C(18)	1.386
C(7)−C(8)	1.490	C(18)−C(19)#2	1.387
C(8)−C(9)	1.385	C(18)−C(18)#2	1.387
C(8)−C(13)	1.386	C(19)−C(18)#2	1.387
C(9)−C(10)	1.385		

C(6)−C(1)−C(2)	120.0	C(9)−C(10)−C(11)	120.1
C(1)−C(2)−C(3)	124.3	C(12)−C(11)−C(10)	119.8
C(4)−C(3)−C(2)	113.5	C(12)−C(11)−O(14)	115.7
C(4)−C(3)−C(3)#1	123.3	C(10)−C(11)−O(14)	124.4
C(2)−C(3)−C(3)#1	123.2	C(11)−C(12)−C(13)	120.1
C(5)−C(4)−C(3)	124.3	C(12)−C(13)−C(8)	120.1
C(6)−C(5)−C(4)	120.0	C(11)−O(14)−C(15)	121.7
C(5)−C(6)−C(1)	117.8	C(16)−C(15)−O(14)	125.7
C(5)−C(6)−C(7)	119.3	C(16)−C(15)−C(19)	120.0
C(1)−C(6)−C(7)	122.8	O(14)−C(15)−C(19)	114.2
O(7)−C(7)−C(6)	119.2	C(17)−C(16)−C(15)	120.1
O(7)−C(7)−C(8)	119.2	C(16)−C(17)−C(18)	120.1
C(6)−C(7)−C(8)	121.6	C(17)−C(18)−C(19)#2	119.9
C(9)−C(8)−C(13)	119.8	C(17)−C(18)−C(18)#2	119.8
C(9)−C(8)−C(7)	118.1	C(19)#2−C(18)−C(18)#2	120.3
C(13)−C(8)−C(7)	122.1	C(18)#2−C(19)−C(15)	119.7
C(10)−C(9)−C(8)	120.1		

[a] Symmetry transformations used to generate equivalent atoms: #1, −*x* + 1, −*y* + 1, −*z* + 1; #2, −*x* + 1, −*y* + 1, −*z*.

Conclusions

The first structural characterization of a naphthalene-based aromatic poly(ether ketone) has been achieved using computational modeling interfaced to X-ray powder data. Atomic coordinates were successfully determined by energy-minimization of the model within an experimentally determined unit cell, using a force-field optimized for this type of polymer on the basis of single-crystal oligomer data. The 2,6-naphthylene residue, like the 4,4′-biphenylene unit, packs edge-to-face with its corresponding residues in neighboring chains, but the "offset" linking geometry associated with the naphthalene residue results in a noticeably unsymmetrical interaction between such units. This feature of the chain-packing may well be responsible for the observed reduction in polymer melting point relative to analogous biphenyl-based polymers.

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Supporting Information Available: Tables of full crystallographic data, including crystal and refinement data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates for the single-crystal X-ray structure of oligomer **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hanna, S.; Coulter, P. D.; Windle, A. H. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2615.

(2) (a) Colquhoun, H. M.; Williams, D. J. *Acc. Chem. Res.* **2000**, *33*, 189. (b) Colquhoun, H. M.; Aldred, P. L.; Kohnke, F. H.; Herbertson, P. L.; Baxter, I.; Williams, D. J. *Macromolecules* **2002**, *35*, 1685.

(3) Colquhoun, H. M.; Herbertson, P. L.; Wade, K.; Baxter, I.; Williams, D. J. *Macromolecules* **1998**, *31*, 1694.

(4) Baxter, I.; Colquhoun, H. M.; Kohnke, F. H.; Lewis, D. F.; Williams, D. J. *Polymer* **1998**, *40*, 607.

(5) Liu, J.; Rybnikar, F.; Geil, P. H. *Kor. Polym. J.* **1998**, *6*, 75.

(6) (a) Colquhoun, H. M.; Lewis, D. F.; Williams, D. J. *Polymer* **1999**, *40*, 5415. (b) Colquhoun, H. M.; Lewis, D. F.; Williams, D. J. *Macromolecules* **1999**, *32*, 3384.

(7) (a) Yang, J.; Sidoti, G.; Liu, J.; Geil, P. H.; Li, C. Y.; Cheng, S. Z. D. *Polymer* **2001**, *42*, 7181. (b) Bao, H.; Rybnikar, F.; Saha, P.; Yang, J.; Geil. P. H. *J. Macromol. Sci., Phys.* **2001**, *B40*, 869.

(8) Colquhoun, H. M.; Aldred, P. L.; Blundell, D. J.; Williams, D. J. *Macromolecules* **2002**, *35*, 9420.
(9) Ohno, M.; Takata, T.; Endo, T. *React. Funct. Polym.* **1996** *30*, 149.
(10) Yoshida, S.; Hay, A. S. *J. Macromol. Sci., Macromol. Chem.* **1997**, *A34*, 1299.
(11) Douglas, J. E.; Wang, Z. Y. *Can. J. Chem.* **1997**, *75*, 1340.
(12) Bottino, F. A.; Di Pasquale, G.; Leonardi, N.; Pollicino, A. *Polymer* **1998**, *39*, 3199.
(13) Ruan, R. X.; Jiang, Z. H.; Xu, W. L.; Shibata, M.; Yosomiya, R. *Angew. Makromol. Chem.*. **1999**, *270*, 33.
(14) Sakaguchi, Y. *High Perform. Polym.* **2002**, *14*, 341.
(15) Colquhoun, H. M.; Dudman, C. C.; Blundell, D. J.; Bunn, A.; Mackenzie, P. D.; McGrail, P. T.; Nield, E.; Rose, J. B.; Williams, D. J. *Macromolecules* **1993**, *26*, 107.
(16) Statton, W. O. *J. Polym. Sci.* **1962**, *58*, 205.

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