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Crystal and Molecular Structure of Poly(thioether−ketone) from Single-Crystal Oligomer Data and Diffraction Modeling. 2. Polymer Crystallized from the Melt or from Solution

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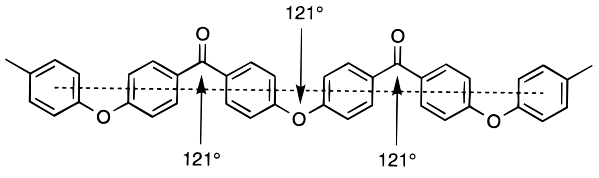
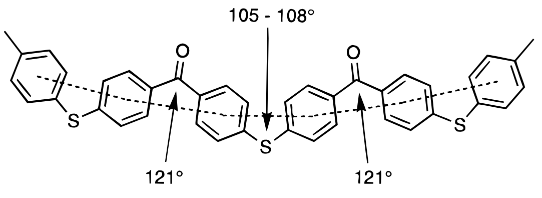
ABSTRACT: The aromatic poly(thioether−ketone) $[ArSArCO]_n$ (Ar = 1,4-phenylene), PTEK, is known to exist in at least two different crystalline forms, one produced by orientation of the amorphous polymer and the other by crystallization from the melt. In the present work, X-ray powder diffraction studies interfaced to molecular modeling and diffraction simulation techniques have been used to determine the crystal and molecular structure of melt- or solution-crystallized PTEK. In this phase, the thioether−ketone polymer chains adopt a packing arrangement very different from that of their ether−ketone analogues. For solution-crystallized polymer, the unit cell is body-centered monoclinic (two chains per cell), space group *I*2, $a = 7.58$, $b = 6.09$, $c = 10.25$ Å, $\beta = 93.7°$, density = 1.49 g cm^{-3}. The thermal parameters required for this model are however rather high, suggesting the possibility of a disordered structure (in space group *I*2/*a*,) whereby thioether and ketone linkages are distributed at random over the available sites. Melt crystallization results in a very slight expansion of the crystal lattice in the *a*-direction, relative to the solution-crystallized form, but the structure is otherwise unchanged.

Introduction

The ability of poly(ether−ketone)s to crystallize rapidly from the melt is generally ascribed to the geometrical equivalence of aromatic ether and carbonyl linkages.[1] Bond angles (C−O−C and C−C−C) at both these linkages are close to 121° so that the linear chain geometry required for thermal crystallization of poly(ether−ketone), PEK (**1**), is readily achieved.[2] The aromatic *thioether* unit, however, is far from geometrically equivalent to a carbonyl group, as the unconstrained $C_{Ar}-S-C_{Ar}$ bond angle lies in the range 105−108°.[3] Nevertheless, the aromatic poly(thioether−ketone) $[ArSArCO]_n$ (Ar = 1,4-phenylene), PTEK (**2**), is known to crystallize readily from the melt.[4]



PEK (**1**)



PTEK (**2**)

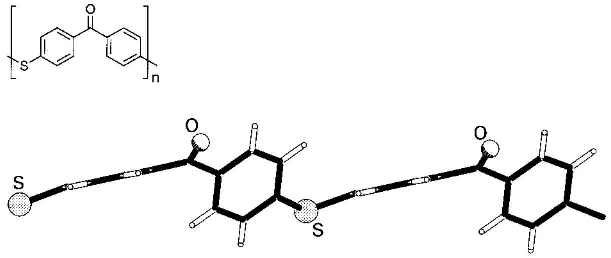


Figure 1. Molecular geometry of $[ArCOArS]_n$ (Ar = 1,4-phenylene). Pyramidalization of the arene carbon linked to sulfur, resulting in a 0.24 Å out-of-ring plane displacement of the sulfur atom, is clearly evident.

It might be imagined that, to achieve linearity, the C−S−C bond angle in **2** must open up by some 10−15° from its normal value. This however seems inherently unlikely on energy grounds, and it has in fact recently been shown by X-ray analysis of the oligomer [ArCOArSArCOAr] (Ar = phenyl or 1,4-phenylene) that the chain geometry necessary for crystallization of (**2**) is achieved, *not* by any significant opening of the C−S−C bridge bond angle, but by a series of distortions elsewhere within the molecule—notably by pyramidalization of the carbon atoms adjacent to the thioether bridge (Figure 1). The C−S−C bond angle (108°) in the oligomer structure does lie at the upper end of its normal range, but the difference (13°) between this value and that observed at the carbonyl groups in the same oligomer (121°) remains extremely significant.[5]

Preliminary studies of the crystal structure and morphology of PTEK (**2**) have only recently been reported. Takahashi and co-workers found that the polymer exists in two different crystalline forms, one phase produced by orientation of the amorphous material and the other by thermal treatment of quenched polymer or by crystallization from the melt.[6] In part 1 of the present work,[5] we showed that the structure of *orientation*-crystallized poly(thioether−ketone) (orthorhombic,

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space group *Pb2n*, $a = 4.12$, $b = 11.30$, $c = 10.44$ Å) is analogous to that of the metastable “form II” phase already known for poly(ether−ketone)s containing a high proportion of carbonyl groups.[7] Takahashi et al. have proposed (on the basis of an extremely weak X-ray powder pattern) that the *melt*-crystallized phase is probably analogous to the “form I” structure generally found for poly(ether−ketone)s (orthorhombic, $a = 7.67$, $b = 6.20$, $c = 10.44$ Å).[6] In the present work, however, we describe a detailed X-ray powder diffraction and molecular simulation study of PTEK crystallized both from the melt and from solution which demonstrates that, although the crystal structure adopted is the same in both cases, it is in fact very different from the conventional poly(ether−ketone)-type structure.

Experimental Section

The poly(thioether−ketone) $[ArSArCO]_n$ (Ar = 1,4-phenylene) was obtained by reaction of sodium sulfide with 4,4′-difluorobenzophenone in *N*-cyclohexylpyrrolidone at 290 °C and was crystallized directly from the reaction mixture by slow cooling (0.5 °C/min).[8] Residual salts and solvent were removed by exhaustive extractions with boiling water and with methanol, and the resulting pale cream polymer was dried at 120 °C under vacuum. Its melting point was 353 °C, and its inherent viscosity (0.1% in 98% sulfuric acid) was 0.46 dL g^{-1}. A melt-crystallized sample was obtained by slow cooling from 380 to 250 °C, followed by annealing at 275 °C under nitrogen for 30 min. X-ray powder data were obtained in the reflection mode using a Siemens D5000 powder diffractometer (Cu Kα radiation). Molecular modeling and diffraction simulation studies were carried out using Cerius2 software, version 3.5 (Molecular Simulations Ltd, Cambridge, UK) running on a Silicon Graphics O2 workstation. The single-crystal X-ray structure of the oligomer [ArCOArSArCOAr] (Ar = phenyl or 1,4-phenylene) has been described in part 1 of this work.[5] Tables of atomic coordinates, bond lengths, bond angles, and thermal parameters for this oligomer are available as Supporting Information.

Results and Discussion

Slow crystallization of PTEK from a solution in *N*-cyclohexylpyrrolidone yielded a fine powder giving the very well-resolved X-ray powder pattern which, after subtraction of a fitted curve representing the scattering from the amorphous phase, is shown in Figure 2. This pattern was virtually identical to a powder pattern obtained from a sample of PTEK crystallized from the melt, although though some very slight shifts in peak positions suggested that minor changes in lattice parameters had occurred. The “solution-crystallized” pattern appeared to contain enough detail to justify a diffraction-modeling study of this polymer, especially in view of the structural data available from an earlier single-crystal oligomer study.[5] The unit cell of this model oligomer, [ArCOArSArCOAr], is monoclinic, space group $P2_1/n$, [$a = 6.051(1)$, $b = 41.826(1)$, $c = 7.589(1)$ Å, $\beta = 90.04(1)°$]. The scarcely significant departure of β from 90° means that there is negligible offset in the chain direction between laterally disposed oligomer molecules. Despite the difference in bond angle between the thioether and carbonyl linkages (107.8° and 121.1°, respectively), the oligomer succeeds in attaining a near-linear geometry by a series of bond angle distortions at the arene carbons adjacent to sulfur (C−C−S averaging 124.3° and 115.4°) and by a remarkable 0.21 Å out of arene plane displacement of the sulfur atom which, taken together, open up the “effective” angle at sulfur very significantly. The *a* and *c* dimensions of the oligomer cell are close to the *b* and *a* dimensions, respectively, proposed earlier for the unit cell of melt-crystallized PTEK,[6] and the oligomer crystal packing is essentially identical to that found in PEK.[1]

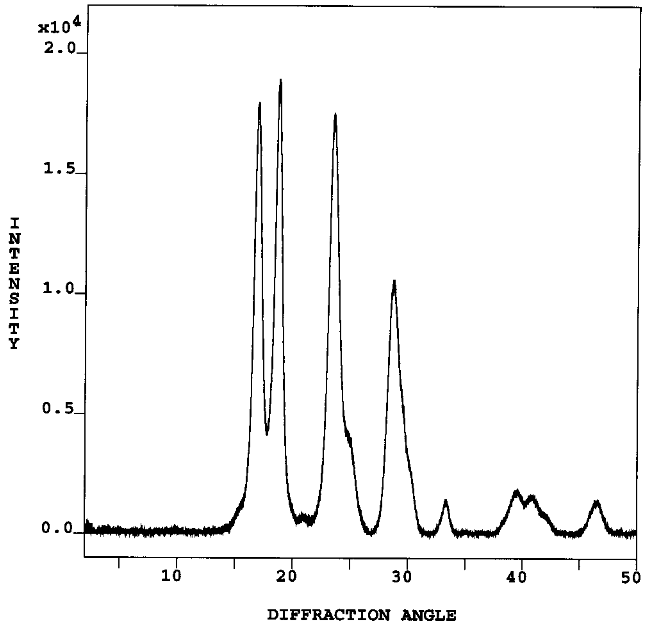

Figure 2. X-ray powder diffraction pattern (Cu Kα radiation) of solution-crystallized PTEK, after subtraction of a fitted curve representing scattering from the amorphous phase (diffraction angle = 2θ).

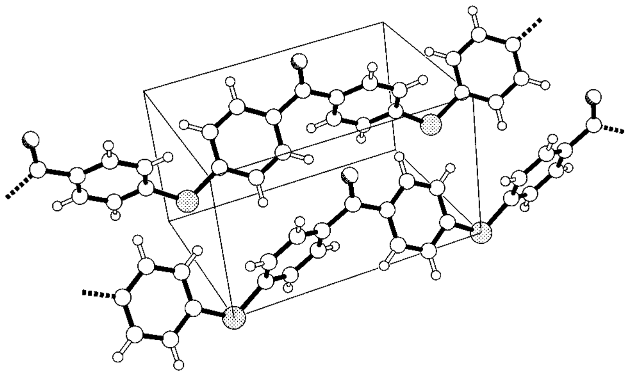

Figure 3. Preliminary model for the crystal structure of solution-crystallized PTEK (orthorhombic, two *n*-glide-related chains, $a = 7.67$, $b = 6.20$, $c = 10.44$ Å), based on the structure of PEK.

A preliminary model for PTEK was thus constructed in an orthorhombic unit cell having the same lateral dimensions as those found for the oligomer ($a = 7.59$, $b = 6.05$ Å) and with the same symmetry relationship (an *n*-glide) between adjacent chains in the unit cell. The *c*-dimension was based on the oligomer carbonyl−carbonyl (C···C) separation (10.25 Å). The Cerius2 Universal force field was modified to reproduce the bond lengths and bond angles (but not necessarily the torsion angles or out-of-plane distortions) found in the oligomer, and the energy of the polymer model was then minimized in a fixed unit cell. This minimization, for which the chain geometry was *required* to be linear, generated a somewhat greater out-of-plane displacement at the arene−sulfur linkage than observed in the oligomer structure, the sulfur atom now lying 0.24 Å from the plane of the adjacent aromatic ring and the C−S bond subtending an angle of 10° to this plane. Molecular simulation thus confirms the requirement for a very

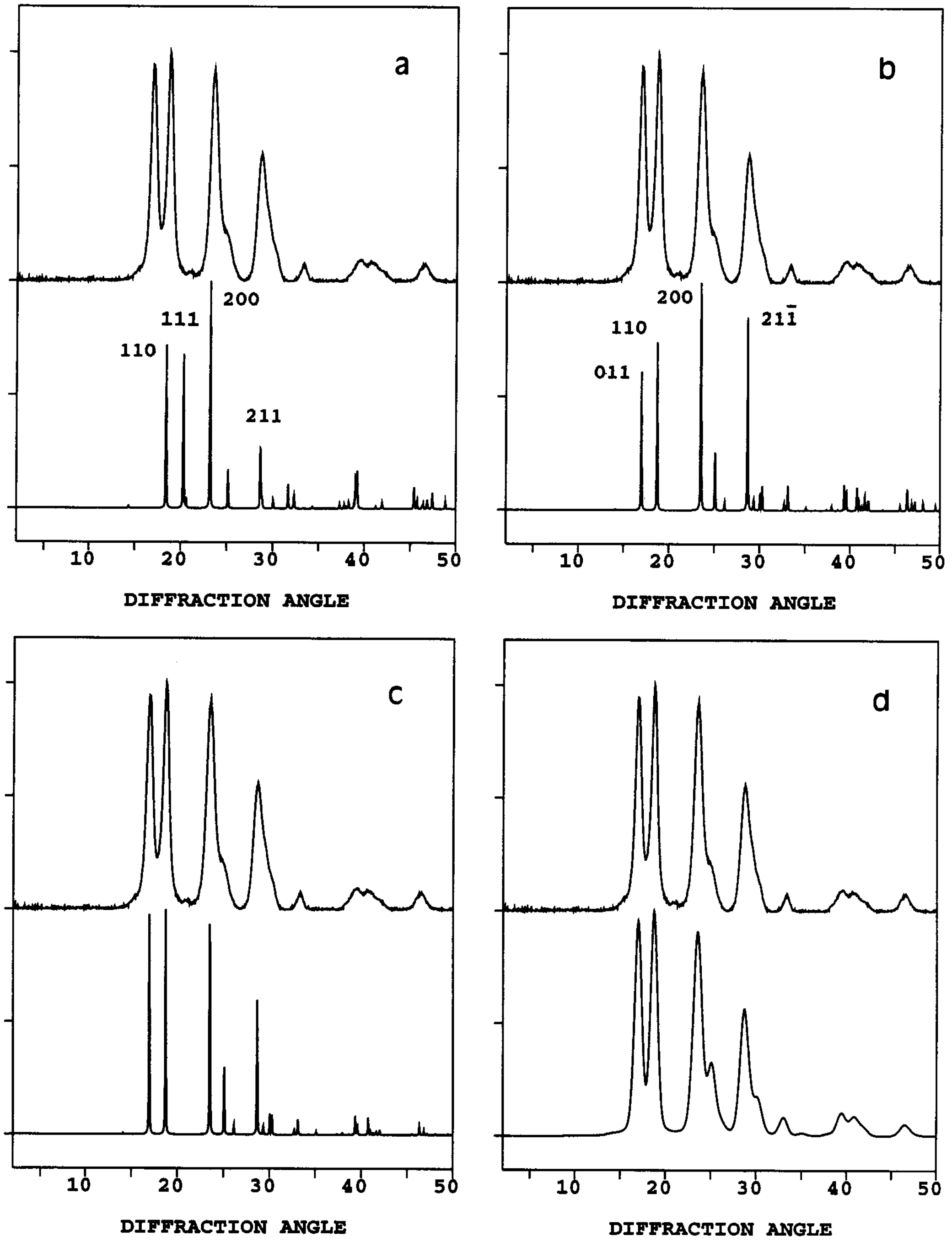

Figure 4. (a) Experimental powder pattern for solution-crystallized PTEK (above) and simulated pattern (below) for the structure shown in Figure 3. Crystallite dimensions for the simulation were 1000 × 1000 × 1000 Å, and thermal parameters were set to zero. (b) Experimental pattern and a simulated pattern for the body-centered structure shown in Figure 5. (c) As for (b) but with simulated thermal parameters $U_a = 0.30$, $U_b = 0.23$, and $U_c = 0.10$ Å^2. (d) As for (c) but with simulated crystallite dimensions $a = 90$, $b = 160$, and $c = 85$ Å. Thompson peak shape parameter for the final simulation was 0.25.

significant out-of-plane distortion at the C−S linkage, if PTEK is to achieve a linear chain geometry in the solid state.

In terms of unit cell dimensions and chain packing, this preliminary orthorhombic model for PTEK corresponded very closely to that of its ether anologue PEK.[1] Next, the cell dimensions were adjusted very slightly to those proposed by Takahashi and co-workers for melt-crystallized PTEK (Figure 3, $a = 7.67$, $b = 6.20$, $c = 10.44$ Å),[6] and an X-ray powder pattern was generated from the model. This simulated pattern is shown in Figure 4a, together with our experimental data. Although a number of peaks in the simulation (specifically the 110, 200, and 211 reflections) appear to correspond to reflections observed in our experimental pattern, the strong 111 peak at $2\theta = 20.29°$ in the simulation is not seen experimentally. Moreover, the intense reflection at $2\theta = 16.94°$ in the experimental pattern is absent from the simulation. It can thus be concluded that the structure of melt- or solution-crystallized PTEK is not in fact analogous to that of PEK.

We therefore screened a number of alternative symmetry relationships between the two chains in the unit cell. From this study it emerged that, if the second chain is related to the first by simple *body-centering* rather than by the *n*-glide found in PEK, then the simulated powder pattern is in vastly better agreement with

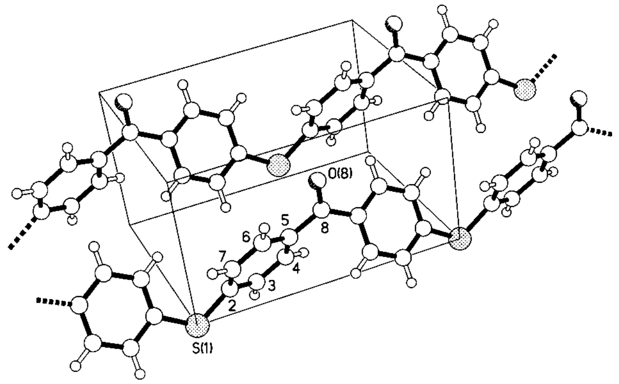

Figure 5. Final model for the crystal structure of solution-crystallized PTEK (body-centered monoclinic, space group *I*2, $a = 7.58$, $b = 6.09$, $c = 10.25$ Å, $\beta = 93.7°$). The C−S bond length is 1.77 Å, and the C−S−C and C−C_{ket}−C bond angles are 107° and 122° respectively. The C−S bond subtends an angle of 10° to the mean plane of its associated aromatic ring, with the sulfur atom lying 0.24 Å out of this plane.

Table 1. Fractional Atomic Coordinates for Solution-Crystallized PTEK, in Space Group *I*2

	x	*y*	*z*
S(1)	0.0000	0.0000	0.0000
C(2)	0.0099	0.1725	0.1394
C(3)	0.0898	0.0847	0.2530
C(4)	0.0861	0.1987	0.3696
C(5)	0.0023	0.4007	0.3728
C(6)	−0.0770	0.4890	0.2591
C(7)	−0.0734	0.3748	0.1424
C(8)	0.0000	0.5189	0.5000
O(8)	0.0000	0.7198	0.5000
H(3A)	0.1485	−0.0578	0.2509
H(4A)	0.1424	0.1367	0.4496
H(6A)	−0.1359	0.6313	0.2613
H(7A)	−0.1299	0.4367	0.0624

Table 2. Principal X-ray Reflections and *d*-Spacings (Å) for Solution-Crystallized PTEK, from Experimental Powder Data and from the Final Diffraction Simulation

h k l	d_{expt}	I_{expt}	d_{simuln}	I_{simuln} (%)
0 1 1	5.24	vs	5.23	86
1 1 0	4.75	vs	4.74	88
2 0 0	3.79	vs	3.78	100
$2\ 1\ \bar{1}$	3.11	s	3.11	57
1 2 1	2.69	w	2.71	6
$1\ 1\ \bar{4}$	2.28	w	2.29	8
1 1 4	2.21	w	2.21	7
0 2 4	1.95	w	1.96	4

experiment. In the new, body-centered structure, thioether linkages in symmetry-related chains are no longer adjacent and "in register" but are offset in the *c* direction by half a unit cell (Figure 5). Minimization of the crystal packing energy for this structure led to a monoclinic, rather than an orthorhombic, cell, and optimization of the unit cell parameters eventually gave a structure ($a = 7.58$, $b = 6.09$, $c = 10.25$ Å, $\beta = 93.7°$) for which the agreement between experimental and simulated peak positions is excellent (Figure 4b). Evaluation of the symmetry elements present in the final model (Figure 5) resulted in the assignment of space group *I*2 (an alternative setting of the standard space group *C*2 and required here by the convention which aligns the polymer chain with the crystallographic *c*-direction). As noted above, the powder pattern from a *melt*-crystallized sample of PTEK shows very slight shifts of the 200 and $21\bar{1}$ reflections to lower angle when compared to the pattern from solution-crystallized material. The shifts are consistent with an expansion of the *a*-dimension of the unit cell from 7.58 to 7.70 Å, but no other changes in the structure are required to account for the positions of these reflections.

It will be noted from Figure 4b that the relative *intensities* of the simulated reflections for this model do not match the experimental intensities as well as might be expected, and these cannot be brought into agreement simply by adjustment of simulated crystallite dimensions and/or crystallite strain. However, by also applying very high anisotropic vibrational parameters ($U_a = 0.30$, $U_b = 0.23$, and $U_c = 0.10$ Å^2) to the model, a very good match in intensities was achieved (Figure 4c). Adjustment of the simulated polymer crystallite dimensions to $a = 90$, $b = 160$, and $c = 85$ Å gave satisfactory peak profiles when compared to the experimental X-ray data, as shown in Figure 4d. The final model is shown in Figure 5, and atomic coordinates for the asymmetric unit are given in Table 1. Simulated and experimental X-ray data for this model are compared in Table 2.

The most probable explanation for the very high thermal parameters required to simulate the experimental X-ray powder pattern is that the crystal is significantly disordered. This has some precedent in the structure of the conventional poly(ether−ketone), PEK, where substitutional disorder of geometrically equivalent ether and ketone linkages raises the apparent space group symmetry from *Pb*2*n* to *Pbcn*.[1] In the present structure the differences in bond lengths and bond angles for the thioether and carbonyl groups mean that crystallographic randomization of these linkages would lead to substantial *positional* as well as substitutional disorder for all the atoms in the structure, thus giving rise to unusually high apparent thermal parameters.

An alternative space group (*P*2/*a*) can in fact be identified for PTEK, differing from that shown in Figure 5 only by the interchange of thioether and carbonyl linkages in the "centered" chain. Analysis of the model confirms that such interchange can be accommodated without giving rise to unfavorable intermolecular contacts. Furthermore, diffraction simulation from the *P*2/*a* structure generates a powder pattern that is very similar to that shown in Figure 4c, though with some slight variation in intensities. A disordered crystal lattice (in the higher symmetry space group *I*2/*a*) would result from superposition of these two structures, though further work on this and related polymers is needed to confirm the interchangeability of thioether and carbonyl linkages.

Conclusions

In the crystal phase of poly(thioether−ketone) which is formed by crystallization from the melt or from solution, the polymer chains pack very differently from their ether−ketone analogues. The unit cell of solution-crystallized PTEK is found to be body-centered monoclinic (two chains per cell), space group *I*2, $a = 7.58$ (7.70 for melt-crystallized polymer), $b = 6.09$, $c = 10.25$ Å, $\beta = 93.7°$, density = 1.49 g cm^{-3}. The very high thermal parameters required for this structure, however, also suggest the possibility of a disordered crystal, in space group *I*2/*a*, whereby equal numbers of thioether and ketone linkages are distributed at random over the available sites.

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Supporting Information Available: Molecular structure of [ArCOArSArCOAr] (Ar = phenyl or 1,4-phenylene) and tables of atomic coordinates, bond lengths, bond angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Dawson, P. C.; Blundell, D. J. *Polymer* **1980**, *21*, 577.

(2) Colquhoun, H. M.; O'Mahoney, C. A.; Williams, D. J. *Polymer* **1993**, *34*, 218.

(3) Hasebe, K.; Asahi, T.; Ishazawa, A.; Izumi, K. *Acta Crystallogr.* **1989**, *C45*, 2023. Ovchinnikov, Y. E.; Nedel'kin, V. I.; Ovsyannikova, S. I.; Struchkov, Y. T. *Russ. Chem. Bull.* **1994**, *43*, 1384.

(4) Feasey, R. G.; Rose, J. B. German Patent, 2,156345, 1972 (to ICI).

(5) Colquhoun, H. M.; Lewis, D. F.; Williams, D. J. *Polymer*, in press.

(6) Takahashi, T.; Hii, S.-H.; Sakurai, K. *J. Macromol. Sci., Phys.* **1998**, *B37*, 59.

(7) Blundell, D. J.; Newton, A. B. *Polymer* **1991**, *32*, 308.

(8) Durvasula, V. R.; Stuber, F. A.; Bhattacharjee, D. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 661.

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