*Acc. Chem. Res.* **2000,** *33,* 189−198

# Crystal and Molecular Simulation of High-Performance Polymers

HOWARD M. COLQUHOUN*,† AND
DAVID J. WILLIAMS*,‡

*Department of Chemistry, University of Salford, Salford M5 4WT, U.K., and Department of Chemistry, Imperial College, London, SW7 2AY U.K.*

Received August 25, 1999

**ABSTRACT**

Single-crystal X-ray analyses of oligomeric models for high-performance aromatic polymers, interfaced to computer-based molecular modeling and diffraction simulation, have enabled the determination of a range of previously unknown polymer crystal structures from X-ray powder data. Materials which have been successfully analyzed using this approach include aromatic polyesters, polyetherketones, polythioetherketones, polyphenylenes, and polycarboranes. Pure macrocyclic homologues of noncrystalline polyethersulfones afford high-quality single crystals—even at very large ring sizes—and have provided the first examples of a "protein crystallographic" approach to the structures of conventionally amorphous synthetic polymers.

"*What Linus did [in discovering the α-helix] was to insist that, from his data on the crystal structures of simple molecules, he could extrapolate. For example that the peptide bond had to be planar.*" (H. F. Judson, *The Eighth Day of Creation*; Simon and Schuster: New York, 1979).

## History: Polymers and X-rays

Following the discovery of X-ray diffraction by von Laue in 1912, and its interpretation in the same year by W. L. Bragg, the technique was almost immediately used to determine the structures of simple ionic crystals, of metals, and, within a few years, of small organic molecules. At the same time, attempts were made, though with much less success, to unravel the structures of crystalline polymers such as fibroin (the protein of silk) and cellulose.[1] Polymer crystallography was slow to yield definitive results because, in comparison with the highly resolved X-ray diffraction patterns obtained from crystals of small molecules, reflections from crystalline polymers were generally rather diffuse, poorly resolved, and few in number.[2] One family of polymers, the globular proteins, did prove an exception to this rule. By the 1930s, a number of such biopolymers had yielded high-quality, macroscopic crystals, giving many thousands of X-ray reflections[3] susceptible in principle, and ultimately (after decades of effort) in practice,[4] to direct analysis by single-crystal methods.

Among the reasons purified enzymes and other globular proteins such as myoglobin and hemoglobin are able to form macroscopic single crystals giving well-resolved, three-dimensional diffraction data are that (i) every molecule in the sample is chemically and stereochemically identical and (ii) strong intramolecular interactions cause the polymer chain to adopt a compact, tightly chain-folded conformation which enables the molecule to pack readily into a conventional crystal lattice. In contrast, synthetic polymers generally contain molecules having a statistical distribution of molecular weights, adopting extended rather than compact chain conformations and, in the case of copolymers, exhibiting a marked nonuniformity of molecular composition. These factors all militate strongly against the formation of macroscopic single crystals so that, although *one*-dimensional diffraction data can be obtained from crystalline polymer powders and *two*-dimensional data may be available from highly oriented polymer fibers,[5] there are few reports of synthetic polymers affording single crystals large enough to yield *three*-dimensional X-ray diffraction patterns.[6]

It is perhaps ironic that the crystal and molecular structures of globular proteins—the most complex of all known macromolecules—can now be almost routinely determined by sophisticated single-crystal methods,[7] while analysis of the far simpler structures of synthetic polymers still remains largely dependent on the trial-and-error approach developed in the 1920s.[8] This latter method involves (i) constructing a three-dimensional trial model for the crystal structure in question, (ii) calculating the diffraction pattern it would produce, and then (iii) progressively refining the model to obtain the best possible fit to the experimental X-ray data. Crucial to this approach is the construction of a *realistic* trial model, without which the method is almost guaranteed to fail. Pauling's approach to protein structure in the 1950s, for example, depended heavily on single-crystal data for peptide oligomers,[9] and in the context of nucleic acid structure Crick has noted that "Furburg's nucleotide (the single-crystal X-ray structure of cytidine) was essential to us".[10]

## Trial Structures from Oligomer Data

Bond lengths and bond angles vary only very slightly between closely related molecular systems, so reliable data of this type can be obtained from single-crystal analyses of small molecules related to the polymer in question.

Howard Colquhoun was educated at Washington Grammar School and Cambridge University. After obtaining a Ph.D. in inorganic chemistry from London University, he carried out research on metallocarboranes at the University of Warwick, before joining ICI plc in 1977, where he was able to develop a latent interest in polymer chemistry. In 1994 he moved to Manchester University as a Royal Society Industrial Fellow, and in 1997 to Salford University, where he is currently Professor of Inorganic Chemistry. His research interests include homogeneous catalysis, molecular assembly, and the structural chemistry of high-performance polymers.

David Williams was educated at the City of London School for Boys and, after a period working in industry, took a degree in physics at the University of Portsmouth. He subsequently gained a Ph.D. in crystallography at Imperial College, London, where he has since held the posts of Research Fellow, Lecturer, Reader, and currently, Professor of Structural Chemistry. His research interests are wide-ranging but center on supramolecular chemistry, noncovalent interactions and their role in controlling crystal structure, metallacyclic network structures, and structure prediction in aromatic polymer systems.

† University of Salford.
‡ Imperial College.

10.1021/ar980123c CCC: $19.00 
Published on Web 02/25/2000

However, these data cannot of themselves define a polymer crystal; conformational and packing data are also required. Here, single-crystal studies of *oligomers* containing a number of repeat units of the polymer itself can provide strong indications of the preferred values of torsion angles within and between monomer residues, though these values are naturally less constrained than are bonding parameters. It has long been established that synthetic polymers generally crystallize by adopting extended molecular conformations which enable the chains to pack parallel to one another,[11] and oligomer structures often reflect this packing mode, enabling the identification of preferred intermolecular interactions and symmetry relationships between adjacent chains.

## High-Performance Polymers

High-performance polymers are here defined as those exhibiting good oxidative stability and mechanical strength above ca. 180 °C. In molecular terms this translates to polymers comprising mainly aromatic or heterocyclic units, connected by thermo-oxidatively stable linkages such as ether, sulfone, sulfide, and ketone, or by direct bonds.[12] Unfortunately, the degree of crystallinity achieved by such materials is often relatively low because of the inflexible character of the chains, and scattering from the amorphous component can obscure significant details of the crystalline diffraction pattern. Moreover, the crystallite dimensions in such polymers are generally restricted to only a few tens of nanometers, resulting in broad and overlapping diffraction peaks. Finally, many crystalline aromatic polymers are both insoluble and infusible below their decomposition temperatures, so that the experimental information can be limited to a simple, one-dimensional, powder pattern. In this situation, the number of unique X-ray data will be very much smaller than the number of independent structural parameters. Bond lengths and bond angles must then be fully constrained in any analysis, and the conformation of the polymer chain and its mode of crystal packing must somehow be restricted to a very small number of possible options.

## Aromatic Polyesters—The Origins of Diffraction Modeling

Although aromatic homopolyesters such as poly(1,4-phenylene terephthalate) (**1**) and poly(4-oxybenzoate) (**2**) are themselves virtually unprocessable, having extremely high crystal melting points and very low solubilities, *co*polyesters of this type (produced commercially as engineering thermoplastics) can display thermotropic mesophase behavior, which enables them to be processed in the liquid-crystalline state.[13] In the solid phase, these random copolymers also display an unusually high degree of three-dimensional crystallinity, the nature of which continues to be the subject of much debate.[14] To clarify the molecular basis of this problem, Windle and coworkers at Cambridge University developed an interactive diffraction-modeling program, which enabled the structure of the "parent" homopolyester (**1**) to be determined from X-ray powder data,[15] an analysis based in part on the single-crystal structure of the oligomer bis(4-biphenylyl)terephthalate (**3**).[16]

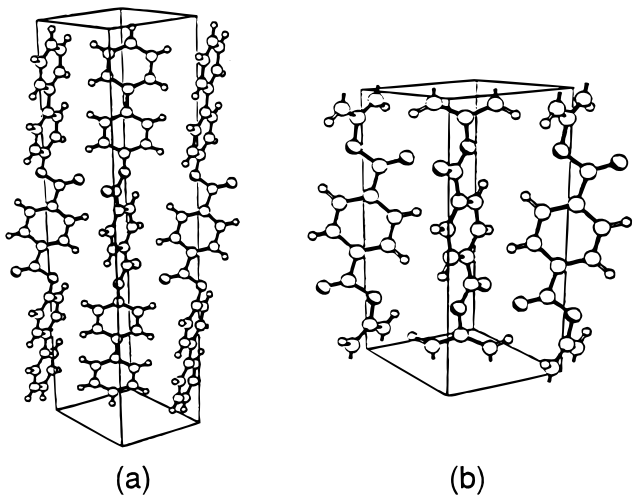
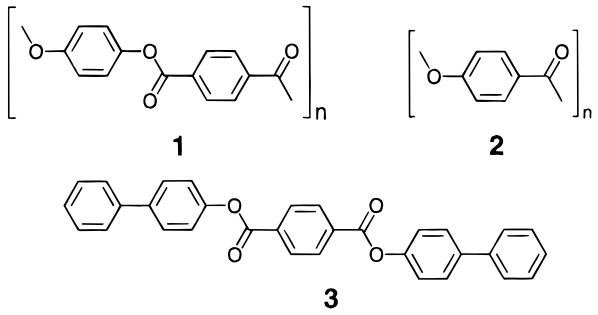



**FIGURE 1.** Crystal and molecular structures of (a) bis(4-biphenylyl)-terephthalate (**3**) and (b) poly(1,4-phenylene terephthalate) (**1**).

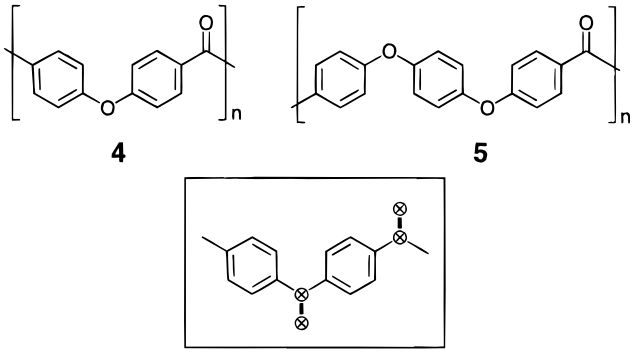



Striking parallels between the crystal structures of oligomer **3** and polymer **1** are evident from Figure 1. Not only are the torsional relationships betwen the ester linkage and its associated aromatic rings in the two structures very similar, but the packing relationships within the unit cell are identical. The oligomer and polymer structures share the same space group ($P2_1/a$), and even the unit cell dimensions of the oligomer crystal ($a = 7.89$, $b = 5.58$, and $c = 12.71$ Å, $\beta = 96.57°$) provide a reasonable model for the polymer cell ($a = 7.98$, $b = 5.33$, and $c = 12.65$ Å, $\beta = 98.98°$).[15]

The commercial diffraction-modeling package *Cerius*$^2$ (Molecular Simulations Inc.) is descended directly from the original Cambridge program, though it now includes facilities for molecular mechanics and crystal-packing calculations, as well as model-building and interactive diffraction simulation.[17] In the context of the present review, it should be noted that single-crystal oligomer data enable the force fields available within such software to be reparameterized so as to accurately reproduce the crystal structure of an oligomer. A high degree of confidence can then be placed on calculations involving the corresponding polymer.

## Aromatic Polyetherketones and Polythioetherketones

Early X-ray fiber diffraction studies of the crystalline, high-temperature thermoplastics known as "polyetherketone" (PEK) (**4**) and "polyetheretherketone" (PEEK) (**5**) suggested strongly that aromatic ether and ketone linkages are crystallographically interchangeable.[18] Thus, polymers **4**

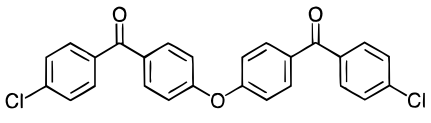


**4** **5**

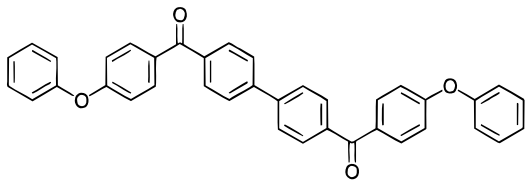


**6**

and **5** adopt the same disordered crystal structure (space group *Pbcn*), based on a two-ring polymer-repeat (**6**) in which the linking groups represent a weighted average of ether and ketone units. It was concluded, from the length of the polymer *c*-axis (which by convention is oriented parallel to the polymer chain), that the average in-chain ether/ketone bond angle must lie in the range 124−127°.[19] However, this result requires a considerable distortion of these bond angles from the accepted range of 121−122° found in small molecules, and we therefore synthesized a number of ether−ketone oligomers, including **7** and **8**, to look for more definitive evidence of such distortions.[20]



**7**



**8**

The single-crystal structure of oligomer **7** is shown in Figure 2, viewed down the *c*-axis, together with a similar view of the (disordered) structure of PEK (**4**). The polymer structure reflects the oligomer structure very closely indeed, even to the extent of their sharing the same space group (*Pcan* is just an alternative setting of *Pbcn*). However, the proposed distortions of bridge-bond angles are *not* evident in the oligomer structure, the angles at ether and ketone remaining in the range 121−122°. It emerged from this study that the structural perturbations required to produce the observed *c*-axis length do not arise from

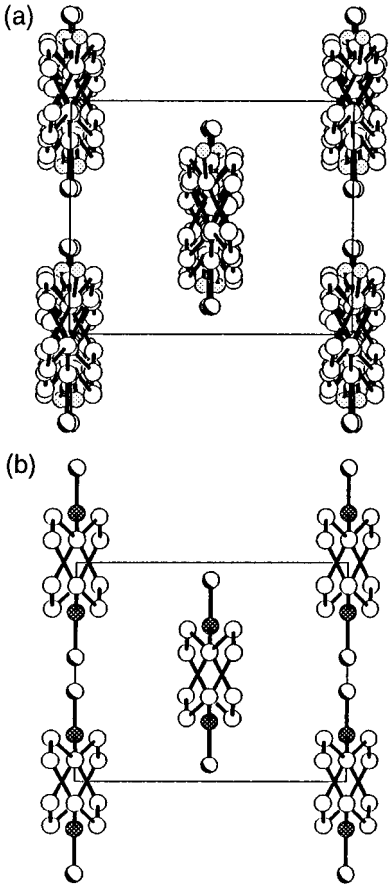



**FIGURE 2.** Crystal structures of (a) 4,4′-bis(4-chlorobenzoyl)-diphenylether (**7**) and (b) polyetherketone (**4**) viewed along the crystallographic *c*-direction.

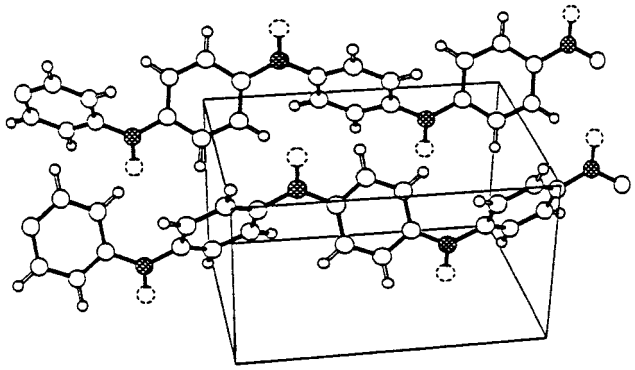
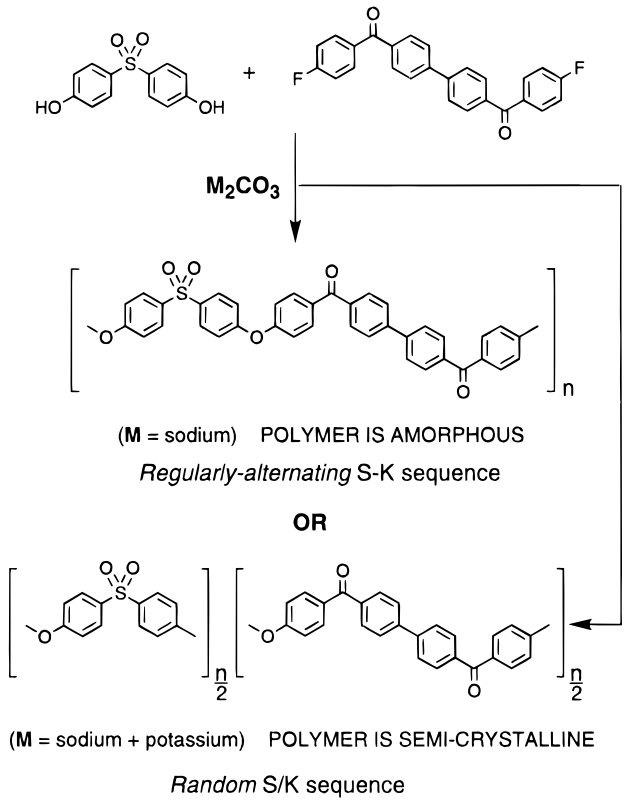


**FIGURE 3.** Crystal and molecular structure of polyetherketone (**4**) in space group *Pbcn*. Crosshatched circles represent an averaged superposition of ether oxygen and carbonyl carbon atoms, and dashed circles represent half-occupancy carbonyl oxygen atoms.

opening up the bridge bonds (C−O−C or C−C−C) but, perhaps surprisingly, from *in-plane distortions* at the arene carbons adjacent to them.[20] Only minor modifications to the *Cerius*[2] universal force field were needed to reproduce these distortions, and a very satisfactory model for PEK (**4**) was thus obtained (Figure 3).

A significant early success of oligomer-based diffraction modeling was the analysis of a remarkable polymer system, in which monomer sequence randomization within a formerly alternating polymer chain leads to

**Scheme 1. Synthesis of the Two Forms (One Alternating, One Random) of Polymer 9**




induction of crystallinity.[21] Thus, the aromatic polyether (**9**) formed by high-temperature polycondensation of 4,4′-dihydroxydiphenylsulfone with 4,4′-bis(4-fluorobenzoyl)-biphenyl was found (depending on polymerization conditions) to be either amorphous, with alternating subunits-[−OArSO$_2$Ar−] ("S") and [−OArCOArArCOAr−] ("K"), or semicrystalline, with the distribution of "S" and "K" units now unexpectedly *random* (Scheme 1). This latter polymer results from extensive transetherification, catalyzed by the coproduct fluoride ion, and the system in fact represents a classic example (more often seen in biology than in chemistry) of the way in which a random sequence of monomer residues contains more information than a regular one. The "information" in this case is represented by consecutive sequences of the "K" subunits [−OArCOArArCOAr−]$_n$ ($n \geq 3$) which are statistically present inthe random polymer (but not in its regularly alternating isomer) and which can thus aggregate and crystallize on cooling from the melt.[21]

This interpretation of an, at first sight, rather improbable result was confirmed when the crystalline phase of the random polymer was identified by X-ray fiber diffraction as [−OArCOArArCOAr−]$_n$. The crystal structure of this previously unknown phase was finally determined by diffraction modeling using data from the single-crystal structure of oligomer **8** (Figure 4). The polymer chain was generated simply by removing the terminal phenyl rings from an oligomer molecule and placing a twofold rotation axis at each terminal ether oxygen. After minor adjustments were made to the oligomer-derived unit cell

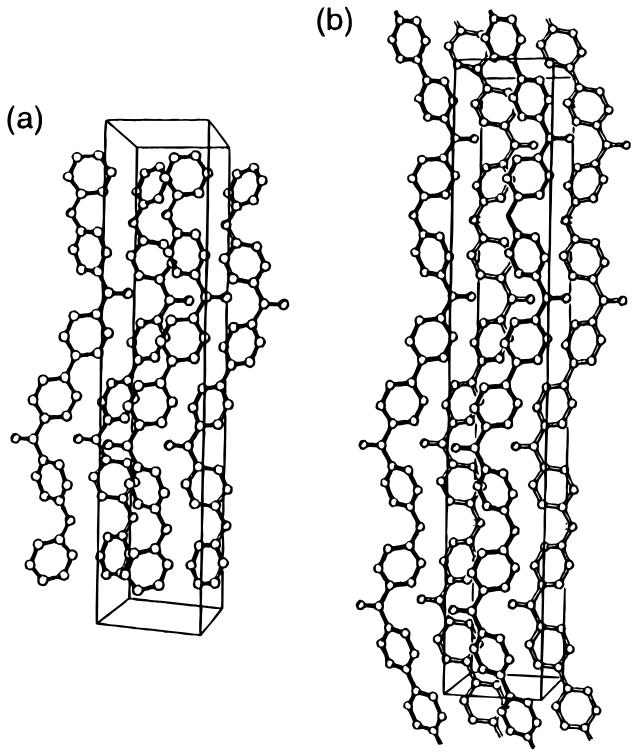



**FIGURE 4.** Structures of (a) 4,4′-bis(4-phenoxybenzoyl)biphenyl (**8**) and (b) the crystalline phase [−OArCOArArCOAr−]$_n$ of polymer **9** (Ar = 1,4-phenylene).

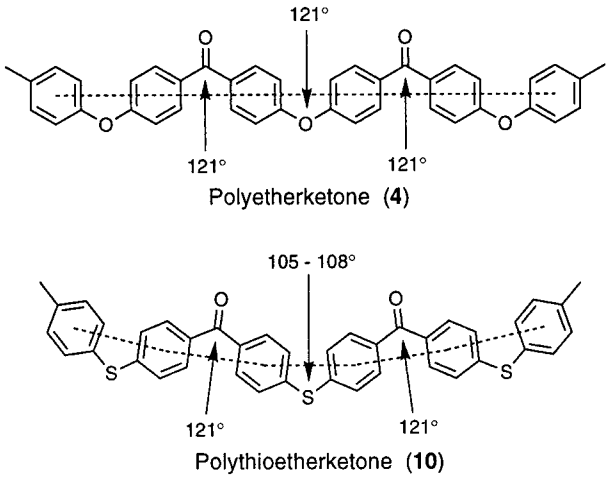
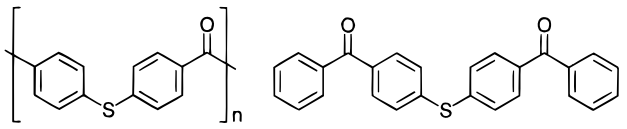



**FIGURE 5.** Predicted bond angles and chain geometries in polyetherketone (**4**) and polythioetherketone (**10**).

dimensions, an excellent match between observed and simulated polymer fiber diffraction patterns was obtained.[21]

The ability of polyetherketones to crystallize rapidly from the melt is generally ascribed to the geometrical equivalence of aromatic ether and carbonyl linkages noted above, which leads directly to the linear chain geometry required for polymer crystallization (Figure 5).[18] A conceptual challenge was thus posed by the facile thermal crystallization observed for aromatic poly*thio*etherketones such such as polymer **10**,[22] since the accepted bond angles

at thioether (105−108°) and carbonyl groups (120−122°)are very different indeed (Figure 5).[23]



**10** **11**

Single-crystal X-ray data for oligomer **11** showed that bond angles at the thioether and carbonyl linkages are in the expected ranges, at 108° and 121°, respectively, but the oligomer is nevertheless essentially linear. Linearization of the oligomer chain (presumably driven by an enhancement of crystal lattice energy) is achieved by pyramidalization of the carbon atoms adjacent to the thioether bridge, which opens up the *effective* angle between aromatic rings linked by the thioether group very considerably. On this basis, a geometrically linear model for polythioetherketone **10** was readily constructed.[24]

The crystal structure of melt-crystallized polymer **10** was originally suggested (from very limited X-ray powder data)[25] to be analogous to that shown in Figure 3 for PEK (**4**). However, we recently obtained a greatly improved experimental powder pattern for polymer **10** which showed clearly that this proposal could not be correct (Figure 6a). We have now established 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 calculated powder pattern is in vastly better agreement with experiment (Figure 6b).[26]

In this new, body-centered structure (Figure 7) the thioether linkages in symmetry-related chains are no longer in register but are offset in the *c*-direction by half a unit cell, so avoiding a number of sub-van der Waals [S····H] contacts which are present in the original PEK-type model. Minimization of crystal-packing energy for the body-centered structure leads to a monoclinic rather than an orthorhombic cell, and optimization of the unit cell and broadening parameters eventually yielded a crystal structure for which the agreement between experimental and simulated peak positions was very good indeed.[26] Evaluation of the symmetry elements in the model (Figure 7) resulted in assignment of the space group *I*2.

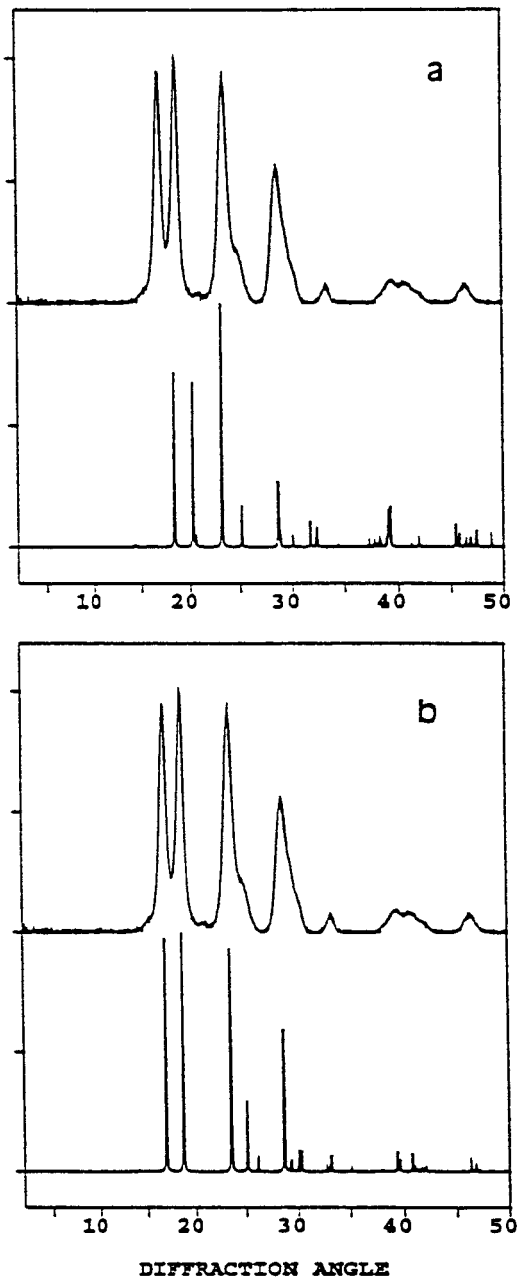



**FIGURE 6.** (a) Experimental powder pattern for melt-crystallized polymer **10** and a simulated pattern (unbroadened) for an ordered PEK-type structure. (b) Experimental powder pattern and a simulated pattern for the body-centered crystal structure shown in Figure 9.

## Aromatic Polysulfones

Structural analysis of aromatic polysulfones has always been restricted by the amorphous character of poly*ether*-sulfones such as **12**, **13**, and **14** (see later) and by the extreme intractability of crystalline materials such as poly-(1,4-phenylenesulfone) (**15**).[27]

A unit cell *was* reported for poly(1,4-phenylenesulfone) in 1980,[28] but doubt has been cast on this result by suggestions that oxidation of the oriented poly(1,4-phenylenesulfide) films ultimately used for fiber diffraction may have resulted in cross-linking rather than conversion to poly(1,4-phenylenesulfone).[29] Even recent attempts to approach the problem of polysulfone structure via computer simulation have reached conflicting conclusions regarding the preferred torsional relationships between the sulfone unit and its adjacent aromatic rings.[30] Our preliminary analysis of single-crystal data for small molecules, however, revealed that, in unstrained systems, the diarylsulfone unit most frequently adopts an "open-book" conformation in which the rings lie essentially orthogonal to the C−S−C plane. This conformation has been qualitatively interpreted as arising from maximization of $\pi$-overlap between vacant d-orbitals on sulfur and filled arene p-$\pi$ orbitals,[31] although higher level theoretical studies are probably needed to substantiate this idea.

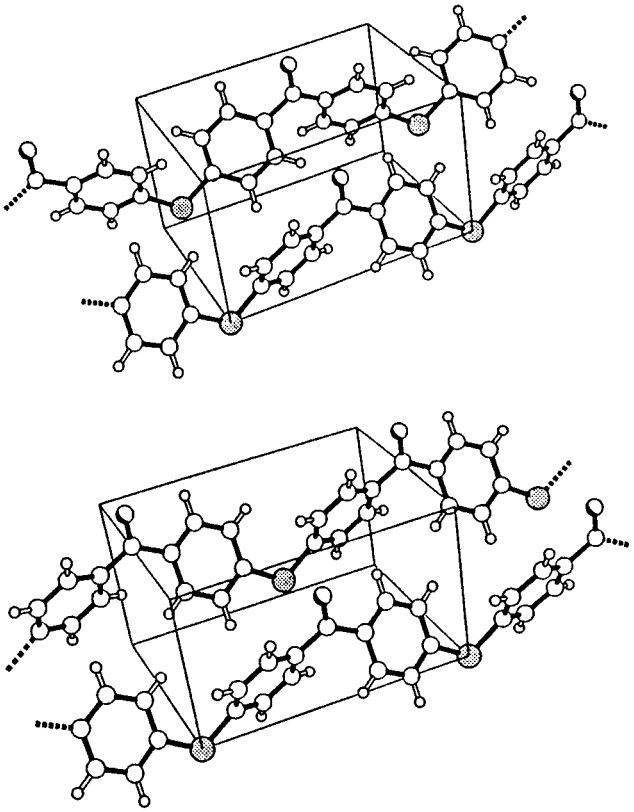
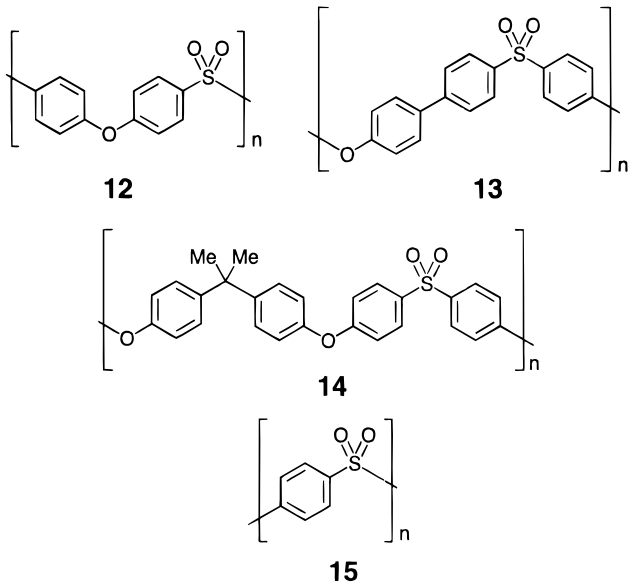


**FIGURE 7.** Initial model (above) and final model (below) for the crystal structure of polymer **10**. The final model is body-centered monoclinic, space group *I*2. The C−S−C and C−$C_{ket}$−C bond angles are 107 and 122° respectively. The C−S bond subtends an angle of 10° to the mean plane of its associated aromatic ring, with the sulfur atom lying 0.24 Å out of this plane.




The recent report of an unequivocal synthesis of polymer **15**, and the availablity of good-quality X-ray powder data,[32] suggested that the previously conflicting views concerning polysulfone structures might be resolved by a diffraction-modeling study. Poly(1,4-phenylenesulfone) (**15**) was thus modeled using a force field edited to reproduce not only crystallographically derived bond lengths and angles for aromatic sulfones but also the 90° torsion angle between aromatic rings and the C−S−C plane. Minimization of crystal packing energy led to a primitive monoclinic lattice which transformed to centered orthorhombic symmetry, and adjustment of simulated crystallite size, lattice strain, and temperature factors eventually produced an extremely good overall match with the experimental powder pattern (Figure 8). Evaluation of the symmetry elements present in the final model (Figure 9) identified the space group as *Cmcm*.[33]

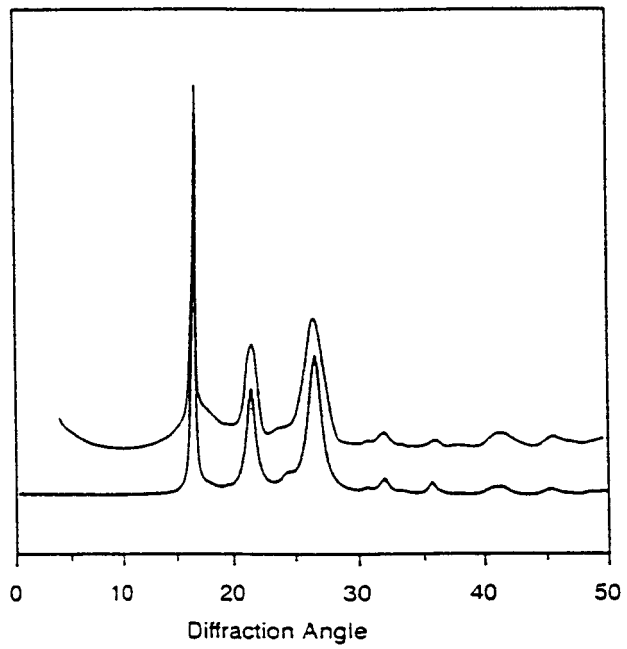



**FIGURE 8.** Experimental (upper trace) and simulated (lower trace) X-ray powder patterns for poly(1,4-phenylenesulfone) (**15**).

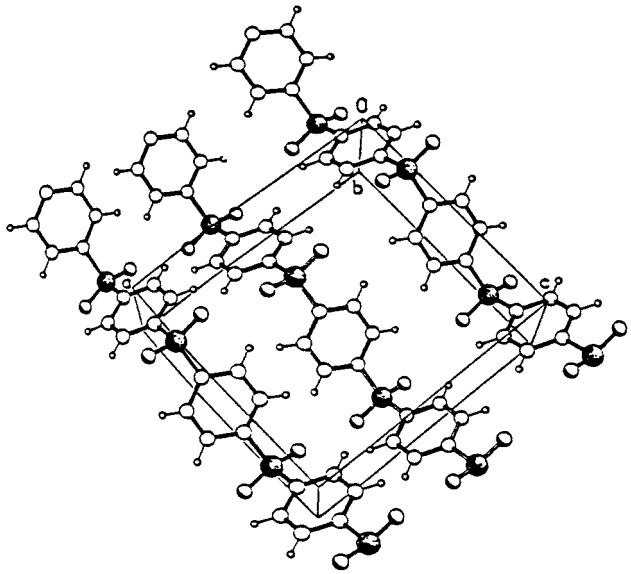
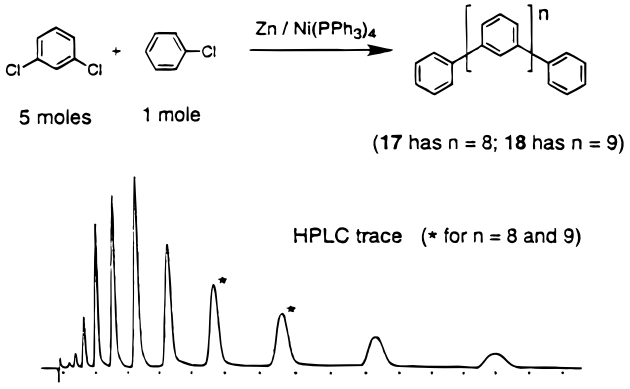



**FIGURE 9.** Perspective view of the crystal structure of poly(1,4-phenylenesulfone) (**15**).

## Polyphenylenes

In recent years, poly(*p*-phenylene) has been intensively studied, not only as a high-performance material [34] but

**Scheme 2. Synthesis and Fractionation by HPLC of *m*-Phenylene Oligomers**




also, after doping, for its potential as an organic conductor.[35] In contrast, very little was known until recently of the isomeric poly(*m*-phenylene) (**16**), though an X-ray powder pattern published in 1978 showed the polymer to be crystalline.[36] In 1993, we were able to isolate milligram quantities of the oligomers $C_6H_5-(m\text{-}C_6H_4)_n-C_6H_5$ ($n = 6-10$) by analytical-scale HPLC fractionation of low-molecular-weight poly(*m*-phenylene) (Scheme 2), and it ultimately proved possible to obtain small but high-quality single crystals of both the 10- and 11-ring oligomers **17** and **18**.[37]

To our astonishment, the X-ray structure of *m*-deciphenyl ($C_6H_5-(m\text{-}C_6H_4)_8-C_6H_5$, **17**) revealed a lattice of apparently *infinite* helical chains, with five aromatic rings to each turn of the helix (Figure 10). Individual chains have crystallographic $C_2$ symmetry normal to the chain axis and are all of the same helicity, as required by the polar tetragonal space group ($P4_12_12$ or $P4_32_12$). Chains are oriented with their long axes parallel to the crystallographic *c*-direction. Analysis of the site occupancies for individual atoms in the crystal (ca. 90%) strongly suggests that the positions of the oligomer chain ends are not correlated between pseudo-polymer chains but occur as random point defects in the crystal. Moreover, since oligomers **17** and **18** are isomorphous, it seems almost certain that higher oligo-*m*-phenylenes will adopt the same type of structure.[37] This result—that an oligomer can form macrocopic single crystals *in which it simply adopts the corresponding polymer lattice*—appears to be unprecedented. Nevertheless, comparison of the X-ray powder pattern predicted from the single-crystal structure of *m*-deciphenyl with experimental powder data from a sample of poly(*m*-phenylene) leaves little doubt as to the accuracy of the predicted polymer structure,[37] and we are currently attempting to extend this approach to other polymer systems.

As part of a related synthetic program, aimed at generating polyphenylenes in which icosahedral carborane units are incorporated into the polymer chain, we found that catalytic polycondensation of the all-*para* bifunctional monomer 1,12-bis(4-chlorophenyl)-1,12-dicarbadodecaborane (**19**) gave a rodlike polymer (**20**) which crystallized spontaneously from the reaction solution

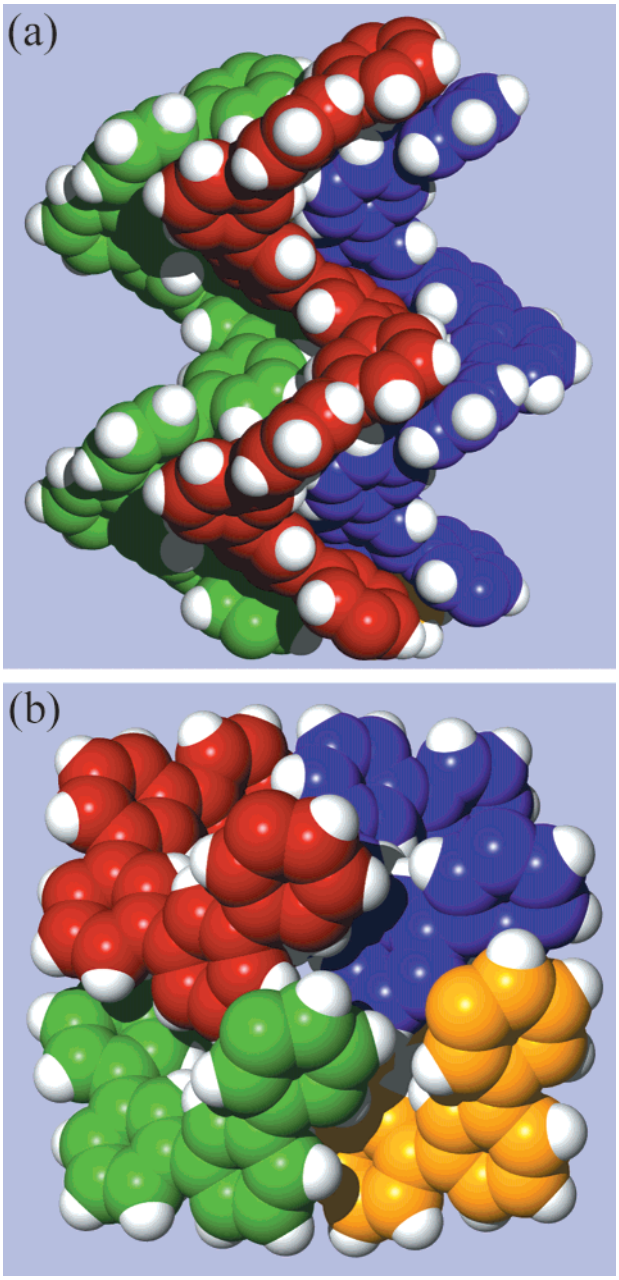
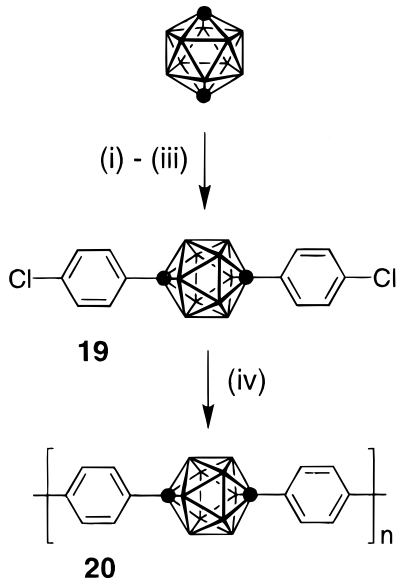



**FIGURE 10.** (a) Single-crystal X-ray structure of *m*-deciphenyl (**17**) showing four molecules (one partially hidden), each forming a continuous pseudo-polymeric helical chain. (b) Tetragonally packed, interleaving helical chains in the crystal of *m*-deciphenyl (**17**) viewed along the crystallographic *c*-direction.

(Scheme 3).[38] This material showed no evidence of melting or softening up to 600 °C, but it gave a well-defined X-ray powder diffraction pattern (Figure 11), suggesting that its intractability stems from a very high crystal melting point and not from cross-linking or other side reactions associated with the synthesis.

The X-ray powder pattern of polymer **20** (Figure 11, upper trace) could be indexed in terms of a *C*-face-centered monoclinic unit cell with dimensions $a = 9.11$, $b = 11.77$, and $c = 13.33$ Å, $\beta = 144.4°$. On the basis of a known, single-crystal oligomer structure,[38] crystallographic inversion centers were placed both at the center of the

**Scheme 3. Synthesis of Rigid-Rod Poly(biphenylene-carborane) 20[a]**




[a] Reagents: (i) BuLi, (ii) CuCl, (iii) 1,4-$ClC_6H_4I$, (iv) Zn, $Ni(PPh_3)_4$.

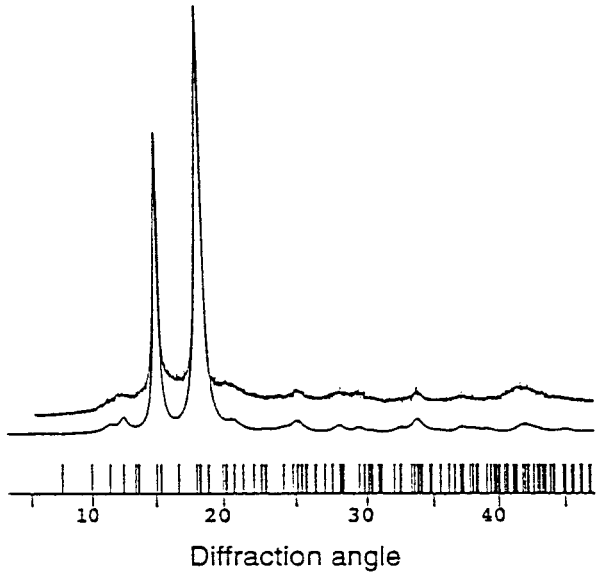



**FIGURE 11.** Experimental (upper trace) and simulated (lower trace) powder diffraction patterns for poly(4,4′-biphenylene-1,12-dicarba-dodecaborane) (**20**), for the crystal structure shown in Figure 12.

carborane cage and at the center of the biphenyl linkage, so defining a polymer chain in which the aromatic rings are effectively coplanar and leaving only the torsion angle Δ between the carborane cage and its associated aromatic rings to be determined. Crystal-packing calculations indicated an energy minimum for the chain conformation in which Δ = 18°, and a simulated powder diffraction pattern based on this structure (space group *C*2/*m*, Figure 12) is shown in Figure 11, together with the experimental powder pattern. The agreement is clearly very good indeed.[38] Crystalline polymers based on carborane units have been known for more than 30 years,[39] yet this appears to be the first polymeric carborane whose crystal structure has been determined.

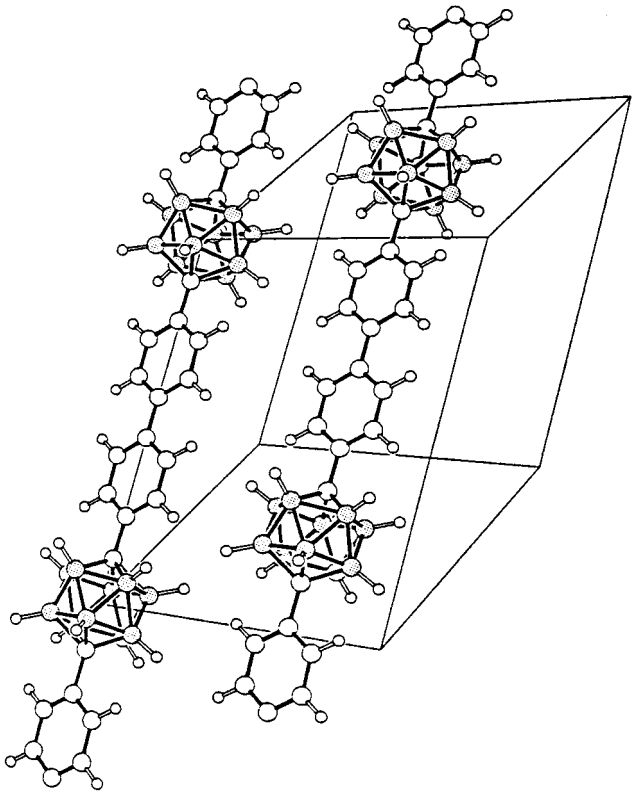


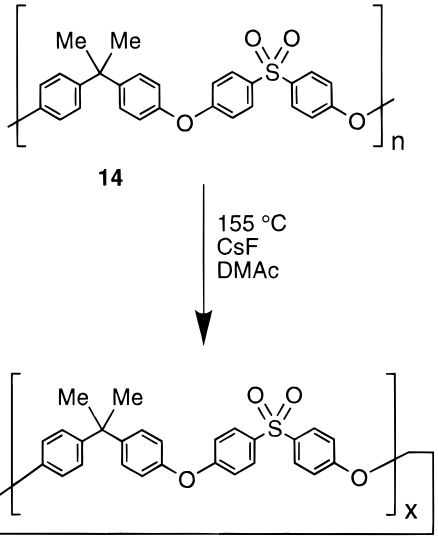
**FIGURE 12.** Crystal and molecular structure of polymer **20** from diffraction modeling (centered monoclinic, space group *C*2/*m*).

## Crystalline Models for Amorphous Polymers

In view of the inevitable lack of detailed structural information for *non*crystalline high-performance polymer such as the polyethersulfones,[40] we set out to isolate monodisperse oligomers of these materials in an attempt to obtain single-crystal X-ray data. Although linear oligomers turned out to have little greater tendency to crystallize than their parent polymers, we have recently discovered that very large *cyclic* oligomers of aromatic polyethersulfones often afford high-quality single crystals.[41] Perhaps the best examples here are macrocyclic homologues of thermoplastic **14**, which undergoes fluoride-promoted cyclo-depolymerization in dipolar aprotic solvents (Scheme 4) to give a family of macrocyclic oligomers ranging from the cyclic [2 + 2] dimer (MW 906) up to at least the cyclic [18 + 18] octadecamer (MW 7980).[42] The situation seems analogous to that for globular proteins in that the crystallizability of these macrocycles can be associated with fully defined, monodisperse, and conformationally compact molecular structures. It might be noted in passing that many globular proteins are themselves macrocyclic, the nominally linear polypeptide chains being intramolecularly cross-linked by one or more covalent disulfide bridges.

Single-crystal X-ray data have so far been obtained for three macrocyclic homologues of polymer **14**,[42,43] and here we comment specifically on the cyclic *trimer* (**21**). This compound not only folds spontaneously into the approximate shape of a tennis ball seam but also self-

**Scheme 4. Ring-Closing Depolymerization of Bisphenol-A Polysulfone (14)**




(x = 2 to >18; Macrocycle **21** has x = 3

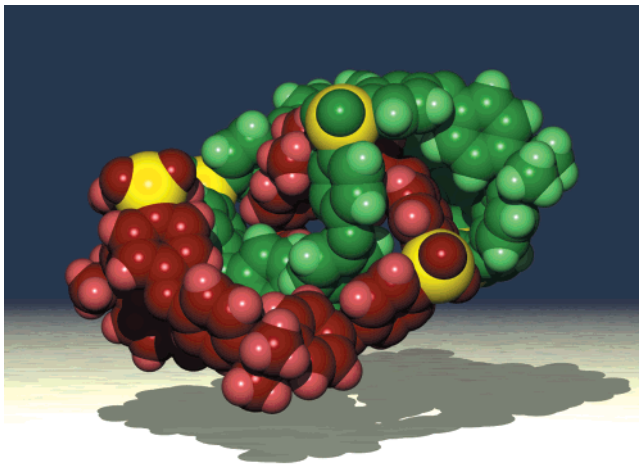


**FIGURE 13.** Molecular structure of the cyclic trimer **21**, illustrating its tennis-ball-seam-like conformation, and the mutual interpenetration of paired enantiomeric macrocycles found in the solid state.

associates in the solid state to form a centrosymmetric, noncovalent dimer containing pairs of intertwined enantiomeric macrocycles (Figure 13). Isopropylidene groups mutually insert through the loops of complementary oligomer chains, and residual clefts in the surface of the dimer are populated by included acetonitrile molecules. The diarylsulfone units largely retain the open-book conformation established for poly(1,4-phenylenesulfone), and stabilization of the dimer is achieved through a combination of face-to-face $\pi$-stacking and C—H$\cdots\pi$ interactions. It is not yet clear how far such a structure actually *does* reflect that of (amorphous) bisphenol A polysulfone (**14**), but in this context it is by far the most relevant experimental result so far obtained.

## Concluding Remarks

The oligomer crystallographic/diffraction-modeling technique outlined in this Account clearly provides a highly effective approach to the determination of aromatic polymer structure from limited X-ray data, though it remains to be seen whether the remarkable case of poly(*m*-phenylene), in which the crystal structure of the polymer is revealed directly in the structure of its 10-ring oligomer, can be generalized to other polymer systems. Readers should also note that a different approach to the structural analysis of aromatic polymer systems, involving simulation of electron diffraction patterns from melt-grown microcrystals, has been developed by Geil and coworkers,[44] and that we ourselves have also successfully investigated a number of materials not discussed in the present review.[45]

Finally, the isolation of crystalline, *macrocyclic* oligomers of amorphous polyethersulfones has enabled previously inaccessible structural data to be obtained for these materials. In the longer term, it seems likely that crystallization of very much higher macrocyclic oligomers (when eventually isolated as pure, monodisperse compounds) may well allow a "protein crystallographic" approach to the structural analysis of conventionally amorphous polymers.

*We thank the Royal Society, the Engineering and Physical Sciences Research Council of the United Kingdom, and the University of Salford Academic Development Fund for grants in support of this work.*

## References

(1) Herzog, R. O. The fine structure of fibrous materials. *Naturwissenschaften* **1924**, *12*, 255.
(2) Astbury, W. T. X-ray diffraction photographs of vegetable and animal fibers. *Photogr. J.* **1932**, *72*, 318.
(3) Bernal, J. D.; Crowfoot, D. X-ray photographs of crystalline pepsin. *Nature* **1934,** *133*, 794.
(4) Perutz, M. F. Recent advances in molecular biology. *Endeavour* **1958**, *17*, 190.
(5) Tadokoro, H. Structure and properties of crystalline polymers. *Polymer* **1984**, *25*, 147.
(6) Polymer single crystals are occasionally accessible by solid-state polymerisation; single crystals of polyoxymethylene, $[CH_2O]_n$, can for example be obtained by polymerization of the cyclic tetramer $[CH_2O]_4$ in the crystalline state. See: Tadokoro, H. Structural studies of several helical polymers. *J. Polym. Sci.* **1966**, *C15*, 1.
(7) Helliwell, J. R.; Helliwell, M. X-ray crystallography in structural chemistry and molecular biology. *Chem. Commun.* **1996**, 1595.
(8) See, for example: Hengstenberg, J. X-ray investigation of the structure of the carbon chain in hydrocarbons. *Z. Kristallogr.* **1928**, *67*, 583.
(9) Carpenter, G. B.; Donohue, J. The crystal structure of N-acetylglycine. *J. Am. Chem. Soc.* **1950**, *72*, 2315. Pauling, L.; Corey, R. B.; Branson, H. R. The structure of proteins: two hydrogen bonded helical configurations of the polypeptide chain. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 205.
(10) Crick, F. H. C., quoted in: Judson, H. F. *The Eighth Day of Creation*; Simon and Schuster: New York, 1979; p 324. Furberg, S. Crystal structure of cytidine. *Nature* **1949**, *164*, 22.
(11) Bunn, C. W. The crystal structure of long-chain normal paraffin hydrocarbons. The "shape" of the $CH_2$ group. *Trans. Faraday Soc.* **1939**, *35*, 482.
(12) *High Performance Polymers: Their Origin and Development*; Seymour, R. B., Kirshenbaum, G. S., Eds.; Elsevier: New York, 1986.
(13) Economy, J. Aromatic polyesters of *p*-hydroxybenzoic acid. *Mol. Cryst. Liq. Cryst.* **1989**, *169*, 1. Jackson, W. J. Liquid crystal polymers XI: early history and future trends. *Mol. Cryst. Liq. Cryst.* **1989**, *169*, 23.
(14) Mitchell, G. R.; Windle, A. H. Structural analysis of an oriented liquid crystal copolyester. *Polymer* **1982**, *23*, 1269. Blackwell, J.; Biswas, A.; Gutierrez, G. A.; Chivers, R. A. X-ray analysis of some liquid crystalline polyesters. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 73. Windle, A. H.; Viney, C.; Golombok, R.; Donald, A. M.;

Mitchell, G. R. Molecular correlation in thermotropic copolyesters. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 55. Blackwell, J.; Cheng, H.-M.; Biswas, A. X-ray analysis of the structure of the thermotropic copolyester XYDAR. *Macromolecules* **1988**, *21*, 39. Lemmon, J. T.; Hanna, S.; Windle, A. H. Non-periodic layer crystallites in a thermotropic random copolymer. *Polym. Commun.* **1989**, *30*, 2.

(15) Coulter, P. D.; Hanna, S.; Windle, A. H. A methodology for determining the crystal structures of polymers using powder X-ray diffraction and molecular modelling. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1989**, *30* (2), 140. Hanna, S.; Coulter, P. D.; Windle, A. H. Determination of the crystal structure of poly(*p*-phenylene terephthalate) from powder diffraction data. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2615.

(16) O'Mahoney, C. A.; Williams, D. J.; Colquhoun, H. M.; Blundell, D. J. Single crystal X-ray studies of aromatic oligomers: conformation and packing in oligomeric isophthalate and terephthalate esters. *Polymer* **1990**, *31*, 1603.

(17) *Cerius*$^2$ V. 3.5; Molecular Simulations Inc., San Diego, CA, 1997.

(18) Dawson, P. C.; Blundell, D. J. X-ray data for poly(aryl ether ketones). *Polymer* **1980**, *21*, 577

(19) Rueda, D. R.; Ania F.; Richardson, A.; Ward, M.; Balta Calleja, F. J. X-ray diffraction study of die drawn poly(aryletherketone) (PEEK). *Polym. Commun.* **1983**, *24*, 258. Wakelyn, N. T. On the structure of poly(etheretherketone) (PEEK). *Polym. Commun.* **1984**, *25*, 306. Hay, J. N.; Kemmish, D. J. The conformation of crystalline poly(aryl ether ketones). *Polym. Commun.* **1989**, *30*, 77.

(20) Colquhoun, H. M.; O'Mahoney, C. A.; Williams, D. J. Single-crystal X-ray diffraction studies of aromatic oligomers: resolution of the bond-angle anomaly in poly(aryletherketone)s. *Polymer* **1993**, *34*, 218.

(21) 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. An aromatic polyether in which sequence-randomisation leads to induction of crystallinity: X-ray structure of the crystalline phase $[-OArCOArArCOAr-]_n$ (Ar = 1.4-phenylene). *Macromolecules* **1993**, *26*, 107.

(22) Feasey, R. G. (ICI). Thiophenol polymers. German Patent 2,164,-291, 1972.

(23) Hasebe, K.; Asahi, T.; Ishazawa, A.; Izumi, K. Structure of *p*-bis-(phenylthio)benzene: a redetermination. *Acta Crystallogr.* **1989**, *C45*, 2023.

(24) Colquhoun, H. M.; Lewis, D. F.; Williams, D. J. Crystal and molecular structure of poly(thioether-ketone) from single-crystal oligomer data and diffraction modeling. 1. Polymer crystallised by orientation. *Polymer* **1999**, *40*, 5415.

(25) Takahashi, T.; Hii, S.-H.; Sakurai, K. J. Crystal morphology and polymorphism of a wholly aromatic thermoplastic polymer, poly-(ketone sulfide). *J. Macromol. Sci.–Phys.* **1998**, *B37*, 59.

(26) Colquhoun, H. M.; Lewis, D. F.; Williams, D. J. Crystal and molecular structure of poly(thioether-ketone) from single-crystal oligomer data and diffraction modeling. 2. Polymer crystallised from the melt or from solution. *Macromolecules* **1999**, *32*, 3384.

(27) Gabler, R.; Studinka, J. Novel poly(phenylenesulfone) reactions on solid polymers. *Chimia* **1974**, *28*, 567.

(28) Tsvankin, D. Y.; Papkov, V. S.; Dubovik, I. I.; Sergeev, V. A.; Nedel'kin, V. I. Structure of crystalline poly(*p*-phenylenesulfone). *Vysokomol. Soedin., Ser. B* **1980**, *22*, 366.

(29) Hawkins, R. T. Chemistry of the cure of poly(phenylenesulfide). *Macromolecules* **1976**, *9*, 189.

(30) Fan, C. F.; Hsu, S. L. Application of the molecular simulation technique to generate the structure of an aromatic polysulfone system. *Macromolecules* **1991**, *24*, 6244. Hamerton, I.; Heald, C. R.; Howlin, B. J. Molecular simulation of the comparative flexibility of bridging linkages in poly(aryl ether sulfone)s and poly-(aryl ether ketone)s from a study of isolated oligomers. *Macromol. Theory Simul.* **1996**, *5*, 305.

(31) Koch, H. P.; Moffit, W. E. Conjugation in sulfones. *J. Chem. Soc.* **1951**, 7.

(32) Robello, D. R.; Ulman, U.; Urankar, E. J. Poly(*p*-phenylenesulfone). *Macromolecules* **1993**, *26*, 6718.

(33) Colquhoun, H. M. Crystal and molecular simulation of poly(1,4-phenylenesulfone). *Polymer* **1997**, *38*, 991.

(34) Kovacic, P.; Jones, M. B. Dehydro coupling of aromatic nuclei by catalyst-oxidant systems: poly(*p*-phenylene). *Chem. Rev.* **1987**, *87*, 357.

(35) Elsenbaumer, R. L.; Shacklette, L. W. Phenylene-based conducting polymers. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol.1, p 213.

(36) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. A novel type of polycondensation reaction utilizing transition-metal catalyzed C–C coupling. 1. Preparation of thermostable polyphenylene type polymers. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091.

(37) Williams, D. J.; Colquhoun, H. M.; O'Mahoney, C. A. The structure of poly(*m*-phenylene): a prediction from single-crystal X-ray studies of *m*-deciphenyl and *m*- undeciphenyl. *J. Chem. Soc., Chem. Commun.* **1994**, 1643.

(38) Colquhoun, H. M.; Herbertson, P. L.; Wade, K.; Baxter, I.; Williams, D. J. A carborane-based analogue of poly(*p*-phenylene). *Macromolecules* **1998**, *31*, 1694.

(39) Peters, E. N. Poly(dodecacarborane-siloxanes). *J. Macromol. Sci., Rev. Macromol. Chem.* **1979**, *C17*, 173.

(40) Methods are, however, being developed which may enable structural information for amorphous polymers to be obtained using neutron scattering techniques. See, for example: Rosi-Schwartz, B.; Mitchell, G. R. Extracting quantitative structural parameters for disordered polymers from neutron scattering data. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1995**, *354*, 17.

(41) Ben-Haida, A.; Baxter, I.; Colquhoun, H. M.; Hodge, P.; Kohnke, F. H.; Williams, D. J. Ring-closing depolymerisation of aromatic polyethers. *J. Chem. Soc., Chem. Commun.* **1997**, 1553.

(42) Baxter, I.; Ben-Haida, A.; Colquhoun, H. M.; Hodge, P.; Kohnke, F. H.; Williams, D. J. Cyclodepolymerisation of bisphenol A polysulfone: evidence for self-complementarity in macrocyclic poly(ether sulfones). *J. Chem. Soc., Chem. Commun.* **1998**, 2213.

(43) Colquhoun, H. M.; Williams, D. J. Isolation and structural characterisation of the macrocyclic dimer present in bisphenol-A polysulfone. *Macromolecules* **1996**, *29*, 3311.

(44) See, for example: Liu, J.; Yuan, B. L.; Geil, P. H.; Dorset H. L. Chain conformation and crystal packing in poly(*p*-oxybenzoate) single crystals at ambient temperature. *Polymer* **1997**, *38*, 6031. Liu, J.; Cheng, S. Z. D.; Geil, P. H. Morphology and crystal structure of poly(*p*-phenylene terephthalamide) prepared by melt polymerisation. *Polymer* **1996**, *37*, 1413 and references therein.

(45) Baxter, I.; Colquhoun, H. M.; Kohnke, F. H.; Lewis, D. F.; Williams, D. J. Chain- conformation and chain-folding in 'PK 99': Evidence from single-crystal X-ray studies of linear and cyclic oligomers. *Polymer* **1999**, *40*, 607. Baxter, I.; Colquhoun, H. M.; Hodge, P.; Kohnke, F. H.; Lewis, D. F.; Williams, D. J. Macrocyclic oligomers of the aromatic polyetherketone 'PK99': Synthesis, fractionation, structural characterisation and ring-opening polymerisation. *J. Mater. Chem.* **2000**, *10*, 309.

AR980123C