Polyethersulfone polymers and oligomers – Morphology and crystallization

Abdelkader Benhalima, François Hudon, Finda Koulibaly, Christian Tessier, and Josée Brisson

Abstract: Crystal forms of polyethersulfones (PES) were investigated by using a model compound and a low molecular weight oligomer. These are amorphous as-synthesized, and can undergo solvent-induced crystallization under the appropriate conditions. The model compound, 4,4'-bis(*p*-methoxyphenoxy)diphenyl sulfone, yielded monocrystals, and its structure was solved using X-ray diffraction. Conformational disorder is present, two conformers cohabiting in 55:45 proportions. This model compound, combined to previous structural studies published in the literature, served as a basis for conformational studies of polyethersulfone. Low molecular weight polymers submitted to solvent-induced crystallization resulted in a PES crystal form different from that previously published in the literature, as shown by powder X-ray diffraction.

Key words: polyethersulfone, solvent-induced crystallization, crystal structure, polymorphism, X-ray diffraction.

Résumé : On a étudié les formes cristallines de sulfones de polyéthers (SPE) en se basant sur un composé modèle et un oligomère de faible poids moléculaire. Ces sont des produits amorphes obtenus par une synthèse-as et, dans des conditions appropriées, ils peuvent donner lieu à une cristallisation induite par un solvant. Le composé modèle, le sulfone de 4,4'-bis(*p*-méthoxyphénoxy)diphényle, peut être isolé sous la forme de monocristaux et on a déterminé sa structure par diffraction des rayons-X. On a décelé un désordre conformationnel alors que deux conformères coexistent dans des proportions de 55 : 45. Les données relatives au composé modèle combinées aux études publiées antérieurement sur les structures ont servi de base pour les études conformationnelles des sulfones de polyéthers. Les polymères de faibles poids moléculaires soumis à une cristallisation induite par un solvant ont conduit à la formation de SPE dont la forme cristalline, d'après la diffraction des rayons-X, serait différente de celles rapportées antérieurement dans la littérature.

Mots-clés : sulfone de polyéther, cristallisation induite par un solvant, structure cristalline, polymorphie, diffraction des rayons X.

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Introduction

Polyethersulfones, abbreviated PES, stand out among other high-performance thermoplastic polymers because of their thermal stability, amorphous morphology, and good solubility in low polarity solvents (ketones and chlorinated aromatic hydrocarbons). They are finding increasing use as membranes for a variety of applications, such as hemodialysis, water filtration, and gas separation, and are serious candidates for fuel cell membranes.

A regular polymer such as PES is rarely entirely amorphous. Blackadder et al.¹ showed that PES can undergo solventinduced crystallization in dichloromethane under specific conditions. Upon crystallization, PES solubility markedly decreases because of the increase in interchain interactions that must be weakened before dissolution occurs.

Improving crystallization of PES could yield a better range of properties and therefore applications. On the other hand, solvent-induced crystallization has been identified as a cause for the increase in brittleness in PES upon contact with chlorinated solvents, and techniques to inhibit this crystallization could, in turn, be useful for specific applications where this crystallization issue causes problems.² For this, a better knowledge of the crystal phase of PES and conditions that favour its growth is needed.

The limited crystallization of regular PES and its oligomers is an exception in the world of rigid polymers. For example, polyetheretherketones (PEEKs) have a similar rigidity, but nevertheless crystallize extremely well, as reported in the literature.³ Polythioethersulfones (PTES) and polyparaphenylenesulfone (PPS), which are also similar in chemical repeat unit and rigidity, also crystallize readily.³ Atwood et al.⁴ suggested that the combined effect of a T_g higher than that of PEEK, and a difference in the valence angle of C–S–C diarylsulfone versus C–C–C diarylketone links may explain the low PES crystallinity, whereas other authors mention the limited difference between glass transition temperature and melt temperature as the cause for the limited crystallinity observed.⁵ However, this behaviour may also be related in part to the adopted crystal phase conformation. Polyethylene te-

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rephtalate is usually obtained in an amorphous form, which does not crystallize easily unless submitted to annealing, stretching, or solvent-induced crystallization. It has been proposed that the key in its amorphous phase stability lies in the fact that the lowest energy conformation is not the all-trans conformation found in the crystal form and favoured by packing interactions, but a gauche conformation.^{6–8} A similar origin for the limited crystallization may exist for PES.

With limited data on the PES crystalline form itself, crystal structures of model compounds become of utmost interest. Few have been studied in the literature, and the present work testifies to the difficulty in crystallizing model compounds composed of a little as two repeat units. A four-ring oligomer bearing amine terminal groups was studied by Bocelli and Rizzoli.⁹ Cyclic ethersulfone oligomer crystal structures were reported by the group of Colquhoum and Williams,³ as these yield high-quality single crystals. However, packing of these cyclic analogues is incompatible with that of polymer chains, and ring constraints may favour conformations different from those adopted in long polymeric chains. From the study of these cyclic oligomers, it was observed that face-to-face π -stacking and C–H··· π interactions provided the main stabilization mechanism for crystallization.³ Whether such interactions are at play in PES is unknown.

In recent years, our group has focussed on the design of rigid–flexible copolymers with rigid block lengths close to the thickness of a single crystalline lamellae.¹⁰ These rigid blocks adopt the same crystal structure as the homopolymers and, because of their lower molecular weights, crystallize more readily. Furthermore, during the course of the synthesis, various low molecular weight model compounds were synthesized and attempts to crystallize them were made. The present article therefore reports the crystal structure of a new model compound, X-ray diffraction of an oligomer as well as conformational analysis, in the aim of shedding light on the crystallization of polyethersulfones for future applications.

Experimental

Synthesis and crystallization of

4,4'-bis(p-methoxyphenoxy)diphenyl sulfone (MPDS)

4,4'-Bis(*p*-methoxyphenoxy)diphenyl sulfone, abbreviated MDPS, was synthesized by reacting 5.085 g (20.0 mmol) of 4,4'-difluorodiphenyl sulfone, 4.967 g (40.0 mmol) of 4-methoxyphenol, and 6.08 g (44.0 mmol) of potassium carbonate in a round-bottomed flask. Thirty millilitres of dimethylacetamide (DMAc) was added to this mixture and the resulting solution was heated to 160 °C overnight under argon atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturated NaCl water three times to remove DMAc and potassium carbonate. The organic layer was washed three times with distilled water and dried over MgSO4, filtered, evaporated, and dried in vacuo at 60 °C to give a white solid (MDPS). The MDPS was crystallized by solvent evaporation of the toluene/methanol solutions (3:1).

Synthesis and characterization of polyethersulfone oligomers

PPS oligomers were synthesized by chain-growth polymerization of 4-fluoro-4'-hydroxydiphenylsulfone, following the work of Yokozawa et al.,¹¹ which was end-capped by the addition of 4-methoxy phenol in dimethylacetamide. Methoxy end groups were deprotected by the addition of BBr₃ in CH₂Cl₂. Molecular weights of ethersulfones oligomers were determined by MALDI-TOF mass spectroscopy in positive linear mode, using a Bruker Autoflex mass spectrometer equipped with an UV laser ($\lambda = 337$ nm, 3 ns second pulse). NaCl was used as a cationizating agent in a dithranol matrix. $M_{\rm p}$ was found to be 1600 g mol⁻¹ and the polydispersity index was 1.15. Oligomer crystallization was performed following the work of Blackadder et al.¹ by first dissolving the PES copolymer in dichloromethane and then lowering the temperature of the 20 wt % solutions to 5 °C for 24 h. The resulting powder was dried in air until the powder did not feel sticky any more, then introduced into a 1 mm diameter glass capillary (Charles Supper Company), and sealed using a match. X-ray diffraction diagrams were registered right away on a Bruker diffractometer equipped with a Kristalloflex 760 generator, a three-circle goniometer, and a Hi-Star area detector. The generator produced a graphite-monochromatized copper radiation (Cu K α = 1.5418 Å) at 40 kV and 40 mA. For the MPDS model compound, the X-ray powder pattern was also calculated from the x, y, and z coordinates fo the resolved crystal structure using the Mercury 2.3¹² program (Cambridge Crystallographic Data Centre) and imposing a constant full-width at a half-height of 0.4° .

Single crystal determination of MPDS

A yellow crystal of MDPS having approximate dimensions of 0.16 mm × 0.15 mm × 0.07 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. Measurements were made at 200(2) K on a Bruker APEX II area detector diffractometer equipped with graphite-monochromated Mo K α radiation. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.5° counted for a total of 30 seconds per frame. An orientation matrix corresponding to the cell constants listed in Table 1, along with additional details on data acquisition, was obtained from a least-squares refinement using the measured positions of 3181 centered reflections in the range 2.23° < θ < 18.44°. The APEX 2 program was used for cell parameter retrieval and data collection.¹³

Data were integrated using the SAINT program.¹⁴ The data were corrected for Lorentz and polarization effects. A multiscan absorption correction was performed using the SADABS program.¹⁵ The structure was solved and refined using SHELXS-97 and SHELXL-97.¹⁶ All non-H atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions. Neutral atom scattering factors were taken from the *International Tables for X-ray Crystallography*.¹⁷ All calculations and drawings for this crystal structure were performed using the SHELXTL package.¹⁸ The final model was checked either for missed symmetry or voids in the crystal structure using the PLATON software.^{19,20} None was found. The crystal structure gives a satisfactory chekcif report (available in the Supplementary data).

Results and discussion

Polyethersulfone crystallinity

Experimental data on PES crystallization present in the literature is limited, to the best of our knowledge, to mainly two publications, which report X-ray diffraction of a sample crystallized at low temperature in the presence of a solvent¹ and spherulite-like structures.²¹ The same crystallization

procedure was applied to the low molecular weight PES blocks available in our lab, and the results are reported in Fig. 1, along with diffraction of the initial polymer assynthesized and of the only oligomer studied from which we were able to obtain single crystals, MPDS. Whereas, as synthesized, PES oligomer samples showed only a broad peak due to scattering of the amorphous phase, small narrow peaks began to be observed after solvent treatment, although the amorphous halo was still predominant. These, however, disappeared if the sample was dried too much, indicating that solvent molecules may be included as an adduct in the crystal

form, as previously proposed in the literature.^{1,21} Observed diffraction peak positions are reported in Table 2, along with those previously reported for PES by Blackadder

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Fig. 1. X-ray diffraction powder diagrams of polyethersulfone (PES) and of a model compound, 4,4'-bis(*p*-methoxyphenoxy)diphenyl sulfone (MPDS), experimental powder spectrum (Powder) and as calculated from single crystal structure (Calcd.).



et al,¹ and those of similar rigid–flexible polymers.^{22–27} The diagram observed in the present work presents two intense diffraction spots at approximately 4.9 Å (18°) and 4.2 Å (21°). This does not match the previous report by Blackadder et al.,¹ in which the two most intense spots were positioned at 4.50 Å (19.7°) and 3.32 Å (26.9°), as reported in Table 2.

The experimental powder X-ray diffraction diagram of the MPDS model compound, as well as the diagram calculated from the single crystal structure of this compound (which is discussed in the following section) are shown in Fig. 1. As observed in the figure, experimental and calculated MPDS spectra do not match, indicating that this compound is polymorphic. The main difference lies in the relative intensity of the peak at 17.3°, the most intense for MPDS as calculated from the crystal structure, which is of much lower relative intensity in the observed spectrum, although many of the smaller intensity peaks also change in intensity below at higher diffraction angles. The main diffraction peak positions remain unchanged, within experimental error.

The strongest peaks are at similar 2θ positions for PES from this work and for MPDS, although smaller intensity peaks

Empirical formula

Formula weight Temperature (K)

Wavelength (Å)

Unit cell dimension

Crystal system

Space group

a (Å)

b (Å)

c (Å)

α (°)

β (°)

γ (°)

Ζ

Volume (Å³)

 (mm^{-1}) *F*(000)

Density (calcd) (Mg/m³)

Absorption coefficient

Crystal size (mm³)

Reflections collected

Observed reflections

Absorption correction

Refinement method

Completeness to $\theta = 25.00^{\circ}$ (%)

Max and min transmission

Data/restraints/

parameters Goodness-of-fit on F^2

Final *R* indices $(I \ge 2\sigma(I))$

R indices (all data)

Absolute structure

Largest diff. peak

and hole (e Å-3)

parameter

Independent reflections

θ range for data collection (°)Index range

Table 1. Crystal data and structure refinement for 4,4'-bis(*p*-methoxyphenoxy)diphenyl sulfone.

 $C_{26}H_{22}O_6S$

462.50

200 (2)

0.71073

10.069(4)

10.350(4)

21.607(9)

2251.7(16) Å³

0.16×0.15×0.07

2838 ($I > 2\sigma(I)$)

0.9872 and 0.9610

3955/193/352

3955 (R(int) = 0.0560)

 $-11 \le h \le 11, -12 \le k \le 12, -25 \le l \le 25$

Semi-empirical from equivalents

Full-matrix least-squares on F^2

R1 = 0.0450, wR2 = 0.0790

R1 = 0.0727, wR2 = 0.0871

(Hooft, Straver and Spek y)

0.10(9) (Flack x), 0.07(5)

0.229 and -0.165

1.88-25.00

22624

100.0

1.238

90

90

90

4

1.364

0.185

968

Orthorhombic

P2(1)2(1)2(1)

PES PEEK PTEK Form I^{22,23} Form I¹ Form II^{22,23} Form I25 Form II²⁴ PPS^{26,27} This work 2θ (°) d (Å) Ι Ι Ι hkl Ι hkl Ι hkl Ι hkl hkl Ι 14.0 6.3 W 5.7 020 020 15.6 ____ S S 16.4 5.4 011 200 sh vs VS 18.0 4.9 021 021 W S m m ____ ____ ____ 18.7 4.8 110 110 ____ ____ VS vs ____ ____ ____ 19.7 4.5 S _____ ____ 20.7 4.3 s 111 S _____ 21.1 4.2 100 ____ 111 vs 22.8 3.9 200 110 200 110,022 VS vs VS m ____ 3.6 24.5 111 m W m ____ 26.5 3.3 112 S W ____ 3.2 27.8 102 121 m m ____ 28.9 3.1 211 21-1 vw S s 29.5 3.0 310 W W 31.6 2.8 040 040 311, 114 W W W

Table 2. X-ray powder diffraction data for the main peaks of various rigid copolymer structures (polyetheretherketone (PEEK) peak positions calculated using unit cell dimensions proposed by Ho and Cheng^{22,23}).

Note: PES, polyethersulfone; PTEK, polythioetherketone; PPS, polyparaphenylenesulfone.

differ. This indicates that a similarity in structural features may occur between PES and this model compound.

Crystal structure of the MPDS model compound

The crystal structure of the MPDS model compound is reported in the present work. Atomic positions are given in Table 3, and Table 4 lists anisotropic displacement parameters. This structure is different from any of the ethersulfone model compounds reported in the literature. As depicted in Fig. 2, which also shows the numbering of the atoms, the chain exhibits conformational disorder, two different conformations appearing in the crystal packing with 55% and 45% occupancy factors at the site of a phenoxy group. This disorder is located at one of the phenyl ether groups, the rest of the structure remaining well-ordered, as if multiple conformations were possible at this specific position. Further, these two conformations are well-defined in the crystal state, as illustrated by the occurrence of similar temperature factors for the ordered and disordered parts of the molecules, as reported in Table 4. This highly unusual phenomenon points to a large conformational flexibility, and already gives insights on the possible cause for a low crystallinity of the parent PES polymer.

Geometry of the sulfonic group is comparable to that of various previously determined sulfone structures, which have been the object of a review:²⁸ S=O distances are short, (1.435(2) and 1.446(2) Å), corresponding to strong double bonds; the large O–S–O bond angle of 120.10(13)° is comparable to values of 116.9(8)° to 120.61(8)° for previously reported sulfones; and the C–S–C of 104.11(13)° is small for a tetrahedral angle, again as observed for other sulfones (104.11(13)°), which has been attributed to the effect of lone-pair repulsion on the sulfone group oxygen atoms.²⁸ Ether groups have normal geometries, with distances varying from 1.380(3) to 1.419(11) Å, with one exception, at 1.431(7) Å in one of the two disordered conformations. This may, however, be related to a slightly incorrect position of the C4 carbon

atom common to both disordered conformations, as the temperature factor is larger perpendicular to the ring plane for this atom, and as an abnormally low valence C–O–C angle of $113.5(10)^{\circ}$ is also observed, significantly lower than the average 120° – 121° diaryl ether bond angle.^{3,4} However, two distinct positions of this carbon atom could not be resolved, the two positions being most probably too close.

Conformational features of this structure can be described either by the dihedral angle between the two aromatic ring planes or by the two successive torsion angles C-X-C-C and C-C-X-C related to the two C-X bonds of the sulfone or ether groups. For the sulfone group, the dihedral angle is 81.0° and the torsion angles (C–S–C–C) are $87.4(3)^{\circ}$ and $91.5(2)^{\circ}$, in agreement with the 90° value predicted by Koch and Moffitt²⁹ for maximum conjugation between aromatic rings and a sulfone group, and are also in agreement with a recent X-ray study of sulfones in which the dihedral angle between the ring plane and the sulfone plane varied from 75.3° to 86.6°.28 A few values were found to depart from this optimal value in the literature: a value of -67°9 and one of -102.3°30 were observed for hydrogen-bond-forming NH2-terminated aryl ether sulfones and an ortho-substituted nitro compound that showed steric hindrance exhibited a value of 61.2°.28 The SO_2 plane, therefore, generally lies between the two phenyl planes in an "open-book" conformation. This conformation is also the one proposed by Tabor et al.³¹ for PPS, and no evidence suggests that it should be any different for PES.

Phenoxy groups show a much larger variability in conformation than sulfone groups do. The number of aryl ethersulfone crystal structures is limited, but variations are large even within this selected group, with two main conformations having been observed: the first is analogous to the open-book conformation, although dihedral angles between aromatic rings are closer to 70° than to 90° , with successive torsion angles of 87.3° and -61.6° ;⁹ in the second conformation

Table 3. Atomic coordinates ($\times 10^4$), occupancy factors (Occ.), and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for 4,4'-bis(*p*-methoxyphenoxy)diphenyl sulfone. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

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Atom	Occ.	X	У	Z	U(eq)
S(1)	1	2060 (1)	2303 (1)	7667 (1)	61 (1)
O(1)	1	5086 (2)	-1573 (2)	6265 (1)	70(1)
O(2)	1	6921 (2)	-720 (2)	3894 (1)	74 (1)
O(5)	1	1780 (2)	1781 (2)	8269 (1)	74 (1)
O(6)	1	2681 (2)	3556 (2)	7609 (1)	69 (1)
C(1)	1	575 (3)	2348 (3)	7250(1)	52 (1)
C(2)	1	-488 (3)	1539 (3)	7397 (1)	66 (1)
C(3)	1	-1631 (3)	1571 (3)	7055 (2)	74 (1)
C(4)	1	-1723 (3)	2398 (4)	6563 (1)	74 (1)
C(5)	1	-685 (3)	3200 (3)	6406 (1)	66 (1)
C(6)	1	451 (3)	3185 (3)	6753 (1)	59 (1)
C(7)	1	3040 (3)	1186 (3)	7265 (1)	55 (1)
C(8)	1	2980 (4)	-110 (3)	7416 (2)	84 (1)
C(9)	1	3703 (4)	-1006 (4)	7086 (2)	86(1)
C(10)	1	4436 (3)	-611 (3)	6587 (2)	59 (1)
C(11)	1	4506 (3)	672 (3)	6432 (2)	71 (1)
C(12)	1	3818 (3)	1564 (3)	6780 (2)	71 (1)
C(13)	1	5572 (3)	-1292 (3)	5671 (2)	57 (1)
C(14)	1	6912 (3)	-1170 (3)	5586(1)	59 (1)
C(15)	1	7394 (3)	-980 (3)	4990 (1)	59 (1)
C(16)	1	6538 (3)	-910 (3)	4499 (1)	58 (1)
C(17)	1	5183 (3)	-1047 (3)	4593 (2)	64 (1)
C(18)	1	4711 (3)	-1220 (3)	5182 (2)	63 (1)
C(19)	1	8291 (4)	-508 (4)	3776 (2)	89 (1)
O(3A)	0.55	-2791 (6)	2146 (5)	6164 (3)	69 (2)
C(20A)	0.55	-3180 (17)	3087 (11)	5724 (4)	56 (2)
C(21A)	0.55	-3328 (13)	4375 (10)	5888 (5)	73 (3)
C(22A)	0.55	-3593 (8)	5288 (8)	5457 (3)	65 (2)
C(23A)	0.55	-3806 (15)	4935 (11)	4850 (4)	82 (2)
C(24A)	0.55	-3699 (10)	3669 (7)	4695 (4)	69 (2)
C(25A)	0.55	-3391 (8)	2727 (9)	5132 (3)	75 (2)
O(4A)	0.55	-4146 (5)	5910 (4)	4456 (2)	81 (1)
C(26A)	0.55	-4447 (19)	5587 (15)	3844 (7)	81 (3)
O(3B)	0.45	-3036 (7)	2692 (6)	6353 (3)	64 (2)
C(20B)	0.45	-3070 (20)	3297 (13)	5763 (5)	56 (2)
C(21B)	0.45	-2838 (10)	2520 (11)	5253 (4)	75 (2)
C(22B)	0.45	-3058 (9)	3038 (7)	4687 (4)	82 (2)
C(23B)	0.45	-3523 (13)	4265 (8)	4587 (5)	69 (2)
C(24B)	0.45	-3765 (10)	5015 (10)	5096 (4)	51 (3)
C(25B)	0.45	-3461 (18)	4556 (13)	5689 (5)	71 (4)
O(4B)	0.45	-3723 (6)	4659 (5)	4003 (2)	86 (2)
C(26B)	0.45	-4220 (20)	5907 (18)	3889 (9)	81 (3)

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torsions angles of $-0.6(9)^{\circ}$ and $1.8(19)^{\circ}$, or corresponds to a new conformation with torsion angles of $-28.8(9)^{\circ}$ and $-46.5(15)^{\circ}$. The variety of possible conformations, and the disorder observed, are in part due to a large flexibility of the phenoxy conformation, which has been established by theoretical calculations of diphenyl ether derivatives using ab initio^{33,34} and semi-empirical DFT calculations.³⁵ An energy rotation barrier around the ether C–O bond of approximately 8 kcal/mol (1 cal = 4.184 J) was found, with a global minimum at approximately 35° , associated with a large, flat minimum

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 4,4'-bis(*p*-methoxyphenoxy) diphenyl sulfone. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2hka^{*b}*U^{12}]$.

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
S(1)	67 (1)	69 (1)	46 (1)	-5 (1)	1(1)	8 (1)
O(1)	69 (2)	69 (1)	72 (2)	3 (1)	12(1)	15 (1)
O(2)	79 (2)	85 (2)	58 (1)	2(1)	-5 (1)	15 (1)
O(5)	93 (2)	89 (2)	40 (1)	-1 (1)	5 (1)	16(1)
O(6)	75 (1)	65 (1)	69 (1)	-11(1)	-5 (1)	-3 (1)
C(1)	55 (2)	58 (2)	44 (2)	-1 (2)	8 (1)	2 (2)
C(2)	76 (2)	66 (2)	54 (2)	14 (2)	11 (2)	-1 (2)
C(3)	58 (2)	91 (3)	71 (2)	25 (2)	7 (2)	-16 (2)
C(4)	55 (2)	98 (3)	67 (2)	24 (2)	-2 (2)	-16 (2)
C(5)	49 (2)	83 (2)	67 (2)	23 (2)	-2 (2)	-10 (2)
C(6)	49 (2)	67 (2)	61 (2)	5 (2)	11 (2)	-6 (2)
C(7)	54 (2)	63 (2)	48 (2)	-3 (2)	3 (2)	3 (2)
C(8)	106 (3)	86 (3)	60 (2)	24 (2)	30 (2)	31 (2)
C(9)	112 (3)	75 (2)	70 (2)	24 (2)	31 (2)	38 (2)
C(10)	48 (2)	66 (2)	64 (2)	-10(2)	0(2)	10 (2)
C(11)	63 (2)	60 (2)	90 (3)	-17 (2)	32 (2)	-14 (2)
C(12)	69 (2)	56 (2)	88 (2)	-15 (2)	24 (2)	-16 (2)
C(13)	58 (2)	54 (2)	59 (2)	-6(2)	2 (2)	12 (2)
C(14)	52 (2)	68 (2)	57 (2)	1 (2)	-7 (2)	9 (2)
C(15)	50 (2)	61 (2)	66 (2)	-5 (2)	-7 (2)	7 (2)
C(16)	68 (2)	52 (2)	54 (2)	-6(2)	-14(2)	12 (2)
C(17)	61 (2)	55 (2)	76 (3)	-7 (2)	-26 (2)	11 (2)
C(18)	49 (2)	56 (2)	82 (3)	-4 (2)	-3 (2)	5 (2)
C(19)	85 (3)	111 (3)	70 (2)	9 (2)	6 (2)	23 (2)
O(3A)	56 (3)	62 (4)	89 (4)	14 (3)	-8 (3)	-10 (3)
C(20A)	50 (3)	56 (4)	62 (2)	4 (2)	-4 (2)	-16 (3)
C(21A)	84 (6)	68 (6)	67 (5)	-7 (4)	2 (5)	7 (5)
C(22A)	67 (4)	59 (5)	69 (5)	-13 (4)	-21 (4)	5 (4)
C(23A)	103 (5)	73 (4)	70 (4)	-8 (3)	10 (4)	16 (4)
C(24A)	68 (4)	82 (6)	57 (3)	-5 (4)	-3 (3)	9 (5)
C(25A)	98 (6)	52 (3)	74 (3)	-7 (3)	-6 (4)	6 (4)
O(4A)	96 (3)	67 (3)	78 (3)	6 (3)	-16 (3)	16 (2)
C(26A)	82 (6)	82 (7)	80 (4)	2 (4)	-13 (3)	11 (5)
O(3B)	50 (4)	78 (5)	63 (4)	5 (3)	10 (3)	-6 (4)
C(20B)	50 (3)	56 (4)	62 (2)	4 (2)	-4 (2)	-16 (3)
C(21B)	98 (6)	52 (3)	74 (3)	-7 (3)	-6 (4)	6 (4)
C(22B)	103 (5)	73 (4)	70 (4)	-8 (3)	10 (4)	16 (4)
C(23B)	68 (4)	82 (6)	57 (3)	-5 (4)	-3 (3)	9 (5)
C(24B)	25 (4)	49 (5)	78 (7)	-2(5)	2 (6)	11 (4)
C(25B)	78 (7)	68 (7)	68 (8)	-14 (6)	23 (6)	-1 (6)
O(4B)	127 (5)	65 (3)	67 (3)	5 (3)	8 (3)	21 (3)
C(26B)	82 (6)	82 (7)	80 (4)	2 (4)	-13 (3)	11 (5)

region between 30° and 95°.³³ This feature of the potential energy surface explains why, in the absence of stabilizing contacts, two different conformations are adopted with almost equal probabilities in MPDS.

The packing adopted by this molecule is presented in Fig. 3, and is clearly incompatible with that of an extended chain polymer. In the present MPDS ethersulfone model compound, as in polysulfones and poly(ethersulfones), there are no hydrogen atoms on polar atoms, and therefore no classical hydrogen bonds can form. Nevertheless, as observed

previously,^{28,36} soft hydrogen bonds can form between aromatic hydrogen atoms and sulfone oxygen atoms. In the present case, two short contacts are observed between the oxygen atoms of the sulfone group and the hydrogen atoms of the aromatic rings, with distances of 2.634 Å for O6…H3 and 2.651 Å for O5…H17. It is worth noting that the two S=O bond distances are significantly different, with values of 1.435(2)Å for S1–O5 and 1.446(2) Å for S1–O6, the longer distance corresponding to the weakest O…H contact. This difference in S=O bonds is therefore proposed to be the effect



Fig. 2. Single molecule of 4,4'-bis(*p*-methoxyphenoxy)diphenyl sulfone in its two observed conformers (labelled A and B), present in a 55:45 ratio. Hydrogen atoms are omitted for clarity. (*a*) Numbering of atoms. (*b*) ORTEP view with 50% probability.

of a weakening of the S=O bond due to a soft hydrogen bond interaction.

As shown in Fig. 4, for MPDS, one soft hydrogen bond is formed between the sulfonic group and a hydrogen atom of an aromatic ring bonded to both the sulfonic and the ether group, whereas a second bond is formed between the sulfonic group and a ring bonded to the ether and a methoxy end group. Although only one of the two disordered conformers is depicted in the figure for clarity, interestingly, the disordered ring is the one not interacting with the sulfone group; neither of the two disordered conformations observed showed such interactions. Therefore, it is proposed that sulfone – aromatic ring interactions are important and play a role in either stabilizing the crystal phase, if such interactions can exist in a regular close packing of polyethersulfones or, alternatively, stabilizing the amorphous phase, thereby contributing to a high energy barrier for crystallization and to a decrease in resulting crystallinity. The absence of such interactions may lead to disorder, and may therefore inhibit crystallization.

Comparison with similar rigid polymer structures

It is also interesting to compare the X-ray diffraction patterns and crystal structures of related rigid polymers, as strong similarities exist between some of these rigid polymers. Figure 5 illustrates conformations adopted in the crystal phase by a few representative rigid polymers. In poly(etherketone) (PEK) and PEEK, the aromatic ether and ketone linkages are crystalloFig. 3. Packing of the major conformation (55%) of 4,4'-bis(*p*-methoxyphenoxy)diphenyl sulfone (*ac* plane). Hydrogen atoms are omitted for clarity.



Fig. 4. Soft hydrogen bonds between the SO_2 group and the aromatic hydrogen atoms of 4,4'-bis(*p*-methoxyphenoxy)diphenyl sulfone.



Fig. 5. Comparison between crystal structure conformations of rigid polymers. From left to right: polyetherketone (PEK), polythioetherketone (PTEK), polyparaphenylenesulfone (PPS), and possible conformations for polyethersulfone (PES).



graphically interchangeable, only slight variations in unit cell dimensions and relative intensity of the diffraction spots being observed.³⁷ These polymers are highly crystalline, surprisingly so for aromatic polymers, which are often low in crystallinity.³ This has been attributed to the geometrical equivalence of aromatic ether and carbonyl linkages, which allows the chain to remain in a linear geometry favourable to crystallization.³⁷ Two crystal polymorphs are known, each having the same planar conformation and differing by the packing mode. Form I, obtained by

crystallization from the melt, exhibits diffraction peaks at 3.8 and 4.8 Å and has been proposed to be monoclinic, with one chain at the center of the unit cell and another at the corner of the cell.³⁸ Its packing has been described as an edge-to-face phenyl packing.³⁹ Form II, obtained from the solution of cold crystallization, has an intense peak at 4.2 Å. Two different structures have been proposed for this form, a two-chain orthorhombic structure, also with one chain at the center and the other at the corner, but with slightly different chain organization,³⁸ and a one-chain or-

	Torsion ang				
PES	C-C-S-C	C–S–C–C	ССОС	С-О-С-С	Helix pitch (Å)
Model compound (ref. 9)	96.2	-67.0	87.3	-62.0	
MDPS conformation I	91.5 (2)	87.4 (3)	-16.1 (4)	-75.8 (4)	_
MDPS conformation IIa	91.5 (2)	87.4 (3)	-28.8(9)	-46.5 (15)	_
MDPD conformation IIb	91.5 (2)	87.4 (3)	33.1 (7)	75.5 (16)	_
2 ₁ Helix	90	78	20	-30	15.7
3 ₁ Helix	90	90	-30	90	25.0
4 ₁ Helix	90	78	20	60	26.2

Table 5. Torsion angles and helix pitch of polyethersulfone (PES) models.

Note: MPDS, 4,4'-bis(p-methoxyphenoxy)diphenyl sulfone.

thorhombic structure.³⁹ Random etherketone copolymers are even more crystalline than regular polymers, which further illustrates the crystallographic equivalence of ether and ketone groups in this class of rigid polymers.⁴⁰

Polythioetherketone (PTEK), in which the ether group of PEK is replaced by a thioether group, also crystallizes well, in spite of the fact that thioether bond lengths and C-S-C bond angles are different from those of the ketone group.³ Deformations occur on carbon atoms adjacent to the thioether bridge, opening up the thioether bond angle. This allows the polymer and related oligomers to remain essentially linear, and the conformation is very similar to that of PEK. This polymer is known to crystallize as two different polymorphs. Comparison of peak positions for the most intense reflections, as reported in Table 2, show strong similarity with PEK form I. Strong similarities in peak positions and relative intensities are also found between PEK form II and PTEK form II.24,41 Form I is a body-centered monoclinic structure, whereas chains are at the corner and middle of the unit cell in the orthorhombic form II.

A third rigid polymer for which the crystal structure is known is presented in Table 2, PPS, in which the only linker between aromatic rings is a sulfone group.^{27,42} Data on oligomers of PPS and proposed crystal structure show that the favoured conformation is not planar but of the open-book type, where rings are orthogonal (or nearly so) to the C–S–C plane,^{42,43} as depicted in Fig. 5. This leads to a completely different chain packing and unit cell dimensions than in the case of PEK, PEEK, and PTEK. Two crystal polymorphs are also observed in this case, with peak positions bearing little similarity to those of PEK or PTEK, which can be attributed to the different chain conformation adopted.

In contrast to these rigid polymers, the crystal structure of PES has never been solved, and its repeat distance is also unknown, this polymer usually being amorphous as synthesized or even after annealing at higher temperatures in spite of its regularity, which is highly unusual. Further, when a low crystallinity is observed as synthesized, it disappears upon heating above the melt ing point.

The conformation adopted by the MPDS molecule is not all-trans nor reminiscent of a conformation leading to extended chains, as in the zig-zag conformation adopted in forms I and II of PEK and PTEK. It is also different from that of the crystal phase of PPS, which is an open-book zig-zag conformation, as shown in Fig. 5. The most interesting feature of this conformation is the fact that the open-book conformation is adopted for the sulfone group, but not for the ether groups.

As can be seen in Table 2, the diffraction diagrams of PEK, PTEK, and PPS do not match that observed in the present work for PES, the closest one being that of PPS, which exhibits three intense diffraction peaks at 16.4°, 21.1°, and 26.5°, as compared with two intense peaks at 18.0° and 21.1° for PES. PES is therefore proposed to exhibit a different crystal packing and possibly different conformation than that of related previously studied rigid polymers. Changing the carbonyl group by a sulfone group, therefore, has a more profound effect on the crystal form that by changing an ether group to a thioether group, which leads one to suspect that the change is not merely related to packing but may also relate to the conformation adopted by the chains.

Investigation of possible conformations of PES

In the absence of a repeat distance value, it is very difficult to determine without ambiguity the conformation adopted by PES in its crystal forms. In the present study, a few low-energy conformations were built and compared. These are reported at the right in Fig. 5. In all cases, helices were investigated, although pseudohelical forms cannot be excluded.

The 2_1 helix is the simplest form, conformationwise. It is similar to that of PPS, combining open-book around the sulfone group and parallel ring arrangements around the ether linkage. As reported in Table 5, torsion angles around the sulfone groups have values of 90° and 78°, and are both close to the minimum energy conformation of 90°. The ether group shows torsion angle values of 20° and -30° , close to those observed for MDPS conformation IIa (although in this conformation successive torsion angles were of the same sign, which is not the case for the 2_1 helix). This yields a zig-zag conformation reminiscent of the PPS conformation, but with bends occurring every two aromatic cycles. The chain "bends" at each sulfone group, whereas the ether groups remain in the same plane at the aromatic cycles to which they are linked. A packing similar to that of PPS would be possible with this conformation.

Various helices could be built using slight variations in the torsion angles of one of the conformations of MDPS. For example, the 3_1 helix shown in Fig. 5 is relatively compact, and its conformation angles are 90° around the sulfone group, as in the case of most crystal structures. Around the ether group, a first torsion angle of -30° is found, which is close to one value observed for MDPS conformations I and IIa However, the second torsion angle is 90° , which deviates signifi-

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cantly from values observed for model compounds, a value close to the one observed by Bocelli et al.⁹ for a PES model compound, although the two successive torsion angles were not the same. The 4_1 helix was obtained from slight deviations from the torsion angles adopted by the MPDS conformation IIb and is a more "open" helix, exhibiting a void at the center. It is also close, but with opposite signs, to MDPS conformation I. This similarity, and the previously noted similarity in powder diffraction diagrams, indicates this could be the conformation adopted by the crystal structure of PES that was observed in the present work.

A top view of each of these three helices is presented in Fig. 6. The 2_1 and 3_1 helices are relatively compact, whereas a void is present at the center of the 4_1 helix. In all cases, the oxygen atoms (shown in black in this figure) lie on the outer surface of the helix. If soft hydrogen bonds between the helix and solvent molecules stabilize this crystal form, solvent molecules would be present between helices. On the other hand, as can be seen in Fig. 5, some solvent molecules could also be trapped at the middle of a 4_1 helix.

The presence of solvent molecules in the crystal structure, stabilizing the helical conformation, is in agreement with observations by Blackadder and Ghavamikia²¹ that birefringent spherulitic structures and crystal-like globules can be observed in chloroform of dichloromethane, and that structures loose their birefringence and crystallinity upon drying.

Conclusion

A new crystal form for PES was observed from solventinduced crystallization of low molecular weight PES. X-ray diffraction shows a strong similarity with X-ray diffraction patterns of the small molecule model MPDS. The crystal structure of MPDS is disordered, illustrating the relative flexibility for rotation around ether linkages, as compared with relatively more rigid sulfone bonds. For this reason, it is proposed that ether and sulfone bonds are not crystallographically interchangeable, thus destabilizing the crystal form of this polymer as compared with that of other rigid polymers, where all aryl bonding groups are crystallographically interchangeable.

Various low-energy helical forms exist for PES, and all have oxygen atoms at their outer surface with which solvent molecules can form soft hydrogen bonds to stabilize the conformation. Further, a 4_1 helix PES model built using torsion

angles close to those of a MPDS conformation presents a void at the center and can therefore accommodate additional solvent molecules. Upon drying, evaporation of the solvent increases the free volume, allowing the chain to adopt other conformations and resulting in a loss of short-range order and crystallinity. It is proposed as a possible conformation for the new PES crystal form reported in the present work.

Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/ 10.1139/v2012-066. CCDC 871798 contains the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/ request (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44 1223 336033; or e-mail:deposit@ccdc.cam.ac.uk.

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