Polymorphism in an oligo(aryl ether ketone)

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Abstract The molecular compound 1,3-bis(4-phenoxybenzoyl) benzene (**1**) shows a single melting peak at $T_1=120^\circ\text{C}$ when **rapidly crystallized** from a methanol/benzene mixture (10:1) (sample A) and a double melting peak at $T_1=120^\circ\text{C}$ and $T_2=130^\circ\text{C}$ when **crystallized slowly (overnight)** (sample B). A slow recrystallization of **1** using ethanol instead of methanol induces the formation of large single crystals which only show a single melting peak at $T_2=130^\circ\text{C}$ (sample C). Analysis of powder X-ray diffractograms obtained for A, B and C samples clearly point out to the coexistence of two crystalline phases in sample B: phase 1 (observed for sample A) and phase 2 (sample C). From optical microscopy and thermal (DSC) observations it can be concluded that, upon heating, phase 1 melts at T_1 and the molten material converts itself into phase 2 if some crystals of phase 2 are present. Single crystal structure determination of, both, phase 1 and 2 reveal conformational differences of the molecule in both phases which pack in an orthorhombic and a monoclinic unit cell, respectively.

Dedicated to Prof. Dr. F.J. Baltá Calleja on the occasion of his 60th birthday

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Introduction

Polymorphism is frequently observed in polymers and molecular compounds as a consequence of different molecular conformations each one demanding a particular arrangement of atoms in the crystal [1,2]. As a result crystal polymorphs show differences in most of their physical properties, so that phase transitions are of basic interest in material science. In the case of aromatic polyketones, with high melting points the development of polymorphism is of interest to facilitate the processing of the material. Recently, Gardner reported on the polymorphism observed in polyketones containing 1,3 substituted phenylene rings [3,4]. Particularly, polyketones made up with 1:1 terephthalic/isophthalic (T/I) ratio show a very complex thermal behaviour.

In the present paper we report the polymorphism observed in oligomer **1** depending on the solvent and crystallization conditions. The molecular compound **1** is of interest as a monomer as it is used in the synthesis of polyketones PEKK with different T/I ratio. A characterization of the crystalline phases and of their transformation has been carried out by means of powder X-ray diffraction, differential scanning calorimetry (DSC), optical microscopy and by means of single crystal structure determination. The information obtained from the monomer will be useful for the understanding of the thermal behaviour observed for related polyketones.

The behaviour of this molecular compound as glassy material ($T_g = 24^\circ\text{C}$) and its crystallization from the glassy state will be reported separately.

Experimental

The schematic chemical formula of 1,3-bis(4-phenoxybenzoyl) benzene (**1**) is:

1 was prepared by reaction synthesis of diphenyl ether with isophthaloyl chloride in the presence of aluminium chloride. The bulk synthesis product was washed with methanol and allowed to dry in air. The air-dried product was recrystallized from alcohol/benzene

mixtures. A rapid crystallization from methanol/benzene (10:1) gives a fine, white crystalline powder (sample A). On the other hand, slow recrystallization (overnight) from the same mixture produces white, crystalline powder (sample B) with particle sizes larger than those of sample A. A further slow recrystallization of the sample B from ethanol/benzene mixture gives, much larger yellow crystals (single crystals, sample C).

Thermograms were obtained by means of a Perkin-Elmer DSC calorimeter (DSC-7 and DSC-4 models) working at usual conditions: a heating rate of 10K/min and a cooling rate of 320K/min and about 5 mg of sample. Different heating rates (from 3K/min up to 40K/min) and cooling rates (320K/min and 1K/min) were also used.

A Mettler hot stage coupled with a Leitz microscope, and polarized light, was used to follow optically the thermal behaviour and for morphological identification of the samples.

Powder X-ray diffractograms were obtained with a vertical goniometer using a scanning rate of 1°/min and a chart recording speed of 1cm/min. Ni filtered, Cu K α radiation from a rotating anode working at 8 kW was used. Particularly, samples B and C were grinded, before recording X-ray diffractograms, to reduce particle sizes.

Crystal data and refinement details for both phase 1 (single crystal from sample B) and phase 2 (sample C) are given in Table 1. Both structures were solved by direct methods (SIR92 [5]) and refined by full-matrix least-squares analysis (SHELX93 [6])

Results

X-ray diffraction

Fig. 1 shows the low 2θ angular region (3–25°) of the X-ray diffractograms of samples A, B and C. The sharpness of reflexions observed for A and B samples reveals their highly crystalline nature which is similar to that of grinded single crystals (sample C). A and B diffractograms mainly differ in some of the reflexions (noted with a star) which are present in C. Furthermore, the reflexions below 12° which appear at similar positions (at 5.3, 7.1, 9.7, 10.3, 11 and 11.4°) for A and B samples do not appear in the diffractogram of sample

C. Thus, a different crystal packing should be found for A and C samples, suggesting the presence of different crystal phases. If we denote the phase of sample A as phase 1 and the phase of sample C as phase 2 it turns out that sample B consists of, both, phase 1 and phase 2. The differences in intensity of common reflexions of A and B diffractograms could be attributed to orientation problems of sample.

Taking into account the relative intensity of the reflexions from phase 2 (noted with a star in B) in relation to that of those from phase 1, phase 2 represents some few per cent of the material of sample B.

The drawing [7] of the molecular structures found for phase 1 and phase 2 are shown in Figs. 2a-b, respectively, with the atomic labels used in the crystallographic description. Figs. 2c-d show a different view of the two molecular structures with the isophthalic ring plane perpendicular to the plane of paper. The bond lengths and angles show standard values and are very similar for both molecular conformations. The main differences found correspond to the torsional angles at both molecular ends, i.e. those ones involving the ether group.(see Table 2 and Fig. 2). The small difference of the calculated densities (Table 1) can also be shown in terms of the total packing coefficients (0.659 for phase 1 and 0.662 for phase 2) calculated using an atomic model [8].

Thermal properties

Fig. 3 shows the first and second DSC traces observed for B sample. In the first DSC trace two melting peaks at $\sim 120^{\circ}\text{C}$ (T_1) and $\sim 130^{\circ}\text{C}$ (T_2) are observed. The consecutive, second DSC trace is rather flat and the small inflection observed at $\sim 24^{\circ}\text{C}$ (T_g) would correspond to a glass transition temperature. This thermogram would also indicate that the material does not crystallize by cooling from the melt at 320K/min. Even, using a very low cooling rate (1K/min) no crystallization was observed.

Fig. 4 illustrates the upper temperature region of DSC traces observed for samples A, B and C. The lower temperature peak (T_1) of sample B coincides with the single peak observed for sample A while the higher temperature peak (T_2) observed for sample B, appearing about 10 degrees above T_1 , coincides with the peak observed for sample C. Thus, it seems that the

melting peaks from A and C samples are contributing to the DSC trace of sample B.

We remain surprised because the observed melting temperatures are in total disagreement with the value reported (169.7°C) for the same molecular compound [9].

In order to understand the origin of the double melting peak observed for sample B different heating rates were used as illustrated in Fig. 5. Thus, for small heating rates a clear exothermic area is observed above the T_1 peak, that could indicate a recrystallization of the molten material above T_1 . For high heating rates no exotherm was observed and an appreciable intensity reduction of the peak at T_2 in comparison to that of T_1 peak occurred. For a heating rate of 40K/min (not shown in figure) the area of the second peak was negligible in comparison to that of the first one. This suggests that at these high heating rate values the molten material cannot recrystallize totally. i.e. the rate of the recrystallization process is not as high as the heating rate used.

It is worth mentioning that optical microscopic observations of sample A revealed the presence of some few crystals above T_1 (see below Fig. 7) which were not detected by DSC. However, sample A upon a prolonged (about 5 h) thermal treatment at 122°C showed a similar DSC trace to that of sample C.

Optical microscopic observations upon thermal treatment.

While the rapidly crystallized oligomer (samples A) consists of very small, flattened crystals, showing different shapes and sizes, the slowly crystallized one (sample B) exhibit notably larger crystals.(Fig. 6).

The thermal behaviour of samples in the vicinity of melting temperatures was additionally examined by optical microscopy. Thus, samples were first heated up to 110°C and then a heating rate of 1K/min was used to reach temperatures 10 degrees above the melting temperature of crystals.

In the case of the sample B we observed that most of the crystals melted (at temperatures around T_1) by losing their original shape though they recovered a new crystal habit. We observed that birefringence of particles never disappeared during the first melting tem-

perature range and that the molten material surrounding crystalline material becomes to crystallize again. Finally, all material melted around the second melting temperature (T_2).

Sample A shows a narrow melting range ($\sim 1.5^\circ\text{C}$) around T_1 . Each one of the isolated crystals gave rise to a drop of molten material (no birefringence was observed) (Fig. 7) which did not crystallize above T_1 temperature. It is worthy to mention that for all the optical preparations of sample A we observed at least one drop of molten material which contained a (or few) very small crystal inside. When the sample was heated at constant temperature (above T_1 , i.e. 123°C) the growing of the crystal at expenses of the molten material of the drop could be observed (Fig. 7). The time required for the consumption of the molten material depended on the drop size, and on whether there was only one or more crystals inside the drop.

Discussion

Polymorphism

We have seen that the oligomer 1 crystallizes from solution in two different polymorphs (orthorhombic and monoclinic) each one showing a different molecular conformation (Fig. 2). The presence of the isophthalic moiety in the center of this relatively short molecule seems to determine the molecular conformation observed which differs from the linear extended one detected for normal poly(aryl ether ketone) (all para-linked phenylenes) [10,11]. Furthermore, the free ends of the oligomer facilitate the rotation of phenylene rings around the ether linkages giving rise to the two molecular conformations found. These are responsible for the two crystal phases observed. The orthorhombic form is associated to the less stable phase 1 while the monoclinic one is assigned to the phase 2. According to crystallographic data (Table 1) the phase 2 has a slightly higher density than the phase 1. Thus, phase 2 is more stable than phase 1 in agreement with their corresponding melting temperatures ($T_2 > T_1$).

The presence of two endothermic peaks for the samples B (Fig. 3 and 4) and their thermal behaviour (Fig. 5) together with the corresponding X-ray diffractograms (Fig. 1) support

the coexistence of two crystal phases (1 and 2). As far as the relative amount of phases is concerned, from the X-ray diffractograms recorded at room temperature one could argue that phase 2 (reflections noted with a star) represents some percentage of sample B. However, from the endotherm of sample B one may expect that both phases could similarly contribute to sample B. On the other hand, since a heating DSC trace is a dynamic representation of the sample as a function of temperature, the endotherm of sample B shown in Fig. 4 would not describe exclusively the original nature of the sample but the one evolving with increasing temperature.

The thermal behaviour shown in Fig. 5 using different heating rates offers information about the rate of recrystallization of molten material of phase 1 and about the speed of transformation of phase 1 (now in molten state) into phase 2. However, both informations are connected with a unique process. Thus, the crystallization rate should be somewhat larger than 10K/min because a small exothermic contribution is still detected for the DSC trace recorded at a heating rate of 10K/min. On the other hand, from the DSC trace recorded at 20K/min no exothermic contribution is observed and the endothermic area of peak 2 is now smaller than that of peak 1. This result suggests that the molten material (above T_1) cannot crystallize totally and, therefore, that it is not contributing to the endothermic area of peak 2.

Phase transformation mechanism

The single endothermic peak T_1 observed for sample A (Fig. 4, top) together with the optical observations carried out above T_1 (Fig. 7) suggests that the material of sample A remains in the molten state. However, occasionally a drop of molten material, in the presence of a crystal of phase 2 is capable to crystallize in the more stable crystals of phase 2 (Fig. 7). This can be interpreted by saying that crystals of phase 2 act as nuclei (seed) of crystallization for the molten phase of sample A. In the case of sample B crystals of phase 2 are always present. Thus, crystals of phase 2, (stable above T_1) will allow the molten material (phase 1) to crystallize on them. Therefore, the molecular conformation 1

is capable to change into the molecular conformation 2 only upon solidification onto crystals of phase 2. Since phase 2 has a higher density than phase 1 it is assumed that the driving force of the phase transition observed is the densification of the system induced by phase 2.

Conclusions

- The oligomer 1, crystallized using a methanol/benzene mixture, appears in two different crystal phases whose melting temperatures differ by about 10 degrees. The less stable crystals, phase 1, appear using rapid crystallization conditions (samples A). The more stable crystals, phase 2, tend to appear under slow crystallization conditions (sample B). A further slow crystallization of sample B (mixture of phase 1 and 2) using an ethanol/benzene mixture induces the appearance of only phase 2 single crystals (sample C).
- The pure phase 1 upon melting does not transform itself into phase 2. However, the molten material in the presence of crystals of phase 2, which act as nuclei of crystallization, crystallizes onto phase 2.
- Two molecular conformations which mainly differ in the orientation of chain ends with respect to the isophthalic unit, are responsible of the polymorphism observed. The phase transformation detected upon heating is governed by a densification of the system from the orthorhombic (phase 1) into the monoclinic phase 2.

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Caption to Figures

- Fig. 1 Powder X-ray diffractograms from A, B and C samples.
- Fig. 2 Molecular conformations of phase 1 (a,c) and phase 2 (b,d), showing the atom labels, with the isophthalic ring plane oriented parallel (a,b) and perpendicular (c,d) to the plane of the paper.
- Fig. 3 First (top) and second (bottom) DSC traces of sample B.
- Fig. 4 Upper temperature region of DSC traces for A (top), B (middle) and C (bottom) samples.
- Fig. 5 Upper temperature region of DSC traces of sample B for different heating rates values.
- Fig. 6 Optical micrographs of samples A (top) and B (bottom).
- Fig. 7 Optical micrographs of the molten sample A at 123°C showing: a crystal of phase 2 (top) and a grown crystal of phase 2 inside of a molten drop (bottom).

Table 1 . Crystal data for phases 1 and 2.

	Phase 1	Phase 2
Empirical formula	$C_{32}H_{22}O_4$	$C_{32}H_{22}O_4$
Formula weight	470.50	470.50
Temperature	293 K	293 K
Wavelength (Å)	1.5418	1.5418
Crystal system	Orthorhombic	Monoclinic
Space group	P bca	P 2 ₁ /n
Unit cell dimensions (Å, °)		
a	18.428(3)	12.398(2)
b	7.7150(4)	7.811(1)
c	34.426(3)	25.623(2)
β	90	100.49(1)
V (Å ³)	4894.4(9)	2439.9(5)
Z (molecules per cell)	8	4
Calc. density (Mg m ⁻³)	1.277	1.281
Absorption coeff. (mm ⁻¹)	0.671	0.673
F(000)	1968	984
Crystal size (mm)	0.70 x 0.24 x 0.04	0.50 x 0.23 x 0.16
Data collection equipment	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Data collection method	ω/2θ scans	ω/2θ scans
θ range for data (°)	2 - 50	2 - 65
Index ranges	0 ≤ h ≤ 18, 0 ≤ k ≤ 7, 0 ≤ l ≤ 34	0 ≤ h ≤ 14, 0 ≤ k ≤ 9, -30 ≤ l ≤ 29
Reflexions collected	2612	4215
Reflexions independent	2517	4148
R(int)	0.012	0.008
Intensity decay	none	none
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	2517/0/325	4148/0/326
Extinction coefficient	none	0.0037(3)
Max. and min. absorp. coef.	1.00, 0.70	no correction done
Goodness-of-fit on F ²	1.070	1.047
Final R and R _w [I > 2σ(I)]	0.058, 0.135	0.036, 0.103
Final R and R _w (all data)	0.101, 0.171	0.045, 0.110
Largest Δρ peak and hole (e Å ⁻³)	0.201, -0.185	0.189, -0.171

Table 2 . Selected torsional angles (°) for phases 1 and 2.

	Phase 1	Phase 2
C(2) -C(1) -C(110)-C(111)	-38.1(7)	-36.4(2)
C(6) -C(1) -C(110)-O(11)	-37.5(8)	-33.6(2)
O(11) -C(110)-C(111)-C(112)	-23.1(8)	-26.2(2)
C(115)-C(114)-O(12) -C(121)	13.1(8)	172.6(1)
C(114)-O(12) -C(121)-C(122)	-134.2(5)	93.9(2)
C(2) -C(3) -C(210)-C(211)	-35.3(7)	-43.1(2)
C(4) -C(3) -C(210)-O(21)	-32.6(7)	-38.6(2)
O(21) -C(210)-C(211)-C(216)	-24.4(7)	-21.5(2)
C(215)-C(214)-O(22) -C(221)	0.8(8)	27.3(2)
C(214)-O(22) -C(221)-C(222)	-96.9(6)	-138.5(2)

Fig. 1
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(a)

(b)

(c)

(d)

Fig. 2
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Fig. 3

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Fig 4

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Fig 5
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Fig. 6

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Fig. 7