Crystalline Structure of PEO−Resorcinol and PEO−Methylresorcinol Complexes

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ABSTRACT: The molecular structure of the polyethylene oxide (PEO) molecular complexes with resorcinol (RES) and 2-methylresorcinol (two allotropic forms α-2MR and β-2MR) have been solved and refined by an X-ray diffraction technique (the "whole-pattern method"). The space group is $Pna2_1$ for RES (a = 10.54 Å, b = 10.18 Å, c = 9.89 Å), $Pbca$ for β-2MR (a = 11.07 Å, b = 18.60 Å, c = 10.74 Å), and $P2_1/a$, unique axis c, for α-2MR (a = 16.24 Å, b = 10.57 Å, c = 18.79 Å, γ = 89.2°). Although for RES no direct chain-to-chain interactions are established in the molecular packing, for 2MR, the layered organization of chains and small molecules is present with chain-to-chain contact. Moreover, although hydrogen bonds are clearly established in the case of RES and β-2MR, α-2MR should be regarded as a simple intercalated complex, in agreement with a previous solid state NMR and IR investigation.

Introduction

The ability of polyethylene oxide (PEO) to form molecular complexes with a large variety of inorganic[1−3] and organic[4−7] molecules has been investigated a great deal. Depending on the chemical nature of the small molecule, the PEO chain-to-small molecule interactions may be weak or strong. Examples of the former are the intercalated complexes of PEO with *p*-dihalogenobenzenes, for which the crystalline structure modifications are controlled mainly by van der Waals interactions.[4−7] When small molecule bear polar substituents, strong interactions may take place between the oxygen atoms along the PEO chain and the small molecule itself, as is the case for resorcinol (RES),[8−14] 2-methylresorcinol (2MR),[9,15−17] hydroquinone (HYD),[15,16] and *p*-nitrophenol (PNP)[12,13,18−21] complexes. In this case, the crystalline phases are strongly stabilized by hydrogen bonding, showing, among other significant features, higher melting temperatures.

Another interesting feature of PEO is that it frequently shows an intricate phase diagram when mixed with small molecules. For instance, this was the case of 2MR for which some of us isolated three complexes, each with different PEO-to-small molecule stoichiometric ratios.[17] Only two of them are stable crystalline phases, α-2MR and β-2MR, and the other, γ-2MR, is unstable and spontaneously transforms to the β form after 1 day at room temperature.

To understand the role that hydrogen bonding plays in establishing the crystalline structure, in this paper, we report and discuss the analysis and the refinement of the crystalline structure of RES and 2MR (α and β) supramolecular complexes by means of X-ray diffraction techniques.

Experimental Section

Complexes. PEO complexes were prepared according to the procedure discussed in Spevacek et al.[14] PEO of molecular weight 6000 (Hoechst) was used. Resorcinol (from Janssen Chimica) and 2-methylresorcinol (from Aldrich) were used as received. Molecular complexes were prepared by melting and recrystallizing stoichiometric mixtures of PEO and the respective aromatic molecule. The molar ratio of PEO monomeric units and small molecules is 2:1 for RES and β-2MR[9−11,17] and 7:2 for α-2MR.[17]

X-ray Measurements. Fiber diffraction spectra were collected on a Fuji BAS-UR type image plate by means of a flat camera with a sample-to-film distance of 70.0 mm. Ni-filtered Cu Kα radiation, supplied by a Seifert X-ray generator, was employed. The X-ray pattern was read out by means of a Fujix Bas 3000 (0.100 μm final resolution) in the range of the linear response of the instrument.

Samples. Oriented samples for X-ray measurement were obtained by stretching thin films of complexes at room temperature. Thin films were prepared by melting the correspondent material at 20 °C higher than the melting temperature, followed by a fast quenching in liquid nitrogen to avoid crystallization.

Structure Refinement Procedure

In the following sections, the "whole pattern" method[22−27] is employed to carry out the analysis and refinement of the crystalline structure of PEO complexes. The method applies the least-square fitting procedure to obtain the best match between the two-dimensional experimental and calculated X-ray diffraction patterns. Computation is carried out in the reciprocal space.[23] Background intensity due to the incoherent scattering is not subtracted ab initio and is considered at the subsequent fitting stage. To ensure the convergence of the fitting, it is always necessary to have a reliable starting model of the molecular structure. Usually, the fitting is carried out by first considering the equatorial part of the diffraction pattern and then later considering the whole set of data. Refinable parameters are of two kinds: (i) nonstructural ones, such as the crystalline size and the degree of crystallites orientation with respect to the fiber axis, and (ii) structural ones, such as the bond and torsional angles

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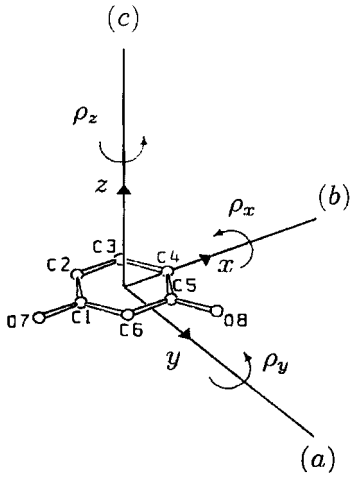

Figure 1. Overall translational and rotational parameters setting the aromatic molecule position in the unit cell. The case of resorcinol is shown as an example.

which define the chain conformation. The former set the shape and the latter the diffraction intensity of each diffraction spot.

In this article, we have considered the following nonstructural parameters: (i) the main crystallite size ($\Delta a - \Delta c$) taken along a direction parallel to the lattice axes ($a-c$, respectively); (ii) the angle (α_0) made by the axis of the preferential orientation of the crystallites and the fiber axis; and (iii) the background intensity (B) in the observed diffraction pattern fitted with the following function[23]

$$B(\xi_i, \zeta_i) = \epsilon_1 + \epsilon_2\xi_i + \epsilon_3\xi_i^2 + \epsilon_4\zeta_i + \epsilon_5\zeta_i^2$$

where ξ_i and ζ_i are the fractional coordinates at the generic ith point in reciprocal space and $\epsilon_1-\epsilon_5$ are parameters to be evaluated by fitting that have no physical meaning.

The refinable structural parameters are the following.

(1) The lattice parameters.

(2) The overall fractional coordinates of the center of mass of the chain (X_0-Z_0), when they are not fixed according to the space group symmetry, and the angle of rotation (Φ_0) of the chain around its own axis [Φ_0 is defined as the intersection angle between two planes both containing the chain axis; the first is parallel to (010), whereas the second contains the first atom of the chain].

(3) The overall fractional coordinates of the center of mass of the aromatic ring (x_0-z_0) and the three angles setting the orientation of the small molecule ($\rho_x-\rho_z$) [These are defined according to Figure 1: (i) a cartesian frame is placed with the origin at the center of mass of the aromatic ring, (ii) the x axis goes through the atom labeled with the lowest number, and (iii) the y axis lies in the aromatic ring. With reference to this frame, the small molecule is first placed with the aromatic ring (xy plane) parallel to (001) and the x axis parallel to the lattice axis b; then, rotations are applied in the sequence around a by ρ_y, around b by ρ_x, and around c by ρ_z].

(4) The six torsion angles τ_i defining the PEO chain conformation as shown in Figure 2. In the case of α-2MR, as will be discussed later, only three torsion angles are considered to set the $^7/_2$ chain conformation.

The following structural parameters are taken to be fixed during refinement: bond lengths C−C = 1.54 Å, C−O = 1.43 Å, and C−H = 1.08 Å and bond angle

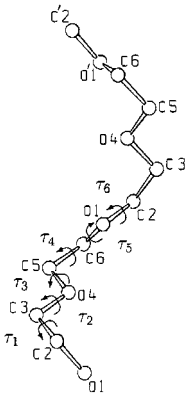

Figure 2. PEO chain backbone showing torsional angles.

O−C−C = 109.5°, C−O−C = 109.5°, and H−C−H = 109.5°. The isotropic thermal parameter B_{iso} = 7.11 Å^2, taken to be equal for all atoms, is not refined because of its strong correlation with the scale factor. Hydrogen atoms, placed using the canonical sp^2 and sp^3 geometry, are included in the calculation. During refinement, two constraints are imposed on the chain backbone to force the chain length to match the c axis length. As shown in Figure 2, they are that (1) the distance $O_1-O'_1$ must match the c axis length and (2) the x and y fractional coordinates of atoms C_2 and C'_2 must be equal.

PEO−Resorcinol Complex (RES)

RES possesses two allotropic forms, α and β, with a PEO monomer-to-RES molecule ratio of 2:1.[9−12] The latter is metastable and transforms spontaneously into the stable α form; thus, the β form will not be considered in this article. Myasnikova et al.[8] proposed for RES a monoclinic unit cell with a = 16.05 Å, b = 14.25 Å, c = 9.84 Å, and β = 112°, whereas some of us[11] suggested an orthorhombic unit cell with a = 10.50 Å, b = 10.13 Å, c = 9.776 Å, and the $Pna2_1$ space group, according to the extinction conditions. This cell will be used in the following structure refinement stage.

Structure Refinement. In the first stage of the analysis, the *ttg* conformation and screw symmetry, which is one of the symmetry operators of the space group, are imposed on the PEO chain (4 monomeric units/chain). Thus, the center of mass of PEO is placed at the origin of the cell ($X_0 = 0$, $Y_0 = 0$, $Z_0 = 0$). Because the asymmetric unit contains two monomers and the stoichiometric ratio of monomeric units to small molecules is 2:1, only one resorcinol unit has to be accommodated in the asymmetric unit. We decided to place the center of mass of the small molecule at $x_0 = 0.25$, $y_0 = 0$, and $z_0 = 0$, both to avoid steric interactions and to ensure strong 200 and 110 reflections, according to the equatorial observed data.

By following the procedure described in the previous section, the convergence of refinement is reached in a few cycles, and the experimental diffraction pattern is well-reproduced, but a short (2.27 Å) PEO chain-to-resorcinol contact takes place between an oxygen ether atom of the chain (O_{12}) and a hydroxy oxygen atom of resorcinol (O_7). Indeed, short contacts are expected according to a previous IR and NMR investigation,[12] but 2.27 Å is clearly not a realistic value. The anomalous result may be due to the presence of two independent

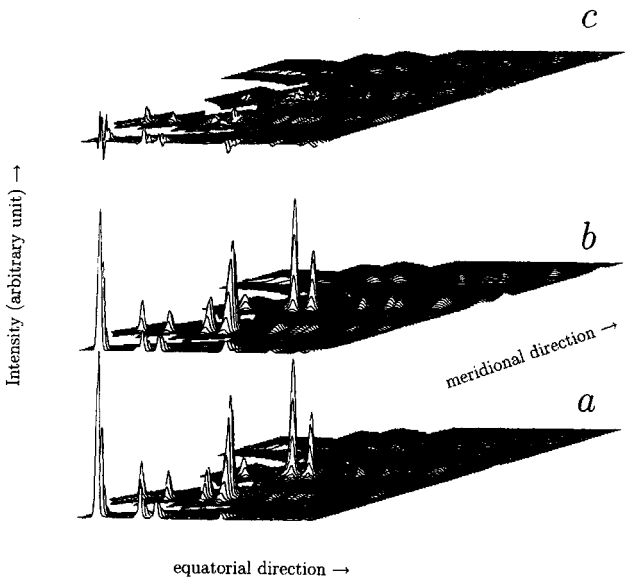

Figure 3. Three-dimensional representation of X-ray diffraction pattern of RES: (a) observed data; (b) calculated data according to this article; (c) the difference between (a) and (b).

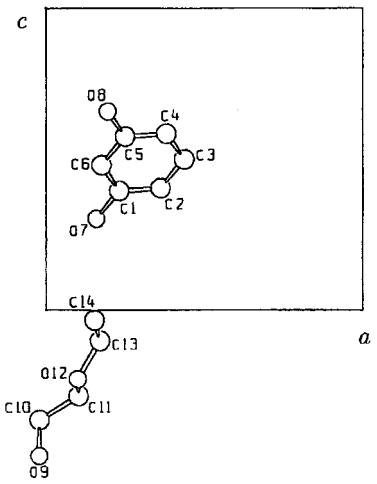

Figure 4. Asymmetric unit showing atomic labeling of RES according to Tables 1 and 2.

molecules (one chain and one small molecule) in the same asymmetric unit, which is a less favorable situation compared to a single molecular frame in which atoms constrain each other by bond lengths and angles. The problem may be solved by applying a constraint to this distance, which may be forced to be, for instance, 2.80 Å, as would be expected for a hydrogen bond. In this way, a new run is carried out, and the convergence is reached in few cycles.

The observed and calculated diffraction data at the end of the refinement are compared in Figure 3. A representation of the asymmetric unit and the crystalline packing are shown in Figures 4 and 5, respectively. The refined atomic fractional coordinates and the refined parameters are listed in Tables 1 and 2, respectively. The packing is characterized by two hydrogen bonds between resorcinol and the PEO chain (2.80 Å for O_7-O_{12}, imposed by constraint, and 2.98 Å for O_7-O_9) and one between two resorcinol units (2.84 Å for O_7-O_8). All of the other intra- and intermolecular atomic distances are in agreement with the standard values (the shortest intermolecular contacts are 3.13 Å for O_7-C_{10} and 3.38 Å for C_5-C_{13}). Concerning the chain conformation, the *ttgttg* torsion angles sequence is almost retained with little distortion from the exact one. The PEO chains are organized to give a body-centered molecular packing with each chain surrounded by resorcinol units; therefore no direct chain-to-chain interaction takes place. The resorcinol units are tilted with respect to the *c* axis direction so that they fill the free space left in the cell by the PEO chain sinuous conformation.

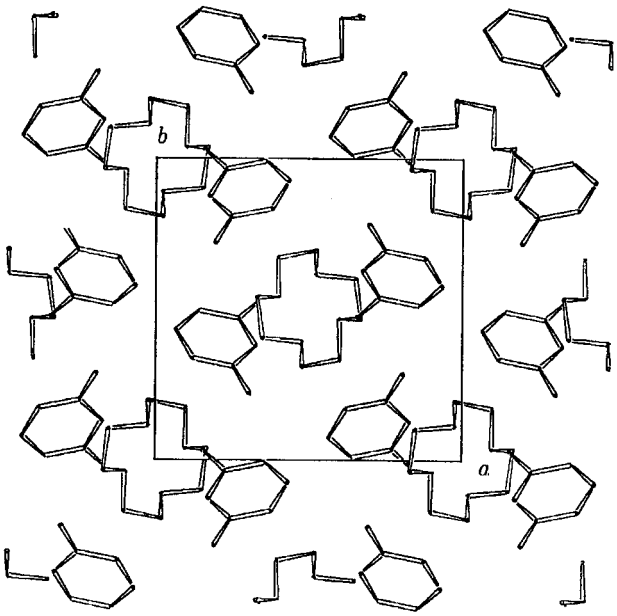

Figure 5. Molecular packing of RES along the *c* axis.

Table 1. Atomic Fractional Coordinates As Obtained after Structural Refinement of RES

atom label	*x*	*y*	*z*
C_1	0.230(2)	−0.035(1)	0.392(2)
C_2	0.360(1)	−0.009(2)	0.401(2)
C_3	0.434(3)	−0.075(1)	0.497(1)
C_4	0.378(2)	−0.168(1)	0.583(2)
C_5	0.248(1)	−0.194(2)	0.574(2)
C_6	0.174(3)	−0.127(1)	0.478(1)
O_7	0.158(3)	0.029(3)	0.299(4)
O_8	0.193(3)	−0.283(4)	0.657(3)
O_9	−0.023(1)	0.112(3)	−0.485(9)
C_{10}	−0.022(1)	0.194(4)	−0.365(7)
C_{11}	0.101(3)	0.169(4)	−0.285(6)
O_{12}	0.099(2)	0.037(1)	−0.229(4)
C_{13}	0.168(4)	0.035(1)	−0.102(2)
C_{14}	0.152(4)	−0.100(2)	−0.034(1)

Table 2. Structural and Nonstructural Parameters As Obtained at the End of Structural Refinement of RES[a]

parameter	value	parameter	value
τ_1 ($C_{10}-C_{11}$)	68.3(4)°	τ_2 ($C_{11}-O_{12}$)	148.9(2)°
τ_3 ($C_{12}-C_{13}$)	187.2(2)°	τ_4 ($C_{13}-C_{14}$)	70.7(2)°
τ_5 ($C_{14}-C_{9'}$)	148.6(3)°	τ_6 ($C_{9'}-C_{10'}$)	199.7(2)°
a	10.54(1) Å	*b*	10.18(1) Å
c	9.89(1) Å		
x_0	0.3037(3)	y_0	−0.1013(2)
z_0	0.4874(5)	ρ_x	45.4(1)
ρ_y	18.3(1)	ρ_z	−148.4(1)
X_0	0	Y_0	0
Z_0	0	Φ_0	−78.2(1)°
Δa	139.4(4) Å	Δb	225(1) Å
Δc	186(1) Å	α_0	4.41(1)°

[a] Standard deviation is given in parentheses only for the refined parameters.

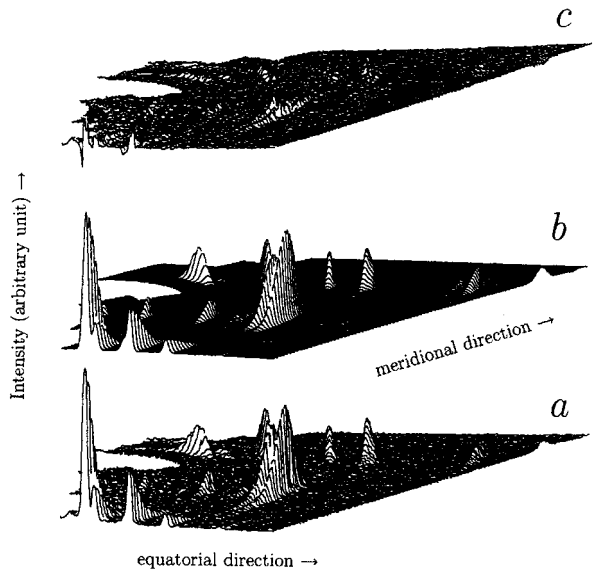

Figure 6. Three-dimensional representation of X-ray diffraction pattern of β-2MR: (a) observed data, (b) calculated data according to this article, and (c) the difference between (a) and (b).

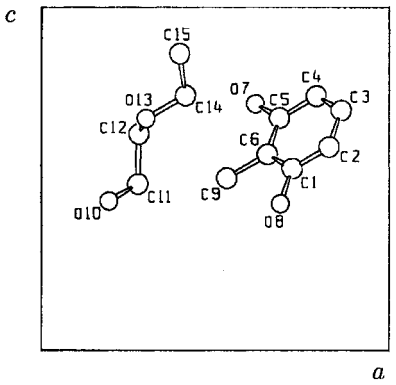

Figure 7. Asymmetric unit showing atomic labeling of β-2MR according to Tables 3 and 4.

PEP−2-Methylresorcinol Complex: β Form (β-2MR)

For β-2MR, a structure of an orthorhombic unit cell with $a = 11.1$ Å, $b = 18.6$ Å, and $c = 10.6$ Å, a *Pbca* space group, and four monomeric units in the repeating unit along the PEO chain[17] was proposed. The unit cell, the space group, and the proposed *ttg* chain conformation are used in the following structure refinement.

Structure Refinement. In analogy to RES, in the first stage of the analysis, the *ttg* conformation and the screw symmetry are imposed on the PEO chain. In this way, according to the space group, the center of mass of PEO is placed at $X_0 = 0.25$, $Y_0 = 0.0$, and $Z_0 = 0.0$. As in the case of RES, only one methylresorcinol unit has to be accommodated in the asymmetric unit. In the first hypothesis, the center of mass of the small molecule is placed at $x_0 = 0.25$, $y_0 = 0.25$, and $z_0 = 0$ in order to have strong 200 and 040 and weak 020 reflections, according to the equatorial data. Differing from RES, the overall coordinate $Z_0 = 0.0$ of the PEO chain has to be refined because of the centrosymmetric space group.

After the refinement was begun, convergence was reached in few runs. The observed and calculated diffraction data at the end of the refinement are compared in Figure 6. A representation of the asymmetric unit and the crystalline packing are shown in Figures 7 and 8, respectively. Refined atomic fractional coordinates and refined parameters are listed in Tables 3 and 4, respectively. Only two hydrogen bonds between small molecules and the PEO chain (2.87 Å for O_8-O_{13} and 2.98 Å for O_8-O_{10}) are present in the packing with no interactions between methylresorcinols. The other intra- and intermolecular atomic distances are in agreement with the standard values (the shortest intermolecular contacts are 3.21 Å for O_7-C_{12} and 3.34 Å for C_3-C_9).

On the basis of the torsion angles in Table 4, it is evident that the PEO chain conformation is distorted from that of the standard *ttg*. Moreover, compared to RES, PEO chains and small molecules are packed to give a layered structure with chain-to-chain interaction. Because RES and β-2MR have the same stoichiometric ratio of monomeric units to small molecules, it is clear that the methyl group is responsible for such a deep-structure modification. As with RES, the aromatic molecules are tilted with respect to the *c* axis to fill the

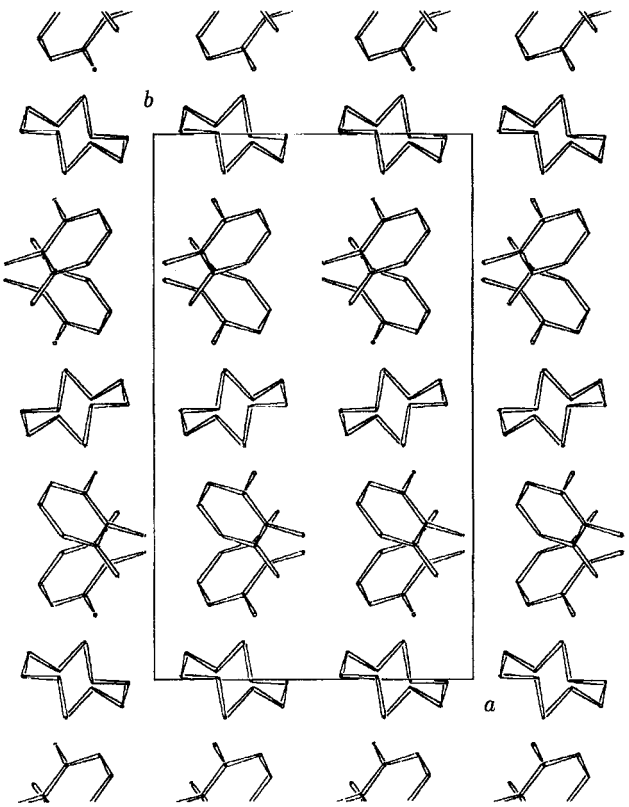

Figure 8. Molecular packing of β-2MR along the *c* axis.

Table 3. Atomic Fractional Coordinates As Obtained after Structural Refinement of β-2MR

atom label	*x*	*y*	*z*
C_1	0.721(1)	0.657(5)	−0.468(3)
C_2	0.827(2)	0.639(7)	−0.405(1)
C_3	0.862(3)	0.677(2)	−0.299(2)
C_4	0.790(1)	0.735(5)	−0.257(3)
C_5	0.685(2)	0.753(7)	−0.320(1)
C_6	0.650(3)	0.714(2)	−0.426(2)
O_7	0.615(4)	0.809(14)	−0.280(2)
O_8	0.687(2)	0.619(10)	−0.571(5)
C_9	0.533(6)	0.734(5)	−0.496(3)
O_{10}	0.195(2)	0.016(2)	−0.563(11)
C_{11}	0.278(2)	0.069(9)	−0.513(10)
C_{12}	0.281(2)	0.069(9)	−0.367(6)
O_{13}	0.302(1)	−0.003(1)	−0.322(5)
C_{14}	0.415(4)	−0.006(2)	−0.255(4)
C_{15}	0.398(4)	−0.049(7)	−0.134(1)

Table 4. Structural and Nonstructural Parameters As Obtained at the End of Structural Refinement of *β*-2MR[a]

parameter	value	parameter	value
τ_1 ($C_{11} - C_{12}$)	−52.2(1)°	τ_2 ($C_{12} - O_{13}$)	243.1(3)°
τ_3 ($O_{13} - C_{14}$)	224.5(6)°	τ_4 ($C_{14} - C_{15}$)	58.7(2)°
τ_5 ($C_{15} - O_{10'}$)	227.3(6)°	τ_6 ($O_{10'} - C_{11'}$)	239.0(4)°
a	11.07(1) Å	b	18.60(2) Å
c	10.74(1) Å		
x_0	0.756(1)	y_0	0.696(1)
z_0	−0.363(1)	ρ_x	−54.6(1)
ρ_y	185.5(2)	ρ_z	−35.7(1)
X_0	0.25	Y_0	0
Z_0	−0.110(1)	Φ_0	−25.3(6)°
Δa	202(1) Å	Δb	234(1) Å
Δc	338(3) Å	α_0	6.33(1)°

[a] Standard deviation is given in parentheses only for the refined parameters.

free space left by the sinuous shape of PEO chain in the unit cell.

PEO−2-Methylresorcinol Complex: α Form (α-2MR)

For α-2MR, the following orthorhombic unit cell was proposed: $a = 10.4$ Å, $b = 15.9$ Å, $c = 18.5$ Å, a $Pm2_1b$ space group, and a $^7/_2$ PEO chain conformation.[17] According to the experimental density, four chains and eight resorcinols are accommodated in the unit cell. The $^7/_2$ chain conformation was suggested to explain the appearance of weak layer lines at high angle in the diffraction pattern that cannot be indexed with a halved c axis (about 10 Å) corresponding to the typical $^4/_1$ chain conformation. This hypothesis is supported by the occurrence of the same chain conformation in the case of pure PEO.[28] In the same article, a monoclinic unit cell, metrically orthorhombic, was suggested to explain the few extinctions in the diffraction pattern and to remove the mirror plane (parallel to the chain axis, thus not acceptable in terms of molecular packing) imposed by the space group $Pm2_1b$.

The unit cell and the proposed $^7/_2$ chain conformation are used in the following structure refinement to set the starting model. The only difference is the exchange between a and b axes.

Structure Refinement. A structure with 4 PEO chains/unit cell restricts the choice of space group to only those with four general positons. In fact, because of the absence of any symmetry for the $^7/_2$ conformation (rejecting the hypothesis of a two-fold axis perpendicular to the C−C bond along the chain as too restrictive), space groups with a higher number of general positions cannot be taken into account. Consequently, there are two methylresorcinols in the asymmetric unit. This is unusual, but it should be kept in mind that the shape of the $^7/_2$ chain is close to that corresponding to two turns of the $^4/_1$ (*ttg*) chain; thus, the two small molecules may have the same x and y atomic coordinates, remaining only shifted to each other by $c/2$ along the chain axis. In other words, the two small molecules are surrounded by the same "environment", thus resulting in very similar steric interactions with the PEO chains. This hypothesis is compatible with the very weak odd layer lines in the diffraction pattern (the first and the third ones are practically absent), and any attempt to modify the relative position of the two methylresorcinols along c gives strong odd layer lines. Because of the extinctions ($h0l$ and $h00$; h = even), in the orthorhombic case only the space group $P2_1mb$ may be considered, as already

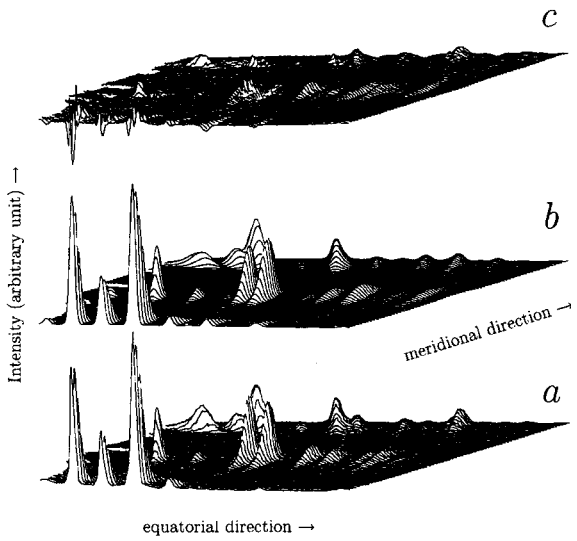

Figure 9. Three-dimensional representation of X-ray diffraction pattern of α-2MR (structure I): (a) observed data, (b) calculated data according to this article, (c) the difference between (a) and (b).

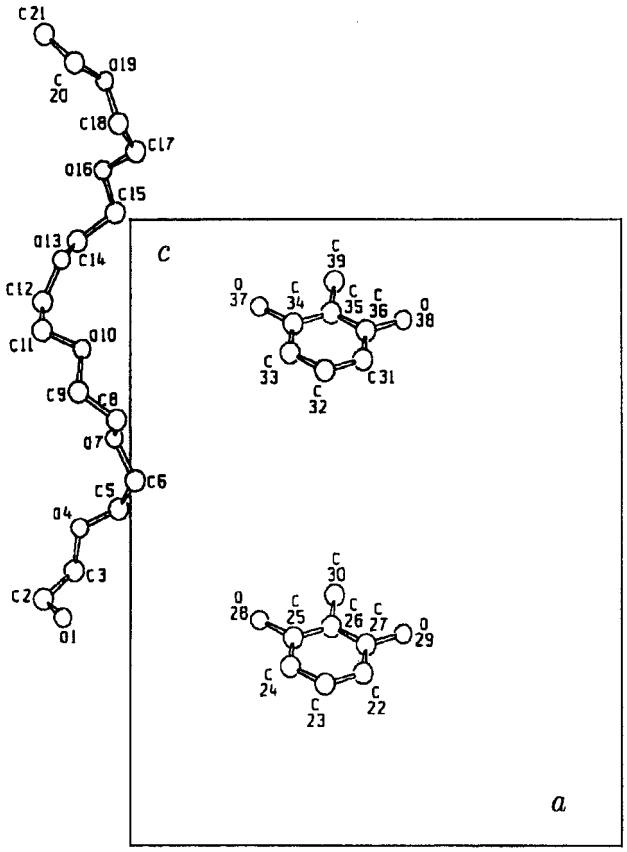

Figure 10. Asymmetric unit showing atomic labeling of α-2MR according to Tables 5 and 6.

suggested in Paternostre et al.[17] (here given as $Pm2_1b$ because of the exchange of a and b axes). But any attempt to use this space group in the refinement failed because it is not possible to reproduce exactly the three strong equatorial reflections with indices 200, 210, and 020. In fact, the 210 is always weak, and any attempt to increase its intensity gives lower 200 or 020 peaks or lowers both. Then, the less symmetric monoclinic cell was tried in an effort to better model the intensity of the equatorial line in the diffraction pattern. Among the monoclinic space groups, the $P2_1/a$, c axis unique, meets

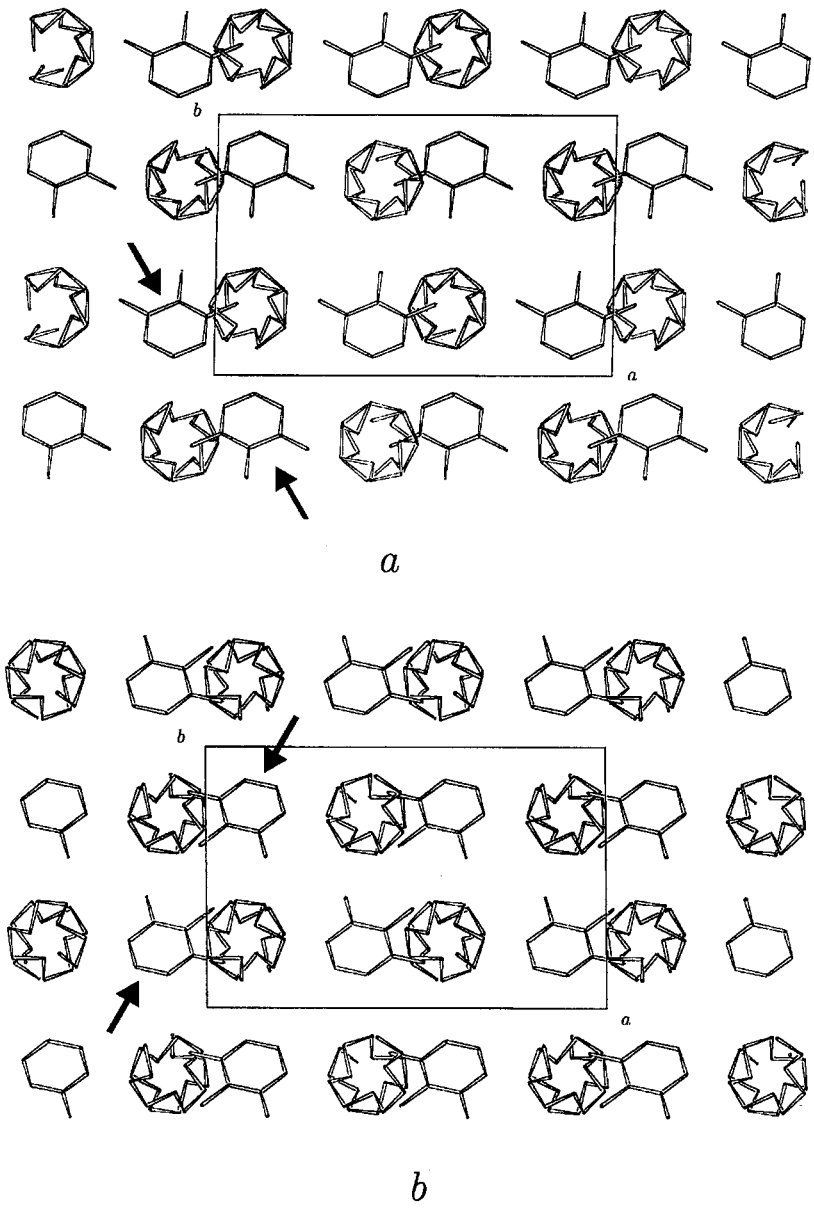

Figure 11. View of the molecular packing along the *c* axis of α-2MR for the two structures corresponding to the two minima in the observed-to-calculated fitting: *a* = model I and *b* = model II.

the selected extinction rule and is thus considered. In the starting model, the center of mass of the chain is placed at $X_0 = 0.25$, $Y_0 = 0.25$, and $Z_0 = 0$, and the two aromatic molecules are placed at $x_0 = 0.50$, $y_0 = 0.25$, $z_0 = 0$ and $x_0 = 0.50$, $y_0 = 0.25$, $z_0 = 0.5$, respectively. The refinement procedure converges in few runs with a good experimental-to-calculated fitting but with very short chain-to-resorcinol contact (the shortest is 1.45 Å for O_1-O_{38} and 2.42 Å for C_2-O_{38}). As in the previous complexes, the observed-to-calculated diffraction data fit is shown in Figure 9, and the asymmetric unit and the crystalline packing are shown in Figures 10 and 11a, respectively. Moreover, the refined atomic fractional coordinates and the refined parameters are listed in Tables 5 and 6.

The strong interactions are shown clearly in Figure 11a, with the aromatic molecule placed very close to the PEO chain. It is not clear why the small molecule should leave empty space on its left side where another PEO chain is clearly too far away. Moreover, the atomic coordinates are affected by a large error (standard deviations given in paraentheses in Table 5), especially the *z* coordinates of atoms belonging to the PEO chain (O_1-C_{21}) and the coordinates of some atoms of the methylresorcinols (for instance, hydroxy and methyl groups). These may suggest some statistical displacement of molecules or disorder in the unit cell. With this idea in mind, we performed a new run starting from the refined structure with a small change of the coordinates of the resorcinol, seeking another minimum in the refinement. Then, another convergence is reached in a few cycles corresponding to a new molecular structure close to the previous one but with some interesting differences; the calculated diffraction pattern is practically the same. To better compare the two structures, I and II, the projection along the *a* axis is compared in Figure 12. It is evident that the aromatic molecules may move in two different places to fill in the available space in the cell (this is in agreement with the lower experimental density, $d = 1.2$ g/cm^3, compared to that of the β-2MR, $d = 1.27$ g/cm^3; see Paternostre et al.[17]) by simply shifting a little in the *c* direction. In both packings, the two methylresorcinols are placed in such a way as to touch each other, and because they lie with

Table 5. Atomic Fractional Coordinates As Obtained after Structural Refinement of α-2MR

atom label	*x*	*y*	*z*
O_1	−0.134(4)	−0.296(2)	0.365(61)
C_2	−0.175(8)	−0.185(4)	0.394(58)
C_3	−0.133(3)	−0.110(4)	0.439(52)
O_4	−0.102(2)	−0.173(2)	0.507(43)
C_5	−0.023(6)	−0.138(4)	0.537(39)
C_6	0.012(8)	−0.249(4)	0.582(33)
O_7	−0.030(5)	−0.251(2)	0.650(24)
C_8	−0.025(6)	−0.377(4)	0.680(20)
C_9	−0.102(3)	−0.403(4)	0.725(14)
O_{10}	−0.095(2)	−0.339(2)	0.793(5)
C_{11}	−0.176(8)	−0.317(4)	0.823(2)
C_{12}	−0.176(8)	−0.196(4)	0.868(6)
O_{13}	−0.137(4)	−0.222(2)	0.936(14)
C_{14}	−0.107(3)	−0.105(4)	0.966(18)
C_{15}	−0.030(6)	−0.134(4)	1.011(24)
O_{16}	−0.054(3)	−0.186(3)	1.079(33)
C_{17}	0.014(8)	−0.259(5)	1.109(37)
C_{18}	−0.021(6)	−0.368(4)	1.154(43)
O_{19}	−0.049(3)	−0.319(2)	1.222(52)
C_{20}	−0.109(3)	−0.403(4)	1.251(56)
C_{21}	−0.171(7)	−0.326(4)	1.297(62)
C_{22}	0.473(6)	0.119(1)	0.276(4)
C_{23}	0.396(1)	0.070(2)	0.259(6)
C_{24}	0.325(7)	0.125(1)	0.287(2)
C_{25}	0.330(6)	0.229(1)	0.333(4)
C_{26}	0.407(1)	0.278(2)	0.350(6)
C_{27}	0.479(7)	0.223(1)	0.322(2)
O_{28}	0.261(12)	0.283(3)	0.360(7)
O_{29}	0.554(13)	0.270(3)	0.339(5)
C_{30}	0.413(2)	0.393(5)	0.400(13)
C_{31}	0.473(6)	0.119(2)	0.776(4)
C_{32}	0.396(1)	0.070(2)	0.759(6)
C_{33}	0.325(7)	0.125(1)	0.787(2)
C_{34}	0.330(6)	0.229(1)	0.833(4)
C_{35}	0.407(1)	0.278(3)	0.850(6)
C_{36}	0.479(7)	0.223(1)	0.822(2)
O_{37}	0.261(12)	0.283(3)	0.860(7)
O_{38}	0.554(13)	0.270(3)	0.839(5)
C_{39}	0.413(2)	0.393(5)	0.900(13)

Table 6. Structural and Nonstructural Parameters As Obtained at the End of Structural Refinement of α-2MR[a]

parameter	value	parameter	value
τ_1 ($C_2 - C_3$)	77.4(3)°	τ_2 ($C_3 - O_4$)	−156.7(2)°
τ_3 ($O_4 - C_5$)	−211.0(5)°		
a	16.24(2) Å	*b*	10.57(1) Å
c	18.79(2) Å	γ	89.2(1)°
x_0	0.402(1)	y_0	0.174(1)
z_0	−0.696(1)	ρ_x	25.8(1)
ρ_y	−330.7(3)	ρ_z	−310.1(3)
X_0	−0.0860(1)	Y_0	−0.2550(3)
Z_0	0.828(2)	Φ_0	−36(2)°
Δa	143(1) Å	Δb	136(1) Å
Δc	130(1) Å	α_0	6.58(1)°

[a] Standard deviation is given in parentheses only for the refined parameters.

their aromatic planes in the same direction, they give a "pair" moiety. For the sake of clarity, the two resorcinols involved in this interaction are marked with arrows in Figures 11 and 12. Particularly in Figure 12, it is clear that structure I may transform into structure II, and vice versa, by dividing a "pair" and making a new one. This strongly suggests that the real structure is a statistical average of the two (and perhaps other ones also involving rotations of methylresorcinol around the *z* axes).

Discussion and Conclusion

The stability of mixed crystals containing a polymer counterpart depends on several energetic contributions,

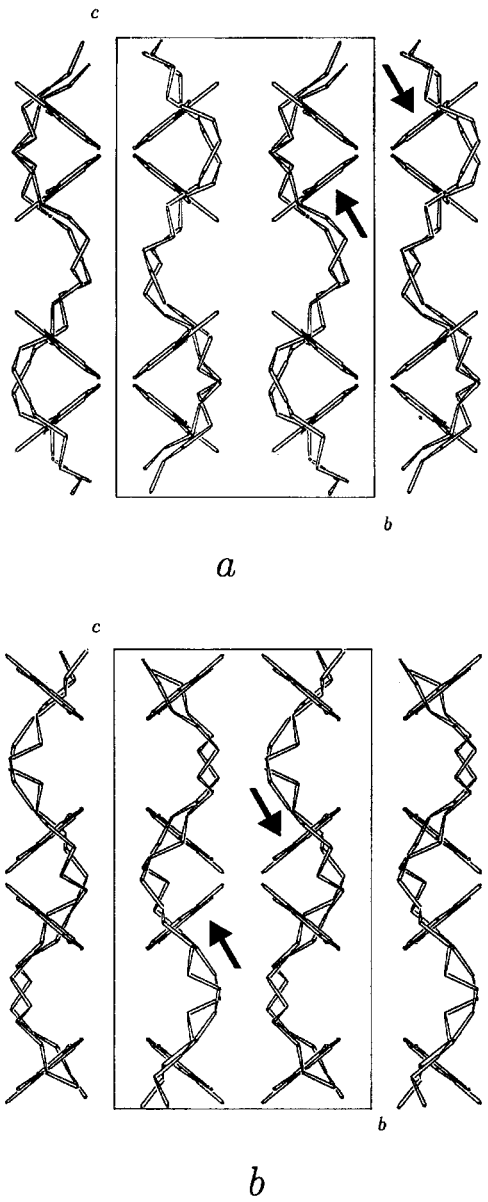

Figure 12. Molecular packing view of α-2MR along the lattice axis *a* for structures I (*a*) and II (*b*).

i.e., the polymer−guest molecules, guest−guest molecules, and polymer−polymer intermolecular interactions and an intramolecular energetic contribution related to the chain conformation. For pure PEO chains, several experimental and theoretical studies have demonstrated that the most stable chain conformation corresponds to the *ttg* conformers, with the C−O and C−C bonds being trans and gauche, respectively.[29,30] In the solid state, the stability of this *ttg* conformer and the interchains interactions yield the well-known $^7/_2$ helical conformation observed in the $P2_1/a$ monoclinic crystal structure.[28] For PEO molecular complexes, the crystal structure reflects the balance between the following tendencies, sometimes opposed: (i) to form intermolecular interactions with guest molecules (e.g., electrostatic interactions, hydrogen bonds, ...) and (ii) to maintain a chain conformation close to the canonical (*ttg*) conformation. Any large departure from the *ttg* conformation has to be compensated for by strong intermolecular interactions.

As shown in Figure 11, the α-2MR molecular complex exhibits an intercalated structure. This complex can be

formed by the diffusion of aromatic molecules inside the pure PEO unit cell[28] with only slight modifications of the chain packing, i.e., the increased distance between adjacent polymer layers to accommodate the guest molecules (see also the structure of PEO-*p*-dihalogenobenzene intercalates[4−7]). Because this structure only involves weak interactions (van der Waals contact or weak hydrogen bonds), the PEO chains still maintain a helical conformation very close to the canonical $^7/_2$ helix of pure PEO.

Contrary to these intercalates, RES and β-2MR exhibit a network of hydrogen bonds which can be prepared only from melted or dissolved polymer. As shown by an NMR investigation,[14] the chain mobility in these molecular complexes is considerably reduced by the interactions with the guest molecules. However, the intermolecular interactions are not strong enough to induce a large departure from a *ttg*like conformation (see Tables 2 and 4). For the PEO-*p*-nitrophenol complex, the structure contains one PEO chain of six monomers surrounded by four stacked *p*-nitrophenol molecules.[18,19] The stacks of antiparallel aromatic molecules are formed because of the strong dipole−dipole interactions. In this case, the PEO chains adopt an unusual glide (*ttg ttg ttt tt-g tt-g ttt*) conformation so that the four oxygen atoms of PEO interact with the hydroxyl groups of the *p*-nitrophenol molecules. For all of these different complexes, the crystal structure is fully determined by the formation of hydrogen bonds between host and guest molecules, the distortion of the PEO chains, and by molecular packing considerations.

On the basis of the structure, an explanation can be proposed to account for the polymorphism observed for the 2MR system, whereas only one stable crystal form each exists for the PEO-*p*-dihalogenobenzene, RES, and the HYD[15,16] molecular complexes. In fact, we suggest that the methyl group of methylresorcinol favors van der Waals or electrostatic interactions or a combination of both with the PEO chains and thus greatly stabilizes the low-methylresorcinol-content intercalated structure (α-2MR), as it does for the *p*-dihalogenobenzene complexes.[4−7] In addition, because the methyl group donates electron density on the aromatic ring, the ability of methylresorcinols to form hydrogen bonds is slightly lower than that of the resorcinol.

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