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Supramolecular Tubular Structures of a Polymethacrylate with Tapered Side Groups in Aligned Hexagonal Phases

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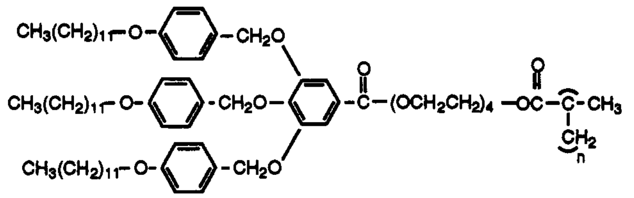
ABSTRACT: X-ray methods have been used to analyze the supramolecular tubular structures in the hexagonal solid state and columnar hexagonal liquid crystalline (ϕ_h) phases of a polymethacrylate with tapered side groups: specifically, poly{2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((*p*-(dodecyloxy)benzyl)oxy)benzoate}, abbreviated as 12-ABG-4EO-PMA. Oriented fibers were drawn from the ϕ_h liquid crystalline phase at ~60 °C and annealed for several days at 4 °C. The X-ray pattern for these fibers recorded at room temperature (25 °C) contained eight equatorial reflections that are orders predicted for a hexagonal unit cell with $a = b = 60.4$ Å. The similarity of the data to those for unoriented specimens in the ϕ_h phase suggests that both phases contain the same type of supramolecular cylindrical moieties. In addition, wide-angle maxima are observed on the equator and two layer lines that suggest formation of a three-dimensionally-ordered structure at room temperature. These data give the first available information on the supramolecular structure within the columns. The layer line spacings define a repeat of $c = 5.03$ Å along the column axis, containing eight monomeric units based on the observed density. Strong off-meridional maxima at $d = 4.30$ and 3.84 Å on the first layer line suggest that the "planes" of the aromatic moieties are tilted rather than perpendicular to the cylinder axis. Possible "pine tree" models are discussed in which the tapered side groups are stacked in 8-fold layers or form 8-fold helices within the columns. Increasing the temperature to 60 °C leads to a reduction in the cylinder diameter to 58.0 Å. Stacking correlations remain along the fiber axis direction, but otherwise the internal structure of the cylinder is much more disordered than at room temperature. On cooling, the three-dimensional order is restored.

Introduction

In this paper we describe an investigation of the tubular supramolecular structures formed by a thermotropic liquid crystalline polymethacrylate with tapered side groups: specifically, poly{2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((*p*-(dodecyloxy)benzyl)oxy)benzoate}, abbreviated as 12-ABG-4EO-PMA, as shown below:



Both 12-ABG-4EO-PMA and its low molar mass precursor, 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((*p*-(dodecyloxy)benzyl)oxy)benzoate (abbreviated as 12-ABG-4EO-OH), self-assemble to form supramolecular tubular architectures which generate ϕ_h liquid crystalline phases.[1a–c] The mechanism for this self-assembly was discussed by Percec *et al.*[1a,b] The planar tapered side group 12-ABG-4EO-OH, based on the 3,4,5-tris((*p*-(dodecyloxy)benzyl)oxy)benzoic acid (12-ABG) moiety, plays an important role in this process. Extensively tapered groups based on 12-ABG and other related structures have been used[1] to generate molecular and macromolecular structures that self-assemble into supramolecular architectures, following the principles resembling those of the self-assembly of tobacco mosaic virus (TMV)[2] and of other rodlike viruses. The bulky tapered group mimics the shape of the protein subunits of the viral coat and could possibly lead to a self-assembled helical tubular supramolecular structure, in which the polymer backbone forms the core of the column.[1a–c] 12-ABG and other tapered groups have also been used in other laboratories to design molecular[3] and supramolecular[4] liquid crystals displaying ϕ_h and other liquid crystalline phases. Alternative methods to generate self-assembled supramolecular disklike and cylindrical structures that form ϕ_h phases have also been reported.[5]

DSC and X-ray experiments have shown that 12-ABG-4EO-PMA and 12-ABG-4EO-OH are crystalline at room temperature and undergo transitions at approximately 47 and 66 °C, respectively (the actual temperatures depend on thermal history), to form a ϕ_h liquid crystalline phase,[1a,b] analogous to the ϕ_h phase seen for low molecular weight discotic liquid crystals.[6] The ϕ_h phase of 12-ABG-4EO-PMA becomes an isotropic melt above 103 °C.[1a] The existence of a ϕ_h phase was demonstrated by X-ray studies of unoriented specimens: three small-angle maxima are observed, with Bragg *d*-spacings in the ratio of $1:1/\sqrt{3}:1/2$, which indicate a hexagonal packing of cylinders with a diameter of 57.2 Å at 74 °C, increasing to 60 Å on cooling to 25 °C.[1a] Similar data were obtained for a family of polymers with different tapered side groups and backbones, indicating that the same type of supramolecular cylinders are formed.[1] In addition, the monomer 12-ABG-4EO-OH appears to self-assemble in an analogous manner, forming cylinders in which a noncovalent supramolecular structure replaces the covalent backbone of the polymer.[1a]

Other than the three intense small-angle maxima that define the cylinder diameter, the reported X-ray data contained only an "amorphous halo" at d = 4–5 Å. Thus so far there has been no information available to define the structure along the axis of the cylinders. Percec *et al.*[1a] have shown that the cylinder diameter is significantly less than that predicted for a structure in which the side chains radiate from the backbone and have fully extended

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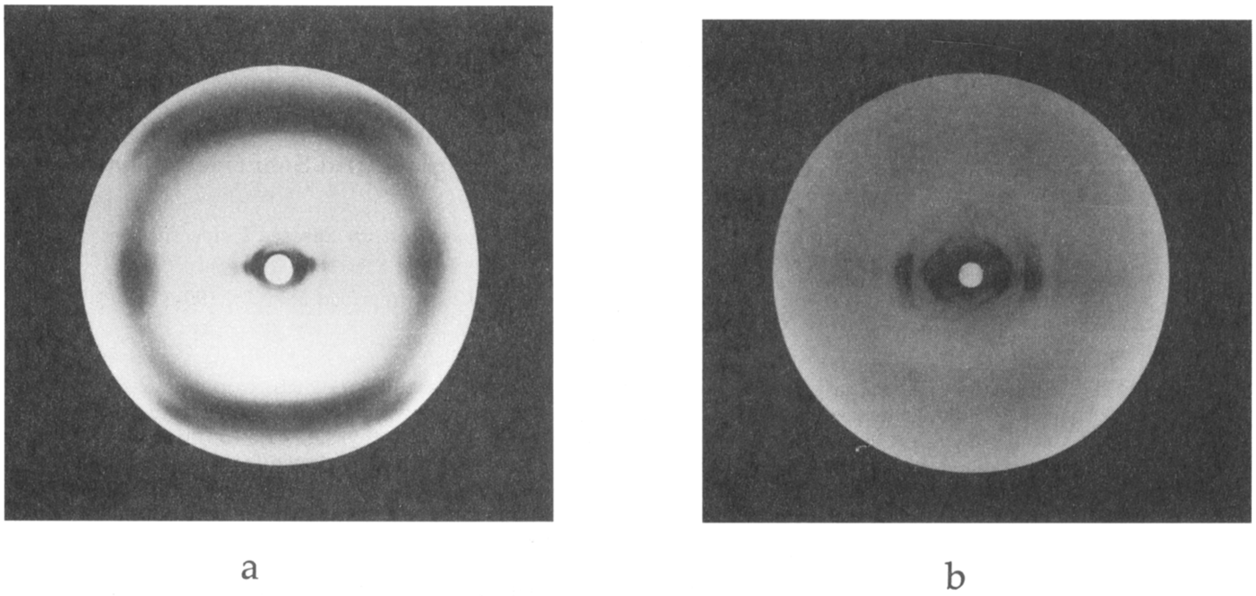

Figure 1. (a) Wide-angle and (b) small-angle X-ray diffraction patterns for melt-drawn fibers of 12-ABG-4EO-PMA at 25 °C. The fiber axis is vertical.

(all-*trans*) oligo(oxyethylenic) spacers and terminal alkyl groups. Therefore, it was suggested that the spacer and terminal groups must contain significant numbers of *gauche* conformations. If the 3,4,5-tris(benzyloxy)benzoate units are planar and are arranged so that they are stacked perpendicular to the cylinder axis, the measured density is compatible with six monomer units in an axial advance of 3.74 Å (the approximate thickness of an aromatic ring).[1a] Such a structure could be helical, with a staggering of the tapered groups along the backbone chain, but the monomers could also be grouped in disks of six that are stacked to form cylinders.

For a more detailed understanding of these supramolecular structures, it is essential to have X-ray data for oriented specimens, from which one can determine the structural parameters in the axial direction. We have prepared oriented fibers by stretching samples of 12-ABG-4EO-PMA in the ϕ_h liquid crystalline phase. It will be seen that these preparations yield higher quality X-ray data than those available previously and provide insight into the three-dimensional structure.

Experimental Section

Specimens of 12-ABG-4EO-PMA were prepared as described elsewhere,[1a] with a scale-up to generate 1 g of material. The molecular weight was determined by GPC to be M_n = 24000 (M_w/M_n = 1.42) based on polystyrene standards. This corresponds to a degree of polymerization of approximately 19. A homogeneous film of the polymer on a microscope slide at 60 °C was drawn as a fiber. Cut sections of such a fiber were aligned approximately parallel to each other as a bundle. This manipulation was made difficult by the stickiness of the fibers at room temperature, and the alignment in the resultant bundle was less than perfect. A fiber bundle was placed with its axis parallel to a magnetic field of 2.0 T at 90 °C for 20 min, in an effort to improve the ordering. The specimens were stored in a refrigerator at 4 °C for several days prior to recording the X-ray data. Wide-angle X-ray fiber diagrams were recorded at room temperature and at 60 °C on Kodak Direct Exposure scientific imaging film using a Searle toroidal focusing camera and Ni-filtered Cu Kα radiation. Pinhole collimation was used to record the data at small angles. The wide-angle d-spacings are calibrated using CaF_2 powder. The density of the specimen was determined by flotation in DMSO–water at 25 °C. Thermal analyses were performed using a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) at a scan rate of 20 °C/min. Details of the characterization by GPC and DSC are given elsewhere.[1a]

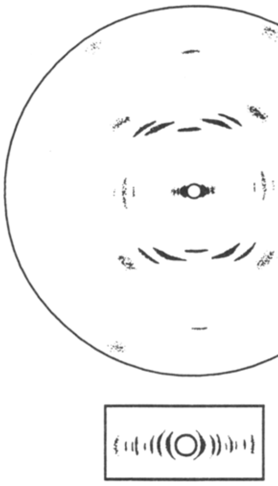

Figure 2. Schematic of the X-ray data presented in Figure 1.

Results

Figure 1 shows the wide- and small-angle diffraction patterns for the fiber bundle of 12-ABG-4EO-PMA recorded at room temperature (approximately 25 °C). We also present schematics of the data in Figure 2 in view of the difficulties in photographic reproduction. These data are for the specimen first subjected to a magnetic field of 2.0 T parallel to the fiber axis. Without application of the magnetic field, the wide-angle pattern was more diffuse, but the layer lines were still resolved. It was subsequently found that annealing for several days at 4 °C led to a steady improvement in the pattern, which became essentially identical to that in Figure 1b after ~5 days. The d-spacings of the observed intensity maxima are given in Table 1. The data consist of a series of eight small-angle maxima on the equator, plus intense wide-angle maxima on the equator and two layer lines. It is striking that the small-angle maxima consist of a number of components that can be assigned to the individual fibers in the bundle. The sharpness of these components points to the large size of the ordered domains. The d-spacings of the small-angle equatorials are indexed by a hexagonal unit cell with dimensions $a = b = 60.4 \pm 0.5$ Å. The layer lines are the first and second orders of an axial repeat of $c = 5.03$ Å. The meridional location for the innermost reflection on

Table 1. Observed and Calculated d-Spacings and hkl Indices for 12-ABG-4EO-PMA at Room Temperature (~25 °C)

d (Å) obsd	d (Å) calcd	hkl
52.3 ± 0.4	52.3	100
30.1 ± 0.2	30.2	110
26.2 ± 0.1	26.2	200
20.1 ± 0.1	19.8	210
17.7 ± 0.1	17.4	300
14.4 ± 0.1	15.1/14.5	220/310
9.98 ± 0.1	10.07/9.88	330/420
7.58 ± 0.1	7.52/7.47	440/530 or 700
5.24 ± 0.03		equator, $l = 0$
4.58 ± 0.02		equator, $l = 0$
3.80 ± 0.05		equator, $l = 0$
5.03 ± 0.03		meridian, $l = 1$
4.30 ± 0.04		$l = 1$
3.84 ± 0.03		$l = 1$
3.02 ± 0.04		$l = 1$
2.46 ± 0.02		meridian, $l = 2$
2.06 ± 0.02		$l = 2$

the second layer line was confirmed by tilting the specimen at the Bragg angle. The wide-angle maxima on the equator and those on the layer lines can be indexed by a hexagonal unit cell with the above dimensions and suggest that the structure has three-dimensional crystallinity. The calculated density for a unit cell with $a = b = 60.4$ Å, $c = 5.03$ Å, and $\gamma = 120°$ containing 8 monomer units is 1.034 g/cm^3, which is close to the measured density of 1.033 ± 0.005 g/cm^3.

Figure 3 shows the fiber diagram of a similar specimen recorded at 60 °C, above the crystal-to-ϕ_h transition temperature. A schematic of these data is shown in Figure 4, which also includes a sketch of the small-angle data. In comparison to Figure 1, we see that the amorphous halo is much more intense, and the layer line intensities are not detected, except for a strong broad arc at $d \sim 4.3$ Å along the fiber axis direction. Six small-angle maxima are observed on the equator, which are indexed by a hexagonal unit cell with $a = b = 58$ Å. These maxima are comparable in sharpness to those seen at room temperature. The unit cell dimensions indicate significant lateral contraction of the cylinders on transition to the ϕ_h phase, consistent with work on other supramolecular structures of this kind.[1] From the changes off the equator, it appears that the ordering within the columns of the ϕ_h phase is much less regular than at 25 °C, but there is still some preferred stacking of the monomer units. After cooling and allowing to stand in the refrigerator for several days, the characteristics seen in Figure 1 are restored. These data are a further indication that the ordered structure is not simply the product of mechanical deformation.

Discussion

The lateral packing dimensions at 25 and 60 °C are comparable to those reported previously for the ϕ_h liquid crystalline phase of this material.[1a] It appears that the specimen at room temperature contains cylindrical units that are more ordered but nevertheless quite similar to those that exist in the ϕ_h phase. The wide-angle maxima seen at room temperature on the equator and layer lines 1 and 2 indicate that we have three-dimensional order under these conditions. The breadths of these maxima suggest that they arise simply from the Fourier transform of the cylindrical moiety; i.e., the three-dimensional order exists only within the cylinders, which are then packed on the hexagonal two-dimensional net.

For the structure at 25 °C we are able to define a c-axis dimension of 5.03 Å, which requires 8 monomer units within the repeat. The strong off-meridionals at $d = 4.30$ and 3.84 Å on the first layer line probably arise as a result of the stacking of aromatic rings that are tilted with respect to the column, rather than perpendicular thereto. In this regard it is interesting that the d-spacing of the second of these maxima is approximately the same as the thickness of a phenyl ring (≅3.74 Å). This maximum is inclined at approximately 50° to the axial direction.

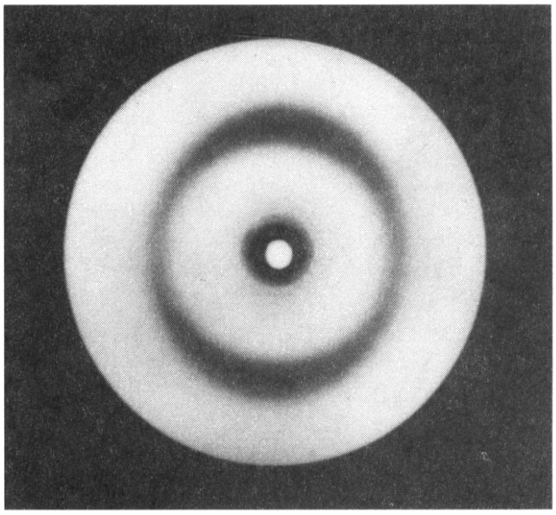

Figure 3. Wide-angle X-ray diffraction pattern for melt-drawn fibers of 12-ABG-4EO-PMA at 60 °C. The fiber axis is vertical.

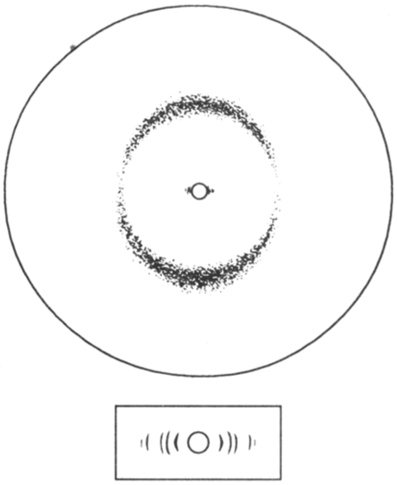

Figure 4. Schematic of the X-ray data presented in Figure 3. The data in the small-angle region are sketched in the rectangle.

The repeat of 5.03 Å would correspond to a dimer repeat for the polymer if the backbone had an all-*trans* conformation, but such a structure is not possible since it would result in bad contacts between the side chains. Since similar columnar structures are formed by the low molar mass compound 12-ABG-4EO-OH,[1a] it is likely that the structure adopted by the polymer 12-ABG-4EO-PMA is dictated by the conformation and stacking of the tapered side groups. As proposed previously,[1] we envisage that these stack to form a cylindrical tube, with the backbone and spacer units filling the central region. Given the length of the spacer units, these should be able to adjust to a conformation compatible with the packing of the tapered groups. The X-ray scattering should be dominated by the stacking of the aromatic moieties, and hence it is unlikely that we can determine the backbone conformation given that it is not stereoregular.

Within the constraints of the data, several possibilities exist for the arrangement of the monomers in the

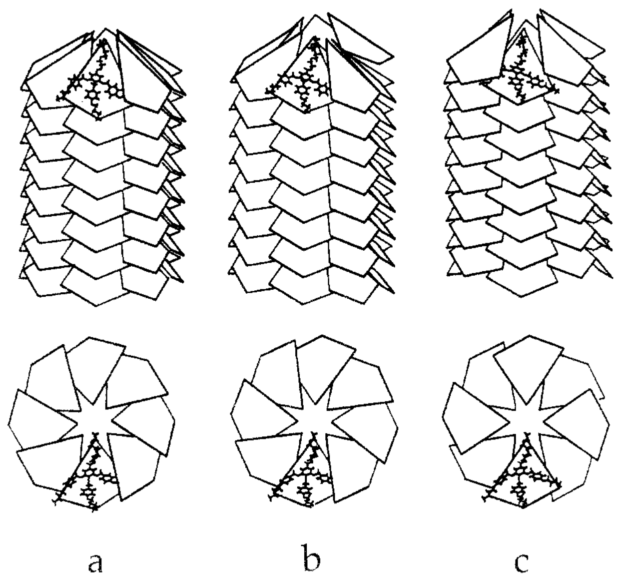

Figure 5. Possible models for the structure of the supramolecular cylindrical columns formed by 12-ABG-4EO-PMA at 25 °C: (a) 8-fold stacked disk structure; (b) 8_1 helix; (c) 8_4 helix. Lateral and axial projections are shown in each case. The monomer units are represented as tilted plates. The atomic structure is shown for one monomer in each case, omitting the backbone and most of the alkyl tails.

cylindrical units. At first glance, the presence of meridional maxima on the first and second layers would argue against any type of 8-fold helical structure and in favor of a stacked arrangement of disklike layers of 8 tilted monomers, as shown in Figure 5a. It seems most likely that the 8 monomers in the repeat would be all from one molecule, but they could derive from more than one, via lateral association of the backbones. The tilting of the "planes" of the tapered groups could be effected by twisting about the spokes of a wheel (giving a propeller-like structure), but they are also likely to be tilted below the plane, in what we describe as a "pine tree" model, which would allow for a more extended spacer and terminal group conformations. However, helical models must also be considered, because, given the large diameter of the cylinders, it is not possible to differentiate between meridional and near-axis off-meridional intensities. Helices appear to have an advantage over the stacked-disk model in that they can more easily accommodate the propagation of the side chains along the backbone in the core of the cylinders. Examples are the 8_1 (Figure 5b) and 8_4 (Figure 5c) models shown in Figure 5. The 8_4 model may deserve further consideration because of the relative weakness of the meridional on the first layer line compared to that of the second. The structure has a repeat consisting of a stack of two disks each of 4 monomers related by a rotation of 45° about the *c*-axis and is analogous to the 10_5 arrangement of the coat protein subunits in filamentous bacteriophage M13.[7] Trial molecular models for the three possibilities described here show that arrangement of the backbone and spacer units within the core probably involve distortions from the local minimum energy conformations that are compensated by the favorable stacking of the tapered side groups. The supramolecular pine tree structures shown in Figure 5 are analogous to those of pyramidic mesophases obtained from cone-shaped cyclotriveratriylenic cores[8] and also bowlic liquid crystals.[3e,9]

In analyzing the data we have considered the possibility that the structure obtained in the oriented specimens occurs only as a result of the mechanical deformation. If this was the case, however, we could not expect the structure to be re-formed after repeated transformations to the ϕ_h phase. It could also be argued that at room temperature we have a mixture of a quenched ϕ_h liquid crystalline phase and a very different crystalline structure, in which case the diffraction data contain the characteristics of both forms superimposed. Following this argument, the data for the layer lines might not relate to the same structure as that giving rise to the hexagonal maxima for the columnar phase. However, the improved ordering achieved on annealing at 4 °C occurs uniformly, whereas increased crystallinity of a new structure might be expected to occur at the expense of the quenched ϕ_h phase. Thus it appears likely that the X-ray data arise from a single structure that is an ordered arrangement of cylindrical moieties that are similar to those present in the ϕ_h liquid crystalline structure.

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