


**Experiment title:**

Aromatic Semirigid Chain Polymers: Studies of Semicrystalline Morphology and its Reorganization upon Annealing

**Experiment number:**

26-02-219

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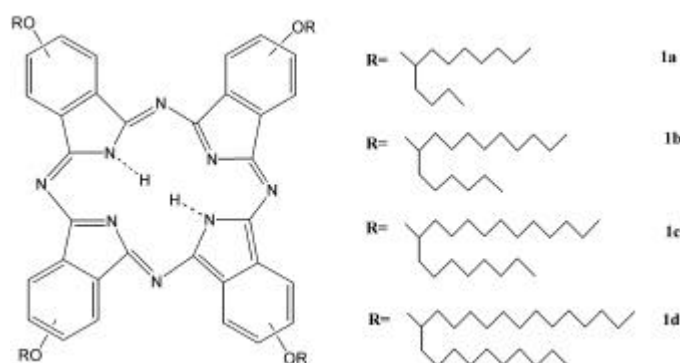
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**Report:**

Since the very discovery of mesogenic phtalocyanines (Pc's) by *Piechocki* and co-authors in 1982 [1], there has been a great, and growing, interest in these materials due to their fascinating optical and electronic properties [2-5], which make them potential candidates for (opto-)electronic devices. Here we report on the structure of four newly synthesized metal-free alkoxy tetrasubstituted Pc's with branched aliphatic chains [6]. Phase characterization was done with X-ray diffraction. X-ray diffraction measurements on oriented samples were performed on BM26 beamline at the European Synchrotron Facility in Grenoble (France) using the energy of 10 KeV. The data were collected in transmission employing 2048x2560 pixels image plates with a pixel size of 98x98  $\mu\text{m}^2$ . The temperature was controlled by a Linkam heating stage operated under a  $\text{LN}_2$  flow. The modulus of the scattering vector  $\underline{s}$  ( $s = 2\sin\theta/\lambda$ , where  $\theta$  is the Bragg angle and  $\lambda$  - wavelength) was calibrated using three diffraction orders of silver behenate. Fibers with diameter of 0.7 mm were obtained by extruding the material in the liquid crystalline phase with a home build mini-extruder. All the compounds show a columnar rectangular disordered mesophase,  $\text{Col}_{\text{rd}}$ , at RT and a columnar hexagonal ordered mesophase,  $\text{Col}_{\text{ho}}$ , at 110°C. Fiber diffraction patterns of both phases are shown in Figure 2. The small-angle fiber diffraction patterns in the  $\text{Col}_{\text{ho}}$  mesophase (Fig. 2A) show a set of equatorial reflections with s-spacings given by the ratio: 1:  $\sqrt{3}$  : 2 :  $\sqrt{7}$ . These can be indexed as the 100, 110, 200 and 210 reflections of an oriented hexagonal columnar mesophase. The wide-angle diffraction region of the same pattern displays two diffraction features. Firstly, a broad halo is found at  $s=0.23 \text{ \AA}^{-1}$ . This is believed to arise from the diffraction by the side-chains in the liquid-like state [7]. The corresponding distance is approximately 4.5  $\text{\AA}$ , which is in good agreement with the van der Waals radius of the carbon atom [8]. Secondly, a wide-angle peak (denoted P in the figure) can be accounted for by assuming stacking of molecules in columns with an average nearest neighbor distance of 3.4-3.5  $\text{\AA}$ . The presence of this reflection implies a certain degree of order in the placement of molecules in the column. Therefore the corresponding mesophase was identified as hexagonal ordered columnar mesophase. Note that the distinction between the



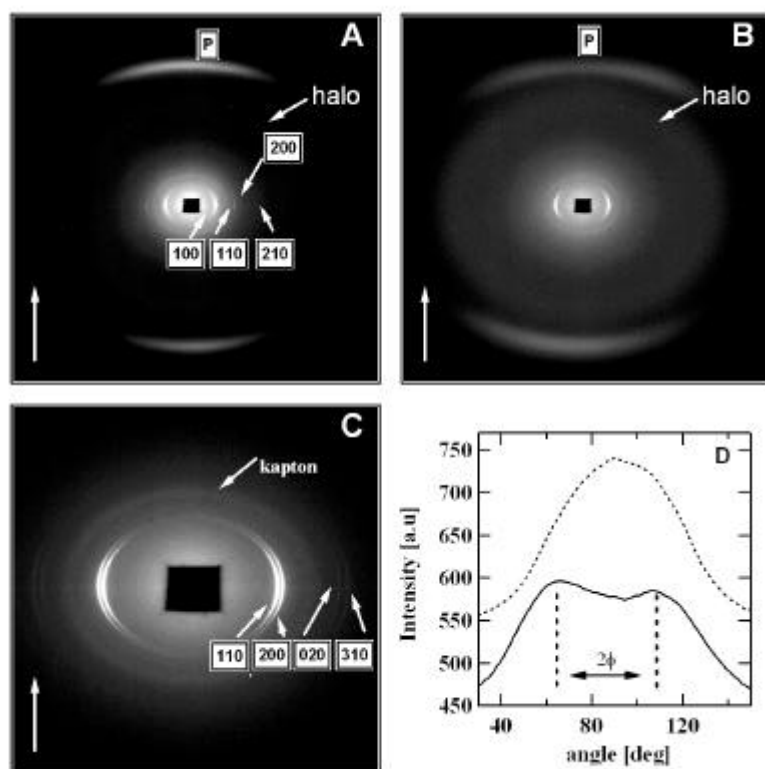
**Fig.1.** Molecular structure of Pc derivatives 1a-d.

ordered and disordered columnar phases is more a matter of convention. Despite the fact that the P peak in the low-temperature mesophase is characterized by about the same width at half maximum ( $0.027 \text{ \AA}^{-1}$ ) as the corresponding peak of the  $\text{Col}_{\text{ho}}$  phase ( $0.024 \text{ \AA}^{-1}$ ), it is a common practice to identify the columnar rectangular mesophase as  $\text{Col}_{\text{rd}}$  (disordered) [9]. Interestingly, some years ago, a claim was made that the ordered mesophases cannot exist for non-hexagonal columnar mesophases. The latter statement does not seem to hold for the systems studied in this work, i.e. rectangular mesophases that are only slightly different from hexagonal structures (pseudo-hexagonal lattices).

In the diffractograms corresponding to the low-temperature mesophase of **1a-d** derivatives (cf. Fig. 2B,C) six reflections are present in the small-angle region. Since all  $hk0$  reflections, denoted further as  $hk$  with  $h+k \neq 2n$ ,  $h0$  with  $h \neq 2n$  and  $0k$  with  $k \neq 2n$ , are absent, this is consistent with the sample being in the crystallographic register described by the two-dimensional space group  $\text{C2mm}$  [10]. At high scattering angles the diffraction patterns exhibit only a broad peak, reflecting the disordered state of the lateral chains and the P reflection corresponding to the form-factor of the column.

The tilt of the molecules with respect to the columnar axis was measured from the angular dispersion of the scattering intensity of the P peak (Fig. 2D). Note that the azimuthal scan (Fig. 2D) displays two broad maxima, which indicate a certain distribution of the tilt angles of the disks. The location of the intensity maxima was taken as the most probable disk tilt angle, which ranges between  $15$  and  $18^\circ$ . If we assume that the sample is described by  $\text{C2mm}$  group, one can conclude that the disks are tilted either along  $a$  or along  $b$  directions. Since the smallest of the  $a$  and  $b$  lattice parameters (chosen in this work as  $b$ ) is close to the  $a$  parameter of the corresponding hexagonal mesophase, whereas the other (in this case  $a$ ) is systematically smaller than  $\sqrt{3}$  times the hexagonal lattice parameter, one can conclude that the disks are tilted along  $a$ .

The lattice parameter of the  $\text{Col}_{\text{ho}}$  phase increases with the main chain length, from  $26.5 \text{ \AA}$  for molecule **1a**, which has short lateral chains, to  $31.8 \text{ \AA}$  for the **1d** molecule having long lateral chains. By approximating the variation of  $a$ , as a function of the number of carbons ( $n$ ) in the main chain, by a straight line and by extrapolating the fit to the intersection with the  $y$ -axis, one can estimate the diameter of the molecular core including the bridging ether oxygens. This value ( $19.2 \text{ \AA}$ ) is found to be comparable to the literature diameter of  $16 \text{ \AA}$  [11]. Taking the core size as  $16 \text{ \AA}$  and assuming the alkyl chains to adopt the *all-trans* conformation, the calculated molecular diameter of the studied Pc's was found to vary between  $40.0$  and  $55.2 \text{ \AA}$ . These values are larger than the ones derived from the X-ray measurements. A possible explanation of this discrepancy can be given if we assume that the lateral chains, belonging to the molecules in the neighboring columns, are interdigitated. More insights in the lateral chain conformation can be obtained from the estimate of the molecular volume. On the one hand, by using the lattice parameters determined from the X-ray measurements, the volume of one molecule in the hexagonal and rectangular mesophases can be written as:  $a^2 \cdot c \cdot \sqrt{3}/2$  and  $a \cdot b \cdot c/2$ , respectively. On the other hand, the molecular volume  $V_c$  can be expressed as  $V_c = V_0 + Z n V_{\text{CH}_2}$ , where  $V_0$  is the volume of the molecular core without the methylene groups and  $Z$  - the



**Fig.2.** 2D X-ray diffraction data on oriented samples, the white arrows in A-C indicate the fiber axis orientation. **A:** diffraction pattern of **1a** recorded at  $110^\circ\text{C}$ ; **B:** the same as in **A** recorded at room temperature, with a zoom of the low  $s$  range given in **C**. The diffuse reflection in the small-angle region indicated by the oblique arrow in **C** corresponds to the kapton tape used to fix the sample. **D:** angular dispersion of the P reflection for the rectangular and hexagonal (dotted line) mesophases of **1a** (the curves are vertically offset for clarity). The integration in **D** was performed between the  $s$ -values of  $0.28$  and  $0.33 \text{ \AA}^{-1}$ .

number of lateral chains. Equating both volumes, one can find that the  $V_{CH_2}$  value varies between 24.7 and 28.4 Å<sup>3</sup>. Similar estimates are also found for the low-temperature rectangular mesophase Col<sub>rd</sub>. These values are in some instances smaller than the literature values for the columnar mesophases (27-28 Å<sup>3</sup>) [12]; this discrepancy can be explained by the fact that the  $V_{CH_2}$  can differ for linear and branched alkyl chains.

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