

Study of 1,15-pentadecanediol by Powder X-ray Diffraction and Polarized Light Microscopy

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α,ω -alkanediols are simple aliphatic compounds with two hydroxyl groups at both sides of chain, but their crystal structures are quite complex showing melting point alternation and two kinds of crystal packing (herringbone and parallel motif), which depends on the parity of the number of carbon atoms. Even-odd behavior in α,ω -alkanediols has been widely studied [1-3] and the crystal structures displays marked differences between both even and odd number of carbon atoms compounds. In this work we present the Rietveld refinement of 1, 15-pentadecanediol (PTDOL) with data obtained from Glancing Incidence X-ray Diffraction (GIXD). Two samples of PTDOL were analyzed, the recrystallized from ethyl ether (PTDOL-R) and sample used as obtained from synthesis (PTDOL-NR). The studied compound crystallizes in space group $P2_12_12_1$ with unit cell parameters: $a = 7.256(2) \text{ \AA}$, $b = 42.7680(6) \text{ \AA}$, $c = 5.1103(2) \text{ \AA}$ (for PTDOL-R) and $a = 7.3614(1) \text{ \AA}$, $b = 41.8048(6) \text{ \AA}$, $c = 5.1732(4) \text{ \AA}$ (for PTDOL-NR). High temperature phase at 70°C was also studied by Polarized Light Microscopy.

GIXD experiments were carried out using a RIGAKU Ultima-IV diffractometer (40 kV, 30 mA) with Cu $K\alpha_{1,2}$ ($\lambda_1 = 1.5406 \text{ \AA}$, $\lambda_2 = 1.5443 \text{ \AA}$) radiation in asymmetric configuration (fixed incident angle at 5°). A primary graphite monochromator was used. X-ray data processing, energetic calculations and synthesis of PTDOL from 15-hydroxypentadecanoic acid were performed according to our previously reported work, [4]. Optical microscopy analysis was performed with an Olympus BX51-P Polarized Light Microscope (PLM) incorporating a Linkham THMS600 stage. Both analyzed samples crystallize in the same space group; however, in the Rietveld analysis it has been found that the refined structure of the PTDOL samples shows slight differences. Figure 1 displays the GIXD patterns of PTDOL for both PTDOL-R and PTDOL-NR samples and also the Rietveld refinement of the PTDOL-R data. It is possible to observe from Figure 2 differences in the herringbone (quasi-parallel) motif of the PTDOL-R sample contrasting with the totally parallel arrangement of the as-arrived sample, the molecular packing is not perfectly parallel to the b long axis, the molecules has a slightly inclination (Figure 2a) and forms an angle of 171.79° between molecules separated by the H-bond layer, while in Figure 2b parallel arrangement is close to 180° (179.32°). This latter result is consistent with that from single-crystal X-ray diffraction reported earlier [5]. The asymmetric diffraction data analysis allowed the identification and refinement of two different planes (101) and (141) by the March-Dollase [6] approach from PTDOL-R sample data. Results obtained from PLM exhibit a solid to solid transition at 70°C between liquid and solid in a cooling process as can be seen in Figure 3a and the crystallized solid at 30°C (Figure 3b).

References

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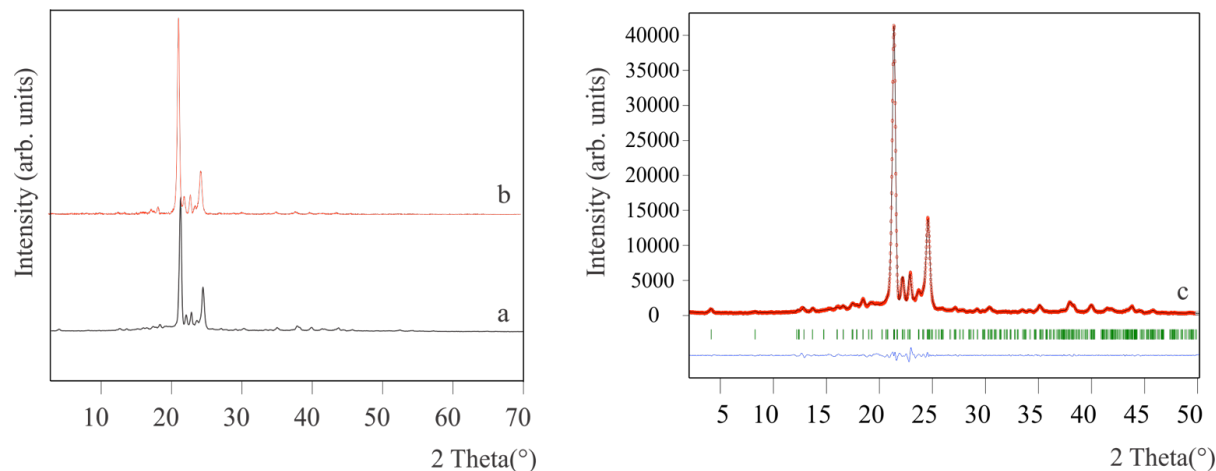


Figure 1. Diffraction patterns obtained from three different samples of PTDOL; a) recrystallized sample from ethyl ether b) non-recrystallized sample and c) Example of the final Rietveld plot of crystal structure from recrystallized sample showing: observed data (red dots), the fit profile (black line) and the difference pattern (blue lower line). Vertical bars correspond to the position of Bragg peaks.

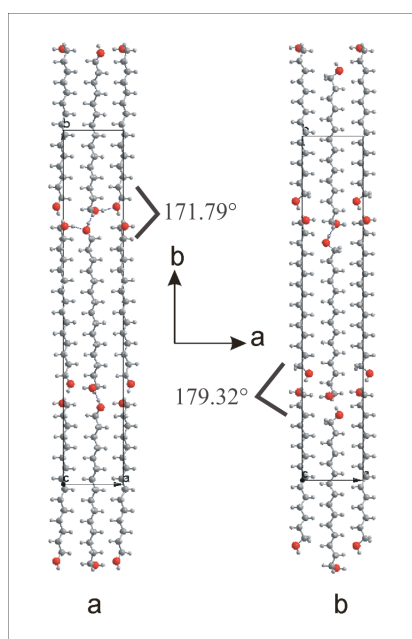


Figure 2. Crystal packing of PTDOL after Rietveld refinement of a) PTDOL-R and b) PTDOL-NR.

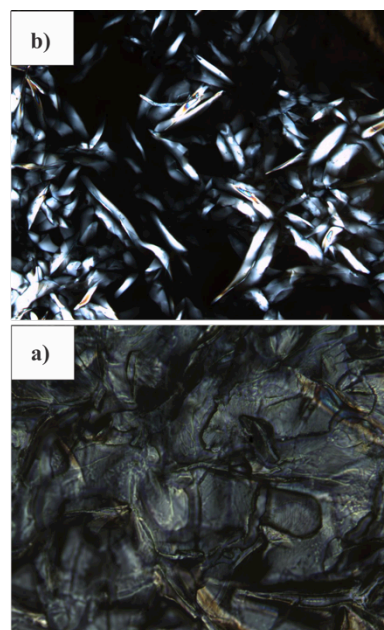


Figure 3. PLM images of PTDOL-R taken from melt (cooling) with a magnification of 100X at: a) 70°C showing acicular morphology and b) 30°C showing the low temperature