

SOFT-CONFINEMENTS OF CHIRAL SMECTIC PHASES ON CRYSTALLIZATION IN THE MACROSCOPIC MONODOMAINS OF A MAIN-CHAIN NON-RACEMIC LIQUID CRYSTALLINE POLYMER

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A main-chain non-racemic chiral liquid crystalline (LC) polyester was synthesized using a condensation reaction of an A-B type chiral monomer, R-(-)-4'-{(ω)-[2-(p-hydroxy-o-nitrophenyloxy)-1-propyloxy]-1-heptyloxy}-4-biphenyl carboxylic acid. It was abbreviated as PET(R*-7). Wide-angle X-ray diffraction (WAXD) experiments combined with differential scanning calorimetry measurements revealed multiple phase transitions: chiral twist grain boundary A (TGBA*), chiral smectic A (SmA*), chiral smectic C (SmC*), and highly ordered monoclinic crystalline (K_M) phases with decreasing temperatures. Flat-elongated and double-twisted helical single crystals were grown thermotropically in the smectic LC states. The helical crystals were all right-handed. Both types of crystals possessed the identical monoclinic unit cell: $a = 1.03$ nm, $b = 0.46$ nm, $c = 5.38$ nm, $\alpha = \beta = 90^\circ$ and $\gamma = 84.2^\circ$ based on both the WAXD and selected area electron diffraction results. Macroscopic quasi-monodomains in a film form up to centimeters in lateral sizes and sub-millimeter thickness could be obtained by uniaxial elongation. Analysis of the detailed 2D WAXD results indicated that in the SmA* phase the molecules were parallel to the layer normal and the elongation direction. However, in the SmC* phase, the quasi-monodomain was constructed by two sheets of mirror imaged structures. This structure was identified to be that the layers in the quasi-monodomains were synclinically organized in a 13°-tilted arrangement with respect to the elongation direction, yet this layer normal was also 13°-deviated from the elongation direction towards the film sample normal. The molecular orientation direction in the quasi-monodomain was found to be ~8°-tilted also synclinically with respect to the layer normal. This leads to a ~21°-tilting with respect to the layer normal. During the crystallization of the K_M Phase in the quasi-monodomains of the SmA* phase, the c axis of K_M crystal was along the elongation direction, yet the d -spacing of the (00 l) ($l = \text{even number}$) planes were only slightly larger than the layer spacing of the SmA* phase. When the crystallization occurred in the quasi-monodomain of the SmC* phase, on the other hand, the synclinic tilted LC layers and the tilted layer normal orientation with respect to the elongation direction were retained in the K_M crystal, although the d -spacing of the (00 l) ($l = \text{even number}$) planes was significantly larger than the layer spacing of the SmC* phase. The most striking observation was that in order to form the K_M crystals in the SmC* phase, the molecules must undergo a remarkable re-orientation (~21° tilting) to fit into the crystal lattice.