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ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JULY 2005

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## Frustrated Molecular Packing in Highly Ordered Smectic Phase of Side-Chain Liquid Crystalline Polymer with Rigid Polyacetylene Backbone

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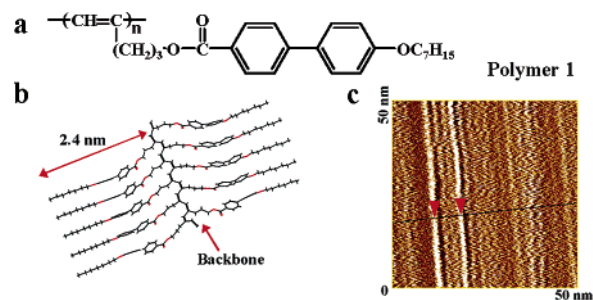
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Conventional side-chain liquid crystalline (LC) polymers are based on flexible backbones, of which the LC phase structures are generally determined by the mesogens in the side chains.<sup>1</sup> When mesogens are attached to conjugated rigid polyacetylene (PA) backbones through flexible spacers, the resultant side-chain LC PA (SCLCPA) bears novelty not only with respect to the chemical structures but also for the combination of the different molecular electronic and optical properties.<sup>2</sup> What the role of the rigid PA backbone plays when chains are packed in a condensed state is an interesting question. Although the insertion of spacers with reasonable lengths may decouple the dynamics of the backbone and the mesogens, the effect of the rigid backbones cannot be simply ruled out. In SCLCPAs, nematic (N) and several smectic (Sm) phases were reported.<sup>3</sup> Mechanical shear on SCLCPAs can produce unusual, high-strength disclinations and well-ordered parallel microbands, implying that the backbones at least affect the molecular relaxation and the orientation of the LC domains.<sup>3c</sup>

In this communication, by using poly(5-[(4'-heptoxy-4-biphenyl)carbonyl]oxy-1-pentyne) (**1** in Figure 1a) as an example, we intend to describe the incorporative accommodation of the rigid PA backbones and mesogenic pendants, which leads to a highly ordered Sm phase with a frustrated structure. Polymer **1** exhibits recognizable molecular shape persistence due to its rigid backbone and relatively short spacer (three methylene units), and the building blocks of the LC phase are sheetlike molecules.

The detailed synthetic procedure of **1** has been published.<sup>2,3c</sup> The polymer has a molecular weight ( $M_w$ ) of  $4.8 \times 10^4$  g/mol (by static laser light scattering), a polydispersity index of 2.1 (by GPC using polystyrene standards), and a trans content of >80% (by <sup>1</sup>H NMR). Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) were used to examine the molecular shape and dimension of **1**. The LC phase structure and transition were investigated by differential scanning calorimetry (DSC), one- and two-dimensional (1D and 2D) wide-angle X-ray diffractions (WAXD), and polarized light microscopy (PLM). Molecular simulation was also performed to study the single molecules and their packing in the highly ordered Sm phase. The experimental and modeling details are provided in Supporting Information.

Figure 1b presents the molecular structure after energy minimization using Smart Minimizer of Materials Studio (see Supporting Information). The PA backbone with a trans-cisoid conformation remains extended despite its twisting by the large appendages. The side chain has a length ( $l_{SC}$ ) of 2.4 nm if the spacer and tail are



**Figure 1.** The chemical structure of **1** (a) and the single molecular structure after energy minimization (b). (c) An STM image of the ultrathin film of **1** on HOPG surface. The 7.3 nm between two red arrows contains three periods. Therefore, the  $d$  spacing of the bright lines is equal to an  $l_{SC}$  of 2.4 nm.

assumed to be all in the trans conformation. On both sides of a backbone, the side chains are parallel to each other but extend to opposite directions. The whole width of a molecular sheet is thus 4.8 nm. Moreover, with respect to the plane of the backbones, the ester (OCO) bridges between the spacers and mesogens may be slightly bent, giving rise to curved sheetlike shape, with an apparent sheet thickness of  $\sim 0.8$  nm. This simulated value is close to the AFM observations of the single molecular layer thickness of  $\sim 1$  nm, which was obtained via casting the dilute solution sample on a fresh mica surface (see Supporting Information).

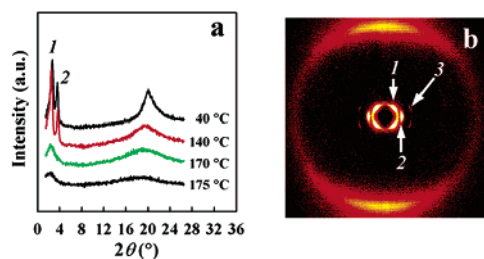
The  $l_{SC}$  can be directly measured by STM on ultrathin film (20–30 nm thick) of **1** on highly oriented pyrolytic graphite (HOPG) (Figure 1c). The alternative bright and dark lines are aligned parallel with a periodicity of 2.4 nm. Although the electron conductivity of **1** is poor, STM is able to detect the conductivity difference between backbones and side chains,<sup>4</sup> as evidenced in Figure 1c. The bright lines should correspond to the backbones separated by the side chains. During scanning, the STM tip might scrape the film and align the side chains that are lower in conductivity, leading to the lines nearly perpendicular to the scanning direction.

The phase behavior of **1** exhibits two broad endotherms with the peak temperatures at 95 and 160 °C, followed by a relatively narrow transition that leads to an isotropic state after 175 °C (see Supporting Information). Figure 2a represents the 1D WAXD patterns of **1** recorded at four temperatures upon heating in different phases. The scattering at  $2\theta$  of  $\sim 20^\circ$  ( $d$  spacing of  $\sim 0.44$  nm) is relatively sharp at 40 °C, but a typical amorphous halo at 140 °C, indicating that the sample has lost some degrees of order on the subnanometer scale after the lowest transition at 95 °C. On the other hand, two strong reflection peaks (1 and 2 in Figure 2a) in the low  $2\theta$  region exist at both 40 and 140 °C, which only slightly

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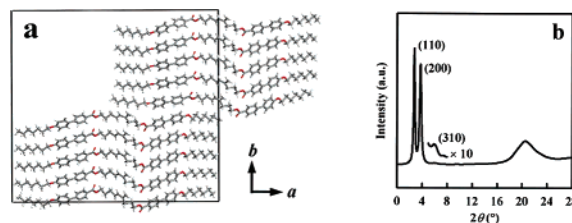
**Figure 2.** (a) One-dimensional WAXD powder patterns of **1** at 40, 140, 170, and 175 °C. (b) Two-dimensional WAXD pattern obtained at room temperature after the sample had been sheared and annealed at 140 °C with the shear direction on the meridian. In addition to diffractions 1 and 2, the high-order diffraction 3 can be seen after a prolonged exposure time.

shifts the  $2\theta$  angles upon heating. At 170 °C, a weak peak 1 remains, while peak 2 completely disappears. At 175 °C, two amorphous halos in both the low and high  $2\theta$  regions were observed, indicating the isotropic state of **1**.

Herein, we focus our analysis on the LC structure of **1** at low temperatures. Below 160 °C, the WAXD result reveals that the sample possesses the same packing character on the nanometer scale, where the PLM textures observed are also identical (see Supporting Information). In Figure 2a, peaks 2 and 1 correspond to the  $d$  spacings of almost exactly  $l_{SC}$  and 1.3 times of  $l_{SC}$  of **1**, respectively. These  $d$  spacing data may result from a mixture of smectic A (SmA) and interdigitated smectic A (SmAd) phases in the sample. Yet, this assignment is in question due to the assumed coexistence of the two phases.

Figure 2b shows a 2D WAXD pattern of **1** at room temperature. The sample was obtained by a mild mechanical shear at 140 °C followed by annealing at that temperature for 1 h in the LC state. In this figure, the X-ray incident beam is perpendicular to the shear direction that is along the meridian, where the high  $2\theta$  angle scattering halo appears. The pair of diffraction 2 at  $2\theta$  of 3.7° locates on the equator, and the pair of diffraction 1 at  $2\theta$  of 2.7° appears on quadrants, with an angle of 45° away from the equator. A pair of high-order diffraction (3 in Figure 2b) at  $2\theta$  of 6.0° on the same layer as that of diffraction 1 can be seen after a prolonged exposure time. This WAXD pattern is, in fact, identical to the electron diffraction pattern obtained from the thin film of **1** without mechanical shearing, wherein the backbone direction is parallel to the electron beam.<sup>3i</sup> This implies that the mild shear force has aligned the LC domains rather than the polymer backbones. In this case, the X-ray incident beam is parallel to the backbones.

This unusual 2D WAXD pattern is reminiscent of frustrated Sm phases due to the 2D escape from incommensurability.<sup>5</sup> During packing, the sheetlike molecules of **1** have to stack layer by layer with an average distance between two adjacent layers of ~0.44 nm. Assuming the diffractions 1, 2, and 3 to be the (110), (200), and (310) diffractions, we may obtain an orthorhombic cell including 10 chains, with  $a = 4.8$  nm,  $b = 4.4$  nm, and  $c = 0.47$  nm (length of two chemical repeating units), wherein the sheetlike molecules are parallel to the  $ac$  plane. Figure 3a illustrates the projection of the molecular layer packing structure along the  $c$ -axis (backbone direction) after energy minimization with above cell parameters. To satisfy extinctions of the (100) and (010) diffractions as shown in experiments, most likely, the upper and lower five layers of molecules, which stacked as two SmA blocks, must glide halfway to each other along the  $a$ -axis. This chain packing gives rise to the diffraction pattern (Figure 3b) that fits our experimental results. Moreover, the density of the annealed sample was measured



**Figure 3.** (a) Molecular layer packing model of **1** (viewed along the chain direction) with the orthorhombic cell parameters of  $a = 4.8$  nm,  $b = 4.4$  nm, and  $c = 0.47$  nm. With respect to the lower five layers, the upper five layers glide halfway along the  $a$ -axis. (b) The simulated 1D WAXD pattern obtained from the model after Lorentzian fitting.

to be 1.25 g/cm<sup>3</sup>, which agrees well to the calculated value of 1.26 g/cm<sup>3</sup>. In principle, such a frustration structure is caused by the coupling of the density and dipole moment modulations, as interpreted by Prost.<sup>5a</sup> We expect that the sheetlike molecules are easy to glide within the LC states and facilitate the highly ordered frustrated Sm phase. However, this LC phase may be modified by strong external forces. As shown in Figure 1c, upon STM scanning, the ultrathin film of **1** presents an SmA pattern with the  $d$  spacing determined by the length of the side chain.

In summary, we have demonstrated in this study that the SCLCPA (**1**) is shape persistent, and the building block of its LC phase is the sheetlike molecules. The sheet stacks may easily slide halfway along the  $a$ -axis to form the highly ordered frustrated Sm phase. The detailed thermodynamics and kinetics of the phase transitions are currently being investigated. We are also working on the STM-induced SmA structures of the series of samples, which may pave the way to the fabrications of nanodimensional patterns with periodic electron conductivity using the side-chain-conjugated polymers as templates.

**Acknowledgment.** We are grateful to Prof. H. Finkelmann for his useful discussions. This work was supported by the National Natural Science Foundation of China (20025414 and 20129001).

**Supporting Information Available:** Experimental and modeling details, and results of AFM, DSC, and PLM. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA050643K