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ScienceDirect
Chinese Chemical Letters 22 (2011) 1355–1358
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Monotropic smectic A to double layer smectic C transition of biphenyl containing liquid crystal acetylene

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Received 31 March 2011
Available online 28 July 2011

Abstract

5-[(4′-Heptoxy-4-biphenylyl)carbonyloxy]-1-pentyne (A-3, 7) was synthesized and the phase structures and transitions were investigated by differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), polarized light microscopy (PLM) and the molecular packing in the crystal and liquid crystalline phases were simulated by molecular dynamic simulation. The results showed that the sample formed thermodynamically metastable SmA and SmC_2 phases before crystallized during cooling and the crystal phase directly transformed into isotropic phase during heating.

Keywords: Liquid crystal; Phase structure; Phase transition; Smectic phase; X-ray diffraction

Liquid crystal (LC) is mesomorphic phase lying between isotropic liquids and three dimensional ordered crystals, which can be used as functional materials [1]. Owing to the unique features, LC materials can be applied in a wide range of fields, such as liquid crystal display [2], light modulators [3,4], and switches [5]. For a thermotropic LC system, there are two kinds of phase transformations, namely, enantiotropic and monotropic, which can be identified when more than one ordered phases exists [6]. Monotropic LC behavior possesses thermodynamic metastability throughout the entire temperature and experimentally, monotropic LC phases can only be observed during cooling, in which the crystallization process is bypassed by undercooling due to the kinetically controlled nucleation process.

Understanding the phase behaviors of the monomers is of importance to understand the structures and properties of the corresponding polymers [7,8]. In a recent research [9], we have reported the phase structures and transitions of 5-[(4′-pentoxy-4-biphenylyl)carbonyloxy]-1-pentyne (denoted as A-3, 5 in the literature), which is an enantiotropic LC and exhibits a sequence of smectic A (SmA), smectic B (SmB), smectic E (SmE) and crystal phase during cooling. 5-[(4′-heptoxy-4-biphenylyl)carbonyloxy]-1-pentyne (abbreviated as A-3, 7) is a homologous of A-3, 5 with drastically different phase transition behavior from that of A-3, 5 [9–11]. Previously, the sample was regarded as metastable SmC phase when the sample was cooled to the second LC phase. In this research, by using A-3, 7 as an example, we

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1001-8417/$ – see front matter
doi:10.1016/j.cclet.2011.06.013

reinvestigate the metastable SmC phase by annealing the sample in the metastable SmA phase. Luckily, we detected a peak at $2\theta = 1.89^\circ$, which reveals that the structure of the metastable SmC phase having a double layer periodicity, *i.e.*, double layer SmC phase.

Fig. 1a presents the DSC curves at different rate (20–1.25 °C/min) during cooling and subsequent heating. There exhibits only one transition in the heating process, which can be assigned to the crystal melting. However, the results obtained during cooling exhibits quite different from that during heating. The first two exothermic peaks (T_1 and T_2) at relative high temperature always take place at 71 and 52 °C, and the transition temperatures are only slightly cooling-rate dependent, which represent the two transitions are associated with LC phase transitions. The third exothermic peak (T_3) exhibits cooling-rate dependent, suggesting crystallization or highly ordered LC phase formed [6]. The DSC results show that the sample forms monotropic LC, which is thermodynamically metastable with respect to the corresponding crystalline phase.

Fig. 1b shows a set of 1D WAXD powder patterns obtained during cooling. Only an amorphous scattering halo at high 2θ region recorded when the temperature higher than 70 °C, indicating an isotropic melt with the aids of PLM texture observation. When the sample cooled to 70 °C, an amorphous scattering halo at ~20° and three reflection peaks at $2\theta = 3.42^\circ$, 6.83°, and 10.26° with the corresponding q-ratio ($q = 4\pi \sin\theta/\lambda$, with λ the X-ray wavelength) of 1:2:3 recorded. The d-spacing of the first order reflection peak is comparable to the extended molecular length, indicating a SmA phase. Upon further cooling to 55 °C, several new diffractions with the first reflection peak at a 2θ of 1.94° appeared at low 2θ region and multiple sharp peaks observed at high 2θ region, suggesting a crystal phase formed. PLM textures also confirm the formation of crystal phase. It should be noted that only SmA phase was detected during cooling and the second LC phase was not detected, this may be because the lifetime of the second LC phase is smaller than the time a scanning of 1D WAXD curve needed.

To capture the second LC phase not recorded in the cooling experiment, we annealed the sample at 64 °C and conducted WAXD experiments at an interval of 12 min, as described in Fig. 2. The reason 64 °C was chosen is in that at that temperature, the transition of isotropic melts to SmA phase completed and can be transformed into another LC phase by thermal annealing and the annealing time is not too short and not too long. At wide angle region, the spacing of the scattering halo at 2θ of ~21° (indicated by solid line) corresponding to the lateral distance of the liquid-like alkyl tails. When the annealing time reached to 36 min, another four reflection peaks at 2θ of 1.89°, 3.76°, 5.65°, and 7.50° with a q-ratio of 1:2:3:4 were detected, while the reflection peaks of the SmA phase still exist, indicating a new smectic phase formed during annealing and the sample states in a coexistence of two LC phases. The d-spacing of the first peak

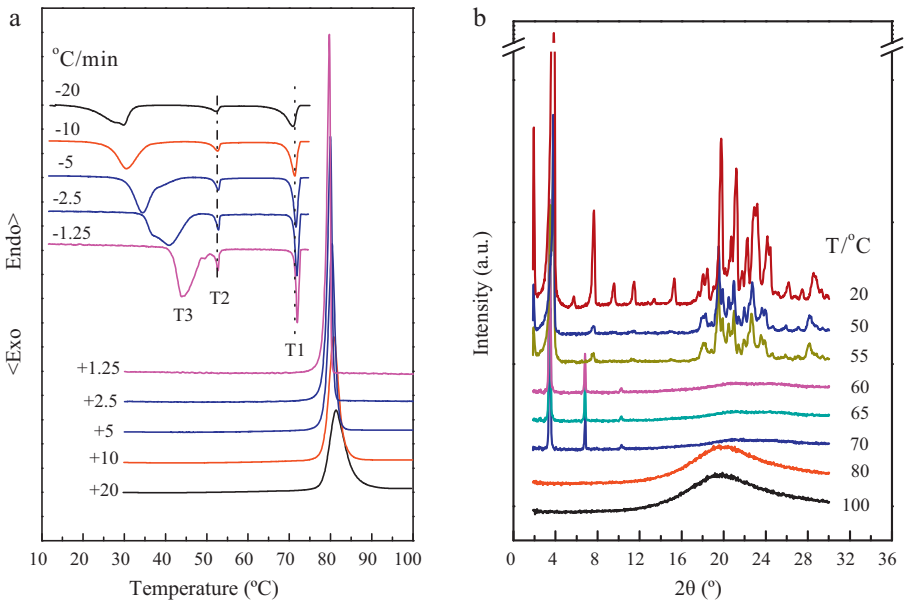

Fig. 1. (a) The DSC curves recorded during cooling and heating with the cooling/heating rate indicated and (b) 1D WAXD powder patterns recorded during cooling.

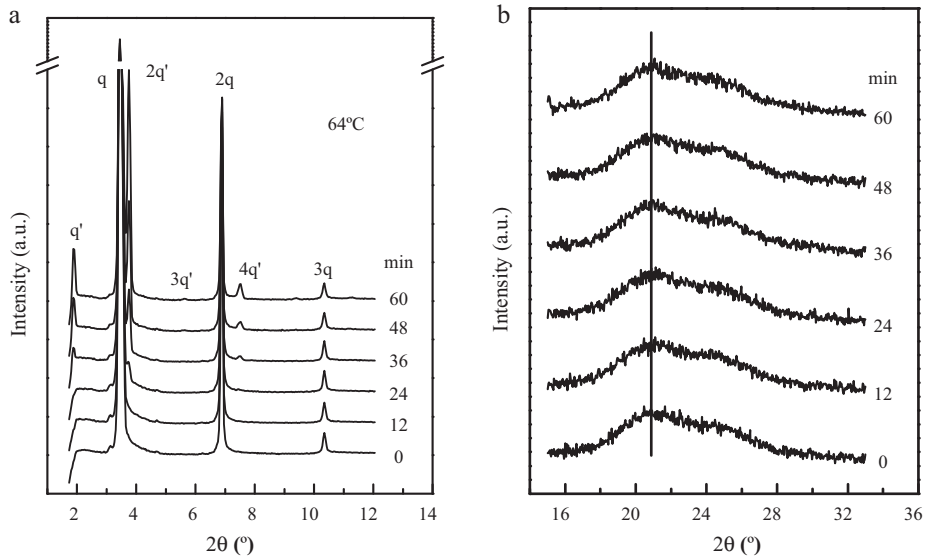

Fig. 2. 1D WAXD powder patterns at low (a) and high (b) 2θ angle region during annealing at 64 °C. q is the scattering vector of SmA phase and q' is that of SmC_2.

is 46.74 Å, which is much larger than the extended molecular length but comparable to the layer thickness of the crystal phase, indicating a double layer SmC (SmC_2) phase formed [11]. In the SmC_2 phase, the molecules tilt away from the normal direction about a calculated angle of 24°. With increasing of the annealing time, the intensity of the SmC_2 phase increased and that of the SmA decreased. Before the SmA phase completely disappeared, the sample was in the coexistence of SmA and SmC_2 phase. With continued annealing, the SmC_2 phase would transform into crystal phase. For the short lifetime of SmC_2 phase, it is prone to transform into crystal phase, we anneal the sample at 64 °C, which is a relatively high temperature to avoid the SmC_2 phase transformed into crystal phase before we can observe.

To further investigate the phase behavior of A-3, 7, PLM experiments were conducted to observe the textures. Upon cooling from isotropic melts to 70 °C, a characteristic fan-shaped texture observed, as illustrated in Fig. 3a, which confirm the SmA phase. Further cooling to 64 °C and annealing, fan-shaped texture transformed to broken fan-shaped texture, as shown in Fig. 3b, confirming the formation of SmC_2 phase [12]. With continued annealing, broken fan-shaped texture transformed into crystalline texture, as illustrated in Fig. 3c, which was the coexistence state of crystal and SmC_2. The SmC_2 phase is in the thermodynamically metastable state and is prone to crystallize, accordingly, the broken fan-shaped texture is prone to transform to the crystal texture upon annealing.

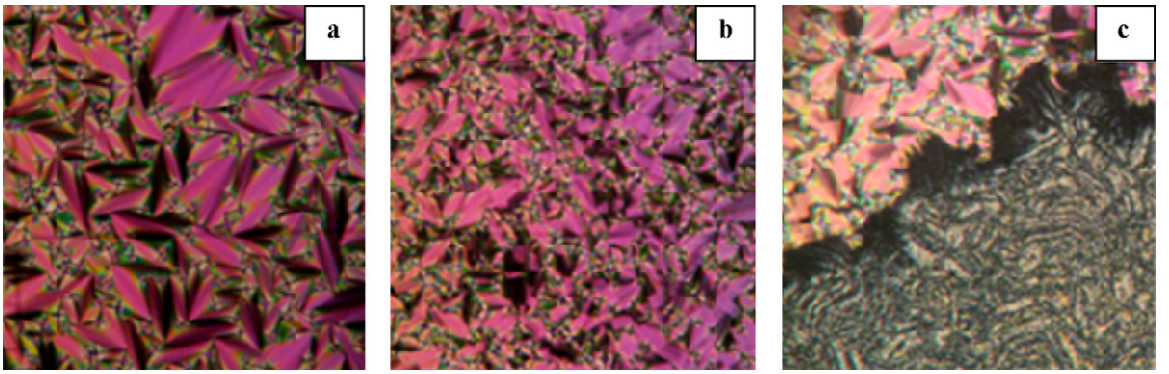

Fig. 3. PLM textures (400×) of A-3, 7 observed on cooling to (a) 70 °C, (b) 64 °C followed by annealing for 0.5 h, and (c) 64 °C followed by annealing for 2 h from isotropic liquids at a cooling rate of 1 °C/min.

The molecular packing model of crystal phase and LC phase were also simulated by Materials Studio 5.0 (Accelrys). In the crystal phase, the alkyl tails of the molecules take an extended conformation and form a double layer structure with the triple bonds of neighboring layers meet together in the inner part and the alkyl tails in the outer part. The SmC_2 phase is similar to that of the crystal structure and the molecules tilt an angle of about 24° away from the normal direction of the layer plane.

In summary, 5-[(4′-heptoxy-4-biphenylyl)carbonyloxy]-1-pentyne shows a thermodynamically metastable SmA to SmC_2 liquid crystal phase transition followed by a crystal phase, while in the heating process, only a crystal to isotropic melts transition detected. Upon thermal annealing the sample in the SmA phase, SmC_2 phase detected and identified.

Acknowledgments

The author (Z.Q. Yu) would like to thank the financial supports of National Natural Science Foundation of China (No. 21074073) and Shenzhen Key Laboratory of Functional Polymers (No. FP20100011).

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