



Original article

Liquid crystal character controlled by complementary discotic molecules mixtures: Columnar stacking type and mesophase temperature range



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ABSTRACT

In this work, the mesophase properties were tuned *via* mixing two discotic molecules with structural complementarity. Compared with the liquid crystalline hexakis(*n*-hexyloxy)triphenylene (H6TP) materials (columnar hexagonal phase from 53 °C to 91 °C), mesophase types as well as phase transition temperatures varied with the introduction of crystalline hexaazatriphenylene derivative (PBH) molecules. The introduction of less than 33% amount of PBH disrupted the columnar hexagonal phase formed by H6TP remarkably, followed by the decreased clearing temperatures of liquid crystals. As the PBH amount was further increased, the destroyed columnar hexagonal phase was turned into the columnar rectangular phase, in which H6TP and PBH molecules together formed the columnar mesophase. The formation of new mesophase contributed to the enlarged mesophase temperature (from 44 °C to 144 °C). We speculated that the alkyl chains interaction induced by the PBH component competed with the strong π - π stacking between H6TP molecules, thus altering the liquid crystalline properties including mesophase types and phase transition temperatures.

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1. Introduction

As a new generation of organic semiconductor, discotic liquid crystals (DLCs) have attracted intensive attention in the last decade. Because of the large π - π overlap within columnar stacks, one-dimensional high charge transport mobility can be achieved. Prospective applications for the DLCs in opto-electronic devices, such as field effect transistors (FETs), photovoltaic solar cells (PSCs) have been developed [1–10]. To fulfill the device application of the DLCs, the materials should exhibit the mesophase behavior within a broad temperature range. Moreover, disc-shaped mesogens could arrange in different columnar stacking types, such as the columnar hexagonal (Colh) phase and the columnar rectangular (Colr) phase, which definitely influences charge transport along

the column axis [11]. Besides, the alignment of disc-shaped molecules is desirable to construct efficient devices. For example, the planar and homeotropic orientations are needed for FETs and PSCs, respectively. Although several factors influence the alignment process, the mesophase type plays a critical role in the orientation process. As has been reported [12], the Colh phase and the Colr phase are preferred for face-on and edge-on alignments, respectively.

Among different kinds of DLCs, triphenylene-based compound is one of the most widely investigated materials, because they are relatively easy to synthesis. In the past years, efforts have been made to modify the mesophase properties. One approach to this aim is the modification of the cores and the side chains [13]. However, it takes more effort for the design and synthesis of desired materials. An alternative way to this synthesis-intensive requirement is blending triphenylene DLCs with other materials, such as 2,4,7-trinitro-9-fluorenone (TNF) [14,15] and hexaazatriphenylene derivatives [16]. These molecules can form face-to-face alternating stacks, leading to the enhanced mesophase temperature range. The extended stability of these mixtures is

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the result of either the complementary polytopic interaction (CPI) [17–20] or the charge transfer interaction [21–24].

Though physical methods have been widely adopted to tune the liquid crystal properties [12,16,17,21,25,26], little attention has been paid to the close relationship between columnar stacking type and properties of materials mixture upon incorporating guest component [12]. In this work, we blended hexakis(*n*-hexyloxy)-triphenylene (H6TP) with hexaazatriphenylene derivative (PBH) (Scheme 1) to form alternatively stacking columns. These two molecules are complementary in both shape and electronic characteristics. The mesophase types of mixtures change from the Colh phase to the Colr phase with the increase of PBH content, resulting in the novel trend of the isotropic temperatures. The clearing temperatures decreased firstly and then rose up with the increasing amount of PBH molecules. Moreover, it is inferred that the structure variation was possibly driven by the competition of the alkyl chains interaction induced by PBH molecules with the strong π - π interaction between H6TP molecules.

2. Experimental

2.1. Materials

H6TP was purchased from Sichuan Normal University. PBH was synthesized as in Ref. [27]. Chloroform (99%) was purchased from Beijing Chemical, China. All the materials were used as received without further purification.

The glass and silicon substrates (1.5 cm × 1.5 cm) were cleaned in a piranha solution (70/30, v/v of concentrated H₂SO₄ and 30% H₂O₂) at 90 °C for 20 min, then thoroughly rinsed with deionized water, and finally blown dry under nitrogen.

2.2. Sample preparation

All H6TP/PBH mixtures with desired molar ratios were obtained by blending the corresponding individual chloroform solutions, and the total concentration was 10 mg/mL.

Thin films of H6TP, PBH and H6TP/PBH blends were prepared through spin-coating and drop-casting processes. In the spin-coating procedure, the solution was cast for 18 s at a rate of 500 rpm. The thicknesses of the spin-coating films are about 140–180 nm. In the drop-casting process, 50 μ L solution was deposited on the glass/silicon substrate with a size of 1.5 cm × 1.5 cm. All the experiments were performed at room temperature.

2.3. Characterization

Polarized optical microscopy (POM), differential scanning calorimetry (DSC) and grazing incidence X-ray diffraction (GIXD) analysis were performed to characterize the thermotropic behaviors and the structures of the mixtures. The thermal stability of the mixtures was investigated by Thermal gravimetric analysis (TGA). The interaction between H6TP and PBH in solution and thin

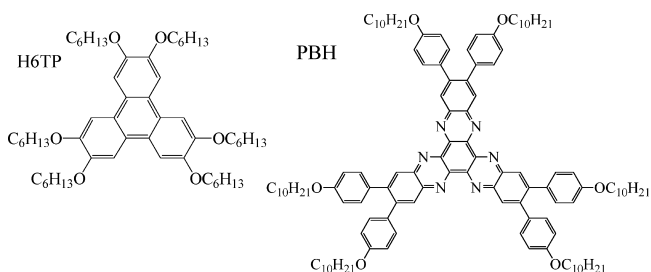
film state was characterized through UV–vis absorption spectroscopy, fluorescence emission spectroscopy and nuclear magnetic resonance (¹H NMR) spectroscopy. The detailed procedures are collected in the Supporting information.

3. Results and discussion

3.1. Phase transition temperatures variation with the increase of PBH content

DSC and POM was used to characterize the transition points of the individual components and the mixtures (Table 1). Since the transition points variation with the increase of PBH content in the heating cycle is similar to that in the cooling cycle, only the transition temperatures in the cooling cycle were utilized to show the variation trend. Firstly, *prior* to discuss the thermotropic behaviors of the mixtures, we focused on the individual components. Upon cooling from the isotropic state, H6TP exhibited the liquid crystalline phase from 91 °C to 53 °C as previously reported (Fig. 1a) [28], and gave the focal conic texture representative of the Colh phase (Fig. 2a). In contrast, PBH showed complex polymorphism. After heating at 200 °C, five exothermic transitions at 155 °C, 131 °C, 99 °C, 51 °C and 28 °C were observed in subsequent cooling to 20 °C (Fig. S1 in Supporting information). The temperature-dependent GIXD patterns of PBH showed a series of reflections during these transition points, indicating the crystalline phase (Fig. S2 in Supporting information). Furthermore, no significant changes of textures were observed during the transition points in POM. (Fig. S3 in Supporting information). In addition, it is difficult for the PBH film to be sheared with a cover slide even at 200 °C. Hence, PBH is clearly in crystalline phase. The thermal stability of mixtures has also been investigated by TGA. The TGA measurements show that both H6TP and PBH compounds were thermally stable with 1% weight loss at 327 °C and 395 °C, respectively. The H6TP/PBH = 1/1 compound was stable up to 340 °C with 1% weight loss (Fig. S4 in Supporting information). The decomposition temperature of the H6TP/PBH = 1/1 mixture is different to those of individual components, indicating the existence of the superstructure between H6TP and PBH.

Blending H6TP with PBH in different molar ratios results in two transitions in DSC traces except for the H6TP/PBH = 1/4 blend of which the DSC trace shows only one single phase transition (Fig. 1). As shown in Fig. 1c, when the molar ratio of H6TP/PBH changes from 1/0 to 1/0.5, the clearing temperatures decrease from 91 °C to 59 °C. While for the H6TP/PBH = 1/1 blend, the isotropic temperatures are augmented to 144 °C in comparison to the H6TP/PBH = 1/0.5 blend. Besides, the transition enthalpies follow the similar trend. In contrary to the tendency of the clearing points, as the molar fraction of PBH raises, the crystallization temperatures of the H6TP/PBH blends decrease. In the heating and cooling cycles, none of the blends shows the characteristic of their components undergoing individual



Scheme 1. The chemical structures of H6TP and PBH molecules.

Table 1

The phase transition temperatures (°C) and enthalpies (J/g) of H6TP/PBH mixtures upon cooling from the isotropic state. T_c = the crystalline temperature; T_{iso} = the isotropic temperature.

H6TP/PBH	$T_c/\Delta H$	$T_{iso}/\Delta H$
1/0	53/50.4	91/6.0
1/0.05	49/38.6	86/3.7
1/0.25	45/30.4	65/2.3
1/0.5	45/19	59/0.6
1/1	44/10.8	144/2.4
1/2	40/5.3	141/3.1
1/4	–	151/4.8

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