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Liquid Crystal Structures of Spirobenzopyran Derivatives

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Two thermotropic liquid crystalline (LC) compounds containing chiral spirobenzopyran were examined by DSC, polarizing optical microscope, and X-ray diffraction. The fine structural differences of the two compounds resulted in entirely different LC phases. Both compounds showed monotropic LC phases, even though PSBPI-OOBP showed identical thermal transitions in heating and cooling of DSC scans.

Keywords: liquid crystal phases; non-activated spirobenzopyran derivatives; DSC; optical texture; X-ray scattering

INTRODUCTION

One of the most important classes of photochromic materials is a spiropyran compound.[1],[2] Upon irradiation with UV light the spiropyran undergoes heterolytic cleavage of the carbon-oxygen bond to form a colored isomer. The reversal of the isomerization immediately occurs by the thermal or photo-chemical energy. On the other hand, much less attention has been paid to the non-activated spiropyrans.[3],[4] Upon irradiation with UV light, these compounds usually display a photostationary state, which is undesirable for most photochromic applications. However, the photostationary state effectively results in a photoracemerization of the chiral spiropyran group, which is the key requirement for photoresolution. To maximize the switching efficiency of these

materials, smectic C mesogens with non-activated spiropyran moiety are sought.

In this report, we discuss the liquid crystalline behaviors of two non-activated spirobenzopyran derivatives based on the results of DSC, optical microscopy, and X-ray scattering.

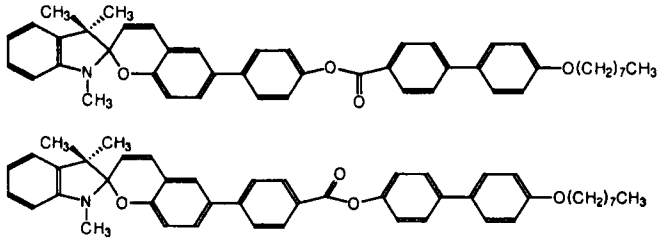

FIGURE 1. Chemical structures of spirobenzopyran containing compounds, PSBPI-OOBP (top) and OOBP-SBPIB(bottom).

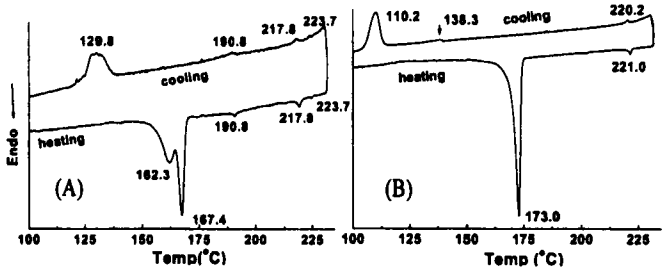

FIGURE 2. DSC thermograms of PSBPI-OOBP (A) and OOBP-SBPIB (B).

MATERIALS AND EXPERIMENTAL METHODS

As depicted in Figure 1, chemical structures of the two compounds are nearly identical except that the biphenylcarboxylate in PSBPI-OOBP is directly linked to the carbonyl group while the biphenyl carboxylate in OOBP-SBPIB is to the ether group. Transition temperatures and thermal behaviors of the compounds were determined by a differential scanning calorimeter (Perkin-Elmer DSC-7). The phase transitions were then confirmed

by the texture change as observed by a polarizing optical microscope (Nikon) equipped with a Mettler hot stage (FP82HT). Wide angle X-ray scattering utilizing the synchrotron radiation source and one-dimensional diode array detector was also performed to determine the molecular packing state and the LC phases.

RESULTS AND DISCUSSION

The DSC heating scan of PSBPI-OOBP (Figure 2) exhibits 5 thermal transitions at 162.2, 167.4, 190.8, 217.8 and 223.7 °C. The first two strong transitions at 162.2 and 167.4 °C are found to be associated with the crystal phase. The phase between 167.4 and 190.8 °C is probably another crystal phase because X-ray pattern obtained in this temperature range still maintains crystalline order but with a marked reduction in intensity and peak numbers. When the temperature is raised above the transition at 190.8 °C, the X-ray pattern reveals a layer structure whose spacing corresponds to the molecular length of PSBPI-OOBP, indicating a smectic A phase. Optical texture of total extinct also suggests that the molecules are oriented perpendicular to the two glass plates. The next transition at 217.8 °C is found to be from smectic A to nematic phase and 223.7 °C is for the nematic to isotropic transition, as can be confirmed by the optical texture and X-ray pattern. The three thermal transitions at 223.7, 217.8, and 190.8 °C observed upon cooling are identical to those of heating cycle. The texture observed between 217.8 and 190.8 C, however, differs from that of heating cycle but it becomes identical to that of heating below the transition temperature of 190.8 °C. The X-ray pattern indicating smectic A, however, remains unchanged through the transition point at 190.8 °C until the crystal phase appears.

The DSC heating scan of OOBP-SBPIB compound exhibits only two thermal transitions. The first strong peak at 173.0 °C apparently denotes the crystal to LC transition. The change from the crystal spherulite to a mosaic texture can be seen. The

X-ray pattern indicates a smectic A phase above 173.0 °C. The smectic A phase is maintained until the temperature reaches another transition to an isotropic liquid at 221. 0 °C. Upon cooling the compound, we also note the transition at 220.2 °C. Texture below this temperature is identical to that observed during the heating cycle. The X-ray pattern also reveals smectic A phase. Upon lowering the temperature further, we note another transition at 138. 3 °C both in DSC and optical texture. The X-ray pattern shows a smectic C phase, even though the texture is almost identical to that of crystal phase.

TABLE 1. Transition temperatures and LC phases.

Compound	heating	cooling
PSBPI-OOBP	Cr 167.4 Cr(?) 190.8 S_A 217.8 N 223.7 I	Cr 129.8 S_A 217.8 N 223.7 I
OOBP-SBPIB	Cr 173.0 S_A 221.0 I	Cr 110.2 S_C 138.3 S_A 220.2 I

LC phases and transition temperatures of the two compounds are summarized in Table 1. Both compounds exhibit a monotropic behavior. The fine structural difference of the two compounds results in an entirely different LC behavior, manifesting the effects of the molecular architecture on the interactions between the neighboring molecules.

Acknowledgments

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