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Thermotropic Liquid Crystalline Behavior of Dihydroxyphenylene Benzobisthiazole Derivatives

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Thermotropic liquid crystalline behaviors of dihydoxyphenylene benzobisthiazole with alkyl moieties of three different lengths at both ends were studied by d.s.c. polarizing optical microscope. and X-ray scattering. All three samples showed tilted smectic phases. Higher transition temperature and wider Sc interval were noted in DiOH-PBT-Cn. The alkoxy chain length lowered the transition temperature and temperature interval.

Keywords: dihydroxyphenylene benzobisthiazole derivatives; tilted smectic phases; thermal behavior; optical texture; x-ray scattering

INTRODUCTION

Poly(p-phenylene benzobisthiazole) (PBT)[1] is a highly ordered rigid rod polymer consisting of benzobisthiazole (BBT) and phenyl and is essentially collinear. But the minimum energy conformation prefers the rotation between the phenyl and BBT unit. resulting in a non-coplanar molecular conformation between the two units. When the PBT is incorporated with 2.5-dihydroxy-1.4-phenylene moieties. however. the polymer becomes a coplanar structure similar to benzimidazobenzophenanthroline ladder polymer. BBL[2]. The coplanar structure can be attributed to intramolecular hydrogen bonds between the hydroxyl unit and the nitrogen atom of BBT.

Some years ago Kim et al.[3] reported the first example of thermotropic liquid crystalline behaviors of the benzobisthiazole model compounds with alkyl moieties at both ends. Following

Kim and coworker's work a similar series of model compounds of dihydroxyphenylene benzobisthiazole was synthesized by Seng et al.[4] In this synthesis it was hypothesized that intramolecular hydrogen bonding would provide the coplanarity between the BBT and the adjacent phenyl ring and the planar structure would result in a different liquid crystalline behavior from those of nonplanar model compounds of alkoxylated benzobisthiazole.

In this report we present liquid crystalline behaviors of the series of model compounds with dihydroxyphenylene moiety as studied by d.s.c. polarizing optical microscope. and wide angle X-ray scattering.

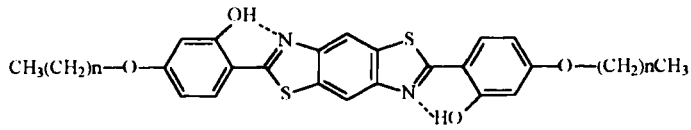

FIGURE 1 Chemical structure of DiOH-PBT-Cn (n=7, 11, 15).

MATERIALS AND EXPERIMENTAL METHODS

Chemical structures of the three model compounds of dihydorxyphenylene BBT derivatives having 8, 12, and 16 alkoxy chains (DiOH-PBT-C8, DiOH-PBT-C12, and DiOH-PBT-C16) are presented in Figure 1. Their brief synthetic route has been described elsewhere. A d.s.c. (DuPont 950) was used to investigate the thermal behavior of the compounds under the nitrogen atmosphere at a heating rate of 5 °C/min. For an optical texture a polarizing optical microscope and a Mettler hot stage (FP82HT) were used under the nitrogen atmosphere. The molecular packing of the compounds was studied by the wide angle X-ray scattering using a synchrotron radiation source at the Pohang Accelerator Laboratoty.

RESULTS AND DISCUSSION

Among the three samples, results of DiOH-PBT-C16 are only shown for a representative example. A d.s.c thermogram of DiOH-PBT-C16 is depicted in Figure 2. Optical micrographs and wide angle X-ray patterns of DiOH-PBT-C16 obtained at temperatures between the endothermic

peaks indicated by the d.s.c thermograms are shown in Figure 3 and 4, respectively.

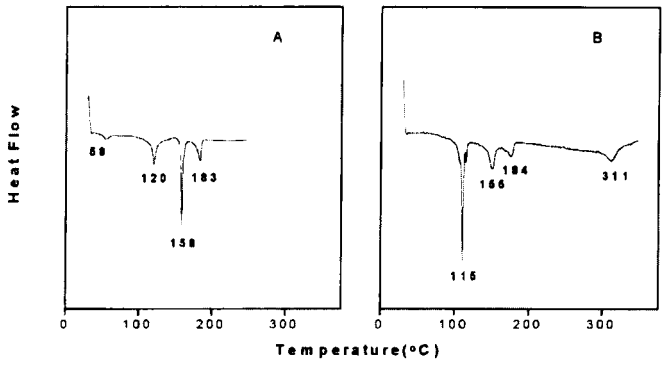

FIGURE 2. Differential scanning calorimeter thermograms of DiOH-PBT-C16. Curve A denotes the first scan and curve B the second scan.

FIGURE 3. Textures of DiOH-PBT-C16 at 220 °C (A) and 180 °C (B).
(See Color Plate III at the back of this issue)

Curves plotted in Figure 2-A and 2-B represent the first heating scan and the second scan followed by the first one, respectively. The two curves show different thermal behaviors in peak sharpness and thermal transition temperatures, indicating a thermal history effect. Similar history effect was also observed in DiOH-PBT-C8 and DiOH-PBT-C12. Schlieren texture (Figure 3) and X-ray diffractogram (Figure 4) demonstrate a smectic C phase below the transition at 311 °C and an isotropic phase above it. A mosaic texture of smectic F phase is noted below the transition at

184 °C. X-ray pattern at 170 °C shows an evolution of local order within the layer, confirming smectic F phase. Smectic G and H phases can be seen on further cooling. Similar liquid crystalline behavior was also observed in DiOH-PBT-C12. But in DiOH-PBT-C8, only smectic C and G were observed. Comparing the results of DiOH-PBT-Cn with those of PBT-Cn, it was found that model compound with dihydroxy moiety has wider temperature interval for smectic C phase and higher transition temperature from smectic C to isotropic phase. With the increase of alkoxy chain length the transition temperature decreased and the transition interval between the phases became narrower.

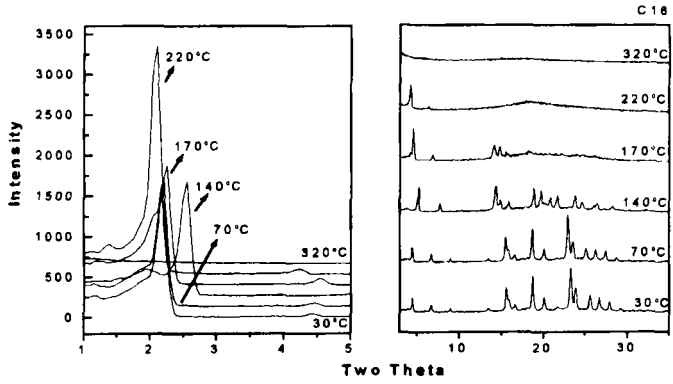

FIGURE 4. X-ray diffractomgrams of DiOH-PBT-C16 at various temperatures.

Acknowledgments

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