

NOTES

Thermotropic Liquid Crystals of Polyesters Having a Mesogenic *p,p'*-Bibenzoate Unit IV. Mesophase Behavior of Polyesters with Branched Spacers

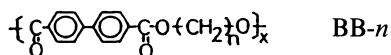
Junji WATANABE, Manabu HAYASHI, Satoshi KINOSHITA,
and Teruki NIORI

*Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan*

(Received January 16, 1992)

KEY WORDS Liquid Crystalline Polyester / Smectic C Phase / Phase Transition / Smectic Layered Structure /

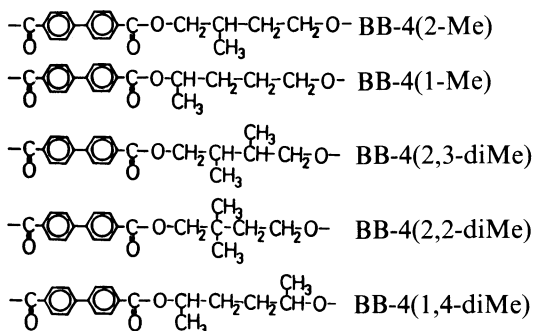
In the first paper of this series,¹ we reported the thermotropic mesophase properties of main-chain polyesters that can be constructed by an alternative arrangement of the *p,p'*-bibenzoate unit as a mesogenic group and alkanediol as a flexible spacer:



The polyesters are designated BB-*n* where *n* is the number of methylene units in the diol. This homologous series of BB-*n* (*n*=3—9) invariably forms smectic mesophases whose isotropization temperatures and entropies exhibit an even-odd oscillation with the number of intervening methylene units, *n*. The even-odd oscillation can also be seen on the thickness of smectic layer, with a larger layer thickness in the even-membered polyesters. These even-odd effects suggest that the mesophase properties are strongly related to the polymer chain conformations and that different types of smectic structures should be formed between the even- and odd-membered polyesters. In succeeding papers,^{2,3} these were confirmed from observations of oriented X-ray patterns and optical properties. In even-membered polyesters there is formed a normal smectic A

phase in which both axes of the polymer chain and mesogenic group lie perpendicular to the layers. In odd-membered ones, in contrast, the smectic structure was identified as a new type of smectic phase, smectic C₂, in which the tilt direction of mesogenic groups is invariable in every second neighboring layer but opposite to the other between neighboring layers.³ These results show the importance of the flexible spacer understanding the mesophase structure and properties for these polyesters.

In this study, we prepared another homologous series of BB-*n* polyesters as follows:



The polyesters are analogous to the BB-4 polyester by having the butylene spacer, but different by containing branched methyl groups. The mesophase behavior of these

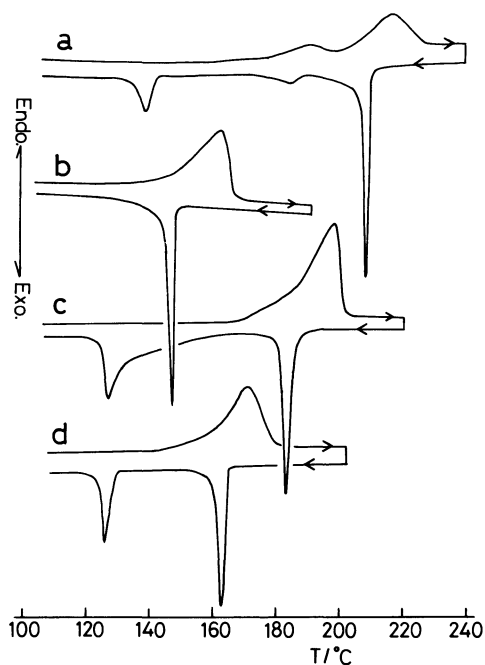
Table I. Phase transitions ($^{\circ}\text{C}$) based on cooling DSC data for the BB-polyesters; K =crystal; S_C =smectic C; S_A =smectic A; N =nematic; I =isotropic melt; ()=transition entropies (ΔS) in kcal mol^{-1} of repeat unit K

	$\eta_{\text{inh}}/\text{dl g}^{-1}$	Phase transitions						
		K		S_C	S_A		I	
BB-4	0.32	●	251 (2.0)	—	●	—	298 (3.3)	●
BB-4 (2-Me)	0.41	●	139 (1.4)	●	—	185 (0.5)	●	210 (2.9)
BB-4 (1-Me)	0.40	—	—	●	—	—	148 (3.7)	●
BB-4 (2,3-diMe)	0.45	●	127 (3.9)	—	—	—	182 (2.7)	●
BB-4 (2,2-diMe)	0.42	●	124 (1.8)	—	—	—	162 (2.4)	●
BB-4 (1,4-diMe)	0.35	—	—	—	—	—	—	●

polyesters was examined by DSC, optical microscopic and X-ray methods, and the effects of the branched methyl groups on the mesophase structure and properties are discussed in a comparison with the BB-4 polyester forming a S_A phase.

All the polymers were synthesized by melt transesterification from the dimethyl *p,p'*-bibenzoate and the appropriate diol.^{1,2} Inherent viscosities of polymers (η_{inh}), as determined at 25°C by using 0.5 g dl^{-1} solutions in a 60/40 w/w mixture of phenol and tetrachloroethane, ranged from 0.3 to 0.5 dl g^{-1} as listed in the second column of Table I. DSC measurements were performed with a Perkin-Elmer DSC-II calorimeter at a scanning rate of $10^{\circ}\text{C min}^{-1}$. Wide-angle X-ray diffraction patterns of the polymers were recorded with a flat-plate camera mounted in a Rigaku-Denki X-ray generator. Optical microscopic observations of the liquid crystalline textures were made with an Olympus BH-2 polarizing microscope.

BB-4(2-Me) The DSC thermograms of BB-4(2-Me) are shown in Figure 1a. Two transitions are observed at 190 and 218°C on heating. The lower one is attributed to the transition of the crystal to mesophase and the higher one to the isotropization of mesophase.

**Figure 1.** DSC thermograms of BB-polyesters. a, BB-4 (2-Me); b, BB-4 (1-Me); c, BB-4 (2,3-diMe); d, BB-4 (2,2-diMe).

On cooling, the material exhibits three transitions at 210, 185, and 139°C , and hence forms two types of mesophases. One is a nematic and another a smectic C (S_C) as described below. The nematic phase is

enantiotropic while the S_C phase is monotropic and was thus observed only on cooling from 185°C to 139°C.

The nematic phase is easily confirmed by its appearance as droplets on cooling the isotropic melt. It is also identified from the characteristic schlieren texture as shown in Figure 2a. On further cooling, the S_C phase appears as a sanded texture from the nematic phase. Shearing the specimen gives a well aligned fan-shaped texture (Figure 2b), exhibiting a smectic character of the mesophase.⁴

Direct evidence of the S_C phase is offered by the X-ray pattern of fibrous specimen. A typical X-ray pattern is shown in Figure 3. The fibrous specimen was prepared by drawing the isotropic melt so that the fiber axis placed in the vertical direction of Figure 3 corresponded to the polymer chain axis. The X-ray pattern includes two major reflections. One is a sharp

reflection and another, a broad reflection. These are assigned to the smectic structure; the inner reflection, the so called layer reflection, is attributed to the layered structure and the broad reflection to the disordered lateral packing of molecules within a layer. Further, it is found that the inner reflections are split into two portions around a meridional line while the broad reflections are centered on an equatorial line. Thus, the type of mesophase can be assigned as a S_C phase in which the axis of the mesogenic group is parallel to the axis of the polymer chain and both axes are tilted to the layer normal.²

The tilt angle in the S_C phase was directly estimated from the splitting angle of the layer reflections and plotted against the temperature in Figure 4a. Although the observations were limited within a temperature region from 180°C to 150°C, one can see a clear trend in which the tilt angle increases from 0° to 15° with a decreasing temperature. This trend is similar to that observed in the S_C phases of the low-molecular weight materials.⁵

The variation in the spacings of layer reflections with the temperature also reflects the tilted association of molecules to the layer (see Figure 4b). Comparing the tilt angle elucidated from the layer spacing with the observed one, we can conclude that the polymer chain conformation is not varied with temperature and has an averaged repeat length of

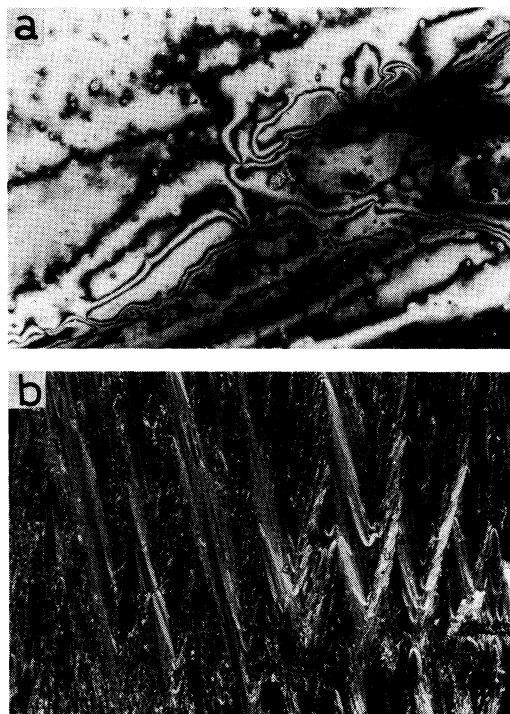


Figure 2. Optical microscopic textures for the mesophases of BB-4 (2-Me) polyester. a, nematic schlieren texture observed at 200°C; b, smectic fan-shaped texture observed at 180°C.

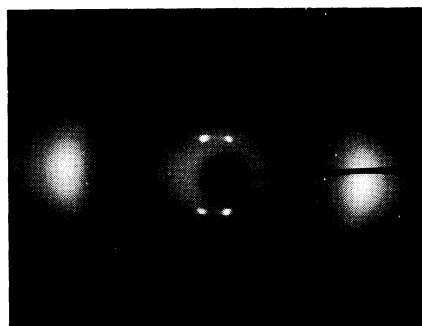


Figure 3. X-ray pattern of the fibrous smectic C phase in BB-4 (2-Me) observed at 155°C. The fiber axis is in the vertical direction.

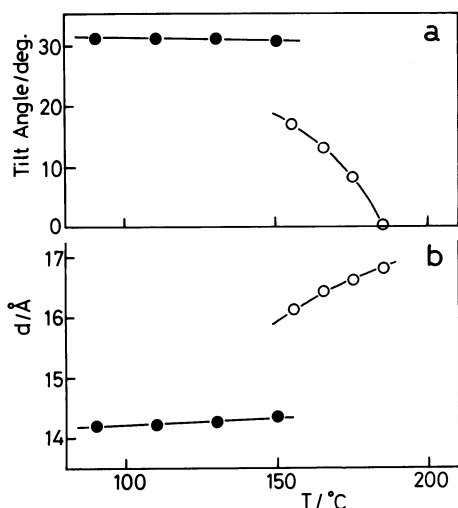


Figure 4. Temperature dependence of (a) the tilt angle and (b) the spacing of layer reflection in smectic C phases of BB-4 (2-Me) and BB-4 (1-Me) polyesters. (O), BB-4 (2-Me); (●), BB-4 (1-Me).

16.5 Å. This value of 16.5 Å is slightly larger than 15.8 Å elucidated in the smectic A phase of BB-4.¹ The chain conformation assumed in this S_C phase is thus similar to that in the S_A phase of BB-4, indicating that the tilting is caused only by the tilted association of polymer chains. In Figure 5a, the S_C structure for the BB-4(2-Me) is illustrated and compared with the S_A structure of BB-4 in Figure 5b.

BB-4(1-Me) Figure 1b shows the DSC thermograms of BB-4(1-Me). On heating, one can see only a peak at 162°C attributed to the crystal-isotropic phase transition. Cooling the isotropic melt results in the mesophase at 148°C. This monotropic mesophase is smectic, since it appears as battonnets from the isotropic melt and also exhibits a fan-shaped texture after the battonnets coalesce with each other. No other transition appears on cooling to the room temperature and the mesophase is likely to be glassified. The mesophase is metastable since annealing the specimen at the mesophase temperatures above 100°C causes the significant crystallization. This specimen thus crystallized gives the heating DSC data of Figure 1b.

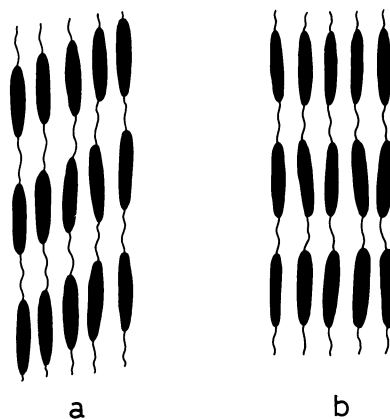


Figure 5. Illustration of the layer structure for (a) the smectic C phase of BB-4 (2-Me) and (b) smectic A phase of BB-4.

The oriented X-ray pattern of fibrous mesophase appears similar to that in the S_C phase of BB-4(2-Me), showing that layer reflections split into two portions around a meridional line and the outer broad reflection on an equatorial line. Thus, the S_C phase is also formed for this material, but in this case different from the S_C phase of BB-4(2-Me), the tilt angles are large and relatively constant around 30° with temperature variation as shown in Figure 4a. The small spacings of layer reflections also reflect the large tilt angles (see Figure 4b). The calculated tilt angle based on the layer spacing corresponds to the observed one if an averaged repeat length of polymer chain is 16.5 Å which is the same value as in the S_C phase of BB-4(2-Me). A similar S_C structure as in BB-4(2-Me), thus can be figured up for this material.

BB-4(2,3-diMe) The DSC thermograms of this material are shown in Figure 1c. Also in this case, only a monotropic mesophase is observed in the temperature region of 182°C to 127°C on cooling. The type of mesophase is nematic, which is assured from observation of the optical schlieren texture.

BB-4(2,2-diMe) Similar to BB-4(2,3-diMe), this material indicates the monotropic nematic phase appearing in the temperature region from

162°C to 124°C on cooling (see Figure 1d).

BB-4(1,4-diMe) This material indicates only the isotropic phase, which is glassified on cooling to room temperature. The mesophase and crystalline phase cannot be obtained even if the specimen is annealed at any temperature.

Table I summarizes the transition temperatures and types of liquid crystals collected on cooling. The data for BB-4 polyester are also listed in the table.

Comparing the branched polyesters with the BB-4 polyester,^{1,2} we can extract two significant effects of the branched methyl group on mesophase behavior. One is observed with respect to the mesophase temperature regions. As can be seen in Figure 1 and Table I, the mesophase temperature region falls by branching the methyl groups. Also, the temperature region becomes narrow and hence the mesophase tends to arise only on cooling. These trends seem more remarkable by branching the methyl group to the α -carbon than to the β -carbon or by branching two methyl groups than one methyl group. Reduction in the lateral packing interaction of polymer chains due to the branched methyl groups may be attributable to these effects. The second effect can be seen on the type of liquid crystal. With a comparison of BB-4 and BB-4 (2-Me) or BB-4 (1-Me), the branching of the methyl group

tends to alter the smectic A to the smectic C. In this alteration of the mesophase structure, no conformational change is included and only polymer chains are forced to assume tilted packing. The effect on the phase structure appears more remarkable by branching two methyl groups. In this case, the smectic liquid crystal is replaced by the nematic liquid crystal which has only an orientational order with a lack of positional order. These effects can be simply explained as due to the steric hindrance of the branched methyl groups; an effective accommodation of branched methyl groups into the mesophase structure may be achieved by tilted association of polymer chains in a system with one branched methyl group or by random packing in a system with two branched methyl groups.

REFERENCES

1. J. Watanabe and M. Hayashi, *Macromolecules*, **21**, 278 (1988).
2. J. Watanabe and M. Hayashi, *Macromolecules*, **22**, 4083 (1989).
3. J. Watanabe and S. Kinoshita, *J. Phys. (France)*, in press (1992).
4. D. Demus and L. Ritcher, "Texture of Liquid Crystals," Verlag Chemie, New York, 1978.
5. G. W. Gray and J. W. G. Goodby, "Smectic Liquid Crystals," Leonard Hill, Glasgow and London, 1984.