Frustrated bilayer smectic phase in main-chain polymers with two different spacers

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Classification
Physics Abstracts
61.30 — 61.30E

Frustrated bilayer smectic phase in main-chain polymers with two different spacers
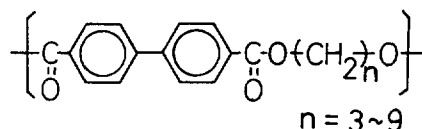
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Abstract . — We have studied the structural characteristics of the smectic phases formed by the main-chain type of polymers in which the mesogenic biphenyl moieties are linked by two different odd-numbered aliphatic spacers in a regularly alternate fashion. The first interesting result of this study is that the two different types of layer structures are formed depending on the difference in the lengths of two aliphatic spacers. In the polymers with the two spacers having a small difference in their lengths, the single layer structure is formed as a result of the random mixing of the two different spacers. In contrast, if there is a sufficiently large difference in lengths, the two different spacers participate into different layers and so the smectic phase appears to have a bilayer character. The second interesting result is that the bilayer smectic phase pretends the frustrated structure with the unusual density modulation in the direction parallel to the layer. This frustrated structure has been explained as resulting from a two-dimensional escape of the spontaneous polarization.

We have so far reported the thermotropic mesophase properties of main-chain BB-n polyesters that can be constructed by an alternate arrangement of the mesogenic p,p'-bibenzoate unit and the flexible alkylene spacer with the carbon number of n [1-7]:

$$\left[\begin{array}{c} C \\ \parallel \\ O \end{array} \bigcirc - \bigcirc \begin{array}{c} C \\ \parallel \\ O \end{array} O(CH_2)_n O \right]$$

$$n = 3 \sim 9$$

This homologous series of BB-n ($n = 3$-9) invariably form smectic mesophases whose isotropization temperatures and entropies exhibit an even-odd oscillation with the number of intervening methylene units, n. The even-odd oscillation was also observed on the types of smectic phases. In even-membered BB-n 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 contrast, the smectic

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structure in odd-membered ones was identified as a new type of smectic phase, smectic C_A [8], in which the tilt direction of mesogenic groups is invariable in every second neighboring layer but opposite to the other between neighboring layers (refer to Fig. 6 of Ref. [2]). The formation of such a distinct S_{CA} structure as well as the odd-even appearance of smectic structures have been explained as resulting from a coupling of the polymeric and mesogenic effects in which the spatial arrangement of mesogenic groups is strongly confined by the conformation of the intervening alkylene spacers [2, 4, 7, 9].

In addition to this conformational constraint effect, another interesting effect can be considered on the smectic structure in the main-chain type of polymers [10]. If there are two different alkylene spacers within a polymer molecule which are incompatible sterically, and if there is sufficient lateral attraction between identical spacers of adjacent polymer molecules, segregation into bilayer may occur. Then, four possible types of bilayer structures will arise as a result of a coupling with the conformational constraint mentioned above. These are illustrated in figures 1a to 1d. The bilayer structures of figures 1a and 1b may be formed from the polymers in which both different spacers have even number of carbons. The bilayer smectic phase in figure 1c may arise in the polymers with the two spacers different in an odd-even parity of their carbon numbers. Finally, the bilayer phase of figure 1d can be expected for the polymers with the two odd-numbered spacers.
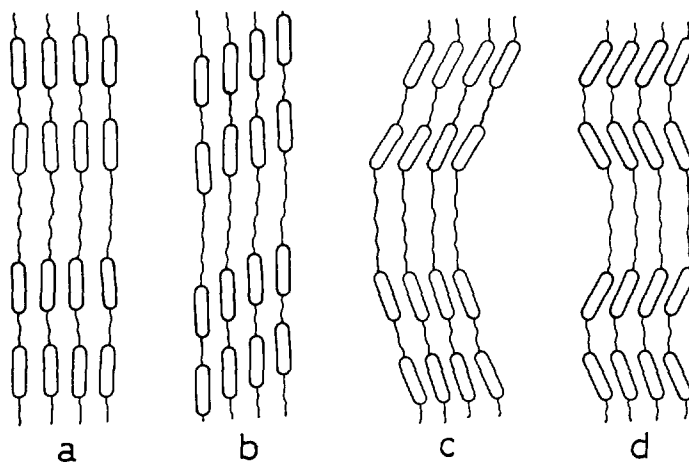

Fig. 1. — Four possible smectic structures with the bilayer modifications which may be formed in the main-chain polymers with the two different spacers sequenced in a regularly alternate fashion.

Among these, the bilayer smectic phase of figure 1d is especially interesting since it should be ferroelectric even in nonchiral system. The ferroelectricity can be understood by considering the space group. As illustrated in figure 2, the space group is analogous to the crystallographic C_{2v}^1; there are two fold axes along y-axis and mirror planes perpendicular to x- and z-axes [11, 12]. Since there is no mirror plane perpendicular to the two fold axes, the spontaneous polarization can be expected to arise along the y-axis, i.e., in a tilted direction in a layer [13].

The present study has been performed to seek this type of ferroelectric smectic liquid crystal

in the following main-chain polymers in which two mesogenic biphenyl moieties and two odd-numbered aliphatic chains are sequenced in a regularly alternate fashion [14].
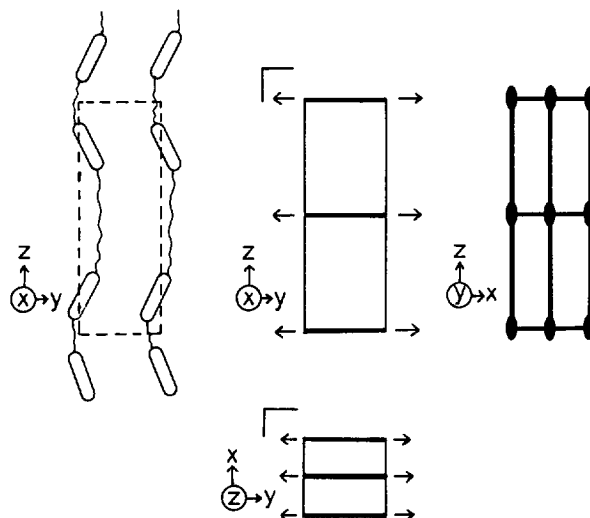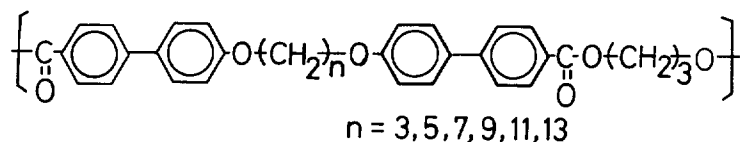
$$n = 3, 5, 7, 9, 11, 13$$

Fig. 2. — Space-group symmetry for the bilayer smectic structure of figure 1d [11].

Here, the aliphatic chain containing three methylene units is connected to the mesogenic cores by two ester linking groups, while the other aliphatic chain is linked to the mesogenic cores by two ether groups containing a variable odd number of methylene groups with $n = 3$, 5, 7, 9, 11 and 13. The polymers were designated BP-C03-0n where 3 and n indicates the number of methylene groups in the spacers. These were prepared by a polycondensation of the corresponding 4,4'-dicarboxy-α,ω-diphenylphenoxyalkane and 1,3-propanediol, which have been described elsewhere [14]. All the polymers form the smectic mesophases. The phase transition temperatures and enthalpies, collected from the DSC cooling curves, are listed in table I.

Depending on the compatibility of two flexible spacers, two possible types of smectic structures can be considered to be formed. One is the single-layer smectic phase in which the two different spacers are compatible and so randomly mixed. Another is the bilayer smectic phase with the different spacers segregated from each other. These two types of layer structures can be easily distinguished from each other through the x-ray observations. In random mixing system, the first-order layer reflection should arise with a spacing corresponding to half the length of a repeat unit of polymer ($L/2$) while in the bilayer system it arises with a spacing corresponding to the length of a repeat unit (L).

Figure 3a shows the X-ray diffraction pattern observed for the oriented smectic phase of BP-C03-07. Here, the oriented specimen has been prepared as a fiber by pulling up the isotropic

Table I. — *Phase transitions (°C) of BP-C03-0n polymers based on cooling DSC data; K =
crystal; S_m = smectic; I = isotropic melt; ( ) = transition enthalpies (ΔH) in kJ/mol of
repeat unit.*

| | η_{inh}/dlg^{-1} [*] | Phase transitions | | |
		K	S_m	I
BP-C03-03	0.43	169 (4.6)	248 (13.4)	
BP-C03-05	0.41	155 (4.6)	249 (18.4)	
BP-C03-07	0.54	161 (7.5)	236 (17.1)	
BP-C03-09	0.38	149 (3.3)	213 (18.0)	
BP-C03-011	0.58	145 (3.8)	202 (19.2)	
BP-C03-013	0.37	157 (3.8)	196 (23.4)	

[*]Inherent viscosities were determined at 25 °C by using 0.5 dlg^{-1} solutions in a 60/40 w/w mixture
of phenol and tetrachloroethane.

melt and the fiber axis corresponding to the polymer chain axis is placed in the vertical direction
[2]. The similar X-ray pattern was observed for BP-C03-03, BP-C03-05 and BP-C03-09. For
these polymers with n = 3 to 9, the first-order layer reflections (the 001 reflections) appear
having the spacings of 12.9 Å to 16.1 Å as listed in table II. These values approximate to half
the repeat length ($L/2$) [1, 7], meaning that the layer structure is constructed by a random
mixing of the two different spacers. Further, it is found from figure 3a that the layer reflection
arises just on a meridian while the outer broad reflection showing the liquid-like association of
mesogenic groups in a layer are placed above and below the equator. This diffraction geometry
clarifies the S_{CA} type of layer structure [2, 4].

Table II. — *The spacing Å of layer reflections observed for the smectic phases of BP-C03-0n
polymers; ( ), indices of reflections (see the text).*

BP-C03-03	BP-C03-05	BP-C03-07	BP-C03-09	BP-C03-011	BP-C03-013
				21.9 (101)	24.7 (101)
12.9 (001)	13.9 (001)	14.9 (001)	16.1 (001)	17.1 (002)	18.0 (002)
6.43 (002)	6.94 (002)	7.45 (002)		8.54 (004)	9.04 (004)
				6.66 (105)	
				5.70 (006)	

The remarkably distinct X-ray pattern is observed for the smectic phases of the BP-C03-011
and BP-C03-013, as shown in figure 3b. The narrow distribution of reflection intensities also
points to the high degree of orientation in fibers. An interesting aspect of this pattern is that
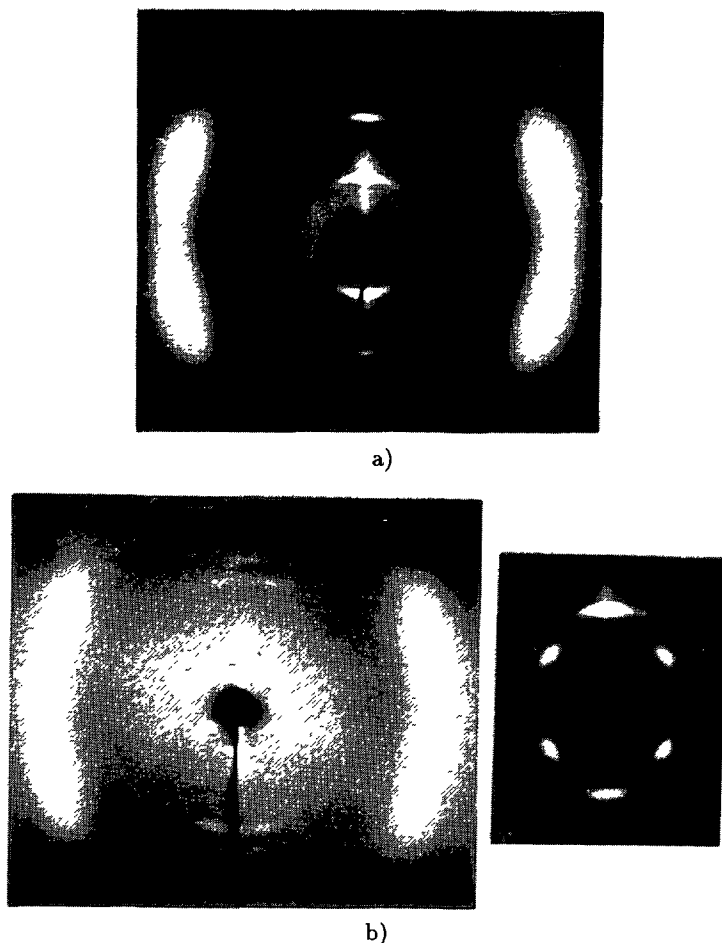
a)

b)

Fig. 3. — X-ray diffraction photographs of the oriented smectic phases observed in (a) BP-C03-07 and (b) BP-C03-011 fibers at 200 °C. The fiber specimen was prepared by pulling up the isotropic melt and its axis is placed in the vertical direction. The enlarged photograph in (b) shows the X-ray pattern in the small-angle region.

the meridional layer reflection is accompanied by four point (off-meridional) reflections (see enlarged photograph in Fig. 3b). The relative intensities of these reflections are maintained constant with the variation of mesophase temperatures, showing that these come from a single phase. As listed in table II, the spacing of the first meridional reflection corresponds to half the length of repeat unit $(L/2)$ while the off-meridional reflections appear with the height of $1/L$ far from the equator. This dictates that there is a density modulation with a periodicity of L along the layer normal. The X-ray photograph shows additionally weak but distinct higher-order reflections on meridian and off-meridian, which are also listed in table II. All of these reflections can be interpreted as $00l$ ($l = 2m$) and $10l$ ($l = 2m+1$) reflections based on the two-dimensional rectangular lattice. The lattice parameters are determined as $a = 28.5$ Å and $c = 34.2$ Å for BP-C03-011, and $a = 33.8$ Å and $c = 36.2$ Å for BP-C03-013. Here, the c-axis corresponds to the polymer chain axis and a-axis lies perpendicularly to the polymer chain. Considering that the averaged diameter of molecule is more or less than 4.5 Å, six to eight

molecules are located in these lattices. The diffuse outer reflections are also observed here, lying above and below the equator. Hence, the mesogenic groups are liquid-like in a layer with their axes alternately tilted to the layer normal similarly as in the S_{CA} phase of the random mixing system. Overall results show that the smectic phase pretends the bilayer structure of figure 1d although it also has another periodic density modulation in a direction parallel to the layer irrespective of the liquid-like lateral association of mesogenic groups. We thus come to a preliminary conclusion that even the compatible aliphatic spacers can form different layers if there is a sufficiently large difference (8 or more in the carbon number) in their lengths.

Let us consider the layer structure responsible for showing the distinct X-ray pattern of figure 3b. This characteristic pattern containing the meridional and off-meridional layer reflections is reminiscent of those reported for the frustrated smectic phases [15-17]. Using the concept developed for the frustrated smectic phases, we can tentatively propose a structural model as illustrated in figure 4, according to which the internal structure of the smectic layers displays an unusual density modulation parallel to the tilt direction of mesogenic groups [18]. The unusual density modulation is produced in such a way that the bilayer is constructed by a repeat unit of polymer chain in a small domain but the polymer chains in adjacent small domain slide halfway along the layer normal after the 180° rotation around their chain axes. In other words, it can be described by a periodic structure of domain walls, in each domain the basic layer structure being the same as the bilayer structure of figure 1d. Observation of a series of reflections with $l = 1$ to 5 dictates the highly positional order along the layer normal (c-axis) while the positional order along the layer (a-axis) is low because of the observation of reflections with only $h = 1$. This shows that the density modulation along the layer is not necessarily regular. Furthermore, one can find that the tilted orientation correlation of the mesogenic groups, which should be required in the liquid crystalline field, has been maintained irrespective of the frustration (see dashed curves).
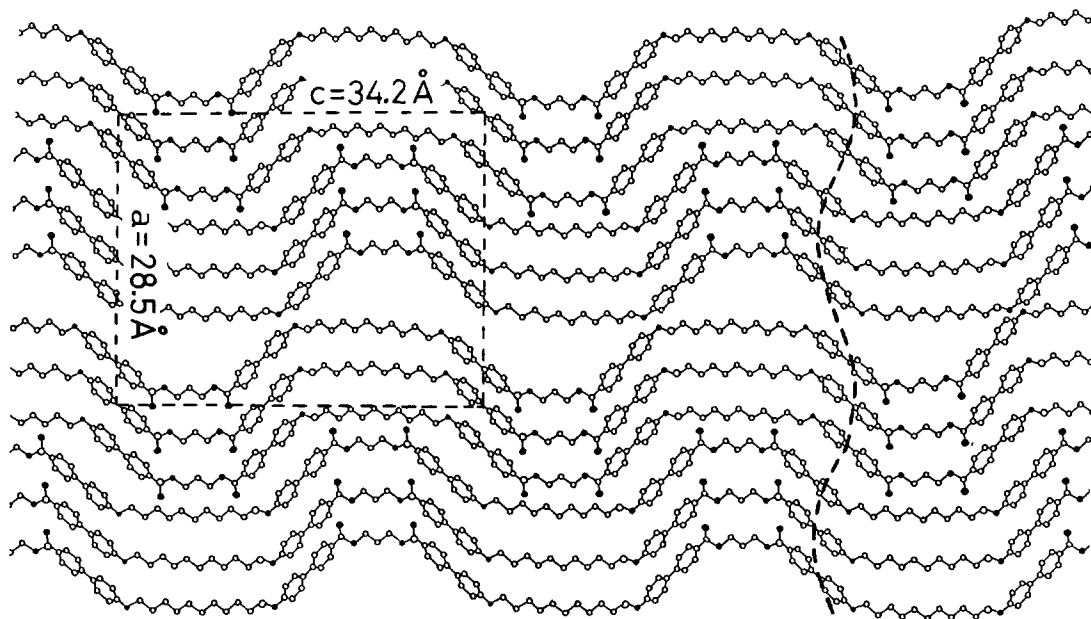

Fig. 4. — Tentative structural model for the frustrated smectic phase of BP-C03-011. For convenience, the polymer chains in an all-trans conformation are illustrated.

The frustrated smectic phases with a two-dimensionally positional order have been firstly observed for low molar mass compounds such as the derivatives of cyanobiphenyl *possessing* a strong longitudinal dipole [15]. Frustration effects arise in such a system because of the incommensurability of two types of characteristic lengths, namely, the molecular length and the pair length, the pair formation being controlled by dipolar forces [16, 17]. The frustrated smectic structure, as an another example, has been observed in the combined main-chain/side-chain polymers. It has been explained to be caused by the combined orientation of side-chain and main-chain mesogens [19, 20], showing that the frustrated smectic phase can be induced by an appropriate design of polymer molecule. In the present system, can one make sense for the driving force for the adoption of such a frustrated smectic phase? If the fundamental bilayer smectic phase of figure 1d is ferroelectric, it turns out that the answer is rather simple. By a comparison with the ferroelectric bilayer phase of figure 1d, one can find that there is a two-dimensional escape of polarization, i.e., an antiferroelectric arrangement of polarization in the frustrated smectic phase of figure 4. It is thus postulated that the frustration has been induced to eliminate the strong interaction of the spontaneous polarization. Any other reasons can be hardly considered since the frustration effects have never been observed in the other types of bilayer smectic phases of figures 1b and 1c which have no spontaneous polarization [14]. The present frustrated smectic phase with the two-dimensionally positional order is the third example which is caused by the different reason.

References

[1] Watanabe J. and Hayashi M., *Macromolecules* **21** (1988) 278.

[2] Watanabe J. and Hayashi M., *Macromolecules* **22** (1989) 4083.

[3] Watanabe J., Hayashi M., Kinoshita S. and Niori T., *Polym. J. (Japan)* **24** (1992) 597.

[4] Watanabe J. and Kinoshita S., *J. Phys. II France* **2** (1992) 1237.

[5] Takanishi Y., Takezoe H., Fukuda A. and Watanabe J., *Phys. Rev. B* **45** (1992) 7684.

[6] Watanabe J., Komura H. and Niori T., *Liq. Cryst.* **13** (1993) 455.

[7] Watanabe J., Hayashi M., Morita A. and Niori T., *Mol. Cryst. Liq. Cryst.*, in press.

[8] In the previous reports, this phase has been termed S_{C2} phase, but S_{C2} is a confusing notation in the context of the nomenclature described in low molar mass systems. For this reason, we will hereafter adopt the notation of S_{CA} which has been adopted for the same type of smectic phase in low molar mass system by Fukuda *et al.*; Chandani A.D.L., Gorecka E., Ouchi Y., Takezoe H. and Fukuda A., *Jpn J. Appl. Phys.* **28** (1989) L1265.

[9] Abe A., *Macromolecules* **17** (1984) 2280.

[10] Petscheck R.G. and Wiefling K.M., *Phys. Rev. Let.* **59** (1987) 343.

[11] International Table for X-ray Crystallography (1959) Vol. **I** (Birmingham, Kynoch Press) p. 208.

[12] It should be noted here that this space group is essentially different from that of the S_{CA} phase which is analogous to the crystallographic D_{2h}^5 [4, 11].

[13] Meyer R.B., *Mol. Cryst. Liq. Cryst.* **40** (1977) 33.

[14] Nakata Y., Shimizu K. and Watanabe J., to be published.

[15] Sigaud G., Hardouin F., Achard M.F. and Levelut A.M., *J. Phys. France* **42** (1981) 107.

[16] Prost J. and Barois P., *J. Chim. Phys.* **80** (1983) 65.

[17] Prost J., *Adv. Phys.* **33** (1984) 1.

[18] It should noted here that the fundamental bilayer smectic phase has a biaxial character and *so* another frustrated structure can be also proposed such that the unusual density modulation occurs in a direction perpendicular to the tilt direction. In the present time, we cannot select one of these two models since the X-ray pattern has been observed only for the fiber specimen. However, even if any model is adopted, the structural characteristics described here are not essentially altered.

[19] Endres B.M., Ebert M., Wendorff J.H., Reck B. and Ringsdorf H., *Liq. Cryst.* **7** (1990) 217.

[20] Mensinger H., Biswas A. and Poths H., *Macromolecules* **25** (1992) 3156.