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Thermotropic liquid crystals of polyesters having a mesogenic 4, 4-bibenzoate unit

Smectic mesophase properties and structures in dimeric model compounds

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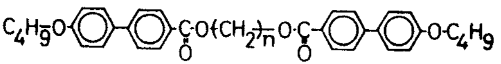
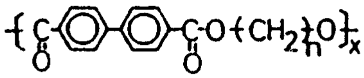
In this study, we prepared a homologous series of dimeric compounds, di-BB-*n*,



These compounds have two mesogenic groups linked by a flexible methylene spacer and so can be regarded as model compounds for main chain liquid crystalline BB-*n* polyesters. In this dimeric system, we observed distinct odd–even effects in which the smectic mesophase properties and structures are significantly affected by the number of carbon atoms in the flexible spacer. The most interesting effect among them was observed for a type of smectic phase. From detailed optical microscopy and X-ray observations, we found that the even-membered di-BB-*n* materials form a smectic A while the odd-membered ones form a smectic C_2 phase. Such a distinct odd–even effect was concluded to result from the confined spatial orientation of mesogenic groups which is controlled by the conformation of the flexible spacer similar to the BB-*n* polymeric system.

1. Introduction

In the first paper of this series [1], we reported the thermotropic mesophase properties of main chain polyesters that can be constructed by an alternating arrangement of the mesogenic 4, 4′-bibenzoate unit and a flexible methylene spacer [2]:



The polyesters are designated BB-*n* where *n* is the number of methylene units in the spacer. The BB-*n* homologous series ($n = 3$–9) invariably form smectic mesophases whose isotropization temperatures and entropies exhibit an odd–even oscillation with the number of intervening methylene units, *n*. An odd–even oscillation was also seen for the thickness of the smectic layer, with a larger layer thickness for even-membered polyesters. These odd–even effects suggested that different types of smectic structures are formed for even- and odd-membered polyesters. In succeeding papers [3–5] this was confirmed from the observations of oriented X-ray patterns and optical properties. In even-membered polyesters a normal smectic A phase is formed 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 C_2, in which the tilt direction of the mesogenic groups is the

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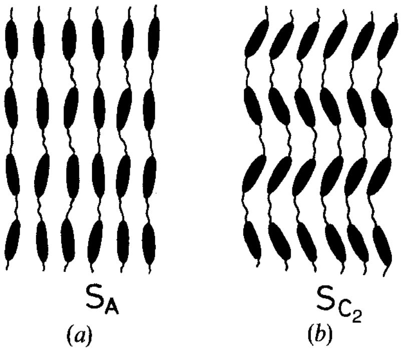


Figure 1. The smectic layered structures which have been elucidated for (*a*) the S_A phase of the even-membered BB-*n* polyesters and (*b*) the S_{C_2} phase of the odd-membered BB-*n* components.

same in every second layer but opposite to that in neighbouring layers. In figure 1 are illustrated the layer structures elucidated for both phases [3–4].

Such an odd–even effect shows how the nature of the flexible spacer is important for the understanding of the mesophase structure and properties for this kind of polyester. The novel S_{C_2} phase formed by the odd-membered BB-*n*, is especially quite interesting since uniaxial ordering cannot be observed for the **n** director but only for the **c** director [3–4]. The formation of such a curious S_{C_2} structure was believed to result from coupling of the polymeric and mesogenic effects in which the spatial arrangement of the mesogenic groups is strongly related to the conformation of the intervening methylene spacers.

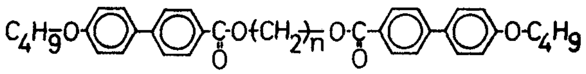
This coupling effect of polymer chain and mesogenic group was examined by Abe [6], who has performed conformational analysis within a framework of the rotational isomeric state model and evaluated the angle Θ, defined by unit vectors attached to two successive mesogenic groups for all possible conformations of the methylene spacer. The results indicate that the angular distribution for the even- and odd-membered BB-*n* polymers appears remarkably different. When *n* is even, Θ are found to be distributed in the two ranges 0° to 30° (30–40 per cent) and 85° to 130° (60–70 per cent). For the system when *n* is odd, the major portion of the angles is located in the region 50° to 90° and to some extent orientations are also permitted in the region above 150°. In each system, the conformers with the smaller angular displacement of successive mesogens are in the more extended form whereas the ones with the larger angular displacement are in the folded form. According to this calculation, we would arrive at the following interesting conclusions that can be closely related to the previously mentioned observations [3–4]:

(i) When *n* is even, the parallel orientation of successive mesogenic groups is allowed, conforming more or less to the concept of an ordinary uniaxial ordering of the **n** director but when *n* is odd uniaxial orientation of successive mesogenic groups is not expected.

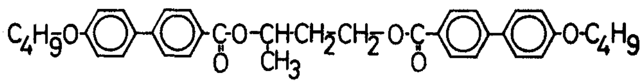
(ii) Conformers with the smaller angular displacement in both odd and even systems correspond to the conformers participating in the observed layer structures.

These points explain the odd–even appearance of the different smectic phases and at the same time, account for the specific formation of the S_{C_2} phase in the odd-membered BB-*n* series [4] (see figure 1).

The same conformational constraint is likely to arise for the smectic phases of the dimeric compounds in which two mesogenic groups are linked by a flexible spacer [7, 8], although a number density in the molecular ends remarkably increases in comparison with the polymers and so the end groups of molecules might significantly affect the smectic structures. In this study to clarify this, we prepared the dimeric model compounds, α, ω-bis(4, 4′-butoxybiphenyl-carbonyloxy) alkanes, with the following formula:



which have a similar chemical structure to the BB-*n* polyesters and invariably form smectic phases. These are abbreviated as di-BB-*n* where *n* indicates the number of carbon atoms in the methylene spacer and was varied here from $n = 4$ to 9. In addition to these, we have also prepared the chiral dimeric compound, 1, 3-bis(4, 4′-butoxybiphenyl-carbonyloxy) (*S*)-1-methyl propane (di-BB-3*):

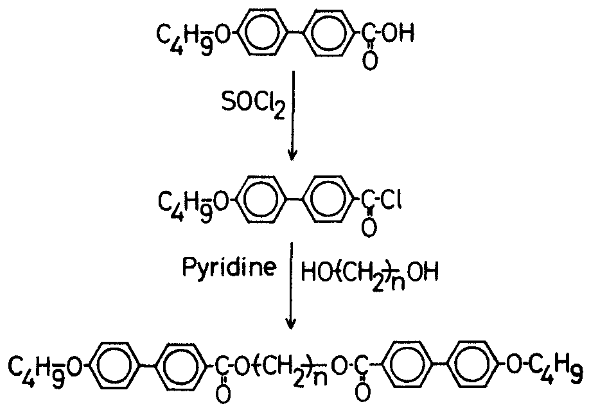


Their thermotropic mesophase behaviours and structures have been analysed by DSC, optical microscopy and X-ray methods, and are discussed in comparison with those for the BB-*n* polymeric system.

2. Experimental

2.1. *Materials*

The di-BB-*n* materials were synthesized according to the route shown in the scheme.



2·0 g of butoxybiphenyl carboxylic acid (from Hamari Chemicals, Ltd) were refluxed with 40 ml of thionyl chloride, until no further evolution of HCl was observed. The excess of thionyl chloride was removed by distillation under reduced pressure and the acid chloride was collected. In a typical preparation of the dimeric compounds, 2·0 g of acid chloride were dissolved in 30 ml of anhydrous pyridine. To this solution, 0·002 mol of diol, previously dissolved in 30 ml of pyridine, were added dropwise under stirring at 100°C. After 10 h, the reaction mixture was then poured into the dilute solution of HCl. The solid precipitate was filtered. The dimeric compound was purified by column chromatography (silica gel, chloroform as eluent) and finally recrystallized from chloroform/ethanol. All the synthesized compounds gave proton NMR spectra, recorded on a JEOL FX90Q spectrometer, which were consistent with their chemical formulae.

2.2. *Methods*

The calorimetric behaviour was investigated with a Perkin–Elmer DSC-II calorimeter at a scanning rate of 10°C min^{-1}. The textures of the mesophases were studied using a polarizing microscope (an Olympus BH-2) equipped with a Mettler FP 80 hot stage. X-ray diffraction photographs were taken at different temperatures by using Ni-filtered Cu–K_α radiation. The temperature was measured and regulated within an accuracy of 0·2°C by using a Mettler FP 80 heater. The film to specimen distance was determined by calibration with silicon powder. The reflection spectra were measured with a Hitachi Model 330 spectrometer.

3. Results and discussion

3.1. *Odd–even effects on mesophase properties and structure*

All specimens prepared, except for di-BB-3*, exhibit a single mesophase as found by the typical DSC thermograms of di-BB-6 in figure 2. Di-BB-3* undergoes a direct transition from crystal to isotropic melt. Figure 3 shows the dependence of the transition temperatures on the number of carbon atoms in the methylene spacer, *n*, and the table lists the fundamental thermodynamic data related to the transitions. The thermotropic phase behaviour of this series is similar to typical dimeric mesogens in the following two ways [7, 9–12]. At first, the isotropization temperatures (T_i), enthalpies (ΔH_i) and entropies (ΔS_i) of the series exhibit a remarkable odd–even alternation with the higher values for the even-membered di-BB-*n*. Secondly, increasing the length of the spacer lowers the mesophase temperature range.

The smectic phase can be confirmed for all specimens from its characteristic X-ray pattern which exhibits an inner sharp reflection, so called the layer reflection, and an outer broad reflection. The spacing of the layer reflection varies from 18Å to 22 Å depending on the length of the flexible spacer (refer to the last column of the Table)

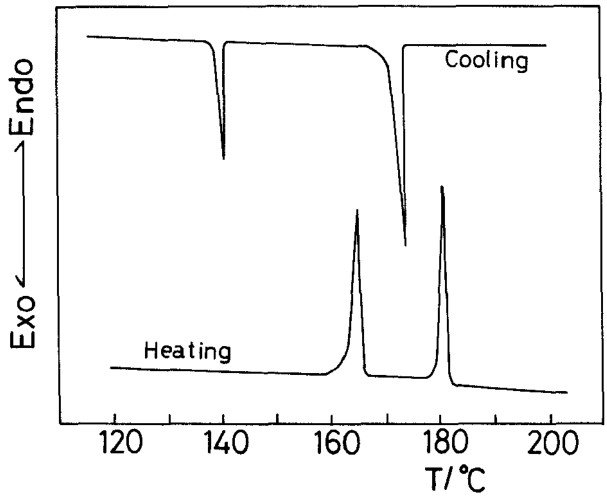


Figure 2. DSC thermograms of di-BB-6.

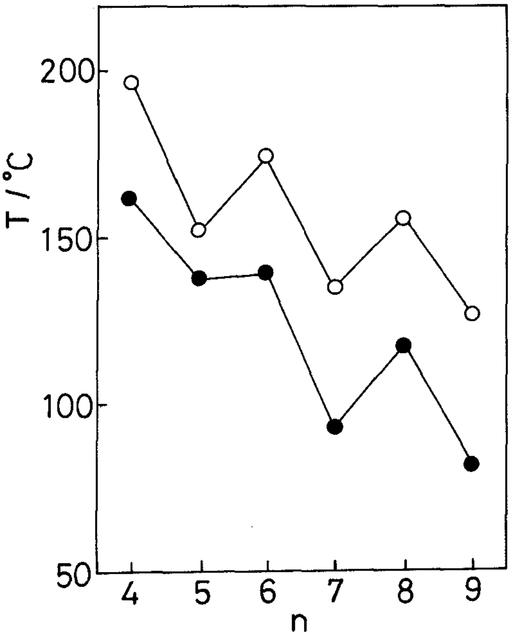


Figure 3. Variation of the transition temperatures with the number of carbon atoms in the methylene spacer, *n*, for di-BB-*n*. The transition temperatures are based in the DSC cooling data.

Characterization of di-BB-*n* compounds.

	T_m/°C	T_i/°C	ΔH_i/kJ mol^{-1}	ΔS_i/kJ mol^{-1} K^{-1}	*d*/Å
di-BB-4	161	198	23·4	49·4	18·8
di-BB-5	138	153	17·6	40·2	18·1
di-BB-6	139	176	20·9	46·4	20·0
di-BB-7	92	135	16·3	39·8	19·0
di-BB-8	117	157	20·1	46·4	21·2
di-BB-9	80	125	14·6	36·8	20·3

Thermodynamic data based on the DSC cooling thermograms.
d is the spacing of smetic layer reflection

while the spacing of the broad reflection is constant around 4·5 Å. Figure 4 shows the variation of the layer spacing with *n*, which exhibits a clear odd–even oscillation. Further, the type of the smectic phase appears different between even- and odd-membered di-BB-*n*; the smectic A (S_A) phase for the even-membered di-BB-*n* and the smectic C_2 (S_{C_2}) for the odd-membered ones will be shown in detail later.

These odd–even oscillations for the mesophase properties are fairly similar to those observed for the polymeric BB-*n* system [3, 4].

3.2. *Identification of the smectic structure*

3.2.1. *S_A phase for the even-membered di-BB-n*

The smectic A phase for the even-membered di-BB-*n* can be confirmed by optical microscopy. Figures 5 (*a*) and (*b*) are the microscopic textures as typically observed for

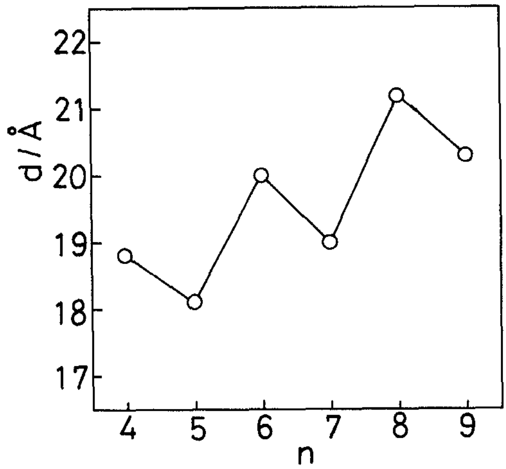


Figure 4. Variation of the layer spacings with the number of carbon atoms in the methylene spacer, *n*, for the smectic phases of di-BB*n*.

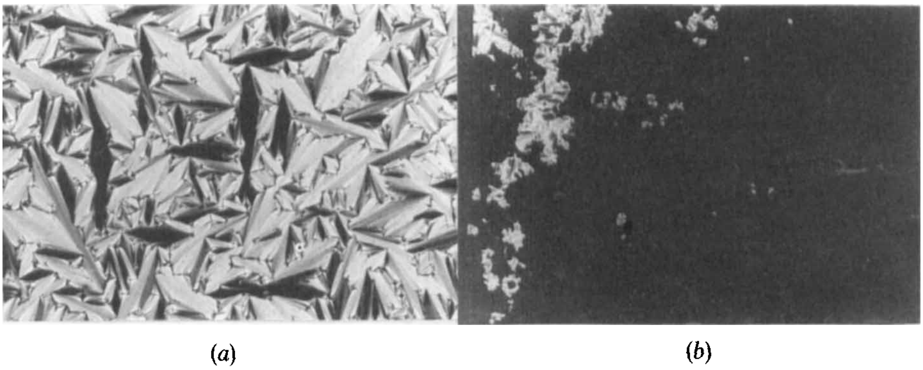


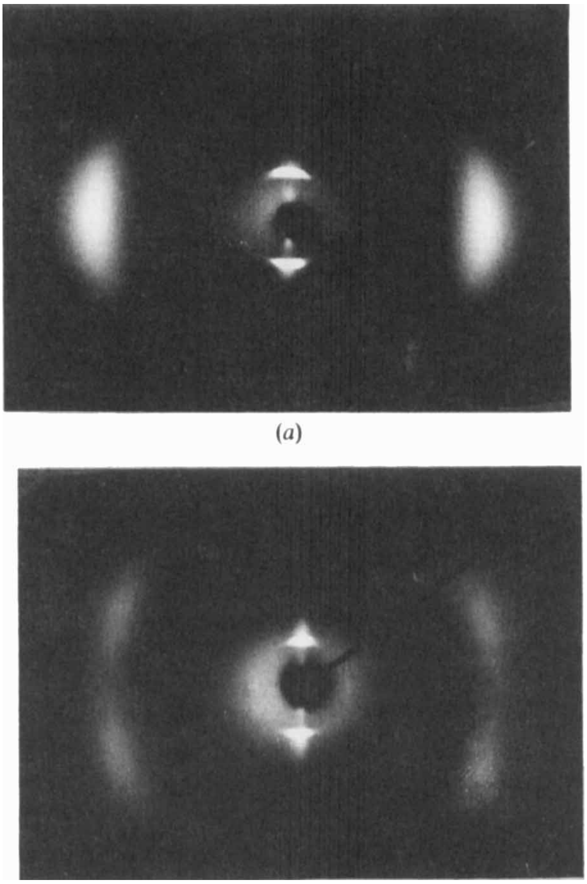
Figure 5. The microscopic textures observed for the S_A phase of di-BB-8; (*a*) the fan-shaped texture and (*b*) the homeotropic texture obtained by shearing the mesophase of (*a*).

di-BB-8. At first on cooling the isotropic melt, bâtonnets appear and coalesce to the fan-shaped texture as in figure 5 (*a*). Shearing the specimen between glasses, the fan-shaped texture can be altered to the homeotropic texture in which no birefringence is observed between crossed polarizers (see figure 5 (*b*)). These optical textures are typical of a S_A phase.

The supplementary evidence for the S_A phase is given by X-ray measurements. Figure 6 (*a*) shows the oriented X-ray pattern taken for a thin homeotropic film with an X-ray beam parallel to the film surface. The X-ray pattern indicates the sharp layer reflection and the outer broad reflection which have an angular displacement of 90° to each other. This angular displacement directly indicates the S_A structure with the mesogenic groups lying perpendicular to the layer.

3.2.2. S_{C_2} *phase for the odd-membered di-BB-n*

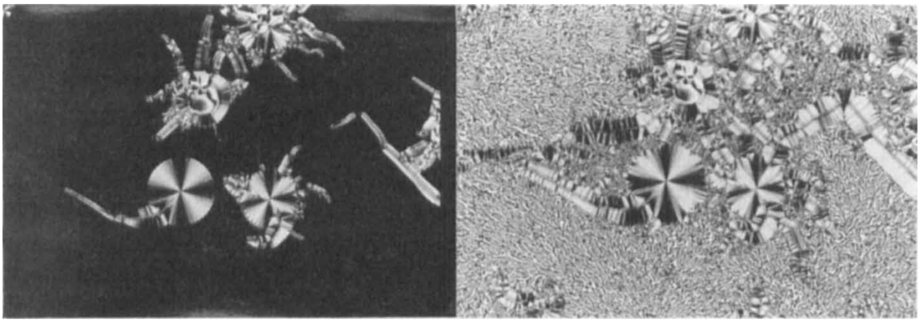
The S_{C_2} phase for the odd-membered system was found to appear with characteristic textures from the isotropic melt as typically shown for di-BB-7 in figures 7 (*a*) and (*b*). On cooling from the isotropic melt, the spherulitic domains, containing the well



(a)

(b)

Figure 6. The X-ray pattern taken for the homeotropic smectic phases with the X-ray beam parallel to the film surface; (a) the S_A phase of di-BB-8 and (b) the S_{C_2} phase of di-BB-7.



(a) (b)

Figure 7. The microscopic textures for the S_{C_2} phase of di-BB-7. On cooling from the isotropic melt, the S_{C_2} phase initially appears as the focal conic texture with the spherulitic domains (a). Their worm-like strings develop surrounding the spherulitic domains (a) and simultaneously, the homeotropic domains occupy the space between the strings (b).

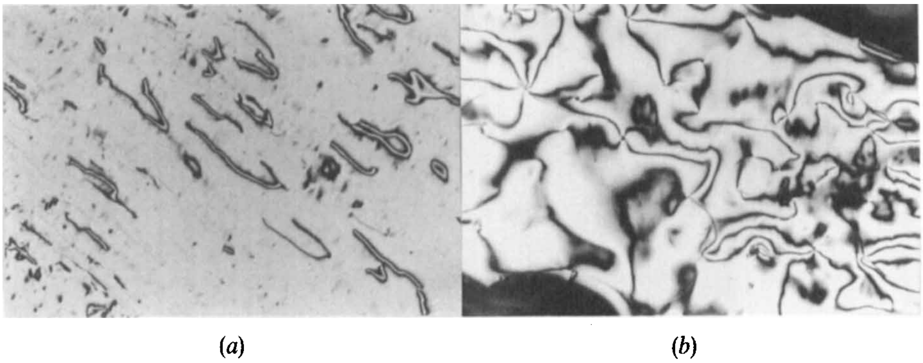

(*a*) (*b*)

Figure 8. The homeotropic texture of the S_{C_2} phase of di-BB-7 exhibition (*a*) the closed inversion walls and (*b*) the schlieren with singularities $s=\pm 1$ and $s=\pm 1/2$.

aligned focal conic textures developed initially (see figure 7 (*a*)). After growing to a limited size, the worm-like strings, which look like oily streaks appear surrounding the spherulitic domains as found in the same figure. Simultaneously, the homeotropic domains appear to occupy the space between the strings (see figure 7 (*b*)). By shearing the specimen unidirectionally between the glass slide and cover slip, such a complex texture is easily altered to a completely homeotropic texture, exhibiting strong birefringence and leaving some marbled textures with closed inversion walls as shown in figure 8 (*a*). Simply pressing the specimen between the glass slide and cover slip also promotes homeotropic alignment of the layers, but in this case the distinct schlieren textures with singularities of $s=\pm 1$ and $\pm 1/2$ can be seen (figure 8 (*b*)).

The orientated X-ray pattern taken for a thin homeotropic film is shown in figure 6 (*a*). We can see that the inner reflection is located on the meridional line as for a S_A phase but the outer broad reflections are split by about 25° above and below the equatorial line.

Both the microscopic and X-ray observations, thus indicate that the mesogenic groups are tilted to the layer normal and hence the **c** director exists in this phase. The tilt angle is around 25° as elucidated from the X-ray photograph. The structure is thus similar to a normal S_C. However, the exhibition of the schlieren texture of $S\ \pm 1/2$ rules out the S_C phase [13] but indicates the S_{C_2} phase in which the tilt directions of the mesogenic groups are opposite in adjacent layers [4, 14, 15].

It is worth noting that the S_{C_2} phase can be converted to the chiral $S_{C_2}^*$ phase by introducing a chiral component. A typical system that adopts a chiral $S_{C_2}^*$ structure is the mixture of di-BB-7 and di-BB-3*. The phase diagram for this binary system is given in figure 9. The helical structure of the chiral $S_{C_2}^*$ phase can be confirmed by the microscopic observation of dechiralization lines superimposed on the fan-shaped texture and also from the ability of this phase to selectively reflect light (see figure 10). The helical pitch, P, evaluated by microscopy and absorption spectroscopy was found to be independent of temperature, but decreases linearly with an increase in the weight fraction of chiral di-BB-3*, $y/(x+y)$, according to the equation, $1/P(\mathrm{nm}^{-1})=7{\cdot}1\times 10^{-3}y/(x+y)$.

The homeotropic chiral $S_{C_2}^*$ phase results in the formation of a Grandjean planar texture, which was confirmed by the observation that the rotation of the sample between crossed polarizers produces no extinction. The helical structure is, thus, formed with its helical axis perpendicular to the layers, in other words, the helical

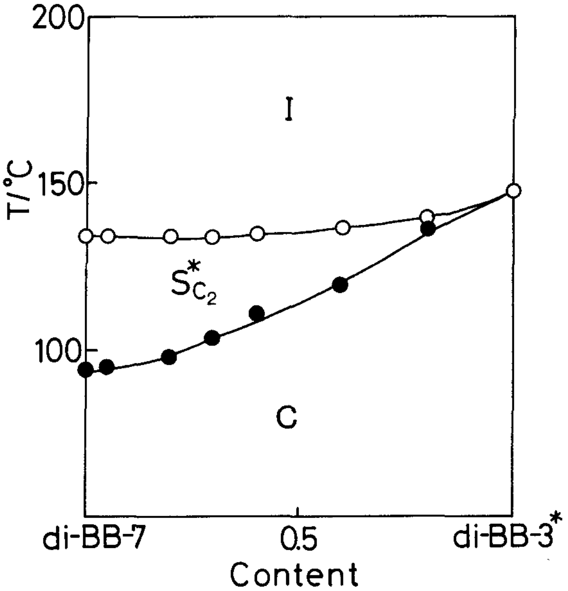


Figure 9. The phase diagram for the binary system composed of di-BB-7 and di-BB-3*. The transition temperatures are based on the DSC cooling data.

structure results from the helical twisting of the c directors as in a chiral S^*_C phase. The chiral $S^*_{C_2}$ phase in such a Grandjean alignment results in the selective reflection of the visible light when the weight fraction of di-BB-3* is in the range of 0·3 to 0·5. Figures 10 (*a*) and (*b*) show the typical reflection spectra that were observed for the mixture with a di-BB-3* weight fraction of 0·4, with incident light normal and oblique to the helical axis. In these figures, we can see the single normal reflection band arising from the periodicity of half the pitch (the so-called half-pitch band) for both normally and obliquely incident light. This observation again indicates that the S_{C_2} phase is essentially different from the normal S_C phase [16, 17] and shows the layered structure with alternate tilting of the mesogenic groups [14, 18]

3.3. *Illustration of the smectic layered structure in the dimeric system*

It can be thus concluded that the even-membered di-BB-*n* materials exhibit the S_A phase while the odd-membered ones the S_{C_2} phase. This odd–even character is completely the same as that observed in the polymeric BB-*n* system [4]. In this case, however, the smectic layered structure is also significantly affected by the conformational constraint of the flexible spacer as mentioned in detail in the Introduction; for even-membered di-BB-*n* the two mesogenic groups within a molecule are parallel to each other on average while for the odd-membered ones they are tilted by 50° to 60° to each other. The smectic structures for the dimeric compounds can be illustrated as in figure 11.

Irrespective of this striking similarity in the fundamental layered structure, it should be noted here that the dimeric compounds are essentially different from the polymers with respect to the molecular length and also the number density of the molecular ends. In the polymeric system, the confined orientation correlation of the mesogenic groups is maintained along the whole polymer chain length (see figure 1) while in the dimeric system it persists only for two mesogenic groups within a molecule (see figure 11). To

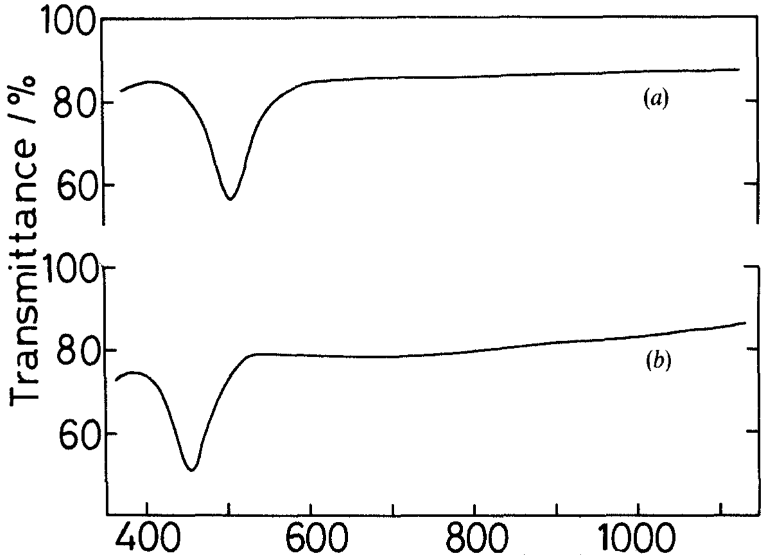


Figure 10. The reflection spectra observed for the chiral $S_{C_2}^*$ phase with a homeotropic Grandjean alignment, as measured by the incident light (*a*) parallel and (*b*) inclined by 60° to the helical axis. Here, the Grandjean chiral $S_{C_2}^*$ phase was prepared by using the binary mixture of di-BB-7 and di-BB-3* with a di-BB-3* weight fraction of 0·4.

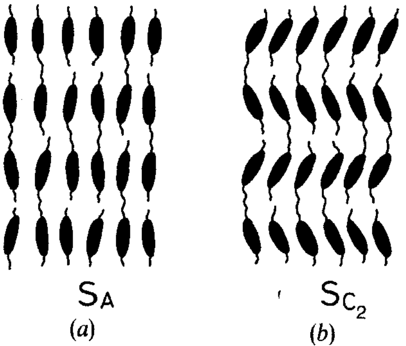


Figure 11. The smectic layered structures proposed for (*a*) the S_A phase of even-membered di-BB-*n* and (*b*) the S_{C_2} phase of odd-membered di-BB-*n*.

give a more detailed illustration of the layered structure in the dimeric system, we have to understand how the end groups are being accommodated in the layers. Two types of layer structure can be considered as has been discussed by Date *et al.* [12]; one is the intercalated layer structure constructed by the random mixing of the spacers and end groups, and another the monolayer structure in which the mesogenic groups, spacers and end groups each constitute a microphase (see figure 25 of [12]). On this point, the observation that the spacings of the layer reflection are in the range of 18 Å to 22 Å (see the table and figure 4) is significant. These values obviously correspond to half the molecular length, signifying that each layer is constructed by each mesogenic group rather than by each molecule. In other words, the intercalated layer structure is formed as illustrated in figure 11. Such a structure requires the random mixing of alkyl end groups and methylene spacer groups, which may be reasonable since both groups are not siginificantly different in property and length [19]. As a result of this random mixing, the orientation correlation forced on the two mesogenic groups of a molecule can be maintained even for mesogenic groups between molecules. This seems the main reason why the odd–even effects for the structure and properties of the smectic phase of the BB-*n* polyesters could be completely reproduced in the dimeric di-BB-*n*.

Finally, we would like to comment on the S_{C_2} phase commonly observed for the odd-membered BB-*n* and di-BB-*n*. According to the classification of liquid crystals so far proposed [9], this phase can be sited as a distinct, new smectic phase. On this point, it should be mentioned that recently two smectic phases with similar structure have been reported by Galerne and Lieber [20, 21] and Fukuda *et al.* [22]. One is called the S_O phase observed in chiral 1-(methyl)-heptyl-tere-phthalidene-bis-amino cinnamate (MHTAC), and another the S_{C_A} phase in chiral 4-(1-methyl-heptyloxycarbonyl) phenyl 4′-carboxylate (MHPOBC). Both have been clarified to be chiral phases and also have antiferroelectric properties. The latter can be expected from the D_2 symmetry of the molecular packing structure [4, 23]. We believe that the present S_{C_2} phase may be classified into the same type as the smectic O and C_A phases. However, if this is the case, another significant reason, in addition to that proposed here, must be presented for such a curious formation of the smectic C_2 structure since in MHTAC and MHPOBC it is unlikely that alternate tilting of the mesogenic groups results from molecular conformational constraints. This point is currently being examined.

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