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Thermotropic liquid crystals in main chain polyesters having a mesogenic 4,4′-biphenyldicarboxylate unit. 9. Chain folding in solid polyesters crystallized from smectic A

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The lamellar structure with chain foldings is formed from the main chain polyesters crystallized from the SmA phase. The lamellar spacing increases with a decrease in crystallization temperature. This trend is contrary to that observed in conventional polymers, and is explainable if the chain foldings exist at a thermodynamic equilibrium as an entropy effect in the preceding SmA phase.

The introduction of flexible methylene spacers between rigid aromatic units into a polymer backbone is a proven method for obtaining liquid crystalline polymers (LCPs), and has generated much interest in recent years because of the challenge of understanding the polymeric effects on liquid crystal structure and properties.

In this series of studies [1–6], we have investigated the following main chain LC polyesters designated as BB-n
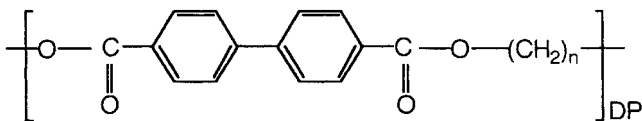
where n is the number of carbon atoms in the methylene spacer. These BB-n polyesters with $n = 3$–9 can form smectic mesophases. In BB-n with an even n, a smectic A (SmA) phase is formed with both the axes of the polymer chain and biphenyl mesogen lying perpendicular to the layers. In contrast, the smectic structure of BB-n with an odd n was identified as a smectic C_A phase, in which the tilt direction of the mesogenic group is the same in every second layer but opposite between neighbouring layers [1, 2, 5]. This odd–even alternation of the smectic structures results from the conformational constraint in which the polymethylene spacer, assuming a more extended conformation, forces the neighbouring mesogens to arrange with characteristic angular displacement that depends on the odd–even parity of n. Thus, we can picture that the polymer takes up the extended con-

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figuration at least in the local space of the smectic LC field.

In a previous paper [7], we reported the solid state morphology of the BB-6 polyester examined by the small angle X-ray scattering (SAXS) method. The BB-6 polyester forms isotropic, SmA and crystal phases in order of decreasing temperature, thereby its crystallization takes place from the SmA phase. SAXS for the crystalline specimens prepared by cooling the smectic melt shows well-defined reflection maxima which are attributable to a stacked lamellar structure [8]. The lamellar spacings are centred around 250 Å so that an appreciable number of chain foldings are included in a chain. Since we can hardly consider that the chain folding takes place on the crystallization from the SmA phase, we suggested that it already exists in the smectic field. Thus, the study has generated much interest because of the challenge of understanding the polymer configuration on a liquid crystalline field.

In this work, we extended our study of the crystalline state morphology for four BB-n polyesters, namely, BB-6, BB-8, BB-10 and BB-12, and found that in BB-6 and BB-8 forming the SmA phase, the crystallization temperature decreased with an increase in the cooling rate but the lamellar spacing increased. This trend in the lamellar spacing is opposite to that observed for the BB-10 and BB-12 polyesters which crystallize from the isotropic liquid as for conventional polymers. Some explanation for this trend will be given with a relation to the chain configuration in the preceding SmA phase.

Figure 1 shows the DSC curves of the BB-n polyesters

SmA phase and the isotropization of the SmA phase, respectively. For BB-8, only one peak is observed on heating, which corresponds to the crystal to isotropic liquid transition. On cooling, two peaks appear and hence a monotropic SmA phase is formed between the two. In BB-6 and BB-8, thus, the crystallization takes place from the SmA phase. On the other hand, BB-10 and BB-12 show only one peak both on heating and cooling; they cannot form a mesophase because of the longer flexible spacer. Thus, the crystallization of BB-10 and BB-12 occurs directly from the isotropic liquid as in conventional polymers. The thermodynamic data as well as the inherent viscosities are listed in the table.

The crystalline BB-*n* specimens were prepared by cooling the preceding phase at various rates in the DSC sample pan. In an effort to prevent a thermal prehistory, all the specimens were heated to the isotropic melt before measurement. After holding the samples in the preceding phase for 10 min (the SmA phase for BB-6 and BB-8 and the isotropic phase for BB-10 and BB-12), the crystallization process, over various rates from 1·25 to 40°C min^{-1}, was monitored by DSC to determine the crystallization temperature, T_c, and the enthalpy, ΔH_c from the exothermic crystallization peak. Here, the peak temperature was regarded as T_c since the exothermic peak was appreciably sharp. After the whole peak was observed, the specimens were quenched to room temperature and removed from the DSC sample pan for SAXS measurements.

The SAXS pattern of all the specimens (using a Rigaku–Denki RU-200) include clear reflection maxima with a spacing (L) within a range of 200–300 Å, showing that a long period exists in the crystals. For BB-6, the long period was attributed to the stacked lamellar
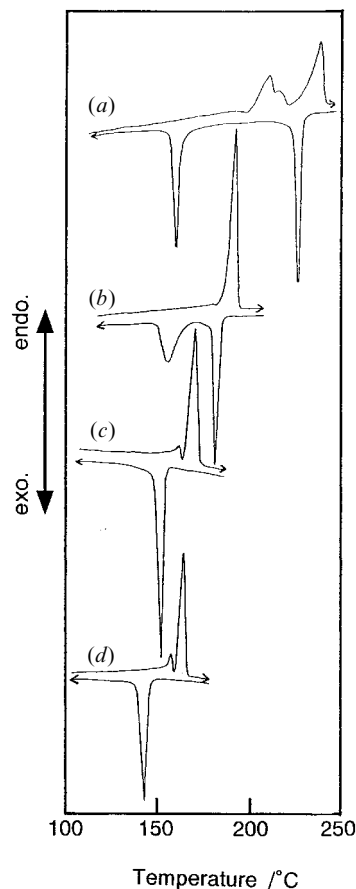

Figure 1.   DSC thermograms of (*a*) BB-6-IV, (*b*) BB-8, (*c*) BB-10 and (*d*) BB-12 measured at a scanning rate of 10°C min^{-1}.

which were observed using a Perkin–Elmer DSC II. BB-6 exhibits two enantiotropic transitions at T_m and T_i which were assigned to the crystal melting to the

Table 1.   Characterization of the BB-*n* polyesters.

Sample	η_{inh}/dL g^{-1}	Calorimetric data[a]						
		Transition temperature				Transition enthalpies		
		Heating		Cooling				
		T_m/°C	T_i/°C	T_c/°C	T_i/°C	ΔH_c/kcal mol^{-1}	ΔH_i/kcal mol^{-1}	Long spacing[b], L/Å
BB-6-I	0·26	210	231	187	218	3·12	1·99	225
BB-6-II	0·34	213	238	167	228	2·09	2·31	244
BB-6-III	0·40	216	239	166	227	2·09	1·97	251
BB-6-IV	0·49	214	240	165	229	1·90	2·01	247
BB-6-V	0·67	220	241	161	227	1·84	2·13	267
BB-6-VI	0·92	210	239	155	224	1·96	2·15	294
BB-8	0·70	193		153	180	1·62	2·27	273
BB-10	0·84	171		151		3·88		251
BB-12	1·05	164		141		4·71		225

[a] Based on DSC data measured at a scanning rate of 10°C min^{-1}.
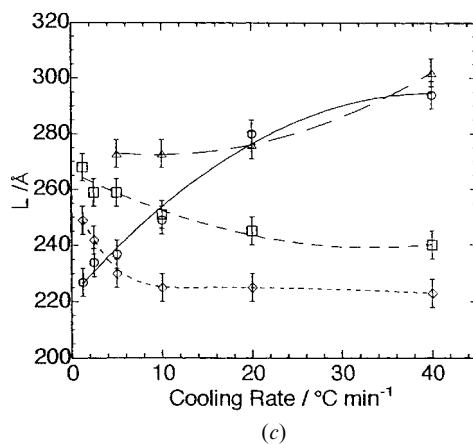[b] Determined for the solid sample prepared by cooling the preceding phase at a rate of 10°C min^{-1}.
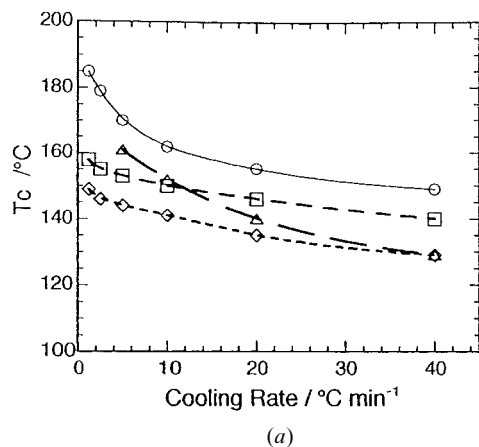
(a)
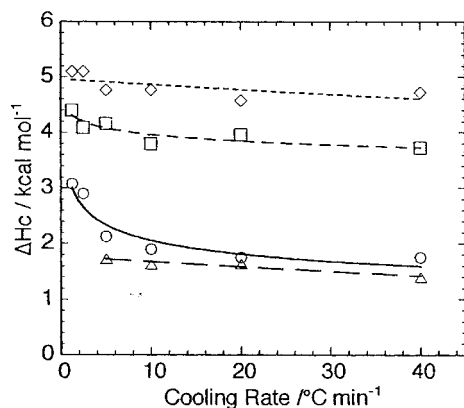
(b)

(c)

Figure 2. (a) Crystallization temperature (T_c), (b) crystallization enthalpy (ΔH_c) and (c) lamellar spacing (L) as a function of the cooling rate observed for BB-6-IV (circle), BB-8 (triangle), BB-10 (square) and BB-12 (lozenge). The data points of BB-8 measured at cooling rates of 1·25 and 2·5°C min^{-1} are omitted because of significant overlapping of the two peaks due to the isotropic to SmA and SmA to crystal transitions.
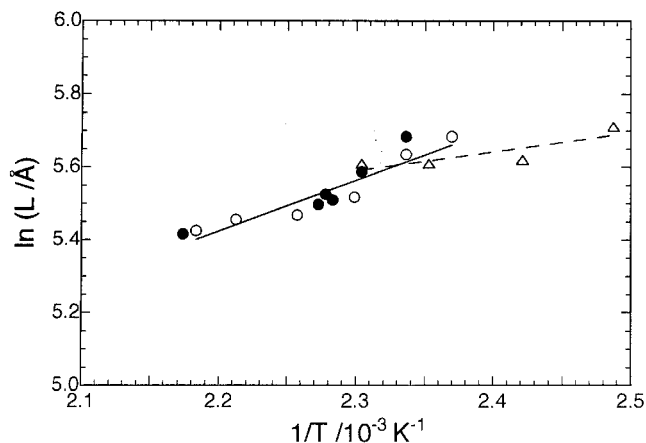

Figure 3. Plots of logarithmic lamellar spacing against the reciprocal of the crystallization temperature (T_c) for BB-6-V (circles) and BB-8 (triangles). The data points given by the open symbols are those observed in figure 2. Also included are the data points given by closed symbols which were collected for the BB-6 polyesters with different molecular weights in a previous study [7].

structure with chain foldings [7, 8]. Hence it is reasonable to assume that the other BB-*n* polyesters with longer methylene spacers could accommodate chain foldings and form the stacked lamellar structure with a lamellar spacing, L.

Figure 2 shows the dependence of (*a*) T_c, (*b*) ΔH_c and (*c*) L, on the cooling rate. As shown in figure 2(*a*), T_c decreases with an increase in the cooling rate for all the specimens owing to supercooling. A much smaller decrease is also observed in the ΔH_c values (see figure 2(*b*)), suggesting that the degree of crystallinity is not much altered from sample to sample. On the other hand, the variation of L is great between the samples crystallized from the isotropic liquid and those from a smectic phase (see figure 2(*c*)). For BB-10 and BB-12 crystallized from the isotropic melt, the lamellar spacing decreases with an increase in the cooling rate, namely, with a decrease of T_c, which can be understood from the kinetical criteria as considered in conventional polymers [9]. On the other hand, the lamellar spacing increases with an increase in the cooling rate for BB-6 and BB-8 crystallized from the SmA phase. This contrary dependence shows that the chain foldings result from a completely different origin from conventional polymers.

The SmA phase has long range orientational order due to the extended configuration of polymer molecules. Further, it has a one-dimensional positional order with the layer spacing nearly equal to the repeat length of a fully extended polymer so that a significant migration of the molecules and significant change of the molecular configuration are not required on crystallization from the SmA phase [7]. We thus speculate that the chain foldings observed in the crystalline phase are not

newly formed on crystallization but already exist in the preceding SmA phase. If this is the case, fold length (the distance between consecutive chain foldings) in the crystalline phase should correspond qualitatively to that in the SmA phase at the temperature just above T_c, and the unusual dependence of the lamellar size on T_c in BB-6 and BB-8 crystals can be interpreted according to the theoretical prediction on the polymer chain configuration in the liquid crystalline (LC) field.

Polymer configuration in a LC field was initially debated theoretically by de Gennes [10]. The chain folding is considered to arise as a result of the counterbalance between its energy cost and entropy gain. In other words, to produce the orientational and positional order in a LC phase, the obvious configuration for a polymer molecule to assume in order to minimize its energy is for it to lie entirely along the director, but a semiflexible long chain may recover some entropy loss due to the ordering of the mesogenic units by forming hairpin folding where the chain executes a counter reversal (180°) with respect to the director. Such an entropy effect leads to the prediction that the fold length increases with decreasing temperature and hence that the lamellar thickness in the resulting crystal increases with decreasing crystallization temperature. The present result corresponds to this prediction.

Along the line of the chain folding (hairpin) theory, Warner and coworkers [11, 12] have developed statics and dynamics of chain foldings in worm-like chains and given the simple theory in which the fold length is proportional to $\exp(U_h/k_B T)$, where $U_h = 2\sqrt{3aS\varepsilon}$ is the hairpin energy; S, the order parameter of the LC field, ε, the elastic bend constant, and a, the LC field coupling constant. To clarify this proportionality, the logarithmic lamellar spacings are plotted against the reciprocal of absolute temperature in figure 3 for BB-6 and BB-8. A linear relationship between the two can be seen as expected from the above equation. Here, it is reasonable that the slope of the line of BB-6 is larger than that of BB-8 since it reflects the chain rigidity estimated by ε in the above equation. The hairpin theory for the preceding LC phase thus explains the variation of lamellar size in BB-6 and BB-8 crystals.

We reconsidered the effect of molecular weight on the lamellar size for BB-6 reported in a previous paper [7]. We used here six specimens of BB-6 with different molecular weights, BB-6-I to BB-6-VI, which were prepared and characterized in the previous paper. They are listed in the table with the inherent viscosity and the thermodynamic data. The lamellar spacings listed in

the ninth column of the table were determined for the specimen prepared by cooling the SmA melt at a constant rate of 10°C min^{-1}. The data are plotted in figure 3 with closed circles, showing the linear relationship identical with that found in this work. It is hence reasonable to assert that the lamellar spacing depends on the crystallization temperature rather than the molecular weight.

In conclusion, BB-6, BB-8, BB-10 and BB-12 polyesters prepared by cooling the preceding phase at various rates exhibit well-defined SAXS maxima showing crystals of the lamellar type. The variation in lamellar size with the cooling rate depends strongly on the preceding phase. In BB-10 and BB-12 which crystallizes from the isotropic liquid as in conventional polymers, longer L values were observed for samples which were cooled at a slower rate and hence crystallized at a higher temperature. In contrast, crystals of BB-6 and BB-8 which were prepared from the SmA phase exhibit the unusual trend where larger values of L were observed for samples crystallized at a lower temperature. The identical dependence of the lamellar spacing on the crystallization temperature was found in the data collected for the BB-6 polyesters with different molecular weights in a previous study [7]. At this stage, this contrary trend can be explained by the hairpin theory based on which the chain folding exists at thermodynamic equilibrium as an entropy effect in the preceding SmA phase.

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