# Inclusion of Chain Ends in Long Period Lamellae of Main-Chain Polyester Smectic Liquid Crystals

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1 Introduction

The degree of polymerization (DP) of liquid crystal polymers (LCPs) affects liquid crystal (LC) temperature range especially in oligomeric range. Even if a monomer does not exhibit LC phase, the polymer can exhibit LC phase to show crystal-to-LC and LC-to-isotropic liquid transitions.[1–3] While both transition temperature increases with DP, the increment of LC isotropization temperature (T_i) is steeper than that of crystal melting temperature (T_m) or the glass transition temperature (T_g) and the LC temperature region enlarges with DP and the transition temperatures and the LC temperature range become constant when DP is larger than 10. A monotropic LCP can alter to enantiotropic one with increasing DP.[4] These DP dependences of LC transition behaviors have been understood thermodynamically by depicting temperature dependence of the free energies of the three phases for different DP with assuming that the entropies of isotropic liquid and LC phases decrease asymptotically with DP.[5]

In this study we examine the LC phase transition behaviors for a series of main-chain LC PB-10 polyester with different DPs. The PB-10 polyester consisting of 4,4′-biphenol and 1,10-dodecanoic acid forms crystal, smectic I (SmI) LC, and isotropic liquid phases in order of increasing temperature.[6] The morphological feature of the PB-10 SmI LC is 40 nm thick lamellae stacking at a spacing of 47 nm along the chain axis and being separated by isotropic liquid. The isotropization behavior of the lamellar LC should be influenced by lamellar thickness like as the melting of lamellar crystal polymers.[7] Here we investigated the correspondence of the lamellar morphology with the phase transitions for three PB-10 polyesters with different DPs. While the lamellar thickness was hardly dependent on DP, T_i decreased by 12 °C with decreasing DP from 50 to 12. The chain contour length of PB-10 polyester with DP = 12 was 1.5 times smaller than the lamella thickness. Such DP dependence of T_i is attributed to the inclusion of chain ends into the lamellar smectic LC.
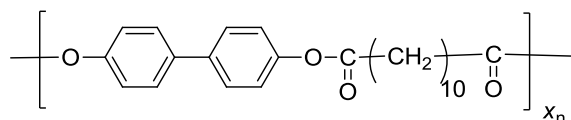
2 Experiment

Materials: Three PB-10 polyesters with different molecular weights were synthesized by melt condensation of 4,4′-biphenol diacetate and 1,10-dodecanoic acid. The melt condensation was followed by solid state polymerization for preparation of the highest molecular weight sample.[6] The number-average molecular weight (M_n) and polydispersity index (PDI) of the polymers were estimated by gel permeation chromatography (GPC) using universal calibration and listed in Table 1. The polymers are identified as PB-10-x_n, where x_n is the number average degree of polymerization.

Table 1: Characterization of PB-10 Polyesters.

	$M_n{}^a$ /g mol^{-1}	PDI	$T_i{}^b$ /°C $\Delta H_i{}^b$ /kJ mol^{-1}	L^c /nm	$\Delta H_i/\Delta H_i°$
PB-10-12	4,500	1.7	246 12.5	27	0.51
PB-10-23	8,600	1.8	253 19.7	52	0.80
PB-10-50	18,900	5.9	258 22.7	115	0.92

[a]determined by GPC. [b]determined by DSC. [c]chain contour length calculated from x_n and the lattice constant $c = 2.31$ nm.

Measurements: Differential scanning calorimetry (DSC) was performed using a PerkinElmer DSC7 calorimeter under a flow of dry nitrogen. The synchrotron radiation (SR)-SAXS measurement was performed at a BL-10C beamline in Photon Factory, Tsukuba, Japan. The scattering intensity was corrected by transmission and subtraction of background scattering and plotted against the scattering vector $q = 4\pi \sin \theta/\lambda$.

3 Results and Discussion

PB-10 polyesters form crystal, smectic I (SmI), isotropic liquid phases in order of increasing temperature. The temperature on the isotropization of SmI LC (T_i) and the corresponding enthalpy change (ΔH_i) were measured by DSC at heating rate of 10 °C min^{-1} and listed in the fifth column of Table 1. Before the measurement, the sample was cooled from the isotropic phase to ambient temperature at a rate of 10 °C min^{-1} to erase any prior history. With increasing x_n, T_i and ΔH_i increase remarkably.

The SmI phase has been identified by the WAXD pattern of a PB-10-50 fiber which includes the reflections attributed to the monoclinic unit cell with $a = 0.64$ nm, $b = 0.90$ nm, $c = 2.31$ nm, and $\beta = 126°$ with the c-axis parallel to the fiber axis.[6] In the C-centered monoclinic unit cells, mesogenic moieties are packed with their long axis parallel to the c-axis. Two mesogens neighboring along the c-axis at a spacing of 2.31 nm are connected by an alkyl spacer assuming most extended configuration. Thus most extended polymer chains lie along the fiber

axis. On the other hand, the same fiber exhibited SAXS pattern including several reflections which are attributed lamellae stacking along the fiber axis at a spacing of 47 nm. By combining the WAXD pattern with SAXS one, we can depict polymer chains are parallel to the fiber axis and form lamellae stacking along the fiber axis at a spacing of 47 nm and SmI structures with the smectic layers stacking in the direction tilted by 36° from the fiber axis at a spacing of 1.87 nm.
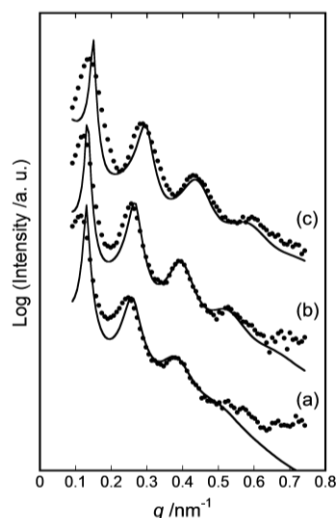

Fig. 1: SR-SAXS intensity profile (dots) of (a) PB-10-12, (b) PB-10-23, and (c) PB-10-50. The samples were initially prepared by cooling the isotropic melt at a rate of 10 °C min^{-1} and heated to a LC temperature of 210 °C. The solid curve shows the calculated intensity based on the paracrystal theory.

The lamella structure as well as the SmI structure is common in PB-10 polyesters with different molecular weights. Figure 1 shows the SAXS profile measured for PB-10 polyesters at 220 °C. The sample was cooled from the isotropic liquid phase to room temperature at a rate of 10 °C min^{-1}, and then the temperature was jumped to 220 °C just moments before the X-ray irradiation. To prevent the morphology change such as lamellar thickening, the SAXS data were obtained by 5 min synchrotron radiation X-ray illumination. These profiles include three or four maxima. The ratios of the scattering vectors (q) at the peaks are 1, 2, 3, and 4, indicating the existence of lamellae staking. These lamellae consist of the smectic LC and isotropic liquid phases.[8] The thickness of each phase lamella can be estimated by comparing the observed intensity with the scattering profile calculated numerically using the paracrystal theory.[9,10] The solid curves in Figure 1 represent the best-fitted calculated profiles. While the third-order peaks are well-fitted to the calculated profile, the first- and second-order peaks are deviated from the calculated profiles of PB-10-12 and PB-10-23, suggesting that the correlation length of lamellae decreases with decrease in x_n. The thicknesses of the LC and isotropic phase lamellae (d_{LC} and d_{am}) and the standard deviations of each lamellar

thickness (σ_{LC} and σ_{am}) are listed in Table 2. Here d_{LC} is assumed to be larger than d_{am} because a sufficient number of smectic layers stack within each lamella to produce the smectic layer reflection in the WAXS pattern.

These structural parameters, however, are not consistent with T_i of SmI LC. T_i of the lamellar SmI LC should be depend on d_{LC} as expected by the Gibbs-Thomson relationship and such a trend has been observed for the homologue PB-14 polyester.[8] Because d_{LC} of these three PB-10 polyesters are almost constant of 40 nm, T_i is expected to be almost constant according to the Gibbs-Thomson relationship. However, T_i increases with x_n and T_i of PB-10-50 becomes 12 °C higher than PB-10-12. Thus T_i of lamellar SmI LC cannot be explained by the lamellar structural parameters.

Table 2: Structural Parameters Determined by the Simulation Method.

	d_0 /nm	d_{LC} /nm	d_{am} /nm	σ_{LC} /nm	σ_{am} /nm	d_{LC}/d_0
PB-10-12	48.0	40.0	8.0	5.0	2.0	0.83
PB-10-23	46.9	40.2	6.7	3.8	2.3	0.86
PB-10-50	42.0	37.0	5.0	3.5	2.3	0.88

The inconsistency between the variations of T_i and d_{LC} can be attributed to incorporation of chain ends in LC lamellae. We can sketch the accommodation of polymer chain in LC lamella by comparing d_{LC} with the average contour length of polymer chain, L calculated from x_n by the equation of L (nm) = 2.31x_n, where 2.31 is the repeat length along the chain axis (c-axis) in the SmI phase in unit of nm. L of PB-10-50 is 115 nm, which is three times larger than d_{LC}. The polymer chains assume most stretched conformation in the lamella inside and fold and assemble chain ends at the lamella boundaries. In contrast, L of PB-10-12 is 27 nm, 1.5 times smaller than d_{LC} = 40 nm. When the one side of end is located at a lamella boundary, the other side of end should be in the lamella. Thus many chain ends can be included in LC lamellae in PB-10-12. The probability of finding chain ends in LC lamellae decreases with increasing x_n.

Assuming such inclusion of chain ends in LC lamellae, the dependence of T_i on x_n can be explained. In Figure 2, the reciprocal of T_i is plotted against the reciprocal of x_n. The data are consistent with a straight line as shown in Figure 2. Indeed, such a relationship is similar to that between the melting point of polymer crystals and DP where the end groups of polymer chains are assumed to be included in the crystal lattice and regarded as a foreign component. Thus T_i can be described by a following equation in the same way as the melting point of polymer crystals:[11,12]

$$\frac{1}{T_i} = \frac{1}{T_i^\circ} + \frac{R}{\Delta H_i} \frac{1}{x_n} \qquad (1)$$

where R is gas constant; T_i°, T_i of the SmI LC formed by infinite length polymer chains, and ΔH_i°, the enthalpy of fusion per structural unit. The data is extrapolated to T_i° of 535 K (262 °C) and the slope of the line yields ΔH_i° = 24.7 kJ mol^{-1}. These estimated values seem reasonable

because they are close to the values observed for PB-10-50 ($T_i = 258$ °C, $\Delta H_i = 22.7$ kJ mol^{-1}).
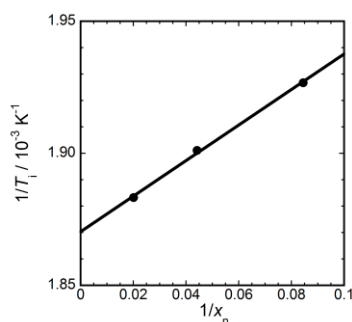

Fig 2: Reciprocal isotropization temperature of PB-10 polyester as a function of the reciprocal of the number average number of repeat units in PB-10 polyesters.

Such an inclusion of polymer chain ends into LC lamellae decreases the LC fraction even in the LC lamellae. The LC fraction can be estimated by the following two ways. First is the volume fraction f_v of LC lamellae in sample which is equal to the ratio of d_{LC} to d_0. The other is the weight fraction f_w which can be determined as $f_w = \Delta H_i/\Delta H_i°$. The values of f_v and f_w should be comparable to each other when the LC and amorphous phases are completely segregated into each lamella. Such a complete segregation may be achieved in PB-10-23 and PB-10-50 which show certain agreement between the values of f_v and f_w. On the other hand, PB-10-12 exhibited f_w whose value is significantly lower than the value of f_v, suggesting that the amorphous phase is not accommodated only in the amorphous lamellae but in the LC lamellae.

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