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Polarized Light Scattering and Synchrotron Radiation Wide-Angle X-ray Diffraction Studies on Smectic Liquid Crystal Formation of Main-Chain Polyester

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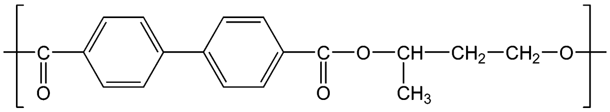
Recent works on polymer crystallization have given considerable attention to the possibility that the crystal phase in the final semicrystalline state could be preceded by transient liquid crystal phases.[1−18] At this aspect, it is interesting to investigate the smectic liquid crystallization process of polymer in which the developments of positional order as well as the orientational one are required. However, the liquid crystallization from the isotropic melt is hardly followed with the conventional scattering techniques which have been applied for the polymer crystallization because it generally takes place close to equilibrium; i.e., it proceeds completely and rapidly even at small supercooling. Recently, we have found that the following main-chain smectic liquid crystalline BB-3(1-Me) polyester shows strong cooling rate dependence of the liquid crystallization temperature.[19]



This polymer forms the smectic CA (S_{CA}) liquid crystal. The S_{CA} phase is formed directly from the isotropic liquid and solidifies without crystallization even on very slow cooling at a rate less than 1 °C min^{-1}. Of interest is that neither liquid crystallization nor crystallization takes place on cooling as rapidly as at a rate of 100 °C min^{-1}. Thus, the smectic liquid crystal formation of the BB-3(1-Me) from the isotropic liquid phase is so slow that the corresponding developments in molecular orientational order and in the smectic layer order are able to be followed by the conventional methods of polarized light scattering (LS) and synchrotron wide-angle X-ray diffraction (SR-WAXD) methods. The results represent the interesting phenomenon that the nematic orientational order develops prior to the formation of smectic layer structure.

The BB-3(1-Me) polyester used for this study has a number-averaged molecular weight, M_w, of 9800 and a polydispersity of $M_w/M_n = 1.83$. The glass transition point and the isotropization temperature of the S_{CA} phase were determined to be 81 °C and 159 °C, respectively, by a Perkin-Elmer Pyris-1 DSC on heating at a scanning rate of 10 °C min^{-1}.

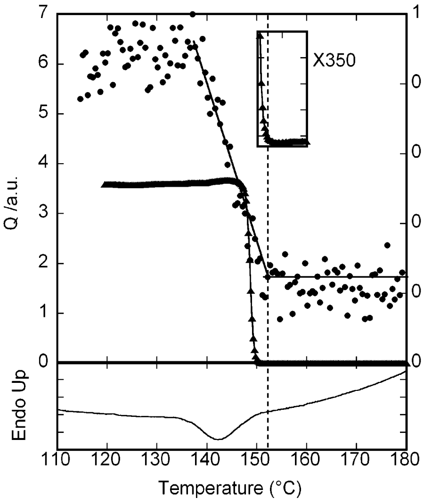


Figure 1. Intensity of the smectic layer reflection appearing at $2\theta = 6.3°$ in the SR-WAXD patterns (I_{WAXD}) (circles), the integrated intensity of the polarized light scattering (Q) (triangles) (in the upper part), and DSC thermogram (in the lower part) measured on cooling from the isotropic liquid phase at 0.5 °C min^{-1}.

In LS measurements, the intensity collected under the H_V condition can be analyzed to reveal information on particles with orientational order (birefringence) or orientation fluctuations. The two-dimensional light scattering patterns were registered by a CCD camera equipped in an Otsuka Electronics DYNA-3000. To discuss the optical anisotropy development during the liquid crystallization, we use the relative invariant of the light scattering, $Q(t)$, defined by

$$Q(t) = \int_0^\infty q^2 I(q,t)\, dq \approx \int_{q_1}^{q_2} q^2 I(q,t)\, dq \qquad (1)$$

$Q(t)$ was obtained by integrating the scattering intensity between the experimentally accessible limits where q_1 and q_2 are 0.54 μm^{-1} and 3.67 μm^{-1}, respectively. The integrated intensity of the scattering, Q, is proportional to the volume fraction of anisotropic domain having dimensions comparable with the wavelength of light (633 nm).

SR-WAXD measurements were carried out at the 4C2 Beamline in Pohang Light Source, Korea. A Princeton two-dimensional CCD camera was used to detect the WAXD signals. The intensity of the smectic layer reflection appearing at $2\theta = 6.3°$ (I_{WAXD}) was used to discuss the development of the layer structure. I_{WAXD} was determined simply by measuring the peak intensity after subtracting the scattering image for the isotropic melt. In the LS and SR-WAXD measurements, the sample temperature was regulated by a Linkam 10039 hot stage with an accuracy of ±0.1 °C.

Figure 1 shows Q, I_{WAXD} (in the upper part), and the DSC thermogram (in the lower part) measured for the BB-3(1-Me) on cooling from the isotropic liquid phase at a rate of 0.5 °C min^{-1}. Two interesting features can be obtained here. First, the increases in Q, I_{WAXD}, and DSC exothermic signal show the same onset temperature of 152 °C. Second, the increase of Q on cooling completes within a few degrees from the onset temperature while the increases in I_{WAXD} and DSC exothermic peak are extended in a relatively wide temperature range from 152 to 138 °C. The latter suggests that the nematic ordering may develop preceding to the smectic layer ordering.

To clarify this characteristic feature of smectic liquid crystallization, we examine the isothermal liquid crystallization. Parts a and b of Figure 2 show developments of Q and I_{WAXD} during

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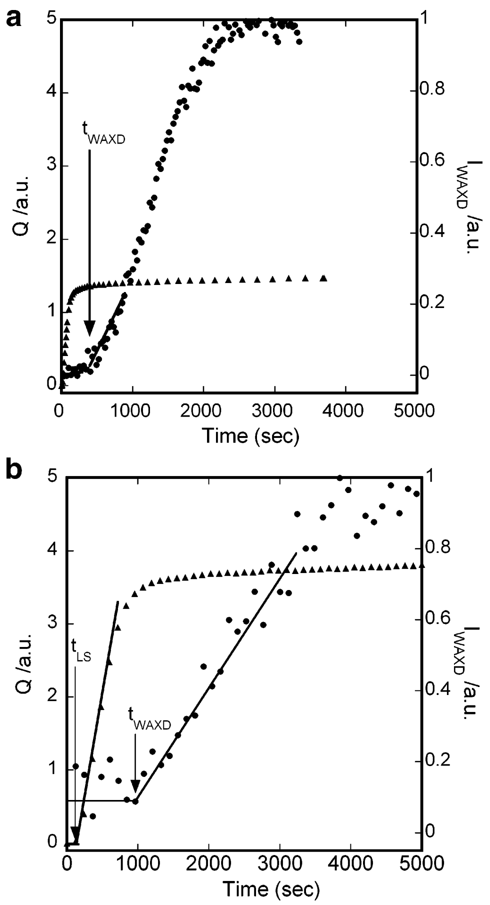

Figure 2. Intensity of the smectic layer reflection appearing at $2\theta = 6.3°$ in the SR-WAXD patterns (I_{WAXD}) (circles) and the integrated intensity of the polarized light scattering (Q) (triangles) measured during isothermal smectic liquid crystal formation from the isotropic liquid phase at T_{LC} of (a) 145 and (b) 150 °C.

the isothermal liquid crystal formation at 145 and 150 °C, respectively. For this isothermal measurement, the sample was first heated to isotropic liquid phase at 180 °C, which was 20 °C higher than the isotropization temperature, and kept for 3 min to ensure the complete isotropization of the smectic phase. Then, it was cooled rapidly to the predetermined temperature, T_{LC}, and the liquid crystallization process was followed. The cooling rate was initially 30 °C min^{-1} and then reduced to 10 °C min^{-1} at a temperature 5 °C higher than the predetermined temperature (T_{LC}) to prevent overcooling the sample. One can see the obvious difference between the two onset times, t_{WAXD} and t_{LS}, determined by the WAXD and LS methods, which is beyond the limits of systematic experimental error. Q first increases, and later I_{WAXD} starts to increase. The differences measured at 145 and 150 °C are 400 and 900 s, respectively. The two onset times, t_{WAXD} and t_{LS}, are plotted logarithmically as a function of T_{LC} in Figure 3. t_{LS} at T_{LC} of 140 °C and below are not plotted in the figure because the light scattering intensity had grown before staring the measurement at the T_{LC}. At temperatures lower than 152 °C where t_{WAXD} could be determined, we know that domains with detectable mean-squared anisotropy by light scattering are formed before the layer structure develops to be detected by SR-WAXD. In other words, the isotropic liquid transforms to a transient nematic phase before the S_{CA} layer formation. With increasing of T_{LC}, t_{LS} increases more rapidly than t_{WAXD}. This trend suggests that the smectic layer structure may develop simultaneously with the molecular orientation at T_{LC} near the isotropization temperature, T_i.

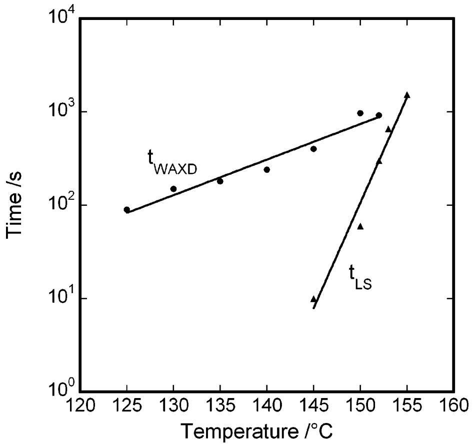

Figure 3. Comparison of the apparent onset time for WAXD (circle) and LS (triangle) at different liquid crystallization temperature, T_{LC}.

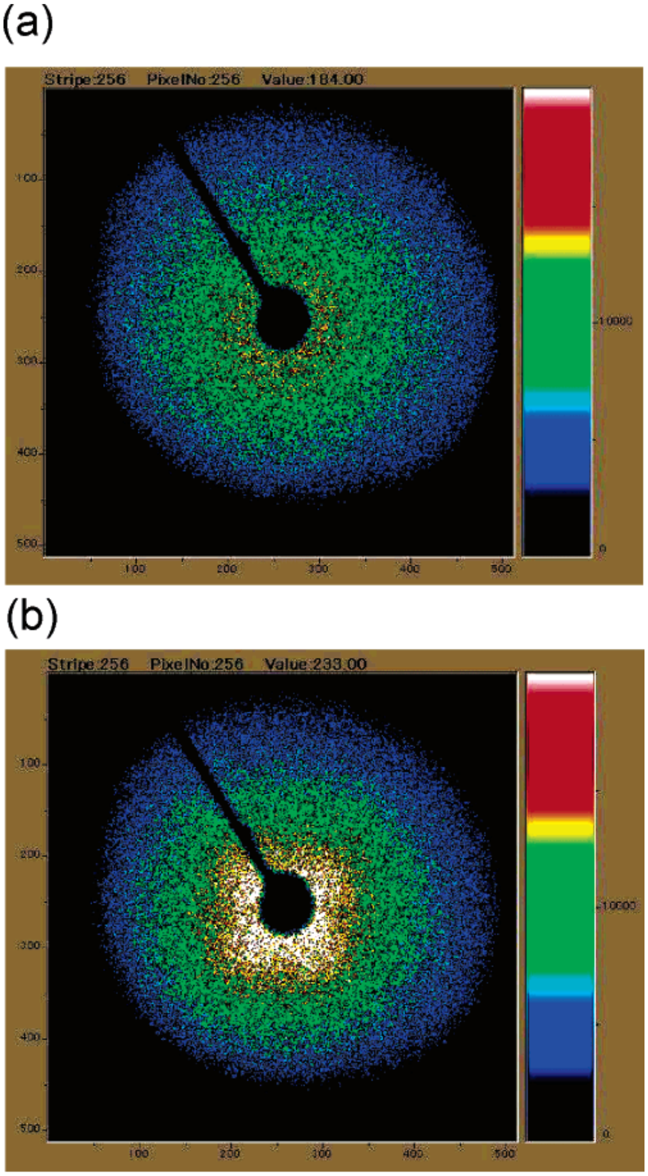

Figure 4. H_V light scattering patterns registered liquid crystallization at T_{LC} of (a) 150 and (b) 152 °C.

It is interesting to note here that the light scattering patterns are dependent on T_{LC}. As found in Figure 4a, the H_V light scattering patterns observed during the isothermal liquid crystallization at T_{LC} below 150 °C were completely isotropic so that the scattered intensity decreased monotonically with the scattered angle independent of an azimuthal direction. This feature indicates that the light scattering objects possess an essentially uniform chain orientation, in other words, resemble hedrites rather than spherulites.[20] On the other hand, with increasing T_{LC} to 152 °C and higher, the H_V patterns changed to the four-leaf-clover patterns characteristic of spherulites (see Figure 4b). These imply that the morphological development of transient nematic liquid crystal is different at the low-rate and high-rate process of liquid crystallization.

The appearance of the transient nematic phase is attributed to a kinetic delay in the smectic layer formation behind the molecular orientation. At large supercooling, strong instability of the isotropic phase is induced by excess excluded volume owing to random arrangement of mesogens. To reduce the excluded volume, this instability forces the mesogens to gain orientation correlation with each other, and simultaneously the polymer chain backbones are stretched and arranged parallel to each other. Thus, the transient nematic phase appears prior to the formation of the thermodynamically stable smectic phase which involves sliding or migration of the polymer chains to achieve the positional order of the mesogens along the chain axis.

In conclusion, the smectic liquid crystal formation in the BB-3(1-Me) polyester was successfully investigated by SR-WAXD and LS measurements. Developments in local anisotropy detected by LS and smectic layer order by SR-WAXD showed the same onset temperature on gradual cooling from the isotropic melt, showing that the smectic phase was formed directly from the isotropic liquid phase. On the other hand, during the isothermal liquid crystal formation from the isotropic liquid phase, the anisotropic domain development was detected prior to the onset of the smectic layer ordering. It indicates that the smectic liquid crystal evolves from the isotropic liquid phase through a transient nematic phase which is attributed to kinetic lag of the smectic layer formation behind the molecular orientation assisted by strong instability of isotropic phase at large supercooling.

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