SHORT COMMUNICATIONS

**A Dynamic Study of Crystallization of Poly(ϵ -caprolactone)
and Poly(ϵ -caprolactone)/Poly(vinyl chloride) Blend**

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The crystallization process of polymers has extensively been studied for last decade by the small angle X-ray scattering (SAXS) method.¹⁻⁵ In these studies, the long period, a repeating length of the alternate stacks of lamella and thin amorphous layer, was examined against crystallization time and temperature. Schultz² reported for a polyethylene (PE) sample that the SAXS curve at higher crystallization temperatures had a peak that increased in intensity with time at an almost invariable wave number, and the behavior of this SAXS curve was different from that at lower temperatures. Recently, use of a strong X-ray source with synchrotron radiation (SOR) made such a study possible to observe the initial stage of crystallization.⁶⁻⁸ Elsner *et al.*^{6,7} found in crystallization process of poly(ethylene terephthalate) (PET) that the long period decreased initially with crystallization time and reached a constant value. In the present study, the process of the crystallization of poly(ϵ -caprolactone) (PCL) and a blend of PCL with

poly(vinyl chloride) (PVC) was studied using the SAXS method with SOR. This blend is known to be compatible throughout the entire composition range.⁹

The PCL supplied from Science Polymer Products, Inc. was fractionated with a benzene/*n*-heptane system. The weight average molecular weight M_w and its ratio, M_w/M_n , to number-average molecular weight M_n determined by gel-permeation chromatography were 23,300 and 1.58, respectively. The melting temperature of PCL, T_m , is about 60°C. The PVC obtained from Aldrich Chemical Company, Inc. was fractionated with a tetrahydrofuran (THF)/water system. The values of M_w and M_w/M_n were 144,000 and 1.56, respectively. The blend with the weight fraction of PCL, $\phi_{PCL} = 0.9$, prepared by casting from THF solution, was used.

The X-ray measurements were carried out using a small angle X-ray equipment for solution (SAXES) with the synchrotron radiation set up at National Laboratory for

High Energy Physics, Japan. The wave length of the X-ray used for the experiment was 1.4881 Å. The scattering intensity was detected by a position sensitive proportional counter (PSPC) with 512 channels, and the distance between the sample and the plane of PSPC was 1,924 mm. The details of the instrumentation and the procedure of SAXES are described elsewhere.¹⁰ The temperature of the sample holder was controlled by circulating water of constant temperature. The temperature fluctuation of the sample was within $\pm 0.2^\circ\text{C}$ throughout the experiments. The temperature drop from the molten state (65°C) to the crystallization temperature T_c (30 – 45°C) was achieved within 60–100 sec. Since this cooling rate was rather slow, the experiment was possible only at rather high temperatures close to T_m , where crystallization did not start until the temperature of the sample reached T_c .

Figure 1 shows the time-resolved measurements of the scattering intensity corrected for Lorentz factor during the crystallization process of pure PCL at $T_c = 40.9^\circ\text{C}$. In a short time after the beginning of crystallization, a peak of the scattering intensity appears at a wave number $s \sim 0.060 \text{ nm}^{-1}$, which corresponds to the long period of 16.6 nm, and becomes higher with the crystallization time. Figure 2 shows the time dependence of the maximum intensity of the peak, I_m . After short induction time, I_m increases linearly with the crystallization time and reaches a constant value. The wave number of I_m , hence the long period, is nearly constant (16–19 nm) during crystallization. From Figure 2, the crystallization seems to be completed at time t^* where the growth of I_m terminates. For oriented polybutadiene⁵ (PB) and PET,⁷ similar behavior was reported by the analysis of the integrated intensity during crystallization; but at relatively low T_c , the long period decreased at the beginning of the crystallization and reached a constant value, where the decrease of the long period was attributed to the generation of a new lamella between lamellae⁵ or

Figure 1. Time-resolved scattering intensity corrected for Lorentz factor for pure PCL at $T_c = 40.9^\circ\text{C}$. Numerals in the figure represent the crystallization time.

Figure 2. The maximum intensity of the peak against crystallization time for pure PCL at $T_c = 40.9^\circ\text{C}$.

the rearrangement of lamellae,⁷ with the crystallization time. At higher T_c for PE, however, it was reported that the long period was nearly constant throughout the primary crystallization.² For PET it was also found⁷ that the change of the long period for the sample with lower molecular weight was smaller than that for the sample with higher molecular weight. Thus the behavior of the long period depends intimately on polymers and factors such as T_c and molecular weight. The crystallization temperatures in the present study are rather high and close to T_m and the molecular weight of PCL is comparatively low, compared to that under

Figure 3. t^* obtained in Figure 2 against T_c . ○, pure PCL; ●, blend with $\phi_{\text{PCL}} = 0.9$.

other experimental conditions. Figure 3 shows the temperature dependence of t^* for a pure PCL and a PCL/PVC blend. It is observed that t^* increases abruptly with the increase of T_c both for the pure PCL and the blend. This behavior is similar to that observed for the spherulite growth of pure crystalline polymers and polymer blends with an optical microscope.¹¹ The scattering behavior of the blend is similar to that of pure PCL except that the crystallization process continues for a longer time than that for pure PCL. The crystallization of a pure polymer is usually faster than that in the blend.¹²

From this study, it is understood that primary crystallization, the early stage of the crystallization, of polymers and polymer blends can be investigated by SAXS method with SOR. At present, the behavior of the spherulite growth under the same crystallization conditions is being studied by an opti-

cal microscope and a comparison between both results is now under way.

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