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SR-SAXS studies on morphology formation in a binary blend of crystalline-amorphous diblock copolymer and crystalline homopolymer. 2.

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Introduction

We have investigated the process of morphology formation in a binary blend of crystalline homopolymer and crystalline-amorphous diblock copolymer. Here, we quantitatively analyze the experimental results[1-3], and clarify the mechanism of morphology formation as a function of characteristic length of composition variation ξ induced by macroscopic phase separation and also crystallization temperature *Tc*.

Experimental Section

Samples We used poly(ε-caprolactone)-block-poly-butadiene (PCL-b-PB) as a block copolymer and poly(ε-caprolactone) (PCL) as a crystalline homopolymer.

SAXS measurements The SR-SAXS experiment was performed at beam line BL-10C. The accumulation time was 10 sec for each measurement. The background scattering and Lorentz factor were taken into account, and finally the relative intensity was obtained as a function of wave number s (= $(2/\lambda)\sin\theta$, 2θ: scattering angle). To evaluate the angular position and relative intensity of each scattering peak accurately, we used the Lorenz function for each scattering peak and the Debye-Bueche equation for the increasing intensity at lower s. The peak position (or spacing) and peak intensity were finally evaluated as a function of crystallization time *tc* at each ξ and *Tc*.

Results and Discussion

The spacing from the microdomain structure is gradually replaced with two kinds of spacing, one from the lamellar morphology formed in the crystallized PCL-*b*-PB region and the other from the crystallized PCL region, at the middle of *tc*. However, the *tc* dependence of the normalized intensity depends significantly on ξ and *Tc*. For example, the normalized intensity from two regions make one master curve at *Tc* = 35 °C while they deviate at *Tc* > 40 °C, indicating that the crystallization rates of PCL and PCL-*b*-PB are equivalent at *Tc* = 35 °C but they differ considerably at *Tc* > 40 °C.

The half-time of crystallization $t_{1/2}$, which is a measure of crystallization rate, can be evaluated from the *tc* dependence of each SAXS peak, and is plotted in Figs 1 and 2 against ξ and *Tc*. Fig 2 shows that when ξ is less than 500 nm the crystallization rate of PCL and PCL-*b*-PB regions is identical and intermediate between those of neat polymers, but the difference becomes significant when ξ goes beyond 500 nm and they approach to the crystallization rate of neat polymers. Fig. 3 shows that at *Tc* = 35 °C the values of $t_{1/2}$ for PCL-*b*-PB and PCL are identical but they deviate significantly with increasing *Tc*. In addition, $t_{1/2}$ for the quenched blend with a smaller ξ takes a middle position between those for PCL and PCL-*b*-PB in the phase-separated blend. These Figures clearly show that the combination of ξ and *Tc* drives the crystallization behavior of this blend.

References

[1] M. Akaba and S. Nojima *Polym. J.,* **37**, 464 (2005).
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[3] M. Akaba and S. Nojima *Polym. J.,* **38**, xxx (2006).

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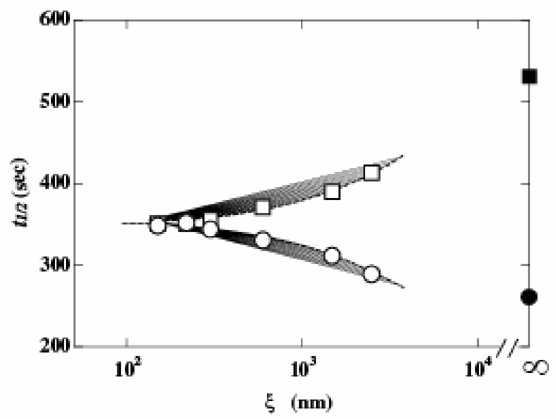

Fig. 1 Half-time of crystallization $t_{1/2}$ for PCL (○) and PCL-*b*-PB (□) regions plotted against ξ for the blend with ϕ_{PCL} = 0.6. The closed symbols stand for $t_{1/2}$ of neat PCL (●) and PCL-*b*-PB (■).

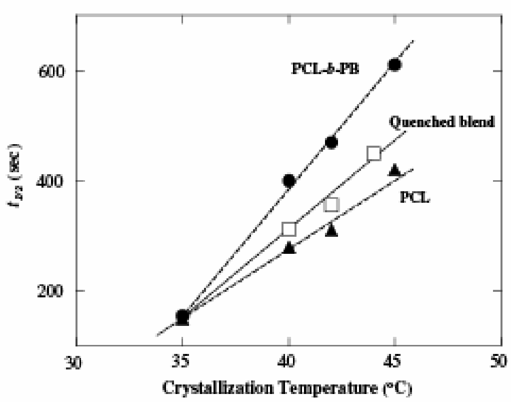

Fig. 2 *Tc* dependence of $t_{1/2}$ for PCL-*b*-PB (●) and PCL (▲) in the phase-separated blend with ξ = 2.5 µm. □ represents the result for the quenched blend, where $t_{1/2}$ is equivalent for PCL and PCL-*b*-PB.