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SR-SAXS studies on morphology formation in a binary blend of crystalline-amorphous diblock copolymer and crystalline homopolymer. 1.

Michiaki AKABA, Takayuki OHSUGI, and Shuichi NOJIMA*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering,
Tokyo Institute of Technology, H-125, 2-12-1 Ookayama, Meguro-ku Tokyo 152-8552, Japan

Introduction

We have previously investigated the morphology formation in a binary blend consisting of amorphous and crystalline homopolymers at various temperatures and compositions by using time-resolved small-angle X-ray scattering with synchrotron radiation (SR-SAXS)[1], where the morphology formation is driven by a combined effect of crystallization and phase separation. We found that two phases, *i.e.*, crystalline phase and amorphous phase, appeared in the system and the ratio of these phases did not change during the morphology formation. However, we did not get information from the amorphous phase because it provided no SAXS signal.

In this study[2], we use a crystalline-amorphous diblock copolymer instead of amorphous homopolymer. The crystalline-amorphous diblock copolymer yields characteristic structures before and after crystallization and therefore we can get information from this region on the process of morphology formation.

Experimental Section

Samples We used poly(ε-caprolactone)-*block*-poly-butadiene (PCL-*b*-PB) as a crystalline block copolymer and poly(ε-caprolactone) (PCL) as a crystalline homo-polymer (Table). The blend was prepared by a solvent-casting method using benzene as a common solvent.

SR-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).

Results and Discussion

Fig. 1 shows the typical time-resolved SR-SAXS curves for the blend (80 wt.%PCL) quenched from 120 °C into 40 °C. Immediately after quenching, we can observe the SAXS peak (A), which arises from the microdomain structure existing at 120 °C. This peak decreases in intensity with crystallization time tc, and simultaneously two peaks at higher (C) and lower (B) angles appear,

which come from the crystallized PCL and PCL-*b*-PB regions, respectively. In addition, we can observe a monotonically increasing scattering toward $s \to 0$ (D), which arises from the mosaic structure consisting of the crystallized two regions.

The tc dependence of normalized intensity, the peak intensity divided by the final intensity, is plotted in Fig. 2 for each SAXS peak. It is found that the crystallization in the PCL and PCL-*b*-PB regions proceeds in a same fashion because the normalized peak intensities make one master curve, though the crystallization rate of neat PCL is sufficiently faster than that of neat PCL-*b*-PB.

References

[1] S. Nojima *et al., Macromolecules*, **25**, 1922 (1992).
[2] M. Akaba and S. Nojima, *Polym. J.,* **37**, 464 (2005).
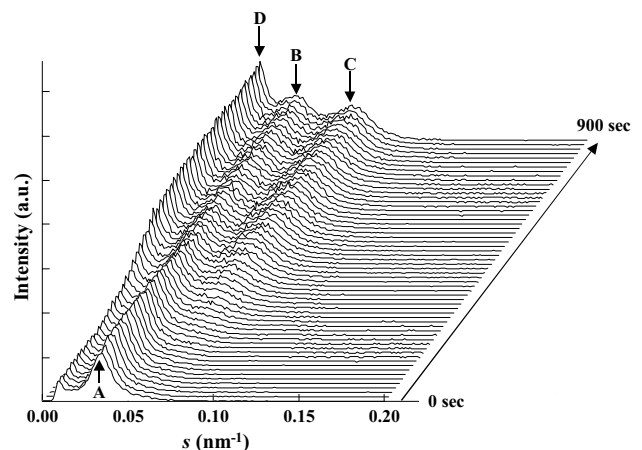* snojima@polymer.titech.ac.jp

Fig. 1 Time-resolved SR-SAXS curves during crystallization for the blend with ϕ_{PCL} = 0.8 after quenching from the microphase-separated melt into Tc = 40 °C.
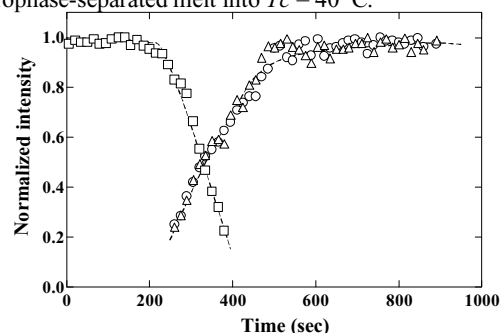
Table Molecular characteristics of the samples used in this study

Sample	Total Mn[a)]	Mw/Mn[b)]	PCL:PB[c)] (vol.%)	Ethyl Branch[c)] (mol%)	Tm[d)] (ºC)
PCL-*b*-PB	13,000	1.16	66:34	7	54
PCL	3,500	1.50	-	-	58

a) Determined by membraneosmometry. b) Determined by GPC. c) Determined by ¹H-NMR. d) Determined by DSC.

Fig. 2 Normalized intensities for the microdomain structure (□), crystallized PCL-*b*-PB region (○), and crystallized PCL region (△) plotted against tc for the blend with ϕ_{PCL} = 0.8 crystallized at 40 °C.