Materials Science

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Breakout and Templated Crystallizations from Microphase Separation of PCL-*b*-polybutadiene Block Copolymer

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Introduction

When semi crystalline block copolymer is crystallized, crystalline structures were categorized into three patterns; crystalline is confined in the microphase separated structure, breaks out microphase structure and changes to an alternative crystalline-amorphous lamellar structure, and is template of microphase separated structure. Some cases have been reported.[1] We reported the crystallized structure of poly(ε-caprolactone)-*b*-polybutadiene (PCL-b-PB) which has a hexagonally packed cylindrical morphology in the molten state.

Results and DIscussion

The characteristics of the block copolymer PCL-*b*-PB sample used here are listed in Table 1. The PCL-*b*-PB formed hexagonally packed cylindrical structure in melt state as revealed by small-angle X-ray scattering (SAXS). Figure 1 shows SAXS profiles which are crystallized at various temperatures except for the bottom. At higher crystallization temperature (T_C), SAXS profile shows the position of the first order reflection peak shifted toward lower q-range. The ratio of the second to the first order peaks is two at high T_C, indicating lamellar structure. The ratio of the first to second order peaks is 1.73 (~ $3^{1/2}$) at low T_C, which means that the melt structure (cylinder) was maintained although the peak was broaden after crystallization. Figure 2 shows the ratio of the second to the first peaks position and domain spacing as a function of T_C. The ratio and domain spacing were found to increase at around 280 K At lower than 270 K, the domain spacing was almost constant and slightly increased as compared with that in molten state. The value of the q_2/q_1 was c.a. 1.7 and the PCL was crystallized in the cylinder that was template of the molten state. At higher than 290 K, the value of the q_2/q_1 was close to two, indicating that its morphology changed from cylindrical to lamellar one (alternative crystalline-amorphous structure). The Flory-Huggins interaction parameter χ and matrix T_g were reported to be keys to determine whether the morphology is maintained after crystallization, or not. For example, if a matrix T_g is higher and lower that *T*c, the crystalline is normally confined and breaks the morphology in a molten state, respectively. If χ is large (strong segregation), a crystalline is confined. In our case, both of the confined (or templated) and breakout crystallization were observed in accordance with T_C.

Table 1: Characteristics of PCL-b-PB

	M_w	M_w/M_n	ϕ_{PCL}
PCL-b-PB	12,400	1.08	22 vol%

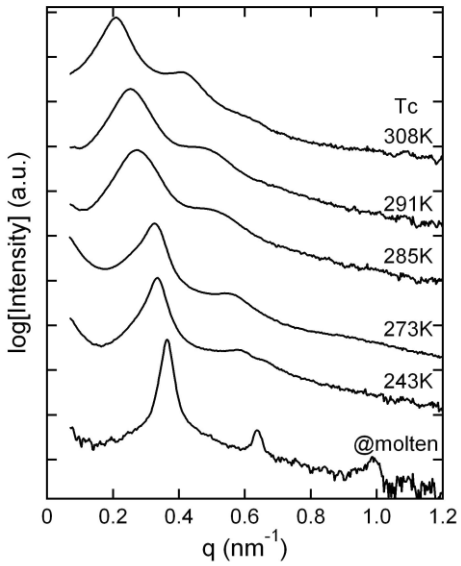

Figure 1. SAXS profiles of PCL-*b*-PB crystallized at various temperatures.

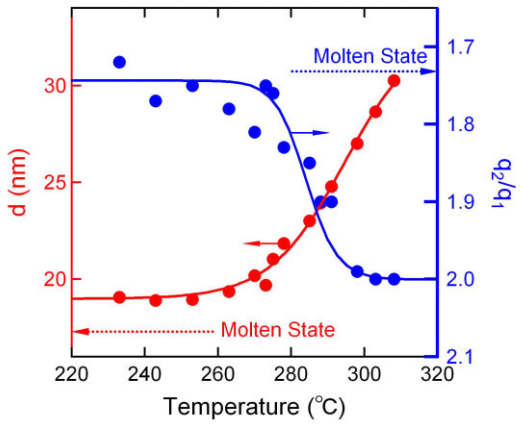

Figure 2. The q_2/q_1 and domains spacing (*d*) as a function of crystallization temperature.

References

[1] A. Register et al., Macromolecules 35, 2365 (2002).

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