10C/2000G034

Structure Formation of Block Copolymers in Crystallizing from Microphase-Separated Melt

T. Shiomi, H. Takeshita*, H. Kawaguchi, M. Nagai, K. Takenaka, and M. Miya
Department of Materials Science and Technology, Nagaoka University of Technology
Nagaoka, Niigata 940-2188, Japan

Introduction

Recently formation of higher-order structure by crystallization of crystalline-amorphous block copolymers from microphase-separated melt has been extensively studied.[1] It has been reported that structure is reorganized to be alternating structure consisting of crystal and amorphous lamellae when the melt is weakly segregated, while crystallization occurs within the microdomain in the melt in the case of the strongly phase-separated melt. Since usually polymers are crystallized in a non-equilibrium state, structure reformation may depend on competition between the crystallization rate of a crystalline component and the diffusion rate of component chains. Even in the weak segregation, therefore, it may be possible that polymers crystallize keeping their melt structure. In this paper, we present structure formation of both kinds of block copolymers in crystallizing from microphase-separated melts: one is poly(butadiene)-poly(ethylene glycol) block copolymers (PBd-PEG) in which the PBd chain can move flexibly, and the other is polystyrene-polyethylene block copolymers (PS-PE) whose microphase separation in the melt is strongly segregated.

Experimental

A molecular weight of PEG in all the PEG-PBd diblock copolymers employed was 5.4x103, and their copolymer compositions of PEG were 34 – 70 wt%, in which the sample names are abbreviated as BE34 – BE70, respectively. PS-PE copolymers, which were named SE-33 –SE72 from the copolymer composition of PE, were prepared by hydrogenation of (high-1,4-PBd)-PS block copolymers. The structure change in the crystallization and melting processes was observed by time-resolved small-angle X-ray scattering (SAXS) with synchrotron radiation in beam line 10C at Institute of Materials Structure Science, Tsukuba, Japan.

Results and discussion

Fig. 1 shows SAXS profiles of PBd-PEG crystallized at the indicated crystallization temperatures Tc together with those in the melt. The microstructure in the melt is lamellar for BE51 while a hexagonal-packed cylinder for BE70 and BE34. In BE51, although the structure in the crystalline state is also lamellar, the peak position shifted discontinuously in both the crystallization and melting processes. In BE34 the peak position shifted continuously so that the cylindrical structure was maintained in the crystallization at all Tc studied here, which suggests that the crystallization occurred within the microdomain. On the other hand, the structure in BE70 was changed from cylindrical to lamellar at a low Tc while remained cylindrical at a higher Tc with a discontinuous peak shift. These results shows that even block copolymers with a flexibly movable amorphous chain can maintain the melt structure in crystallization even though the structure reorganization depends on the melt structure and Tc.

In all PS-PE block copolymers crystallized below the glass transition temperature of PS, the peak position did not shift in both the crystallizaion and melting process, which means that crystallization occurs within the microdomain in the melt.

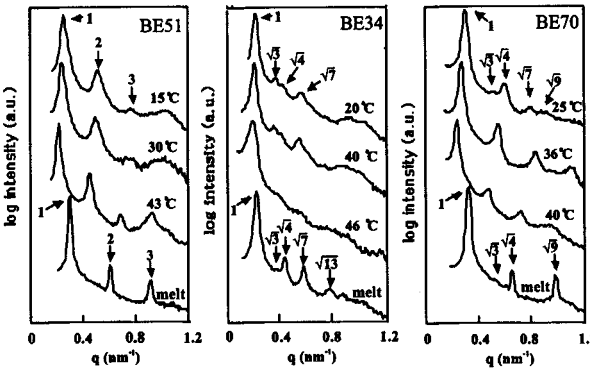

Fig. 1. SAXS profiles of PEG-PBd block copolymers in the crystalline and melt states.

References

[1] I. W. Hamley, “The Physics of Block Copolymers”, Oxford U. P., 1998.

*takesita@chem.nagaokaut.ac.jp