Time-resolved small- and wide-angle X-ray scattering studies on structure formation in crystalline graft copolymers

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Introduction

Structure formation in block copolymers continues to be of considerable experimental and theoretical interest. In block copolymer containing a crystallizable component, structural changes resulting from crystallization will compete with those occurring due to microphase separation.

This report is concerned with the structure of polyethylene-poly(ethylene propylene) (PE-PEP) diblock copolymer quenched from lamellar microphase-separated phase below the polyethylene crystallization temperature. We present that time-resolved synchrotron SAXS and WAXS data for and DSC measurement was carried out simultaneously.

Experiment

The block copolymer used was synthesized by catalytic hydrogenation of polydiene precursor, which was anionically polymerized from butadiene and isoprene monomers. The number average molecular weight, M_n is 4.42×10^4, the M_w/M_n is 1.05, and weight fraction of polybutadiene (PB) is 0.52, where M_w denotes weight-average molecular weight. The simultaneous SAXS, WAXD and DSC (Mettler FP90) measurements were performed at BL9C and BL15A. The wavelength of X-rays was tuned at 0.1499 nm. The PE-PEP sample was heated up to 180°C at a rate of 2-20K/min and then cooled rapidly to crystallization temperature (T_c), where was slightly below melting temperature (T_m=108°C DSC peak top) of the hydrogenated PB block.

Results

Figure 1a shows time-resolved SAXS data detailing the crystallization of PE-PEP at 100°C. During this experiment, the sample was cooled at 100 at 20°C/min from 180°C down to 100°C. The intensities increase of the SAXS peaks beginning near 3 min is due to crystallization of PE block. The simultaneous growth of 4 peaks (q ratio of 1:2:3:4) indicates that crystallization results in the development of a lamellar morphology. Figure 1b also demonstrates the results of the simultaneous WAXS/SAXS/DSC measurements, which is corresponding to data in Figure 1a. DSC exothermic peak was observed during the crystallization. In the WAXS data, the increase intensities of (11) and (200) reflections of the orthorhombic PE crystal were observed. These crystalline reflections appear to develop on the almost same time scale as the increase in SAXS primary peak intensity during 100°C crystallization.

To analyze crystallization process, it is useful to replot the data in the Avrami form: $\ln(1-X_C)=-kt^n$, where, X_C is the fraction of crystallization that has occurred at elapsed time t, n is the Avrami exponent, and k is a constant. We obtain X_C from $X_C = (I(t)- I_0)/(I_m-I_0)$, where I_0 is the melt scattering intensity at T_C, I_m is the intensity at the end of the experiment, and $I(t)$ represents the intensity at time t.

Avrami plots for PE-PEP crystallized at 100 and 103°C are shown in Figure 2, based on the intensities of the primary SAXS peak. The Avrami exponents for PE-PEP were 1.7 and 3.0 at 100 and 103°C crystallization, respectively. These values were commonly observed for polymers that crystallize in spherulites.

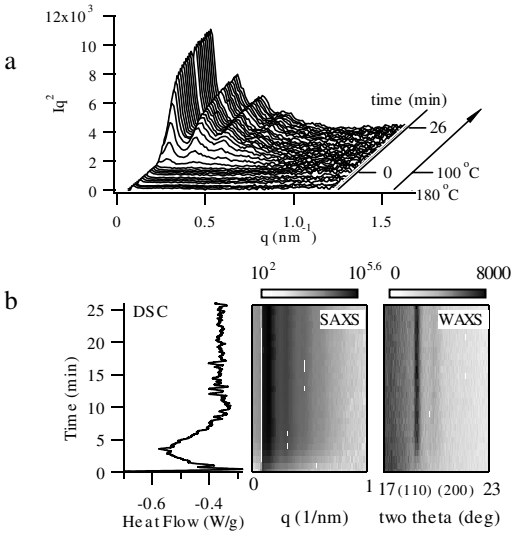

Figure 1. Time-resolved simultaneous WAXS/SAXS/DSC measurements during the crystallization at 100°C. Intensity graduations of SAXS and WAXS are in logarithmic and in linear scales, respectively.

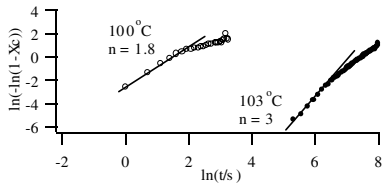

Figure 2. Avrami plots of the crystallization processes.

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