First Detection of Lamella-Gyroid-Cylinder Phase Transition of Neat Polyethylene-Poly(ethylene Oxide) Diblock Copolymers on the Basis of Synchrotron WAXD/SAXS and Infrared/Raman Spectral Measurements

Cao Weiyu1, Kohji Tashiro1, Makoto Hanesaka1, Shinichi Takeda1, Hiroyasu Masunaga2, Sono Sasaki2 and Masaki Takata2

1 Department of Future Industry-oriented Basic Science and Materials, Toyota Technological Institute, Nagoya 468-8511, Japan
2 Japan Synchrotron Radiation Research Institute (JASRI), Kouto, Sayo-gun, Hyogo, 679-5198, Japan
E-mail: ktashiro@toyota-ti.ac.jp

Abstract. The phase transition behaviour of polyethylene-b-poly(ethylene oxide) (PE-b-PEO) diblock copolymer with relatively short chain lengths has been studied on the basis of temperature dependent infrared and Raman spectral measurements and synchrotron WAXD/SAXS simultaneous measurements, from which the concrete structural changes were deduced successfully from the various levels of molecular chain conformation, chain packing mode and higher-order structure. The higher-order structure has been found to transform between lamella, perforated lamella, gyroid, cylinder and sphere structures. The inner structural changes occurring in the polyethylene and poly(ethylene oxide) parts have been related with these morphological changes. The morphological transition from lamella to gyroid occurs with keeping the crystalline state of polyethylene parts. This apparently curious transition can be interpreted reasonably by assuming the thermally-activated chain motion in the crystal lattice, which may play an important role as a trigger to induce the morphological change from lamella to gyroid. This idea was supported by the measurement of half-width of Raman anti-symmetric CH2 stretching band sensitive to the thermal mobility of alkyl chains.

1. Introduction

In a diblock copolymer consisting of two immiscible polymer components, the phase separation on the macroscopic level is prevented by a direct covalent linkage of these polymer chains. The tendency of segregation of these chain blocks leads to a so-called microphase separation, where the separation of the components occurs in nanoscale domains. As a result, they can exhibit various morphologies such as lamella, gyroid, cylinder, sphere structures. The two polymer components studied for a long time were mainly amorphous. In these years the crystalline-amorphous and crystalline-crystalline diblock copolymers have been investigated actively because they exhibit the various types of phase transitions in the crystalline regions which should be related with the drastic morphological changes. But the details of transition behaviors of crystalline-crystalline diblock copolymers have not yet been clarified enough satisfactorily.

Polyethylene-block-poly(ethylene oxide) is one of the typical crystalline-crystalline diblock copolymers. In the aqueous solution it exhibits the various kinds of morphology like cylinder, gyroid
and lamella depending on the concentration and temperature. About the neat PE-b-PEO system without any water content, Sun et al. studied the low-molecular-weight PE-b-PEO diblock copolymer and proposed the lamellar structure in a wide temperature region without any transition to the other types of morphology. Castillo et al. reported a possibility of sphere phase in a high temperature region, but the SAXS profile was too broad to identify the detailed morphology because of relatively high content of side branches. We have investigated the phase transition behaviors of PE-b-PEO diblock copolymers with different chain length combinations on the basis of simultaneous synchrotron WAXD/SAXS measurements as well as vibrational spectral data. We observed successfully the transitions between lamella, gyroid, cylinder and sphere morphologies for PE-b-PEO copolymers with the segmental lengths of PE and PEO similar to those utilized by the previous researchers. The results obtained for PE-b-PEO diblock copolymer with PE and PEO segmental lengths of 39 and 86 monomeric units (E39EO86), respectively, will be mainly described here.

2. Experimental

The sample E39EO86 was purchased from Polymer Source Inc. The molecular weight distribution was 1.10. The infrared spectral measurement was performed using a Varian FTS7000 Fourier-transform infrared spectrometer at a resolution power 1 cm\(^{-1}\). The simultaneous measurement of 2D-WAXD and SAXS data was performed at BL40B2 beamline at SPring-8 (Japan Synchrotron Radiation Research Institute, Japan). The thermal behavior was investigated using a TA Instruments DSC Q1000 under nitrogen gas atmosphere at a heating rate of 10°C/min.

3. Results and Discussion

3.1. Morphological changes

The SAXS profiles of E39EO86 obtained in the heating process are shown in Figure 1. At room temperature, the peaks were detected at the positions of the ratio 1 : 2 : 3, indicating a lamellar lamellar morphology. By heating the sample to above 60°C, the ratio of the peak positions changed to
Before transforming to gyroid structure, the SAXS peaks characteristic of a metastable perforated lamella was detected although the details were not clear enough well. By heating furthermore, the hexagonally-packed cylindrical phase was observed at around 90°C, giving the ratios of peak positions 1 : 1.73 : 2 : 2.65 : 3. As the temperature was increased to above 100°C, the sphere structure started to appear. In the cooling process these morphological changes were detected almost reversibly with some thermal hysteresis.

3.2 Structural Changes in Crystal Lattice

Figure 2 (a) and (b) show the temperature dependences of WAXD profile and infrared spectral pattern measured in the heating process. The X-ray reflection peaks intrinsic to PEO crystal disappeared above 55°C. The reflections of PE orthorhombic phase were observed up to 80°C. The infrared spectra detected not only the melting of PEO crystal at around 54°C but also the transition of PE segments from the orthorhombic crystal to the pseudo-hexagonal or rotator phase as seen in the disappearance of a pair of bands at 730 and 720 cm⁻¹ and the appearance of a single band at 721 cm⁻¹ at around 90°C. Figure 3 shows the comparison of DSC, IR, WAXD and SAXS data as a function of temperature. Once the PEO segments are melted, the transition from lamella to gyroid occurs. It should be noticed here that the PE segments are still in the orthorhombic crystalline phase. Similarly, the gyroid to cylinder transition occurs while the orthorhombic PE crystal transfers to the pseudo-hexagonal form. In this way, the morphological transition is found to occur even in the solid state of PE segmental parts. It may be speculated that the PE chains are thermally activated and can move along the interfacial boundary surface to cause the lamella-to-gyroid transition. This hypothesis could be confirmed using the half-width of Raman band at 2880 cm⁻¹ [the methylene anti-symmetric stretching mode νas(CH₂)] which is sensitive to the thermal mobility of methylene chains. The Raman spectra were measured for the PE-b-deuterated PEO block copolymer E39dEO25 with the same PE segmental length as that of E39EO86. The deuterated sample was needed to separate the νas(CH₂) band of PE from those of PEO species by deuteration of ethylene oxide parts. Figure 4 shows the experimental data collected for E39dEO25 sample. The half-width of νas(CH₂) band was
found to increase largely just when the lamella-to-gyroid and gyroid-to-cylinder phase transitions occurred. That is to say, the enhancement of thermal mobility occurred in the orthorhombic crystal region of PE segmental parts, resulting in the transition of lamella-to-gyroid phases.

4. Conclusions

As reported in the present paper, the complicated morphological changes were found out for PE-b-PEO diblock copolymer with relatively short segmental lengths. By viewing from the various levels these morphological transitions were related intimately with the structural changes occurring in each chain parts. The lamella-gyroid (and gyroid-cylinder) transition was observed even when PE parts were still in the crystalline state, unexpected from the reports on many crystalline-crystalline diblock copolymers with lamellar morphology only. This phenomenon was ascribed to the activation of thermal motion of PE chains in the crystalline state.

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