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Preferential orientation or crystallines spatially confined in lamellar microdomains of polyethylene-block-[atactic poly(propylene)]

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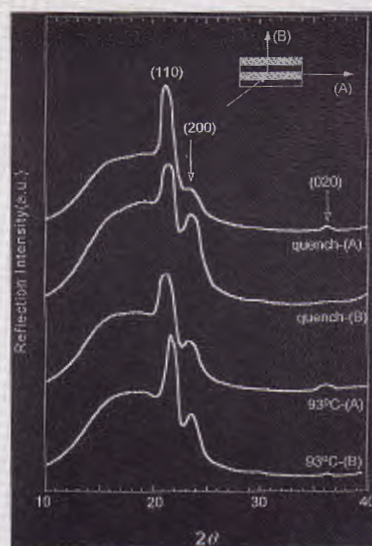
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Communication: Synchrotron small angle X-ray scattering (SAXS), wide angle X-ray scattering (WAXS), and transmission electron microscopy were carried out for an oriented polyethylene-*block*-[atactic poly(propylene)] with a molecular weight of 1.13×10^5 and a volume fraction of polyethylene of 0.5. Isothermal crystallization at 93 °C did not destroy the pre-formed microdomain, however, with a higher crystallization temperature, the microdomain was more heavily deformed and more crystalline lamella grew. In WAXS profiles, preferential orientation of (020) reflection peak was observed, indicating that the crystalline lamella grew in parallel with the micro domain interface.

Comparison of the WAXS patterns for quenched and isothermally crystallized samples at 93 °C. The definitions of the reflection configurations (A) and (B) are described in the text.



Preferential orientation of crystallites spatially confined in lamellar microdomains of polyethylene-*block*-[atactic poly(propylene)]^a

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Introduction

The spatial constraint provided by microphase separation should play a crucial role in the crystallization of semi-crystalline block copolymers which consist of crystalline and amorphous blocks. Whitmore and Noolandi^[1] and DiMarzio et al.^[2] independently predicted that when the crystalline block crystallizes in lamellar microdomains the thermodynamically most stable structure is such that the chain stems align perpendicularly to the microdomain interface.^[3] The theoretical prediction was experimentally examined by Cohen et al.^[4] They performed small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) on a polyethylene-*block*-poly(ethylene) and found that the polyethylene (PE) crystallization is

confined in the preceded lamellar domain, and the PE stems align parallel to the domain interface, which is opposed to the theoretical prediction. The confined crystallization was confirmed by Quiram et al.,^[5] however, they stated that the PE stems orient perpendicularly to the microdomain interface as predicted by the theories. The perpendicular orientation was also found by Ryan et al.^[6] for the case of PE-*block*-poly(ethylene). At the same time, they claimed the parallel orientation for PE-*block*-poly(vinylcyclohexane).^[7] On the other hand, we have shown in previous studies^[8,9] of a series of PE-*block*-[atactic poly(propylene)] (DEP) samples that the PE crystallites orient randomly in the lamellar microdomain, which is not compatible with either the parallel or perpendicular orientation. Although all groups examined the same type of polyethylene, which was prepared through hydrogenation of an anionically polymerized polybuta-

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diene, there seems to be no consistency among the results.

In the present work, we prepared a DEP sample having highly oriented lamellae and crystallized it under different conditions to clarify the preferential orientation of the PE stems with respect to the microdomains by the SAXS and WAXS measurements.

Experimental part

The DEP sample was prepared through hydrogenation of poly(2-methyl-1,3-pentadiene)-*block*-polybutadiene according to Fetters' method.^[10] The weight-average molecular weight ($\bar{M}_w$) is 1.13×10^5 , the molecular weight distribution defined as $\bar{M}_w/\bar{M}_n$ is 1.1, (where $\bar{M}_n$ is the number-average molecular weight), and the volume fraction of the PE block in the melt state is 0.48. The DEP sample with this $\bar{M}_w$ is strongly segregated in the melt state and, therefore, forms a lamellar microdomain structure with a domain spacing (D) of 78–83 nm.^[8,9]

The lamellar microdomain was oriented by applying a planar shear extension at about 150°C (above the melting temperature of PE), and the sample was subsequently immersed in a mixture of isopropyl alcohol and dry ice (about -40°C, below the glass transition temperature of atactic polypropylene).^[8] This procedure could "freeze" the morphology formed in the melt state and the sample maintained this structure while stored at room temperature.^[8] The sample was melted again in a SAXS cell at 150°C, and the cell temperature was lowered quickly to a given isothermal crystallization temperature. The synchrotron SAXS measurement was carried out at a BL-15A SAXS station at the Photon Factory High Energy Research Organization in Japan.^[11] The SAXS intensity was collected as an accumulation of the scattered intensity during 100 s by use of a one-dimensional position sensitive detector with 20 cm length and 512 channels. Details of the optics and the instrumentation is described elsewhere.^[11] Transmission electron microscopy (TEM) was taken for a cryosectioned slice made from an oriented and "frozen" sample with a Hitachi H-7100. WAXS was carried out for the quenched and isothermally crystallized samples with a Mac Science MX-P18. In our measurement, the X-ray beam was incident parallel to the microdomain interface and the reflection profiles were obtained by moving the goniometer parallel to the interface (configuration A) and then perpendicularly (configuration B).

Results and discussions

Deformation of the microdomain structures caused by the crystallization of the polyethylene block

Fig. 1 compares the SAXS profiles (i.e., I vs q plot) for the quenched sample and the ones crystallized at the three different temperatures, where I is the scattering intensity without the Lorentz correction, and q is the magnitude of the scattering vector defined by $q = (4\pi/\lambda)\sin(\theta/2)$; λ is the X-ray wavelength and θ is the scattered angle. In the

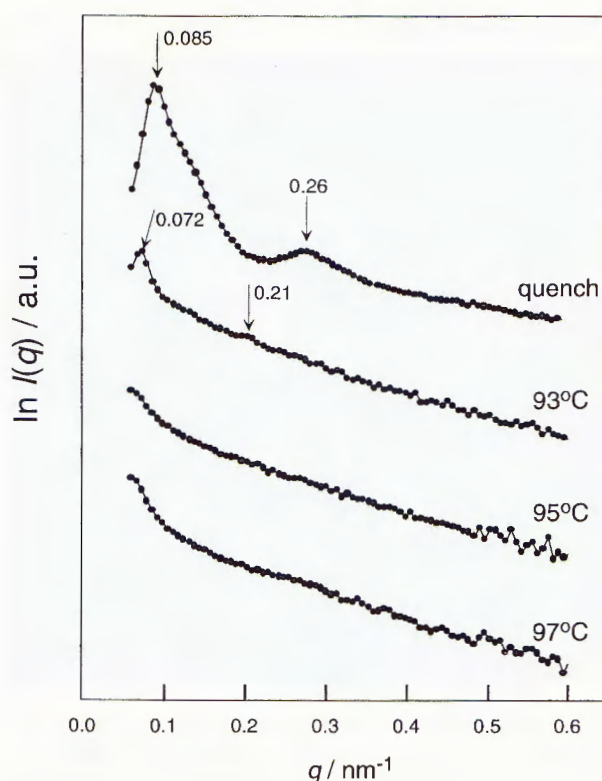


Fig. 1. Comparison of the SAXS profiles for the quenched and isothermally crystallized samples. The arrows indicate the diffraction peak positions due to the lamellar microdomain.

quenched sample, the first and third diffraction peaks due to the lamellar microdomains are observed at $q = 0.085$ and $q = 0.26 \text{ nm}^{-1}$, respectively. The absence of the second order peak is due to its being multiplied by the vanishingly small particle scattering function at the same q where the second peak would emerge if the thickness of each lamella was equal. From the peak positions, D was estimated to be 73.9 nm and this size is comparable with that from the TEM image shown in Fig. 2. When crystallized at 93°C, the peak height is drastically suppressed, indicating that the crystallization at this temperature distorts the preceding microdomain structure. However, the ordering of the lamella is still present to some extent enough to give the third order peak. Another distinctive difference in the 93°C profile is that the $D = 87 \text{ nm}$ obtained from the peak position is larger than that of the quenched sample. Noticing the absence of the second order peak also for this sample, the equal lamellar thickness is still maintained.

In the scattering profiles of the 95 and 97°C crystallizations, there is no peak observed due to the microdomain, and the scattering intensity increases monotonically with decreasing q . This feature indicates that the crystallite growth is more progressed than at 93°C, and the resulting crystalline structures may overwhelm the preceding lamellar microdomain structure.

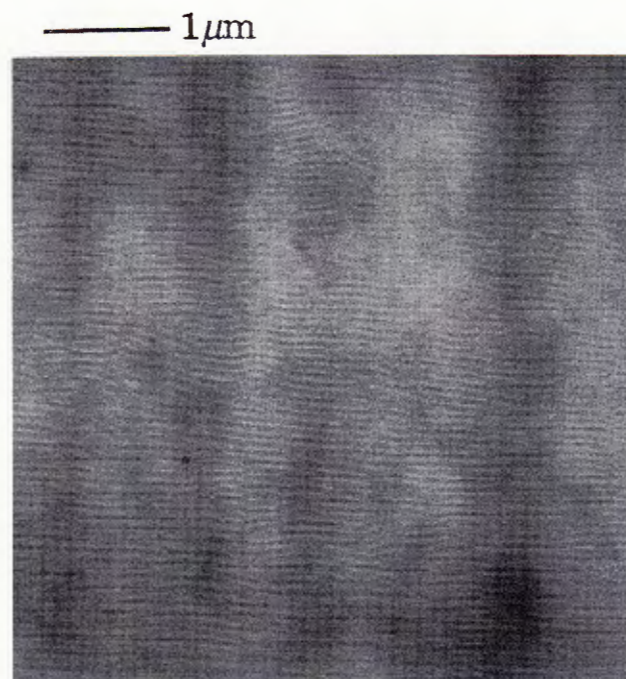


Fig. 2. TEM bright field micrograph for the oriented and "frozen" DEP sample. The bright area consists of the atactic poly(propylene) block and the dark area of the mixture of amorphous and crystallized PE, because the polyethylene crystallites diffract the electron beam to cause dark images in the bright field mode.

Preferential orientation of the *b*-axis of the crystallite

Fig. 3 compares the WAXS profiles of configurations (A) and (B) for the two samples which were quenched or crystallized at 93°C. In the quench-(A) (the configuration (A) for the quenched sample and we denote the reflection in the same manner hereafter) there is a peak from the (020) plane, on the other hand, the quench-(B) shows no trace of it. This fact indicates that the *b*-axis of the PE crystallite orients parallel to the microdomain interface. Furthermore, the feature that the (110) peak is larger in (A) than in (B) and that the (200) peak is smaller in (A) than in (B) is essentially identical to that for the uniaxially oriented PE^[12] when we take the normal direction of the interface as the stretching direction. Therefore, we can conclude that the PE crystallite takes an oriented row structure in the domain, namely, the *b*-axis of the PE crystallite orients parallel to the interface. On the other hand, the *a*-axis and *c*-axis (chain stem direction) rotate around the *b*-axis, as represented by the upper illustration in Fig. 4. The crystalline lamellae lay along the *c*-axis, and the *c*-axis rotates around the *b*-axis, therefore, the scattering between the crystalline lamellae should be identical for all directions. It has already been shown in our previous SAXS experiment^[9] that the Lorentz corrected scattering intensities from oriented and "frozen" DEP were identical for all directions. In the previous work, we interpreted the

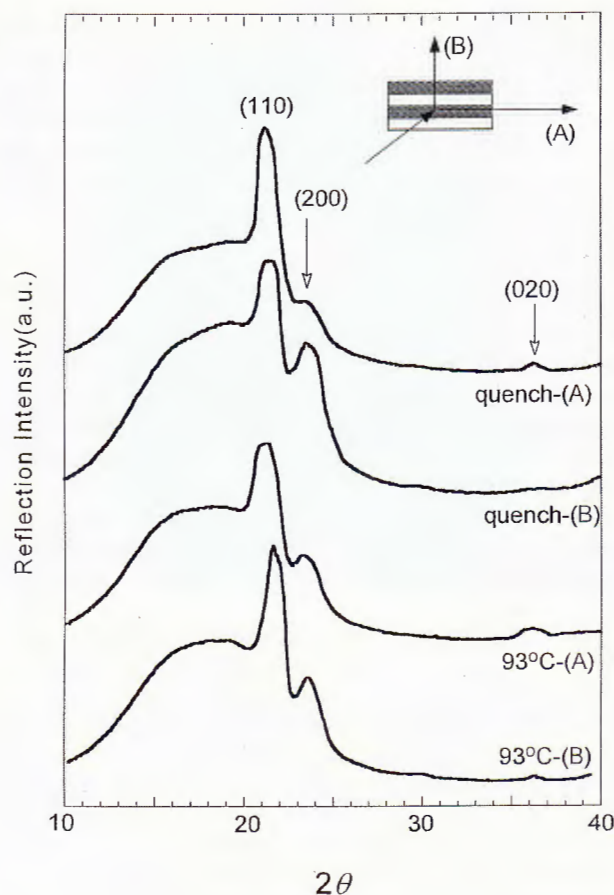


Fig. 3. Comparison of the WAXS patterns for quenched and isothermally crystallized samples at 93°C. The definitions of the reflection configurations (A) and (B) are described in the text.

identical scattering for all directions as the random orientation of the crystallite, however, the interpretation should be corrected as mentioned in this section.

The 93°C-(B) has an appreciable (020) peak although the magnitude is smaller than in 93°C-(A). In contrast there is not much difference in the (110) and (200) peaks between (A) and (B). Although not presented here, the 95 and 97°C samples (A) showed essentially similar WAXS patterns to those of the corresponding (B). These results indicate that the *b*-axis becomes less oriented with increasing the crystallization temperature. This can be explained if we assume that the PE crystallite branches with growth of the crystallization in the same manner as in bulk (see Fig. 4). The crystallite branching proceeds so as to form a spherulite, and usually spherulites can grow larger than the microdomain. Thus, the branching may be the driving force to destroy the preceding lamellar structure, which was observed by SAXS as shown in Fig. 1. Moreover, clear evidence of the formation of spherulites in the 95 and 97°C samples was obtained by the depolarized (Hv) light scattering pattern.^[13]

The present work clarifies that the spatial constraint of the microdomain lamella induces the preferential orienta-

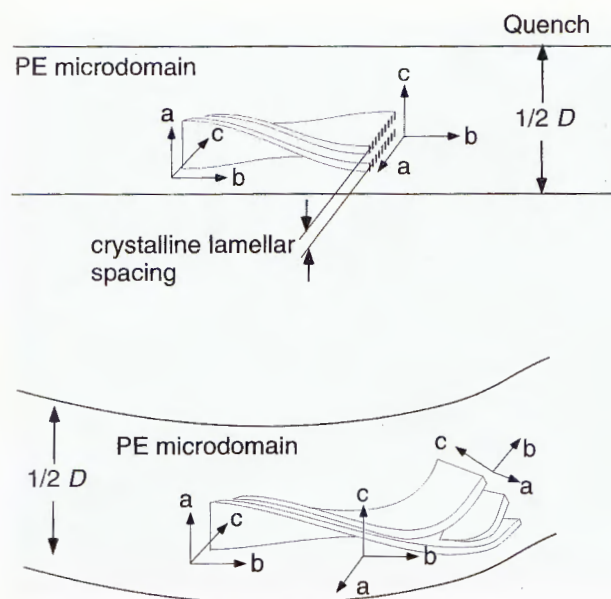


Fig. 4. Illustrations to show the morphology for the quenched sample where the b-axis orients in parallel with the domain interface and the other two axes rotate around the b-axis (upper). Accompanying with the crystallite growth, the crystalline lamellae branch, and the branching may deform the microdomain.

tion of the b-axis rather than that of the chain stems. We are in the process of investigating the relation of the morphological change and the crystallization kinetics by synchrotron SAXS.

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