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Crystal structure analysis of cylindrical phase of polystyrene-*b*-polyethylenebutylene-*b*-polystyrene triblock copolymer

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Abstract

Crystal structure analysis of cylindrical phase of polystyrene-*b*-polyethylenebutylene-*b*-polystyrene triblock polymer was carried out. One cylinder with radius 74.20 Å passes through a hexagonal unit cell with $a = b = 294.42$ Å, $c = \infty$, $\beta = 120°$. The temperature factor which reflects the disorder of the cylinder is 14,525 and $\langle \Delta r^2 \rangle^{1/2}$ is estimated as 13.56 Å. This suggests that the cylinder is distorted and the surface of the cylinder is disordered.

Keywords: X-ray scattering; Crystal structure; Block copolymer

1. Introduction

Block polymer forms various regular structures, so to speak, crystals, depending upon the composition [1]. Many works have been done on the morphology and morphological changes of the structure [1]. The structure has been qualitatively characterized as sphere, cylinder, gyroid etc. Detailed and quantitative descriptions of the structure have not been made so far. Some of block copolymers give fiber diagrams in small angle X-ray scattering region, i.e., uniaxially oriented specimen. In the present study, the small angle scattering of uniaxially oriented sample of polystyrene-*b*-polyethylenebutylene-*b*-polystyrene triblock copolymer is interpreted and the detailed structure is described.

2. Experimental

The uniaxially oriented sample of polystyrene-*b*-polyethylenebutylene-*b*-polystyrene (SEBS) triblock copolymer is kindly supplied by Dr Y. Kobori and Prof T. Kotaka of Toyota Technological Institute. The original sample was supplied by Asahi Chemical Industry Co Ltd, which contains 30% styrene ($M_w = 92.6 \times 10^3$, $M_w/M_n = 1.17$). The uniaxially oriented sample was prepared by the following procedure. The cast film was roll-processed at 160 °C for about 10 min by applying high shear strain along a chosen direction in order to induce the alignment of the polystyrene cylinder in one direction, and, the elongation flow opt-rheometry measurement was made at 180 °C under the condition of Hencky strain rate $\varepsilon_0 = 0.01\ s^{-1}$ [2]. This sample was served for the small angle X-ray scattering measurements after annealing at 160 °C for 30 h in vacuo.

Small angle X-ray scattering (SAXS) was recorded by an imaging plate by using Cu K_α radiation. The details of the camera are described elsewhere [3]. The camera length is 707.6 mm which is corrected by using lead stearate. The imaging plate was digitally read by R-AXIS DS2 (Rigaku Denki Co Ltd). The SAXS pattern is shown in Fig. 1. One dimensional intensity curve was obtained by summing up the digital data of one pixel ($50 \times 50\ \mu m^2$) along constant 2θ and by plotting them to $q = 2 \sin \theta/\lambda$. One dimensional intensity curve was fitted and separated under the assumption of pseudo-voigt function: a linear combination of Gauss and Cauchy functions [4]. The sample was rotated around the orientation axis of the cylinder because the orientation around the orientation axis is observed. Thus, the intensities of four reflections were estimated. The intensity curve is shown in Fig. 2.

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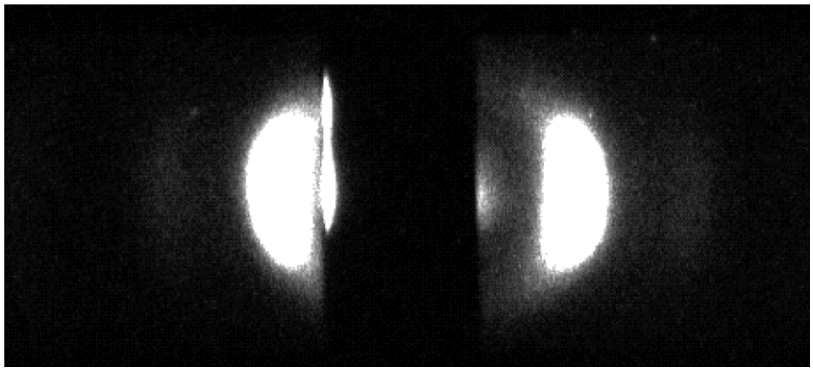

Fig. 1. Fiber diagram (small angle scattering pattern) of the cylindrical phase of polystyrene-*b*-polyethylenebutylene-*b*-polystyrene triblock copolymer. The vertical is the cylindrical axis: fiber axis.

3. Basis for calculation

3.1. Fourier transform of a cylinder

Fourier transform F of a cylinder with radius r_0 is given by [5]

$$F(R) = r_0 J_1(2\pi R r_0)/R \tag{1}$$

Where J_1 is the first order of Bessel function and R is a cylindrical coordinate in the reciprocal space. This suggests that the structure factor depends only on the value of $R = q = 2 \sin \theta/\lambda$.

3.2. Structure factor of a disordered cylinder

In block copolymer, the cross section of the cylinder is generaly distorted from the circle [1], and furthermore, the density difference on the boundary is not necessarily steep.

These disorders from the cylinder were taken into consideration by using so-called temperature factor. Accordingly, the Fourier transform of a disordered cylinder is given by

$$F(R) = r_0 J_1(2\pi R r_0)\exp\left(-\frac{1}{4}BR^2\right)/R \tag{2}$$

where B is the disorder parameter:temperature parameter.

The electron density can be calculated by the Fourier transform of Eq. (2). The Fourier transform of the product of two functions is given by the convolution of the Fourier transforms of two functions (Eq. (5)).

$$f_1(\mathbf{x}) = \int F_1(\mathbf{s})\exp(2\pi \mathbf{s}\mathbf{x})\mathrm{d}v_s \tag{3}$$

$$f_2(\mathbf{x}) = \int F_2(\mathbf{s})\exp(2\pi \mathbf{s}\mathbf{x})\mathrm{d}v_s \tag{4}$$

$$\rho(\mathbf{x}) = \int_{-\infty}^{\infty} f_1(\mathbf{y}) f_2(\mathbf{x}-\mathbf{y})\mathrm{d}\mathbf{y} \tag{5}$$

Where $\mathrm{d}v_s$ is the volume element in the reciprocal space and

$$F_1(\mathbf{s}) = rJ_1(2\pi R r)/R$$

$$F_2(\mathbf{s}) = \exp\left(-\frac{1}{4}BR^2\right)$$

$$f_1(\mathbf{x}) = \begin{cases} 1 & \text{for } |r| \le r_0 \\ 0 & \text{for } |r| > r_0 \end{cases}$$

$$f_2(\mathbf{x}) = \frac{\sqrt{4\pi}}{\sqrt{B}}\exp\left(-\frac{4\pi^2}{B}r^2\right)$$

Accordingly,

$$\rho(r) = \frac{\sqrt{4\pi}}{\sqrt{B}}\int_{r-r_0}^{r+r_0}\exp\left(-\frac{4\pi^2}{B}y^2\right)\mathrm{d}y \tag{6}$$

This density (6) is schematically shown in Fig. 3, where $r = 1.0$ Å and $B = 0.1$ Å^2.

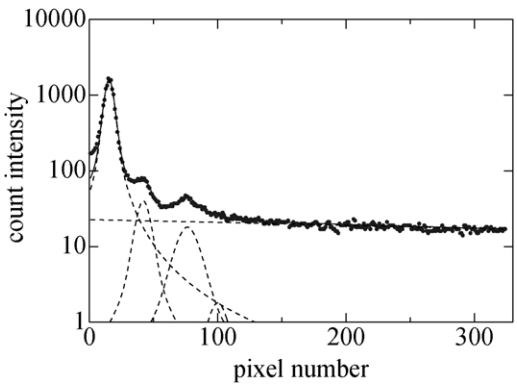

Fig. 2. Intensity distribution along the equator and the curve separation.

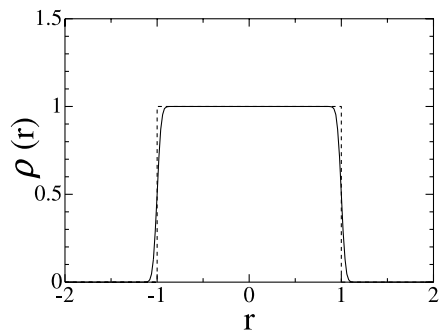

Fig. 3. Electron density distribution when $r = 1.0$ Å and $B = 0.1$ Å^2.

Table 1
Final parameters refined by the least-squares method

Parameters	Values	Standard deviations
Radius r (Å)	74.20	0.08
Temperature parameter B (Å^2)	14,525	242

3.3. Least-squares method

The least-squares method is to minimize the following function Φ,

$$\Phi = \sum w_m\left(\sqrt{I_{obs}} - \sqrt{I_{calc}}\right)^2$$

Where, I_{obs} and I_{calc} are the observed and calculated intensities, respectively, and w_m is the weight. The least-squares program was written in Fortran. Here, the variable parameters are the radius of cylinder r_0, the temperature parameter B, and the scale factor S. And the weights were assumed to be unity.

4. Results and discussion

As shown in Fig. 1, the reflections can be observed only on the equator. This is reflected by the cylinder with $c = \infty$. All the observed equatorial reflections can be indexed by a hexagonal unit cell with parameters $a = 292.42$ Å and $c = \infty$.

The least-squares refinement was carried out. The R-factor converged to 1.2%. Here, R-factor is given by the following equation,

$$R = \frac{\sum|\sqrt{I_{obs}} - \sqrt{I_{calc}}|}{\sum\sqrt{I_{obs}}} \quad (7)$$

where I_{obs} and I_{calc} are the observed and calculated intensities, respectively. The refined parameters: r_0 and B are shown in Table 1 along with the standard deviations. The comparison between the observed and calculated intensities is given in Table 2. The crystal structure of the cylindrical phase of the polystyrene-*b*-polyethylenebutylene-*b*-polystyrene triblock copolymer is shown in Fig. 4 schematically. The radius of the cylinder and the standard deviation are estimated to be 74.20 Å and 0.08 Å, respectively. The small value of the standard deviation shows that the temperature parameter reproduces very well the disorder of the cylinder in the block copolymer. When the density of at-polystyrene is assumed to be 1.06 and that of polyethylenebutylene is assumed to be 0.86: the intermediate value between polyethylene and polybutene [6], the content of polystyrene is calculated to be 27% from the radius of the cylinder, which corresponds well to the original content 30%. The large temperature parameter 14,525 Å^2 shows that the surface of the cylinder is diordered, the cross section of the cylinder is not necessarily to be the circle, and the boundary is not necessarily steep. The temperature parameter B can be related to the mean-square displacements $\langle u^2\rangle$ of the cylinder surface by the following equation,

$$B = 8\pi^2\langle u^2\rangle \quad (8)$$

From the value of B, the root-mean-square displacements $\sqrt{\langle u^2\rangle}$ is calculated to be 13.56 Å, which corresponds to 18.27% of the radius of the cylinder, 74.20 Å. The density is schematically shown in Fig. 5.

Table 2
Comparison between the observed and calculated intensities

Index	$\sqrt{I_{obs}}$	$\sqrt{I_{calc}}$
100	274.8	275.0
110	63.0	61.8
200		
120	65.6	64.9
300		
220	19.3	22.4

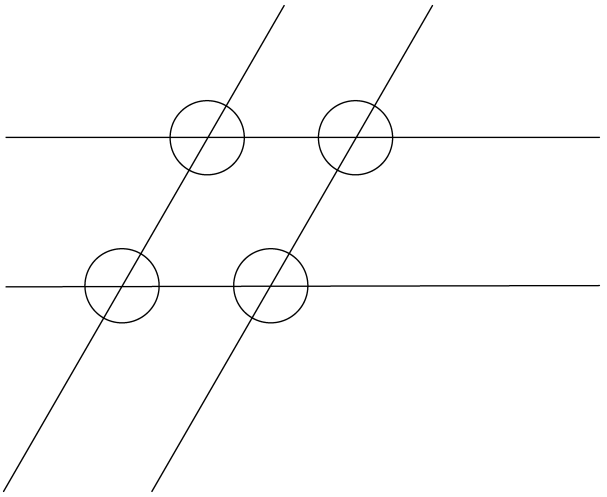

Fig. 4. Schematic representation of the crystal structure.

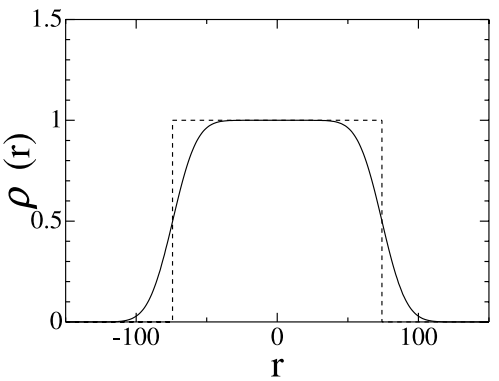

Fig. 5. Electron density distribution of the cylinder of polystyrene-*b*-polyethylenebutylene-*b*-polystyrene triblock copolymer.

Acknowledgements

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