

Evaluation of Grain Size by Small-Angle X-Ray Scattering for a Block Copolymer Film in Which Cylindrical Microdomains Are Perpendicularly Oriented

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Summary: Method of evaluation of grain size of hexagonally-packed cylindrical microdomains is presented by taking as an example the data from the polystyrene-block-polyethylenebutylene-block-polystyrene (SEBS) triblock copolymer film, where the polystyrene cylinders are embedded in the polyethylenebutylene matrix with being oriented perpendicular to the surface of the film. For this purpose, the two-dimensional small-angle X-ray scattering was measured by illuminating X-ray beam from the side of the film. The procedure is similar to the method how to evaluate the crystallite size of polymer, using the peak width of crystalline reflection in the wide-angle X-ray diffraction (WAXD) measurement. While single crystal is used as the standard sample for the case of WAXD because it can be postulated that the crystallite size is infinity in the single crystal, we propose here to use collagen as a standard sample for the SAXS measurement, since collagen forms very regular stacking of texture with 65.3 nm repeating period and the number of the stacking texture is infinitely large. It was confirmed that the grain size evaluated by the SAXS method was in sufficient accord with the result of the transmission electron microscopic observation.

Keywords: block copolymers; cylinder; evaluation of grain size; hexagonal lattice; microdomains; small-angle X-ray scattering

Introduction

Close relation between structure and property is required to reveal for appropriately designing a method of production of functional materials. In case of block copolymer, details of a grain (shape, size and orientation) of microdomains are more important for better understanding of the relation connected to the materials properties as compared to the microdomain structure itself. This is simply because when the polygrain state as depicted in Figure 1 is considered in the block copolymer materials, the macroscopic materials property becomes

isotropic although the microdomains with anisotropic shape such as cylinders or lamellae have intrinsic feature of anisotropic properties. In order to impart anisotropic properties to the block copolymer materials, microdomains are requested to orient and efficiency of imposing the external field such as the shear and extensional flows have been intensively examined.^[1–9] Although application of the external field is effective for inducing the microdomain orientation, the grain would not become large.

To check this, it is required to establish a method of evaluation of the grain size. In this current study, we have tried to evaluate the grain size of the cylindrical microdomains in the polystyrene-block-polyethylenebutylene-block-polystyrene (SEBS) triblock copolymer film, where the polystyrene (PS) cylinders are embedded in the

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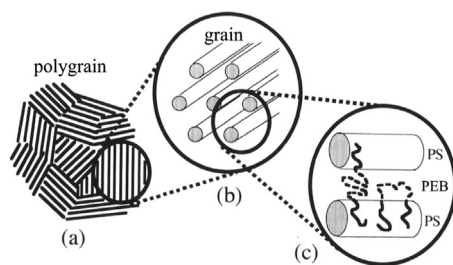


Figure 1.

Schematic illustration of the polygrain state in case of cylindrical microdomains.

polyethylenebutylene (PEB) matrix with the cylinders being oriented perpendicular to the surface of the film. Figure 2 shows schematically the polygrain state in the material where the cylindrical axes are oriented perpendicularly. Note that the white arrows exhibit the orientation direction of the hexagonal lattice (one of the three $\langle 10\text{--}10 \rangle$ directions). We evaluated the average size of such grains.

While the transmission electron microscopic (TEM) and the atomic force microscopic (AFM) observation techniques are straightforward methods for qualitative evaluation of the grain size,^[10–14] the ultra-small-angle X-ray scattering (USAXS) has been utilized for the quantitative evaluation of the grain size^[15] because in this reference it is reported that a peak due to the form factor of a grain of several micrometers (in other words, the particle scattering peak due

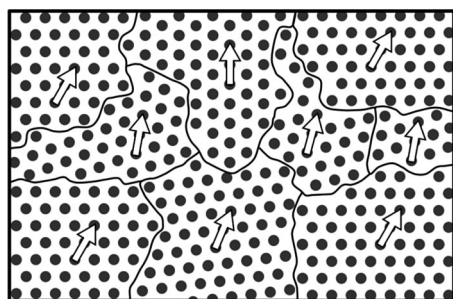


Figure 2.

Schematic illustration of the polygrain state in the material where the cylindrical axes are oriented perpendicularly. Note that the white arrows exhibit the orientation direction of the hexagonal lattice (one of the three $\langle 10\text{--}10 \rangle$ directions).

to the intraparticle interference) appeared in the very small-angle region. Our method hiring ordinary small-angle X-ray scattering (SAXS; the sample-to-detector distance is in the range of 2000 mm) can be referred to as an indirect detection while USAXS can directly detect information of the grain. However, USAXS technique is not easy to conduct because a special beamline (utilizing the sample-to-detector distance in the range of several hundreds of meters) is required in case of using synchrotron radiation facility or special camera such as the Bonsehart camera is required. As compared to USAXS, the ordinary SAXS is much easier to conduct and recently becomes more and more accessible and familiar to public.

It is well known that SAXS is a useful technique to quantitatively analyze the block copolymer microdomain structure.^[1–9,16–20] But unfortunately the SAXS method has never been applied for the evaluation of the grain size of the microdomains because of the lack of the standard sample to estimate the extent of the peak breadth due to the collimation error in the SAXS camera, and may be also due to some other factors (thoroughly referred to as the instrumental broadening). Since the collagen contains a texture with practically infinite size of the colloidal crystals, we considered that it can be used as a standard sample for the SAXS method to estimate the instrumental broadening. Then we applied this method to evaluate the grain size of the hexagonally-packed cylindrical microdomains perpendicularly oriented in the SEBS triblock copolymer film^[20] for which we have evaluated the grain size by the image analyses on the TEM micrograph, reported in our previous publication.^[14] It was confirmed that the grain size evaluated by the SAXS method was in sufficient accord with the result of the TEM observation.

Experimental Section

A bundle of collagen fibrils taken from chicken leg tendon (from a law-market-

price by-product) was fully dried and used as a standard sample in this current study to evaluate the extent of the instrumental broadening. Since collagen forms very regular stacking of texture with 65.3 nm repeating period,^[21] it is used generally as a standard sample to calibrate the magnitude of the scattering vector, q , being defined by

$$q = (4\pi/\lambda)\sin(\theta/2) \quad (1)$$

with λ and θ being the X-ray wavelength and the scattering angle, respectively.

To check the validity of the method of the evaluation of the grain size by the ordinary SAXS, we used an SEBS triblock copolymer sample with $M_n = 66.0$ kDa and $M_w/M_n = 1.03$ (M_n : number-average molecular weight, M_w : weight-average molecular weight). The total volume fraction of PS end-blocks is 0.16, and the volume fraction of butylene moiety in PEB block chain is 0.41. Namely, volume fractions of PS (one of PS end-blocks)/butylene moiety in PEB/ethylene moiety in PEB/PS (the other PS end-block) are 0.08/0.34/0.50/0.08, respectively. A selective solvent, *n*-heptane, was used for the solution casting, where *n*-heptane is good for PEB and poor for PS. To enhance solubility, methylene chloride, which is an inversely selective solvent (good for PS while very poor for PEB) was used as a co-solvent, such that the 1:1 mixture of *n*-heptane/methylene chloride was actually used. Since the methylene chloride is volatile at room temperature, it evaporates rapidly from the 5% solution of the SEBS sample. After complete evaporation of methylene chloride, *n*-heptane still remains in the solution. In this way, *n*-heptane solution of the SEBS sample was finally obtained. Complete evaporation of *n*-heptane from the solution took more several days at room temperature. The as-cast film with 0.5 mm thickness was further subjected to thermal annealing at 210 °C for 3 hours, and then subjected to the two-dimensional (2d) SAXS measurement at room temperature.

To cross-check the grain size, the annealed SEBS sample was subjected to

the TEM observation, using a H-600 instrument (HITACHI Co., Ltd) being operated at 75 kV. The ultra-thin section (a thickness of ca 80 nm) of the sample was made by cryo-microtoming at 183 K using a Reichert-Jung Ultracut T with a cryo-sectioning system (Reichert-Nissei FC-S). A diamond knife was used to cut the sample parallel to its surface so as to observe the TEM image of the cross-section of the cylinders perpendicularly oriented. The thin section was picked up on 400-mesh copper grids and exposed to ruthenium tetroxide (RuO₄) vapour to stain selectively PS microdomains. Therefore, the PS microdomains are stained with RuO₄ so that they appear dark in the TEM micrographs, while the unstained PEB microdomains appear bright.

The 2d-SAXS measurements were carried out at the BL-10C beamline of the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan,^[22] using X-ray with a wavelength of 0.1488 nm. This beamline provides a quasi-point focused beam by using a toroidal mirror, and the beam size was measured at the detector position, which was 850 μm in the vertical direction and 1000 μm in the horizontal direction. A standard slit system with widths of 0.7 × 0.7 mm² was used for the SAXS collimation. At this condition, the brightness of the X-ray beam was 4.1 × 10⁹ phs/sec. A PILATUS300K-W (Dectris Ltd, Baden, Switzerland), which has three pieces of rectangular shaped X-ray-sensitive elements (83.8 × 33.5 mm² in size and 487 × 195 pixel with 172 μm pixel size), being arranged in a series that the long edges of the elements were in line with each other (in total the actual size was 254 × 33.5 mm²), was settled with its long axis being parallel to the vertical direction. The sample-to-detector distance was 2040 mm. Along the long edge of the detector the sensitive q -range was $-2.62 \text{ nm}^{-1} < q < 2.62 \text{ nm}^{-1}$ (because of symmetrical displacement of the detector), and along the short edge of the detector the sensitive q -range was $-0.35 \text{ nm}^{-1} < q < 0.35 \text{ nm}^{-1}$. The 2d-SAXS patterns were further converted to one-dimensional profiles

by sector averaging. As for the SEBS sample, air scattering was subtracted from the 1d-SAXS profile after being normalized by measuring time and X-ray absorption (transmission correction).

In order to evaluate accurately peak width from the 1d-SAXS profile, as being free from the q -dependent background intensity, computational peak decomposition was conducted. For this purpose, the background intensity was assumed to be the functional shape of $a + b q^{-n}$, where a , b , and n are the numerical constants, whilst the Voigt function was used to fit to the lattice peak. Thus, the scattering intensity as a function of q is expressed by

$$I(q) = k\{G^*L(q - q_m)\} + a + b q^{-n} \quad (2)$$

where $G^*L(x)$ denotes the convolution of Gauss and Lorentz functions, i.e.,

$$G(x) = \exp[-x^2/(2\sigma^2)] / [(2\pi)^{0.5} \sigma] \quad (3)$$

$$L(x) = \gamma / [\pi(x^2 + \gamma^2)] \quad (4)$$

The peak decomposition was conducted by fitting this equation to the measured SAXS profile with floating all the parameters, k , q_m , σ , γ , a , b , and n . Then, using a set of the parameters (q_m , σ , and γ) a single peak was retrieved, from which we finally evaluated the integral width ($\Delta q = S/I_m$ where S and I_m denote, respectively, the peak area (integrated intensity) and the scattered intensity at the peak top).

Results and Discussion

Figure 3 shows a TEM image of perpendicularly oriented cylinders of the SEBS triblock copolymers. Since the PS phase is stained with RuO_4 , a hexagonal array of dark cylinders is observed in the bright matrix of unstained PEB. The ideally hexagonal pattern is identified thoroughly in Figure 3 with the size of $2.0 \mu\text{m} \times 2.4 \mu\text{m}$. Therefore, grain size is qualitatively considered to be larger than $3 \mu\text{m}$.

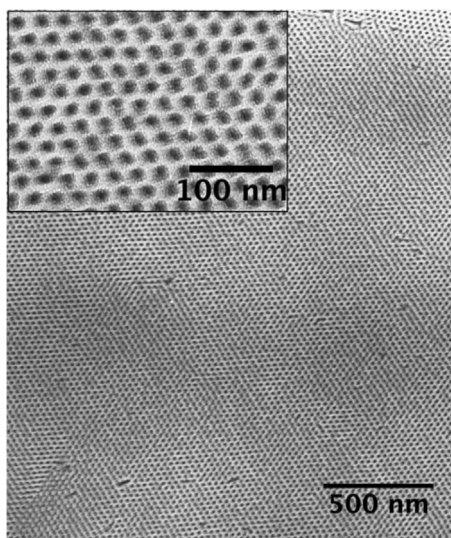


Figure 3.

Transmission electron microscopic (TEM) images of perpendicularly oriented cylinders of the SEBS triblock copolymers. The polystyrene (PS) microphase was stained with RuO_4 so that it appears dark in the TEM images. The PS cylinders are embedded in the unstained poly (ethylenebutylene) matrix and they are oriented perpendicular to the surface of SEBS film.

The 2d-SAXS pattern measured for 30 s for the collagen sample at room temperature was displayed in Figure 4(a) and the 1d-SAXS profile along the q direction parallel to the collagen fibril was shown in Figure 4(b). Many reflections up to the 11th-order peaks were clearly observed, indicating very regular ordering of the texture. Nevertheless, the TEM image of the collagen reported in the literature^[21]

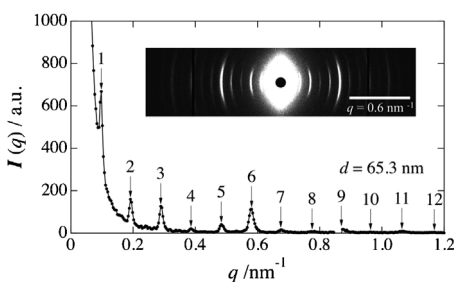


Figure 4.

2d-SAXS pattern and corresponding 1d-SAXS profile (in the q direction parallel to the collagen fibril) measured for collagen taken from chicken tendon.

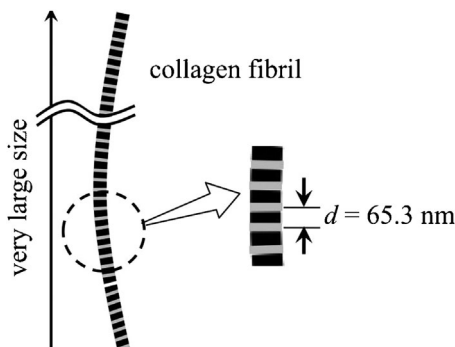


Figure 5.

Schematic illustration of collagen fibril.

shows more or less curling of the fibril, as depicted schematically in Figure 5 where the banding is due to the overlapping arrangement of tropocollagen molecules. Although the TEM image shows the bundle of the collagen fibrils are curling, the one-dimensional repeating of the texture can be considered to continue almost infinitely. Therefore, it is suggested that the collagen texture has paracrystalline feature with lattice distortion. Thus, we can consider that the grain size along the fibril direction is infinite, as the length of the bundle of the fibrils is much longer than the repeating period of the collagen texture (band spacing $d = 65.3$ nm). Based on this idea, we estimate the extent of the instrumental broadening by plotting the square of the integral width of the lattice peak as a function of the fourth power of m (the peak order with integer number), as shown in Figure 6. This plot is to evaluate the distortion factor g ($= \Delta d / \langle d \rangle$ where Δd and $\langle d \rangle$ denote the standard deviation in the spacing d and the number average of d , respectively) and the grain size, D_G , along the direction in which the lattice planes repeat. After Hosemann^[23] (from eq. (16) in ref. 23), Δq is rationalized to m as

$$(\Delta q)^2 = \left(\frac{2\pi}{D_G} \right)^2 + \left(\frac{2\pi^3 g^2}{\langle d \rangle} \right) m^2 \quad (5)$$

In Figure 6, data points with $m = 1$ to 7 were plotted. From the slope and the intercept of the approximated line, the g -factor and the grain size D_G would be evaluated,

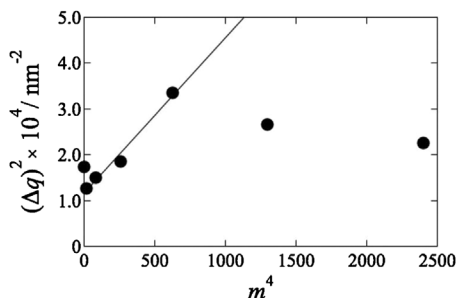


Figure 6.

Plot of $(\Delta q)^2$ vs. m^4 in order to evaluate the grain size and the g factor (the degree of lattice distortion) for the standard collagen sample, where Δq and m denote the width (integral width) of reflection peaks and the peak order, respectively.

respectively. Although unfortunately the data points with $m = 2$ to 5 can only be approximated by the straight line, $g = 0.0249$ is evaluated, indicating low lattice distortion. As discussed above, it can be assumed that the grain size (the size measured along the collagen fibril as schematically illustrated in Figure 5) is infinity. Therefore, the intercept should be zero and therefore the practical intercept of the approximated line in Figure 6 gives the contribution (B^2) due to the instrumental broadening. Note here that $B^2 = 1.16 \times 10^{-4} (\text{nm}^{-2})$ is estimated from the plot of Figure 6. This value corresponds to 3 pixels of the detector, indicating that the experimental error of determination of the peak position is ± 1.5 pixel which is sufficiently small but cause a tremendous error in the determination of size of grain with several micrometers.

In order to take into account of the contribution, Δq in eq. (5) should be taken as follows:

$$(\Delta q)^2 = (\Delta q')^2 - B^2 \quad (6)$$

where $\Delta q'$ denotes the observed peak width (integral width). Figure 7(a) and (b) show the 2d-SAXS pattern (edge view) and the corresponding 1d-SAXS profile, respectively, measured for the SEBS sample for 30 s. The 2d-SAXS pattern exhibits several reflection peaks with $1: \sqrt{3}: \sqrt{4}$ (relative q -values of the peak position) just in the

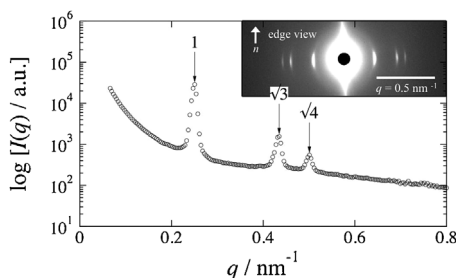


Figure 7. 2d-SAXS pattern (edge view) and corresponding 1d-SAXS profile (in the q direction perpendicular to the normal vector of the film sample, ν) measured for the SEBS film in which the PS cylinders are oriented perpendicular to the sample film.

direction perpendicular to \mathbf{n} (the film normal), indicating clearly that the hexagonal lattice of the cylindrical microdomains are oriented perpendicular to the sample film with the polygrain state likely as depicted in Figure 2. For this sample, the plot of $(\Delta q)^2$ vs. m^4 is made as shown in Figure 8 after the correction according to eq. (6). Here, it should be noted that two data points are plotted in Figure 8, although three peaks clearly appear in the SAXS profile in Figure 7. For the evaluation of the grain size according to eq. (5), peak width for m -th order peaks should be used for the evaluation. The first-order peak of the SAXS profile in Figure 7 is due to reflection by the (1 0–1 0) plane of hexagonal lattice. On the other hand, the second peak assigned with $\sqrt{3}$ is due to reflection by the (1 1–2 0) plane,

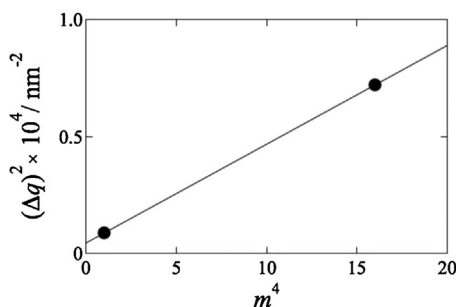


Figure 8. Plot of $(\Delta q)^2$ versus m^4 in order to evaluate the grain size and the g factor for the SEBS film in which the PS cylinders are oriented perpendicular to the sample film.

which is not the second-order peak of reflection by the (1 0–1 0) plane (i.e., $m \neq 2$).

The true second-order peak (i.e., $m = 2$) is the one assigned with $\sqrt{4}$. Therefore, only two data points are plotted in Figure 8, which are those with $m = 1$ and 2 (integer number). From the slope and the intercept of the approximated line shown in Figure 8, $g = 0.0288$ and $D_G = 3.00 \mu\text{m}$ were evaluated, respectively, for this SEBS sample. The grain size of $D_G = 3.00 \mu\text{m}$ is found to be in sufficient accord with the evaluated value by TEM with appropriate image analyses previously reported ($D_G = 2.8 \mu\text{m}$). This confirms the validity of the method proposed in this current paper.

Conclusion

The quantitative method of evaluation of the grain size using SAXS is presented. For this purpose, collagen taken from chicken leg tendon was used as a standard sample to estimate the extent of the instrumental broadening. Then this method was applied for the SEBS triblock copolymer sample in which cylindrical microdomains are oriented parallel to the surface of the film sample. The evaluated value of the grain size of the block copolymer sample was in sufficient accord with the result of the TEM observation, implying the validity of the method proposed in this current paper. Finally, it should be noted that the SAXS method requires at least two peaks. And ambiguity still exists in the result by the SAXS method in the case of using widths of only two peaks (likely as shown in Figure 8). This might imply that the SAXS method is less superior than the USAXS method utilizing the peak directly detected in the very small q range.^[15] However, this is not always true because such a peak which is due to the grain shape (i.e., the peak is resulted by form factor) becomes broader and may disappear when the distribution of grain size is wide. Furthermore, the USAXS experiment is not so easy to conduct as compared to do the ordinary SAXS experiment. Therefore, it should be

stated that the ordinary SAXS and the USAXS methods should be complementarily utilized case by case.

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- [1] F. J. Balta Calleja, Z. Roslaniec, *Block Copolymers*. Marcel-Dekker Publishers, New York **2000**.
- [2] S. Sakurai, D. Isobe, S. Okamoto, T. Yao, S. Nomura, *Phys. Rev. E* **2001**, 63, 061803.
- [3] S. Sakurai, S. Aida, S. Okamoto, T. Ono, K. Imaizumi, S. Nomura, *Macromolecules* **2001**, 34, 3672.
- [4] K. Imaizumi, T. Ono, T. Kota, S. Okamoto, S. Sakurai, *J. Appl. Cryst.* **2003**, 36, 976.
- [5] S. Sakurai, S. Aida, S. Okamoto, K. Sakurai, S. Nomura, *Macromolecules* **2003**, 36, 1930.
- [6] W. Hamley, *Developments in Block Copolymer Science and Technology*. John Wiley & Sons, London **2004**.
- [7] S. Sakurai, T. Kota, D. Isobe, S. Okamoto, K. Sakurai, T. Ono, K. Imaizumi, S. Nomura, *J. Macromol. Sci., Physics* **2004**, B43, 1.
- [8] N. Stribeck, B. Smarsly, “Scattering Methods and the Properties of Polymer Materials”, *Progress in Colloid and Polymer Science*, Springer, Heidelberg **2005**. Vol. 130.
- [9] S. Sakurai, *Polymer* **2008**, 49, 2781.
- [10] F. L. Beyer, S. P. Gido, C. Buschl, H. Iatrou, D. Uhrig, J. W. Mays, M. Y. Chang, B. A. Garetz, N. P. Balsara, N. B. Tan, N. Hadjichristidis, *Macromolecules* **2000**, 33, 2039.
- [11] C. Harrison, D. H. Adamson, Z. D. Cheng, J. M. Sebastian, S. Sethuraman, D. A. Huse, R. A. Register, P. M. Chaikin, *Science* **2000**, 290, 1558.
- [12] M. Y. Chang, F. M. Abuzaina, W. G. Kim, J. P. Gupton, B. A. Garetz, M. C. Newstein, N. P. Balsara, L. Yang, S. P. Gido, R. E. Cohen, Y. Boontongkong, A. Bellare, *Macromolecules* **2002**, 35, 4437.
- [13] X. Hu, Y. Zhu, S. P. Gido, T. P. Russell, H. Iatrou, N. Hadjichristidis, F. M. Abuzaina, B. A. Garetz, *Faraday Discuss.* **2005**, 128, 103.
- [14] H. Ohnogi, T. Isshiki, S. Sasaki, S. Sakurai, *Nanoscale* **2014**, 6, 10817.
- [15] R. T. Myers, R. E. Cohen, A. Bellare, *Macromolecules* **1999**, 32, 2706.
- [16] M. Shibayama, T. Hashimoto, *Macromolecules* **1986**, 19, 740.
- [17] T. Wolff, C. Burger, W. Ruland, *Macromolecules* **1994**, 27, 3301.
- [18] S. Sakurai, *Trends in Polymer Science*, Elsevier, **1995**, Vol. 3, p. 90.
- [19] U. Jeong, H. H. Lee, H. Yang, J. K. Kim, S. Okamoto, S. Aida, S. Sakurai, *Macromolecules* **2003**, 36, 1685.
- [20] S. Sakurai, H. Bando, H. Yoshida, R. Fukuoka, M. Mouri, K. Yamamoto, S. Okamoto, *Macromolecules* **2009**, 42, 2115.
- [21] D. F. Holmes, H. K. Graham, J. A. Trotter, K. E. Kadler, *Micron* **2001**, 32, 273.
- [22] N. Igarashi, Y. Watanabe, Y. Shinohara, Y. Inoko, G. Matsuba, H. Okuda, T. Mori, K. Ito, *J. Phys.: Conf. Ser.* **2011**, 272, 012026.
- [23] R. Hosemann, K. Lemm, W. Wilke, *Mol. Cryst.* **1967**, 1, 333. Note here that the original equation (eq. (16)) in this reference used the different type of the definition of the magnitude of the scattering vector $b (= 2\sin\theta/\lambda)$, and therefore the integral width $\delta\beta$ in terms of b in eq. (16) in this reference was replaced by $\Delta q (= 2\pi \delta\beta)$.