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Apoptotic Path of Transition between Regid Network Structures - Gyroid to Gyroid Transition in Temperature Drop -

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Abstract. We measured temperature change of the nanopatterns formed in polystyrene-*b*-polyisoprene/polyisoprene/dioctylphthalate (PS-*b*-PI/DOP) by Small-Angle X-ray Scattering (SAXS); PS-*b*-PI/DOP formed Ordered Bicontinuous Double Diamond structure (OBDD) below 70˚C and Ordered Bicontinuous Double Diamond (OBDG) above 90˚C. With a temperature drop from the temperature above 90˚C to that below 70˚C, we observed gradual decrease of scattering from OBDG and increase of that from OBDD. It seems rational simply because OBDG disappears and OBDD is formed. Surprisingly, we found an interesting change in a temperature drop from 150 to 110˚C in the OBDG region. First, the SAXS intensity increased with a constant peak position followed by a abrupt intensity drop and successively the intensity increased with the peak position shifted toward the smaller scattering-angle region with more or less constant peak width, meaning the degree of order was not altered. The abrupt intensity drop may indicate "apoptotic" vanishing; in other words, a new OBDG phase was formed in the former OBDG phase by a nucleation and growth.

1. Introduction

A Block Copolymer is a polymer in which different polymers are connected mostly by the covalent bonds; each constituent polymer is called a block chain or simply a block. Even if the block chains undergo phase separation, they do not macroscopically separate but microscopically because of the connectivity between the blocks; thus the phenomenon is called "microphase separation". Consequently, they form periodical nanopatterns with a variety of morphologies, such as alternating lamellae, hexagonally close-packed cylinders, spheres on a body-centered cubic lattice and some bicontinuous network structures. These structures are recently applied to industrial use. Thus, it is important to investigate a temperature dependence of the nanopatterns including order-disorder and order-order transitions between above-mentioned morphologies. Here, we found an interesting temporal structure change after a temperature drop within the temperature region where OBDG is kept, using the time-resolved SAXS with a very short time interval (15 sec).

2. Materials and Method

2.1 Sample

A polystyrene-*b*-polyisoprene diblock copolymer (SI0426; M_n = 45000, f_{PS} = 0.70), and a polyisoprene homopolymer (PI0313; M_n = 18000) were synthesized by the living anionic polymerization under vacuum. Here, M_n and f_{PS} are a number-averaged molecular weight and a volume fraction of polystyrene. Dioctyl phthalate (DOP) was added to the blend, SI0426/PI0313 (=75/25 wt./wt.), by 40 wt.%, denoted SI/PI/DOP(45/15/40). The total volume fractions of polyisoprene were 48.9 %.

2.2 Small-Angle X-ray Scattering

SAXS after a temperature drop was measured for 10 sec with a time interval of 15 sec by imaging plates (R-AXIS IV, Rigaku) and PILATUS 100K (Rigaku) at BL8S3 of Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan. Temperature equilibrium was achieved within ca. 30 sec.

3. Results and Discussion

The SAXS from SI/PI/ DOP(45/15/40) was measured at temperatures from 30 to 150˚C with the step of 20˚C. Above 90˚C, the profiles showed multiple scattering peaks; the relative peak position ratios to the primary peak was close to $1:\sqrt{8/6}:\sqrt{14/6}:\sqrt{16/6}:\sqrt{20/6}:\sqrt{22/6}$ that are typical to an ordered bicontinuous double gyroid (OBDG) structure, while those below 70 ˚C showed multiple peaks; the relative peak position ratios to the primary peak were $1:\sqrt{3/2}:\sqrt{4/2}:\sqrt{6/2}:\sqrt{8/2}$ typical to an ordered bicontinuous double diamond (OBDD) structure. The temperature dependence of the peak positions, i.e., the periods of the nanopatterns, *d*, were negligibly small compared with the other morphologies; generally, the others show $d \sim T^{-1/3}$. Here, *T* is an absolute temperature. This indicates that the OBDG and OBDG are more rigid against temperature change than the others.

The time-resolved SAXS from SI/PI/ DOP(45/15/40) was measured with a very short time interval of 15 sec. Figures 1(a) to 1(d) shows the SAXS patterns obtained at 0, 30, 90 and 585 sec after the temperature drop from 150 to 110˚C. The temperature equilibrium was attained within 35 sec after the drop during the measurement of the pattern shown in Figure 1(b). Although all the SAXS patterns have spot-like intensities as shown in Figure 1, the overall shape of the patterns were identical to each other; the orientation of grains were unchanging during the process. Therefore, we analyze and discuss the data with circular-averaged profiles.

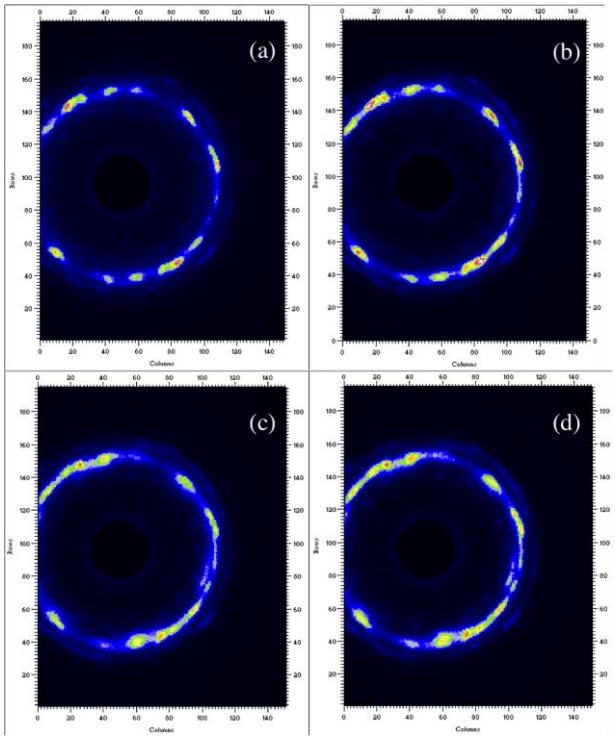

Fig. 1 SAXS patterns obtained at 0 (a), 30 (b), 90 (c) and 585 sec (d).

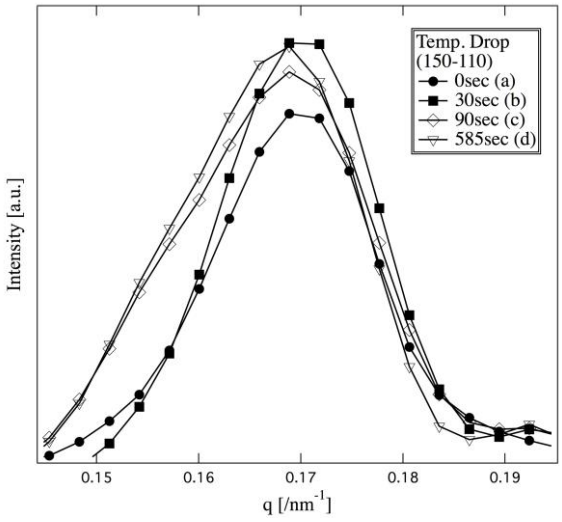

Fig. 2 Circular averaged profiles obtained at 0 (a), 30 (b), 90 (c) and 585 sec (d).

The circular-averaged 1D profiles obtained from the 2D-SAXS corresponding to Figure 1(a) to 1(d) are shown in Figure 2. It is seen that SAXS intensity increases for ca. 30 sec during the temperature drop from 150 to 110˚C, followed by the abrupt intensity drop. Successively, the intensity increased gradually for ca. 8 min.

Here, we evaluated the maximum SAXS intensities (I_m) of the first peak, the peak positions (q_m) and the full width at half maximum (σ) quantitatively, as shown in Figure 3(a) to 3(c), respectively. Note that inverse squared width ($1/\sigma^2$) was plotted in Figure 3(c) because it corresponds to correlation length of the concentration fluctuation in the nanopattern, i.e., the degree of order; the longer the correlation length is, the higher the degree is. The maximum SAXS intensity increased during the first ca. 30 sec after the temperature drop, while the peak position slightly shifted toward the larger q region: The temperature decrease for the first 35 sec enhanced the segregation power and hence the scattering contrast, while the structure was thermally shrunk during the short time. Generally, the domain spacing, i.e., the period of the nanopattern should increase under the stronger segregation power, but in this case, it involves large-scale chain rearrangement because the network domains are percolated throughout the sample. That is why it may have some difficulty in increasing the size of the strucuture; this is in good agreement with the indication that OBDG is rigid as mentioned above. Therefore, the previous structure may have to be apoptotically abandoned for a new structure to be formed as evidenced by the abrupt decrease during the next 60 sec and the successive gradual increase of the peak intensity.

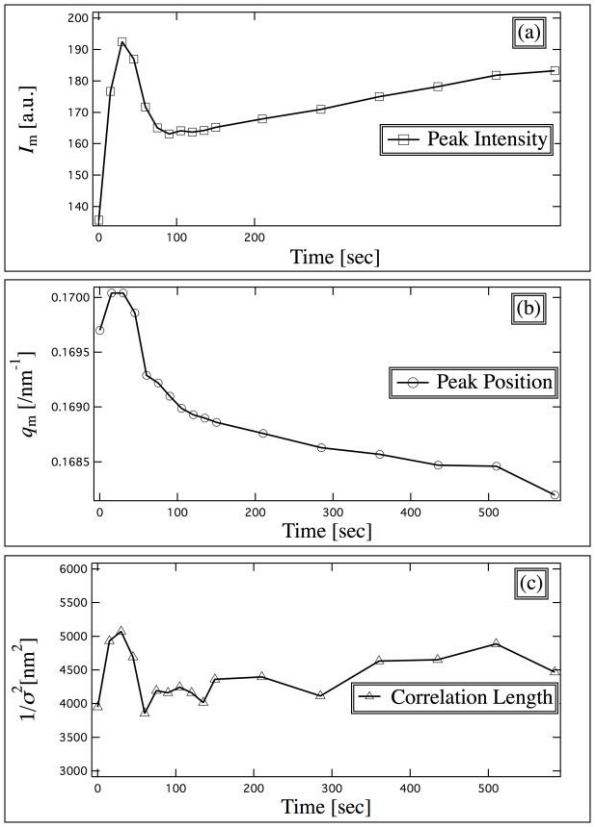

Fig. 3 (a) the SAXS intensities (I_m) of the first peak, (b) the peak positions (q_m) and (c) the full width at half maximum (σ)

It is also worthy to note that the value of $1/\sigma^2$ was more or less constant though it scattered a little bit, indicating the order of the structure was sustained. Therefore, it can be said that the structure did not change via short-range disordering. The total vanishing, i.e., the apoptosis and the formation of the new OBDG were necessary to change the period.

4. Conclusion

The time-resolved SAXS from SI/PI/ DOP(45/15/40) was measured with a very short time interval of 15 sec. It was found that the OBDG structure is too regid to change its period. Consequently, the previous OBDG abruptly disappeared (apoptosis) and the new OBDG was formed as revealed by the sudden drop and gradual increase of the SAXS.

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References

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