Surface Fractals in Block Copolymers

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ABSTRACT: A surface fractal model was presented to describe the interface in block copolymers. It gives a simple power-law relationship between the scattering intensity $I(q)$ and the wave vector $\mathbf{q}$ in a relatively wide range as $q\xi \gg 1$, $I(q) \propto q^{D-6}$, where ξ is the length characterizing the size of the structure producing scattering, D is the fractal dimension of the interface. Small-angle X-ray scattering experiment results of both linear and star styrene–butadiene–styrene triblock copolymers show that the model is quite reasonable. It seems that the interface constructed by the joints of different blocks is a fractal surface with a fractal dimension D from 2 to 3.

Introduction

Block copolymers have gained more and more interests during the past decades.[1–3] Both their morphology and properties have been studied widely. Usually, the block copolymers exhibit a multiphase structure at room temperature. As shown in Figure 1, when the volume fraction varies, the microdomain exhibits sphere, cylinder, optical bicontinuous double diamond, and lamellar morphology.[4] For a binary composition block copolymer, such as styrene–butadiene–styrene triblock copolymers, a clear two-phase system can be observed, as shown in Figure 2 where the white spots are styrene while the black matrix is butadiene. However, up to now, the description of the interface in block copolymers is still somewhat questionable. Despite the fact that the mechanism of the formation of microdomains in block copolymers suggests that the interface must be irregular, classical models have treated the interface as if it is a smooth wall.[2,3]

This can be traced back to Porod.[5] In small-angle X-ray scattering (SAXS), the information of the surface structure can be obtained by measurements of the intensity $I(q)$ in the relatively large scattering angle region known as Porod's region, where $q = 4\pi \sin(\theta/2)\lambda^{-1}$ is scattering vector with scattering angle θ and the wavelength λ. In this region, $I(q) \sim q^{-4}$ for a smooth and sharp boundary, which is known as Porod's law. To some extent, the idealization results from the lack of theories for the geometrical interpretation of structures with random geometry. Nevertheless, this "flat sharp surface" idealization has caused both quantitative inaccuracies in interpretation and conceptual difficulties.[6,7] Many materials give scattered intensities in Porod's region that have the form given by $I(q) \sim q^{-\alpha}$ with an exponent α that is not equal to 4.

The situation has been changed since the fractal concept was presented.[8] Fractal geometry has recently provided a solution of the structures with random geometry. This solution is based on a very simple power–law relation between the magnitude of a measurable property and the size of the yardstick used to measure this property. These power laws are so common in nature that the fractal concept has been applied in a surprising wide scope.[9,10] The fractal concept was first introduced to small-angle scattering studies by Schmidt et al.[11,12] Their valuable investigation has provided a key to understand the structure of the disordered, porous, and fractal systems,[13,14] especially the irregular surface resulting in deviation from the Porod law. However, such systems investigated mainly concern colloids and silicas. As for polymers in a condensed bulk state, apart from a few exceptions,[15,16] there is still lack of the description of the random geometry based on the fractal concepts, for example, the interface in block copolymers.

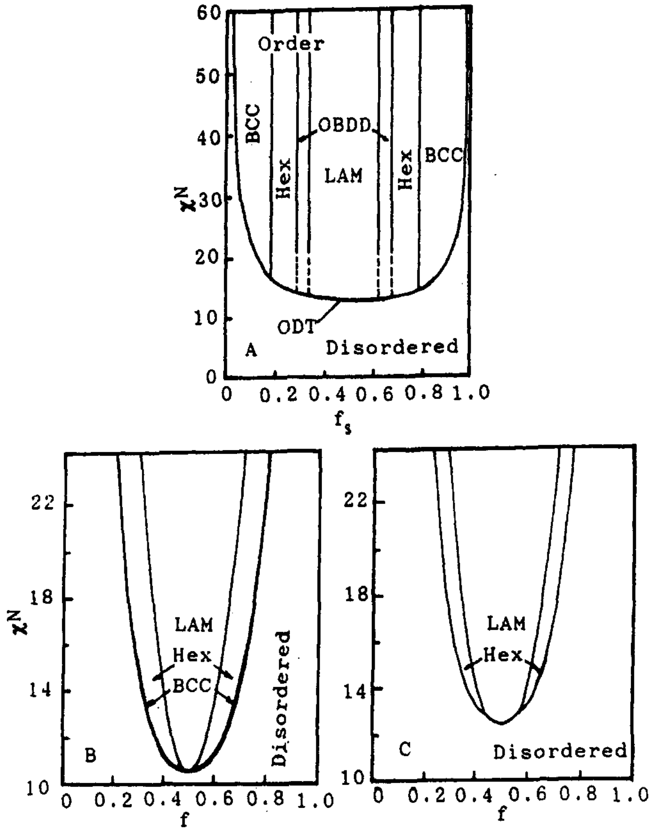

Figure 1. (a) Experimental phase diagram for polystyrene–polyisoprene (PS–PI) diblock copolymers.[4] (b) Theoretical meaning-field phase diagram for diblock copolymers. (c) Fluctuation–corrected mean-field phase diagram.

In this paper, a fractal model was first presented to describe the irregular interface in block copolymers. The physics of the model was manifested by small-angle X-ray scattering data from six triblock copolymers with different molecular weights and architectures. The deviation from Porod's law was reported in the light of fractal. The measurements showed that on a length scale smaller than the average microdomain radius but larger than the diameters of atoms or small molecules, the interfaces in these six triblock copolymers are fractals and have a fractal dimension D from 2 to 3. It demonstrates that a fractal description of the irregular interface in block copolymers is quite reasonable.

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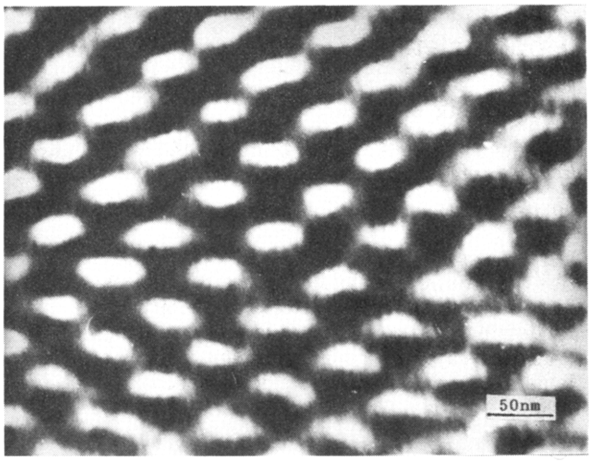

Figure 2. Electron micrographs of OsO_4-stained ultrathin sections of SBS-28 triblock copolymer film cast from toluene solution.

Table 1. Triblock Copolymer Characteristics

designation used here	commercial designation	end-block M_W	midblock M_W	wt % PS
SIS-14	18,292–3	14 000	172 000	14
SBS-28	20,054–7	10 000	51 000	28
SBS-30	18,287–7	24 000	112 000	30
SBS-48	exptl	28 000	60 000	48
SBS-37	exptl	25 000	85 000	37
SB-37-4A	exptl	23 000	39 000	37

Experimental Section

Materials. The triblock copolymers used in present paper, SIS-14, SBS-28, and SBS-30, are commercial products of Aldrich Chemical Co. The others were synthesized in our laboratory via anionic polymerization. The molecular parameters are shown in Table 1.

Preparation of Samples. The six triblock copolymers were first dissolved into toluene with a polymer concentration of 3 wt %. The solutions were then allowed to stand overnight after several hours of stirring until clear solutions were obtained. Next, these solutions were cast into a TFE model and allowed to evaporate slowly at the room temperature under a dry atmosphere. Films obtained in such a way were dried further in a vacuum oven at 80 °C for at least 1 week and cooled to the room temperature slowly before the small-angle X-ray scattering experiments were carried out for them.

Measurement. The small-angle X-ray scattering experiments were carried out on the Karatky Compact Small Angle System with a stationary-anode copper-target X-ray tube (wavelength 1.542 Å) at room temperature. The fine-focus X-ray generator was operated at 45 kV and 40 mA. The measured intensity was desmeared and corrected for background scattering and photoelectric absorption in the sample.

Fractal Description of the Interface in Block Copolymers

The interface in block copolymers has been viewed as an "interphase" between different microdomains with a thickness of 10–20 Å.[2,3] The interphase is composed of different kinds of segments so that it is also called "transition layer", which has been viewed as a smooth, smear wall. Under this idealization, the deviation from Porod's law has been attributed to the thickness of the interphase.[17] After introducing a smoothing function to the electron density profile, the thickness of the interphase can be determined. Obviously, this consideration has neglected the detailed structure of the interface because only the average effect has been considered. The fact is that the interface made from the joints of different kinds of segments is an irregular sharp surface. Nevertheless, since there was a lack of theories to describe such a kind of surface at that time, the forerunners had to view it as a smooth, smear surface of thicknesses in order to make it simple.

Now, we know the real morphology of the interface in block copolymers, a sharp irregular surface, and describe it in terms of fractals. As shown in Figure 2, the binary block copolymer consists of a three-dimensional dispersed phase in the matrix of the continuous phase. If n_1 and n_2 represent the scattering amplitudes for the dispersed phase and the matrix, respectively, and the matrix occupies a fraction ϕ of the sample volume V, then the scattered intensity can be given by[18]

$$I(q) = 4\pi\langle\eta^2\rangle V\int_0^\infty r^2\gamma(r)\sin(qr)/(qr)\,dr \qquad (1)$$

where $\gamma(r) = \langle\eta(0)\eta(r)\rangle/\langle\eta^2\rangle$ is the correlation function and $\eta(r) = n(r) - \langle n\rangle$ describes the fluctuation of the scattered amplitude $n(r)$ from the average value $\langle n\rangle$. For the binary block copolymers, $\langle n\rangle = \phi n_2 + (1-\phi)n_1$. As suggested by Dybye et al.,

$$\gamma(r) = 1 - Z(r)/(2\phi(1-\phi)) \qquad (2)$$

where $Z(r)$ is the probability of placing a rod of length r randomly in the two-phase system and having its two ends be in different phases. For small r, one has

$$Z(r) = Sr/(2V) = V_b/(2V) \qquad (3)$$

where S is the surface area and V_b is the volume of a boundary layer of thickness r at the surface in which one end of the rod must lie for it to penetrate the surface.

Supposing that the interface in block copolymers is a fractal surface, according to the definition of the fractal or Hausdorff dimension D of the fractal surface, as r approaches zero, the number N of spheres needed to cover all points of the fractal surface can be given by

$$N = N_0 r^{-D} \qquad (4)$$

where N_0 is a constant to characterize the fractal surface. The area of the interface can be expressed as

$$S = 4\pi N_0 r^{2-D} \qquad (5)$$

Thus, the domain boundary region has the volume

$$V_b = \int_0^r S\,dr = 4\pi N_0 r^{3-D}/(3-D) \qquad (6)$$

Combining eqs 3 and 6, it is found that

$$Z(r) = 2\pi N_0 r^{3-D}/(V(3-D)) \qquad (7)$$

Then one finds from eq 1 for $q \neq 0$

$$I(q) = -4\pi^2\langle\eta^2\rangle N_0/[\phi(1-\phi)(3-D)]\int_0^\infty r^{5-D} \times \sin(qr)/(qr)\,dr \qquad (8)$$

For large q, one can use the Erdelyi's theorem for asymptotic expansion of Fourier integrals.[19] Then

$$I(q) = 4\pi^2 N_0\langle\eta^2\rangle/[(\phi(1-\phi)]\Gamma(5-D) \times \sin(\pi(D-1)/2)q^{D-6}/(3-D) \qquad (9)$$

Under this approximation, $I(q)$ is proportional to q^{D-6} in the large q region, where D is the fractal dimension of the interface in block copolymers. For a smooth domain

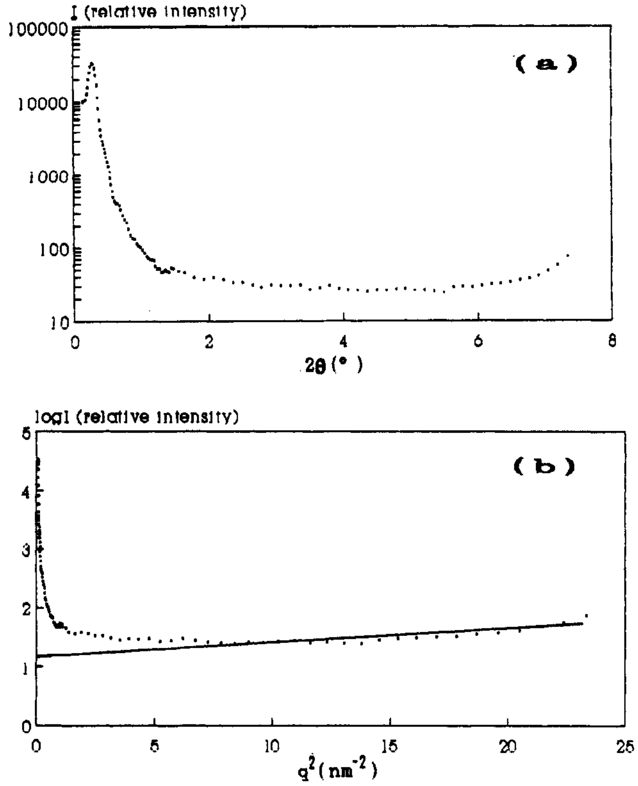

Figure 3. (a) SAXS curve for SIS-14 in the larger angle region. (b) log $I(q)$ vs q^2 plot of the SAXS curves for SIS-14; the solid line is subtracted to get $I(q)$.

boundary surface with $D = 2$, one gets the Porod's estimation for $I(q)$, $I(q) \propto q^4$. While as D approaches 3, it can be deduced that $I(q) \propto q^3$.

Since eq 9 neglects the short-range atomic structure in the sample, it does not apply when q is large enough to permit resolution of structures with atomic dimensions. On the other hand, for the use of the approximation to get eq 9, it is needed to estimate $q_{\min}$, the smallest value of q at which eq 9 describes the scattering. Because $q_{\min}$ is determined by the average domain dimension ξ, a length scale in which eq 9 holds is essentially fixed once the domain and the atomic size are ascertained. This will be discussed in detail afterward.

In the next section, the scattering behavior of six triblock copolymers in the large q region is discussed according to eq 9. The relationship between the length scale in which eq 9 holds and the molecular parameters is manifested; the physics of D for the interface of block copolymers is also discussed.

Results and Discussion

Figure 3a shows the SAXS intensity $I(q)$ for the neat SIS-14 triblock copolymer. The gradual increase in $I(q)$ at large angles comes from the tail of the amorphous halo, multiple scattering, and the density fluctuation with long wavelength. It is shown that $I(q)$ at this region can be fitted empirically by[20]

$$I(q) = a \exp(bq^2) \tag{10}$$

In Figure 3b, the logarithm of the intensity $I(q)$ obtained from SIS-14 is plotted against q^2, the linear relation exhibited by the larger angle data indicates the validity of eq 10. The intensity $I(0)$, obtained by extrapolation of the linear region in Figure 3b to $q = 0$, represents the extent of the thermally induced density fluctuation present in homogeneous liquids. In the all scattering data shown hereafter, the observed intensity has been corrected for the background by subtracting $I(0)$, the contribution of the thermal density fluctuation.

In the scattering curves for all of the triblock copolymers, there is a relatively wide region in which the scattering behavior can be described by a power law like eq 9, as shown in Figure 4. However, the length scale in which eq 9 holds is different from sample to sample. In Table 2, we list the fractal dimension D calculated by least-square fits of eq 9 over the length scale $q_{\min} < q < q_{\max}$.

From the results, it is obvious that the length scale in which eq 9 holds varies from sample to sample. The upper point $q_{\max}$ depends on the size of the atomic or the small molecules with definite physics, while the low point $q_{\min}$ is somewhat obscure. Many researchers ascertained it by least-square fits other than determined according to its physical essence. Schmidt et al. have first found out that the range of length scale varies with pore size; unfortunately, they have not given an explicit interpretation.[21] As the materials used in previous investigations are disordered systems, there is only one peak in the scattering curve which characterizes the size of the structure producing the scattering; the ignorance of the physical meaning of the $q_{\min}$ has not brought into effect the investigations of those fractal structures. However, the block copolymer studied here is an ordered system; there are usually several high-order peaks in the scattering curve. Neglecting of the physical meaning of $q_{\min}$ will lead to a completely contrary conclusion. First, the derived eq 9 describes the scattering behavior of a structure with fractal surface; it is necessary to determine the part in the scattering profile that reflects the information of the structure. In the present paper, the fractal surface is supposed to be the domain boundary; therefore, only the part that reflects the scattering of the isolated domains can be described by eq 9. For block copolymers, the first- and second-order peaks are due to the intraparticle interference of the single spherical microdomains at q's satisfying $qR = 5.765$ and 9.10, where R is the average radius of the spheres. As for the cylindrical microdomain,[22] there is $qR = 5.03$ for the first-order peak arising from the intraparticle interference of the single cylinder, as marked by thick arrows in Figure 5. Furthermore, one can expect that the features in the interface cannot be larger than the radius of the spherical or the cylindrical microdomain. Thus, we have

$$q_{\min} \geq 5.765/R \tag{11}$$

and

$$q_{\min} \geq 5.03/R \tag{12}$$

for spherical and cylindrical microdomains, respectively. As for the lamellar domain, since the relationship describing the intralamellar interference is not available, after approximated with $qd = 6.283$, where d is the periodicity, similar equation can be obtained

$$q_{\min} \geq 6.283/d \tag{13}$$

In column 3 of Table 2, we have listed the values of radii for PS spheres and cylinders and the size of PS lamellars obtained from the SAXS curves. Compared with the results in column 4, the values of R_S are very close to the maximum size of the features which resemble self-similarity in the interface, as deduced from eqs 11–13 by submitting $q_{\min}$ in column 5. As for the peaks marked

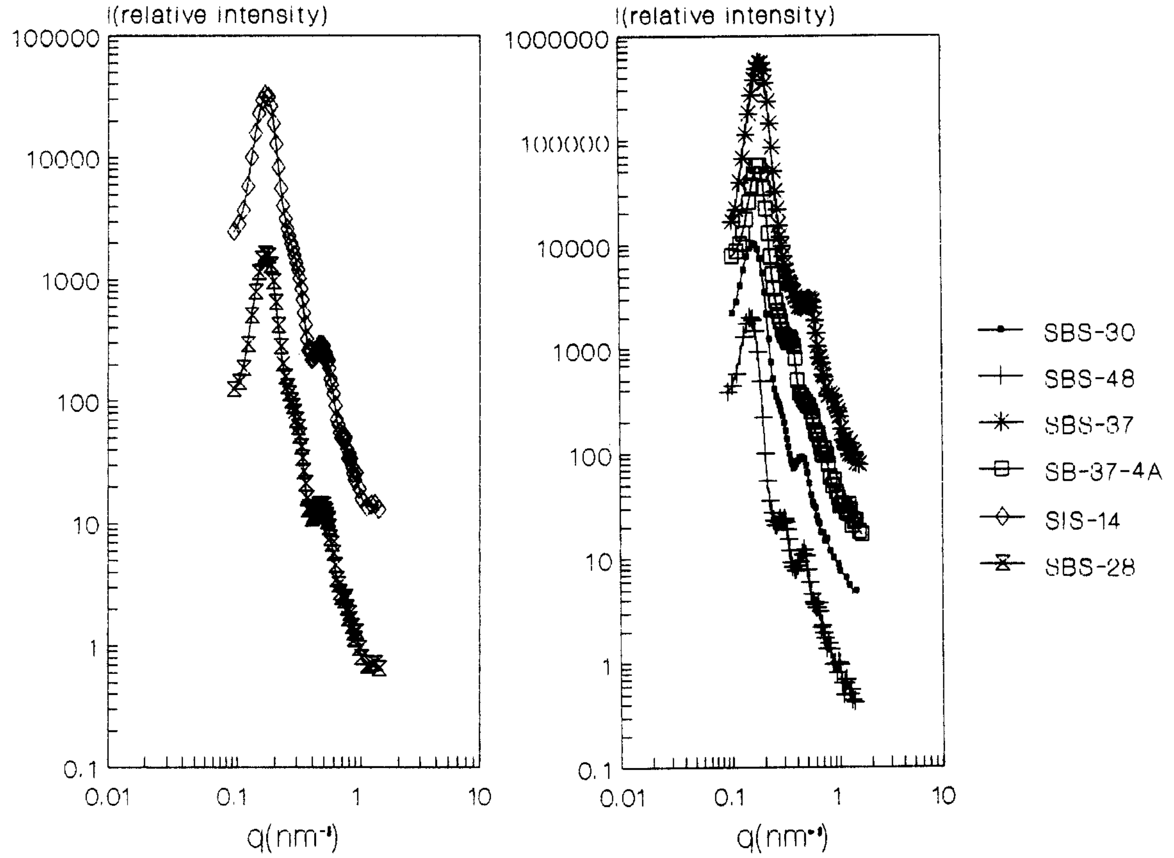

Figure 4. Small-angle X-ray scattering curves for the triblock copolymers. The curves has been displaced vertically by different distances in order to avoid crowding the plot.

Table 2. Fractal Dimension D calculated from the Scattering Curves

sample	domain morphology	domain spacing R_S (Å)	size of feature (Å)	q_{min} (nm^{-1})	q_{max} (nm^{-1})	D
SIS-14	sphere	135.7	134.0	0.43	1.43	2.24
SBS-28	cylinder	100.0	98.6	0.51	1.39	2.09
SBS-30	cylinder	118.0	123.0	0.41	1.67	2.18
SBS-48	lamellar	178.0^a	169.8	0.37	1.39	2.09
SBS-37	lamellar	110.0^a	114.2	0.55	1.67	2.12
SB-37-4A	lamellar	110.0^a	114.2	0.55	1.77	2.38

^{a} Size of the PS lamellar domain.

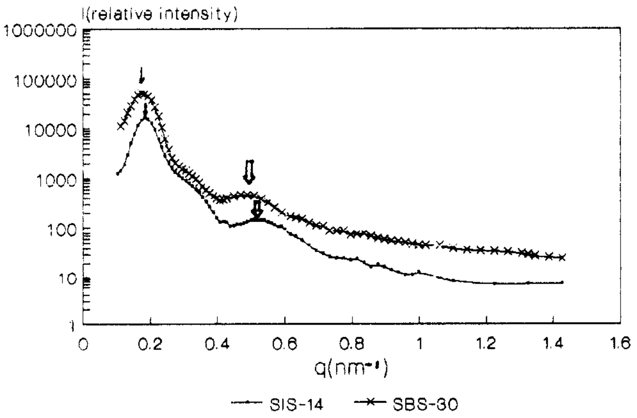

Figure 5. Small-angle X-ray scattering curves for the triblock copolymers SIS-14 and SBS-30 showing interparticle and intraparticle interference.

with thin arrows in Figure 5, they reflect the information between domains, due to interparticle interference of the microdomains. In this part of the curve, the scattering behavior should not be described by eq 9. Even though it can be described by eq 9, we still have to discard the

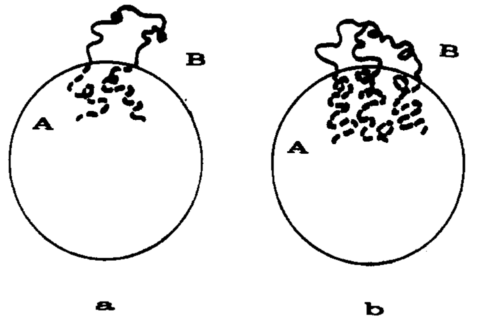

Figure 6. Schematic representations of microphase separation in (a) a triblock copolymer and (b) a three-arm star block copolymer.

data since the feature in the interface should not be larger than the radius of the microdomain.

The results have also shown that both linear and star triblock copolymers exhibit a fractal interface. Nevertheless, the fractal dimension and the length scale are different as the molecular architecture changes. Star SB-37-4A is of a higher fractal dimension than that of the linear SBS-37. Although q_{min} is the same for both linear and star copolymers, q_{max} for star SB-37-4A is much larger than that for the linear SBS-37. As shown in Table 1, both block copolymers have the same weight fraction of PS and almost equal total molecular weight of PS blocks. Thus, the differences can only be attributed to the change of the molecule architecture. According to the theory of Helfand,[24-27] the molecular architecture has much effect on the domain boundary. For triblock copolymer, any chains in the domains have two joints in the interface region while the other ends are free, as shown in Figure 6. The thermodynamic requirement of uniform density in the domains can be salified if the chains possess some unfavorable conformations that entail entropy loss. In the case of a linear triblock copolymer, only each central block has two joints in the surface region, while for the three-arm star block copolymer, besides the restriction of keeping the A–B joints in the interface region, the common joint for the three central blocks results in a structure that entails even more entropy loss for keeping uniform density in a much more complex interface for star block copolymer as compared with that of the linear triblock copolymer. This may be also why the value of q_{max} for star SB-37-4A is much larger than that for linear SBS-37.

It is also found that the fractal dimension of SIS-14 is larger than that of other linear triblock copolymers. Since D is a parameter describing the irregularity of the interface, we can only find the reason among the differences between SIS-14 and other linear triblock copolymers that greatly affect the interface morphology in the block copolymers. It is argued that the interphase thickness a_I is equal to $(2/6^{1/2})b/\chi$ for a symmetric pair of polymers, where b is the Kuhn statistical length and χ is the interact parameter. a_I is related to t (the interphase thickness measured by Hashimoto et al.[2]) in the expression[24]

$$a_I = (2/\pi)t = 0.637t \qquad (14)$$

Thus, the interphase thickness in block copolymers is actually proportional to the reversion of the interaction parameter χ between different blocks. Since χ_{SI} is smaller than χ_{SB}, the interface in SIS-14 should be much more complex than that in SBS triblock copolymers with the same molecular architecture.

The size of the microdomain in block copolymers is determined by the molecular weight, the weight fraction of one block, and the molecular architecture.[25-27] Thus, both q_{min} and q_{max} are essentially determined by the molecular parameters. Therefore, the length scale $q_{min} < q < q_{max}$ for which eq 9 holds is of definite physics; it is actually the span of the size of the feature that resembles self-similarity in the interface in block copolymers. While the fractal dimension D, obtained in the length scale, is a description of the roughness of the interface, it is also a portrait of the interaction between different blocks as it is sensitive to the interaction parameter χ. As for the architecture of the molecules, it has an effect on both the length scale and D. One can then see the fractal dimension D of the interface in block copolymers and the length scale in which D exists essentially describes the characteristics of the block copolymers, including architectures, molecular weights, and interaction between blocks.

Conclusion

We have first viewed the interface in block copolymers as a irregular, rough, sharp surface instead of a smooth, smear wall with thickness. The irregularity of the interface is described in the term of fractals; this eventually leads to a power-law relationship between $I(q)$ and q in the large q region which is similar to Porod's law, where D is the fractal dimension. The length scale $q_{min} < q < q_{max}$ in which the relationship holds is determined by the size of the fractal structure producing scattering and that of the atoms or the small molecules. A series of block copolymers has been studied using small-angle X-ray scattering technique, the experimental data in the large q region have been found to be well described by the surface fractals other than Porod's law. The fractal dimension D is sensitive to the interaction parameter χ and the molecular architecture. As for the length scale $q_{min} < q < q_{max}$, q_{min} is determined by the molecular weight, the weight fraction of one block, and the molecular architecture of block copolymers, while q_{max} is determined by the size of the atoms or the small molecules. Thus, D and the length scale can describe not only the feature in the interface but also reflect the properties of the block copolymer molecules.

In one word, our experimental results have shown that a fractal description of the interface in block copolymers is reasonable. In a companion paper,[28] the differences in physics between the fractal and the traditional descriptions of the interface in block copolymers were manifested.

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