Preparation and morphology of multiblock copolymers of the $(AB)_n$ type

Yushu Matsushita*, Yasuhiro Mogi†, Hiroaki Mukai‡, Jun Watanabe and Ichiro Noda
Department of Applied Chemistry, Nagoya University, Furo-cho Chikusa-ku,
Nagoya 464-01, Japan
(Received 6 May 1993)

Styrene(S)–isoprene(I) multiblock copolymers of the $(SI)_n$ type ($n=1, 2, 3, 4$) were prepared by a multistep monomer addition technique of anionic polymerization. Molecular weights of SI diblock units are almost the same and the total polystyrene volume fractions are about 0.5. All the film specimens cast from toluene solutions were found to have alternating lamellar structures. The lamellar domain spacing monotonically decreases and approaches an asymptotic value with increasing the number of blocks.

(Keywords: multiblock copolymers; styrene; isoprene)

INTRODUCTION

It is well established that AB diblock copolymers with incompatible components form microphase-separated structures in bulk and the morphologies change systematically with the composition of block components[1–5]. Among several basic morphologies, alternating lamellar structures have been most extensively studied, and it is known that the lamellar domain spacing D increases with increasing the molecular weight M as

$$D \propto M^a \tag{1}$$

where the exponent a is 2/3 or very close to 2/3 in the strong segregation limit[6–11]. Moreover, the single-chain conformation of a block polymer in this structure was studied, and it was concluded that the chain is elongated toward the direction perpendicular to the lamellae[12,13], while it shrinks along the longitudinal direction[12–14] so as to compensate for the expansion.

The feature of AB multiblock copolymers of the $(AB)_n$ type in microphase-separated structures is to have inner block polymers, like a B block polymer of ABA triblock copolymers, which exhibit either a 'bridge' or a 'loop' conformation in contrast to block polymers of AB diblock copolymers, which have a free chain end. In this work, therefore, we studied the microdomain spacings of di-, tetra-, hexa- and octablock copolymers of the $(AB)_n$ type ($n=1, 2, 3, 4$) with well defined molecular structures, in comparison with those of diblock copolymers.

EXPERIMENTAL

Preparation and characterization

Multiblock copolymer samples were prepared by a multistep monomer addition technique of anionic polymerization; styrene and isoprene were alternately polymerized in benzene as a solvent with *sec*-butyllithium as an initiator at 30°C *in vacuo*. The monomers and benzene were purified in the same manner as reported previously[15]. A small amount of solution was removed from the polymerization vessel every time after the complete consumption of isoprene monomer to obtain precursors, of which the molecular weights and the compositions were determined.

The number-average molecular weight, M_n, of multiblock copolymers and their precursors was measured with a Hewlett Packard High Speed Membrane Osmometer type 502. Their molecular weight distributions were measured with a Tosoh Gel Permeation Chromatography type 802A equipped with two GMH_{XL} columns. Polystyrene contents were determined with a Simadzu UV spectrometer type UV-8.

Morphological observation

Film specimens for small-angle X-ray scattering (SAXS) measurements and transmission electron microscopy (t.e.m.) were prepared by solvent-casting from a dilute solution of toluene, which is a common good solvent for both block components. The film specimens were completely dried under vacuum at room temperature, and some of the specimens were annealed at 120°C for more than a week to attain equilibrium. Hereafter, they are called as-cast films and annealed films, respectively. SAXS measurements were carried out at room temperature (25°C) with a Kratky U-slit camera (Anton Paar Co.), equipped with a step scanner and a scintillation counter. The widths of entrance and counter slits were 100 and 250 μm, respectively. X-rays were incident toward the direction parallel to the film surface ('edge' view). The measured intensities were desmeared by the method of Strobl[16]. The microphase-separated structures in ultrathin sections cut normal to the surface of film specimens stained by osmium tetroxide were observed directly using a transmission electron microscope Jeol Model 2000FX. Details of these experimental procedures were reported previously[11,17].

---

* To whom correspondence should be addressed

† Present address: Idemitsu Petrochemical Co., Ltd, 1-1 Anesaki-kaigan, Ichihara, Chiba 299-01, Japan

‡ Present address: Nippon Carbide Industries Co., Inc., 751 Motoshin, Uozu, Toyama 937, Japan

0032-3861/94/020246-04

RESULTS

The molecular characteristics of samples are summarized in *Table 1*. The sample $(SI)_1$ is actually a precursor of $(SI)_2$ and the sample $(SI)_3$ is a precursor of $(SI)_4$, both obtained by the procedure described in the Experimental section. The numbers in the middle column denote M_n values of each SI diblock unit and they are in good agreement with the calculated values. The polydispersity indices, M_w/M_n, indicate that the molecular weight distributions of all the block copolymers are narrow. The volume fractions of polystyrene block, ϕ_s, are the average values for the whole molecules. Since ϕ_s values for the first and second SI units in the hexablock copolymer were determined to be 0.54 and 0.52, respectively, we can see from this table that the ϕ_s values of every SI unit of all the samples are around 0.5.

As shown by the typical t.e.m. images for the as-cast films given in *Figure 1*, all the film specimens have an alternating lamellar structure, though the micrographs for tetra- and hexablock copolymers are not shown here. Desmeared SAXS intensities from the annealed films of multiblock copolymers with different numbers of blocks at the edge views are shown in *Figure 2*. The data for diblock, tetrablock, hexablock and octablock copolymers are shown from top to bottom. Peaks of integer-order are observed in every intensity curve, though the heights of peaks for multiblock copolymers are lower than those of diblock copolymer, reflecting the fact that the orientation of the former lamellae to the film surface is worse than that of the latter one.

The domain spacings D for both as-cast and annealed films were evaluated by applying the Bragg condition to the magnitudes of the scattering vector at each peak position. They are summarized in *Table 2* and plotted against the number of blocks in *Figure 3*. *Table 2* and *Figure 3* indicate that D decreases with an increasing number of blocks and the D values of annealed films are significantly larger than those of as-cast films. The latter result indicates that non-equilibrium factors significantly affect the domain size of as-cast films.

DISCUSSION

The dependence of D on the number of blocks can be understood if we consider the effective number-average

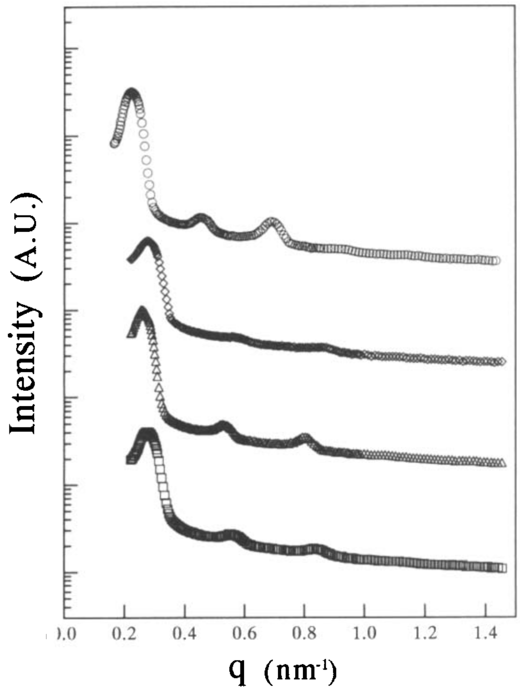

Figure 2 Comparison of SAXS intensity profiles of multiblock copolymers with different numbers of blocks. From top to bottom, the profiles, which are shifted vertically to avoid overlapping, are for $(SI)_1$, $(SI)_2$, $(SI)_3$ and $(SI)_4$

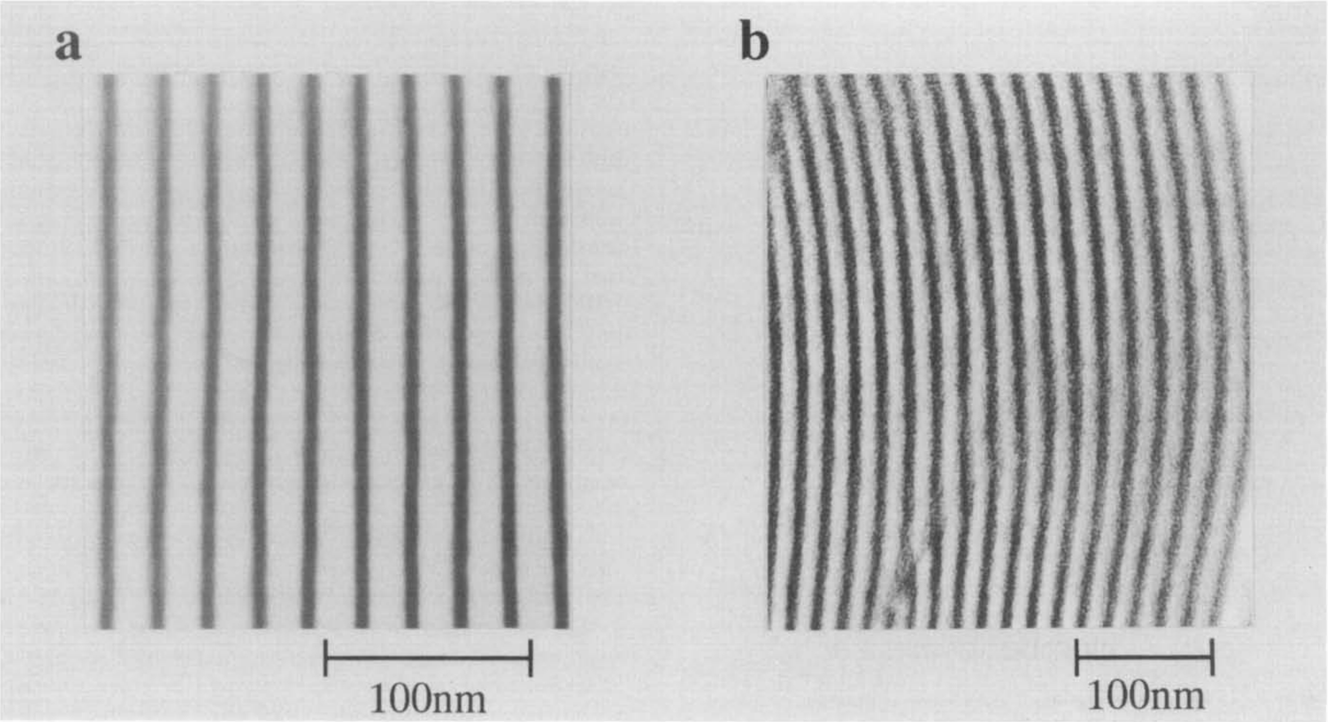

Figure 1 Examples of transmission electron micrographs of block copolymers. Samples: (a) $(SI)_1$ diblock copolymer; (b) $(SI)_4$ octablock copolymer

molecular weight of block chains which constitute one pair of lamellae. In the case of $n=1$, that is, AB diblock copolymers, the domain spacing consists of two molecules along the direction normal to lamellae so that the repeating unit is A–BB–A as shown in *Figure 4a*, and the lamellar domain spacing–molecular weight relationship is well understood by the theories of microphase separation in the strong segregation limit. In the other extreme case, that is, in the case of the multiblock copolymers with $n=\infty$, on the other hand, the repeating unit is A–B as shown in *Figure 4b* and both ends of all the blocks are held in the boundaries like the middle B block chain of ABA triblock copolymers. According to the experimental data[18] and the theoretical prediction of Helfand–Wasserman[6], the ABA triblock copolymers with the ratio of chain lengths of A:B:A = 1:2:1 can be approximately treated as AB diblock copolymers obtained by cutting the middle B block chain at the centre. If this treatment is also applicable to the multiblock copolymers, their lamellar domain spacings may be almost equal to those formed by hypothetical (A/2)(B/2) diblock copolymers obtained by cutting the block chains at the centres. Actually, however, the present multiblock copolymers have two end-block chains as shown in *Figure 4c*. Since the molecular weight of end-block chains is twice that of block chains of (A/2)(B/2) diblock copolymers, the end-block chains can be safely assumed to be distributed uniformly among domains. Although the repeating unit is also A–B in this case, the domain spacings must be determined by the number-average molecular weight of the mixture of (A/2)(B/2), A(B/2) and (A/2)B diblock copolymers, where A(B/2) and (A/2)B denote the diblock copolymers having one end-block A and B, respectively, as shown in *Figure 4c*. If the molecular weight of the AB unit is M_u, the effective number-average molecular weight M_{eff} of a multiblock copolymer of the $(AB)_n$ type with $n=2$ is $2M_u/3$, as shown in *Figure 4c*. In general, therefore, M_{eff} is given by

$$M_{eff}=nM_u/(2n-1) \qquad (2)$$

Introducing the M_{eff} values evaluated from equation (2) into the empirical relationship between D and M for styrene–isoprene diblock copolymers[9], $D=KM^{2/3}$, where K is evaluated from the present experimental value of D (28.2 nm) for a diblock copolymer with $M_n=3.5\times10^4$, we have the calculated values of D (D_{calc}), which are in good agreement with the data for annealed films shown

Table 1 Molecular characteristics of samples

Sample code	M_n (total) $\times10^{-3}$	M_n (SI unit) $\times10^{-3}$ 1	2	3	4	M_w/M_n	ϕ_s
$(SI)_1$	35	35	–	–	–	1.02	0.55
$(SI)_2$	78	35	43	–	–	1.06	0.54
$(SI)_3$	119	42	38	39	–	1.08	0.55
$(SI)_4$	168	42	38	39	49	1.05	0.56

Table 2 Comparison of observed and calculated domain spacings

Sample code	M_n (total) $\times10^{-3}$	M_u $\times10^{-3}$	M_{eff} $\times10^{-3}$	D (nm) As-cast	Annealed	D_{calc} (nm)
$(SI)_1$	35	35	35	23.4	28.2	28.2
$(SI)_2$	78	39	26	18.2	22.7	23.1
$(SI)_3$	119	40	24	18.4	22.9	21.9
$(SI)_4$	168	42	24	18.3	21.6	21.9

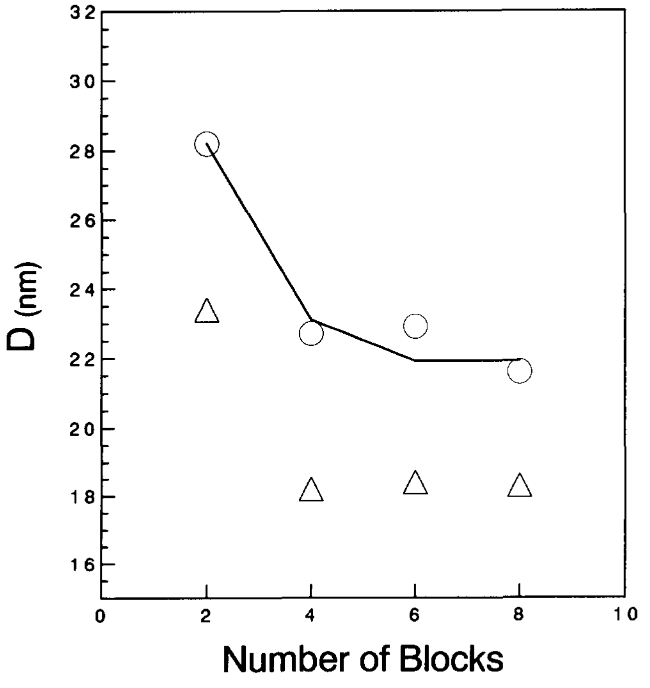

Figure 3 Domain spacing as a function of number of blocks: (△) as-cast films; (○) annealed films. The solid line corresponds to equation (2)

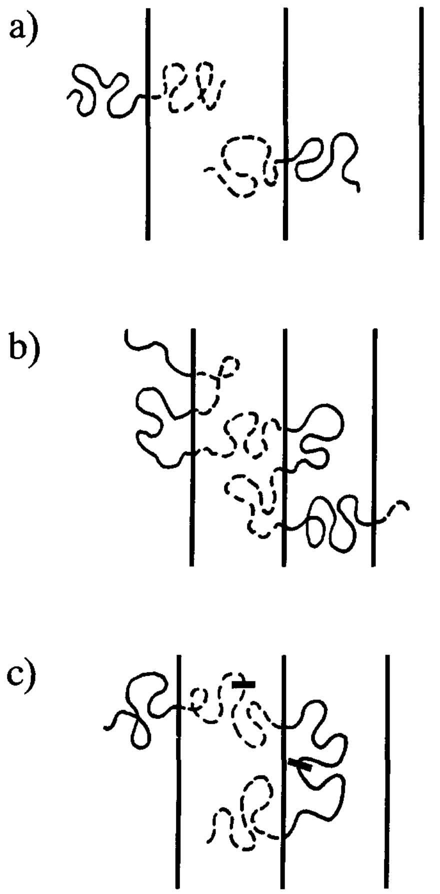

Figure 4 Schematic diagrams of the chain conformations of multiblock copolymers in comparison with that of a diblock copolymer: (a) $(SI)_1$ diblock copolymer; (b) $(SI)_\infty$ multiblock copolymer; (c) $(SI)_2$ tetrablock copolymer

in *Table 2* and *Figure 3*. This means that the lamellar structures of the multiblock copolymers of the $(AB)_n$ type can be well explained by the 'effective diblock copolymer model' mentioned above.

ACKNOWLEDGEMENTS

The authors thank Mr T. Watanabe and Mr T. Imura of the glass-blowing shop in the School of Engineering for their assistance in making the polymerization system and Mr H. Choshi for his help in preparing the polymer samples. The authors also thank Mr M. Nomura for his help in measuring u.v. absorbance and in preparing drafts.

REFERENCES

1 Molau, G. E. 'Block Polymers' (Ed. S. L. Aggarwal) Plenum Press, New York, 1970
2 Meier, D. J. 'Block and Graft Copolymers' (Eds J. J. Burke and V. Weiss) Syracuse University Press, Syracuse, NY, 1973
3 Gallot, B. R. M. *Adv. Polym. Sci.* 1978, **29**, 85
4 Inoue, T., Soen, T., Hashimoto, T. and Kawai, H. *J. Polym. Sci. Part A-2* 1969, **7**, 1283
5 Richards, R. W. and Thomason, J. L. *Polymer* 1981, **22**, 581
6 Helfand, E. and Wasserman, Z. R. *Macromolecules* 1976, **9**, 879
7 Semenov, A. V. *Sov. Phys.-JETP* 1985, **61** (4), 733
8 Ohta, T. and Kawasaki, K. *Macromolecules* 1986, **19**, 2621
9 Hashimoto, T., Shibayama, M. and Kawai, H. *Macromolecules* 1980, **13**, 1237
10 Hadziioannou, G. and Skoulios, A. *Macromolecules* 1982, **15**, 258
11 Matsushita, Y., Mori, K., Saguchi, R., Nakao, Y., Noda, I. and Nagasawa, M. *Macromolecules* 1990, **23**, 4313
12 Hasegawa, H., Hashimoto, T., Kawai, H., Lodge, T. P., Amis, A. J., Glinka, C. J. and Han, C. C. *Macromolecules* 1985, **18**, 67
13 Matsushita, Y., Mori, K., Mogi, Y., Saguchi, R., Noda, I., Nagasawa, M. *et al. Macromolecules* 1990, **23**, 4317
14 Hadziioannou, G., Picot, C., Skoulios, A., Ionescu, M.-L., Mathis, A., Duplessix, R. *et al. Macromolecules* 1982, **15**, 263
15 Matsushita, Y., Choshi, H., Fujimoto, T. and Nagasawa, M. *Macromolecules* 1980, **13**, 1053
16 Strobl, G. R. *Acta. Cryst.* 1970, **A26**, 367
17 Mogi, Y., Kotsuji, H., Kaneko, Y., Matsushita, Y. and Noda, I. *Macromolecules* 1992, **25**, 5408
18 Uchida, T., Soen, T., Inoue, T. and Kawai, H. *J. Polym. Sci., Part A-2* 1972, **10**, 101