Effect of Composition Distribution on Microphase-Separated Structure from Diblock Copolymers

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Received February 28, 2003

ABSTRACT: Microphase-separated structures of diblock copolymers with narrow molecular weight distributions but with various composition distributions were investigated. Monodisperse nine parent block copolymers composed of polystyrene and poly(2-vinylpyridine) having almost the same molecular weight but with different polystyrene volume fraction, ϕ_s, covering 0.1−0.9, were prepared. Successively they were blended variously to produce samples with various composition distributions but with constant average composition; that is, ϕ_s was kept constant at approximately 0.5. Structures from solvent-cast and well-annealed films were observed through transmission electron microscopy and small-angle X-ray scattering. It has been found that the blends with wide composition distributions show periodic alternating lamellar structure up to 1.7 in terms of $M_w(S)/M_n(S)$, where $M_w(S)$ and $M_n(S)$ denote weight-average and number-average molecular weights of polystyrene block, respectively, and that the microdomain spacing increases with increase of polydispersity of each block. Further, it was clarified that the blend shows macrophase separation in between two kinds of regular microphase-separated structures if $M_w(S)/M_n(S)$ reaches approximately 1.8.

Introduction

Microphase-separated structures of block copolymers have been extensively studied, and many scientific and application achievements have been attained. Most of the studies ever done particularly in the academic field have focused on the structures of polymer samples with narrow molecular weight distribution and also with composition distribution. For example, the molecular weight dependence of domain spacing has been investigated,[1−6] while the composition dependence of morphology has been studied sufficiently.[7−11] This is because morphology changes very sensitively to these molecular parameters. The copolymer samples used in most of these studies were monodisperse in both molecular weight and composition. As a result, the effect of these distributions on microphase-separated structures of block copolymers has not been well studied so far, though the polymers in application field in general possess relatively wide molecular weight and composition distributions.

Hashimoto et al.[12] studied structures from binary blends of styrene−isoprene (SI) diblock copolymers with different molecular weights and concluded that lamellar domain spacing D can be scaled by $D \propto M_n^{2/3}$, where M_n denotes overall number-average molecular weight of the constituent copolymers within the criterion where blends show a simple mixed phase. Further, Court et al.[13] observed the variation of domain spacing of also binary blends of SI diblock copolymers with different molecular weights as well as compositions. In these works, however, the composition distribution has not been treated quantitatively, so force its effect on phase separation behavior has not been fully clarified yet.

In this work, therefore, the effects of composition distribution on microphase-separated structures of diblock copolymers were investigated by using nearly monodisperse samples with wide composition distributions which were prepared by blending parent monodisperse samples with respect to both molecular weight and composition and having almost the same molecular weight.

Experimental Section

Parent diblock copolymers were prepared by sequential anionic polymerization in tetrahydrofuran (THF) at −78 °C with cumyl−potassium as an initiator. The details of the polymerization procedure were reported previously.[14] A small amount of polystyrene solutions for all copolymers was separated as precursors to check the molecular weight of polystyrene blocks in the course of polymerization reaction.

The weight-average molecular weights of samples were measured by a multiangle laser light scattering, DAWN EOS enhanced optical system of Wyatt Technology at 35 °C in THF. The reflective index increment, $\partial n/\partial c$, of polystyrene and poly(2-vinylpyridine) in THF are 0.185 and 0.180, respectively, these being very close to each other; therefore, the difference was ignored in evaluating M_w. The molecular weight distribution of polystyrene precursors and block copolymers was estimated by gel permeation chromatography (GPC) using HLC-8020 of TOSOH Co., with THF as an elusive solvent at 38 °C using two GMH_{XL} columns of TOSOH. About 2 vol % of tetramethylethylenediamine was added to THF to avoid adsorption of poly(2-vinylpyridine) block chains on polystyrene gel.[14] Volume fractions of all parent block copolymers were measured by pyrolysis−gas chromatography using a gas chromatograph GC-2010 of Shimadzu equipped with a microfurnace pyrolyzer PY-2020s of Frontier Lab having an ultra alloy column and a flame ionization detector.[15]

Molecular characteristics of parent polymers thus obtained are listed in Table 1. From this table, it is apparent that ϕ_s of these polymers is covering the range $0.1 < \phi_s < 0.9$ with its constant step width of about 0.1 and all having the molecular weights between 100K and 160K. By using these parent copolymers, basically three series of blend samples were prepared. The first and the simplest one, series I, is equal mass

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10.1021/ma0301496 CCC: $25.00
Published on Web 09/23/2003

Table 1. Molecular Characteristics of Parent Polymers

sample	M_w[a]/10^5	M_w/M_n[b]	ϕ_s[c]	M(S)[d]/10^4
SP-19	1.05	1.03	0.100	0.975
SP-28	1.14	1.03	0.193	2.06
SP-37	1.14	1.05	0.302	3.25
SP-46	1.36	1.05	0.399	5.16
SP-55	1.35	1.04	0.462	5.96
SP-64	1.36	1.06	0.591	7.77
SP-73	1.30	1.05	0.687	8.70
SP-82	1.51	1.04	0.792	11.7
SP-91	1.60	1.05	0.896	14.2

[a] Weight-average molecular weights measured by multiangle laser light scattering. [b] Apparent molecular weight distribution determined by gel-permeation chromatography. [c] Volume fractions of polystyrene blocks measured by pyrolysis−gas chromatography. [d] Molecular weights of polystyrene blocks calculated by using M_w, ϕ_s, and bulk densities of two component polymers, i.e., 1.05 for polystyrene and 1.14 for poly(2-vinylpyridine).

amount blends from 3, 5, 7, and 9 parent copolymers, whose code names are E3, E5, E7, and E9, respectively. The second series, II, consists of nonequal amount blends that have Gaussian distribution of the form in eq 1

$$w(\phi_s) = (2\pi)^{-1/2}\sigma^{-1} \exp\{-(\phi_s - 0.5)^2/2\sigma^2\} \quad (1)$$

with its distribution center at 0.5 with respect to ϕ_s, where $w(\phi_s)$ denotes weight fraction of parent polymers and σ is the standard deviation. Several σ^2 values were adopted, and various blends were prepared changing the numbers of parent polymers used. The sample code Gh(k) is used to express blends with Gaussian distribution, where h denotes the numbers of parent polymers blended while k is σ^2 values. For example, G9(4.5) means the blend composed of nine polymers having Gaussian distribution with σ^2 of 4.5. Six different blends, that is, G3(0.2), G5(1.13), G7(2.5), G9(4.5), G9(7.5), and G9(20), were prepared. The third one, series III, which is all composed of nine polymers, has a distribution of the type quadratic and quartic functions according to eq 2

$$w(\phi_s) = (\phi_s - 0.5)^m + A \quad (2)$$

where A is a small constant value and the exponent m equals 2 and 4 and so they were coded Q-2 and Q-4, respectively. As another aspect of the third series, the blends with modified Gaussian distribution expressed by eq 3 were also prepared

$$w(\phi_s) = B - (2\pi)^{-1/2}\sigma^{-1} \exp\{-(\phi_s - 0.5)^2/2\sigma^2\} \quad (3)$$

where B is a constant chosen so as to satisfy the condition $\sum w(\phi_s) = 1$ for normalization. Two code names for this blend are MG(0.02) and MG(0.06) because 0.02 and 0.06 were used for B with σ^2 of 2.55 in eq 3. The average composition of all blends is basically the same to ensure the volume fraction of polystyrene block is around 0.5. The characteristics of all the blend samples from series I through III are listed in Table 2, and the blending manners for G9(4.5), G9(20), E9, MG(0.06), MG(0.02), Q-2, and Q-4 are compared in Figure 1.

The sample films for morphological observations were obtained by casting for 3 days from dilute solutions of constituent copolymers in THF, followed by drying for 1 day in a vacuum oven.[16] Further, they were annealed at 150 °C for a week under vacuum to attain equilibrium structures. The sample films were stained with osmium tetroxide and cut into ultrathin sections with thickness of ca. 50 nm by an ultramicrotome, Ultracut UCT of LEICA, and their microphase-separated structures were observed by a transmission electron microscope (TEM), H-800, of Hitachi under an acceleration voltage of 100K V. Small-angle X-ray scattering (SAXS) was performed also to investigate structures quantitatively using the SAXS apparatus installed in the beamline 15A at Photon Factory in Tsukuba.[17]

Results and Discussion

To deal with the data more quantitatively, we consider the polydispersity of one block, i.e., polystyrene.

Table 2. Composition Distributions and Domain Spacing of All Blend Samples

blend no.	code	M[a]/10^5	M_w(S)/M_n(S)	D/nm	D/D_0[b]
I	E3	1.36	1.03	60.8	1.00
	E5	1.30	1.11	61.8	1.02
	E7	1.30	1.25	63.2	1.04
	E9	1.29	1.45	66.9	1.10
II	G3(0.2)	1.36	1.01	61.2	1.01
	G5(1.13)	1.33	1.05	61.4	1.01
	G7(2.5)	1.32	1.12	61.6	1.01
	G9(4.5)	1.31	1.23	62.7	1.03
	G9(7.5)	1.30	1.30	64.1	1.05
	G9(20)	1.30	1.38	65.4	1.08
III	Q-2	1.28	1.73	69.9	1.15
	Q-4	1.28	1.85	macro	
	MG(0.02)	1.28	1.63	68.5	1.13
	MG(0.06)	1.28	1.55	67.5	1.11

[a] The calculated average molecular weight using M_w values in Table 1. [b] D_0, 60.8nm, is lamellar domain spacing for SP-55.

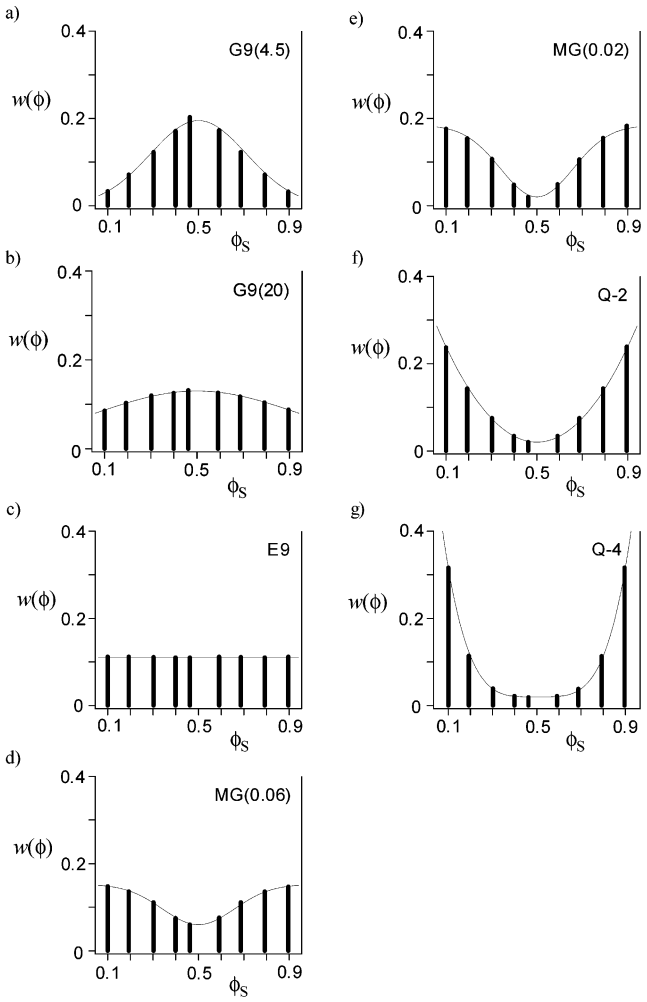

Figure 1. Relative amounts of parent polymers used for preparing various blends. Vertical axes express weight fractions, $w(\phi_s)$, of the nine parent polymers, while horizontal axes are polystyrene volume fractions of the parent polymers in bulk.

Then the polydispersity in molecular weight of polystyrene, M_w(S)/M_n(S), could be regarded as the index of composition distribution in the present case. In calculating M_w(S)/M_n(S) for each blend, all the polystyrene blocks in the parent copolymers were assumed to be monodisperse perfectly since this assumption cannot be considered to affect the results seriously. Molecular weights of polystyrene blocks were estimated by using

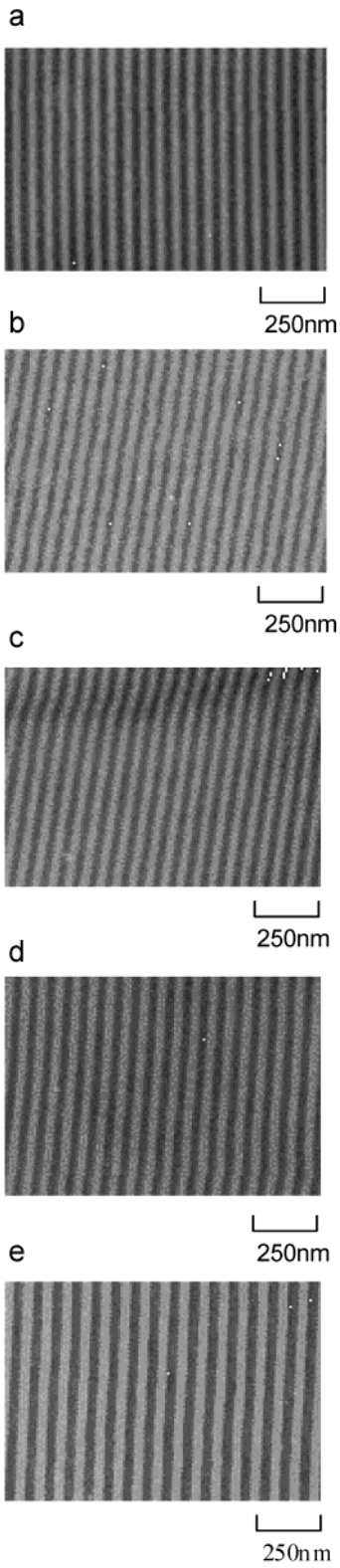

Figure 2. Comparison of transmission electron micrographs for blend series I: a, SP-55; b, E3; c, E5; d, E7; e, E9.

the measured M_w for block copolymers, volume fractions of polystyrene blocks, and the bulk densities of two component polymers. The estimated values, $M(S)$, are listed in Table 1, and the calculated $M_w(S)/M_n(S)$ values obtained by using the data in Table 1 are also listed in Table 2.

Figure 2 compares bright field transmission electron micrographs for blend series I. It is apparent from these micrographs that all the samples studied possess very

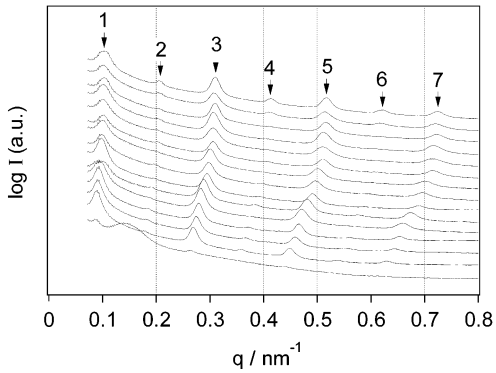

Figure 3. Comparison of SAXS diffraction patterns for all the blends. Scattering profile for one parent polymer, SP-55, is added as a reference. The curves are displayed in the order of the magnitude of composition distribution in Table 2, that is, SP-55, G3(0.2), E3, G5(1.13), E5, G7(2.5), E5, G9(4.5), E7, G9-(7.5), G9(20), E9, MG(0.06), MG(0.02), Q-2, and Q-4 from top to bottom.

periodic lamellar structures with flat interfaces. All the other samples except Q-4 were confirmed to show very periodic lamellar structures which is qualitatively similar to the ones as shown in Figure 2, though they were not shown here to avoid duplicated information. Alternatively, Figure 3 shows SAXS diffraction patterns of all the blends studied. All the curves except the bottom one include interger number order peaks reflecting lamellar structures, where the odd number peaks are stronger while the even number peaks are relatively weak because the compositions of two component blocks are close to each other.[6] From these results, we understand any molecules with different compositions do not localize in lamellar microdomains but might be mixed together randomly so as not to stand out heterogeneity in block chain length spontaneously if the composition distribution is not so extremely wide. The situation in poly(2-vinylpyridine) microdomain is just opposite to that in polystyrene, but essentially two block chains are in the same circumstance in microdomains. This simple experimental fact is a very important result that has been first found clearly by using well-defined and essentially monodisperse samples with respect to molecular weight but with various composition distributions, while the simple microdomain formation was reported on the asymmetric binary blend system.[18]

In Figure 3, small-angle X-ray scattering (SAXS) data are displayed for all blends in the order of composition distribution as defined above. One easily notices that the locations of diffraction peaks shift to lower q value with increasing polydispersity in composition from top to bottom, indicating the increase of domain spacing with composition distribution.

By applying Bragg's condition to the magnitude of scattering vectors corresponding to the locations of the diffracted peaks, microdomain spacings were evaluated, and they are listed in Table 2. The relative magnitude of domain spacings D/D_0 for all blend samples, where D_0, 60.8 nm, denotes that of the pure parent block copolymer, SP-55, are plotted against $M_w(S)/M_n(S)$ in Figure 4. In evaluating D_0, strictly speaking, the difference in average molecular weight of each blend has to be taken into account; however, they were ignored since the average M_n is almost constant at around 130K, as shown in Table 2. From this figure one notices that lamellar domain spacing increases with increase of polydispersity in composition, namely, the heterogeneity

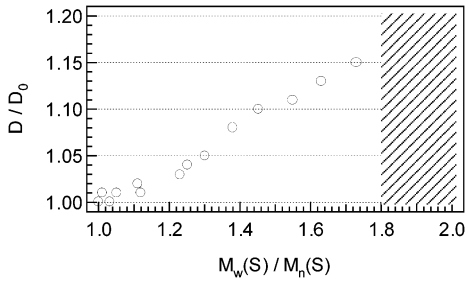

Figure 4. Composition distribution dependence of the reduced domain spacing, D/D_0, of all blends with single microphase-separated structure. D_0, 60.8 nm, is the domain spacing of one of the parent copolymer; SP-55. The hatched region is for the macrophase-separated one.

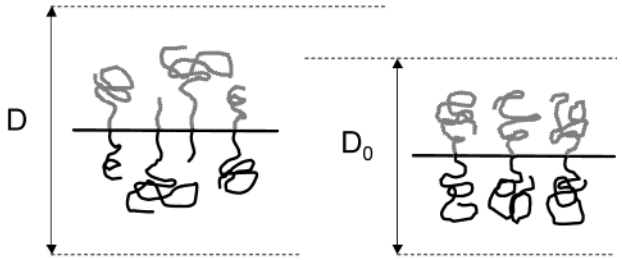

Figure 5. Schematic comparison of microdomains formed by block copolymers with narrow and wide composition distributions.

in block chain length ratio affects domain formation manner; even the constituent block copolymer is monodisperse in total chain length. This fact tells that the domain spacing is governed not merely by number-average molecular weight of copolymers composed but also by composition distribution in satisfying the condition for polymer segments to fill three-dimensional space constantly.[12]

Figure 5 schematically compares lameller domain spacing in between monodisperse and uniform compositional block copolymer and monodisperse but nonuniform compositional block copolymer molecules. Compensating the shortage of the segment for the shorter chain, the segment for the longer chain is apparently responsible for the increase of domain spacing. In another words, the average surface area for a junction point of each block copolymer in blend with wide composition distribution is smaller than that for the regular monodisperse copolymers, though the effect is not so extremely strong. As a result, the longer is the chain, the degree of nonuniform deformation in a microdomain might be more as shown in this figure, though this is merely a speculation at present. Neutron scattering experiments are under way to observe the localization manner of the longer and the shorter molecules in the blend.

Considering the $M_w(S)/M_n(S)$ value for polystyrene as an indicator for macrophase separation, we can discuss the limit of the uniform microphase separation region.[19] Figure 6 shows a typical transmission electron micrograph for blend Q-4, whose $M_w(S)/M_n(S)$ is 1.85, which exhibits macrophase-separated behavior. That is, this micrograph includes two kinds of microphase-separated structures, i.e., the spherical structure and the lamellar one, which are macroscopically phase-separated. Thus, the limit may lie between 1.73 and 1.85, though the limit value could depend on the molecular weight of block copolymer used.

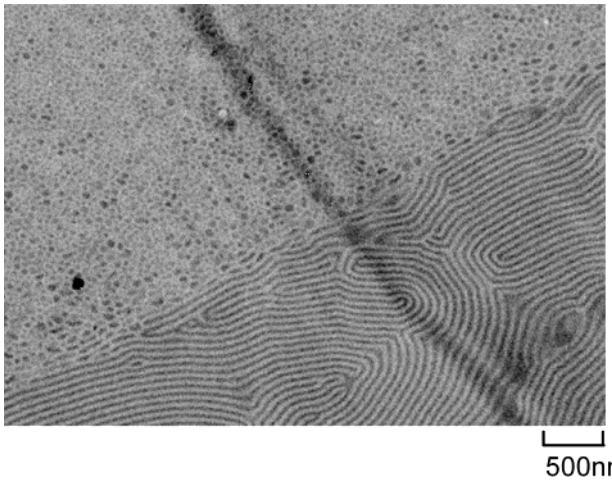

Figure 6. Transmission electron micrograph showing macrophase separation in between two microphase-separated regions. The sample is Q-4.

From these experimental results obtained, we conclude that (1) monodisperse polystyrene-*block*-poly(2-vinylpyridine) block copolymer with relatively wide composition distribution shows very periodic and uniform lamellar structures, their microdomain interface being flat, if the polydispersity index of each component block is lower than 1.7, (2) lamellar domain spacing increases with increase of composition distribution, and (3) macrophase separation takes place if the polydispersity index of each block exceeds 1.8 for block copolymers with molecular weight of around 130K.

Acknowledgment. The authors thank Professor T. Tanji at the Department of Electrical Engineering in Graduate School of Engineering, Nagoya University, and Mr. S. Arai at the Center for Integrated Research in Science and Engineering in Nagoya University for their help in taking transmission electron micrographs.

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MA0301496