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Surface Ordering of Block Copolymers

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ABSTRACT: A linear relationship between fractional surface excess of PDMS (Ψ) and PDMS block length (N_A), $\Psi = \alpha' - \beta' N_A^{-1/2}$, is found for the PS–PDMS–PS type triblock copolymers from ESCA results over three different sampling depths, ranging from 27 to 103 Å. The effect of PDMS surface segregation Ψ is compared within the PS–PDMS diblock, PS–PDMS–PS and PDMS–PS–PDMS triblock copolymer series as N_A changes. At similar bulk composition, the PDMS segments in the PS–PDMS diblock copolymers are the most apt to segregate in the free surface region, while the PDMS segments of the PS–PDMS–PS triblock copolymers are the least probable to segregate in the free surface region. The surface morphologies of the PS–PDMS diblock and PS–PDMS–PS triblock copolymers are lamellar with the periods of 600 and 450 Å respectively, which are revealed by TEM micrographs of the cross sections of the films both near the free surface and in the bulk. A morphology of PS spheres in PDMS matrix is found for the PDMS–PS–PDMS triblock copolymer. The period of the lined PS sphere arrays separated by the PDMS domains is measured to be 130 Å.

Introduction

Ordering of microphases for block copolymers has been studied for more than two decades both in solution[1,2] and in solvent-free bulk.[3-7] Recently, these investigations have been extended to the polymer surfaces.[8-10] The spatially ordered morphological structures can exist in various forms such as one-dimensional lamellae, hexagonally packed cylinders, and body-centered-cubic (BCC) arrays of spheres, depending on the architecture of blocks, bulk composition, block lengths, and interaction parameters between different blocks. On the basis of compositional variations in domains and thickness of the interface between domains, theoretical treatments of the phase separation of block copolymers are classified into two types, namely, strong segregation theories[3-5] and weak segregation theories.[6-11]

The strong segregation theories deal with block copolymers having a strong tendency to phase separate.[4,5] The thickness of the interface which divides the A-rich and the B-rich domains is sufficiently small compared with the period D of the spatially ordered morphological structure. The two kinds of domains differ widely in their compositions. The thermodynamic equilibrium period, D_e, for an ordered lamellar structure is given by

$$D_e \propto N^{\gamma} \qquad (1)$$

where γ varies from 0.636 to 0.667 by mean field theoretical treatments[4,5] for a diblock copolymer with N as the total degree of polymerization of the copolymer. For a triblock copolymer, N is half of the total degree of polymerization of the copolymer. The relationship between period D_e and polymer chain length N described by eq 1 is in very good agreement with experiment.[12] The interface thickness has been found to be independent of the polymer chain length in the strong segregation limit both theoretically[4] and experimentally.[12] For hexagonal–cylindrical[13] or spherically[14] ordered structures, similar good agreement has been found between theoretical treatments and experimental results.[15] A triblock copolymer can be treated as a diblock copolymer achieved by cutting the triblock molecule at the middle of the central block.[4,13,14]

In the weak segregation regime, the major features are a wide interface between microdomains and relatively small deviations of compositions in different microdomains, compared with those in the strong segregation regime. The weak segregation limit theories, such as mean field theory,[6] were believed to be applicable to the disordered phase of block[8,9] or star[7] copolymers and to the ordered microphases at temperatures very close to the microphase separation transition (or MST). They could even be extended to the ordered microphases in strong segregation limit at temperatures well below the MST.[5,8,9]

According to mean field theories, there are two variables determining morphologies of the two-component block copolymers, such as AB diblock copolymers and $(AB)_n$ star block copolymers,[7] at equilibrium conditions. The first varible is χN. Here χ is the dimensionless Flory interaction parameter describing the enthalpic interactions between the two different segments and N is the total number of repeat units for a diblock copolymer or the total number of repeat units per arm for an $(AB)_n$ star block copolymer. The second variable determining the morphology is the bulk composition which is described by $f = N_A/(N_A + N_B)$, where f is the fraction of the number of repeat units of A block of a block (or star block) copolymer chain. N_A and N_B are the numbers of repeat units of the A block and B block, respectively. When $n = 2$, an $(AB)_n$ star block copolymer is a BAB triblock copolymer.

Recently, Green et al.[10,11] presented an equation describing the relation between chain length and surface excess of one component in symmetric PS–PMMA diblock copolymers:

$$\psi = \alpha - \beta N^{-1/2} \qquad (2)$$

This equation was simplified from Fredrickson's mean field theory equation by making some approximations.[9] Here N is the total number of repeat units of a symmetric A–B diblock copolymer. Both α and β are constants. The constants α and β are related to how the unlike segment interactions are different between surface and bulk and to surface energy differences between the components.

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Parameter ψ is the surface excess of the lower surface energy component A defined by the equation

$$\psi = \langle \rho_A \rangle / \rho - f \qquad (3)$$

where $\langle \rho_A \rangle$ is the average density of A segments of lower surface energy at the surface, and ρ is the total segment density expressed in the equation

$$\rho = \langle \rho_A \rangle + \langle \rho_B \rangle \qquad (4)$$

The unique feature of eq 2 is that it establishes a relation between the strong surface segregation regime (when N is very large) and the weak surface segregation regime (when N is very small) and describes how the surface segregation effect changes as chain length changes in the range between the two limits.

An analogue to eq 2 is postulated in the present paper for the asymmetric diblock and triblock copolymers of styrene and dimethylsiloxane:

$$\Psi = \alpha' - \beta' N_A^{-1/2} \qquad (5)$$

Where α' and β' are constants, and N_A is the chain length of the PDMS block for the PS–PDMS diblock copolymers and PDMS–PS–PDMS triblock copolymers and is one half of the chain length of the PDMS block for the PS–PDMS–PS triblock copolymers. The block length in this equation is in term of the number of repeat units of PDMS, the lower surface energy component of the PS–PDMS block copolymers. The parameter Ψ, defined as the fractional surface excess of PDMS averaged over a certain sampling depth, is given by

$$\Psi = \psi / (1 - f) \qquad (6)$$

This parameter is constituted so that it connects both block length and bulk composition to surface excess. It should be noted that $\Psi = 0$ if the bulk concentration prevails in the defined surface region, while $\Psi = 1$ when the surface region is composed of pure PDMS. The term which describes the largest possible deviation of PDMS concentration in the surface region, $(1 - f)$, is so arranged to scale down the trend that the measured deviation of PDMS surface concentration increases as PDMS bulk concentration f decreases.

In a relatively small bulk composition variation range (f ranging from 0.727 to 0.837 in terms of DMS molar fraction), we demonstrate in the present paper that a linear relationship described by eq 5 exists experimentally for the PS–PDMS–PS type triblock copolymers.

Transmission electron microscopy (or TEM) studies reported in this paper provide information about domain sizes and shapes, which are very important to the surface excess discussion. If the surface domain sizes of the PS–PDMS block copolymers are larger than the ESCA sampling depths, the excess of PDMS component measured by ESCA could be defined as the surface excess.

Table I
Architectures and Molecular Weights of Block Copolymers of St and DMS

sample	type	A block (PS)	B block (PDMS)	wt % B	copolymer M_n
1	A–B	27 000	94 000	77.5	121 000
2	A–B	16 600	38 700	70	55 300
3	A–B	70 000	99 000	58.5	169 000
4	A–B–A	2 × 8 600	33 100	65.5	50 000
5	A–B–A	2 × 12 900	94 200	78.5	120 000
6	A–B–A	2 × 12 500	56 000	69.1	81 000
7	A–B–A	2 × 11 250	67 500	75	90 000
8	B–A–B	6 600	2 × 13 200	80	33 000
9	B–A–B	9 090	2 × 1 520	25	12 120

Experimental Section

The PS–PDMS block copolymer samples in one diblock and two triblock types are described in Table I. The block copolymer films (thicker than 100 μm) for ESCA measurements were cast from about 1% chloroform solutions in clean Al weighing pans, allowed to air dry at least 24 h, and analyzed without further preparation. The angle-dependent ESCA experiments were described in a companion paper.[16]

The microdomain structures of the PS–PDMS block copolymers were examined by cross-sectional transmission electron microscopy. For this purpose, relatively thick (>500 μm) PS–PDMS block copolymer films were obtained by casting 1–2 wt % polymer solutions in chloroform into glass Petri dishes. The dry films in the glass Petri dishes were annealed at 140 °C in a vacuum oven for at least 24 h. The Petri dishes with films were immersed in triple-distilled boiling water for 10 min. Then the films were able to be peeled from the Petri dishes. The films were dried again before ultrathin sectioning. The high electron density of PDMS, as compared to PS, led to sufficient contrast without the need for staining. The ultrathin cross sections of the films were sliced normal to the film surface at −120 °C using a Reichert-Jung Ultracut E ultratome with a FC4E cryosectioning attachment. A transverse cross section was microtomed parallel with the air surface to avoid stretching the materials in the surface region. The electron micrographs were taken on a JEOL 100CX-II transmission electron microscope operating at 80 kV.

TEM Studies of the Block Copolymers

TEM Results of the PS–PDMS Diblock Copolymers. Samples 1 and 3, considered to be representatives of the A–B diblock copolymers, were examined by TEM. Figure 1a shows a typical electron micrograph of a cross section of a PS–PDMS diblock copolymer (sample 1) film in the near free surface region. The top bright area without structure represents the air. The remainder of the area, with structural patterns, corresponds to the cross section of the polymer film. A lamellar morphology of alternating PDMS (dark domains) and PS (bright domains) layers exists in the near surface region. The lamellae are aligned parallel to the free surface at least over a few periods. The distance over which the lamellae orient parallel to the surface varies from about 1 μm to several microns from spot to spot for both samples 1 and 3 as determined by TEM studies. In the bulk region (shown in Figure 1b), the microdomains are basically randomly oriented. The average periods of the lamellae in the near free surface region (over several periods) and the bulk are of the same order. They are about 600 Å for sample 1 and about 500 Å for sample 3.

Our ESCA data[16] indicated that the outermost 27 Å free surface region of the PS–PDMS diblock copolymers was composed of pure PDMS. TEM micrographs of the surface region of the PS–PDMS diblock copolymers also show that the free surface region is topped with a PDMS layer. This is consistent with the results obtained by Hashimoto on a polystyrene–polyisoprene diblock copolymer,[17] in which the topmost free surface region was covered with a lamellar PI (the lower surface energy component) domain.

In the free surface region of the PS–PDMS diblock copolymers, one noticeable feature is that the outermost PDMS layer is very hairy in the part very close to the interface. This is not a result caused by a possible stretching effect of microtoming, since the microtoming direction was parallel with the interface and the sectioning process was done at −120 °C, a temperature close to the glass transition temperature of PDMS (−127 °C). This hairy feature indicates that the density of the polymer chains is less than that in the bulk. Another feature of the outermost PDMS layer is that its thickness is at least of

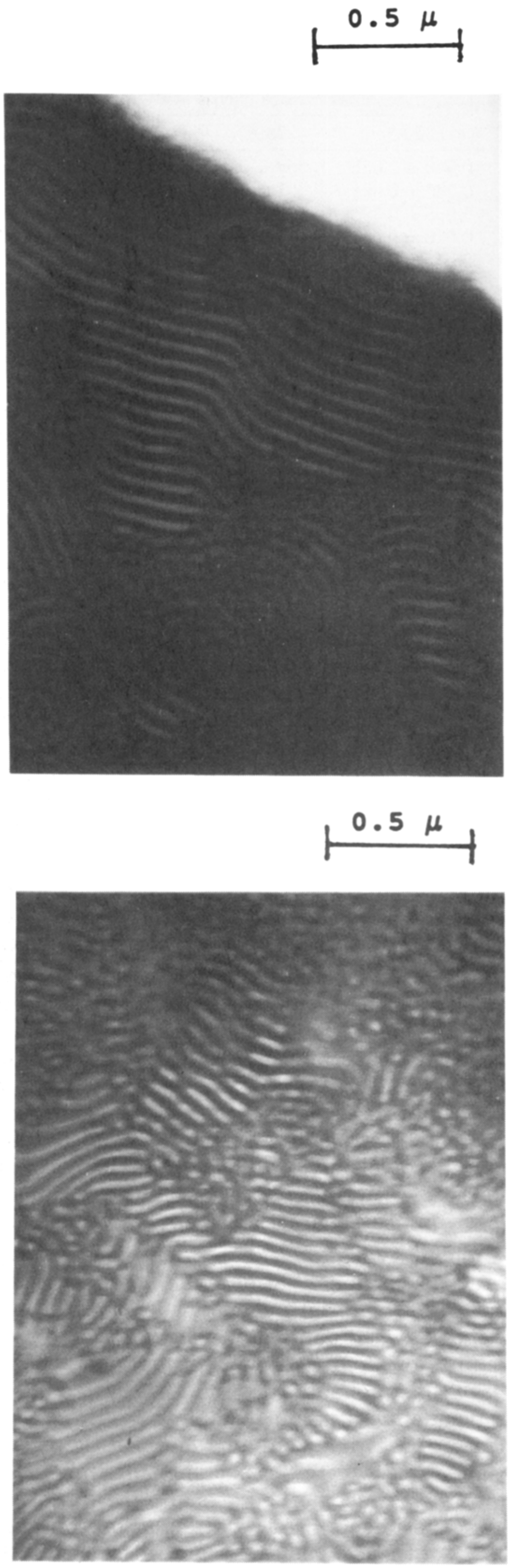

Figure 1. TEM micrographs of the ultrathin cross sections of (a, top) the free surface vicinity and (b, bottom) the bulk of a PS–PDMS diblock copolymer (sample 1). The period is about 600 Å. PDMS and PS domains are visible as dark area and bright area with structural patterns respectively.

the same order as in the bulk, not half of the thickness of the bulk layer found in Hashimoto's studies of a PS–PI diblock copolymer.[17]

TEM Results of the PS–PDMS–PS Triblock Copolymers. Samples 6 and 7 were chosen to represent the PS–PDMS–PS triblock copolymers under TEM study. The basic morphological features of the PS–PDMS–PS triblock copolymers, shown in Figure 2 are the same as those of the PS–PDMS diblock copolymers. The distance over which the PDMS and PS layers in the vicinity of the free surface orient parallel to the free surface for the triblock copolymers is generally much thicker than that

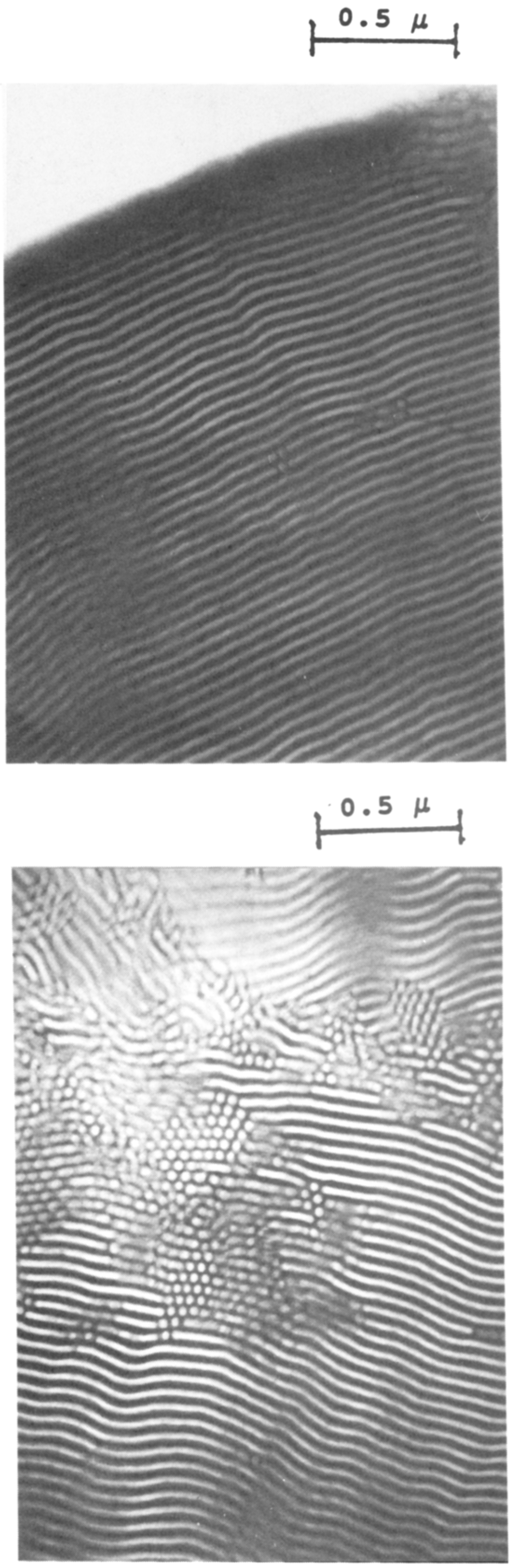

Figure 2. TEM micrographs of the ultrathin cross sections of (a, top) the free surface vicinity and (b, bottom) the bulk of a PS–PDMS–PS triblock copolymer (sample 7). The period is about 450 Å.

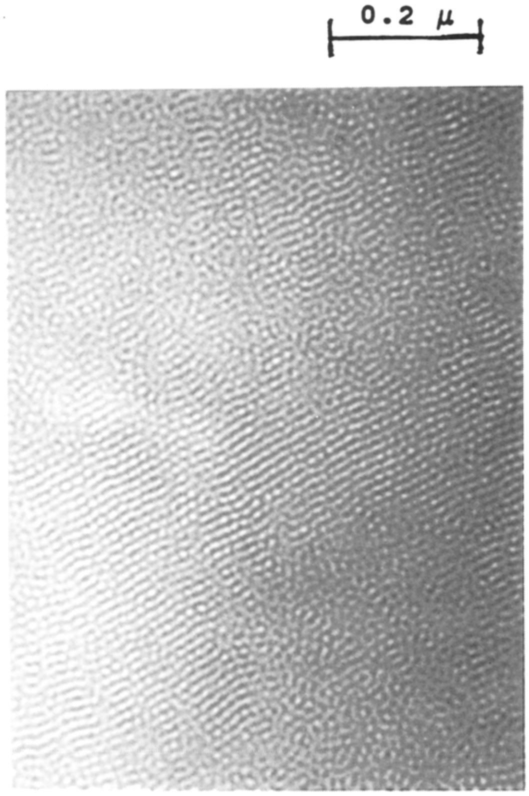

Figure 3. TEM micrograph of the ultrathin cross section of the bulk of a PDMS–PS–PDMS triblock copolymer (sample 8). The period is about 130 Å.

observed on the PS–PDMS diblock copolymers. The bulk morphology of the triblock copolymers is more or less randomly oriented.

A less dense outermost PDMS layer is also observed at the free surface of the PS–PDMS–PS triblock copolymers (samples 6 and 7 under TEM studies). However, the outermost free surface region of the PS–PDMS–PS triblock copolymers is less hairy than that of the diblock copolymers, probably due to the folded middle PDMS segments presented in the region for the PS–PDMS–PS triblock copolymers instead of free PDMS block ends, as well as middle segments, presented in the region for the PS–PDMS diblock copolymers. The thickness of the first PDMS layer, again, is no less than that of the inner PDMS layers.

The average periods of the lamellae in the free surface vicinity (over several periods) and the bulk are of the same order. They are about 450 Å for both sample 6 and sample 7.

TEM Results of the PDMS–PS–PDMS Triblock Copolymers. Figure 3 shows an electron micrograph of a PDMS–PS–PDMS triblock copolymer (sample 8) in the bulk region. Due to manipulation problems, TEM micrographs of sample 9 and sample 8 in the surface vicinity were unable to be obtained.

The block lengths and overall molecular weight of sample 8 are much smaller than those of the other two types of block copolymer samples. A morphology displaying PS spherical domains in PDMS matrix is found for the PDMS–PS–PDMS triblock copolymer. The PS sphere arrays separated by the continuous PDMS domains are in an ordered arrangement. The average period of the PDMS layers which separate the lined PS spherical domains is about 130 Å, a value much smaller than the periods of the other two type PS–PDMS block copolymer samples.

Table II
Fractional Surface Excess of PDMS and PDMS Block Length of PS–PDMS Block Copolymers

	fractional surface excess of PDMS			
sample	27 Å[a]	73 Å[a]	103 Å[a]	$N_A^{-1/2}$ [b]
1	0.959 ± 0.035	0.953 ± 0.047	1.000 ± 0.023	0.028
2	0.983 ± 0.021	0.991 ± 0.034	1.000 ± 0.038	0.044
3	0.955 ± 0.098	0.932 ± 0.054	0.914 ± 0.036	0.027
4	0.516 ± 0.051	0.161 ± 0.078	0.015 ± 0.073	0.067
5	0.945 ± 0.067	0.853 ± 0.043	0.859 ± 0.025	0.040
6	0.838 ± 0.054	0.710 ± 0.062	0.531 ± 0.033	0.051
7	0.896 ± 0.068	0.703 ± 0.141	0.635 ± 0.161	0.047
8	0.656 ± 0.053	0.252 ± 0.079	0.000 ± 0.093	0.075
9	0.656 ± 0.056	0.366 ± 0.019	0.278 ± 0.025	0.221

[a] ESCA sampling depths at different takeoff angles. [b] N_A is the average number of the repeat units of each PDMS block for PS–PDMS type diblock copolymers and PDMS–PS–PDMS type triblock copolymers, and half of the average number of the repeat units of a PDMS block for the PS–PDMS–PS type triblock copolymers.

Surface Excess of the Block Copolymers

ESCA results of PDMS surface concentrations of the as-cast films for all the diblock and triblock copolymers were summarized in Table III of ref 16. The DMS molar fraction in a surface region is $\langle \rho_A \rangle / \rho$, taking component A as the PDMS blocks. The parameter f in eq 3 is defined as the bulk DMS molar fraction. The fractional surface excesses of PDMS, Ψ, for the PS–PDMS block copolymers are calculated according to eqs 3 and 6 and summarized in Table II. The surface composition change of the as-cast films after annealing is relatively small, which had been proved in the previous ESCA studies.[16]

The largest sampling depth of the ESCA measurements is 103 Å, which is smaller than the periods of the morphologies of all three PS–PDMS block copolymers. A surface excess of PDMS is therefore measured by ESCA.

The effect of attenuation on the emitted photoelectrons must be considered when reporting angle dependent analysis of the surface morphology of polymer samples.[18] Though the incident X-rays in the ESCA experiment typically penetrate several microns into the material, the emitted photoelectrons in the energy range 50–1000 eV typically will travel only 20–100 Å before they lose energy from inelastic scattering events and cannot contribute the photoelectron peak characteristic for a given element.

The probability of an inelastic scattering event occurring is governed by exponential decay. The inelastic mean free path, λ, is a material and energy dependent constant which represents the depth at which photoelectrons have a probability of $1/e$ of escaping without energy loss.[19,20] Because of the exponential decay of the emitted intensity one cannot define a unique sampling depth. For most practical purposes the sampling depth (d) is related to both λ and $\sin \theta$, where θ is the angle of emission with respect to the surface normal (θ is also the takeoff angle of ESCA experiments). At a particular takeoff angle θ, about 65% of the total emitted photoelectrons (TEPEs) originate within $\lambda \sin \theta$ of the surface, 86% originate within $2\lambda \sin \theta$, and approximately 95% originate within $3\lambda \sin \theta$ of the surface. In this paper $3\lambda \sin \theta$ is utilized as the sampling depth.

As a result of nonequivalent contributions of the emitted photoelectron signal, the surface layer closest to surface has the highest contribution to the ESCA measurement at each analysis angle. Therefore, direct comparison of ESCA measurements at different sampling depths could be problematic if the surface is not homogeneous. With the caveat that the results of analysis are not equivalent

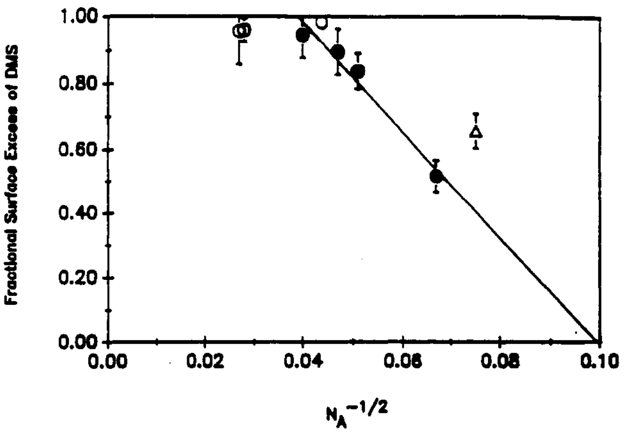

Figure 4. Plot of the fractional surface excess of PDMS versus $N_A^{-1/2}$ in a 27 Å thick free surface region. N_A is the number of repeat units for one PDMS block of the PS-PDMS diblock copolymers (hollow circles) and one of the PDMS blocks for the PDMS-PS-PDMS triblock copolymers (triangle) and is half of the repeat units of the PDMS block for PS-PDMS-PS triblock copolymers (filled circles). The regression line was drown only for the four PS-PDMS-PS triblock copolymers.

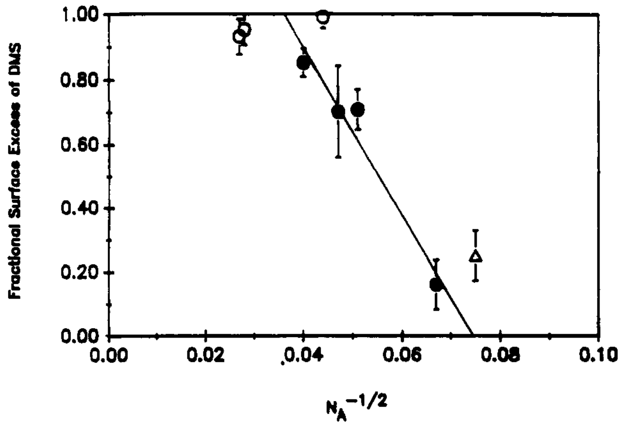

Figure 5. Plot of the fractional surface excess of PDMS versus $N_A^{-1/2}$ in a 73 Å thick free surface region. N_A is defined as the same of Figure 4. The regression line was drown only for the four PS-PDMS-PS triblock copolymers.

across the transverse section, it is still important to note the results under all conditions. Deviation from linearity of the model could therefore be due to two effects, attenuation and/or morphology.

Fractional Surface Excess of PDMS in the Surface Region up to 27 Å. A plot of $N_A^{-1/2}$ vs fractional surface excess of PDMS, Ψ, is shown in Figure 4 for all three types of block copolymers. Sample 9 has much lower molecular weight and much higher $N_A^{-1/2}$ value than the other eight samples so sample 9 is not included in this figure. The fractional surface excess data were calculated from ESCA measurements at a takeoff angle of 15°. Among the three types of block copolymers, the PS-PDMS-PS type triblock copolymers exhibit a linear relation between the fractional surface excess of PDMS (Ψ) and $N_A^{-1/2}$ as shown by the regression line in the figure:

$$\Psi = 1.65 - 16.7N_A^{-1/2} \tag{7}$$

The surface excess of PDMS for these four block copolymers varies from a moderate amount ($\Psi = 0.52$ for sample 4) to a very strong segregation regime ($\Psi = 0.95$ for sample 5). From eq 7, the fractional surface excess is projected to 1.0 when $N_A^{-1/2}$ is 0.039, which corresponds to $N_A = 657$. Therefore, for PS-PDMS-PS triblock copolymers with PDMS block length larger than 1314 ($2N_A$), the free surface region up to 27 Å deep from the interface is expected to be composed of pure PDMS. The fractional surface excess becomes zero when $N_A^{-1/2}$ is larger than 0.099, which corresponds to $N_A = 102$. If the PDMS block length of a PS-PDMS-PS triblock copolymer is less than 204 ($2N_A$), there should be no effect of surface segregation of PDMS observed when the composition is averaged up to the 27 Å deep layer. So, $N_A = 657$ could be defined as a critical PDMS block length of the PS-PDMS-PS triblock copolymers for the strong surface segregation regime, and $N_A = 102$ as a critical PDMS block length of the PS-PDMS-PS triblock copolymers for the weak surface segregation regime.

The fractional surface excess data for the three PS-PDMS diblock copolymers are also plotted in Figure 4. All these three Ψ data are very close to unity, and they fall in the strong surface segregation regime. The N_A is 516 (which corresponds to $N_A^{-1/2} = 0.044$) for the PS-PDMS diblock copolymer with the shortest PDMS block among these three samples. Therefore, the critical PDMS block length of the PS-PDMS diblock copolymers for strong surface segregation regime should be less than 516. Compared with the PS-PDMS-PS triblock copolymers for which the critical N_A is 657 for the same regime, PS-PDMS has lower critical N_A value. Hence, the PS-PDMS diblock copolymers have stronger tendency to have PDMS component segregate in the free surface region than the PS-PDMS-PS type triblock copolymers under similar conditions.

From Figure 4 and Table II, the fractional surface excess of PDMS for the PDMS-PS-PDMS type triblock copolymers is higher than that for PS-PDMS-PS type triblock copolymers at the same value of $N_A^{-1/2}$, even though the N_A is counted as half of the PDMS block length for the PS-PDMS-PS type triblock copolymers. For a PS-PDMS-PS type triblock copolymer to achieve the same amount of PDMS surface excess, it should have its PDMS block length more than twice of each PDMS block length of a PDMS-PS-PDMS type triblock copolymers. A PDMS-PS-PDMS type block copolymer with $N_A = 178$ ($N_A^{-1/2} = 0.075$) has fractional surface excess of 0.66, while a PS-PDMS-PS type triblock copolymer with PDMS block repeat units of 2 × 178 = 356 at the same bulk composition has its fractional surface excess only 0.40. To reach the fractional surface excess of 0.66, a PS-PDMS-PS type triblock copolymer has to have PDMS block length larger than 556 ($N_A \geq 276$). Thus, in the PDMS-PS-PDMS type block copolymers the PDMS segments segregate more extensively to the free surface region than in the PS-PDMS-PS type triblock copolymers of the similar PDMS block length and bulk composition.

Fractional Surface Excess of PDMS in the Surface Region up to 73 Å. Figure 5 shows a plot of the fractional surface excess of PDMS as a function of $N_A^{-1/2}$. The values of PDMS fractional surface excess were converted from the ESCA data obtained at a takeoff angle of 45°, which leads to the sampling depth of 73 Å. The four samples of the PS-PDMS-PS type triblock copolymers exhibit a linear relation of the fractional surface excess of PDMS (Ψ) as a function of $N_A^{-1/2}$ as shown by the regression line in the figure:

$$\Psi = 1.95 - 26.3N_A^{-1/2} \tag{8}$$

The surface segregation of PDMS for the four PS-PDMS-PS triblock copolymers ranges from the weak PDMS surface segregation regime ($\Psi = 0.16$) to the very strong DMS surface segregation regime ($\Psi = 0.85$). When N_A is 772 or larger (or $N_A^{-1/2} \geq 0.036$), the free surface of a PS-PDMS-PS triblock copolymer is composed of pure PDMS

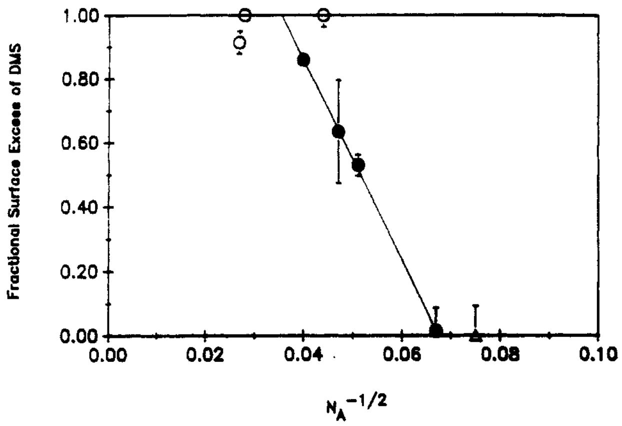

Figure 6. Plot of the fractional surface excess of PDMS versus $N_A^{-1/2}$ in a 103 Å thick free surface region. N_A is defined as the same of Figure 4. The regression line was drawn only for the four PS-PDMS-PS triblock copolymers.

segments down to at least 73 Å. But if N_A is 183 or less (or $N_A^{-1/2} \geq 0.074$), there is no surface segregation effect and the composition down to 73 Å should be the same as the bulk composition.

The three samples of PS-PDMS diblock copolymers still present essentially pure PDMS segments in the top 73 Å surface region. The one with the shortest PDMS block length (sample 2) has its N_A (516) less than the critical N_A of the strong segregation regime for the PS-PDMS-PS triblock copolymers. Again, the critical N_A of the strong segregation regime for a PS-PDMS diblock copolymer should be much lower than that for a PS-PDMS-PS triblock copolymer. The PS-PDMS diblock copolymers allow easier segregation of PDMS segments to the free surface region. The PDMS-PS-PDMS type triblock copolymer with $N_A = 178$ ($N_A^{-1/2} = 0.075$), which is shorter than the critical $N_A = 183$ of the weak segregation of PDMS for the PS-PDMS-PS type triblock copolymers, exhibits moderate surface segregation of PDMS ($\Psi = 0.25$).

Fractional Surface Excess of PDMS in the Surface Region up to 103 Å. Figure 6 illustrates the relationship between the fractional surface excess of PDMS (Ψ) and PDMS block length ($N_A^{-1/2}$) for the three types of PS-PDMS block copolymers. The fractional surface excess data were calculated from ESCA measurements at a takeoff angle of 90°. Among the three types of PS-PDMS block copolymer samples, the four samples of the PS-PDMS-PS type triblock copolymers show a linear relationship between Ψ and $N_A^{-1/2}$ as shown by the regression line in the figure:

$$\Psi = 2.09 - 31.2N_A^{-1/2} \tag{9}$$

The critical N_A of the strong segregation of PDMS over the defined surface region for the PS-PDMS-PS type block copolymers is 816 ($N^{-1/2} = 0.035$), and the critical N_A of the weak segregation of PDMS is 223 ($N^{-1/2} = 0.067$). The PS-PDMS-PS samples present a linear relationship ranging from very high PDMS surface segregation (Ψ = 0.86) to eventually no PDMS surface segregation (Ψ = 0.02). All three samples of the PS-PDMS diblock copolymers retain the feature that the PDMS segments are present almost exclusively in the sampling free surface region. The one with the shortest PDMS block of the three samples has a N_A value of 516, which is much smaller than the critical N_A (816) of the strong segregation of PDMS for the PS-PDMS-PS type triblock copolymers. Therefore, the critical N_A of the strong segregation of PDMS for the PS-PDMS diblock copolymers at the 103 Å thick free surface region must have been much smaller than that for the PS-PDMS-PS type triblock copolymers in the same surface region. There is no surface segregation of PDMS for the PDMS-PS-PDMS sample with high PDMS bulk composition (sample 8 with $f = 0.849$). The critical N_A of the weak segregation limit for the PDMS-PS-PDMS type block copolymers should be larger than 178. However, the PDMS surface segregation still exists in the defined surface region for the sample with low PDMS bulk composition (sample 9 with $f = 0.319$).

Conclusions

A linear relationship between fractional surface excess of PDMS (the lower suface energy component) and block length of PDMS can be used to describe the transition of surface segregation of PDMS in the free surface region from the strong segregation limit to the weak segregation limit for PS-PDMS-PS type triblock copolymers. The equation $\Psi = \alpha' - \beta' N_A^{-1/2}$ for the above block copolymers holds over different ESCA sampling depths, ranging from 27 to 103 Å. But the constants α' and β' vary with sampling depth. This relation between surface morphology and molecular composition can be viewed as a guide for the design of a specific polymer surface. Among one diblock and two triblock type PS-PDMS copolymers, the PDMS segments of PS-PDMS diblock copolymers are the easiest to segregate in the free surface region, while PDMS segments of PS-PDMS-PS triblock copolymers are the least probable to segregate on the free surface over the three sampling depths ranging from 27 to 103 Å at similar bulk composition.

The surface morphologies of the PS-PDMS diblock and PS-PDMS-PS triblock copolymers are lamellar with the periods of 600 and 450 Å, respectively, which are revealed by TEM micrographs of the cross sections of the films both near the free surface and in the bulk. It is also found from those electron micrographs of the two type PS-PDMS block copolymers that the outermost layer is the PDMS lamellar domain, which has a size no less than the PDMS domain size in the bulk. The outer part of the first PDMS layer is less dense and very hairy. The lamellar morphology in the free surface vicinity is oriented parallel to the interface, while the bulk morphology is basically randomly oriented.

A morphology of PS spheres in PDMS matrix is found for the PDMS-PS-PDMS type triblock copolymer. The period of the ordered PS sphere arrays separated by the PDMS domains is measured to be 130 Å. The bulk morphology of this PDMS-PS-PDMS triblock copolymer is randomly oriented.

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