Surface Modification of Polymers by Blending Siloxane Block Copolymers

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ABSTRACT: The surface modification of a series of homopolymers is accomplished through mixing an AB block copolymer, where B is a poly(dimethylsiloxane) (PDMS) block and A is the block of the same chemical identity as of the homopolymers. The homopolymers are polystyrene, poly(α-methylstyrene), and Bisphenol A polycarbonate. The surface composition of PDMS is measured by angle-dependent electron spectroscopy for chemical analysis (ESCA). The PDMS blocks are segregated in the topmost surface region and constitute up to 90 wt % of the surface of the AB/A blends, even though the overall bulk PDMS concentrations of the blends are 6% or less. The effects of the bulk concentration of the block copolymers, molecular weight, and block copolymer architecture on the surface composition of the AB/A blends are discussed.

I. Introduction

The surface properties of polymeric materials are important to many of their applications. A desired polymer surface sometimes cannot be obtained from the material itself but through modification. Modification of a polymer surface can be achieved by means of various chemical or physical processes. The most common surface modification techniques include plasma treatment,[1,2] surface grafting,[3,4] chemical reaction,[1,5] vapor deposition of metals,[6] and flame treatment.[7] Blending a small amount of a block copolymer (AB) into a homopolymer (A) has also been demonstrated as an effective way to change the surface composition and lower the surface tension of the polymeric alloys, if the B blocks have a substantially lower surface energy than the A blocks.[8,9] The block copolymer added in small amounts behaves like a surfactant and segregates to the surface region; only the properties of this region are changed and the bulk properties remain the same as the homopolymer.

For the blend of an AB block copolymer and an A homopolymer (designated as AB/A), a homogeneous mixture of AB copolymer and A homopolymer occurs in the blend bulk when the concentration of the AB copolymer is low.[10,11] Formation of AB block copolymer micelles occurs as the concentration of the AB block copolymer increases beyond a critical micelle concentration (cmc). The cmc and morphology of the micelles depend on the molecular weights of the homopolymer A (M_H) and the blocks of the block copolymer AB (M_A and M_B), as well as the ratio of M_H/M_A.

The surface composition of an AB/A binary polymer blend has been studied recently both theoretically[12-15] and experimentally.[16-18] ESCA was used to compare the surface behavior in binary blends of poly(dimethylsiloxane) (PDMS) with poly(Bisphenol A sulfone) and Bisphenol A polycarbonate.[18] Though a pronounced surface enrichment of the lower surface energy component (PDMS) and the dependence of surface composition on bulk composition of the blends have been revealed, the effects of the relative molecular weights of the components (M_H/M_A) and architecture of the block copolymers on the surface composition of the AB/A blends have not been clearly demonstrated by experiments. In the present investigation, block copolymers of polystyrene–poly(dimethylsiloxane) (PS–PDMS), poly(α-methylstyrene)–poly(dimethylsiloxane) (PMS–PDMS), and (Bisphenol A polycarbonate)–poly(dimethylsiloxane) (BPAC–PDMS) were used in various AB/A type binary blends, where B is denoted as the PDMS component. Surface compositions of the AB/A blends are measured by using angle-dependent ESCA to monitor how these block copolymers change the air side surface of the homopolymers. In particular, the effects of the relative molecular weights of block copolymers and homopolymers, bulk concentration of block copolymers, and architecture of block copolymers on the surface composition of the AB/A blends are the focus of this paper.

II. Experimental Section

Homopolymers of polystyrene, poly(α-methylstyrene), and Bisphenol A polycarbonate were purchased from Scientific Polymer Products. Block copolymers of PS–PDMS, PMS–PDMS, and BPAC–PDMS were obtained as donations, and the details of their structure were described in previous papers.[19-21] All the polymers were used as received. The polymers were dissolved in chloroform to prepare 0.5% solutions, cast into aluminum weighing dishes, and then allowed to air dry. They were further dried in a vacuum oven over 1 day at 150 °C for the polystyrene- and poly(α-methylstyrene)-based blends and 180 °C for the BPAC-based blends. The thickness of the films on aluminum substrate was estimated to be 50 μm from the volume and concentration of the polymer solutions used in casting.

Angle-dependent ESCA analysis of the polymer blend films was performed on a Perkin-Elmer PHI 5300 ESCA spectrometer with a single-channel detector and a hemispherical energy analyzer. The Mg Kα X-ray source of the ESCA spectrometer was operated at 300 W (15 kV and 20 mA). A pass energy of 35.75 eV was chosen for all angle-dependent acquisitions. Take-off angles of 10°, 15°, 45°, and 90° were used for all samples and lead to sampling depths of 18, 27, 73, and 103 Å, respectively.[20,22] The calculation of PDMS surface concentrations was based on the ratio of peak areas (Si/C) and illustrated in our previous work.[19-21]

III. Results and Discussion

According to the base homopolymers, the AB/A binary blends studied are divided into three groups. The configurations of the AB/A blends are summarized in Tables 1–3. In all three tables, the numbers followed by the polymer components are the number-average molecular weights of the homopolymers or polymer blocks in the unit of a thousand grams per mole (10^3 g/mol).

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Table 1. PS–PDMS/PS Polymeric Blends

		block copolymers		PDMS
sample	homopolymer[a]	architecture	wt %[b]	wt %[b]
1	PS790	PS70–PDMS99	2	1
2	PS790	PS70–PDMS99	5	3
3	PS790	PS70–PDMS99	10	6
4	PS280	PS70–PDMS99	2	1
5	PS280	PS70–PDMS99	5	3
6	PS280	PS70–PDMS99	10	6
7	PS58	PS70–PDMS99	2	1
8	PS58	PS70–PDMS99	5	3
9	PS58	PS70–PDMS99	10	6
10	PS280	PS12–PDMS56–PS12	2	1
11	PS280	PS12–PDMS56–PS12	5	3.5
12	PS280	PS12–PDMS56–PS12	10	7
13	PS8	PS12–PDMS56–PS12	2	1
14	PS8	PS12–PDMS56–PS12	5	3.5
15	PS8	PS12–PDMS56–PS12	10	7
16	PS280	PDMS13–PS7–PDMS13	2	1.5
17	PS280	PDMS13–PS7–PDMS13	5	4
18	PS280	PDMS13–PS7–PDMS13	10	8
19	PS5	PDMS13–PS7–PDMS13	2	1.5
20	PS5	PDMS13–PS7–PDMS13	5	4
21	PS5	PDMS13–PS7–PDMS13	10	8

[a] Polymers followed by their molecular weights (10^3 g/mol). [b] Weight percent in the overall blend.

Table 2. PMS–PDMS/PMS Polymeric Blends

		block copolymer[a]		PDMS
sample	homopolymer[a]	architecture	wt %[b]	wt %[b]
22	PMS80	(PMS8–PDMS12)$_n$	2	1
23	PMS80	(PMS8–PDMS12)$_n$	5	3
24	PMS80	(PMS8–PDMS12)$_n$	10	6
25	PMS11	(PMS8–PDMS12)$_n$	2	1
26	PMS11	(PMS8–PDMS12)$_n$	5	3
27	PMS11	(PMS8–PDMS12)$_n$	10	6
28	PMS80	(PMS9–PDMS14)$_4$C	2	1
29	PMS80	(PMS9–PDMS14)$_4$C	5	3
30	PMS80	(PMS9–PDMS14)$_4$C	10	6
31	PMS11	(PMS9–PDMS14)$_4$C	2	1
32	PMS11	(PMS9–PDMS14)$_4$C	5	3
33	PMS11	(PMS9–PDMS14)$_4$C	10	6

[a] Polymers followed by their molecular weights (10^3 g/mol). [b] Weight percent in the overall blend.

Table 3. BPAC–PDMS/BPAC Polymeric Blends

		block copolymer[a]		PDMS
sample	homopolymer[a]	architecture	wt %[b]	wt %[b]
34	BPAC38	(BPAC1.5–PDMS1.5)$_n$	2	1
35	BPAC38	(BPAC1.5–PDMS1.5)$_n$	5	2.5
36	BPAC38	(BPAC1.5–PDMS1.5)$_n$	10	5
37	BPAC38	(BPAC5–PDMS3)$_n$	2	1
38	BPAC38	(BPAC5–PDMS3)$_n$	5	2
39	BPAC38	(BPAC5–PDMS3)$_n$	10	4

[a] Polymers followed by their molecular weights (10^3 g/mol). [b] Weight percent in overall blend.

1. Surface of PS–PDMS/PS Blends. The configurations of the PS–PDMS/PS blends are listed in Table I. The PS–PDMS block copolymers mixed in the blends have three architectures (PS–PDMS diblock copolymer and PS–PDMS–PS and PDMS–PS–PDMS triblock copolymers). For examination of the effect of homopolymer molecular weight (M_H) on the surface composition of the blends, PS homopolymers with different molecular weights were mixed with the block copolymers in various amounts. In the present study, the molecular weight of the PS homopolymer (M_H) is selected to be either significantly larger than ($M_H/M_A \geq 10$) or comparable to the molecular weight of the PS block in the block copolymer (M_A) in a PS–PDMS/PS blend.

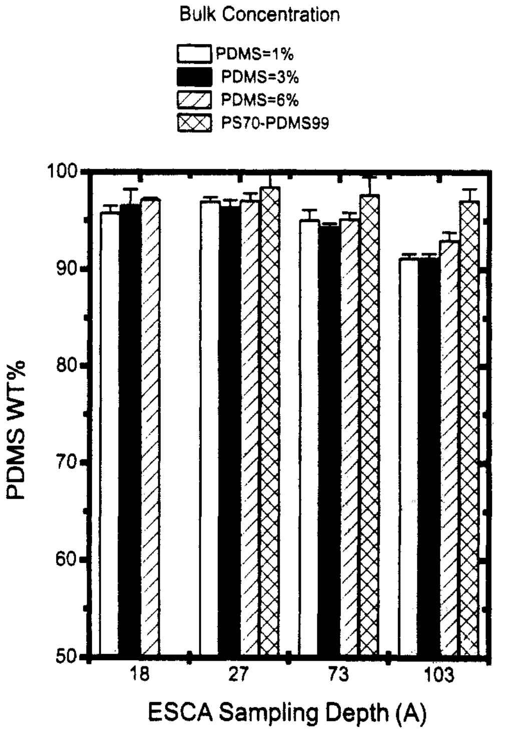

Figure 1. PDMS surface concentration profiles of PS70–PDMS99/PS790 blends and the pure block copolymer PS70–PDMS99. The PDMS bulk concentrations of the blends are 1, 3, and 6% by weight.

To establish a depth profile of surface compositions, four ESCA take-off angles were used. The ESCA sampling depths are from 18 to 103 Å. It should be mentioned that, as of many other surface analysis techniques, the ESCA signals attenuate with depth. The materials in the outer surface region contribute more to the ESCA measurements than the materials of the same volume in the inner surface region. The angle-dependent ESCA measurements in this paper are not deconvoluted and are the complex averages of the measurements from the interface to the sampling depths.

Surface Segregation of PDMS. Since the surface tension of PDMS (20 mN/m) is much smaller than that of PS (41 mN/m), the surface region of the PS–PDMS/PS blends is expected to be rich in PDMS component. The presence of PDMS surface segregation can minimize the total free energy of the blends.

Figure 1 illustrates the surface composition results of the determination for blends of a PS homopolymer (M_H = 790 000) with a PS–PDMS diblock copolymer (M_A = 70 000). The molecular weight of the PS homopolymer is substantially higher than the molecular weight of the PS block ($M_H/M_A = 11.3$). The diblock copolymer was mixed at concentrations of 2, 5, and 10% by weight in the three blends (samples 1–3). The overall bulk PMDS concentrations are 1, 3, and 6% weight, respectively. As shown in this figure, the surface region of the blends are dominated by PDMS (up to values of 97% PDMS), even though the bulk PDMS concentration in the blend is as low as 1%. The surface PDMS concentration attenuates slowly with the ESCA sampling depth. The PDMS blocks comprise more than 90% of the material in a surface region up to 103 Å.

When the PDMS bulk concentration varies from 1 to 6%, the surface compositions do not change significantly. The three PDMS surface concentration profiles in Figure 1 virtually overlap if measurement errors are considered. This result means that mixing as low as 2% of this PS70–PDMS99 diblock copolymer with PS790 is enough to

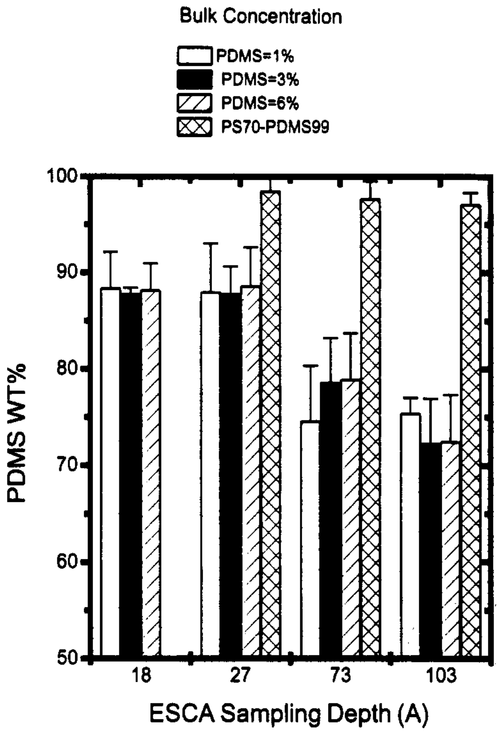

Figure 2. PDMS surface concentration profiles of PS70–PDMS99/PS58 blends and the pure block copolymer PS70–PDMS99. The PDMS bulk concentrations of the blends are 1, 3, and 6% by weight.

achieve drastic surface modification of the polystyrene homopolymer (PS790). If M_H is much larger than M_A in the PS–PDMS/PS blend, the surface of the blend with as low as 2% of the PS–PDMS block copolymer in the overall blend almost exclusively consists of PDMS. The surface concentration profile of the pure block copolymer PS70–PDMS99 is also plotted in this figure.[19] Composition of the profiles of the blends with that of the block copolymer clearly indicates that mixing an excess amount of the diblock copolymer into the blend cannot make any significant change of the composition of the blend in the topmost surface region.

Molecular Weight of PS Homopolymers. Compatibility of polymer components is a major factor governing the compositions and morphology of a polymer blend. In general, block copolymers and polymer blends have a microphase-separated morphology because of the incompatibility between the components. In an AB/A binary blend, the ratio of the molecular weight of the A block (M_A) to the molecular weight of the A homopolymer (M_H) can affect the compatibility of the AB block copolymer with the A homopolymer. When M_H is comparable to or smaller than M_A, the A homopolymer molecules can penetrate into the microdomains of the A blocks. The interface between the A and B microdomains is widened due to the penetration of the A homopolymers into the interfacial region. However, the A homopolymer is less compatible with the AB block copolymer if M_H is much larger than M_A. The penetration of the relatively large A homopolymer molecules would be less probable. In this case, the A homopolymer chains only tether the chains of the A blocks in the interfacial region of the A blocks and A homopolymer.[14]

Figure 2 shows the surface composition profiles of the PS70–PDMS99/PS58 blends (samples 7–9) with M_H slightly smaller than M_A. As found in the PS70–PDMS99/PS790 blends depicted in Figure 1, these PS70–PDMS99/PS58 blends with various bulk concentrations of the PS–PDMS diblock copolymer also exhibit segregation of PDMS in the surface region. From comparison of Figures 1 and 2, it can be noticed that the extent of the PDMS surface segregation of the PS70–PDMS99/PS58 blends in Figure 2 is not as high as that of the PS70–PDMS99/PS790 blends in Figure 1. The surface composition difference between these two groups of blends suggests that the interface of the PDMS block microdomains and PS block microdomains be swollen and widened by the PS homopolymer if M_H is not larger than M_A.

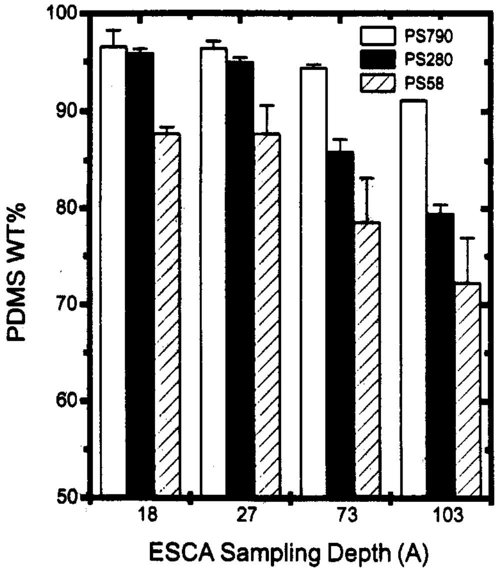

Figure 3. PDMS surface concentration profiles of PS70–PDMS99/PS blends with various molecular weight of PS homopolymers. The PDMS bulk concentration in all three blends is 3%.

The molecular weight effect on the surface composition of the PS–PDMS/PS blends at a controlled blend composition is further illustrated in Figure 3. The three blends analyzed in Figure 3 consist of the PS70–PDMS99 diblock copolymer (5%) and a PS homopolymer of various molecular weights. The molecular weights of the PS homopolymers, M_H, are 790 000, 280 000, and 58 000.

When the composition of the PS–PDMS/PS blend is the same, PDMS surface concentration increases with the molecular weight of PS homopolymer (M_H). Therefore, the surface of a PS homopolymer is more effectively modified by blending a PS–PDMS block copolymer, if the molecular weight of the PS homopolymer is significantly higher than that of the PS block of the block copolymer mixed.

Architecture of Block Copolymers. The surface composition of the PS-PDMS diblock and triblock copolymers were studied in one of our previous papers.[19] The results showed that the architecture of the PS-PDMS block copolymers influenced the surface composition, due to the chain folding patterns in the surface region.

The surface composition profiles of the PS–PDMS/PS blends are shown in Figure 4. The bulk concentration of the PS–PDMS block copolymers in the blends is the same (5%), but their overall bulk PDMS concentrations are slightly different (ranging from 3% to 4%). On the basis of the molecular weights of PS homopolymer and blocks, the architecture effect on the surface compositions of the blends should be discussed in two situations. The block architecture effect on surface composition is not sensitive (as shown in Figure 4a) if the molecular weight of the PS homopolymer (M_H) is much larger than the molecular weight of the PS blocks (M_A). The composition in the topmost surface region (18 Å) is equivalent among the three blends, though some PDMS concentration differ-

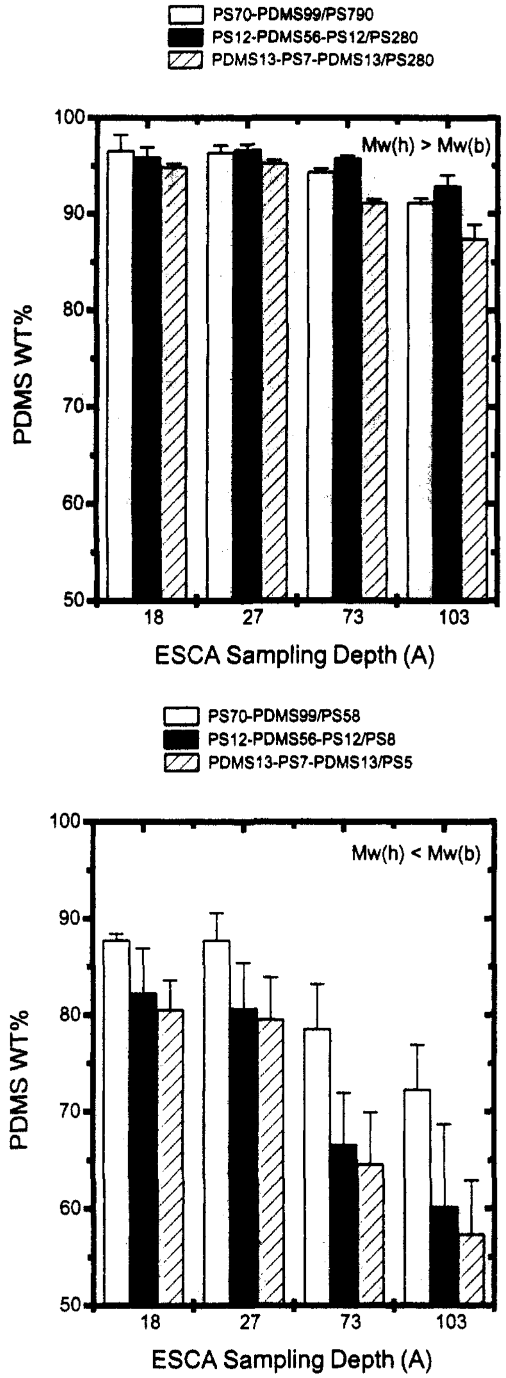

Figure 4. Comparison of the PDMS surface concentration profiles of the PS–PDMS/PS blends. The molecular weight of the PS homopolymer is either larger (a) or smaller (b) than the molecular weight of the PS block in each of the blends.

ences are detected at large ESCA sampling depths (73 and 103 Å). The PDMS concentrations of the PDMS13–PS7–PDMS13/PS280 blend are relatively lower than those of the other two blends. It is most probably due to the short length of the PDMS blocks in this blend, instead of its architecture. However, the effect of block copolymer architecture on the surface composition of the blends is observed (as shown in Figure 4b), if M_H is smaller than M_A. The blend with a diblock copolymer has higher PDMS concentrations in surface regions measured by ESCA than the blend with the PDMS–PS–PDMS triblock copolymer. This result is consistent with the block architecture effect on the surface composition of the pure PS–PDMS block copolymers.[19] The surface composition profiles of the two blends with PS–PDMS–PS and PDMS–PS–PDMS triblock copolymers are completely overlapped.

2. Surface of PMS–PDMS/PMS Blends. Two PMS–PDMS copolymers with different block architectures were used to constitute the PMS–PDMS/PMS blends. A (PMS8–PDMS12)$_n$ multiblock starblock copolymer was blended in samples 22–27 and a (PMS9–PDMS14)$_4$C starblock copolymer was blended in samples 28–33. This starblock copolymer consists of four arms with each arm constituted of a PMS block and a PDMS block. The PDMS blocks are inner blocks and linked to the center of the starblock copolymer.

The surface composition profiles of the PMS–PDMS/PMS blends are shown in Figure 5. In each of the PMS–PDMS/PMS blends, PDMS surface concentration is much higher than the overall bulk PDMS concentration. This means that a small quantity of PMS–PDMS block copolymers can drastically change the surface composition of the PMS homopolymers. The surface properties of the blends should be controlled by the dominated PDMS component.

In Figure 5a, a multiblock copolymer (PMS8–PDMS12)$_n$ was mixed with PMS80 in 2, 5, and 10% by weight. The overall bulk PDMS concentrations are 1, 3, and 6%, respectively. The molecular weight of the PMS homopolymer (M_H = 80 000) is much higher than the molecular weight of the PMS blocks (M_A = 8000). When the overall bulk PDMS concentration in the blends increases from 1 to 3%, the surface PDMS concentrations increase significantly. However, the surface PDMS concentrations measured by ESCA only a slightly increase if the overall bulk PDMS concentration increases from 3 to 6%. The topmost surface region (18 Å) of the PMS–PDMS/PMS blends consists of as much as 90% of PDMS, if there is 3% or more of PDMS in the overall blend. The PDMS surface concentration of the blends attenuates with the ESCA sampling depth. The surface composition measured at an ESCA sampling depth of 103 Å is still dominated by PDMS, if the blend has a relatively high PDMS concentration (3% or more) in the overall blend.

Again, the PDMS surface concentration profile of the pure multiblock copolymer (PMS–PDMS12)$_n$ is plotted with the profiles of the blends.[20] As found in the PS–PDMS/PS blends, the PDMS surface concentration increase is not significant if the bulk concentration of the block copolymer increases from 10 to 100%.

Figure 5b shows the surface composition profiles of the blends of a homopolymer PMS80 and a four-arm starblock copolymer (PMS9–PDMS14)$_4$C. The overall bulk compositions of these PMS blends with the starblock copolymer match those with the multiblock copolymer. The surface composition profiles of the blends containing the starblock copolymer resemble those of the blends containing the multiblock copolymer. The most significant difference between these two groups of blends is that the PDMS surface concentrations of the blends with the starblock copolymer do not increase as much as those with the multiblock copolymer when the overall bulk PDMS concentration increases. If the overall blend consists of 10% of the starblock copolymer (6% PDMS), for instance, the PDMS concentration in the topmost surface region (18 Å) of the (PMS9–PDMS14)$_4$C/PMS80 blend is less than 80%. In the same surface region, the PDMS concentration of the (PMS8–PDMS12)$_n$/PMS80 blend of the same bulk composition is more than 90%. The PDMS surface concentration differences are relatively large between the PDMS surface profile of the blend with 10% of the starblock copolymer and that of the pure starblock copolymer. Therefore, it is less effective to modify the surface of the homopolymer PMS80 by mixing the four-

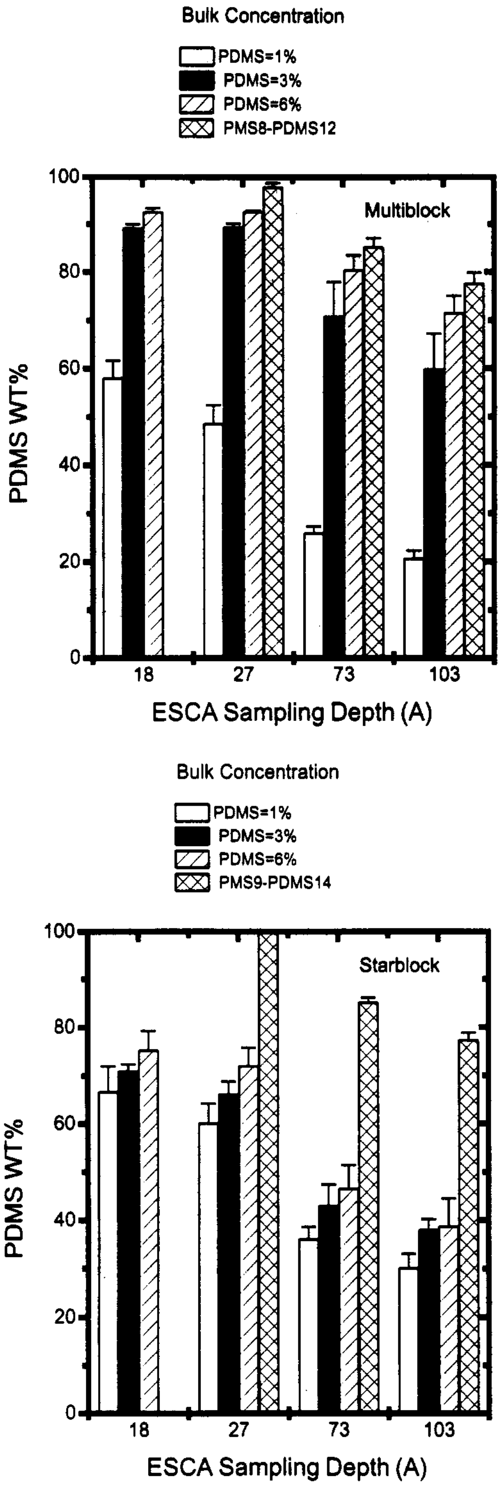

Figure 5. PDMS surface concentration proflies of PMS-PDMS/PMS80 blends and the pure block copolymer PMS-PDMS. The PDMS bulk concentrations of the blends are 1, 3, and 6% by weight. The PMS-PDMS copolymers are (a) multiblock copolymer (PMS8-PDMS12)$_n$ and (b) starblock copolymer (PMS9-PDMS14)$_4$C.

arm starblock copolymer than by mixing the multiblock copolymer.

The effect of the molecular weight of the PMS homopolymer on the surface composition of the PMS-PDMS/PMS blends is illustrated in Figure 6. All these blends in Figure 6 consist of 3% of PDMS in overall blends. Figure 6a compares the surface composition profiles of two (PMS8-PDMS12)$_n$/PMS blends, and Figure 6b compares the surface composition profiles of two (PMS9-PDMS14)$_4$C/PMS blends. For each of the above blend groups, one PMS-PDMS/PMS blend consists of a PMS homopolymer with M_H much higher than M_A, and the other blend consists of a PMS homopolymer with M_H comparable to M_A.

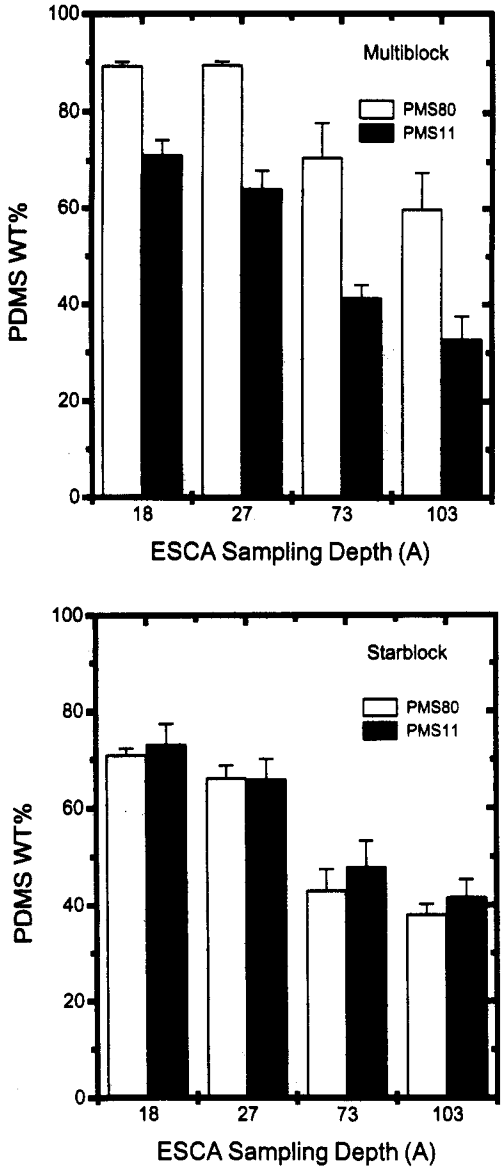

Figure 6. PDMS surface concentration profiles of PMS-PDMS/PMS blends. The PDMS bulk concentration in all these blends is 5%. The molecular weights of PMS homopolymers are 80 000 and 11 000. The block copolymers are (PMS8-PDMS12)$_n$ multiblock copolymer (a) and (PMS9-PDMS14)$_4$C starblock copolymer (b).

For the multiblock copolymer blends, the molecular weight effect on the surface composition is clearly shown in Figure 6a. The PDMS surface concentrations of the blend with PMS80 are much higher than those of the blend with PMS11. However, there is no difference of surface composition detected by ESCA between the starblock copolymer blend with PMS80 and the starblock copolymer blend with PMS11 (Figure 6b).

The surface compositions of the starblock copolymer blends with PMS are not sensitive to both the amount of the block copolymers and the molecular weight of PMS homopolymers. The PDMS blocks in the starblock copolymers are inner blocks, and each PDMS block only links with one PMS block. In a multiblock copolymer architecture, each PDMS block links with two PMS blocks except the end PDMS blocks. Therefore, chain entanglement between a PDMS block and a PMS block is more probable in the multiblock copolymers than in the starblock copolymers. This means that the PDMS mi-

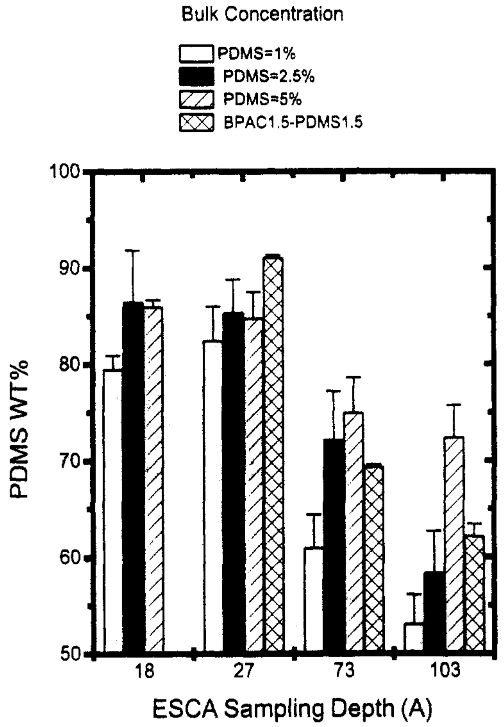

Figure 7. PDMS surface concentration profiles of (BPAC1.5–PDMS1.5)$_n$/BPAC38 blends and the pure block copolymer (BPAC1.5–PDMS1.5)$_n$. The PDMS bulk concentrations of the blends are 1, 2.5, and 5% by weight.

crodomains of the starblock copolymer with PDMS blocks as inner blocks should have narrower interfaces. Any change in the PMS phases does not influence the PDMS microdomains of the starblock copolymer blends as much as the PDMS microdomains of the multiblock copolymer blends.

3. Surface of BPAC–PDMS/BPC Blends. BPAC–PDMS random block copolymers were used to study the surface modification of BPAC homopolymers by mixing block copolymers. The BPAC blocks are relatively short (20 or 40 repeat units) compared with those PS and PMS blocks in the previous sections. Unlike those PS and PMS blocks with a narrow molecular weight distribution, these BPAC blocks have random block lengths due to the nature of polymerization.

A homopolymer BPAC38 was mixed with a random block copolymer (BPAC1.5–PDMS1.5)$_n$ (samples 34–36). The overall bulk PDMS concentrations of these (BPAC1.5–PDMS1.5)$_n$/BPAC38 blends are 1, 2.5, and 5% by weight. The surface composition profiles of these blends are shown in Figure 7. The PDMS surface concentrations in the topmost surface region are as high as 80%, even though there is only 1% PDMS in the overall blend. When more block copolymer is mixed, the PDMS concentrations in the topmost surface region (up to 27 Å) do not increase substantially. The increase in PDMS concentration measured at an ESCA sampling depth of 27 Å is within 5% when the bulk block copolymer concentration increases from 5 to 100%.[21] The surface concentration difference of the blends is significant when a larger span of surface region (73 Å or more) is measured. It is unexpected that the PDMS concentration measured at an ESCA sampling depth of 103 Å from the blend with 10% block copolymer is higher than the PDMS concentration of the pure block copolymer (BPAC1.5–PDMS1.5)$_n$.

A BPAC–PDMS block copolymer with longer blocks was used (samples 37–39) to study the effect of the B block (PDMS) length on the surface of the BPAC–PDMS/BPAC blends. The PDMS block in (BPAC5–PDMS3)$_n$ is twice as long as the PDMS block in (BPAC1.5–PDMS1.5)$_n$. The overall PDMS concentration of the (BPAC5–PDMS3)$_n$/BPAC38 blend is slightly lower than that of the (BPAC1.5–PDMS1.5)$_n$/BPAC38, if the block copolymer concentration in the blends is the same. Figure 8 shows the surface composition profiles of blend (BPAC5–PDMS3)$_n$/BPAC38 and blend (BPAC1.5–PDMS1.5)$_n$/BPAC38. The block copolymers in these two blends were mixed with BPAC38 in 10% by weight. The two profiles overlap in the region of short ESCA sampling depths (18 and 27 Å). The PDMS surface concentrations of the blend with longer PDMS blocks (M_B = 3000) are lower than those of the blend with shorter PDMS blocks (M_B = 1500), when a larger span of surface region is measured (103 Å). The unexpected lower PDMS surface concentration of the (BPAC5–PDMS3)$_n$/BPAC38 blend is most probably due to the lower overall PDMS concentration in blend (BPAC5–PDMS3)$_n$/BPAC38 (4%) than that in blend (BPAC1.5–PDMS1.5)$_n$/BPAC38 (5%). The effect of the overall bulk concentration of the block copolymers on the surface composition averaged in a large span surface region has been illustrated in Figure 7.

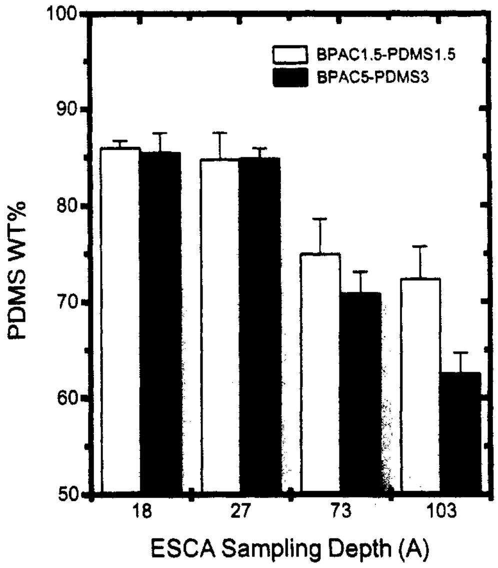

Figure 8. Comparison of the PDMS surface concentration profiles of the BPAC–PDMS/BPAC38 blends with different PDMS block lengths.

IV. Conclusions

Surface modification of a homopolymer A through mixing a block copolymer AB is investigated by measurements from angle-dependent ESCA. The A homopolymers and blocks are polystyrene, poly(α-methylstyrene), and Bisphenol A polycarbonate. The common B blocks are poly(dimethylsiloxane). Because of the low surface energy of the PDMS blocks, surface segregation of the PDMS blocks is found in all these AB/A blends. The amount of the block copolymer AB in the blend, the molecular weight of the homopolymer A, and the block copolymer architecture are among the fractors which affect the surface compositions of the AB/A blends.

When the PDMS from the block copolymers is incorporated into the blends at 6% or less by weight, the surface PDMS concentrations of the blends could be as high as 95%. In most of the AB/A blends, the PDMS surface concentrations do not change substantially when the bulk concentration of the block copolymer in the blend increases from 10 to 100%. Therefore, the surface properties of the AB/A blends should be controlled by the dominated PDMS component in the surface region even if the overall bulk PDMS concentrations in the blends are very low.

The ratio of the molecular weight of the A homopolymer to that of the A blocks (M_H/M_A) is important to the extent of PDMS surface segregation of the AB/A blends. In the PS-PDMS/PS blends and the PMS blends with multiblock copolymer PMS-PDMS, the amount of PDMS surface segregation of the blends with a M_H/M_A ratio larger than 10 is significantly higher than that of the blends with comparable M_H and M_A. However, this effect was not observed in the PMS blends with the starblock copolymer PMS-PDMS, of which PDMS blocks are inner blocks.

The effect of block copolymer architecture on the surface composition is observed on some of the AB/A blends. If the M_H/M_A ratio is large and bulk concentration of the block copolymer is higher than 5%, and PMS-PDMS/PMS blend with PMS-PDMS as the multiblock copolymer has a higher PDMS surface concentration than the PMS-PMDS blend with PMS-PDMS as the starblock copolymer. This effect is not observed if the molecular weight of the PMS homopolymer M_H is comparable to the molecular weight of the PMS blocks M_A.

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Supplementary Material Available: Tables of PDMS weight percent at surfaces of PS-PDMS/PS, PMS-PDMS/PMS, and BPAC-PDMS/PMS blends (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Vargo, T. G.; Thompson, P. M.; Gerenser, L. J.; Valentini, R. F.; Aebischer, P.; Hook, D. J.; Gardella, J. A., Jr. *Langmuir* **1992**, *8*, 130.

(2) Kim, C. Y.; Evans, J.; Goring, D. A. I. *J. Appl. Polym. Sci.* **1971**, *15*, 1365.

(3) Feng, X. D.; Sun, Y. H.; Qin, K. Y. *Macromolecules* **1985**, *16*, 2105.

(4) Liouni, M.; Touloupis, C.; Hadjichristidis, N.; Karvounis, S.; Marston, E. V. *J. Appl. Polym. Sci.* **1992**, *45*, 2199.

(5) Tsukada, M.; Goto, Y.; Freddi, G.; Shiozaki, H. *J. Appl. Polym. Sci.* **1992**, *45*, 1189.

(6) Silvain, J. F.; Ehrhardt, J. J.; Lutgen, P. *Thin Solid Films* **1991**, *L5*, 195.

(7) Briggs, D.; Brewis, D. M.; Konieczko, M. B. *J. Mater. Sci.* **1979**, *14*, 1344.

(8) Dwight, D. W.; McGrath, J. E.; Riffle, J. S.; Smith, S. D.; York, G. A. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *52*, 457.

(9) LeGrand, D. G.; Gaines, G. L., Jr. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1970**, *11*, 442.

(10) Kinning, D. J.; Thomas, E. D.; Fetters, L. J. *J. Chem. Phys.* **1989**, *90*, 5806.

(11) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.

(12) Semenov, A. N. *Macromolecules* **1992**, *25*, 4967.

(13) Cifra, P.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1992**, *25*, 4895.

(14) Shull, K. R.; Winey, K. I. *Macromolecules* **1992**, *25*, 2637.

(15) Banaszak, M.; Whitmore, M. D. *Macromolecules* **1992**, *25*, 2757.

(16) Russell, T. P.; Mayes, A. M.; Deline, V. R.; Chung, T. C. *Macromolecules* **1992**, *25*, 5783.

(17) Green, P. F.; Russell, T. P. *Macromolecules* **1991**, *24*, 2931.

(18) Pertsin, A. J.; Gorelova, M. M.; Levin, V. Y.; Makarova, L. I. *J. Appl. Polym. Sci.* **1992**, *45*, 1195.

(19) Chen, X.; Gardella, J. A., Jr.; Kumler, P. L. *Macromolecules* **1992**, *25*, 6621.

(20) Chen, X.; Gardella, J. A., Jr.; Kumler, P. L. *Macromolecules* **1993**, *26*, 3778.

(21) Chen, X.; Lee, H. F.; Gardella, J. A., Jr. *Macromolecules*, **1993**, *26*, 4601.

(22) Seah, M. P.; Dench, W. A. *Surf. Interface Anal.* **1979**, *1* (1), 2.