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Characteristics of the Surface-Induced Orientation for Symmetric Diblock PS/PMMA Copolymers

T. P. Russell,[*] G. Coulon,[†] V. R. Deline, and D. C. Miller

IBM Research Division, Almaden Research Center, 650 Harry Road,
San Jose, California 95120-6099. *Received January 18, 1989;*
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ABSTRACT: The characterisitics of the surface-induced orientation of symmetric diblock poly(styrene-*b*-methyl methacrylate) copolymers PS/PMMA, as revealed by dynamic secondary ion mass spectroscopy (SIMS) are presented. The lamellar morphology is found to orient parallel to the surface of the substrate with a lateral coherence on the order of 80 μm. On silicon substrates, the total film thickness is given by $(n + {}^1/_2)L$ where L is the lamellar period and n is the number of periods, whereas on a gold substrate the thickness is given by nL. The ordering results from a preferential location of PS on the gold substrate and at the air/copolymer interface and of PMMA on the silicon substrate. Time-dependent annealing studies on thick specimens above the glass transition show that the orientation is induced at both the air/copolymer and the copolymer/substrate interfaces and propagates through the entire specimen. For samples prepared on silicon substrates where the total film thickness is less than L, a microphase-separated morphology is not found. Here only gradients in the composition of each component at the interfaces are found. Finally, the preparation of films under slow-evaporation conditions from solvents that preferentially solvate one of the components induces an oriented, nonequilibrium morphology.

Introduction

In the microphase-separated state, diblock copolymers can exhibit spherical, cylindrical, or lamellar morphologies. This behavior of copolymers in the bulk has been studied by many different laboratories and has provided important insights into the interactions occurring between the two different block constituents.[1] The characteristics of diblock copolymers at surfaces and interfaces in the solid state have, on the other hand, received considerably less attention. However, the use of block copolymers as agents for compatibilizing two immiscible homopolyers and as surface-active components in a multicomponent system has focused attention of the interfacial and surface activity of block copolymers.

Related to these are the characteristics of thin films of block copolymers. For specimens prepared on a substrate, the interactions of the two constituents with the substrate and with the free surface are of critical importance. It is also necessary to consider the total thickness of the film in relation to the periodicity or regular spatial arrangement of the microdomains of the copolymer morphology. While electron microscopy,[2-5] optical microscopy,[6-8] and X-ray photoelectron spectroscopy[9-11] have been used to investigate these questions in the past, we present here the use of dynamic secondary ion mass spectroscopy to characterize the behavior of diblock copolymer in thin-film form and the effect of the air/copolymer and copolymer/substrate interfaces on the copolymer morphology.

Recently, it has been shown that symmetric, diblock copolymers of poly(styrene-*b*-methyl methacrylate), PS/PMMA, prepared on a silicon substrate exhibit a strong orientation of the lamellar microdomains parallel to the surface of the film.[12] It was found that solution-cast films from toluene, a nonselective solvent for either block, while microphase separated,[13,14] showed no preferential alignment of the microdomains. However, annealing these films at temperatures 50 °C higher than the glass transition for 24 h produced a periodic variation in the microdomain morphology normal to the film surface. This orientation was such that PMMA was preferentially located at the Si substrate due, most likely, to polar interactions between the PMMA and the substrate. Since the surface energy of PS is slightly less than that of PMMA, PS is preferentially located at the air/copolymer interface. The reorganization of the solution-cast films was found to be independent of the thickness of the film up to film thicknesses of ca. 5000 Å.

Table I
Copolymer Characterization[d]

		$M_{p,PS}{}^a$	$\frac{M_{w,PS}{}^a}{M_{n,PS}}$	$M_{p,PMMA}{}^{a,b}$	$\frac{M_{w,c}{}^c}{M_{n,c}}$
PSD/PMMAH	15K/15K	12 650	1.05	12 204	1.08
PSH/PMMAD	15K/15K	14 600	1.01	14 100	1.09
PSD/PMMAH	50K/50K	52 800	1.09	48 000	1.07
PSH/PMMAD	50K/50K	56 260	1.13	65 000	1.17
PSD/PMMAH	150K/150K	169 540	1.03	131 900	1.08

[a] Characterization of first block of the copolymer. [b] Derived from the total M_w of the copolymer. [c] Characterization of total copolymer. [d] A deuterium equivalent molecular weights; M_p corresponds to the peak value of the molecular weight.

In this article several different aspects of this orientation process are considered in more detail. First, it is shown that a change in the substrate from silicon to gold, a chemically inert substrate without an oxide layer, shows a preferential adsorption of PS as opposed to PMMA. However, the strong orientation of the lamellar microdomains with a large-scale lateral coherence is maintained. Second, in a kinetic study of the orientation process on thick films, it is shown that oscillatory patterns are established at both the air/copolymer and copolymer/substrate interfaces independently. However, if the film thickness is small, the oscillations from the copolymer/substrate interface dominate. Third, it is shown that with lower molecular weight PS/PMMA diblock copolymers the lamellar orientation is not found, suggesting that this copolymer is phase mixed. Fourth, it is shown that, for films with thicknesses less than one period, the development of a microphase-separated morphology is not seen. Finally, we present some unusual solvent-case results using chloroform, a preferential solvent for PMMA, where the solvent has been evaporated slowly.

Experimental Section

Symmetric, diblock copolymers of PS/PMMA, purchased from Polymer Laboratories, were used in this study. The copolymers were synthesized such that either the PS or PMMA block was deuterated. The molecualr weights and polydispersities of the copolymers, determined from size-exclusion chromatography in reference to PS standards, are shown in Table I. Solutions of

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[*] To whom correspondence should be sent.

[†] U.S.T. Lille Flandres-Artois, 59655 Villeneuve d'Ascq., Cedex, France.

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the copolymers were prepared in either toluene or chloroform. Copolymer films with thicknesses ranging from 300 to 5000 Å in thickness were prepared by spin coating the solutions onto the desired substrate at a spinning speed of 2000 rpm.

Specimens were placed under vacuum at room temperature to remove residual solvents. For those studies where the effect of solvent evaporation rate was examined, the solution was cast onto a wafer and then placed in a chamber saturated with solvent vapors. The solvent was then allowed to slowly evaporate over at least a 72-h period. Annealing studies were performed by placing the dried specimen in a vacuum oven preheated to a desired temperature and then rapidly cooled after a predetermined time period by placing the wafer directly on a cool metal plate.

The substrates were 2.5-cm-diameter silicon wafers, which were cleaned by soaking in an acid bath, rinsing with deionized water, soaking in deionized water to remove water soluble contaminants, rinsing in refluxing ether vapors, and drying. In some cases, the cleaned Si substrates were coated with 2000 Å of gold to alter the characteristics of the substrate.

After the copolymer films were subjected to the desired annealing or solvent-casting condition, a 20-Å layer of gold was evaporated onto the films. This served as a marker for the air/copolymer interface. A separate, 200-Å thick film of PS was spin coated onto a microscope slide and floated off onto a pool of water. The copolymer film on the substrate was then used to remove the PS film. This produced a bilayered film with the copolymer of interest underneath the PS layer separated by a thin layer of gold. The details of the SIMS experiments have been discussed in depth previously.[12] A Cameca IMS-4F secondary ion microsocope was used to obtain the depth profiles in this experiment. The sputtering was accomplished with the use of a 3-keV O_2^+ primary ion beam, which has been shown to provide enhanced positive secodary ion signals and good depth resolution by the low kinetic energy bombarding O_2^+ ions.[12] The primary ion current for these measurements was approximately 200 nA, and the primary ion beam was rastered over an area of 500 μm × 500 μm. An immersion lens and transfer lens are used to extract the secondary ions from the sputtered surface and project an ion image plane on a selected area aperture. Secondary ions passing through the selected area aperture originate from an 80-μm-diameter area at the center of the sputtered crater. A double-focusing magnetic-sector mass spectrometer is used to provide the energy and mass analysis. The mass-separated secondary ions were measured with an electron multiplier, and the intensity of the measured secondary ions versus sputtering time gave the depth profile.

Profiles of H^+, $^2H^+$, $^{12}C^+$, and $^{197}Au^+$ were obtained for each specimen. The $^{197}Au^+$ signal was used as a marker for the surface of the copolymer. The $^{12}C^+$ signal was used as a reference to ensure that the sputtering rate was constant as the ion beam penetrated into the copolymer. The $^1H^+$ and $^2H^+$ were used to determine the depth variation of the PS or PMMA segments depending upon which block was deuterated. The layer of homopolymer placed on top of the copolymer served as a buffer layer where the initial sputtering transition could be surpassed before sputtering into the copolymer. It should be noted that the measured sputtering rate of gold is essentially identical with that of PS under the conditions used. This means that the presence of gold will not perturb the sputtering rate, and, hence, the gold serves as an inert marker.

The constituents of the copolymers, i.e., PS and PMMA, are chemically different. The sputtering rates in each differ by nearly a factor of 2. Thus, the etching rate of the ion beam into a microphase-separated copolymer may vary in the domains rich in PS or PMMA. This is not problematic if the microdomains are randomly oriented in the film. However, if there is a preferential orientation of the microdomains parallel to the surface of the film, then translation of the sputtering time into a distance or modeling $^1H^+$ or $^2H^+$ depth profiles and conversion to a sputtering time require a knowledge of the sputtering rate as a function of composition. In Figure 1 the sputtering rate as a function of weight fraction of PS is shown. These data were obtained by solution-casting mixtures of the PS/PMMA diblock copolymers with PMMA homopolymer. The SIMS profiles showed essentially a constant number of $^1H^+$ and $^2H^+$ as a function of sputtering time, indicating that, on average, the ion beam was sputtering through the desired composition of PS and PMMA. Data were not taken above the 0.5 PS weight fraction since previous studies showed that sputtering rate was close to that of pure PS. The data in Figure 1 confirm these previous observations, showing that the sputtering rate in pure PMMA is ca. 5.3 Å/s and as the weight fraction of PS increases a marked drop in the sputtering rate is observed. At a PS weight fraction of 0.5 the sputtering rate has dropped to ca. 3.3 Å/s, which is only 30% more rapid than that in pure PS. It is apparent from these measurements that the sputtering rate above a PS weight fraction of 0.5 decreases more gradually as more PS is added, and it is not, as indicated previously, equal to that of pure PS.[12] This result points to an important experimental fact, namely, that the sputtering rate appears to be very dependent upon the conditions of the experiment and it is necessary to calibrate the sputtering rate for each experiment.

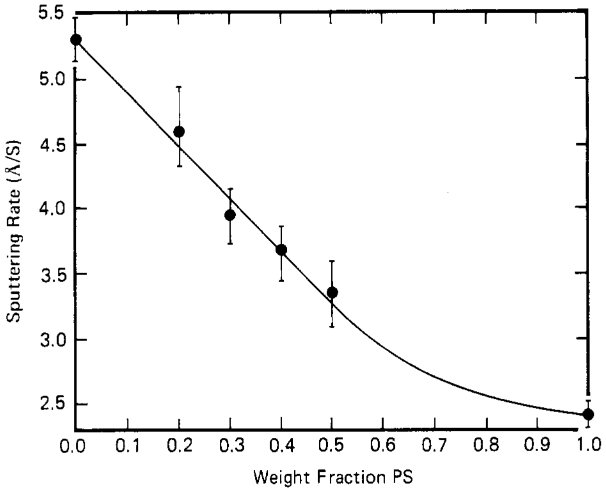

Figure 1. Sputtering rate of the ion beam into a mixture of PS/PMMA copolymer with PMMA rapidly cast from a toluene solution as a function of the weight fraction of poly(styrene).

Results and Discussion

In a previous study it was found that for PS/PMMA diblock copolymers prepared on a silicon substrate the PMMA preferentially adsorbed onto the silicon substrate, whereas the PS was preferentially located at the air/copolymer interface.[12] These results could be understood as follows. The silicon wafer while cleaned thoroughly was not kept under high-vacuum conditions and, hence, has an oxide layer covering the surface. This oxide layer will interact more strongly with the PMMA, the more polar component, giving rise to the preferential adsorption of PMMA. The lower surface energy of the PS, albeit only 0.1 dyn/cm less than that of PMMA, appears to be sufficient to cause a preferential adsorption of PS to the air/copolymer interface.

The influence of the substrate can easily be altered by coating the substrate with gold, which is inert and does not form an oxide overlayer (although exposure to air alters the surface chemistry of the Au). Shown in Figure 2 are the $^1H^+$, $^2H^+$, $^{12}C^+$, and $^{197}Au^+$ signals from a PSD/PMMAH (50K/50K) copolymer after annealing at 170 °C for 72 h. The substrate in this case was a silicon wafer coated with 2000 Å of gold. The vertical dashed line at shorter etching times marks the air/copolymer interface. Data to the left of this line are due to the homopolymer layer on the surface and are not of interest here. The second dashed vertical line to the right is located approximately at the beginning of the gold layer on the silicon substrate. These demarcations are clearly evident in the $^{197}Au^+$ signal. The initial peak corresponds to the 20 Å of gold coated on the copolymer after annealing. It is seen that the gold signal does not rapidly decline to the back-

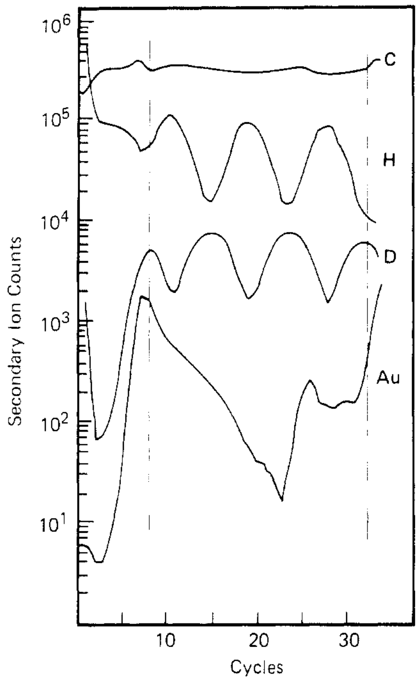

Figure 2. SIMS profile of PSD/PMMAH (50K/50K) diblock copolymer after annealing at 170 °C for 72 h. The specimen was prepared on a gold substrate. Shown are the proton ($^1H^+$), deuterium ($^2H^+$), carbon ($^{12}C^+$), and gold ($^{197}Au^+$) counts as a function of sputtering or etching time, t_{etch}. Total film thickness was measured to be 1150 Å.

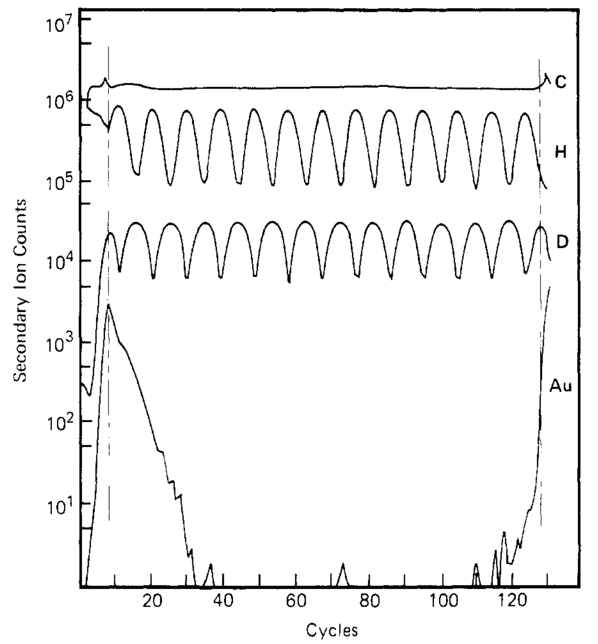

Figure 3. SIMS profile of PSD/PMMAH (50K/50K) diblock copolymer with a total thickness of 5200 Å after annealing at 170 °C for 72 h. The substrate is a gold-coated silicon wafer.

ground level due to possible penetration of the gold into the copolymer during evaporation and due to the discontinuity of the gold, i.e., island formation, on the copolymer. The $^{197}Au^+$ signal, in this profile, also exhibits an increase prior to encountering the bulk of the gold film on the silicon. It will be noticed that the increase in the Au signal occurs at a sputtering time that corresponds to one period in the lamellar structure of the copolymers. Concurrently, a slight depression in the signal from C is also observed. These results strongly suggest that the formation of terraces on the surface of the copolymer, i.e., on the air copolymer surface, is causing this effect. That is to say, the surface topology, due to the constant etching rate of the ion beam over the rastered area, has been maintained throughout the sputtering. Thus, the ion beam impinges on the gold substrate at different times, depending upon the initial surface topology. However, due to the terracing of the surface, the time at which the beam encounters the substrate corresponds to the time required to sputter through one copolymer period. This subject of surface terracing and the surface topology is the subject of a forthcoming paper.[15]

Examination of either the $^1H^+$ signal arising from the PMMA or the $^2H^+$ signal from the PS shows clearly that PS is located preferentially at the air copolymer interface in agreement with previous results.[11,12,16] However, PS is also preferentially located at the gold substrate. In fact, the concentration of PS on the gold substrate appears to be higher than that at the air/copolymer interface. This difference, while subtle, suggests that the partitioning of the two components at the gold/copolymer interface, i.e., at an impenetrable barrier, is much greater than at the air/copolymer interface. This cannot result from the lower surface tension of the PS since the surface tension of gold is much higher than that of either component. It may, however, be associated with the differences in the flexibility and/or polarity of the two components. Finally, while the $^{12}C^+$ signal is constant throughout the sputtering of the film, the marked oscillations in the $^1H^+$ and $^2H^+$ signals are evident. These results are consistent with the previous results.[12] When a trapezoidal model is used to describe the variation $^1H^+$ and $^2H^+$ as a function of depth and the instrumental resolution function, as discussed previously, is taken into account,[12] a period of 400 Å is obtained from the SIMS data in comparison to a value of 390 ± 10 Å obtained from small-angle X-ray scattering. Thus, as in the previous work,[12] the morphology seen in this thin film is identical with that observed in bulk copolymers with the exception of the strong orientation of the lamellar morphology parallel to the film surface. The width of the interface between the PSD and PMMA microdomains is ca. 50 Å. It should be noted that the total film thickness in the case of the gold-coated substrates is given by nL where n is the number of periods and L is the period spacing. Thus, for this specimen, $n = 3$ and a thickness of 1200 Å would be expected, which compares to a value of 1150 Å measured with a profilometer. This quantized film thickness also gives rise to a surface that is terraced where the step height of each terrace corresponds to the period spacing.[15]

A much thicker specimen was cast onto the gold-coated wafer to determine if the film thickness was of significance. The SIMS profiles for $^{12}C^+$, $^1H^+$, $^2H^+$, and $^{197}Au^+$ are shown in Figure 3 for the thicker PSD/PMMAH diblock copolymer after annealing at 170 °C for 72 h under vaccum. As with the data in Figure 2, PS is preferentially located at the air/copolymer and copolymer/gold interfaces and the concentration of the PS at the latter interface is higher. It is also evident from these data that the periodic, lamellar morphology is strongly oriented parallel to the film surface and the ordering persists over 13 periods corresponding to a film thickness of 5200 Å. In addition, since the area being probed is 80 μm in diameter, the lateral coherence of the lamellar domains is quite large. Therefore, these results show that, even on an inert substrate, a very slight difference in surface tension between the two components in a diblock copolymer is sufficient to produce a dramatic orientation of the microdomains parallel to the surface of the substrate that propagates through the entire film thickness.

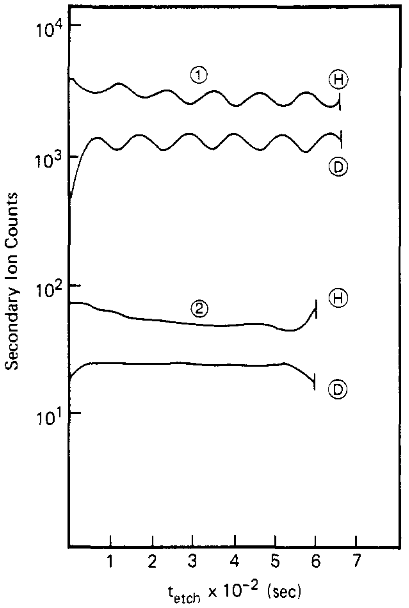

Figure 4. SIMS profile of (1) PSH/PMMAD (15K/15K) and (2) PSD/PMMAH (15K/15K) cast from toluene onto a silicon wafer and annealed at 135 °C for 24 h. The proton (H) and deuterium (D) signals are labeled accordingly.

Up to now, the studies have focused on copolymers where the molecular weight of each block was on the order of 50 000. The copolymers have clearly been microphase separated, albeit with diffuse phase boundaries, and there is a strong orientation of the domains parallel to the substrate. Decreasing the molecular weight of each block to ca. 15 000 produces some interesting results. Shown in Figure 4 are the $^1H^+$ and $^2H^+$ profiles obtained for these lower molecular weight copolymers as a function of the sputtering or etching time. The data have been reduced on the time scale such that a time of zero corresponds to the air/copolymer interface and the vertical line at the end of the profile corresponds to the copolymer/substrate interface. In both cases a silicon wafer served as the substrate. Specimens were annealed at 135 °C for 24 h under vacuum.

The first set of profiles corresponds to the case where the PS is protonated and the PMMA is deuterated. It is evident that the PS and PMMA domains have oriented parallel to the surface as with its higher molecular analogues. As can be seen, PS preferentially resides at the air/copolymer interface, whereas PMMA is preferentially located at the silicon surface. Using model calculations as described previously, it was found that a period corresponded to ca. 245 Å. However, the interface between the two domains was on the order of 50 Å, assuming a linear gradient. Thus, while the morphology is oriented, it is quite diffuse. This result is consistent with our previous study.

By using deuterated PS and protonated PMMA blocks, the results are shown by the lower set of profiles in Figure 4. The $^1H^+$ and $^2H^+$ signals do not show the oscillations characteristic of an orientation of domains parallel to the surface. In fact, only a depletion of the PS near the silicon surface and an enrichment of PS approximately 100 Å from the surface is observed. These results suggest that this copolymer is not microphase separated but rather phase mixed. While SIMS cannot distinguish between a copolymer where the microdomains are randomly oriented or a phase-mixed morphology, independent small-angle neutron scattering studies have shown that the microphase-separation temperature (MST) for this copolymer occurs at 65 °C.[17] In addition, recent neutron reflectivity studies on specimens annealed at 170 °C show that these films are phase mixed.[18] Consequently, the annealing treatment at 130 °C is above the MST and the phase-mixed morphology was frozen in at the glass transition temperature. It is interesting to note that the total molecular weight of the PSH/PMMAD copolymer is slightly larger than that of the PSD/PMMAH copolymer. This difference is sufficient to produce the difference in the morphology, i.e., microphase separated to phase mixed.

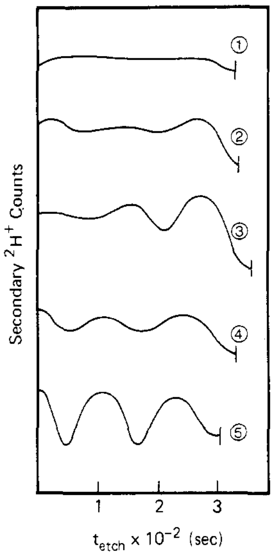

Figure 5. SIMS profiles of $^2H^+$ as a function of sputtering time for a PSD/PMMAH (50K/50K) diblock copolymer with a total thickness of ca. 1000 Å after annealing at 170 °C for different times. The different offset profiles are for (1) as cast, (2) 5 min, (3) 15 min, (4) 60 min, and (5) 480 min.

The strong influence of the surfaces on the orientation of the microdomains is clearly evident for both the 15K/15K and 50K/50K copolymers. However, the data presented up to this point have dealt with the morphology only after extended annealing times. A series of measurements were performed on the PSD/PMMAH (50K/50K) diblock copolymer as a function of time at an annealing temperature of 170 °C. Two separate studies were conducted on films of ca. 1000 and 5000 Å in thickness. Shown in Figure 5 are the $^2H^+$ profiles for the ca. 1000-Å-thick specimen after annealing for 0 min (1), 5 min (2), 15 min (3), 60 min (4), and 480 min (5). The profiles have all been normalized so that a zero etching time corresponds to the air/copolymer interface whereas the vertical line at the end of each profile corresponds to the copolymer/Si interface. The variation in the total etching time for the different profiles is due to the face that each profile was obtained on a different specimen that differed slightly in thickness. The initial profile corresponding to the as-cast film exhibits no variation in the $^2H^+$ counts as a function of depth. After the first 5 min at 170 °C the initiation of the microdomain orientation is evident. Clearly, the PSD is preferentially located at the air/copolymer interface and the PMMAH at the copolymer/Si interface. A distinct oscillation in the PMMAH concentration from the Si interface is already present. Further heating at 170 °C produces an interesting result in that the oscillations from the Si interface intensify and appear to do so at the expense of those at the air/copolymer interface. This result suggests that the adsorption of the PMMAH on the Si interface is stronger than that of the PSD at the air/copolymer interface. This could be a result of polar interactions between the PMMAH and the Si surface. With further annealing, the oscillatory pattern penetrates the

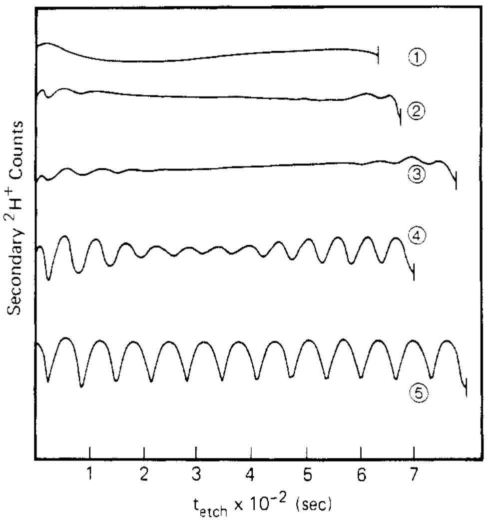

Figure 6. SIMS profile showing the $^2H^+$ counts as a function of etching or sputtering time for a PSD/PMMAH (50K/50K) diblock copolymer with a total thickness of ca. 5000 Å. The different offset profiles correspond to annealing times at 170 °C of (1) as cast, (2) 5 min, (3) 15 min, (4) 240 min, and (5) 480 min.

entire specimen and is perfected at longer times. Thus, these data would indicate that it is the Si surface that gives rise to the orientation of the lamellar microdomains and the air/copolymer interface is playing only a minor role.

In order to investigate this point further, a much thicker film (ca. 5000 Å) of the copolymer was prepared. The results of these experiments are shown in Figure 6 where the different profiles correspond to 0 min (1), 5 min (2), 15 min (3), 120 min (4), and 480 min (5) of annealing at 170 °C. By scanning the entire set of profiles shown, it is evident that the lamellar microdomains orient with respect to both surfaces independently. After 120 min at 170 °C, the periodicity of the microdomain orientation is well established from both interfaces. Careful examination of the profiles shows that the frequency of the oscillation remains constant as a function of distance from either interface up to the point where the two patterns begin to merge (t_{etch} = 250–400 s). Here, the frequency increases and then merges smoothly into the periodic pattern established from the opposite interface. This behavior differs from that seen for the thinner film where the orientation of the microdomains with respect to the copolymer/Si interface dominated. For the thicker specimens the extent of orientation from either interface is sufficiently extensive so that the copolymer at the center is forced to accommodate. Further, annealing at 170 °C produces a uniformly oriented microdomain morphology that pervades the entire specimen.

From previous studies on block copolymers, the thickness of the film has been shown to be dictated by the length of the period of the copolymer morphology. In all cases where silicon is used as the substrate, the total thickness is given by $(n + {}^1/_2)L$ where n is the number of periods and L is the length of the period. The question then arises as to the morphology of a film when the total thickness is less than $3L/2$. To examine this point films of 150K/150K PSD/PMMAH were prepared where the total thickness of the films were ca. 200, 400, and 750 Å. These correspond to thicknesses of $<L/2$, $\sim L/2$, and $\sim L$. Given the depth resolution of SIMS (ca. 125 Å), it was necessary to use these higher molecular weight copolymers so that a large enough value of L could be attained. Films of the desired thickness can be prepared by casting films from solutions of known concentration and known spinning rates as determined from previous work. These copolymers will inherently require a longer time to achieve equilibrium. Therefore, each film was annealed under vacuum for 72 h at 170 °C.

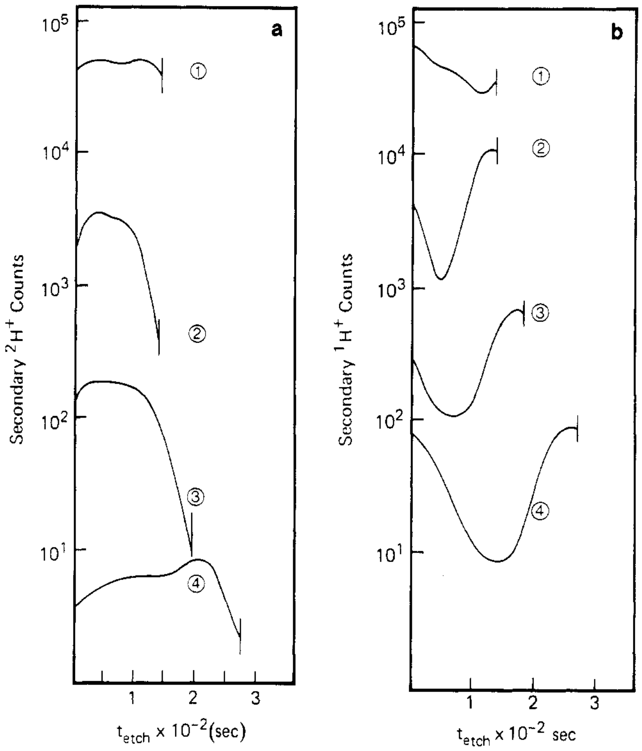

Figure 7. (a) $^2H^1$ counts as a function of etching or sputtering time for PSD/PMMAH (150K/150K) diblock copolymer where the total thickness of the film is (1,2) 200 Å, (3) 400 Å, and (4) 750 Å. All specimens were annealed for 72 h with the exception of (1) where the profile represents that for 200 Å after solvent casting. (b) $^1H^1$ counts as a function of sputtering time for PSD/PMMAH (150K/150K) diblock copolymer. The numbers in these profiles correspond to those in Figure 7a.

Shown in parts a and b of Figure 7 are the $^1H^+$ and $^2H^+$ profiles for the 200-Å film (less than $L/2$), (1) as cast from a toluene solution and (2) after annealing, (3) the 300-Å film where the thickness is $\sim L/2$ after annealing, and (4) the 750-Å film, which is $\sim L$ after annealing. At first glance the data in parts a and b of Figure 7 do not appear to mirror each other as they should. However, it must be recalled that the specimens were prepared with an overlayer of PSH to serve as a region where the initial sputtering transition is established. This, while necessary, causes a smearing of the $^1H^+$ at early sputtering times, i.e., the increase in the $^1H^+$ signal can be attributed, in part, to the presence of this overlayer. Nonetheless, some useful and interesting conclusions can be drawn from these data.

The $^2H^+$ profile of the as-cast 200-Å specimens is virtually constant as a function of the sputtering time. With annealing (2) the profiles change markedly. The $^2H^+$ and $^1H^+$ profiles show a strong adsorption of PMMAH on the Si surface. As one proceeds away from this surface, the concentration of PMMA continually decreases up to the air/copolymer interface. It is also evident that the copolymer has not formed an ordered morphology. This means that the film remains continuous and that formation of isolated patches of ordered domains of the copolymer, which would be necessary to conserve mass, is much too costly energetically. A similar behavior was noted by Henkee et al.[3] in block copolymers of poly(styrene) and poly(isoprene) where for sample thicknesses less than a long period the copolymer morphology was disordered. The results shown here indicate that not only is the morphology disordered but a continuous gradient in the

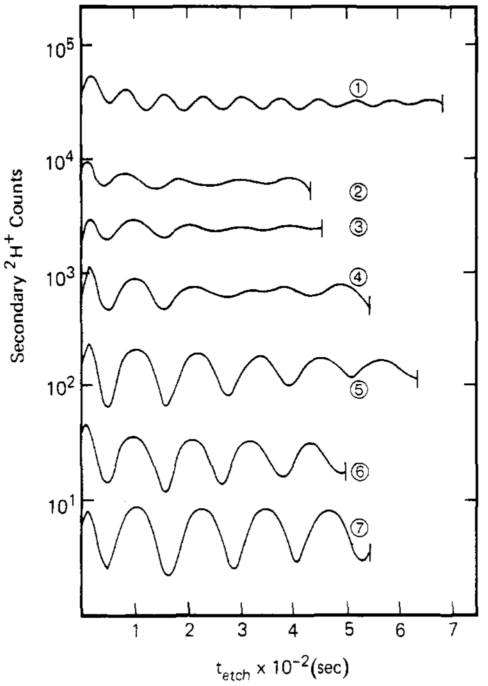

Figure 8. $^2H^+$ counts as a function of sputtering time for PSD/PMMAH (50K/50K) diblock copolymer cast from chloroform under slow solvent evaporation conditions. The profiles correspond to annealing at 170 °C for (1) as cast, (2) 2 min, (3) 5 min, (4) 15 min, (5) 30 min, (6) 60 min, and (7) 240 min.

concentration of the two components is formed. Increasing the specimen thickness to 300 Å (3) shows again a preferential adsorption of PMMAH on the Si surface with a gradient that extends throughout the entire specimen. As with the 200 Å specimen, no ordered morphology is found. Finally, if the specimen thickness is increased to 750 Å, one begins to see the formation of an oscillatory pattern in the profiles. However, it is difficult to assess whether or not a well-ordered morphology is formed. It is also difficult, at this time, to state whether or not the specimens are at equilibrium. For example, interference microscopy indicates the initial formation of a structured morphology, and it is possible that extended annealing may induce further ordering. This is currently under investigation. It is very clear though that, for the annealing times studied, if the specimen has a thickness less than L, an ordered morphology is not found even after extended annealing above T_g.

The solvent from which copolymer films are cast and the rate at which the solvent is removed can alter the morphology and the orientation of the microdomains with respect to the film surface. All the specimens discussed up to now have been prepared by a rapid casting process from toluene solutions. Toluene does not preferentially solvate either the PS or PMMA blocks, consequently, under the casting conditions used, no preferential orientation of the microdomains would be expected. This has been found to be the case in all the PS/PMMA specimens studied since the SIMS profiles of $^2H^+$ and $^1H^+$ are constant as a function of sputtering time. However, if chloroform, which preferentially solvates the PMMA block, is used as the casting solvent and if the solvent is slowly removed from the film, there is clear evidence of ordering the orientation of the microdomains. In Figure 8 are shown a series of SIMS $^2H^+$ profiles for a PSD/PMMAH (15K/15K) copolymer cast from chloroform under slow-evaporation conditions. The sequence of profiles are for annealing times at 170 °C of 0 min (1), 2 min (2), 5 min (3), 15 min (4), 30 min (5), 60 min (6), and 240 min (7). The initial $^2H^+$ profile for the as-cast film (1) shows a very distinct oscillation in the concentration, indicating that the very slow solvent evaporation has induced an orientation of the microdomains parallel to the substrate. However, the spacing of the period is only 240 Å, only 60% of the period evident in the toluene cast films after annealing. Hashimoto and co-workers[19] have observed that block copolymers cast from nonselective solvents can result in a reduction of the long period due to nonequilibrium effects in the high-concentration regime encountered during solvent evaporation. However, only a slight reduction in the period was observed in their studies, whereas that observed in this study is much more pronounced. After a specimen is annealed for 2 min at 170 °C, the amplitude of the oscillations diminishes and the period increases to near its equilibrium value. The oscillatory pattern is only evident from the air/copolymer interface after this brief annealing. The oscillations from the air/copolymer interface continue to grow with more extended annealing times, and after 15 min a noticeable oscillation begins to develop from the Si/copolymer interface with a period equal to that of the period originating at the air/copolymer interface. Where the two oscillations meet, the period changes and the amplitude diminishes dramatically. Continued annealing at 170 °C results in an oscillation with a depth-independent frequency that penetrates through the entire specimen. The amplitude of the oscillation increases with further annealing until, after 240 min, the $^2H^+$ profile of this specimen appears identical with that of annealed films cast from toluene.

It is not possible to describe the SIMS results of the as-cast films in terms of the equilibrium lamellar morphology. The period and amplitude of the $^2H^+$ oscillations and the slow rate of solvent removal would indicate that the morphologies, in fact, are different from lamellar. Variation of the morphology by use of preferential solvents for one component has been shown to induce transformations in the morphology.[20] If the morphology of the as-cast films was comprised of cylinders oriented with their long axes parallel to the films surface, then the observed $^2H^+$ could be explained. However, quantitative assessment of this is not possible by SIMS and must be addressed by other techniques.

In summary, it has been shown that the lamellar microdomain morphology of PS/PMMA symmetric diblock copolymers orients parallel to the surface of an Au or Si substrate. The nature of the substrate will, however, alter the component that is adsorbed preferentially. It has also been shown that the domain orientation occurs at both the air/copolymer and copolymer/substrate interfaces and propagates from these interfaces throughout the film. Results on films prepared on silicon substrates show that, for films with thicknesses less than L, the microphase separation appears to be suppressed and only gradients in the composition at either interface are found. Finally, the use of solvents that preferentially solvate one of the blocks will, under slow-evaporation conditions, induce an oriented nonequilbrium morphology that is rapidly lost upon annealing, whereupon the equilibrium morphology is attained.

Registry No. (PS)(PMMA) (block copolymer), 106911-77-7; Au, 7440-57-5; Si, 7440-21-3.

References and Notes

(1) *Developments in Block Copolymers*; Goodman, I., Ed.; Applied Science Publishing: London, 1982; Vol 1.
(2) Hasegawa, H.; Hashimoto, T. *Macromolecules* **1985**, *18*, 589.
(3) Henkee, C. S.; Thomas, E. L.; Fetters, L. J. *J. Mater. Sci.* **1988**, *23*, 1685.

(4) Hashimoto, T.; Toda, A.; Itoi, H.; Kawai, H. *Macromolecules* **1977**, *10*, 377.
(5) Hashimito, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.
(6) Vanzo, E. J. *J. Polym. Sci.* **1966**, *A4*, 1727.
(7) Bradford, E. B.; Vanzo, E. *J. Polym. Sci.* **1986**, *A1*, 1661.
(8) Whitmann, J. C.; Lotz, B.; Candau, F.; Kovacs, A. J. *J. Polym. Sci. Polym. Phys. Ed.* **1982**, *20*, 1341.
(9) Schmitt, R. L. ; Gardella, J. A.; Magill, J. H.; Salvati, L.; Chin, R. L. *Macromolecules* **1985**, *18*, 2675.
(10) Thomas, H. R.; O'Malley, J. J. *Macromolecules* **1979**, *12*, 323.
(11) Green, P. F.; Christensen, T. M.; Russell, T. P.; Jérôme, R. *Macromolecules*, **1989**, *22*, 2189.
(12) Coulon, G.; Russell, T. P.; Deline, V.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
(13) Green, P. F.; Russell, T. P.; Jérôme, R., Granville, M. *Macromolecules* **1988**, *21*, 3266.
(14) Russell, T. P.; Jérôme, R, unpublished results.
(15) Coulon, G.; Aussêré, D.; Russell, T. P., submitted for publication in *Macromolecules.*
(16) Green, P. F.; Christensen, T.; Russell, T. P.; Jérôme, R. *J. Chem. Phys.*, in press.
(17) Russell, T. P.; Hjelm, R.; Seeger, P. *Macromolecules*, in press.
(18) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrazak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852.
(19) Shibayama, M.; Hashimoto, T.; Hasegawa, H.; Kawai, H. *Macromolecules* **1983**, *16*, 1427.
(20) Meier, D. J. In *Thermoplastic Elastomers—Research and Development*; Legge, N. R., Holden, G., Schroeder, H., Eds.; Hansen Publishing: Munich, 1988.

Neutron Scattering Studies of Blends of Poly(2,6-dimethyl-1,4-phenylene oxide) with Poly(4-methylstyrene) and with Polystyrene: Concentration and Temperature Dependence

Ann Maconnachie,*,† J. R. Fried,‡ and Paul E. Tomlins§

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology, and Medicine, Prince Consort Road, London SW7 2BY, U.K.,
Department of Chemical Engineering, University of Cincinnati,
Cincinnati, Ohio 45221-0171, and DMA Building 95, National Physical Laboratory,
Teddington, Middlesex TW11 0LW, U.K.

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ABSTRACT: Quenched samples of binary blends of polystyrene, PS, and of poly(4-methylstyrene), P4MS, with poly(2,6-dimethyl-1,4-phenylene oxide), PM2PO, have been studied using small-angle neutron scattering, SANS. The composition and temperature dependences of the interaction parameter, χ, and the radius of gyration, R, of PS and P4MS in PM2PO have been measured. No evidence of chain expansion of either PS or P4MS in PM2PO was observed. The interaction parameters, measured in the q range 2×10^{-2}–4×10^{-2} Å^{-1} (where q is the scattering vector), appear to be independent of annealing temperature. This has been interpreted as indicating that over short distance scales the blends equilibrate at temperatures close to their glass transition temperature. For PS/PM2PO blends, χ follows the temperature dependence suggested by mutual diffusion measurements, which assume that it is independent of composition. The values of χ for the P4MS/PM2PO blends are thermodynamically poorer than those of the PS/PM2PO blends.

The range of known miscible polymer pairs grows daily even though until quite recently it was considered highly unusual for high polymers to mix. Why two polymers might or might not mix can be explained by recourse to the thermodynamics of polymer mixtures. In order to achieve a favorable free energy of mixing, it is usually necessary to also have a favorable heat of mixing since the entropy of mixing is essentially zero for high polymers. Unless there is a specific interaction or favorable volume change, the polymers are unlikely to mix. Mixtures of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PM2PO) form miscible single-phase materials in all proportions, and although lower critical solution temperature (LCST) behavior has been indicated,[1-3] phase separation has not been achieved at reasonable temperatures. The PS/PM2PO system has been closely studied, particularly the effect of changing the thermodynamic interactions in the system by substituting halogen atoms into the phenyl or phenylene ring of the polymers.[4-7] The position, number, and size of the halogens have been varied, and the effect on the miscibility of the polymer pairs was reported. Monosubstituted PS, either ortho- or para-substituted with chlorine or fluorine, is immiscible with PM2PO.[4-6] Monosubstituted PM2PO, with bromine in the 3-position, is also immiscible with PS.[7] However, if the substituent in the PS phenyl ring is changed to a methyl group, the effect is much less dramatic, and now the system becomes partially miscible.[8,9] The aim of this work is to compare the thermodynamics of the two blends PS/PM2PO and poly(4-methylstyrene) (P4MS)/PM2PO by measuring the interaction parameter, χ, as a function of composition and temperature. The technique that has been used is small-angle neutron scattering (SANS).

Table I
Characterization Data

	M_w[a]	M_w/M_n[a]	N_w[b]
PS	300 000	2.52	2884
PS-*d*	379 000	2.94	3486
P4MS	80 900	1.09	686
P4MS-*d*	88 500	1.73	708
PM2PO	35 400	1.62	295

[a] Measured by GPC from universal calibration of 10 PS standards in toluene. [b] Degree of polymerization.

Experimental Section

1. **Materials and Sample Preparation.** Poly(4-methylstyrene) and ring-deuterated poly(4-methylstyrene-d_7) (P4MS-*d*) were supplied through the courtesy of Dr. B. Z. Gunesin of the Mobil Chemical Co. Polystyrene was obtained from BASF and ring-deuterated polystyrene-d_5 (PS-*d*) from Cambridge Isotope

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† Imperial College of Science, Technology, and Medicine.
‡ University of Cincinnati.
§ National Physical Laboratory.

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