Surface Study of Diblock Copolymers of Poly(dimethylsiloxane) and Nylon-6 by Electron Spectroscopy for Chemical Analysis

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ABSTRACT: Surface composition of solution-cast films of diblock copolymers of poly(dimethylsiloxane) (PDMS) and nylon-6 was measured by using angle-dependent ESCA. Segregation of PDMS in the free surface region of the block copolymers was detected. The surface composition of these amorphous-semicrystalline block copolymers depends on both their polymer structure and the way the films are prepared. Mixed solvents can be used to control the competition between crystallization and microphase separation and, eventually, to adjust the surface composition of the solution-cast films. Annealing of the solution-cast films drives more PDMS into the surface region. The surface region comprised of the topmost 100 Å of the annealed films is pure PDMS for the PDMS-nylon-6 copolymer with a longer PDMS block length (202 repeat units) and a higher PDMS bulk concentration (34 mol %).

Introduction

The surface morphology and composition of amorphous block copolymers have been intensively investigated.[1-7] However, there has been little study of the surface effect of block copolymers consisting of both amorphous and crystalline components.[8,9] Polystyrene-poly(ethylene oxide) (PS-PEO) diblock copolymers are among the a few amorphous-crystalline block copolymers investigated previously by ESCA. The surface compositions of PS-PEO diblock copolymer thin films are significantly different from their bulk compositions and depend on their polymer structure and the casting solvents.

Diblock copolymers of poly(dimethylsiloxane) (PDMS) and nylon-6 contain both amorphous and crystalline components. They were synthesized and examined previously by transmission electron microscopy (TEM) and wide-angle X-ray scattering (WAXS).[10,11] Results showed that morphology is very sensitive to processing history, such as the choice of casting solvent and annealing conditions.[10] The morphology of solution-cast films is determined by two processes, crystallization and microphase separation. The surface composition of these copolymers should also be subject to the competition between crystallization and microphase separation. This should prove to be an important model system for understanding the quantitative relationships between systems with strong hydrogen bonding and crystallinity, such as nylon, and controlling the microphase separation and surface segregation of a lower surface energy component.

Two PDMS-nylon-6 copolymers, as described in Table 1, were studied. For the copolymer with a short PDMS block length and a low PDMS concentration, a spherulitic morphology was revealed from the TEM micrographs. The TEM ultrathin films were directly cast onto TEM grids from 2,2,2-trifluoroethanol (TFEtOH) solution. The spherulitic morphology changed to a spherical PDMS microdomain morphology after melt annealing the thin films. The WAXS data of the thin films showed that there was a significant crystallinity change in the block copolymers after the samples were annealed.

TEM of the ultrathin cast films, instead of cross sections of films, cannot provide direct information about the surface. Microtoming of the PDMS-nylon-6 films is very difficult due to both the undesirable wetting characteristics of nylon-6 and the very low glass transition temperature of PDMS.[10] This paper presents a quantitative surface study of these PDMS-nylon-6 diblock copolymers by angle-dependent ESCA. The effects of annealing and casting solvent composition on their surface compositions are investigated.

Since PDMS has a very low surface energy, the microphase-separated PDMS-nylon-6 diblock copolymers would be expected to have a low energy surface, due to the PDMS surface segregation. Along with good adhesion of nylon-6 to the substrate, the unique interface properties would make this type of material a potential candidate for nonfouling coatings.[12,13] The surface composition, specifically the degree of PDMS surface segregation, is essential to the nonfouling requirement.

Experimental Section

The two poly(dimethylsiloxane)-nylon-6 diblock copolymers used are designated as (3/100) and (15/44), based on the molecular weights of the blocks. Copolymer (3/100), for example, is a diblock copolymer with a molecular weight of the PDMS block of 3000 and that of nylon-6 of 100 000. The preparation of the block copolymers has been described previously.[11] Details of the structural information are summarized in Table 1. Homopolymers of PDMS (secondary standard, gum) and nylon-6 (pellets) were obtained from Scientific Polymer Products.

Thin films of the two copolymers were prepared by casting 1% solutions of pure 2,2,2-trifluoroethanol (TFEtOH), or the mixed solvents of TFEtOH and toluene, into aluminum dishes. The thickness of the films was estimated to be 50-100 μm from the concentration and the amount of the solution used. Nylon-6 and PDMS homopolymer thin films were cast from TFEtOH and toluene solutions, respectively. The films were first air dried over 24 h. They were subsequently dried in a vacuum oven at ambient temperature over 24 h and designated as as-cast films. To prepare annealed films, the dry films were further heated quickly and held at 235 °C (the melting temperature of nylon-6) for 10 min. The melt-annealed samples were allowed to cool down in air.

Angle-dependent ESCA experiments were performed on a Perkin-Elmer Physical Electronics Model 5300 ESCA spectrom-

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Table 1. Compositions of PDMS-Nylon-6 Diblock Copolymers

		no. of repeat units			composition (mol %)		
sample	polymer structure[a]	PDMS	PMVS	nylon-6	PDMS	PMVS	nylon-6
3/100	(PDMS/PMVS)-nylon-6	40	10	885	4	1	95
15/44	PDMS-nylon-6	202		389	34		66

[a] Diblock copolymers containing PDMS = poly(dimethylsiloxane), PMVS = poly(methylvinylsiloxane), and nylon-6.

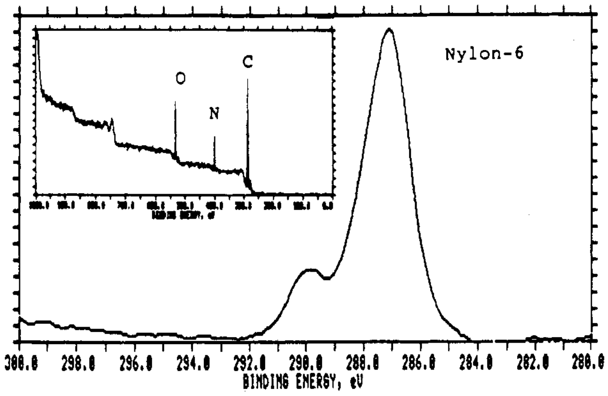

Figure 1. ESCA spectrum of nylon-6 in the C 1s region recorded at a 90° takeoff angle. The ESCA survey spectrum of nylon-6 from 0 to 1000 eV is shown in the inset.

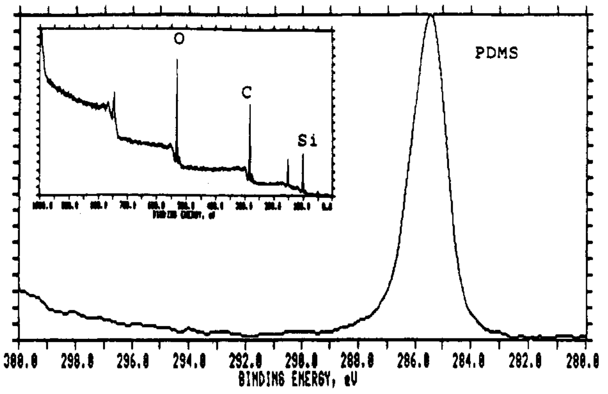

Figure 2. ESCA spectrum of PDMS in the C 1s region recorded at a 90° takeoff angle. The ESCA survey spectrum of PDMS from 0 to 1000 eV is shown in the inset.

eter. It consists of a hemispherical energy analyzer, a single-channel detector, and a Mg K$\alpha_{1,2}$/Ti K$\alpha_{1,2}$ dual-anode source. A Mg K$\alpha_{1,2}$ X-ray source was chosen and operated at 300 W (15.0 kV and 20 mA). Base pressure was maintained at $\leq 3.0 \times 10^{-8}$ Torr. ESCA survey spectra with a binding energy ranging from 0 to 1000 eV were collected at a takeoff angle of 45° and a pass energy of 89.45 eV. A pass energy of 17.9 eV was employed for all high-resolution angle-dependent acquisitions with the range of 20 eV. High-resolution acquisitions of carbon 1s, silicon 2p, and oxygen 1s regions were conducted at takeoff angles of 15°, 30°, 45°, and 90°, which led to the sampling depths under the ESCA experiment conditions ranging from 30 to 100 Å.[7,14]

Possible X-ray radiation-induced degradation of the film surface was examined. During an exposure time *twice as long* as that required for a complete angle-dependent ESCA analysis, the ratio of silicon to carbon measured by ESCA remained the same at a fixed takeoff angle, which means that no significant surface compositional change occurs. This approach has been the standard test utilized in all previous studies[5-7,15,16] from this laboratory.

All data manipulation (peak area calculation, base-line subtraction) was accomplished using a Perkin-Elmer 7500 computer running PHI ESCA version 2.0 software. Surface concentrations of the PDMS-nylon-6 samples were calculated based on the Si 2p/C 1s ratio from ESCA measurements in a manner similar to that of previous work.[5,7]

Results

Homopolymers. ESCA spectra of homopolymers of nylon-6 and PDMS were taken for two reasons, to calibrate the atomic sensitivity factor (ASF) ratio of carbon 1s to silicon 2p and to identify the characteristics on ESCA spectra of the components. When the ESCA takeoff angle of high-resolution angle-dependent acquisition was varied from 15° to 90°, the ASF ratio of C 1s to Si 2p did not change. The ratio was also the same as that calculated from the ASF data reported in an earlier paper under the same conditions.[15]

ESCA spectra of nylon-6 and PDMS pure homopolymers in the C 1s region are shown in Figures 1 and 2, respectively. The entire ESCA survey spectra are also inset in the figures. In Figure 1, nylon-6 gives two peaks in the C 1s region. The main peak at lower binding energy corresponds to the saturated carbon atoms (5 in each repeat unit of nylon-6). The smaller peak at higher binding energy arises from the unsaturated carbons (1 in each repeat unit of nylon-6). The peak area ratio of the main peak to the small peak is 5/1, measured after curve fitting. Signals from three atoms (C, N, and O) are shown in the ESCA survey spectrum of nylon-6. In Figure 2, however, only one peak is shown in the C 1s region. All the carbon atoms in PDMS are saturated and bonded in the same way. The PDMS ESCA survey spectrum yields signals from C 1s, O 1s, and Si 2p peaks.

From the characteristics of the ESCA spectra of nylon-6 and PDMS, we can derive three ways through ESCA measurements to monitor the surface composition of PDMS-nylon-6 copolymers (and PDMS/nylon-6 blends). First, N and Si peaks in the ESCA survey spectrum can be used as atomic labels of nylon-6 and PDMS components in the surface region of PDMS-nylon-6 copolymers. If there is no N peak (binding energy 400 eV) detected, the surface region of the PDMS-nylon-6 film is composed of a pure PDMS overlayer. The estimated ESCA detection limit is about 1 percent atomic. The existence of an unsaturated carbon atom peak in the C 1s region is the second way to monitor the amount of nylon-6 in the surface region, since only the nylon-6 component in the copolymers has unsaturated carbon atoms. Finally, the surface compositions of PDMS-nylon-6 copolymers can be calculated from the peak area ratios of Si 2p to C 1s, which range from 0 (if the surface is completely comprised of nylon-6) to $^1/_2$ (if the surface is completely comprised of PDMS). In this paper, surface compositions of PDMS-nylon-6 copolymers were calculated from Si 2p/C 1s peak area ratios.

Copolymer (3/100). This copolymer has a relatively short PDMS block and a long nylon-6 block. As mentioned in a previous paper,[10] the distribution of the molecular weight of PDMS blocks is very wide, due to the nature of the copolymerization process. The polydispersity of the PDMS block molecular weight may have an important effect on the copolymer morphology, especially in the surface region where PDMS segregates. The PDMS blocks with longer chain lengths could segregate in the surface region to gain maximum coverage of the free surface region and to minimize the total free energy of the films. Figure 3 shows the ESCA spectra of the as-cast film of this copolymer casting from TFEtOH solution. In the survey spectrum, four elements (C, O, N, Si) are detectable, which means that both PDMS and nylon-6 components exist in the surface region. C 1s region of this sample consists of

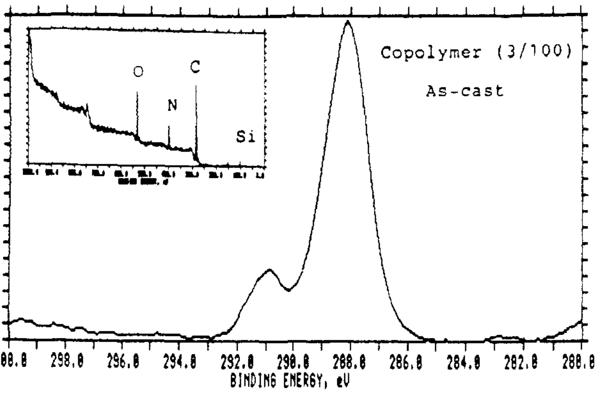

Figure 3. ESCA spectrum of copolymer (3/100) in the C 1s region recorded at a 90° takeoff angle from as-cast films using pure TFEtOH as the solvent. The ESCA survey spectrum of this PDMS–nylon-6 copolymer from 0 to 1000 eV is shown in the inset.

Table 2. Surface PDMS Mol % Concentration of Copolymer (3/100)[a]

film	solvent Tol/TFEtOH[b]	surface PDMS mol % concn ± 1 SD			
		30 Å	50 Å	70 Å	100 Å[c]
as-cast	0	28 ± 6	32 ± 5	28 ± 3	22 ± 2
	1/2	35 ± 8	41 ± 4	36 ± 3	32 ± 2
	1/1	6 ± 6	12 ± 5	13 ± 3	13 ± 3
	2/1	16 ± 3	25 ± 3	22 ± 3	20 ± 1
annealed	0	51 ± 3	54 ± 2	45 ± 1	37 ± 2
	1/2	78 ± 2	79 ± 5	66 ± 4	56 ± 7
	1/1	66 ± 10	60 ± 14	60 ± 16	54 ± 17
	2/1	89 ± 3	89 ± 4	85 ± 1	83 ± 5

[a] The bulk PDMS mol % concentration is 5. [b] Volume ratios of toluene to TFEtOH. [c] ESCA sampling depths.

two peaks, a saturated C peak (lower binding energy) and an unsaturated C peak (higher binding energy). After melt annealing, all four elements are still detectable in the survey spectrum of this copolymer and the unsaturated C peak remains in the C 1s region recorded at all four takeoff angles. The surface compositions of the copolymers cast from different solvents are summarized in Table 2.

The values of cohesive energy of the two blocks are quite different ($\delta = 7.5\ (\mathrm{cal\ cm^{-3}})^{1/2}$ for PDMS and $13\ (\mathrm{cal\ cm^{-3}})^{1/2}$ for nylon-6). A microphase-separated morphology of this copolymer is expected, and it was shown in a previous TEM study.[10] When TFEtOH is used to cast the thin films, the PDMS component partially separates from nylon-6 before this copolymer begins crystallization. The as-cast films have two types of morphological structures simultaneously. The PDMS spherical microdomains of diameter 1000–2000 Å are separated before crystallization and embedded in the crystallized phase, which is a spherulitic morphology with PDMS lamellae as spherulites. The surface composition and morphology remain unknown from the TEM work. However, the PDMS spherical microdomains are expected to segregate in the surface region to minimize the surface energy of the copolymer.

ESCA measurements show that the surface region of the as-cast copolymer (3/100) films from TFEtOH solution consists of PDMS at substantially higher concentrations than its overall bulk concentration. This PDMS surface segregation is best interpreted as the predominant existence of the PDMS-rich microdomains separated before crystallization. The competition between phase separation and crystallization should control the surface morphology and composition of this copolymer.

Table 3. Surface PDMS Mol % Concentration of Copolymer (15/44)[a]

film	solvent Tol/TFEtOH	surface PDMS mol % concn ± 1 SD			
		30 Å	50 Å	70 Å	100 Å
as-cast	0	61 ± 1	61 ± 2	59 ± 1	53 ± 2
	1/2	58 ± 4	56 ± 2	55 ± 1	50 ± 1
	1/1	66 ± 16	79 [illegible] 13	71 ± 13	65 ± 6
	2/1	41 ± 1	55 ± 1	52 ± 3	48 ± 2
annealed	0	100 ± 1	100 ± 0	99 ± 1	97 ± 1
	1/2	99 ± 1	99 ± 1	98 ± 1	98 ± 1
	1/1	101 ± 1	98 ± 0	98 ± 2	96 ± 2
	2/1	96 ± 4	99 ± 1	97 ± 1	96 ± 1

[a] The bulk PDMS mol % concentration is 34.

To adjust the competition between microphase separation and crystallization, mixed solvents of TFEtOH and toluene (Tol) were introduced to cast the films. TFEtOH is a good solvent for nylon-6 and a poor solvent for PDMS, while toluene is a poor solvent for nylon-6 and a good solvent for PDMS. When more toluene is used in casting the films, crystallization should begin earlier. Since the polydispersity of the PDMS block is wide, earlier crystallization of the copolymer means only the PDMS blocks with much higher molecular weight can separate into the microdomains. The microdomain is, in turn, richer in PDMS. The surface PDMS concentrations of the copolymer (3/100) films cast from a mixture solvent of a 1 to 2 Tol/TFEtOH ratio are indeed higher than those from pure TFEtOH solvent.

If the mixed solvent is made of a ratio of 1 to 1, copolymer (3/100) is still completely dissolved. During film casting, a very thin white skin floats on top of the concentrated solution. This skin should be the crystallized portion of the copolymer. ESCA measurements show that the surface compositions are much closer to the overall bulk composition, although the PDMS surface concentration is detectably higher than the overall bulk PDMS concentration. This effect leads to a wider variation of the surface composition as noted by increased standard deviations in Table 2 and 3.

When even more toluene is used (at the Tol/TFEtOH ratio of 2 to 1), no skin is observed during casting. The surface PDMS concentrations of copolymer (3/100) cast from the 2 to 1 Tol/TFEtOH ratio solvent are higher than those cast at a 1 to 1 Tol/TFEtOH ratio but lower than those cast at a 1 to 2 Tol/TFEtOH ratio and from a pure TFEtOH solution. This is most probably due to the fact that there is little PDMS separated into the PDMS-rich phases before crystallization starts. Copolymer (3/100) cannot be dissolved if toluene is used as more than a 2 to 1 Tol/TFEtOH ratio.

Melt annealing of the as-cast copolymer (3/100) films dramatically changes the morphology. After melt annealing, the PDMS spherulites in as-cast films disappear.[10] The PDMS-rich microdomains shrink in terms of the diameter of the domains. The observed morphology of the annealed films is PDMS spheres in a nylon-6 matrix.[10] The surface compositions of the copolymer (3/100) annealed films are also summarized in Table 2. Much higher surface PDMS concentrations were measured after annealing.

The solution-cast copolymer (3/100) films start to melt at 230 °C. The surface of the films becomes yellow if films experience extensive annealing (over 30 min at 235 °C). The melt annealing condition was set to be 10 min at 235 °C. However, the polymer segments of the copolymer may not have enough time for relaxation under this annealing condition. The differences of the surface compositions of the films cast from different solvents are still observed after melt annealing. Insufficient relaxation of the copolymer at melting should be the main reason. Attempts to extensively anneal at 235 °C were made to

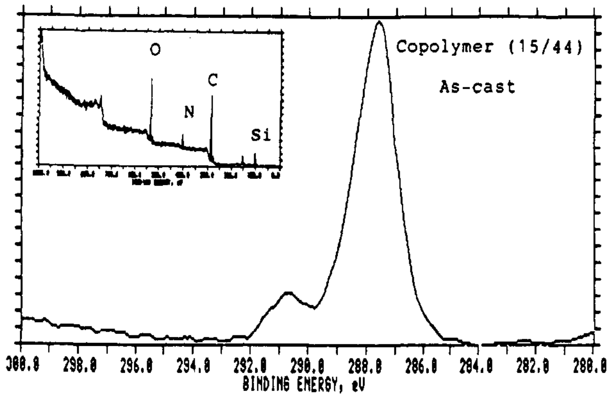

Figure 4. ESCA spectrum of copolymer (15/44) in the C 1s region recorded at a 90° takeoff angle from as-cast films using pure TFEtOH as the solvent. The ESCA survey spectrum of this PDMS–nylon-6 copolymer from 0 to 1000 eV is shown in the inset.

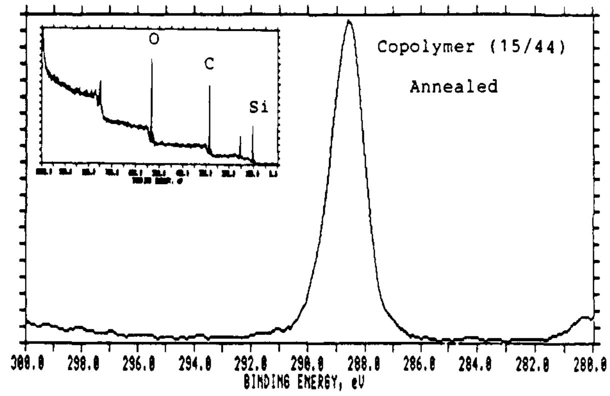

Figure 5. ESCA spectrum of copolymer (15/44) in the C 1s region recorded at a 90° takeoff angle from annealed films using pure TFEtOH as the solvent. The ESCA survey spectrum of this PDMS–nylon-6 copolymer from 0 to 1000 eV is shown in the inset.

complete relaxation of the polymer chains. However, thermal degradation of the films (colorization) was observed at this condition.

Copolymer (15/44). This PDMS–nylon-6 diblock copolymer is composed of a longer PDMS block, and the overall PDMS content is much higher (34 mol %) than copolymer (3/100) (only 5 mol %). The structural difference of the two copolymers should yield large differences in morphology and composition in both the bulk and surface.

Figure 4 shows ESCA spectra of as-cast films of copolymer (15/44) cast from a TFEtOH solution. Again, four elements of C, O, N, and Si are detected in the inset ESCA survey spectrum, and the unsaturated C peak is found in the C 1s region of the high-resolution ESCA spectrum of the copolymer (15/44) films, just as those found in the ESCA spectra of as-cast films of copolymer (3/100). Both nylon-6 and PDMS components exist in the surface region of copolymer (15/44) as-cast films. After melt annealing, both the N peak in the ESCA survey spectrum and the unsaturated C peak in the C 1s region of the high-resolution ESCA spectrum of copolymer (15/44) disappear, as shown in Figure 5. The high-resolution ESCA spectrum of the C 1s region in Figure 5 was recorded at a 90° takeoff angle, and the ESCA sampling depth was 100 Å. This means that the surface of the melt-annealed copolymer (15/44) films is an overlayer of pure PDMS with a thickness over 100 Å.

Surface compositions of copolymer (15/44) films cast from solutions using mixed solvents of TFEtOH and toluene are summarized in Table 3. For the as-cast copolymer (15/44) films prepared from TFEtOH solution, the PDMS concentrations in the surface region up to an ESCA sampling depth of 100 Å are significantly higher than the overall bulk PDMS concentration (34 mol %). The PDMS surface segregation, again, should be attributed to the existence of PDMS-rich microdomains in the surface region. Unlike the as-cast films of copolymer (3/100) (of which the morphology consists of both spherical microdomains of rich PDMS composition and spherulitic phases with nylon-6 as the matrix and PDMS as spherulites), the as-cast film of copolymer (15/44) has only one type of morphological structure, PDMS spherical microdomains immersed in a nylon-6 matrix.[10] During the film-casting process, PDMS blocks separate into the PDMS-rich microdomains well before the copolymer starts to crystallize. The surface region of the as-cast films should be dominated by the PDMS-rich microdomains due to the reason to minimizing the total energy of the PDMS–nylon-6 copolymer film. The surface PDMS concentrations of copolymer (15/44) films are much higher than those of copolymer (3/100), because the overall bulk PDMS concentration and the average molecular weight of PDMS blocks of copolymer (15/44) are both much higher than those of copolymer (3/100).

Since copolymer (15/44) consists of more PDMS than copolymer (3/100), copolymer (15/44) is more soluble in the mixed solvents of toluene and TFEtOH. When toluene is used at a 1 to 2 Tol/TFEtOH ratio to prepare the copolymer (15/44) films, the surface compositions of the as-cast films remain almost the same as those of the copolymer (15/44) films cast from TFEtOH solution. If the mixed solvent is composed of equal amounts of toluene and TFEtOH, the surface concentrations of the as-cast films are higher than those cast from TFEtOH solution. A substantial amount of toluene used for casting the films promotes crystallization and reduces the amount of PDMS separated into PDMS-rich microdomains. The PDMS separated before crystallization should be the portion of PDMS blocks with higher molecular weight. The PDMS-rich microdomains dominate the surface region, and they contribute to the higher surface PDMS concentrations if more toluene is used to cast the films.

When mixed solvent is used at a 2 to 1 Tol/TFEtOH ratio, the surface PDMS concentrations begin to drop. This is also the result of competition between PDMS phase separation and copolymer crystallization. The large amount of toluene promotes more copolymer to crystallize. The size of the PDMS-rich microdomains becomes smaller.[10]

After melt annealing, the surface composition experiences a drastic change. The surface region up to 100 Å for the copolymer (15/44) films, no matter what ratio of the mixed solvent is used to cast the films, is completely or almost completely composed of pure PDMS, as summarized in Table 3.

Discussion

As found in many other PDMS block copolymers,[5-7,16] PDMS surface segregation exists in the PDMS–nylon-6 diblock copolymers. The surface energy of PDMS (20.4 mN/m) is substantially lower than that of nylon-6 (38.4 mN/m).[17] To minimize the overall free energy of the block copolymer films, the lower surface energy blocks, PDMS, should present as much surface area as possible. The amount of PDMS surface segregation of the amorphous–semicrystalline block copolymers depends on the polymer structure (block length and composition).

Polystyrene–poly(ethylene oxide) diblock copolymer is also an amorphous–semicrystalline copolymer. The sur-

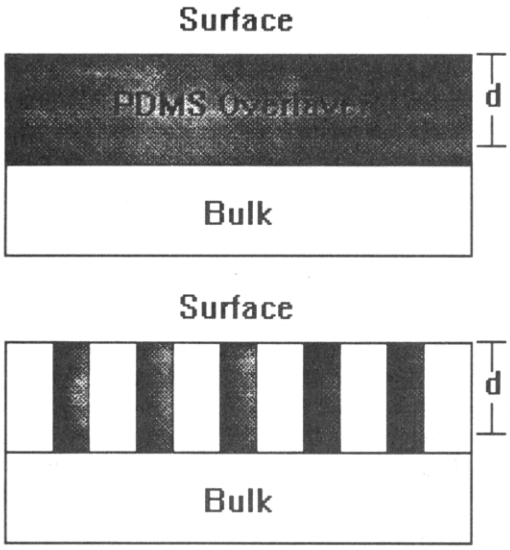

Figure 6. Surface morphology models of (a) as-cast films of copolymer (3/100) and copolymer (15/44) and of (b) melt-annealing films of copolymer (15/44) films.

face of PS–PEO as-cast thin films was previously examined by Thomas and O'Malley using angle-dependent ESCA.[8] In PS–PEO diblock copolymers, PS has a lower surface energy (36 mN/m) thin PEO (44 mN/m). The surface region of the PS–PEO diblock copolymers was found rich in PS. The surface PS content is very sensitive to the casting solvents, and it increases as the solvent becomes more preferential for PS. These results are consistent with the solvent effect on PDMS–nylon-6 diblock copolymers, if the Tol/TFEtOH ratio is under a certain value and PDMS phase separation is not overwhelmed by crystallization.

One feature of all the as-cast PDMS–nylon-6 films is that the PDMS surface compositions do not change substantially when the ESCA sampling depth varies from 30 to 100 Å. For the amorphous–amorphous PDMS block copolymers, the amount of PDMS surface segregation attenuates as the ESCA sampling depth increases.[5–7,16] The surface composition of an as-cast PDMS–nylon-6 film in the region up to at least 100 Å is somewhat uniform, if the casting solvent is preferential for nylon-6 (toluene content is low). This is, again, in good agreement with what Thomas found in PS–PEO diblock copolymers if the casting solvents were preferential for the major component.[8] This surface composition feature of PDMS–nylon-6 copolymers excludes the parallel-to-surface lamellar microdomain structure. A surface morphology model for two as-cast PDMS–nylon-6 diblock copolymers is sketched in Figure 6a. The surface region is composed of cylinders or layers of one component oriented perpendicularly to the surface.

However, the effect of annealing on the surface composition of an amorphous–semicrystalline block copolymer has not been documented. In Figure 6b is shown a surface morphology model for the melt-annealed films of PDMS–nylon-6 diblock copolymer (15/44). An overlayer of pure PDMS is in the surface region.

In this study, only the fast cooling rate of melt annealing was used to preserve the melt morphology of the annealed films. The cooling rate is crucial to the crystallization process. When a fast cooling rate is chosen, the major portion of the morphology of the amorphous–semicrystalline copolymers should be an amorphous phase. If the cooling rate is low, more materials in the copolymers crystallize, and the surface morphology and composition may be quite different from what are observed in this paper.

Conclusion

The surface compositions of two PDMS–nylon-6 diblock copolymers are studied by angle-dependent ESCA measurements. The surface segregation of PDMS is observed for both copolymers used. The surface composition of the amorphous–semicrystalline diblock copolymers depends on both polymer structure (block length and composition) and the film preparation process.

When the copolymer films are prepared by solution casting, the surface of the as-cast films is determined by the competition between PDMS phase separation to form PDMS-rich microdomains and crystallization of the copolymers. If pure TFEtOH (a preferential solvent for nylon-6) is used as the casting solvent, some amount of PDMS separates into PDMS microdomains. These PDMS microdomains dominate the surface region and give rise to PDMS surface segregation. When toluene (a preferential solvent for PDMS) is added to make mixed solvents, toluene promotes crystallization and reduces the amount of PDMS separated into PDMS-rich microdomains. Distribution of molecular weights of the block copolymers is also an important factor of the surface composition of the amorphous–semicrystalline copolymers, since the amorphous PDMS blocks of higher molecular weights separate into the PDMS-rich microdomains first.

Annealing of the as-cast films of PDMS–nylon-6 diblock copolymers drives more PDMS to the surface region. After annealing, the surface region up to 100 Å copolymer (15/44) films is exclusively composed of PDMS regardless of what solvent is used to cast the films.

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