Effects of Structure and Annealing on the Surface Composition of Multiblock Copolymers of Bisphenol A Polycarbonate and Poly(dimethylsiloxane)

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ABSTRACT: The surface compositions of multiblock copolymers of Bisphenol A polycarbonate (BPAC) and poly(dimethylsiloxane) (PDMS) were studied by angle-dependent X-ray photoelectron spectroscopy. Structure and annealing effects on the PDMS surface concentrations of the BPAC-PDMS block copolymers measured at different ESCA sampling depths (up to 103 Å) are discussed. The glass transition temperatures of the block copolymers and BPAC homopolymer were measured by DSC to determine the annealing temperature for the block copolymers.

Introduction

Surface segregation of a component with a low surface energy in multicomponent polymeric systems, such as block copolymers and polymer blends, currently attracts intensive investigations.[1-8] Along with fluorinated polymers, poly(dimethylsiloxane) (PDMS) has a very low surface energy. A substantial amount of PDMS segregation in the near free surface region has been shown consistently in the studies of a wide variety of the PDMS-containing block copolymers. These block copolymers include polystyrene-PDMS diblock and triblock copolymers[9,10] and poly(α-methylstyrene)-PDMS multiblock and starblock copolymers.[11]

The surface compositions of the solution-cast films of multiblock copolymers of Bisphenol A polycarbonate (BPAC) and PDMS, with 20 repeat units of dimethylsiloxane in each PDMS block, were previously studied by ion scattering spectroscopy (ISS),[12] angle-dependent X-ray photoelectron spectroscopy (XPS or ESCA),[12,13] and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).[13,14] Previous applications of angle-dependent ESCA for the analysis of block copolymers have been discussed in earlier work.[9,12] PDMS surface segregation was revealed by all these three surface-sensitive techniques. Because of their properties of low surface energy, excellent mechanical strength, and good adhesion to metal and other base materials, the BPAC-PDMS block copolymers could be used as, for example, ice-release coatings which can drastically reduce the adhesion of ice to surfaces.[15]

When they are added to BPAC homopolymers, BPAC-PDMS block copolymers can dramatically change the surface properties of the blends. Surface wettability studies by contact angle measurements indicates that the wettability of blends of BPAC homopolymer and BPAC-PDMS multiblock copolymers was close to that of pure PDMS, even though the BPAC-PDMS block copolymer was incorporated into the blends at low concentrations.[16] The wettability was shown to be insensitive to both PDMS block length and BPAC-PDMS block copolymer concentration in the blends provided that the PDMS block length was 20 or longer. ESCA studies of the surface of the blends of BPAC homopolymer and BPAC-PDMS multiblock copolymers showed that only 1% PDMS by weight in the overall bulk composition was enough to generate a PDMS surface concentration in the blends equivalent to those of the pure BPAC-PDMS block copolymers; this means that the surface region of the blends was dominated by the incorporated BPAC-PDMS block copolymers.[17-19] Therefore, a basic understanding of the effects determining the surface of block copolymers can also be applied to the surface of those blends.

As revealed by the previous studies on the surfaces of other PDMS-containing block copolymers,[9-14] the bulk composition has a very important effect on the surface composition of these block copolymers. The bulk composition determines the domain structures (mainly domain shape) in the bulks of the block copolymers and affects the surface morphology and composition as well. Block length is the major factor which determines the domain size of block copolymers.[9-11] The primary objective of the present investigation is to systematically examine the surfaces of a series of BPAC-PDMS multiblock copolymers over a wide range of compositions and PDMS block lengths. Specifically, the effects of PDMS block length, bulk composition, and annealing on the PDMS surface concentration of the BPAC-PDMS copolymers within the surface region measured by angle-dependent ESCA are the focus of this work.

Experimental Section

The samples of BPAC homopolymer and BPAC-PDMS multiblock copolymers with various PDMS block lengths and compositions were provided by Dr. Roger Kambour of General Electric Research Laboratory (Schenectady, NY). The BPAC-PDMS block copolymers were prepared by mixing Bisphenol A with α,ω-dichloro-terminated PDMS oligomers and then adding phosgene.[20] The BPAC-PDMS samples were random, alternating multiblock copolymers. Since the PDMS oligomers were prepared by anionic polymerization, the PDMS chain lengths were well-defined. The average numbers of the repeat units of each PDMS block in the BPAC-PDMS multiblock copolymers were 2, 7, 20, and 40. However, the chain lengths of the BPAC block were not well-defined. The repeat unit of a BPAC block could be as low as 2 if a phosgene moiety only linked two Biphenol A-capped PDMS oligomers. The average BPAC block lengths can be calculated from the bulk BPAC concentration and PDMS block length.

The polymers were dissolved in chloroform to prepare 0.5% solutions, cast into aluminum weighing dishes, and then allowed to air dry at ambient temperature. They were further dried in a vacuum oven (5-10 Torr) at room temperature over 3 days. These 50-μm-thick BPAC-PDMS films on Al substrate were used without any more treatment and designated as as-cast films. The

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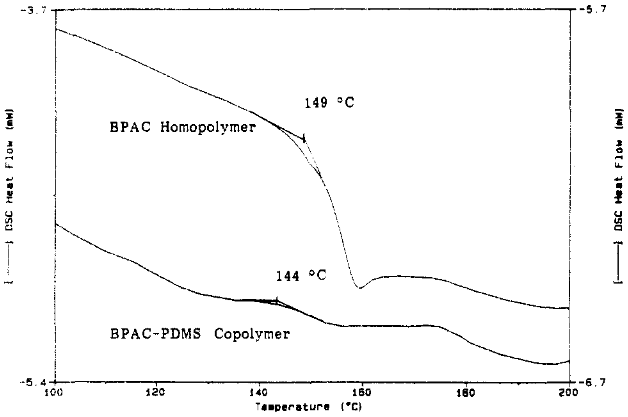

Figure 1. DSC thermographs of a BPAC homopolymer (above) and a BPAC–PDMS multiblock copolymer with a PDMS block length of 20 repeat units and a composition of 50% PDMS (below).

annealed BPAC–PDMS films were obtained by heating the dry films at 180 °C, instead of room temperature, in a vacuum oven over 24 h.

Angle-dependent ESCA analysis of the BPAC–PDMS films was performed on a Perkin-Elmer Physical Electronics Model PHI 5400 ESCA spectrometer operated at 300 W (15 kV and 20 mA). A Mg Kα X-ray source and a pass energy of 35.75 eV were chosen for all angle-dependent acquisitions. Take-off angles of 15°, 45°, and 90° were used for all samples and lead to the sampling depths of 27, 73, and 103 Å, respectively.[11,21] All three elements (carbon, silicon, and oxygen) were recorded. The quantification of PDMS surface concentrations of the copolymers was determined from either the peak area ratio (Si/C) or the curve fit analysis of the C 1s region. There was no significant difference of the results between the two methods.

A TA Instruments 2910/2000 differential scanning calorimeter (DSC) was used for the determination of the glass transition temperature (T_g) of the BPAC–PDMS copolymers and BPAC homopolymer. All samples were heated from 20 to 300 °C at a rate of 20 °C/min with a continuous nitrogen flow at a rate of 20 cm^3/min. The samples were then quench cooled to 20 °C with liquid nitrogen and reheated to 300 °C at the same rate of the first heating. The T_g was taken as the onset of slope change on the thermograph of the second heating.

Results and Discussion

DSC Measurements and Annealing Temperature. Thermal equilibrium morphological structures of block copolymers can be achieved by appropriately annealing the as-cast samples.[5,22] Annealing was used in this current investigation to evaluate the difference of surface compositions between the as-cast samples and the thermal equilibrium samples. In order to choose an appropriate annealing temperature for the BPAC–PDMS block copolymers, DSC experiments were carried out to determine the glass transition temperature (T_g) of BPAC. The thermographs of a BPAC homopolymer and a BPAC–PDMS multiblock copolymer were shown in Figure 1. For the BPAC–PDMS multiblock copolymer in the DSC thermograph, the PDMS block length is 20 repeat units and the bulk composition is 50% PDMS. The T_g of the BPAC homopolymer is determined to be 149 °C, which is close to the T_g reported.[23,24] The T_g's of the BPAC blocks in the BPAC–PDMS multiblock copolymers with high BPAC contents are between 144 and 152 °C. Hence, the annealing temperature for the BPAC–PDMS multiblock copolymers was placed at 180 °C, which is well above the glass transition temperature of the BPAC blocks.

Surface Composition Calculation. The calculation of the PDMS surface concentration of the BPAC–PDMS samples is based on the Si/C atomic ratios measured by ESCA. There are two carbon atoms and one silicon atom in a PDMS repeat unit (MW = 74.2) and 16 carbon atoms but no silicon atoms in each BPAC repeat unit (MW = 254.3), as shown in Figure 2. The overall atomic concentration ratio of silicon to carbon, Si/C, ranging from 0 (the surface region assumed by BPAC exclusively) to $^1/_2$ (the surface region assumed by PDMS exclusively), reflects the ratio of the two components in the surface region of the BPAC–PDMS block copolymers. If X is the molar fraction of the PDMS repeat units, the molar fraction of the BPAC repeat units should be $1 - X$ for these two component copolymers. The Si/C atomic ratio can be expressed as:

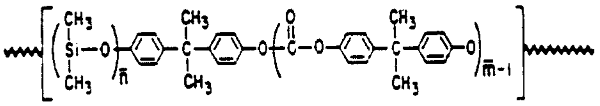

Figure 2. Structure of the repeat units of BPAC and PDMS blocks.

$$\frac{\mathrm{Si}}{\mathrm{C}} = \frac{X}{2X + 16(1 - X)} \tag{1}$$

When weight fraction of PDMS, W, is used, X and $1 - X$ can be replaced by $W/74.2$ and $(1 - W)/254.3$, respectively. The relationship between the Si/C atomic ratio and the weight fraction of PDMS is described in the following equations:

$$\frac{\mathrm{Si}}{\mathrm{C}} = \frac{W/74.2}{2W/74.2 + 16(1 - W)/254.3} \tag{2}$$

or

$$W = \frac{1187.2(\mathrm{Si/C})}{254.3 + 678.6(\mathrm{Si/C})} \tag{3}$$

In ESCA experiments, Si/C atomic ratios were obtained by measuring the areas of Si 2p and C 1s peaks and corrected by using calibrated atomic sensitivity factors as in previous work from this laboratory.[9-13]

The surface composition calculated from ESCA measurement is a complex average over the entire span of a surface region up to the sampling depth. Since the ESCA photoemission intensity is attenuated exponentially with depth, the materials in the upper surface region make more contribution to the measurement than the inner materials of the same volume. In this paper, all the ESCA data are the complex average values without deconvolution.[25]

Surface Compositions of the BPAC–PDMS Block Copolymers. Table I summarizes the PDMS surface concentrations in weight percent of the BPAC–PDMS multiblock copolymers, as well as their bulk PDMS concentrations and PDMS block lengths in number-averaged repeat units.

For all the BPAC–PDMS samples with different PDMS block lengths and bulk concentrations, there are two features shared by both the as-cast films and the annealed films. First, the PDMS surface concentration attenuates as the ESCA sampling depth increases. The surface concentrations of PDMS measured by ESCA at sampling depths up to 103 Å are significantly higher than their bulk PDMS concentrations. The detected surface enrichment of PDMS should be attributed to the lower surface energy of the PDMS component (surface energy γ = 21 mN/m). The surface segregation of the lower surface energy component can minimize the total energy of the block copolymer films. Second, the surface region of these films consists of various amounts of BPAC (the high surface energy component, γ = 43 mN/m), even in the topmost surface region measured (27 Å).

Table I. PDMS Concentrations (wt %) at the Surface of the BPAC–PDMS Samples by ESCA Measurements

PDMS block length	% PDMS (Bulk)	% PDMS (surface), as-cast 27 Å	73 Å	103 Å	% PDMS (surface), annealed 27 Å	73 Å	103 Å
2	15	60.9 ± 2.8	39.7 ± 1.3	34.2 ± 0.7	69.9 ± 2.5	44.2 ± 4.3	36.5 ± 2.4
2	25	71.3 ± 1.6	51.8 ± 0.4	47.3 ± 0.6	72.1 ± 1.6	47.2 ± 1.3	40.9 ± 0.5
7	20	62.7 ± 0.6	46.8 ± 1.2	41.6 ± 0.5	73.0 ± 2.0	47.6 ± 2.5	39.3 ± 0.5
7	45	78.0 ± 2.0	62.8 ± 1.3	58.9 ± 0.4	91.5 ± 4.4	71.8 ± 2.1	64.6 ± 2.0
20	25	82.9 ± 3.9	68.6 ± 4.0	62.6 ± 5.5	89.6 ± 1.8	64.8 ± 0.8	54.3 ± 3.1
20	50	90.1 ± 4.5	77.0 ± 4.2	72.6 ± 4.8	91.1 ± 0.2	69.4 ± 0.2	62.2 ± 1.2
20	65	91.1 ± 5.1	87.8 ± 3.5	86.1 ± 3.9	93.8 ± 2.4	79.9 ± 1.3	75.6 ± 0.8
40	25	80.8 ± 4.3	61.4 ± 5.6	57.6 ± 6.3	87.4 ± 1.8	78.1 ± 4.8	63.7 ± 5.6
40	36.5	82.8 ± 3.8	63.7 ± 6.1	55.9 ± 5.4	84.9 ± 1.8	63.2 ± 2.4	54.6 ± 2.8
40	81	90.9 ± 3.5	88.7 ± 5.2	86.2 ± 3.9	97.8 ± 0.8	91.4 ± 8.0	83.0 ± 1.7

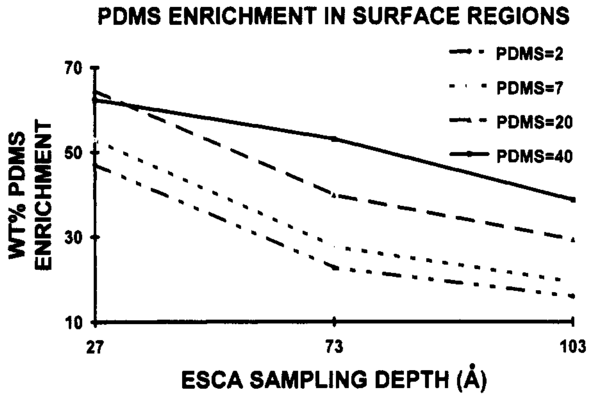

Figure 3. PDMS surface enrichment vs sampling depth profiles of the BPAC–PDMS multiblock copolymers. The bulk PDMS concentration for three samples with PDMS block lengths of 2, 20, and 40 is 25%, and that with a PDMS block length of 7 is 20%. The samples were annealed.

These results are consistent with the morphology model proposed by LeGrand, in which small BPAC domains are separated by a continuous matrix containing both PDMS and BPAC components.[26] The morphology of the BPAC–PDMS multiblock copolymers was studied by using small-angle X-ray scattering, transmission electron microscopy, and thermodynamical analysis.[26,27] A microdomain structure consisting of irregularly-shaped domains was found. If the PDMS block lengths were 20–40 repeat units, the average center-to-center distance of two adjacent BPAC domains was measured to be on the order of 100–500 Å, depending on both the block length and composition. The sizes of the BPAC domains were estimated to be about 10–50 Å. Since there exists a microdomain morphology, the surface region should be composed of the PDMS-rich portion of the morphology. The PDMS surface segregation measured by ESCA suggests that the topmost surface region of the BPAC–PDMS block copolymers is indeed composed of the PDMS-rich phase.

The surface compositions of the BPAC–PDMS samples are related to the polymer structure, such as block length and bulk composition, and also to the preparation process.

PDMS Block Length. For an analysis of the effect of the PDMS block length on the PDMS surface enrichment of BPAC–PDMS multiblock copolymers, PDMS enrichment–depth profiles of four BPAC–PDMS block copolymers with similar bulk compositions but different PDMS block lengths are chosen and shown in Figure 3. The bulk PDMS concentration for three samples with PDMS block lengths of 2, 20, and 40 repeat units is 25%, and that with a PDMS block length of 7 repeat units is 20%. For direct comparison of the effect of the PDMS block length on the PDMS surface segregation, PDMS surface *enrichment* (instead of surface concentration) is used. The PDMS surface concentrations were measured on the annealed samples.

Figure 3 clearly shows the influence of the PDMS block length on the surface composition of the block copolymers. In the topmost surface region (up to 27 Å), the sample with short PDMS blocks (2 repeat units) has substantially lower PDMS enrichment than those samples with longer PDMS blocks (20 and 40 repeat units). The surface enrichment of the BPAC–PDMS samples with PDMS blocks of 20 and 40 in this topmost surface region (27 Å) is the same.

When larger spans of the surface region are measured by ESCA (73 and 103 Å), the surface enrichments of PDMS for the four samples are significantly different. The amount of PDMS surface enrichment is proportional to the PDMS block length. The change of PDMS enrichment is consecutive as the PDMS block length increases from 2 to 40.

Previous contact angle measurements revealed that the critical PDMS block length was 20 repeat units. When the PDMS block length is longer than 20, there is no difference in the wettability of the BPAC–PDMS block copolymers.[16] The wettability of a film is determined by the very topmost surface region (only a few angstroms). It should be best compared with the surface composition measured by ESCA in a small span of the surface region (such as 27 Å). As shown in Figure 3, the PDMS block chain length of 20 repeat units could be considered as a "critical block length" for the topmost surface composition, which is consistent with the contact angle measurements. However, this critical block length is not observed if a larger span of the surface region is considered.

When the PDMS block length is 2 repeat units, PDMS surface segregation is detected up to a sampling depth of 103 Å. Due to the surface attenuation effect of ESCA measurement as mentioned in the surface composition calculation section, this PDMS surface segregation effect could be overestimated. Since the BPAC–PDMS samples are random multiblock copolymers, the polydispersity of the BPAC block length affects the PDMS surface segregation. If the BPAC–PDMS polymer segments with shorter BPAC blocks segregate in the surface region, the local PDMS concentration in this region should be higher than the bulk PDMS concentration. The driving force for the possible effect of BPAC block length dispersity is, again, to minimize the surface energy by deploying a maximum amount of PDMS onto the surface. A further investigation of the block length distribution of the BPAC–PDMS random block copolymers in the surface region is planned by using time-of-flight SIMS.[28]

PDMS Bulk Composition. Three annealed BPAC–PDMS samples with a PDMS block length of 20 repeat units are chosen to show the effect of bulk PDMS concentration on the surface composition (Figure 4). In all surface regions measured by ESCA, the surface PDMS concentration is proportional to the bulk PDMS concentration. For a series of samples with the same PDMS

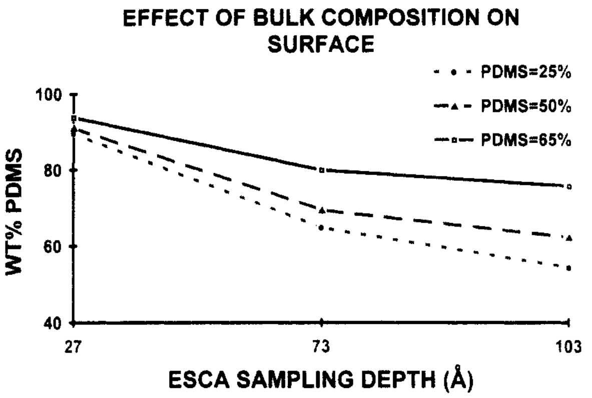

Figure 4. PDMS block lengths of 20 repeat units for all three samples. The PDMS bulk concentrations are 65%, 50%, and 25%. The samples were annealed.

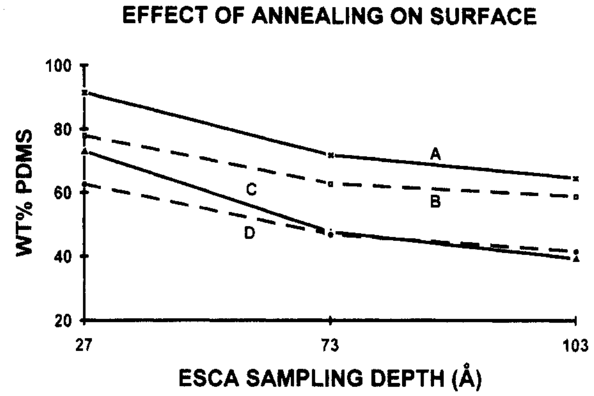

Figure 5. PDMS block lengths of 7 repeat units for all four samples. The bulk PDMS concentration for the annealed film A and the as-cast film B is 45% and that for the annealed film C and as-cast film D is 20%.

block length, the one with a higher bulk PDMS concentration has a higher surface PDMS concentration. The surface concentration difference shrinks as a smaller surface span is measured. The similar surface composition trend can also be found in other series of samples with the same PDMS block lengths.

The same group of samples with a PDMS block length of 20 repeat units were studied by ion scattering spectroscopy (ISS), a more surface-sensitive technique.[12] The sampling depth of ISS is about 1–2 atomic layers (5 Å). The ISS measurements of the PDMS surface concentrations for the as-cast samples of 25% and 50% PDMS in bulk were the same as measured by ESCA in the present study at a sampling depth of 27 Å. However, the PDMS surface concentration of the sample with 65% PDMS in bulk was 99% measured by ISS, while it is 91% by ESCA (from the as-cast samples). This means that the surface composition could be either homogeneous or inhomogeneous even if a very small span of the surface region is considered. These results show the strength of quantification with ISS and ESCA for small amounts over contact angle measurements.[16]

In another previous study[12] on the solution-cast films of the group of BPAC–PDMS samples with a PDMS block length of 20, no difference in the surface composition was observed between the data collected at integrated and 30° take-off angles. This was due to the low angle-dependent resolution of the instrument previously used (a PE PHI 560 ESCA). However, the surface compositions of the PDMS component of the chloroform solution-cast BPAC–PDMS films collected at a 30° take-off angle were consistent with the current results.

Annealing. When a film is prepared by casting from a polymer solution, the solvent used may preferentially solvate one polymer component of a multicomponent polymer and also change the interaction between polymer components. After the solvent is evaporated, the polymer segments are "freezed" (there is no polymer chain movement in large scale) if the glass transition temperature of one of the components is much higher than room temperature. The surface composition of an as-cast film, therefore, could be different from the one at thermodynamic equilibrium conditions. The solvent effect may be removed or at least reduced by annealing the as-cast films at appropriate conditions. The polymer morphology can be readjusted if the sample is heated to a temperature higher than the highest glass transition temperature of the block copolymer, because of the large-scale polymer segment movements (or chain relaxation).

The profiles of ESCA sampling depth versus PDMS surface concentration of the two BPAC–PDMS block copolymers with PDMS block length of 7 repeat units are shown in Figure 5. The top two curves in this figure are the PDMS concentration profiles of the annealed and as-cast (marked as A and B) films which contain 45% PDMS in the bulk. The PDMS surface concentration of the annealed film (A) is considerably higher than that of the as-cast film (B) in the topmost surface region (27 Å). The PDMS concentration difference between the annealed and as-cast films decreases if a larger span of surface region is measured.

A substantial PDMS surface concentration difference in the topmost surface region (27 Å) can also be observed when the annealed and as-cast films (marked as C and D) of the BPAC–PDMS block copolymer with a lower PDMS bulk concentration (20%) are compared in the same figure. The PDMS concentrations become eventually the same when the composition is averaged over larger spans of surface regions (73 and 103 Å).

Quantitative ESCA measurements clearly demonstrate the annealing effect on surface composition change. Quantification of surface composition is a major advantage of ESCA over the singular use of contact angle measurements, which cannot differentiate a small amount of composition change due to the nature of the measurements. This annealing effect has not been reported from previous investigations of BPAC–PDMS block copolymers.

Conclusions

The surface compositions of BPAC–PDMS multiblock copolymers with different block lengths and bulk compositions were investigated by angle-dependent ESCA measurement. All the block copolymers exhibit PDMS surface segregation in the surface region. The PDMS surface concentration averaged over a specific span of the surface region decreases if a larger span of the surface region is measured. Both the block copolymer structure and the film preparation process determine the surface composition of the block copolymers. The BPAC–PDMS multiblock copolymers with longer PDMS blocks or with higher PDMS bulk concentrations have higher PDMS surface concentrations. Annealing of the as-cast BPAC–PDMS films at an elevated temperature drives the more PDMS component into the topmost surface region. After annealing, the composition change in the upper surface region is more significant than that in the inner surface region.

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