Surface Studies on Multicomponent Polymer Systems by X-ray Photoelectron Spectroscopy: Polystyrene/Poly(ethylene oxide) Homopolymer Blends

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ABSTRACT: X-ray photoelectron spectroscopy (XPS) is a surface characterization technique capable of providing detailed information concerning the structure, bonding, morphology, and topography of molecules in the solid state. In this study, we have made XPS measurements as a function of electron takeoff angle [XPS(θ)] to determine the surface composition and topography at the polymer–air or polymer–vacuum interface of thin films containing blends of polystyrene (PS) and poly(ethylene oxide) (PEO) homopolymers. These homopolymers undergo microphase separation when solvent cast into films, and the XPS studies clearly indicate that the composition at the surface (i.e., outermost ~50 Å) is significantly richer in PS than the overall bulk composition. A comparison of these results with those recently obtained in diblock copolymers of identical compositions reveals, unexpectedly, that the concentration of PS at the surface is lower in the blends than in the blocks. The XPS(θ) data indicate that the blend surfaces have isolated domains of PS and PEO which result in lateral inhomogenity at the polymer–air interface. In contrast to the diblock copolymers, it appears from an examination of the core level intensity ratios for the PEO component that there is some mixing of PS in PEO for the blends. This result is surprising since phase separation appeared to be virtually complete in the PS/PEO diblock copolymer system.

Introduction

In the first two papers[2] in this series, we demonstrated, using X-ray photoelectron spectroscopy (XPS), how absolute and relative binding energies and relative peak intensities corresponding to the direct photoionization of core levels (C_{1s} and O_{1s}) in a series of polystyrene/poly(ethylene oxide) diblock and triblock copolymers can provide detailed information about the morphology, topography, and composition in the top few tens of angstroms of the surface. These block copolymers readily undergo phase separation and their film morphology is strongly influenced by molecular weight, thermal and physical history, casting solvent, and temperature.[3] By applying the technique of angular-dependent X-ray photoelectron spectroscopy [XPS(θ)] to the study of solvent-cast diblock copolymer films, we were able to obtain detailed depth profiling of the composition and topography at the air–polymer interface. The results pointed to a surface excess of PS in all the copolymer films studied. A model was proposed for the copolymers which had both the PS and PEO components at the surface but phase separated into vertically homogeneous domains of at least 50 Å thick.

We now report the results of our XPS studies on solvent-cast films containing blends of PS and PEO homopolymers. We contrast these results with those previously obtained on related diblock and triblock copolymers and, in addition, report preliminary results of time-dependent XPS measurements taken on heated bilayer films, PS overcoated with PEO. It was anticipated from the differences in the solid-state surface tensions[4] of PS (36 dyn/cm) and PEO (44 dyn/cm) not only that there would be differences in the equilibrium surface concentrations of each component relative to the bulk for solvent-cast films but that in the bilayered system the PS component would dominate the surface when the system was allowed to equilibrate above the T_g of each homopolymer. Surprisingly, we found that PS did not completely dominate the surface of the polyblends and that, in fact, the blends and the block copolymer systems behave rather similarly.

Experimental Section

A. Samples. Polystyrene/Poly(ethylene oxide) Homopolymer Blends. The polystyrene homopolymer used in this study was prepared by standard anionic polymerization techniques, purified by precipitation into hexane, and recovered as fine powder. The $\bar{M}_n$ of the polystyrene was ~10 000 with an average MWD near 1.1. The poly(ethylene oxide) homopolymer (Union Carbide Carbowax, $\bar{M}_w$ = 25 000) was received in flake form and no further purification was performed.

The PS and PEO homopolymers were dissolved in chloroform (spectroscopic grade, Burdick and Jackson) as dilute solutions and thin films were prepared by dip coating onto flat aluminum substrates. The samples were dried in an argon atmosphere to reduce surface oxidation of the homopolymers, and thick coatings were obtained by multiple dipping to ensure the substrate Al_{2p} core level signals were attenuated to an unobservable level. The blends were not completely soluble in nitromethane and ethylbenzene (preferential solvents for PEO and PS, respectively), used in the XPS study of PS/PEO diblock copolymers,[2] so only the common solvent, chloroform, was used in this work.

The polymers used for Figure 5, poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), poly(vinyl acetate) (PVAc), and poly(oxymethylene) (POM), were all obtained from Scientific Polymer Products and used as received.

Polystyrene/Poly(ethylene oxide) Layer System. The sample for the PS/PEO layer study was prepared by melt casting a thick layer (~100 μm) of polystyrene onto an aluminum substrate and solvent casting a thin layer (~1 μm) of PEO (from nitromethane, a solvent for PEO and not for PS) onto the surface of the PS. The initial core level spectra indicated that a continuous layer of PEO overcoated the PS sublayer.

B. XPS Instrumentation. Spectra were recorded on an AEI ES200B spectrometer by using Mg $K\alpha_{1,2}$ exciting radiation. Typical operating conditions were as follows: X-ray gun, 12 kV, 15 mA; pressure in the source chamber, ca. 10^{-8} torr. Under the experimental conditions employed, the Au $4f_{7/2}$ level at 84-eV binding energy (BE) used for calibration had a full width at half-maximum (fwhm) of 1.2 ± 0.1 eV. No evidence was obtained for radiation damage to the sample from long-term exposure to the X-ray beam. Due to the rather long analysis times required for the angular-dependent studies, a liquid nitrogen cooled X-ray cap was used throughout the study to eliminate hydrocarbon contamination of the sample surface. This device has been described in detail elsewhere.[5]

Calibration of the absolute energy scale was achieved by disconnecting the liquid nitrogen cooling cap on the X-ray anode and allowing hydrocarbon contamination to collect on the sample surface. The value of 285.0 eV was used for the C_{1s} core level of the hydrocarbon and the details of this method of calibration have been discussed elsewhere.[6]

Overlapping peaks were resolved into their individual components by use of a Du Pont 310 curve resolver (an analog computer). The detailed deconvolutions were based on a knowledge of line widths determined from studies of homopolymers and

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Table I
Experimentally Determined Binding Energies, Peak Area Ratios for the Reference Homopolymers, and the Blend Compositions Used in This Study

HOMOPOLYMERS					
		BINDING ENERGY* (IN eV) ± 0.2			PEAK AREA RATIOS
	$M_w \times 10^3$	C_{1s}	$C_{1s}\ \pi^* \leftarrow \pi$	O_{1s}	$\frac{C_{1s}(PS)}{C_{1s}(PEO)} = 1.60 \pm 0.1$
POLYSTYRENE	10	285.0	291.6	—	$\frac{C_{1s}(PEO)}{O_{1s}(PEO)} = 0.73 \pm 0.05$
POLYETHYLENE OXIDE	25	286.5	—	533.3	$\frac{C_{1s}(\pi^* \leftarrow \pi)(PS)}{C_{1s}(PS)} = 0.081 \pm 0.005$
		*REFERENCED TO HYDROCARBON AT 285.0 eV			

BLENDS		
SAMPLE	BULK %PS	
	WT.	MOLE
A	19.6	9.6
B	39.3	21.4
C	70.0	49.5

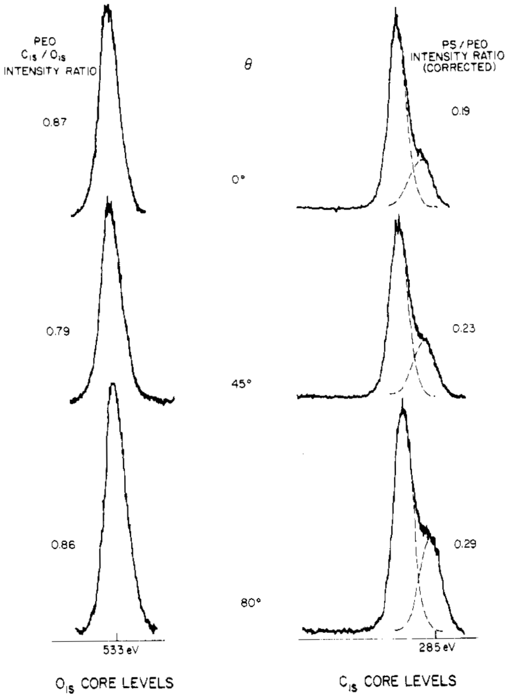

Figure 1. Angular-dependent C_{1s} and O_{1s} core level spectra for the PS/PEO blends at 19.6 wt % PS cast from chloroform. The C_{1s}/O_{1s} intensity ratios for the PEO component are indicated on the left and the corrected intensity ratios for PS/PEO derived from the C_{1s} core level spectra are indicated on the right.

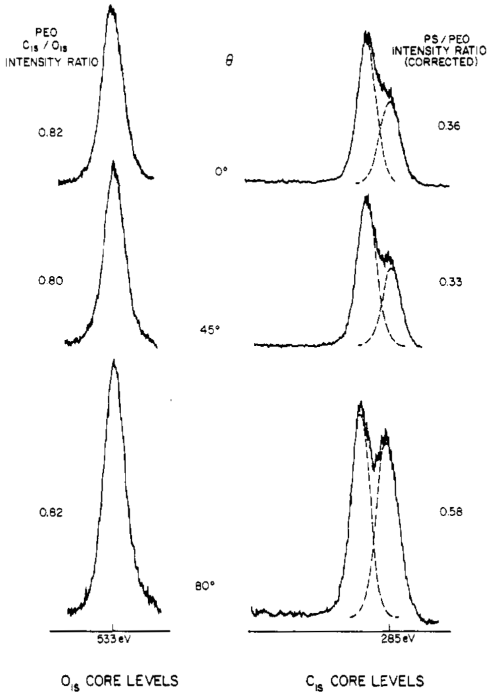

Figure 2. Angular-dependent C_{1s} and O_{1s} core level spectra for the PS/PEO blend at 39 wt % PS cast from chloroform. Intensity ratios are consistent with the description for Figure 1.

model compounds.[7] These studies have shown that for individual components of the core level spectra for C_{1s} and O_{1s} levels, the line shapes approximate a Gaussian distribution.

Results and Discussion

PS/PEO Blends. In previous publications,[2] we established a basis for the interpretation of the diblock and triblock copolymers based upon a study of the individual homopolymer components. Table I contains relevant data on these systems, and it summarizes the differences in the XPS spectra of PS and PEO. These differences, i.e., the 1.5-eV chemical shift in the C_{1s} core level spectra, the uniqueness of the $\pi^* \leftarrow \pi$ shake-up peak associated with the PS component, the O^{1s} core levels associated with the PEO component, and the relative peak intensity ratios (found in Table I) were discussed earlier[2] and, together, they allow for an unambiguous analysis of the surface composition of the PS/PEO blends.

The measured C_{1s} and O_{1s} core level spectra of films of the three different concentration PS/PEO blends cast from chloroform are shown in Figures 1–3. The record of data at more than one electron takeoff angle, θ, allows for a depth profiling of the outermost surface of the sample by controlling the *effective* sampling depth.[2] The spectra were recorded at three different angles, $\theta = 0$, 45, and 80°, to achieve effective sampling depths of ~50, ~25, and ~10 Å, respectively.

Considering first the three samples studied at $\theta = 0°$, where the sampling depth is maximized, it can be seen that as the PS concentration in the bulk increases, the PS concentration at the surface increases. However, in all cases, the PS content, relative to PEO, at the surface exceeds that in the bulk mixture as in the case for the diblock copolymers. A comparison of the PS surface content from

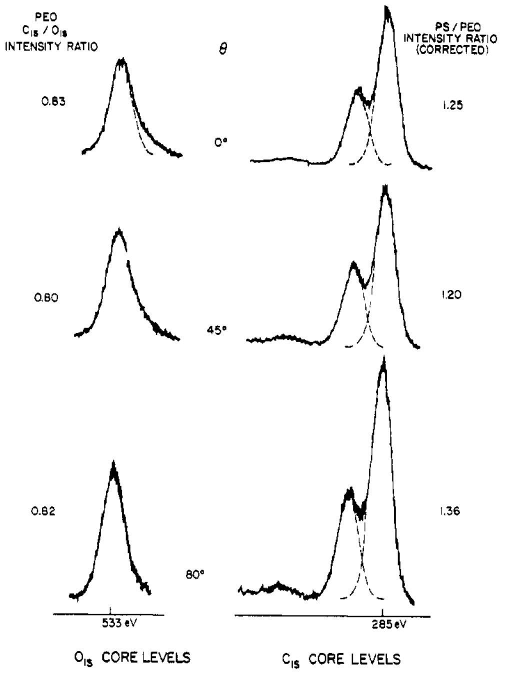

Figure 3. Angular-dependent C_{1s} and O_{1s} core level spectra for the PS/PEO blend at 70 wt % PS cast from chloroform. Intensity ratios are consistent with the description for Figure 1.

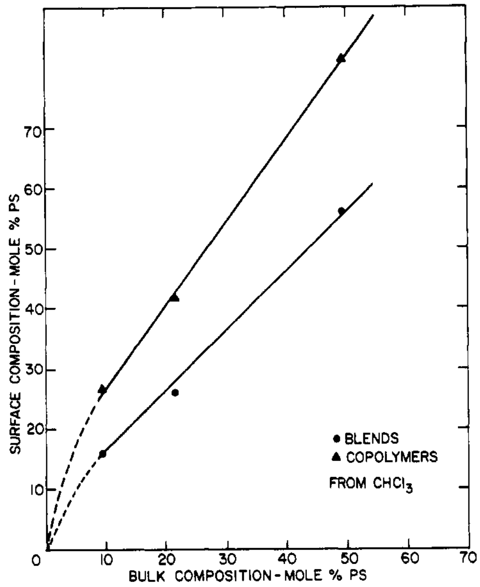

Figure 4. Surface vs. bulk composition for the diblock PS/PEO copolymers from ref 1 compared with the PS/PEO blends from this work taken at $\theta = 0°$.

the XPS data at $\theta = 0°$ for the diblock copolymers and the blends for equivalent bulk concentrations is shown in Figure 4. Considering that there is a thermodynamic driving force for PS to reside preferentially at the surface and that in the blends PS is not linked to a PEO chain, it is surprising to see that the blends have lower surface concentrations of PS than the block copolymer systems for comparable compositions. However, the PS concentration at the surface is certainly dependent upon temperature and rate of solvent evaporation and these variables have not been studied.

A key point to be noted about the spectra in Figures 1–3 is the C_{1s}/O_{1s} intensity ratio for the PEO component in each blend. This ratio for the blend is consistently higher than the value of 0.73 (Table I) found for the pure PEO homopolymer. This increase in the C_{1s}/O_{1s} ratio indicates that the PEO component is somewhat diluted and is not pure PEO within the XPS depth profiling scale, based upon a knowledge of the relative mean free paths for photoelectrons from the C_{1s} and O_{1s} core levels. The C_{1s} core level photoelectrons at binding energy 285 eV have kinetic energies of ~1000 eV with a Mg X-ray source while O_{1s} is at ~700 eV. This difference in kinetic energy results in an electron mean free path difference of about 25% ($\lambda_{C_{1s}} = 15$ Å whereas $\lambda_{O_{1s}} = 11$ Å).[8] Therefore the O_{1s} signal will decay at a faster rate with depth than the C_{1s} signal. A dilution of the PEO with PS effectively decreases the O_{1s} signal relative to the C_{1s} signal, reducing the C_{1s}/O_{1s} ratio. This suggests that the PEO component is either overcoated with a PS layer or that the PEO is mixed with PS, or both.

Table II
Mole Percent PS at the Surface of Films Cast from Chloroform for the Three Blends as a Function of Electron Takeoff Angle (θ) (Effective Sampling Depth)

sample	$\theta = 0°$	$\theta = 45°$	$\theta = 80°$
A	16	19	23
B	26	25	37
C	56	55	58

It is instructive to compare the XPS(θ) results at $\theta = 45$ and 80° with the results at $\theta = 0°$ in Figures 1–3 for the three blends. As we discussed previously,[2] the lateral and vertical homogenity of a sample can be explored by XPS(θ) studies. To summarize this previous discussion, the signal intensities derived from a core level in an overlayer and in a substrate are given by eq 1 and 2, respectively.

For an overlayer

$$I_i^0 = f_i(\theta)F\alpha_i N_i k_i \lambda_i (1 - e^{-d/(\lambda_i \cos \theta)}) \qquad (1)$$

For the substrate

$$I_i^s = f_i(\theta)F\alpha_i N_i k_i \lambda_i e^{-d/(\lambda_i \cos \theta)} \qquad (2)$$

where I_i^0 is the signal intensity arising from the core levels i, $f_i(\theta)$ is the signal intensity as a function of θ for core level i in a homnogeneous sample of the same dimensions, F is the X-ray flux, unattenuated over the sampling depth, α_i is the cross section for photoionization of core level i, N_i is the number of atoms per unit volume on which core level i is localized, k_i is the spectrometer factor for core level i, λ_i is the electron mean free path for core level i, d is the overlayer thickness, and θ is the angle between normal-to-sample surface and electron optics of the energy analyzer.

It can be seen from these equations that the attenuation of the substrate and overlayer signal intensities depends exponentially on d, the overlayer. Detailed analysis of the XPS(θ) spectra in Figures 1–3 reveals a slight angular dependence in the ratios of PS and PEO when considering only the C_{1s} core levels (a more detailed discussion on the basis for these arguments can be found in ref 2). However, if we apply the continuous overlayer model to the analysis of the C_{1s}/O_{1s} signal intensity ratio for the PEO component only, we can see from eq 2, using $\lambda_{C_{1s}}$ of 15 Å,[8] that for as little as 10 Å of PS on PEO that the C_{1s}/O_{1s} ratio for PEO would increase from 0.73 to 0.95. The C_{1s} core level spectra in Figures 1–3 do not show this increase in the C_{1s}/O_{1s} ratio and, therefore, alternative models must be considered.

The calculated mole percent PS from the XPS(θ) studies is shown in Table II for films cast from chloroform. The slight increase in the ratio of PS to PEO with increasing angle θ can be interpreted in a similar manner to the results of the diblock copolymer system. We have ruled out the continuous overlayer model based upon the C_{1s}/O_{1s} ratios

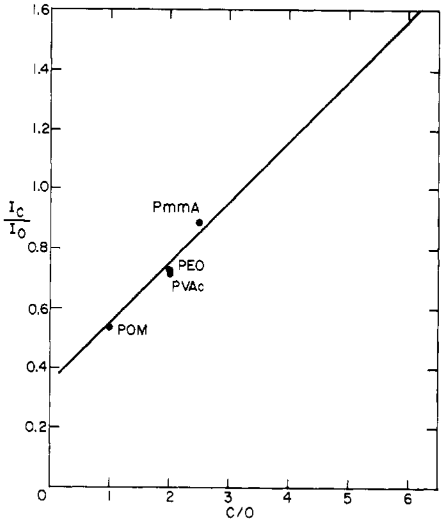

Figure 5. C_{1s}/O_{1s} intensity ratios for a series of homopolymers as a function of carbon-to-oxygen stoichiometry: poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), poly(vinyl acetate) (PVAc), and poly(oxymethylene) (POM).

for the PEO component. However, the slight increase in the PS to PEO relative ratios at the grazing angle ($\theta = 80°$), where the very top surface features are enhanced, can be explained by using the surface topography models developed previously for the diblock copolymers.[2a] The XPS(θ) studies on the three blends, when approached with the same arguments as those applied to the diblock copolymers, reach the inevitable conclusion that the PS/PEO blends have surface topographies similar to those of the PS/PEO diblock copolymers; i.e., the PS and PEO components are both exposed at the surface, and they are organized into domains that are thick compared to the XPS sampling depth. The diblock copolymers when cast as films from chloroform revealed a surface topography where the PS component was somewhat raised above the PEO component as shown in Figure 7d in the previous paper,[2a] and the same conclusions can be drawn for the surfaces of the blends. However, there are two significant differences in the surfaces of the blends compared to the diblocks: (1) The PEO component appears to be diluted with PS because of the high C/O intensity ratio for the PEO component and (2) the surface concentrations of the PS components in the blends cast in this study are significantly lower than that found in the diblock copolymers at identical bulk compositions.

Let us consider now the suggestion that the high C_{1s}/O_{1s} intensity ratio for the PEO component is due to phase mixing of PS and PEO. We can ask the question: How much hydrocarbon would have to be intimately mixed with the PEO component to attenuate the oxygen signal of the PEO component and thereby effectively increase the C_{1s}/O_{1s} intensity ratio from 0.73 to 0.83? In other words, what carbon-to-oxygen stoichiometry will result in a C_{1s}/O_{1s} intensity ratio of 0.83? To determine this stoichiometry, we have measured the C_{1s}/O_{1s} intensity ratios for a series of related homopolymers in which the carbon-to-oxygen stoichiometries range from 1:1 to 2.5:1. In using these homopolymers as model systems, we make the reasonable assumptions that the electron mean free paths differ very little for these series of polymers at the same kinetic energy for photoemitted electrons and that the carbon and oxygen species are randomly arranged in the surface regions of these polymers. The results of the XPS measurements are shown in Figure 5 and, from the curve, we find that a C_{1s}/O_{1s} intensity ratio of 0.83 corresponds to a carbon-to-oxygen stoichiometry of 2.5:1.

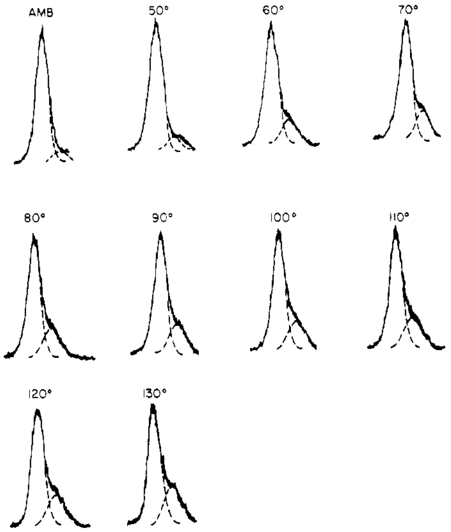

Figure 6. C_{1s} core level spectra for a layered PEO/PS structure as a function of temperature from ambient temperature (~30 °C) to 130 °C.

Continuing this line of reasoning, we assume that PS will only mix with amorphous PEO and that the fraction of PS which is mixed is distributed uniformly throughout the amorphous PEO. Given that the mixed phase has a carbon-to-oxygen stoichiometry of 2.5:1, it is straightforward to show that this is equivalent to homogeneously distributing 1 mol of PS repeat units among 16 mol of PEO repeat units. From calorimetry measurements on bulk samples,[9] we know that the degree of crystallinity of PEO is ~70% for all the polyblends. [Reflection-diffraction (R-D) patterns were obtained in a similar system, PEO-PS-PEO triblock copolymer, using a Philips EM 400 electron microscope with a R-D holder at 80 kV (λ 0.0433 Å). The depth of penetration of the electron beam does not exceed 150 Å; therefore the R-D patterns correspond primarily to the surface crystallinity. In this system the R-D patterns indicated surface crystallinity; however, the paracrystalline reflections did not fall on discrete Debye-Scherrer rings due to the irregularity of the surface. Therefore, the exact measurement of the *d* spacings are difficult due to the undetermined inclination of the diffracting area with respect to the beam. However, the intense spots were believed to correspond to planes with spacings of 3.6-2.5 Å. It is felt that due to the similarity in these two systems it is reasonable to assume a similar crystalline surface for the PEO component of the polyblends.] The remaining 30% of PEO is amorphous and available for mixing with PS in the molar ratio of 16:1. If all the amorphous PEO mixes with PS, calculations indicate that in the 75, 50, and 25% PS/PEO polyblends the mixed phases would contain 1, 2, and 3% PS, respectively.

PEO/PS Layers. The surprising results on the surface composition of the blends of PS and PEO, where the PS component did not dominate the surface and the domains did not appear to be discrete, prompted us to investigate polymer "diffusion" for the blends. A sample was prepared where a PS film was overcoated with a layer of PEO and the sample heated to 130 °C, above the T_g of both homopolymers. The C_{1s} core levels were monitored, Figure 6, as a function of temperature at constant angle $\theta = 25°$ (where the C_{1s} core level signal maximized). It can be seen at ambient temperature that the PEO component dominated the surface, whereas at 130 °C the mole percent PS relative to PEO had increased to ~18%.

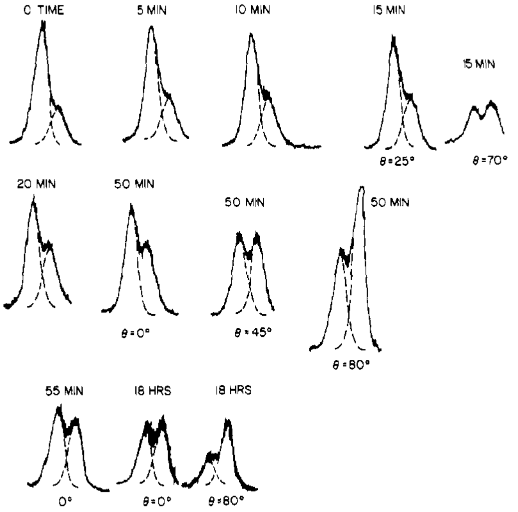

Figure 7. C_{1s} core level spectra for a layered PEO/PS structure as a function of time at 130 °C. (Time zero taken when sample reached 130 °C, from Figure 6.)

The XPS(θ) studies indicate significant angular dependence in the C_{1s} core level spectra, where the PS component increases in intensity relative to the PEO as grazing angles are approached. This effect persists throughout the time involved in the study and is attributed to a topography similar to that assigned to the diblock copolymer and blend surfaces.

Taking into account the fact that the system is not in thermodynamic equilibrium at any sampling period for XPS upon reaching 130 °C, which is designated as $t = 0$ in Figure 7, we carried out a time study for a total of 18 h to establish the surface homogeneity of the layered sample. An examination of the data reveals that an exponential decrease in the rate of appearance of PS at the surface exists, and an extrapolation in time to where a surface of only PS exists yields, for all practical purposes, infinity. An increase from 55 to 1080 min reveals an increase in PS mole percent at the surface of only 6%, from 35 to 41, relative to the PEO component. (There is some concern that just because we are above the T_g's of the homopolymers (130 °C) that this temperature does not necessarily constitute the free-flow regions for the homopolymers; therefore, more extensive studies are needed on the melt flow properties of the homopolymers as well as this particular system to better establish these parameters.) In these studies, we have merely attempted to demonstrate the capability of the XPS technique to study multicomponent layered systems, and further refinement of the experimental conditions are required for more detailed thermodynamic studies on polymer/polymer diffusion.

Conclusions

XPS(θ) studies were performed on blends of PS and PEO homopolymers to determine their surface composition and topography. The experimental results indicate that these blends are similar in surface topography to PS/PEO diblock copolymers cast from chloroform. However, for identical bulk compositions, the concentration of PS on the surfaces of the blends is significantly less than on the surfaces of the copolymers. In general, we can conclude the following:

(1) In the blends, the concentration of PS at the polymer–air interface is higher than the bulk concentration of PS. However, the surface excess of PS in the polyblends is less than that found in the diblock copolymers of comparable bulk composition.

(2) The surfaces of the blends are laterally inhomogeneous in PS and PEO. In a manner similar to the diblock copolymers, we find the PS component raised somewhat above the PEO component. However, our results suggest there is some phase mixing of the PS and PEO components in the blends. In view of the propensity of PEO toward crystallization and the well-known incompatibility of PS and PEO in the bulk, we suspect the degree of mixing to be quite small. In view of current theories[10] on phase mixing in multicomponent systems, it is consistent that evidence is found for phase mixing in the polyblend system but not in the diblock copolymers. More work is obviously needed in this area for a better understanding of these mixing phenomena.

(3) As in the diblock system, the molar composition at the homopolymer blend surface determined by XPS corresponds to the surface area occupied by each copolymer component, with the slight deviation accounted for by the mixing.

The work reported here is a continuation of our studies on multicomponent polymer systems in an attempt to establish a firm understanding of the *surface* structure and bonding for polymer systems in general.

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