Investigation of the Water-Induced Reorganization of Polycaprolactone−Poly(fluoroalkylene oxide)−Polycaprolactone Triblock Copolymer Films by Angle-Dependent X-ray Photoelectron Spectroscopy

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Received September 28, 2001; Revised Manuscript Received May 28, 2002

ABSTRACT: The water-induced reorganization of a series of poly(caprolactone)−poly(fluoroalkylene oxide)−poly(caprolactone) (PCL−PFPE−PCL) thin film surfaces was studied by angle-dependent X-ray photoelectron spectroscopy (XPS). The reorganization was studied as a function of polymer chain length, water exposure time, and XPS sampling depth. The prepared films were exposed to water and then frozen in liquid nitrogen to preserve the surface composition during XPS analysis. The XPS results showed the PFPE block segment length influenced the extent and rate of segment reorganization at the surface. The detected changes were shown to be reversible upon re-exposure to air and the effect of liquid-nitrogen freezing was determined to be negligible.

Introduction

The design and implementation of polymeric materials for applications ranging from biomedical devices[1] to antifouling ship hull coatings[2] requires a fundamental understanding of the interfacial structure and reactivity of the polymer in an aqueous environment. Unlike metal or ceramic surfaces that are relatively fixed, polymer chains at surfaces can be dynamic and can reorient to minimize surface free energy in response to environmental changes.[3,4] For example, low surface energy and low glass-transition temperature (T_g) polymers such as poly(dimethylsiloxane) (PDMS) segments in copolymers of poly(dimethylsiloxane)−polyurethane (PDMS−PU) are known to preferentially segregate to the surface over the PU component at an air interface.[5] Upon exposure to water, however, these surfaces can undergo reorganization whereby the PU component reorients to the surface to form a more thermodynamically favorable interface. The majority of spectroscopic studies of polymer surfaces have focused on the polymer/air interface because of the widespread availability of techniques that are amenable to air or vacuum analysis. However, extracting chemical information from a polymer surface in a water environment is challenging because of sample-handling issues and instrument limitations. Contact angle measurements are useful for in situ analysis of polymer surface reorientation but lack direct analysis of chemical information.[6−10] Therefore, other approaches have been used to extract surface specific molecular information without compromising the integrity of the polymer/water interface.

Attenuated total reflectance infrared spectroscopy (ATR−IR) has been used to study the water-induced reorientation and H_2O/D_2O uptake of poly(ether−urethanes).[11,12]

Although ATR−IR can be used to make "in situ" measurements, it is limited by poor surface sensitivity (≈1000 Å). Atomic force microscopy (AFM) was used with functionalized tips to obtain topographical, friction, and adhesion changes upon hydration of perfluorinated amide−urethane copolymers.[13] The results showed specific hydrophobic/hydrophilic interactions with certain modified tips to segregated regions at the surface before and after hydration. Sum-frequency generation (SFG) spectroscopy was recently used to study the reorientation of hydrogels upon exposure to water.[14] The surface sensitivity (≈5−10 Å) is superior to almost all other surface techniques with the exception of contact angle but quantification is not yet routine.

X-ray photoelectron spectroscopy (XPS) is perhaps the most powerful method for providing both qualitative and quantitative information for polymer surfaces. However, the ultrahigh vacuum conditions in XPS present a number of obstacles for studying hydrated or immersed polymer surfaces. Ratner et al.[15] devised a method to preserve the hydrated surface of grafted 2-hydroxyethyl methacrylate (HEMA) by rapidly freezing the substrate to cryogenic temperatures. This study demonstrated that XPS could be used to monitor the change in HEMA composition at the surface before and after exposure to water. Lewis and Ratner[16] evaluated the effect of freeze-drying and surface contamination on a series of polymer surfaces by angle-dependent XPS. The results from this study showed that the freezing process did not significantly influence the surface composition and that the water-induced reorganization of the polymer surfaces under investigation was reversible. Angle-dependent cryogenic XPS was used to correlate improved cell adhesion to the surface enrichment of polyurethane-grafted peptide sequences in water.[17] Yasuda et al.[18−20] labeled polymer surfaces with fluorine from a CF_4 plasma to investigate water-induced reorganization by cryogenic XPS. By monitoring the spectral intensity of

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10.1021/ma011697r CCC: $22.00
Published on Web 07/11/2002

Scheme 1. General Chemical Formula for Polycaprolactone−Poly(fluoroalkylene oxide)−Polycaprolactone Triblock Copolymer

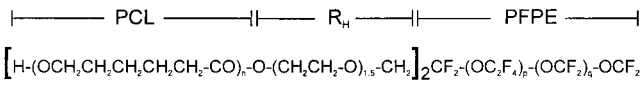

Table 1. Triblock Copolymer Average Molecular Weights

triblock copolymers	number average MW (M_n) PCL−R_H−PFPE−R_H−PCL
PCL(50)−TX1	600−100−900−100−600
PCL(50)−TX2	1100-100-2200-100−1100
PCL(50)−TX3	1600-100-3200-100−1600

the fluorine tag (F 1s peak), they were able to determine the rate and extent of chain mobility at the polymer/water interface for a series of commercial polymer films including poly(ethylene terephthalate), Nylon 6, poly(methyl methacrylate), and polyethylene. Yasuda et al. also investigated the water-induced reorganization for poly(ethylene−vinyl alcohol)[21] and poly(tetrafluoroethylene)−perfluoropropyl vinyl ether[22] by cryogenic XPS without using the fluorine plasma label. In both cases, XPS showed the more hydrophilic components segregated to the surface in water as compared to the air interface surface composition. Similar findings were reported by Lukas et al. using cryogenic XPS to study the water-induced reorganization of a series of statistical methacrylate copolymers. [23]

In this study, the water-induced reorganization of a series of polycaprolactone−poly(fluoroalkylene oxide)−polycaprolactone (PCL−PFPE−PCL) triblock copolymers have been investigated by angle-dependent cryogenic XPS. Previous XPS studies of these polymers at the air interface have shown a preferential segregation of the perfluoropolyether (PFPE) segment to the surface relative to the bulk composition.[24,25] Further, angle-dependent XPS studies showed, for a particular composition, the longer PFPE block segment length yields a higher ultimate surface composition of PFPE and a thicker segregation layer of PFPE.[25] In the present study, the effect of molecular weight and block segment length at a fixed bulk composition on the extent and rate of water-induced reorganization is investigated for a set of PCL−PFPE−PCL triblock copolymers. From our evaluation of the literature, this appears to be the first report of the study of the time course of polymer surface reorganization, showing the effects of structure on the kinetics of reorganization.

Experimental Section

Materials. The synthesis and bulk characterization of the PCL−PFPE−PCL copolymers was reported previously.[26] The general structure for the copolymers used in this study is shown in Scheme 1 and their respective molecular weights are given in Table 1.

XPS Sample Preparation. Thin polymer films of the samples were prepared by solvent casting onto clean glass slides from 30.0% (w/v) methylene chloride solutions. The methylene chloride (Fisher 99.9%) was used as received and the samples were allowed to dry in air for 6 h and then dried under vacuum (1×10^{-3} Torr) for 1 h prior to water exposure. The film thicknesses of the samples were estimated to be ≈150 μm.

XPS Instrumentation and Sample Handling. The angle-dependent XPS data were recorded on a Physical Electronics Model 5300 XPS spectrometer with a hemispherical analyzer and single-channel detector. The achromatic Mg Kα X-ray source was operated at 150 W (15 kV and 10 mA). The base pressure during analysis was maintained at or below 2×10^{-8} Torr. High-resolution spectra were acquired over a 20-eV window with a pass energy of 35.75 eV at 0.1 eV/step. Each sample was analyzed at a takeoff angle of 15°, 20°, 30°, 45°, and 90° (a 90° takeoff angle being defined as the film surface normal to the analyzer) with an X-ray exposure time (analysis time) of 5 min for each angle. The cryogenic UHV system used in this study has been described elsewhere.[27]

The vacuum-dried polymer films were immersed in freshly distilled deionized water for 5 min, 30 min, and 6 h at room temperature. The films were removed from the water and mounted to a sample holder by a small water droplet on the sample holder surface. The sample was then immediately immersed in liquid nitrogen (LN_2) with a stainless steel holder. The removal, mounting, and immersion of the sample into liquid nitrogen took no more than 10 s. When the sample was cooled to −198 °C (indicated by the gentle boiling of the LN_2), the Dewar was brought up to the UHV introduction chamber against flowing nitrogen and the sample was introduced onto a room-temperature UHV transfer arm. The sample was rapidly evacuated to ca. 1×10^{-3} Torr (15 s) in an introduction chamber and then transferred to a precooled sample holder (typical experimental temperatures ranged from −120 to −125 °C) in an isolated preparation chamber. The sample remained on the cryogenic sample holder for 2−3 h whereas the ice film on the surface sublimed. The temperature was maintained below −115 °C during the sublimation period and film analysis in the XPS chamber. After 2−3 h, the sample was introduced into the analysis chamber and analyzed at five takeoff angles. At least three independent measurements were made for each exposure time. To minimize quantitative error from X-ray damage (defluorination),[25] the order of takeoff angle measurements was alternated for the three shallowest angles (15°, 20°, and 30°) and subsequently no changes were detected. The treatment of the raw spectral data has been reported elsewhere.[25]

Results and Discussion

The chemical structure of the polycaprolactone−poly(fluoroalkylene oxide)−polycaprolactone (PCL−PFPE−PCL) is shown in Scheme 1. We chose to use PCL(50)−TX1, PCL(50)−TX2, and PCL(50)−TX3 (Table 1) because the chain lengths of the polycaprolactone (PCL) and perfluoropolyether (PFPE) incrementally increased but their bulk weight percents were approximately the same. We were interested in how different water exposure times changed the measured surface weight percentages of the PFPE, PCL, and poly(ethylene oxide) linker (R_H) and how the changes in molecular weight influenced the rate and extent of reorientation. The interfacial weight percentages for each copolymer segment can be calculated from either the oxygen (O 1s) or carbon (C 1s) region in the XPS spectrum. The O 1s region was not used in this study because of the possibility of frozen water adsorbed to the surface. Therefore, all of the weight percent results were calculated from the C 1s region. The curve-fit XPS C 1s spectrum for a thin film of PCL(50)−TX2 is shown in Figure 1. Peaks G and F correspond to the PFPE segment whereas peaks D, B, and A correspond to the PCL segment. Both peak E and C are due to the R_H linking unit. A detailed discussion on the peak identification, data treatment, and weight percent calculations were reported elsewhere.[25]

The polymer films in this study undergo two significant environmental changes. The first change involved exposing the films to water and the second was the rapid freezing in liquid nitrogen. Because we are interested in investigating the former changes, the latter temperature effects must be either ruled out or corrected for. To rule out any temperature-induced changes, the polymer films were frozen without exposure to water

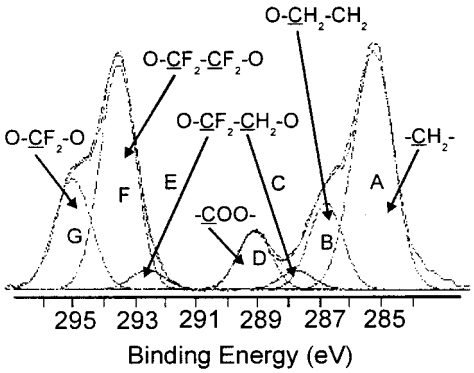

Figure 1. Curve-fit carbon 1s XPS spectrum of a PCL(50)−TX2 thin film. Peaks A, B, and D are assigned to the polycaprolactone segment, F and G are assigned to the perfluoropolyether segment, and peaks C and E are assigned to the poly(ethylene oxide) linker.

and analyzed by XPS. The results are reported in Table 2 for each takeoff angle (TOA) and polymer. The "air" and "air/LN_2" samples are separate polymer films with the latter representing the samples frozen in liquid nitrogen at the air interface. The data reported in Table 2 confirm that the liquid-nitrogen freezing does not significantly change the surface composition of the three polymer samples. The surface weight percentages for the frozen surfaces do not vary by more than 4% compared to the room-temperature samples with the sole exception of the PCL(50)−TX1 at 90° TOA. Even though this change is larger than 4%, it is attributed to experimental error because of further results from samples exposed to water, where no significant differences in composition at 90° TOA were detected. The data for the PCL(50)−TX1 at 90° TOA for the three different exposure times did not show significant changes at this escape depth. Because the "air" and "air/LN_2" data were shown to vary by <4%, we will designate a significant change in weight percent as anything >4%.

The PCL(50)−TX1 films were exposed to water for 5 min, 30 min, and 6 h prior to XPS analysis. The weight percent calculated from the C 1s peak fit data for the PCL(50)−TX1 at the air interface and after 6 h of water exposure are plotted in Figure 2 as a function of takeoff angle. The weight percent results for the 5 and 30 min water-exposed films are not shown because they are within 3% of the 6-h data. The air interface data in Figure 2 shows a preferential surface segregation for the PFPE segment compared to the PCL data at each corresponding takeoff angle. The weight percent of the R_H segment does not change as a function of sampling depth. After the PCL(50)−TX1 films are exposed to water for 6 h, the PFPE weight percent changed by more than 5% at a TOA of 30° (≈51 Å).[28] There were not, however, weight percent changes greater than 4% at 15°, 20°, 45°, and 90° TOAs. This was also observed for the films that were exposed to water for 5 and 30 min. It is expected that the largest changes in surface composition would occur at the shallowest takeoff angles (i.e., shallowest sampling depth) or closest to the surface. However, the combined results from all three exposure times show that there were no changes in the copolymer segment weight percentages from 30 to 35 Å and no detectable changes in the top 30 Å.

The 15° TOA C 1s spectra for PCL(50)−TX2 at four different interface conditions are shown in Figure 3. The spectra indicate a qualitative time-dependent change in weight percent composition for both the PFPE and PCL segments. The PFPE component of the C 1s spectra is very intense relative to the PCL component for the air interface data. After 5 min of water exposure, the PFPE intensity decreases with the PCL peaks subsequently increasing. This trend continues through the 30-min and 6-h water exposure results. Figure 4 shows the calculated weight percentage data at each interface condition as a function of takeoff angle. A decrease in PFPE surface composition is observed between 15° and 45° TOA with a subsequent increase in PCL at the surface. The PFPE increases between 45° and 90° with a decrease in PCL over the same sampling depth. This suggests a restructuring of the copolymer segments at the surface and subsurface in response to the water exposure. To accommodate the excess PCL moving toward the near surface region, the PFPE must relocate to the subsurface region where it forms an excess relative to the air interface. As the water exposure time is increased to 30 min, the excess PFPE has moved below the top 100 Å with weight percentages at each TOA below that of the air interface data. The PFPE weight percent decreases by almost 10% at the shallow takeoff angles after 6 h of water exposure. The PCL consequently increases by close to 10% at those takeoff angles.

The XPS results at a 15° TOA for PCL(50)−TX3 thin films at four different water exposure times are shown in Figure 5. A large increase in PCL C 1s peak intensity is observed after 5 min of water exposure. Continued exposure to water at 30 min and 6 h resulted in no further detectable reorganization. Figure 6 shows the calculated weight percent plots for the PFPE, PCL, and R_H weight percentages for the air interface and the three water exposure times. The data for the three water exposure times were superimposed in these plots to show the stability of the surface composition after 5 min. There was no significant difference in the weight percentages at any of the sampling depths for the three exposure times. The rapid change in copolymer segment reorganization for the PCL(50)−TX3 films compared to the PCL(50)−TX2 films clearly shows a segment length dependence on water-induced reorganization for this class of polymers.

The interesting results from the comparison of the three polymers clearly involve the lack of detectable reorganization for the TX1 polymer, the rapid and continuing reorganization exhibited by the TX2 polymer, and the rapid but then fixed reorganization for the TX3 polymer. The respective T_g's and T_m's for the three polymers[24] are as follows: PCL(50)−TX1, $T_g = -77$ °C, $T_m = 39$ °C; PCL(50)−TX2, $T_g = -115$ °C, $T_m = 54$ °C; all TX3 polymers showed $T_g \sim -112$ to -115 °C and T_m's ~ 50 °C. Thus, the low glass-transition temperatures, ascribed mainly to the PFPE segments, and the melting temperatures, ascribed to the PCL segments, show little significant difference for the TX2 and TX3 polymers and cannot explain the differences in the time course of reorganization for these two materials. The lack of compositional changes in the near surface region for PCL(50)−TX1 thin films is not understood at this time. Water contact angle results for the TX1 films showed hysteresis of 25°, suggesting chemical and or physical changes at the surface.[24] The lack of any detectable changes in the top 30 Å may be attributed to the dimension of the polymer chains and the sampling depth limitations of XPS. The fully extended chain length of PCL(50)−TX1 has been estimated to be ≈100

Table 2. Calculated Segment Weight Percentages for PCL(50) Films in Air at Room Temperature and Liquid-Nitrogen Temperatures

sample conditions	15° TOA			20° TOA			30° TOA			45° TOA			90° TOA		
	PCL	R_H	PFPE	PCL	R_H	PFPE	PCL	R_H	PFPE	PCL	R_H	PFPE	PCL	R_H	PFPE
							PCL(50)−TX1								
air	13.0	2.7	84.3	13.1	3.6	83.3	15.3	4.9	79.8	22.2	5.8	72.0	34.5	5.8	59.7
air/LN_2	9.6	4.8	85.6	11.6	4.1	84.3	15.9	5.2	79.0	20.2	6.7	73.1	25.8	7.2	67.0
							PCL(50)−TX2								
air	8.6	1.8	89.6	10.8	1.8	87.4	16.1	2.6	81.3	22.2	5.8	75.9	30.2	4.7	65.2
air/LN_2	6.6	2.6	90.8	10.1	1.9	88.0	13.6	3.1	83.3	23.6	2.6	73.8	31.2	4.5	64.3
							PCL(50)−TX3								
air	9.5	1.3	89.1	10.4	1.0	88.6	14.2	1.9	83.9	22.8	1.5	75.7	30.9	2.5	66.7
air/LN_2	9.9	1.5	88.6	12.6	1.8	85.7	17.1	2.5	80.5	22.8	3.0	74.3	27.3	4.6	69.1

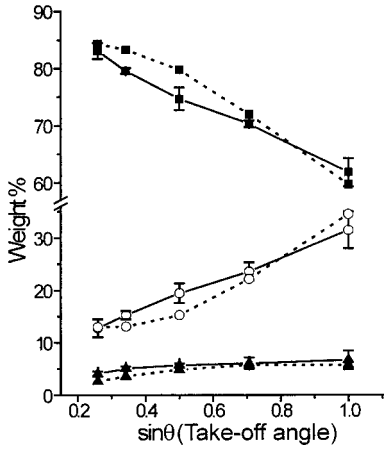

Figure 2. PCL(50)−TX1 segment weight percentages plotted as a function of takeoff angle at the air interface (dashed lines) and water interface after 6 h of exposure (solid lines). (■) PFPE segment, (○) PCL segment, and (▲) R_H segment.

Å. However, a cast thin film of these polymers will almost certainly not have an appreciable amount of extended chains. In reality, these chains are most likely coiled into much smaller dimensions and associated with other chains in microdomain structures. If a water-induced chemical transition occurs in the top 30 Å of a PCL(50)−TX1 film, XPS analysis of the film at a takeoff angle of 15° may not reveal any changes. Another factor may be the weight percent contributions of the R_H linking group. In PCL(50)−TX1, 2, and 3, the weight percentages are 8.4%, 4.3%, and 2.9% respectively. This is significant because the PCL weight percent for all three polymers is ≈50% while the PFPE weight percent fluctuates to accommodate the changes in R_H weight percent. The larger R_H percent would be expected to contribute more significantly to restricting chain mobility. This is supported by the thermal characterization data. The higher overall amount of PCL and R_H coupled with shorter PFPE chains would give rise to reduced chain mobility. However, a better explanation might be the surface T_g of the materials, dominated by the PFPE segments: even still, one might predict that there would be little difference, and all the T_g's are well below room temperature. Further studies of the surface thermal properties are presently underway.

To further demonstrate the influence of interfacial environments on the surface composition, experiments were performed to determine whether the water-induced changes were reversible upon re-exposure to air. All three films were exposed to water for 5 min and analyzed by XPS at a 20° TOA. After analysis, the films were returned to room temperature (25 °C) in a vacuum for 12 h and then re-analyzed at a 20° TOA. The results

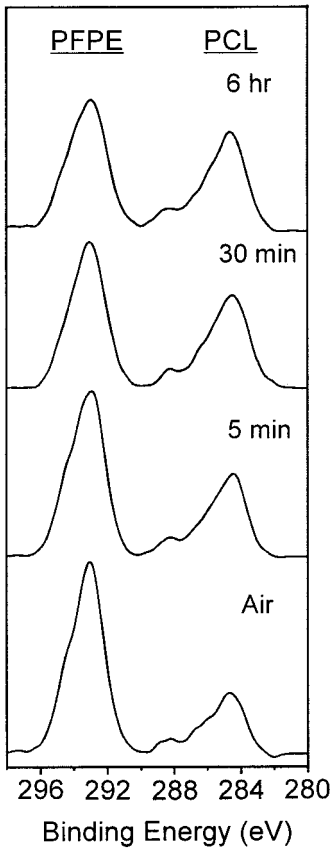

Figure 3. Carbon 1s spectra taken at a 15° TOA of PCL(50)−TX2 films at the air interface and water interface for different exposure times. The lower binding energy peaks correspond to the PCL segment whereas the higher binding energy peaks correspond to the PFPE segments.

are shown in Table 3. The "air" interface data constitutes separate samples while the "5-min H_2O" and "air (reorganize)" data is derived from the same sample. As was discussed earlier, no changes were detected for the PCL(50)−TX1 at the shallow takeoff angles. The results for the PCL(50)−TX2 and PCL(50)−TX3 films indicated reversible systems at a sampling depth of ≈35 Å. The weight percents for both the PFPE and PCL copolymer segments return to the air interface values to within 3%. However, the PCL(50)−TX3 wt % data after 5 min of water exposure was ≈6% higher than the data shown in Figure 6 whereas the data for the PCL(50)−TX2 films were consistent with the data in Figure 4. The reason for this discrepancy in segment weight percentages is not known. However, it should be noted that the sample preparation for the data in Table 3 was different than the procedure outlined in the Experimental Section. Because these films were allowed to warm back up to

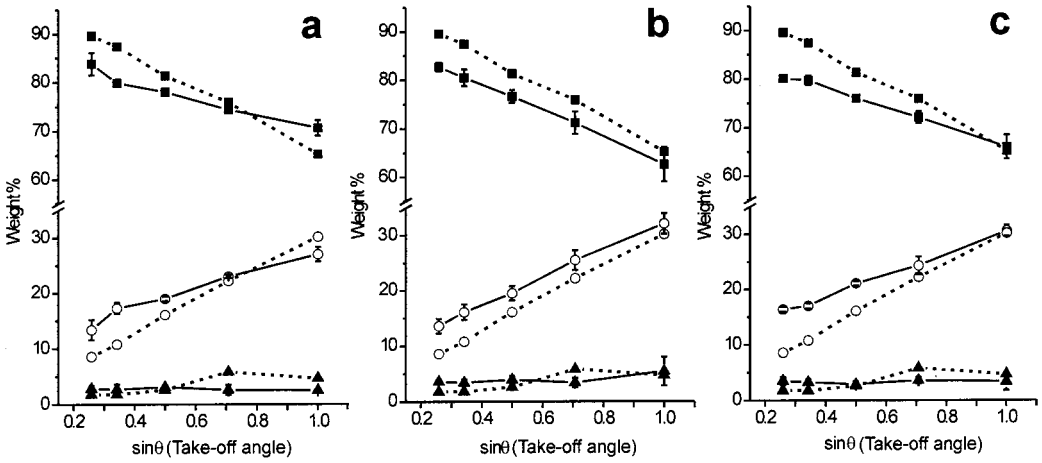

Figure 4. PCL(50)−TX2 segment weight percentages plotted as a function of takeoff angle at the air interface (dashed lines) and water interface (solid lines); (a) 5 min, (b) 30 min, and (c) 6 h of water exposure: (■) PFPE segment, (○) PCL segment, and (▲) R_H segment.

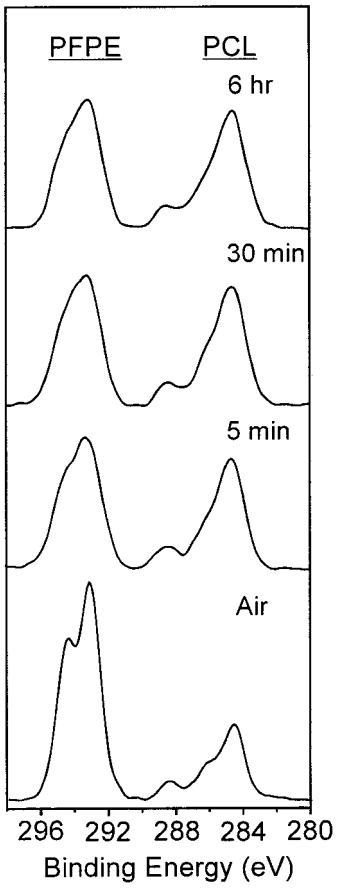

Figure 5. Carbon 1s spectra taken at a 15° TOA of PCL(50)−TX3 films at the air interface and water interface for different exposure times. The lower binding energy peaks correspond to the PCL segment whereas the higher binding energy peaks correspond to the PFPE segments.

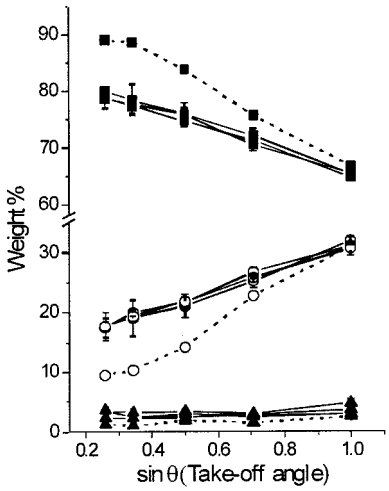

Figure 6. PCL(50)−TX3 segment weight percentages plotted as a function of takeoff angle at the air interface (dashed lines) and water interface (solid lines) at different exposure times: (■) PFPE segment, (○) PCL segment, and (▲) R_H segment.

Table 3. Weight Percentages of the Copolymer Films Taken at a 20° TOA under Different Conditions: Air Interface, after 5 min of Water Exposure (Frozen) and after the Frozen Films Were Allowed To Return to Room Temperature over a 12-h Period of Time in a Vacuum

	PCL(50)−TX1			PCL(50)−TX2			PCL(50)−TX3		
	PCL	R_H	PFPE	PCL	R_H	PFPE	PCL	R_H	PFPE
air	13.1%	3.6%	83.3%	10.8%	1.8%	87.4%	10.4%	1.0%	88.6%
5-min H_2O	14.7%	6.1%	79.2%	15.9%	3.2%	80.9%	23.4%	4.2%	72.3%
air (reorg.)	14.1%	4.4%	81.5%	10.9%	1.4%	87.7%	13.0%	1.5%	85.4%

room temperature, the frozen water drop method used for immersed films would not work (i.e., the glass slides would fall off the sample holder). To mount these samples, a copper clip was used to secure the glass slide to the sample holder. The film was exposed to water by placing a large drop of distilled water onto the top of the surface for 5 min. After exposure, the water was removed by tilting the sample holder to allow the water to drain and then immediately immersing the film in liquid nitrogen. This procedure took less time (≈10% of the time of the normal method). Therefore, it may be possible that the PCL(50)−TX3 was able to reorganize during the normal mounting procedure to give higher PFPE (lower PCL) weight percent values.

Conclusions

Water-induced reorganization of PCL−PFPE−PCL surfaces was studied at cryogenic temperatures by angle-dependent XPS as a function of water exposure time and polymer chain length. XPS results showed that freezing the polymer films in liquid nitrogen did not induce changes in the chemical composition. XPS was not able to detect any changes in surface composition for the PCL(50)−TX1 films upon exposure to water with

the exception of the 30° TOA data. However, previous water contact angle hysteresis data suggested chemical and or physical changes in surface composition. Water-induced changes in PCL(50)−TX3 films occurred within the first 5 min of water exposure with no further changes after 6 h. The calculated weight percentages for PCL(50)−TX2 surfaces were different at each exposure time interval, suggesting a slower rate of reorganization than the PCL(50)−TX3. The water-induced reorganization for each of the film surfaces was reversible at a 20° TOA. These results highlight the importance of block segment length on the rate and extent of water-induced reorganization for copolymer films. The differences in the extent and time course of the reorganization cannot be simply rationalized by the bulk T_g and T_m of the polymers.

Acknowledgment. The authors acknowledge support from grants to J.A.G. from the NSF Analytical and Surface Chemistry program and the Office of Naval Research Chemistry Division Polymers program.

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MA011697R