Surface Segregation and Plasma Oxidation of Polyethylene−Poly(dimethylsiloxane) Copolymer Doped Polyethylene Films

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Received January 24, 2002

ABSTRACT: The surface enrichment of polyethylene−poly(dimethylsiloxane) (ABA) doped polyethylene films has been investigated by XPS, AFM, and contact angle measurements. The poly(dimethylsiloxane) copolymer is found to readily undergo surface segregation during annealing to produce a well-adhered polysiloxane-rich layer. Subsequent oxygen plasma exposure leads to conversion of the surface to SiO_x with a concomitant increase in hydrophilicity. Pulsing the electrical discharge is found to significantly accentuate this behavior.

1. Introduction

There are two generic ways for modifying the surface properties of polymeric materials. First, there are external methods, such as gas plasma treatment,[1] plasma coating deposition,[2] surface grafting,[3] and photochemistry.[4] Alternatively, surface segregation from within the material bulk can be utilized, e.g., polymer blend systems.[5] The latter typically entails blending two homopolymers (A) and (B) or mixing a block copolymer (AB) with a homopolymer (A). A strong perturbation of the surface vs bulk composition occurs if the polymer/polymer segment (B) has a lower surface energy compared to that of the host homopolymer/block (A). The overall driving force in this case is a net lowering of the surface energy for the polymer blend system leading to the surface enrichment of B relative to its bulk concentration. The degree and spatial distribution of polymer segregation at the air−solid interface are governed by a number of factors. These include bulk composition, molecular weight of the constituents (block length and architecture in the case of copolymers), and processing conditions.[6] A major advantage of using copolymers instead of homopolymers is considered to be the fact that potentially better anchoring of the surface segregant (adhesion) to the host bulk polymer can be achieved via the copolymer segment (A) as a result of chain entanglement or cocrystallization.[7,8] Otherwise, there exists the danger of the surface active polymeric constituent undergoing complete phase separation and leaching out from the host homopolymer.

Poly(dimethylsiloxane) (PDMS) is a low surface energy polymer ($\gamma_{\mathrm{PDMS}} = 21$ mJ m^{-2}) and is often found to be incompatible with other polymer systems.[9] Therefore, PDMS can be chosen as a homopolymer or included as a segment in block copolymers for mixing into polymeric materials.[10] Typically this leads to surface enrichment of the PDMS component. For instance, numerous poly(dimethylsiloxane) copolymer/homopolymer blend mixtures have been studied in the past; examples include PDMS-*co*-poly(methyl methacrylate)/poly(methyl methacrylate),[11] PDMS-*co*-polyurethane/phenoxy,[12] PDMS-*co*-bisphenol A polycarbonate/bisphenol A polycarbonate,[13] and PDMS-*co*-polystyrene/polystyrene.[14]

Oxygen plasma treatment of such siloxane-rich polymer surfaces is a potentially attractive route for making ultrathin inorganic silica-like layers.[15] In the case of PDMS-containing polymer blend systems, the primary advantage is that the precursor material is already available at the polymer surface (rather than having to resort to external line-of-sight deposition techniques). Potential applications of such thin oxide layers include hydrophilicity and adhesion.

In this article, the surface segregation behavior of a polyethylene-*co*-poly(dimethylsiloxane)-*co*-polyethylene ABA copolymer blended with polyethylene homopolymer is described. Plasma oxidation of these siloxane enriched surfaces to form silica-like material has also been investigated.

2. Experimental Section

$A_{30}B_{30}A_{30}$ triblock polyethylene-*co*-poly(dimethylsiloxane)-*co*-polyethylene copolymer (Dow Corning, $M_n = 420$ for the PE blocks and $M_n = 2200$ for the PDMS block) was mixed with linear low-density polyethylene/low-density polyethylene (LLDPE/LDPE, $M_n = 29\,000$, prepared by blending a 1:1 (by weight) mix of Dow 5004I LDPE and Dowlex 2045A LLDPE pellets) during film extrusion via the bubble film process to give 2.5 wt % PDMS in the bulk. Solvent washing studies of these polymer blend films were carried out using a 50/50 mixture of cyclohexane (BDH, 99.5% purity)/propan-2-ol (BDH, 99.7% purity) for 30 s in an ultrasonic bath. Subsequent annealing experiments entailed placing the washed films in a vacuum oven (LTE, Qualivac).

Plasma treatment of the polymer blend surfaces was performed using an inductively coupled cylindrical glass

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10.1021/ma020124r CCC: $25.00

Table 1. XPS Analysis Summarizing Changes in Elemental Composition and SiO_x Content at the Surface of ABA Copolymer Doped Polyethylene Film (2.5 wt % PDMS in the Bulk)

	elemental %			% Si(2p)			% SiO_x		
treatment	% C	% O	% Si	PDMS	$\underline{Si}O_{3/2}$	$\underline{Si}O_{4/2}$	% $SiO_{3/2}$	% $SiO_{4/2}$	total
theoretical bulk composition	99.0	0.5	0.5	0.5					
as received (1)	71.3	15.5	13.2	13.2					
washed (2)	92.5	4.3	3.2	3.2					
washed and annealed (3)	63.7	18.2	18.1	18.1					
(3) + 2 W O_2 plasma	31.7	49.3	18.9	2.7	9.1	7.2	22.8	21.6	44.4
(2) + 2 W O_2 plasma (h.s.)[a]	47.6	31.4	21.1	7.8	6.0	7.3	15.0	21.9	36.9
(3) + 20 W O_2 pulsed plasma $t_{on} = 120$ μs, $t_{off} = 1360$ μs	35.5	46.3	18.2	3.7	8.3	6.1	20.8	18.3	39.1
(2) + 20 W O_2 pulsed plasma (h.s) $t_{on} = 120$ μs, $t_{off} = 1360$ μs	26.1	52.6	21.4	0.9	8.6	11.9	21.5	35.7	57.2

[a] h.s. = heated substrate.

reactor (5 cm diameter, 650 cm^3 volume) enclosed in a Faraday cage (Figure 1). This was fitted with a gas inlet, a thermocouple pressure gauge, a heated substrate stage controlled by a thermostatic circulation bath, and a two-stage mechanical rotary pump attached to a liquid air cold trap (base pressure of 2×10^{-3} mbar and a leak rate better than 1.2×10^{-3} cm^3 min^{-1}). The temperature of the substrate was monitored with a thermocouple probe. A 13.56 MHz rf power supply was coupled to a copper coil (5 mm diameter, 10 turns, spanning 8−16 cm from the gas inlet) wound externally around the reactor via an LC matching circuit. Prior to each experiment, the chamber was cleaned with a 40 W air plasma at 0.2 mbar pressure for 10 min. Next, a piece of polymer substrate was placed into the center of the reactor, and oxygen (BOC, 99.6% purity) was introduced at a pressure of 0.2 mbar and 1 cm^3 min^{-1} flow rate for 10 min, followed by plasma ignition. Continuous wave oxygen plasma treatment was carried out for 60 s at 0.2 mbar pressure for powers ranging from 2 to 20 W. In the case of the pulsed plasma exposure, the conditions comprised t_{on} varying between 50 and 2000 μs, t_{off} varying between 100 and 50 000 μs, and peak power set at 20 W. (The oxygen gas pressure and treatment time were kept the same as for continuous wave experiments.)

A Kratos ES300 electron spectrometer equipped with a Mg Kα X-ray source (1253.6 eV) and a concentric hemispherical analyzer (CHA) was used for XPS analysis of the polymer blend surfaces. Photoemitted electrons were collected at a takeoff angle of 30° from the substrate normal, with electron detection in the fixed retarding ratio (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced PC computer and fitted using a Marquardt minimization algorithm assuming Gaussian peak shapes with equal full width at half-maximum (fwhm).[16] Instrument sensitivity factors were calculated using reference chemical standards to be C(1s):O(1s):Si (2p) equal to 1.00:0.57:0.72. An argon ion gun source was used for ion sputter depth profiling studies (operating at 3 keV ion energy, 1.5 μA beam current, and 2×10^{-6} mbar pressure). The etch rate was calibrated to be 0.5 nm min^{-1} by using a known thickness of SiO_2 (as measured by ellipsometry) grown onto a silicon wafer.

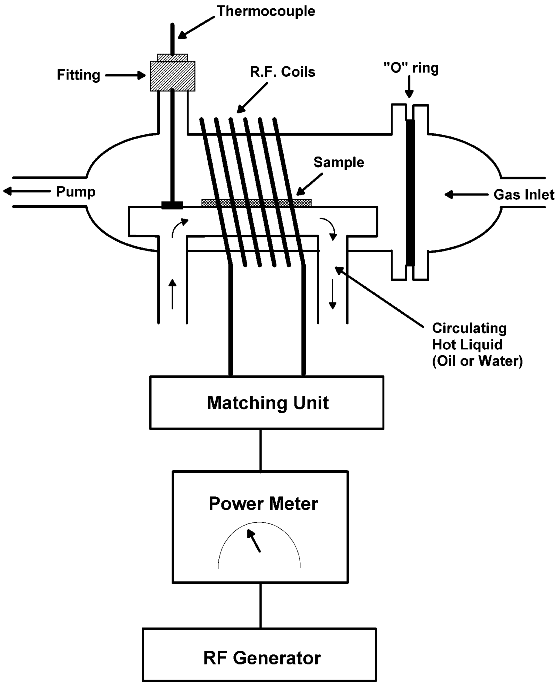

Figure 1. Schematic of heated substrate plasma reactor.

AFM micrographs were acquired with a Digital Instruments Nanoscope III. Damage to the tip or sample was minimized by using Tapping Mode AFM.[17] As well as topographical height images, phase images reflecting the mechanical properties of the surface were obtained by choosing a set point:free amplitude ratio of 0.5 (set point = 50 nm; free amplitude = 100 nm).[18] All images were acquired in air at room temperature and are presented as unfiltered data. Large area scans were taken on the 100 μm scale in order to check that the images presented are representative of the whole surface.

Sessile drop contact angle measurements were carried out at 20 °C using a video capture apparatus (A.S.T. Products VCA2500XE). High-purity water (B.S. 3978 grade 1) was employed as the probe liquid to test hydrophilicity/hydrophobicity of the polymer blend surfaces.

3. Results

Washing of the polymer blend surface with a 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s was sufficient to remove most of the polysiloxane species from the top 3−5 nm of the substrate (i.e., the Si(2p) XPS sampling depth[19]) (Table 1). Subsequent annealing at 80 °C for 30 min led to polysiloxane material diffusing from the bulk into the near-surface region. The absence of any binding energy shift in the XPS Si(2p) spectra confirmed that the PDMS component was not undergoing oxidation during annealing (Figure 2). By using this washing/annealing procedure, a reproducible polymer blend surface composition could be produced (whereas variable amounts of PDMS were present at the surface of the as-prepared films due to contamination from the rollers).

Oxygen plasma treatment of the washed and annealed copolymer doped polyethylene film gave rise to oxygen incorporation at the expense of carbon loss (although not much change in the concentration of silicon at the surface was observed) (Table 1). The relative amounts of oxygenated silicon environments were estimated by fitting the Si(2p) envelope:[20] $\underline{Si}O_{PDMS}$ at 102.0 eV, $\underline{Si}O_{3/2}$ at 103.0 eV, and $\underline{Si}O_2$ at 104.0 eV (Figure 2 and Table 1). A number of electrical discharge parameters were investigated (continuous wave vs

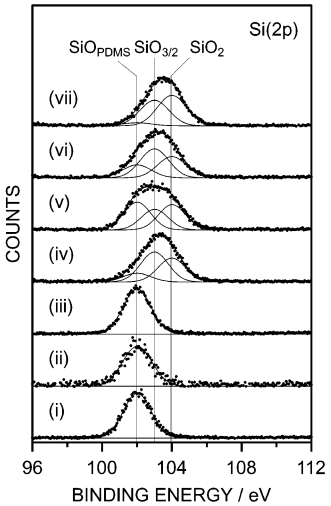

Figure 2. Si(2p) XPS spectra of 2.5% $A_{30}B_{30}A_{30}$ copolymer doped polyethylene blend: (i) as received; (ii) washed; (iii) washed and annealed; (iv) 2 W O_2 plasma treatment of (iii) for 60 s at room temperature; (v) 2 W O_2 plasma treatment of (ii) for 60 s−heated substrate; (vi) O_2 pulsed plasma ($P_p = 20$ W, $t_{on} = 120$ μs, $t_{off} = 1360$ μs) of (iii) for 60 s at room temperature; (vii) O_2 pulsed plasma ($P_p = 20$ W, $t_{on} = 120$ μs, $t_{off} = 1360$ μs) of (ii) for 60 s−heated substrate. (Note that all Si(2p) peak areas have been normalized to 100%.)

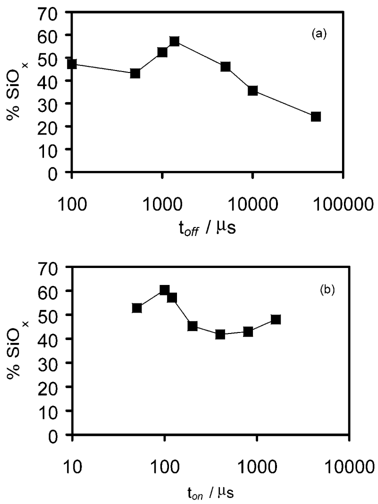

Figure 3. Proportion of silicon present as SiO_x at the surface as a function of (a) t_{off} ($P_p = 20$ W, $t_{on} = 120$ μs, substrate heated to 80 °C, total duration = 60 s) and (b) t_{on} ($P_p = 20$ W, $t_{off} = 1360$ μs, substrate heated to 80 °C, total duration = 60 s).

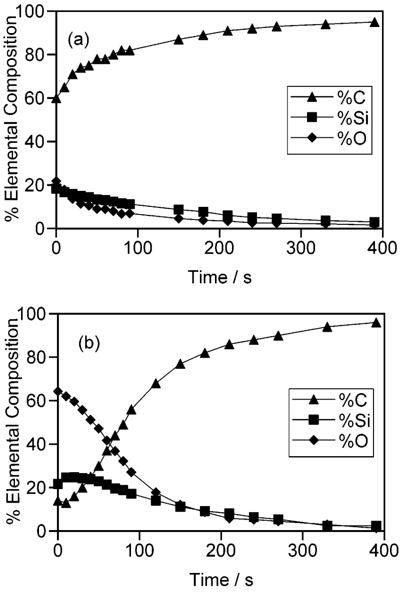

Figure 4. Ar$^+$ ion depth profile in conjunction with XPS of (a) washed and annealed $A_{30}B_{30}A_{30}$ copolymer doped polyethylene blend and (b) oxygen plasma treated $A_{30}B_{30}A_{30}$ copolymer/PE blend ($P_p = 20$ W, $t_{on} = 120$ μs, t_{off} 1360 μs, 60 s, substrate heated to 80 °C).

Table 2. XPS Analysis Summarizing Changes in Elemental Composition at the Surface of the Pulsed Plasma Oxidized $A_{30}B_{30}A_{30}$ Doped Polyethylene upon Annealing

treatment	% C	% Si	% O	O/Si
washed and annealed	63.7	18.1	18.2	1.0
20 W O_2 pulsed plasma (h.s) $t_{on} = 120$ μs, $t_{off} = 1360$ μs (1)	26.1	21.4	52.6	2.5
(1) + heating at 80 °C for 10 min	31.6	19.1	49.2	2.6
(1) + heating at 80 °C for 30 min	32.9	20.1	47.1	2.3
(1) + heating at 80 °C for 41 h	53.8	19.6	26.6	1.4

pulsed plasmas, substrate temperature, and duration of treatment). The greatest amount of SiO_x formation corresponded to oxygen plasma treatment at 80 °C using pulsed conditions (Table 1). These optimum t_{on} and t_{off} settings for the pulsed discharge were attained using computer-aided simplex optimization (Multisimplex). It was found that t_{off} had a greater influence on SiO_x formation at the polymer blend surface compared to t_{on} (Figure 3).

Ar$^+$ ion depth profiling of the ABA copolymer doped polyethylene samples confirmed surface enrichment of PDMS segments during annealing (Figure 4 and Table 1). No periodic variation in the subsurface was found. Pulsed oxygen plasma treatment produced a thin, highly oxidized layer at the surface (~1.3 nm) with a drop in oxidation below the surface.

Heating of the plasma oxidized polymer blend surface beyond extinction of the electrical discharge produced a progressive buildup of PDMS material at the surface. This was evident from the shift in the Si(2p) peak toward lower binding energies: 104.0 eV ($\underline{Si}O_2$) to 102.0 eV ($\underline{Si}O_{PDMS}$) (Figure 5). A drop in intensity of the oxidized C(1s) shoulder was also noted:[21] $\underline{C}-CO_2$ at 285.7 eV, $\underline{C}-O-$ at 286.6 eV, $\underline{C}=O$, $O-\underline{C}-O$ at 287.8 eV, $-O-\underline{C}=O$ at 289.0 eV, and $-O-\underline{C}O-O-$ at 290.0 eV, to leave behind a hydrocarbon-rich environment centered at 285.0 eV (Figure 5 and Table 2). However even after prolonged periods, complete recovery to unoxidized PDMS was not observed.

Polyethylene lamellar features could be clearly seen in the height image[22] following solvent washing of the polymer blend surface (Figure 6). The corresponding phase image confirmed the absence of PDMS at the surface. Subsequent annealing clearly showed the buildup of separate PDMS-rich regions on the polyethylene surface in the AFM phase image, whereas no change was apparent in the corresponding height scan. No discernible change in surface morphology was noted following pulsed plasma oxidation at elevated substrate temperature; this can be taken as being consistent with a very thin layer of SiO_x-like material being formed at the polymer blend surface. Subsequent annealing gave rise to the appearance of cracks and small dropletlike regions of PDMS-containing material. This correlates to the emergence of PDMS moieties in the Si(2p) XPS envelope (Figure 5).

The optimum pulsed plasma oxidized polymer blend surfaces produced a completely wettable surface toward

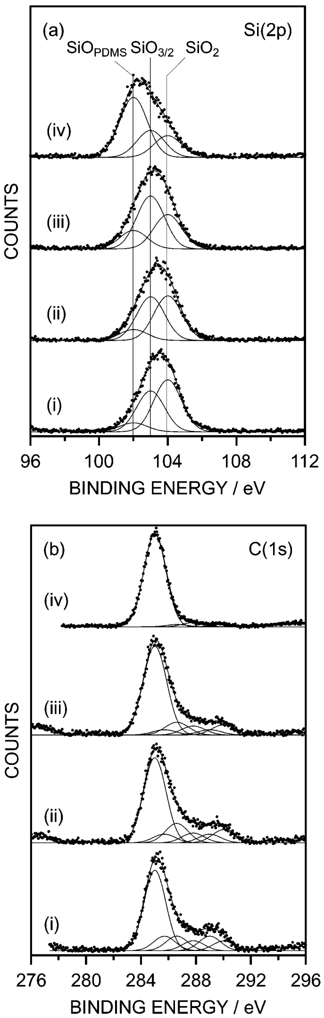

Figure 5. (a) Si(2p) and (b) C(ls) XPS spectra of 2.5% $A_{30}B_{30}A_{30}$ copolymer doped polyethylene blend: (i) O_2 pulsed plasma treatment (P_p = 20 W, t_{on} = 120 μs, t_{off} = 1360 μs, substrate heated to 80 °C); (ii) annealing of (i) at 80 °C for 10 min; (iii) annealing of (i) at 80 °C for 30 min; and (iv) annealing of (i) at 80 °C for 41 h. (Note that the XPS peak areas have been normalized to 100%.)

water, which underwent partial hydrophobic recovery to 46° over the period of a week (Table 3). Hydrophobic recovery occurred at a faster rate if the oxidized polymer blend film was annealed at an elevated temperature (Table 3). A comparison with corresponding plasma treatments performed on bulk PDMS elastomer and pure polyethylene substrates indicated that the polymer blend surface was behaving in an analogous fashion to pure PDMS.

4. Discussion

On the basis of the lower surface energy PDMS segment contained in the PE-*co*-PDMS-*co*-PE block copolymer ($\gamma_{PDMS} = 21$ mJ m^{-2} and $\gamma_{PE} = 36$ mJ m^{-2}),[9] one would expect this additive to migrate toward the air−polyethylene interface.[10] Also, the triblock copolymer has a lower average molecular weight compared to that of the host polymer (M_n = 420 for the PE blocks, M_n = 2200 for the PDMS block, and M_n = 29 000 for the linear low-density polyethylene/low-density polyethylene). This will produce greater segmental motion of the additive polymeric chains to assist their diffusion toward the film surface. The PDMS segments can be envisaged as forming a looplike structure at the air−solid interface, with the polyethylene ends embedded into the polyethylene bulk.[23] XPS analysis of the washed and annealed polymer blend surface confirmed this to be the case (Table 1). The stoichiometry of the segregated polymer blend surface was less than the elemental composition of pure PDMS (50% C, 25% Si, 25% O); this indicates that there is either a thin layer present or incomplete coverage of the polyethylene surface by PDMS segments (the latter is consistent with the AFM phase image; Figure 6). Assuming a uniform distribution throughout the XPS sampling depth (1−2 nm), the XPS data correspond to 72% PDMS coverage. Contact angle analysis supports this description, since the polymer blend surface (after washing and annealing) gave lower water contact angle values compared to pure PDMS films (Table 3).

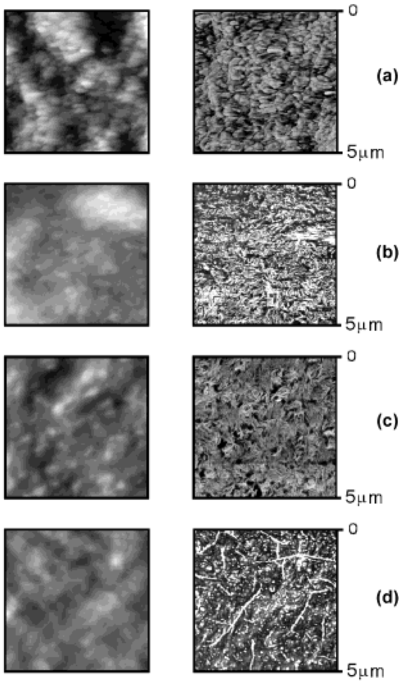

Figure 6. Atomic force height (LHS) and phase (RHS) micrographs of 2.5% $A_{30}B_{30}A_{30}$ copolymer doped polyethylene blend: (a) solvent washed; (b) solvent washed and annealed at 80 °C for 30 min; (c) solvent washed followed by O_2 pulsed plasma treatment (P_p = 20 W, t_{on} = 120 μs, t_{off} = 1360 μs, substrate heated to 80 °C); and (d) annealing of (c) at 80 °C for 30 min.

Table 3. Water Contact Angle Measurements of $A_{30}B_{30}A_{30}$ Doped Polyethylene Blend Surfaces

	contact angle/deg		
treatment	$A_{30}B_{30}A_{30}$/PE	PDMS	PE
as received	107.0 ± 1.0	116.0 ± 2.0	102.8 ± 0.5
washed and annealed at 80 °C for 30 min	109 ± 1.0		
20 W O_2 pulsed plasma (h.s) t_{on} = 120 μs, t_{off} = 1360 μs (1)	0.0 ± 0.0	0.0 ± 0.0	61.8 ± 1.0
(1) + 1 week at room temperature	46.0 ± 2.5	43.8 ± 1.7	76.2 ± 1.8
(1) + annealed at 80 °C for 30 min	43.5 ± 3.5		

In the case of 2 W continuous wave (CW) plasma treatment, maintaining the substrate at room temperature produced more SiO_x compared to heating the film during plasma treatment (Table 1), whereas the converse was true for pulsed plasma exposure. These differences can be explained in terms of PDMS being allowed to thermally segregate to the surface during the off-period of the pulsed plasma duty cycle, whereas the continuous bombardment of the substrate by energetic plasma species during CW heated conditions will lead to greater PDMS chain scission and ablation, i.e., less probability for the formation and growth of extended SiO_x networks. Similarly, the variation in SiO_x formation with plasma duty cycle can be ascribed to the overall balance between surface segregation during the off-period and oxidation /etching within the on-time.

Examination of the pulsed/heated oxygen plasma treated films by XPS and contact angle measurements showed that the polymer blend surface was highly oxidized and fully wettable immediately after plasma treatment. A small degree of hydrophobic recovery was observed over time. Diffusion of unreacted copolymer chains contained in the subsurface region toward the air−solid interface accounts for this behavior. AFM analysis indicated the presence of cracks in the SiO_x surface, which facilitate the transport of PDMS containing moieties toward the air−solid interface.

5. Conclusions

Pulsed plasma oxidation of polyethylene−poly(dimethylsiloxane) (ABA) doped polyethylene films at elevated temperatures gives rise to the formation of a well-adhered hydrophilic layer of SiO_x.

Acknowledgment. C.G.S. thanks Dow Corning for financial support. We are also grateful to R. Drake and A. Brimblecombe for synthesis of the $A_{30}B_{30}A_{30}$ block copolymer and film preparation, respectively.

References and Notes

(1) Yasuda, T.; Yoshida, K.; Okuno, T. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 2061.
(2) Wang, J. H.; Chen, J. J.; Timmons, R. B. *Chem. Mater.* **1996**, *8*, 2212.
(3) Tan, K. L.; Woon, L. L.; Wong, H. K.; Kang, E. T.; Neoh, K. G. *Macromolecules* **1993**, *26*, 2832.
(4) Mailhot, B.; Gardette, J.-L. *Macromolecules* **1992**, *25*, 4119.
(5) Bates, F. S. *Science* **1991**, *251*, 898.
(6) Zhao, J.; Rojstaczer, S. R.; Chen, J.; Xu, M.; Gardella, J. A., Jr. *Macromolecules* **1999**, *32*, 455.
(7) Ndoni, S.; Jannasch, P.; Larsen, N. B.; Almdal, K. *Langmuir* **1999**, *15*, 3859.
(8) Smith, S. D.; Wnuk, A. J.; Gerber, M. S. U.S. Pat. 5,476,901, 1995.
(9) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989.
(10) Garbassi, F.; Morra, M.; Occhiello, E. In *Polymer Surfaces−From Physics to Technology*; Wiley: Chichester, 1994.
(11) Inoue, H.; Matsumoto, A.; Matsukawa, K.; Ueda, A.; Nagai, S. *J. Appl. Polym. Sci.* **1990**, *41*, 1815.
(12) Wen, J.; Somorjai, G.; Lim, F.; Ward, R. *Macromolecules* **1997**, *30*, 7206.
(13) LeGrand, D. G.; Gaines, G. L., Jr. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *11*, 442.
(14) Chen, X.; Gardella, J. A., Jr. *Macromolecules* **1994**, *27*, 3363.
(15) Spanos, C. G.; Ebbens, S. J.; Goodwin, A. J.; Merlin, P. J.; Badyal, J. P. S. *Macromolecules* **2001**, *34*, 8149.
(16) Johanson, G.; Hedman, J.; Berndtsson, A.; Klasson, M.; Nilsson, R. *J. Electron Spectrosc.* **1973**, *2*, 295.
(17) Zhong, Q.; Innis, D.; Kjoller, K. Elings, V. B. *Surf. Sci.* **1993**, *14*, 3045.
(18) Magonov, S. N.; Elings, V. B.; Whangbo, M. H. *Surf. Sci.* **1997**, *375*, L385.
(19) Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.
(20) Alfonsetti, R.; Lozzi, L.; Passacantado, M.; Picozzi, P.; Santucci, S. *Appl. Surf. Sci.* **1993**, *70/71*, 222.
(21) Beamson, G.; Briggs, D. In *High-Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*; Wiley: New York, 1992.
(22) Schonherr, H.; Shetivy, D.; Vancso, G. J. *Polym. Bull. (Berlin)* **1993**, *30*, 567.
(23) Hariharan, A.; Harris, J. G. *J. Phys. Chem.* **1995**, *99*, 2788.

MA020124R