Surface Modification of Polyethylene through Bromination

Noppavan Chanunpanich,[†,‡] Abraham Ulman,*[,†,‡] Y. M. Strzhemechny,[‡,§]
S. A. Schwarz,[‡,§] A. Janke,[∥] H. G. Braun,[∥] and T. Kraztmuller[∥]

*Department of Chemical Engineering, Chemistry, and Materials Science,
Polytechnic University, Brooklyn, New York 11201, Department of Physics,
Queens College of CUNY, Flushing, New York 11367, Institute for Polymer Research,
Hohe Strasse 6, D-01069 Dresden, Germany, and The NSF MRSEC for
Polymers at Engineered Interfaces*

Received August 6, 1998. In Final Form: December 31, 1998

Surface bromination of low-density polyethylene (LDPE) was carried out by brief exposure to gaseous bromine followed by UV irradiation. X-ray photoelectron spectroscopy suggests two different types of C−Br groups. Atomic force microscopy and wetting studies reveal that excessive bromination is accompanied by severe surface roughening. A nucleophilic substitution reaction was used to introduce surface 4-aminobenzenethiolate functionalities. UV spectral analysis indicates a grafting density of 2.9 bromine atoms per 100 Å^2 for the first bromination cycle.

Introduction

Surface modification of polymers gives rise to new surface properties that play an important role in many polymer applications. Using surface modification, properties such as wettability, adhesion, and biocompatibility can be controlled. Polyethylene (PE) is one of the most interesting commodity polymers, and tuning its surface properties is highly desirable. For example, it is not possible to paint the PE surface with water-based paint formulations due to its low surface energy. Also, the adhesion between PE surfaces and most matrixes is poor, because of their hydrophobicity and smoothness, which prevent chemical as well as mechanical bonding.

Modification of the PE surface can be made via a chemical reaction with a contacting solution,[1−7] corona discharge treatment,[8−10] plasma or glow discharge treatment,[10−14] and surface grafting of hydrophilic monomers after photoirradiation.[15−21] Acid etching or chemical oxidation[1−7] and plasma treatments mainly introduce oxygen functionalities which are in the form of ether, hydroxyl, carbonyl, and carboxyl groups into the outer few molecular layers of the polymer film. Polyethylene carboxylic acid films have been used as starting materials for PE-functionalized systems.[1,5,21] Attempts to introduce other functionalities by plasma treatment utilizing N_2,[22] NH_3,[23,24] CCl_4,[25] $CHBr_3$,[26] acrylic acid,[27] and allylamine[27] have been carried out recently.

Bromination is one procedure that can improve adhesion[28] and wettability[29,30] of polymers. Moreover, a brominated surface can serve as an intermediate to other chemical functionalities in nucleophilic substitution reaction.[31] Such reactions have been successful in ω-bromoalkyltrichlorosilane self-assembled monolayers;[26,32] however, rarely has work been done on PE films. Therefore, the purpose of our work is to prepare bromopolyethylene films (PE-Br), to find the optimum conditions for surface bromination, and to use these films as model substrates for studies of consequent substitution reactions.

* Corresponding author. Phone: (718) 260-3119. Fax: (718) 260-3125. E-mail: aulman@poly.edu.

† Polytechnic University.
‡ The NSF MRSEC for Polymers at Engineered Interfaces.
§ Queens College of CUNY.
∥ Institute for Polymer Research.

(1) Olafsen, K.; Stori, A.; Tellefsen, D. A. *J. Appl. Polym. Sci.* **1992**, *54*, 1673−1676.
(2) Zhang, J.; Dato, K.; Uyama, Y.; Ikada, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2629−2638.
(3) Foerch, R.; McIntyre, N. S.; Hunter, D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 193−204.
(4) Chtourou, H.; Riedl, B.; Kokta, B. V. *Polym. Degrad. Stab.* **1994**, 149−156.
(5) Mercx, F. P. M. *Polymer* **1994**, *35*, 2098−2107.
(6) Kang, E. T.; Tan, K. L.; Kato, K.; Uyama, Y.; Ikada, Y. *Macromolecules* **1996**, *29*, 6872−6879.
(7) Tsuchida, M.; Osawa, Z. *Colloid Polym. Sci.* **1994**, *272*, 770−776.
(8) Tan, K. L.; Woon, L. L.; Wong, H. K.; Kang, E. T.; Neoh, K. G. *Macromolecules* **1993**, *26*, 2832−2836.
(9) Curto, D.; Valenza, A.; La Mantia, F. P. *J. Appl. Polym. Sci.* **1990**, *39*, 865−873.
(10) Edge, S.; Walker, S.; Feast, W. J.; Pacynko, W. F. *J. Appl. Polym. Sci.* **1993**, *47*, 1075−1082.
(11) Bai, G.; Hu, X.; Yan, Q. *Polym. Bull.* **1996**, *36*, 503−510.
(12) Lee, A.; Russell, K. E. *Eur. Polym. J.* **1989**, *25*, 709−712.
(13) Gugumus, F. *Angew Makromol. Chem.* **1990**, *182*, 111−134.
(14) Kilkal, K.; Olafsen, K.; Stori, A. *J. Appl. Polym. Sci.* **1992**, *44*, 1893−1898.
(15) Bentjen, S. B.; Nelson, D. A.; Tarasevich, B. J.; Rieke, P. C. *J. Appl. Polym. Sci.* **1992**, *44*, 965−980.
(16) Ferguson, G. S.; Chaudhury, M. K.; Biebuyck, H. A.; Whitesides, G. M. *Macromolecules* **1993**, *26*, 5870−5875.
(17) Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M. *J. Colloid Interface Sci.* **1974**, *47*, 638−551.
(18) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725−740.
(19) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1987**, *3*, 62−76.
(20) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921−937.
(21) Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4736−4745.
(22) Foerch, G.; Hunter, D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 279−286.
(23) Brown, J. R.; Chappell, P. J. C.; Mathys, Z. *J. Mater. Sci.* **1992**, *27*, 3167−3172.
(24) Chappell, P. J. C.; Brown, J. R.; George, G. A.; Willes, H. A. *Surf. Interface Anal.* **1991**, *17*, 143−150.
(25) Inagaki, N.; Tasaka, S.; Imai, M. *J. Appl. Polym. Sci.* **1993**, *48*, 1963−1972.
(26) Baker, M. V.; Watling, J. D. *Langmuir* **1997**, *13*, 2027−2032.
(27) Ko, T.; Cooper, S. L. *J. Appl. Polym. Sci.* **1993**, *47*, 1601−1619.
(28) Chew, A.; Dahm, R. H.; Brewis, D. M.; Briggs, D.; Rance, D. G. *J. Colloid Interface Sci.* **1986**, *110*, 88−95.
(29) Elman, J. F.; Gerenser, L. J.; Goppert-Berarducci, K. E.; Pochan, J. M. *Macromolecules* **1990**, *23*, 3922−3928.
(30) Shah, C. D.; Jain, D. K. *Textile Res. J.* **1984**, *54*, 742−748.
(31) Kiss, E.; Samu, J.; Toth, A.; Bertoti, I. *Langmuir* **1996**, *12*, 1651−1657.
(32) Balachander, A.; Sukenik, C. N. *Langmuir* **1990**, *6*, 1621−1627.

In this paper we report the gas-phase bromination of PE. A detailed account of chemical transformations at PE surfaces will be reported in forthcoming papers. Since the diffusion coefficient of bromine in PE is quite high (10^{-9} cm^2/s),[33] short wavelength UV light has been used to accelerate the bromination reaction. Therefore, no matter how deep the bromine diffuses into PE film, it is subjected to UV light and bromine radicals then immediately react with the PE chains, producing a profile of bromine functional groups as a function of PE depth.

Experimental Section

Chemicals. Low-density polyethylene (LDPE) and 4-nitrobenzaldehyde were purchased from Acros Organic. Bromine, 4-aminothiophenol, and anhydrous ethanol were obtained from Aldrich. All solvents were analytical grade and purchased from Fisher Scientific.

PE Film Preparation. In a typical experiment, a LDPE sample, having 50 000 molecular weight and a density of 0.92 g/cm^3, was used. Pellets were pressed into 0.15 ± 0.02 mm thick films at 120 °C, against polyaramid films that had previously been cleaned with acetone. Before bromination, the PE films were ultrasonically washed in 50% 2-propanol/hexane for 10 min and then washed with ethanol and water and dried under a nitrogen stream. All samples were kept in a desiccator to minimize exposure to oxygen.

Bromination. PE films were brominated by exposure to saturated bromine vapor for 0.70 ± 0.10 s, followed by a 30 s irradiation using a short wavelength UV lamp (Spectroline). The lamp was placed approximately 2 cm away from the films. After being subjected to UV light, the films (PE-Br) were colorless. Additional bromination cycles were used to increase the bromine concentration at the PE surface. The PE-Br films were washed with cold distilled water for 15 s to remove HBr on the surface, dried under a nitrogen stream, and kept under vacuum overnight to remove sorbed Br$_2$ and HBr.

Substitution Reactions with 4-Aminothiophenolate. In a typical experiment, PE-Br samples were immersed in a 0.02 M sodium 4-aminothiophenolate solution (20 mL) at 33 °C for 20 h. The product films (PE—S—Ph—NH$_2$) were washed several times with absolute ethanol to remove the adsorbed 4-aminothiophenolate ion and water to remove the NaBr byproduct and dried under a nitrogen stream.

Reaction with 4-Nitrobenzaldehyde. Four PE—S—Ph—NH$_2$ sample films were immersed in a solution of 0.01 M 4-nitrobenzaldehyde in anhydrous ethanol (20 mL) containing acetic acid (0.04 mL) and 4 Å molecular sieves (1 g) under nitrogen atmosphere at 50 °C for 3 h.[34,35] The PE—S—Ph—N=CH—Ph—NO$_2$ films were then washed several times with absolute ethanol and dried with a stream of nitrogen.

Hydrolysis of Surface Imine Groups. Four PE—S—Ph—N=CH—Ph—NO$_2$ sample films were hydrolyzed in water (10 mL) containing acetic acid (0.02 mL) at 30 °C for 1 h. The amount of 4-nitrobenzaldehyde obtained from the hydrolysis reaction was characterized by UV absorption measurement at a wavelength of 270 nm.

Trifluoroacetamide Derivatives. PE—S—Ph—NH$_2$ films were exposed to gaseous trifluoroacetic anhydride for 16 h, washed with water several times, dried under a nitrogen stream, and kept under vacuum overnight.

Contact Angle Measurements. The static contact angles of water were determined at room temperature by the sessile drop method using a Rame′-Hart Model 100 goniometer, equipped with a high-resolution CCD-IRIS color video-camera (SONY) connected to a computer. The captive drop method was used to measure the advancing and receding angles. A 10 μL droplet was formed at the end of the blunt-ended needle of a syringe and was brought into contact with the surface, water was added, and the advancing angle was measured. Subsequently, water was withdrawn, and the receding contact angle was measured. Stored images of the droplet were analyzed using NIH software. Contact angles were determined from an average of five specimens.

ATR-FTIR Spectra. The attenuated total reflection (ATR) FTIR spectra for the surface of PE films were recorded on a Nicolet 760 spectrophotometer equipped with a He—Ne laser and an MCT detector. A crystal of ZnSe was used, and the incident angle of the IR beam was 45°. In a typical measurement, 500 scans were collected with a 2 cm^{-1} resolution.

UV Spectra. UV—vis spectroscopy was performed on a Perkin-Elmer, Lamda 3 spectrometer.

X-ray Photoelectron Spectroscopy (XPS) Measurements. XPS results were obtained in a Kratos ES300 X-ray photoelectron spectrometer with a non-monochromatic Mg Kα X-ray source (1253.6 eV photons). The hemispherical energy analyzer was operated in the fixed retardation ratio mode. The samples were mounted on standard sample studs with double-sided adhesive tape. The pressure in the analysis chamber was ~10^{-8} Torr during measurements. Core level Br 3d, S 2p, O 1s, N 1s, F 1s, and C 1s spectra were monitored at the electron takeoff angle 15°. To compensate for surface charging effects, all binding energies were referenced to the C 1s neutral carbon peak at 285.0 eV. In the experiment, the C peaks of the sample were shifted from 0.7 to 1.7 eV; hence, the Br 3d, S 2p, O 1s, N 1s, and F 1s peaks were shifted according to C 1s at 285.0 ± 0.1 eV. Deconvolution of complex peaks was performed using an Origin nonlinear curve fit with the full-width at half-maximum (fwhm) of the Gaussian line shape 1.3–1.4 eV. Quantitative measurements were made by correction of integrated peak intensities with the Scofield correction factors.[36] The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors and may be subject to a maximum of $\pm 20\%$ error.

Atomic Force Microscopy (AFM). AFM topography of PE and PE-Br films was made by using Nano Scope IIIa, multimode from Digital Instruments, Santa Barbara, CA. The measurement was done in trapping mode. The phase image shows a hard—soft contrast.

Results and Discussion

Commercial PE films usually contain additives, and when they were studied in our laboratory using atomic force microscopy, they were found to be very rough. Therefore, we have prepared PE samples by pressing the melt of PE between two flat surfaces at 120 °C. Good samples could be prepared by melting the PE on a smooth silicon wafer and pressing it with a flat glass slide. However, the separation of the film from the silicon wafer was difficult. We did not observe any separation problem, on the other hand, when the melt was pressed against polyaramid films. The resulting PE samples were optically smooth and showed relatively small roughness by AFM standards. The ATR-FTIR spectra of untreated PE films show characteristic peaks at 2915 cm^{-1} (asymmetric CH$_2$ stretching), 2847 cm^{-1} (symmetric CH$_2$ stretching), 1471 cm^{-1} (CH$_2$ scissoring), 1462 cm^{-1} (asymmetric CH$_3$ bending), and 1377 cm^{-1} (symmetric CH$_3$ bending) and split peaks at 731 and 721 cm^{-1} (CH$_2$ rocking in the crystalline and amorphous parts, respectively). Some contamination with oxygen-containing groups (C=O stretching band at 1710 cm^{-1}, and other bands at 1018–1079 cm^{-1}) could not be removed even after hot extraction with acetone or 2-propanol over a long period of time. This is supported by XPS data when the carbon peak was resolved into three peaks (fwhm of 1.3 eV), centered at 285.0 ± 0.1 eV (C—C or C—H), 286.8 ± 0.1 eV (C—O), and 289.2 ± 0.1 eV (O—C=O). The result shows 8.7 atomic percent of C—O and a small amount of O—C=O (1.9 atomic percent). In contrast, the advancing water contact angles of the PE

(33) Lewin, M.; Penhasi, A. *Polym. Adv. Technol.* **1993**, *4*, 481–489.

(34) Moon, J. H.; Shin, J. W.; Kim, S. Y.; Park, J. W. *Langmuir* **1996**, *12*, 4621–4624.
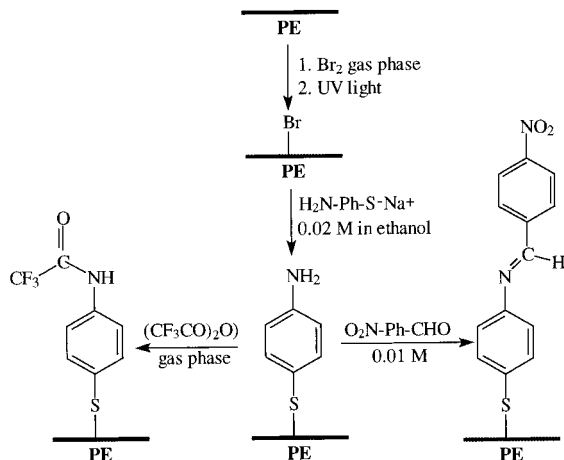
(35) Brüning, C.; Grobe, J. *J. Chem. Soc., Chem. Commun.* **1995**, 2323–2324.

(36) Andrade, J. D. *Surface and Interfacial Aspects of Biomedical Polymers, Vol. 1 Surface Chemistry and Physics;* p 112.

Table 1. Atomic Percent of Elements in PE, in PE-Br Films Resulting from the Three Bromination Cycles, and in PE−S−Ph−NH−CO−CF$_3$[a]

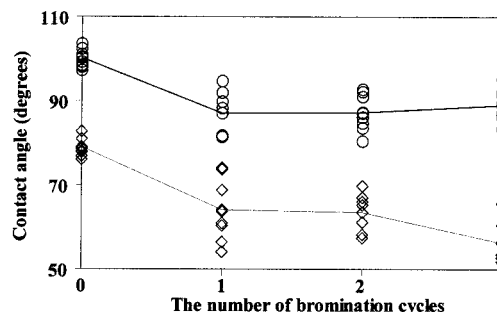| element | PE | PE-Br | | | PESPhNHCOCF$_3$ |
		1 cycle	2 cycles	3 cycles	
C$_{tot}$	96.5−97.3	84.4−89.2	81.0−88.0	78.8−84.1	70.9−75.2
O	2.7−3.5	3.7−5.4	3.2−5.4	4.2−6.7	2.8−6.1
Br$_{70.4}$	0	4.1−5.6	3.1−4.9	3.7−7.6	2.1−3.4
Br$_{68.4}$	0	1.5−6.1	1.6−6.2	4.8−6.8	3.3−4.3
N	0	0	0	0	2.8−3.3
F	0	0	0	0	5.1−6.6
S	0	0	0	0	3.8−5.2

[a] Deconvolution of complex peaks was performed using an Origin nonlinear curve fit with the full-width at half-maximum (fwhm) of the Gaussian line shape 1.3−1.4 eV. Quantitative measurements were made by correction of integrated peak intensities with the Scofield correction factors.

Figure 1. Reaction sequences in surface modification of PE films.

Figure 2. Advancing (○) and receding (◇) water contact angles on PE and after one, two, and three bromination cycles.

films were quite high (100 ± 3°), suggesting that the oxygen moieties are probably buried below the surface.

The first bromination reactions were carried out using Br$_2$/H$_2$O at pH 2. However, irradiation of these samples resulted in PE surfaces with considerable oxygen-containing groups, probably due to water adsorption. Therefore, we turned to gas-phase bromination. We found that a very brief exposure of PE films to Br$_2$ vapor (∼0.7 s) gave colored films, which upon UV irradiation became colorless. After irradiation, the PE-Br sample films were washed very briefly with cold distilled water (temperature 10−15 °C), followed by drying under a nitrogen stream, and were kept under vacuum for 24 h to remove sorbed Br$_2$ and HBr. Water is a nonsolvent for PE or PE-Br films; it is a polar solvent, and hence, the washing process does not swell the film where reorganization will take place after drying. We have never observed an increase in oxygen content after the washing, and we believe the increase in oxygen content (Table 1, discussed below) is the result of the irradiation in ambient atmosphere, where HOBr can be formed from the reaction of Br$_2$ and H$_2$O. Moreover, surface reorganization usually occurs when the PE films are exposed to a hydrophobic environment and also under heating conditions.

The exposure of PE films to bromine followed by irradiation is considered one cycle of bromination (Figure 1), and we applied a number of consecutive cycles to the PE samples to increase the surface bromine concentration. The water contact angle of the brominated sample films is shown in Figure 2. As expected, the advancing water contact angle drops from 100° to ∼90° after the first cycle of bromination. However, insignificant changes in advancing contact angles were observed after additional bromination cycles. That contact angles level off suggests

that after one bromination cycle most of the surface is covered by bromine atoms. This is supported by XPS data that will be discussed later. On the other hand, the receding contact angles decrease with increasing number of bromination cycles, especially at three bromination cycles, where the receding contact angle decreases dramatically, thus increasing the contact angle hysteresis. The increase in hysteresis suggests an increase in surface inhomogeneity and roughness, which is corroborated by AFM results and will be discussed later.

Unfortunately, we could not observe the C−Br stretching vibration at ∼600 cm^{-1} with ATR-FTIR spectroscopy due to the wavelength limit of the detector. However, we observed increased intensities at 1720 and 1263 cm^{-1} and between 1079 and 1018 cm^{-1} that are assigned to carboxylic acid and alcohol functional groups, respectively. Thus, the bromination process introduced not only a bromine functional group but also oxygen moieties on the surface. This is supported by XPS data (Table 1) where the oxygen contents increase from the average of 3.1 (pristine PE) to 4.6, 4.2, and 4.8 atom percent (PE-Br for one to three bromination cycle, respectively). The constant advancing contact angle of 90° for all PE-Br films suggests that the COOH and OH groups are probably buried at least 10 Å below the PE surface.

There are two possibilities to determine the oxygen and bromine compositions on the PE surface by XPS, from resolution of the carbon peak and from the atomic ratio of oxygen or bromine and total carbon. Baker et al.[29] reported the bromine composition in the brominated hexadecylsiloxane monolayer by deconvolution of the C peak. They suggested that there are two types of bromine carbon. First, the peak centered at 286.3 eV is attributed to carbon atoms with one bromine atom attached. Second, the peak at 288.5 eV is assigned to the carbon atoms with two bromine atoms attached. However, it is not easy to evaluate all types of carbon species with carbon peaks, especially if the evaluated peaks are overlapped. In our case we need to resolve the carbon peak into five peaks
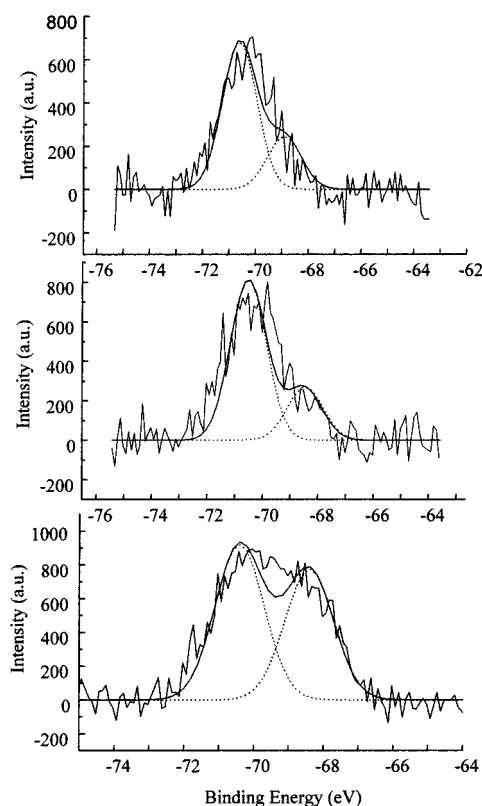
Figure 3. High-resolution XPS spectra of Br 3d in PE-Br films after one to three bromination cycles, after shifting due to charging effects.

(centered at 289.2 (O$-$C$=$O), 288.5 (C$-$Br$_2$), 286.8 (C$-$O), 286.3 (C$-$Br), and 285.0 (C$-$C) with the same fwhm (1.3 eV) where the C$-$Br peak and the C$-$O peak are overlapped). We therefore adopt determination of oxygen and bromine concentrations by means of the ratio of the elements to the total carbon. Table 1 shows the atomic percent of elements in PE and PE-Br films for one to three bromination cycles.

It is found that the increasing number of bromination cycles is accompanied by the bromine peaks becoming broader (Figure 3). The integration width increases from $\sim$2.0 eV (one bromination cycle) to 3.3 eV (three bromination cycles). As a result, the bromine peaks are resolved into two peaks, centered at 70.4 $\pm$ 0.2 and 68.4 $\pm$ 0.2 eV with a constant fwhm of 1.3 eV. Notice that, even after one bromination cycle, there is a small peak at 68.4 eV.

Before getting into the issue of bromine peaks, one should consider if peak asymmetry may be a source of concern, since Gaussian fit is used. We suggest that there are two reasons why overlap of two peaks rather than peak symmetry is the case. The first is the large energy difference between the two peaks (2 eV), and the second is the fact that the second peak increases in intensity to the point where it is almost equal to the first peak after three bromination cycles. Our conclusion is, therefore, that there are two *distinct* bromine peaks and that they result from either structural or environmental effects.

The ratios O/C and Br/C are shown in Figure 4, while the ratios O/C and Br$_{70.4}$/C are roughly constant with an increase in the number of bromination cycles, the Br$_{68.4}$/C ratio preferentially increases, and the data are variable. The concentration of the surface bromine, after the first bromination cycle, based on the 70.4 eV peak is 4.1$-$5.6 atomic percent. Thus, there are 4.6$-$6.6 bromine atoms/ 50 monomer units of PE.
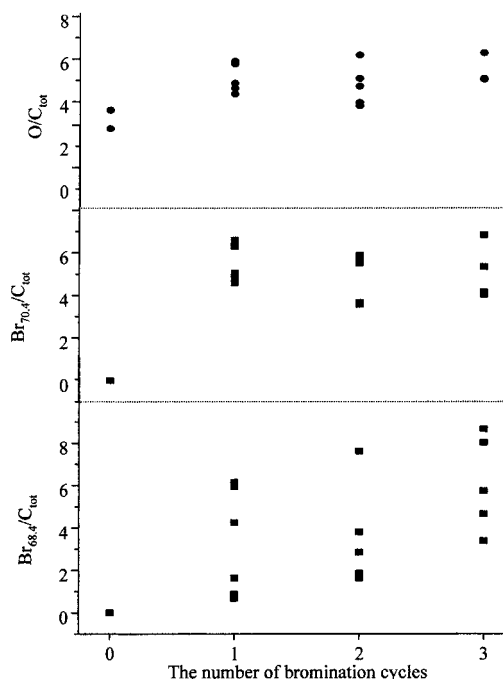

Figure 4. Ratio of elements and total carbon on PE and PE-Br for one to three bromination cycles. Oxygen is calculated from integration of the peak at 532 eV. The bromine peak is deconvoluted into two peaks, centered at 70.4 and 68.4 with a fwhm of 1.3 eV.

Holmes-Farley et al.[18] have discussed the oxidation of PE with chromic acid/sulfuric acid. They explained their observations by describing a process in which a limited surface oxidation results in increased roughness, but with carboxylic groups that reside only at the surface. Further oxidation, however, yields carboxylic groups in the interior of the film, as well as heavy etching. The bromination results presented here show similar trends.

That both the advancing water contact angle (Figure 2) and the ratio of Br$_{70.4}$/C$_{tot}$ level off suggests that the bromine peak at 70.4 eV is possibly a characteristic of C$-$Br groups that cover the PE surface from the first bromination cycle. The additional bromination cycles allow bromine molecules to react either with inner CH$_2$ or with surface CHBr, yielding, in the latter case, CBr$_2$ groups. We propose that the 68.4 eV peak represents the inner CHBr groups, which explains the observed increased intensity. Thus, we suggest that the 70.4 eV peak represents bromine atoms at the top carbon atom in polyethylene chain turns in the lamellar structure, while the 68.4 eV peak results from bromine atoms substituted below the surface. Hence, XPS data suggest that bromination occurs at least at two distinct sites. That the position of an XPS peak is sensitive to the chemical environment of the corresponding functional group has been observed by Evans et al.[37] for C$-$F groups in the case of phase-separated mixed monolayers containing alkyl and perfluoroalkyl groups. They used the stamping technique to prepare mixed monolayers of CH$_3$(CH$_2$)$_{17}$SH and CF$_3$-(CF$_2$)$_{10}$$-S-C_6H_4$-(CH$_2$)$_4$$-$SH and observed two F 1s peaks in their XPS spectra. The energy difference between these peaks was 2 eV, similar to the energy difference in our studies. They have suggested that the two F 1s peaks result from fluorine atoms at the interface between two adjacent domains and from fluorine atoms inside the domain. It is important to note that in ref 37 there was

(37) Evans, S. D.; Cooper, S. D.; Johnson, R. S.; Flynn, T. M.; Ulman, A. *Supramol. Sci.* **1997**, *4*, 247$-$253.
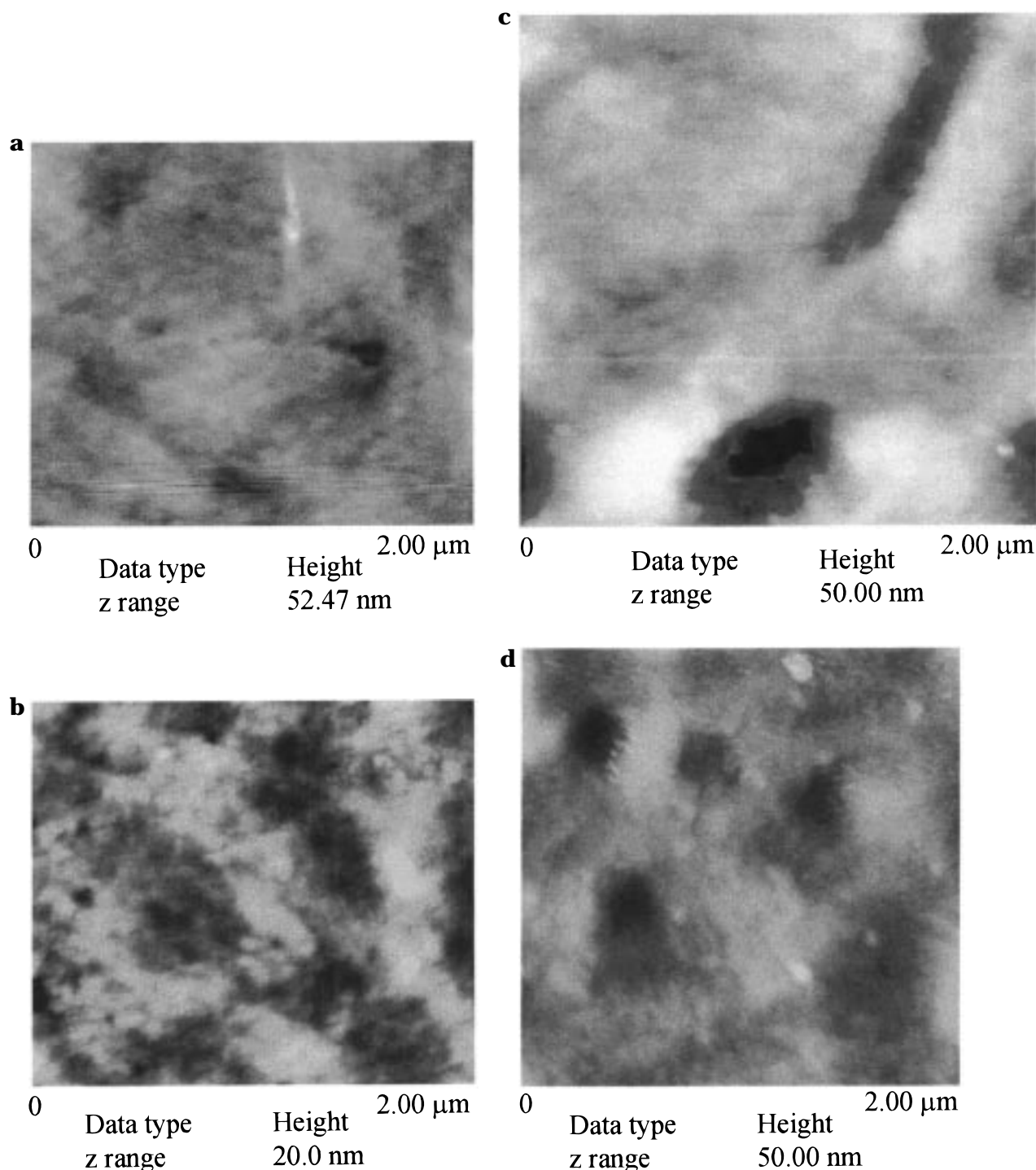
Figure 5. AFM topography of PE before (a) and after one (b), two (c), and three (d) bromination cycles.

no question of where the fluorine atoms are, since the mixed monolayers were constructed from molecules with known structure; therefore, their conclusion was the only feasible one. We suggest the same explanation by way of deduction and propose that one bromination site is at the top carbon atom of PE chain turns, while the other is inside the film. We believe that bromination inside the film occurs preferentially in amorphous regions; however, the present experimental results cannot provide a definite assignment of bromination position.

The reactivity of PE-Br surfaces in substitution reactions corroborates this assignment, as discussed below. Since XPS studies were carried out at a 15° angle—which corresponds to an ∼25 Å depth—only the surface meth-

ylene layers were examined, and little information about bromination in deeper methylene layers can be provided.

The effect of bromination on the topography of the PE film surface has been studied using atomic force microscopy (AFM). Figure 5 shows AFM topography of PE before and after one, two, and three bromination cycles. While the original PE films are optically smooth, they are found to be rough on a submicron length scale, although much smoother than commercial PE films. This is why water contact angle hysteresis on these surfaces was found to be 19°. Roughening of the surface after one bromination cycle can be clearly observed, which explains the increased water contact angle hysteresis to 25°. Roughness (Ra value) calculated by AFM increases from 2.7 (original PE

film) to 3.2, 4.9, and 3.6 nm (1−3 bromination cycles, respectively). Moreover, two and three bromination cycles obviously result in surface damage, suggesting that dibromination may have occurred. Such highly brominated surfaces may be hydrolyzed and UV oxidized, which may result in C−C bond breaking and even loss of material. That the roughness after the third bromination cycle is less than that after the second bromination cycle suggests that low-molecular-weight chain fragments may have been washed out onto the top surface.

We turn now to the determination of surface active bromine concentration using substitution reactions on PE-Br films formed after one bromination cycle. Our model compound for studying substitution reactions is 4-aminothiophenolate. Figure 1 shows the reaction of 4-aminothiophenolate with the PE-Br. On the left, the PE−S−Ph−NH$_2$ was further reacted with trifluoroacetic anhydride in the gas phase, yielding the trifluoroacetamide derivative. On the right, the PE−S−Ph−NH$_2$ was further reacted with 4-nitrobenzaldehyde, yielding the corresponding imine. Since the N=C bond is sensitive to acid and moisture, it can be hydrolyzed quantitatively back to the 4-nitrobenzaldehyde. Therefore, we have used this method to determine the density of amine groups on the PE surface.

There are five advantages for using this compound. First, the thiolate ion is a soft base, and therefore HBr elimination should not compete with the substitution reaction. Second, the electron-donating amino group increases the thiolate nucleophilicity. Third, amino groups have been proven to promote wettability, like oxygen-containing groups. Moreover, they can promote adhesion by forming covalent chemical bonding as well as H-bonding at an interface. Forth, amino and aromatic moieties show unique absorption peaks in ATR-FTIR spectra that may help establish the occurrence of substitution reactions. Finally, the amino groups react with both trifluoroacetic anhydride and 4-nitrobenzaldehyde, resulting in products that have well-defined, strong absorption peaks in infrared and UV spectra.

The grafting density of the reactive surface bromine groups on PE-Br films was first investigated using three subsequent step reactions: a substitution reaction with 4-aminothiophenolate to give grafted aniline moieties (PE−S−Ph−NH$_2$), condensation of the latter with 4-nitrobenzaldehyde to provide the corresponding grafted imine (PE−S−Ph−N=CH−Ph−NO$_2$),[32] and finally hydrolysis of the imine and measurement of the free benzaldehyde by UV absorption. Figure 6 shows ATR-FTIR spectra of the films in all reaction steps. The spectra show the appearance of the NH bending band at 1595 cm^{-1}, aromatic C=C stretching at 1595 and 1496 cm^{-1}, a C−N stretching at 1176 cm^{-1}, and a parasubstituted benzene ring at 824 cm^{-1} for the aniline. The higher intensity of C=C stretching at 1595 cm^{-1} suggests overlapping with the C=N stretching band of the imine. The appearance of a band at 1340 cm^{-1} is characteristic of the nitro group absorption in the last compound.

The amine group density of PE-Br films (after one cycle of bromination) is 2.9 molecules/nm^2. This value was calculated from $A/\epsilon_{ave}a$ mol/cm^2, where A is absorbance, ϵ_{ave} is the molar extinction coefficient (6.33 × 10^4 M^{-1} cm^{-1}), and a is the surface area of sample films (cm^2). Further derivatization of PE−S−Ph−NH$_2$ can be done by the reaction with trifluoroacetic anhydride, yielding
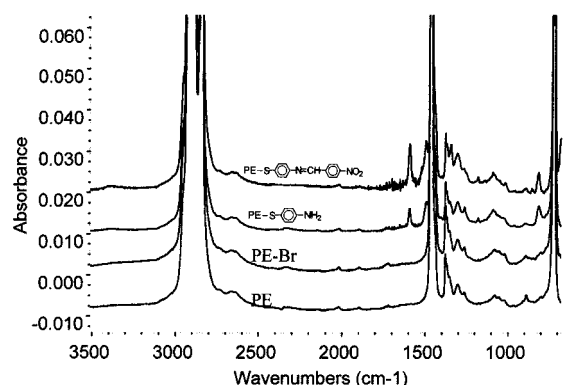

Figure 6. ATR-FTIR spectra of PE, PE-Br, PE−S−Ph−NH$_2$, and PE−S−Ph−N=CH−Ph−NO$_2$.
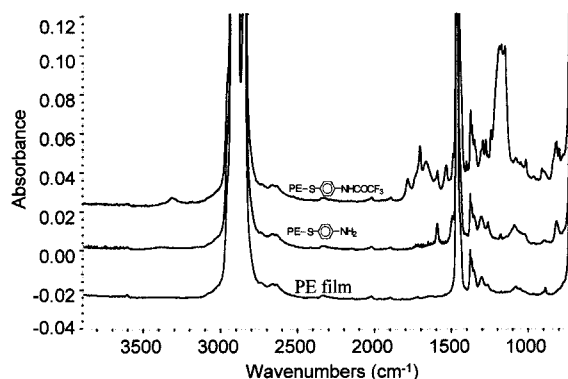

Figure 7. ATR-FTIR spectra of PE, PE−S−Ph−NH$_2$, and PE−S−Ph−NH−COCF$_3$.

PE−S−Ph−NH−CO−CF$_3$, which is shown clearly in ATR-FTIR and XPS spectra. ATR-FTIR (Figure 7) shows strong absorption of CF$_3$ stretching at 1183 cm^{-1} and C=O stretching at 1787 cm^{-1}. The atom percents of elements of PE−S−Ph−NH−CO−CF$_3$ are presented in Table 1. If substitution occurs only on the surface, the reaction yield is an average of 41.5% {(4.7−2.75)100/4.7, which corresponded to a N atomic percent of 2.8−3.3 or 2.7−3.9 atoms/50 monomer units of PE on the surface when calculated from the N 1s peak area}.

In conclusion, we have successfully modified PE surfaces using bromination and demonstrated that surface substitution with thiolate nucleophiles can be easily accomplished. The bromination is carried out with an average of 4.7% bromine incorporated at the surface. Substitution reaction of PE-Br films with 4-aminothiophenolate yields 41.5% and the incorporation of 2.8−3.3 atomic percent of nitrogen, or 2.7−3.9 N atoms/50 monomer units of PE on the surface. We note that since bromination was carried out in the gas phase, taking less than 1 min for each cycle, this method may be of some practical utility in design of in-line reactors for polymer surface modification instead of the more cumbersome batch reactors.