

Surface Modification of Polyethylene Films via Bromination: Reactions of Brominated Polyethylene with Aromatic Thiolate Compounds

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Introduction

Polyethylene (PE) is one of the most interesting commodity polymers. However, one problem associated with PE is its low surface energy. For example, the adhesion between PE surfaces and most matrixes is poor, because of their hydrophobicity and smoothness, which prevent chemical as well as mechanical bonding. One possible route to increase PE surface energy is to modify it. Modification on PE surface has been accomplished via a chemical reaction with a contacting solution,¹ corona discharge treatment,² plasma or glow discharge treatment,³ and surface grafting of hydrophilic monomers after photo-irradiation.^{1f,4} Unfortunately, acid etching or chemical oxidation 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. Attempts to introduce other functionalities by plasma treatment utilizing N₂,⁵ NH₃,⁶ CCl₄,⁷ CF₃Cl,⁸ and CHBr₃⁹ have been reported.

Halogenation has been one route for modification of the PE films,^{7,10} resulting in adhesion improvement.^{10a,c,e} Moreover, halogenated PE surfaces can be further modified to other functionalities using substitution reactions,^{10g,1h} resulting in new, improved surface properties. Fluorination has been reported on PE and polypropylene (PP) films.^{10d,e} There, the film surface became heavily fluorinated within 1 s of exposure to fluorine gas. Chlorination on PE film has been studied to improve hydrophilicity and was found to occur selectively in the amorphous regions of the PE film. Also, chlorination was found more surface-selective in the presence of light due to a decreased rate of Cl₂ diffusion through a highly chlorinated product.^{10f} Thus, the reaction took place in the outermost molecular layers (10 Å) more than deeper in the subsurface (40 Å). In addition, several infrared studies have concluded that no CCl₂ moieties exist in chlorine-saturated samples.¹¹

The kinetics of chlorination, bromination, and iodination of PE were also reported.^{10b} Bromination took place much slower than chlorination. After 11 days, bromine concentration at the PE surface was found only slightly greater than 12%, while after 2 s exposure to chlorine its surface concentration was 6.5%. The rate of iodination on PE film was very slow, and 0.34% iodine was found on the surface after 141 days of exposure to iodine vapor. It has been suggested that the size of the bromine and iodine atoms is larger than that of the chlorine, and surface uptake could be much more facile than subsurface uptake. Moreover, the bond strength of C–halide is 116, 81, 68, and 51 kcal/mol for C–F, C–Cl, C–Br, and C–I, respectively.¹² Hence the exothermicity of halogenation reaction also decreases in this order, and the order of reactivity of halogenation is F₂ > Cl₂ > Br₂ > I₂.

Nucleophilic aliphatic substitution reaction on haloalkanes, on the other hand, depends on the strength of the bond to carbon, the stability of halide anion, its leaving group characteristics, and the nucleophile. Given the decrease in C–halide bond strength from C–F to C–I, the order of displacement reactions on haloalkanes is I > Br > Cl > F.

Attempts at nucleophilic substitution of F and Br in PE surfaces in the presence of nucleophiles such as amines and phenols^{10a,e} were largely unsuccessful. This is because these nucleophiles reacted also as a base and elimination reactions competed with substitution reactions. However, such reactions have been successful on self-assembled monolayers (SAMs) of ω -bromoalkyltrichlorosilane, with less basic nucleophiles such as azide and thiolate compounds.¹³

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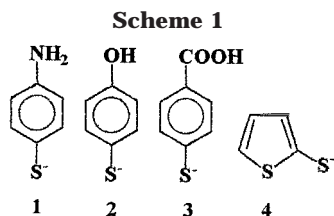


Table 1. Advancing and Receding Contact Angle of PE, PE-Br, PE-S-Ph-NH₂, PE-S-Ph-OH, PE-S-T, and PE-S-Ph-COOH Films

samples	contact angle (deg)	
	advancing angle	receding angle
PE	100.6 ± 2.0	80.7 ± 2.1
PE-Br	86.1 ± 4.2	58.9 ± 4.5
PE-S-Ph-NH ₂	86.0 ± 6.6	54.7 ± 4.3
PE-S-Ph-OH	81.2 ± 4.7	35.2 ± 2.6
PE-S-Ph-COOH	80.8 ± 5.9	37.3 ± 6.6
PE-S-T	90.5 ± 2.5	59.0 ± 6.8

We recently reported a bromination reaction that can improve the wettability of PE films.^{10h} This bromopolyethylene film (PE-Br) could be transformed into amino-terminated PE film (PE-S-Ph-NH₂) using a nucleophilic substitution reaction. We are interested in developing modified PE surfaces with different properties. This requires the development of a family of PE surfaces with a variety of potential chemical modifications. Therefore, in this paper we expand on using aromatic thiolates as nucleophiles and report on the nucleophilic substitution reaction of PE-Br with 4-aminothiophenolate (**1**), 4-hydroxythiophenolate (**2**), 4-carboxythiophenolate (**3**), and 2-thiophenethiolate (**4**). The structures of these compounds are presented in Scheme 1.

Experimental Section

The procedures for the PE film preparation and its bromination are reported elsewhere.^{10h}

Substitution Reaction. The procedures are reported elsewhere,^{10h} except substitution reaction with 4-carboxythiophenolate (**3**), and 2-thiophenethiolate (**4**), which were carried out in 50% ethanol/water and 50% ethanol/DMF, respectively.

Characterization. The PE, PE-Br, PE-S-Ph-NH₂, PE-S-Ph-OH, PE-S-Ph-COOH, and PE-S-T films were characterized by contact angle measurement (captive drop), ATR-FTIR (Nicolet 760 with ZnSe crystal), and XPS (Kratos ES300 with a nonmonochromatic Mg K α X-ray source). The core level S 2p, O 1s, and C 1s spectra were monitored at an electron takeoff angle of 15°. Deconvolution of complex peaks was performed using Origin nonlinear curve fit with the full width at half-maximum (fwhm) of Gaussian line shape of 1.3–1.4 eV. Quantitative measurements were made by correction of integrated peak intensities with the Scofield correction factors of C, S, O, and N are 1.0, 2.63, 2.93, and 1.10, respectively.

Results and Discussions

The LDPE starting material film was first investigated prior to bromination, and subsequent to substitution reactions. Contact angle measurement which affected in the range of 10 Å from the top of the surface showed hydrophobic character with the advancing angle of 100.6 ± 2.0° and receding angle of 80.7 ± 2.1° (Table 1). The ATR-FTIR spectra of untreated PE films showed characteristic peaks at 2919 cm⁻¹ (asymmetric CH₂ stretching), 2848 cm⁻¹ (symmetric CH₂ stretching), 1472 and 1465 cm⁻¹ (CH₂ scissoring, due to crystal-field splitting band

as a result of intermolecular interaction of segments in the orthorhombic cell), 1379 cm⁻¹ (symmetric CH₃ bending), and split peaks at 731 and 720 cm⁻¹ (CH₂ rocking in crystalline and amorphous part, respectively). Some contaminations with oxygen-containing group (at 1008–1127 cm⁻¹) were observed in both the IR and the XPS.

Bromination of PE film was carried out under saturated bromine gas at room temperature. The reaction was finished after a couple of seconds, including sorption, and irradiation with short wavelength UV light. The films were colorless after irradiation with UV light. An attempt to increase bromine concentration on the PE surface by increasing bromine exposure time was unsuccessful. A 2-s exposure to bromine gas resulted in bromine trapped in the bulk of the PE, suggesting that UV light could not pass through and activate the reaction. XPS investigation found oxygen contents increase from ca. 9.7 (pristine PE) to ca. 13.1 atomic percent. The source of oxygen incorporated into the brominated PE film surfaces may be due to two possible processes. First, the oxidation by ozone formed from oxygen during the UV irradiation process, and second the attack by hydroxy radicals formed from hypobromous (HOBr) resulted from the reaction of bromine with water. In fact, one cannot avoid oxygen moieties from incorporating in the film. Chew and co-workers^{10a} reported that oxygen moieties were found on the LDPE surface after bromination *even under nitrogen atmosphere*. Atomic force microscopy studies (see ref 10h for details) suggested that one bromination cycle resulted in PE-Br films with some increase in microroughness, supporting the observed water contact angle hysteresis increase from 19° to 25°. Thus, roughness value (*Ra* value) increased from 2.7 nm (original PE film), to 3.2 nm after one bromination cycle. Further bromination cycles damaged the PE surface.^{10h}

Nucleophilic substitution reactions using thiolates is a new route for the introduction of desired functionalities to the PE surface. We have successfully replaced bromide groups on PE-Br films with 4-aminothiophenolate (**1**).^{10h} The amine group density was 3 molecules per 100 nm². ATR-FTIR of PE-S-Ph-NH₂ (Figure 1a) show the appearance of 3397 cm⁻¹ (N-H stretching), 1593, 1496 cm⁻¹ (aromatic C=C stretching), 1593 cm⁻¹ (N-H bending), 1180 cm⁻¹ (aromatic C-N stretching), and 816 cm⁻¹ (C-H bending for para-substituted benzene). Furthermore, the sulfur and nitrogen peak in XPS clearly showed that 4-aminothiophenolate was introduced onto the surface (Figure 2a) with S/C ratio of 4.9 ± 2.2% and N/C ratio of 3.2 (Table 2). The S/N ratio was ca. 1.5, suggesting that the surface may have reorganized and that the polar amino groups were buried beneath the surface, resulting in the decrease of surface free energy.¹⁴ This is supported by contact angle measurement, which will be discussed later.

The substitution reaction of PE-Br with 4-hydroxythiophenolate was carried out in ethanol solution, yielding hydroxyl-terminated PE (PE-S-Ph-OH) film. The ATR-FTIR spectrum in Figure 1b shows the appearance of 3141 cm⁻¹ (O-H and aromatic C-H stretching), a small peak at ca. 1520 cm⁻¹ (aromatic C=C stretching), 1406 cm⁻¹ (O-H bending), 1263 cm⁻¹ (C-O stretching), and 810 cm⁻¹ (para-substituted benzene). The introduction of 4-hydroxythiophenolate onto PE film was also supported by XPS (Figure 2b), with the S/C ratio of 3.2 ± 0.9% (Table 2). Oxygen concentration was ignored because of contamination in the original PE films.

Substitution reaction of PE-Br with 4-carboxythiophenolate was carried out in 50% water/0.04 M sodium

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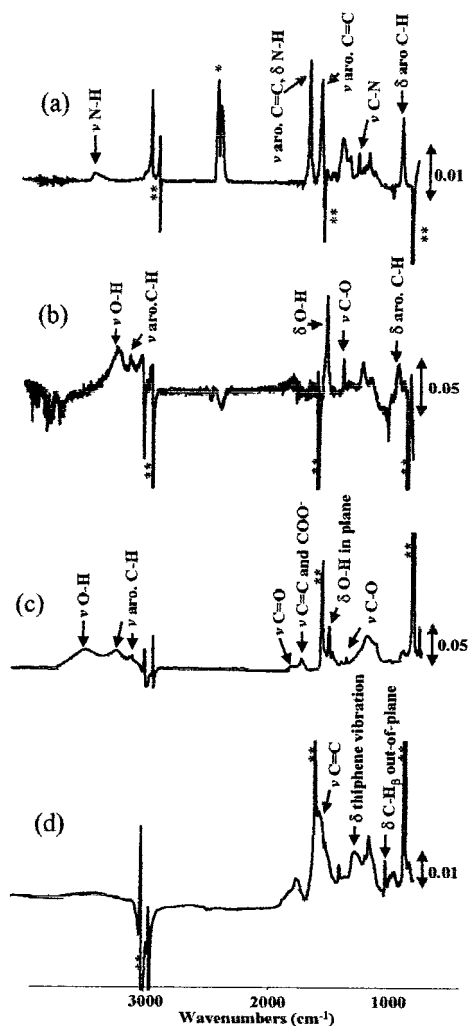


Figure 1. ATR-FTIR spectra of PE-S-Ph-NH₂ (a), PE-S-Ph-OH (b), PE-S-Ph-COOH (c), and PE-S-T (d) after subtraction of the PE spectrum. The asterisk denotes CO₂; ** is polyethylene.

ethanolate, yielding carboxy-terminated PE (PE-S-Ph-COOH). Because of the two acidic protons, 2 equiv of ethanolate was required to ensure the formation of thiolates. Since the thiolate is a much better nucleophile than the carboxylate, the reaction was highly selective; i.e., no evidence for binding through the carboxylate could be detected. Moreover, the carboxylate anion is not a strong enough base, and hence no elimination was observed (based on ATR-FTIR). The ATR-FTIR spectrum of PE-S-Ph-COOH (Figure 1c) showed the appearance of 3401 cm⁻¹ (O-H stretching), 3151 and 3039 cm⁻¹ (aromatic C-H stretching), 1703 cm⁻¹ (COOH stretching), 1632 cm⁻¹ (aromatic C=C stretching, antisymmetric COO⁻ stretching), 1404 cm⁻¹ (symmetric COO⁻ stretching and O-H bending), 1263 cm⁻¹ (C-O stretching), and 800 cm⁻¹ (O-H out-of-plane bending). XPS (Figure 2d) revealed very low displacement with S/C mole ratio of 0.3 ± 0.1% (Table 2), due to the decreased nucleophilicity of the thiolate due to the electron-withdrawing character of the carboxylate group at the para position. This low reactivity of the thiolate may result in a competing hydrolysis that results in surface OH groups.

We turn to grafting thiophene moieties onto PE films by nucleophilic substitution reaction of PE-Br with 2-mercaptothiophene in the presence of sodium ethoxide in DMF, yielding thiophene-terminated PE (PE-S-T). In a forthcoming paper we plan to report on using these

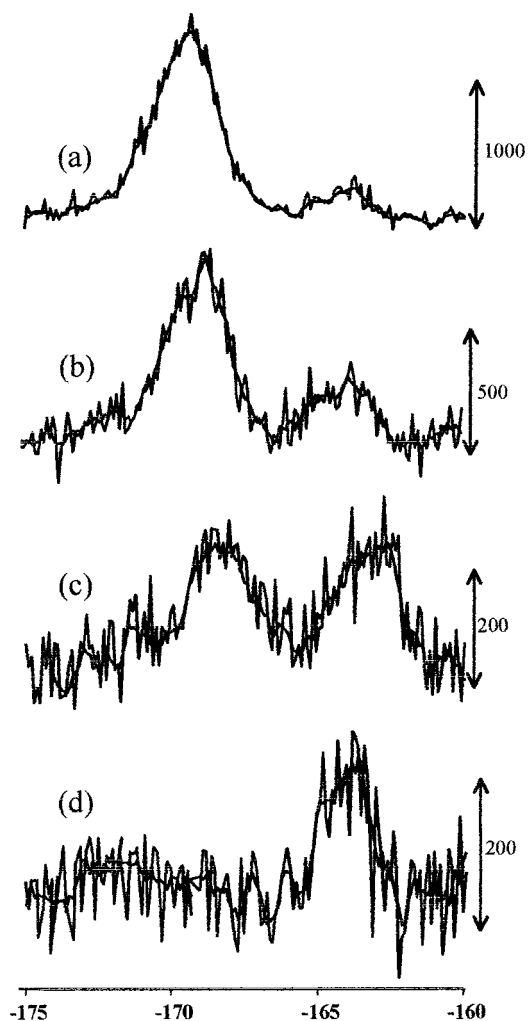
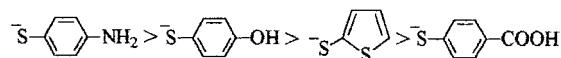


Figure 2. S_{2p} XPS high-resolution spectra of PE-S-Ph-NH₂ (a), PE-S-Ph-OH (b), PE-S-T (c), and PE-S-Ph-COOH (d).

Table 2. XPS Results of S/C and N/C Ratios of PE Film after Replacement with Thiol Compounds on the PE-Br Film

samples	S/C ratios (%)	N/C ratios (%)
PE-S-Ph-NH ₂	4.9 ± 2.2	3.5 ± 1.0
PE-S-Ph-OH	3.2 ± 0.9	
PE-S-Ph-COOH	0.3 ± 0.1	
PE-S-T	1.03 ± 0.1	

Scheme 2



PE-S-T surfaces as substrates in the polymerization of thiophene, resulting in polythiophene-grafted PE. 2-Mercaptothiophene and its anion do not dissolve well in ethanol; hence, DMF was added to increase solubility. ATR-FTIR spectrum of PE-S-T (Figure 1d) showed characteristics of the thiophene ring at 1433 cm⁻¹ (aromatic C=C stretching), a broad range in 1139 cm⁻¹ (stretching vibration of thiophene ring), and 879 cm⁻¹ (C-H_β out-of-plane bending). According to the S/C ratios in Table 2, we conclude that the order of reactivity of thiolate anion is as appears in Scheme 2. This reactivity can be explained by the effect of substituents on the nucleophilicity of the thiolate group. The stronger electron donating the substituent is, the better the thiolate nucleophilicity

and, therefore, the more efficient the displacement reaction.

XPS is not just a surface-sensitive technique for quantitative analysis of surface composition, but shifting in the binding energies of elements under study is indicative of changes in the environment of these elements. The changes in polythiophene oxidation state after doping resulted in shifts of the sulfur peak to higher binding energy. In doping of poly(butylmercaptothiophene)¹⁵ were found three types of sulfur (S 2p): binding energies (BE) of 164.1 and 165.1 eV were assigned to neutral sulfur; BEs of 165.5 and 166.5 eV were associated with the formation of oxidized sulfur S²⁺; and BEs of 168 and 169 eV were ascribed to sulfone due to oxidation of S atoms on the pendant group during the doping process.

We have reported before that XPS showed two Br 3d peaks for PE-Br, and suggested that bromination occurred at least at two distinct sites.^{10h} Evans et al. reported that the position of an XPS peak was sensitive to the chemical environment of the corresponding functional group. They observed two F 1s peaks in the case of phase-separated mixed monolayers containing alkyl and perfluoroalkyl groups.¹⁶

There are two sulfur peaks in PE-S-Ph-NH₂ (Figure 2a), a large peak at 169 eV and a small peak at 164 eV, suggesting either two environments for the grafted molecules or two oxidation states for the grafted sulfur. This is the same for PE-S-Ph-OH (Figure 2b) and PE-S-T (Figure 2c). However, in the case of PE-S-Ph-COOH only one peak appears, at 164 eV (Figure 2d). The energy difference between the peaks (~5 eV) is very significant, suggesting that the idea of two environments, i.e., different concentrations of surface bromide adjacent to the sulfur atom, should be rejected.

When examining the ratio between the 169 and 164 eV peaks, one finds that it decreases in the order presented in Scheme 2. This may suggest that oxidation of the surface thioether has occurred upon exposure of the samples to air, and that the degree of oxidation relates to the electron density at this sulfur. Thus, the 164 eV peak represents the thioether moiety, while the 169 eV peak represents sulfoxide or sulfone moieties. These components appear when the samples were subjected to air and/or XPS studies. No such peaks appear in IR spectra because the spectra were recorded as soon as preparation processes were finished. Furthermore, it is evident that when PE-S-Ph-NH₂ samples were reacted with trifluoroacetic anhydride immediately after formation, XPS studies of the PE-S-Ph-NH-(CO)-CF₃ showed only the 164 eV peak, suggesting that no oxidation had occurred. This is in agreement with all above arguments since the trifluoroacetamido group is not a good electron donor.

The introduction of hydrophilic groups onto the PE surface is expected to improve wettability of the PE surface. Table 1 shows advancing and receding contact angles of PE film before and after modification. The results show that wettability is improved after bromination and subsequent substitution reaction. The effect of functional groups on wettability can be explained using eq 1.^{4e} The

$$\cos \theta = \sum A_i \cos \theta_i \quad (1)$$

influence of a functional group on wettability is related to the normalized fraction of the area (A_i) of the interface occupied by that type of functional group. After bromination, the polar functional groups (bromine) were introduced on the surfaces, which contributed to $\cos \theta$. Thus, the modified surfaces show a lower contact angle. The contact angle reduced from $100.6^\circ \pm 2.0^\circ$ (pristine) to $86.6^\circ \pm 4.2^\circ$ (PE-Br). However, the contact angle did not show significant changes after substitution reaction. This might be because the substitution process is not complete. The previous paper^{10h} showed that the bromine groups were replaced by the aminothiophenolate about 41%. Hence, there was not much change in the hydrophilic area fractions (A_i). As a result, the small change in advancing contact angle after substitution reaction was not unexpected. Higher hydrophilic groups such as -OH and -COOH show little decrease in advancing contact angle. This might be because the difference in $\cos \theta_i$ of OH or COOH and Br group. On the other hand, a significant change in receding contact angle, which is influenced by adhesion between hydrophilic groups on the surface and water, was observed, especially, on the PE-S-Ph-OH and PE-S-Ph-COOH films, where receding contact angle decreased from $58.9^\circ \pm 4.5^\circ$ (PE-Br) to $37.3^\circ \pm 6.6^\circ$. The receding contact angle PE-S-Ph-NH₂ was as high as that of the PE-Br film, although -NH₂ groups are more hydrophilic. This is in agreement with XPS data that amino groups reorganized into the subsurface, probably 10 Å where the contact angle has no effect.¹⁷

In conclusion, we have modified PE-Br by nucleophilic substitution reactions with aromatic thiolate compounds. The amount of replacement was examined in terms of S/C mole ratio using XPS. The stronger electron donating the substituent group on thiolate anion is, the higher the amount of substitution reaction at the PE-Br surface. The S/C ratio is the largest for PE-S-Ph-NH₂ due to the enhancing nucleophilicity of thiolate anion by the amino group. On the other hand, the ratio in PE-S-Ph-COOH is the smallest because of the electron-withdrawing character of the COOH group. However, the film revealed improvement in wettability, due to high hydrophilicity.

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