Radical Chlorination of Polyethylene Film: Control of Surface Selectivity[1]

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ABSTRACT: The heterogeneous (gas–solid) reaction of polyethylene film with chlorine gas has been studied with the objectives of controlling the thickness of the chlorinated layer (depth of chlorination) and the extent of chlorination (density of chlorine atoms on the polyethylene chain). A combination of X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (both transmission and attenuated total reflectance—ATR IR), and gravimetric techniques was used to study the reaction products. Control of chlorination depth and chlorine density was accomplished by varying the pressure of Cl_2 and the photointensity. Control was demonstrated by preparing four "extreme" types of modified film sample: a shallow layer of lightly chlorinated chains (SL), a shallow layer of highly chlorinated chains (SH), a deep layer of lightly chlorinated chains (DL), and a deep layer of highly chlorinated chains (DH).

Introduction

We have been developing synthetic routes to chemically modified polymer surfaces with the objective of preparing substrates with controllable surface structures so that we can control (and understand) macroscopic surface properties. We have focused much of our effort on controlling the surface selectivity of modification reactions so that very thin layers (10–100 Å) of reactive functionality can be introduced to relatively thick (several mil) film samples. This type of sample is amenable to surface structure–property correlations. Surface-selective modifications (with varying success) have been reported for poly(chlorotrifluoroethylene),[3-5] poly(vinylidene fluoride),[5-8] polypropylene,[9] poly(tetrafluoroethylene-*co*-hexafluoropropylene),[5,10] and poly(ether ether ketone).[11] Each of these modification procedures involves a reaction at an interface between the solid polymer film and a reactive solution that does not swell the polymer. We became interested in the heterogeneous (gas–solid) photochlorination of polyethylene with the thought that under certain conditions the reaction may be inherently surface-selective. The product, chlorinated polyethylene, is less permeable[12] to chlorine (and other gases) than is polyethylene so we suspected that, under conditions in which chlorination is more rapid than diffusion of chlorine into polyethylene, a barrier layer of chlorinated polyethylene would form at the surface and inhibit bulk chlorination. This paper reports the results of research that had the objective of simultaneous control of the chlorination depth (thickness of the chlorinated layer) and the density (extent of chlorination of the polyethylene chain). This type of control may have practical applications including minimizing the chlorine content that yields a particular barrier property and controlling the selectivity of membranes for gas separation.

The chlorination of polyethylene has been studied extensively, but not with regard to understanding or controlling the surface selectivity. Chlorinated polyethylene can be prepared (and is commercially produced) by chlorination with the polymer in suspension,[13-18] in chlorinated solvent solution,[17-23] or as a solid.[24] UV irradiation is generally used. In heterogeneous reactions, the chlorination occurs selectively in the amorphous regions, but, in solution, the chlorine is evenly distributed.[18] Analysis by NMR[13,18,25-27] shows that CCl_2 content is greater for suspension vs solution chlorinated polymer of the same Cl content, indicating a less random distribution for suspension chlorination. Several infrared studies[23,28] have been reported that conclude that no CCl_2 is observed in chlorine-saturated samples. As saturated samples contain 73%[28] chlorine by weight (which corresponds to ~1 Cl per C), this suggests that the predominant structure of chlorine-saturated polyethylene is –CHCl–. Heterogeneous chlorinations of polyethylene film have been reported[12,29-32] and the products characterized by elemental analysis,[12,29] X-ray fluorescence,[30] infrared spectroscopy,[31] and X-ray photoelectron spectroscopy.[32] It was noted that "the reaction occurs mainly on the surface" as much more halogenation was observed by ATR IR than by transmission IR.[31] The kinetics of chlorination ($CH_2 \rightarrow CHCl \rightarrow CCl_2$) were followed by XPS, and it was determined that reaction occurs uniformly throughout the XPS sampling depth.[32]

Experimental Section

General Procedures. Linear low-density polyethylene (CdF Chimie Grade FW 2900, ρ = 0.92) was dissolved in refluxing *p*-xylene with a small amount of 2,6-di-*tert*-butyl-4-methylphenol (Aldrich), precipitated in cold (0 °C) methanol, washed with acetone, and dried (25 °C, 0.05 mm, several weeks). Films (4-mil) were hot-pressed between poly(ethylene terephthalate) film (Carver press), extracted with refluxing hexane, and dried (25 °C, 0.05 mm, >48 h). Chlorine was obtained from Aldrich and used as received. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin-Elmer–Physical Electronics 5100 using Mg Kα excitation (300 W) using pass energies of 89.5 eV for survey spectra and 17.9 eV for C_{1s} region spectra. Acquisition time was minimized (1.5–6 min) to avoid X-ray damage; no beam damage (change in C:Cl ratio) was observed under these conditions. Atomic composition and peak area calculations were determined using the instrument's supplied software and programmed sensitivity factors: C_{1s}, 0.25; Cl_{2p}, 0.53. ATR IR spectra were recorded under nitrogen with an IBM 38 FTIR and a KRS-5 (45°) internal reflection element. Gravimetric analysis was performed with a Cahn 29 electrobalance containing a polonium source. The precision of the quantitative XPS and gravimetric data is well within preparative reproducibility.

Chlorination of Polyethylene Film. Chlorine was introduced to a nitrogen-purged Schlenk tube containing a polyethylene film sample (1.5 × 6 cm). For reactions at 1 atm of Cl_2, the tube was purged with chlorine for 2 min through a mineral oil-containing bubbler and closed to achieve 1 atm. For reactions at lower pressure, the desired partial pressure of chlorine was obtained by introducing an appropriate volume of Cl_2 to the nitrogen-filled tube using a gas-tight syringe. For reactions

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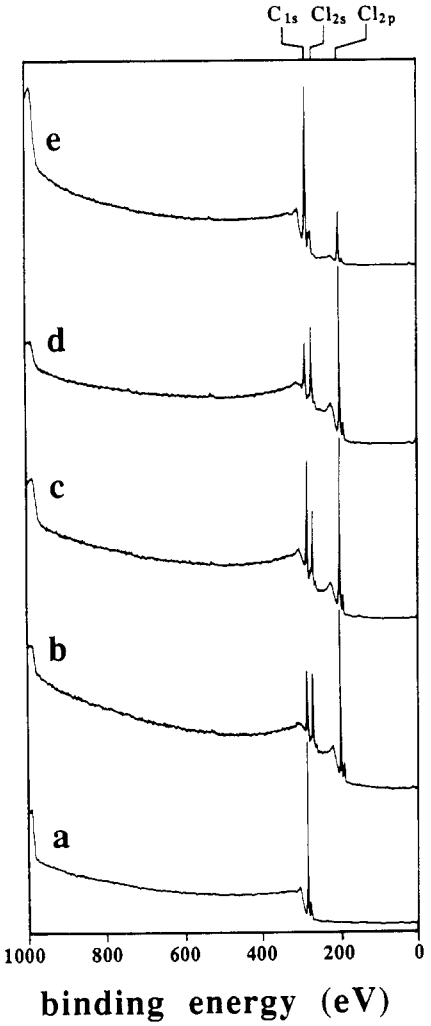

Figure 1. XPS survey spectra of PE film chlorinated at 1 atm of Cl_2: (a) virgin PE; (b) 2 min, ambient light, 15° takeoff angle; (c) 2 min, ambient light, 75° takeoff angle; (d) 22 h, ambient light (15°); (e) 22 h, dark (15°).

performed in the dark, the tube was wrapped with black electrical tape. Reactions in ambient light were performed in a hood with fluorescent lighting. An Ultra-Violet Products B-100A lamp (350 nm) was placed ~20 cm from the tube for reactions with UV irradiation. After the desired reaction time, the tube was purged with nitrogen and evacuated (0.05 mm, 25 °C) for at least 24 h before analysis.

Results and Discussion

Polyethylene film was prepared by hot-pressing purified commercial linear low-density resin. Film samples were cut (1.5 × 6 cm, convenient for our analytical methods), extracted with hexane, dried at reduced pressure to constant mass, and stored under vacuum or nitrogen. This procedure consistently gave film samples (hereafter abbreviated PE) that were free of impurities as evidenced by XPS and ATR IR spectroscopies. Figures 1a, 2a, and 3a show survey XPS, C_{1s} region XPS, and ATR IR spectra of PE.

The objective of our work was to stimultaneously and independently control the depth of chlorination (thickness of the modified layer) and the density of chlorination on the PE chain; we chose four extreme targets to demonstrate this control: a shallow layer of lightly chlorinated chains (SL), a shallow layer of highly chlorinated chains (SH), a deep layer of lightly chlorinated chains (DL), and a deep layer of highly chlorinated chains (DH). Product film samples were analyzed by XPS, ATR IR, and gravimetric

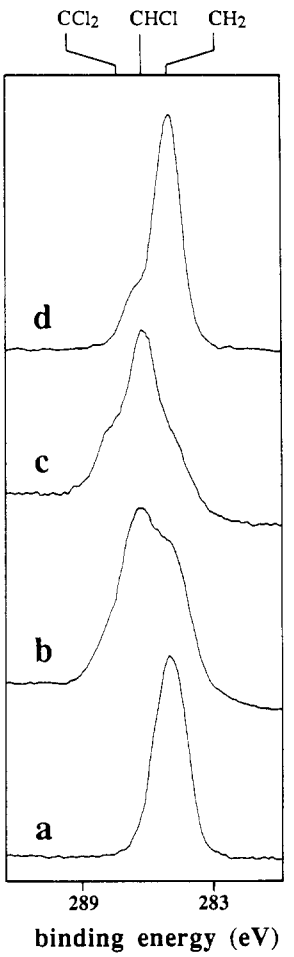

Figure 2. XPS C_{1s} region spectra (15° takeoff angle) of PE film chlorinated at 1 atm of Cl_2: (a) virgin PE; (b) 2 min, ambient light; (C) 22 h, ambient light; (d) 22 h, dark.

analyses. Advancing and receding water contact angles were measured early on in the course of this work; they were found to decrease upon chlorination from (θ_A/θ_R) 105°/83° to ~96°/~68° for all conditions and extents of chlorination. This was judged to be an uninformative analytical tool and abandoned.

Chlorination of PE with 1 atm of Cl_2. Gas–solid interface chlorinations at 1 atm of Cl_2 were performed by purging a Schlenk tube containing a PE film sample with Cl_2 for 2 min, closing the tube (at 1 atm), and, after the desired time period, flushing the tube with nitrogen, and then evacuating the tube at reduced pressure. Reactions were carried out in ambient light, with UV irradiation, and in the dark. XPS and ATR IR spectra of two samples prepared in ambient light are shown in Figures 1–3. These samples were allowed to react (after the initial Cl_2 purge) for 2 min (Figures 1b,c, 2b, and 3b) and 22 h (Figures 1d, 2c, and 3c). The XPS survey spectra show the expected decrease in intensity of the C_{1s} photoelectron line (285 eV) and the appearance of Cl_{2s} (278 eV) and Cl_{2p} (208 eV) lines. Two survey spectra are shown for the 2 min reaction sample: they were recorded at takeoff angles of 15° and 75° (between the film plane and the detector) and assess the composition of the outer ~10 and ~40 Å, respectively (~95% of the measured photoelectrons originate in these regions[33]). Quantitative analysis indicates that the composition of the outer 10 Å is $C_{100}Cl_{81}$ and the outer 40 Å is $C_{100}Cl_{49}$ and demonstrates that the reaction is occurring surface selectively in the initial stages. After 22 h the composition (takeoff angle independent) is $C_{100}Cl_{107}$. This corresponds to 76 wt % chlorine and is close to the 73%

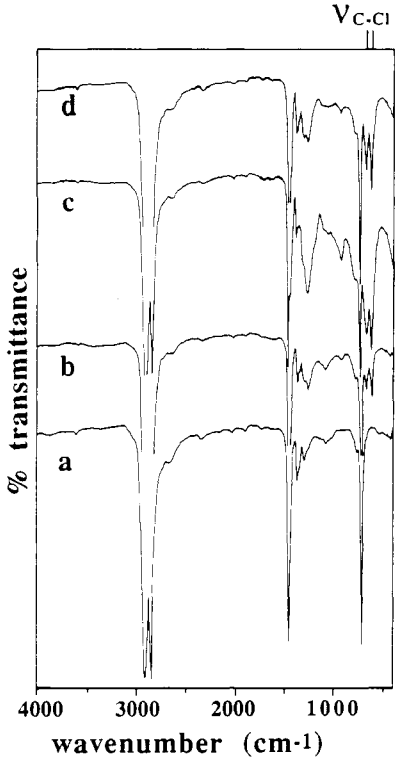

Figure 3. ATR IR spectra (KRS-5, 45°) of PE film chlorinated at 1 atm of Cl_2: (a) virgin PE; (b) 2 min, ambient light; (c) 22 h, ambient light; (d) 22 h, dark.

saturation level observed in solution chlorinations. Attempts to follow the kinetics of the reaction by XPS failed.[34] Samples chlorinated for 30 s to 2 min were indistinguishable. After 5 min of reaction, no takeoff angle dependency was observed. The surface composition ($C_{100}Cl_{82\pm3}$) was invariant in samples chlorinated for 5 min to 1 h. The chlorine content measured by XPS did not increase from 5 to 22 h ($C_{100}Cl_{107\pm2}$). XPS C_{1s} region spectra (Figure 2b,c) indicate a composite of peaks due to CH_2, CHCl, and CCl_2. Areas of curve-fitted peaks for the 22-h reaction (chlorine-saturated) sample give a composition of 29.1% CCl_2, 45.5% CHCl, and 25.4% CH_2; this corresponds to an empirical formula of $C_{100}Cl_{104}$ (75 wt %) and is consistent with the atomic composition analysis. The presence of methyl and methine groups in virgin polyethylene is ignored in this analysis; the infrared spectrum (Figure 3a) indicates that methylene groups are present in large majority. The ATR IR spectra (Figure 3b,c) suggest that the reaction occurs deep in the film, as C–Cl stretching bands (667 and 613 cm^{-1}) are visible in 2-min reacted samples and are still increasing in intensity after 22 h. Gravimetric analysis showed that the PE samples reacted for 2 min and 22 h gained 20 and 790 $\mu g/cm^2$, respectively. A very rough estimate of the reaction depth can be calculated from this data. Assuming compositions of $C_{100}H_{151}Cl_{49}$ (2 min) and $C_{100}H_{93}Cl_{107}$ (22 h), 20 and 790 $\mu g/cm^2$ mass gains correspond to reaction depths of ~0.2 μm (2 min) and ~3.5 μm (22 h). These estimates are minimum depths and assume constant chlorine concentration throughout the modified layer. Figure 1 (b and c) indicates a gradient in chlorine concentration and that this is a poor assumption. Nevertheless, they indicate very deep modifications relative to the XPS sampling depth.

XPS spectra of a sample chlorinated in the dark for 22 h are shown in Figures 1e and 2d. The film surface region is lightly chlorinated and analyzes to have a composition (not takeoff angle dependent) of $C_{100}Cl_{9\pm2}$. Chlorination is not expected in the dark at room temperature and likely results because of incomplete darkness in the reaction tube. The ATR IR spectrum (Figure 3d) indicates extensive chlorination; the C–Cl absorbance bands are as intense as those for the sample prepared in ambient light. Gravimetric analysis of a sample chlorinated in the dark for 24 h indicated a mass increase of 386 $\mu g/cm^2$, which corresponds to an estimated minimum reaction depth of 18.9 μm (assuming a composition of $C_{100}H_{181}Cl_9$).

Reactions run with UV irradiation at 1 atm of Cl_2 gave products essentially identical with those prepared in ambient light as evidenced by ATR IR. XPS indicated a slightly higher and more variable chlorine concentration ($C_{100}Cl_{127\pm10}$) and that the reaction in the XPS sampling depth was faster, reaching saturation in less than 5 min. Gravimetric analysis indicated a slightly higher rate of chlorination at short reaction times: 10- and 30-min chlorinated PE samples gained 26.6 and 54.2 $\mu g/cm^2$, respectively, compared with 22.4 and 49.3 $\mu g/cm^2$ after the same times in ambient light. At longer reaction times, however, the reaction is slower with UV irradiation. After 21 h of reaction, a sample had gained 230 $\mu g/cm^2$, compared with 790 $\mu g/cm^2$ after 22 h in ambient light. This corresponds to a minimum reaction depth, of the type described above, of ~0.8 μm.

The above results demonstrate that the chain density of chlorination and the depth of reaction are controlled by the intensity of light. Greater light intensity increases the rate of the chlorination reaction, and, as a result, the rate of diffusion of Cl_2 is decreased. The depth of reaction can only be crudely controlled with reaction time at 1 atm of Cl_2 pressure. All of the reactions proceed to relatively large depths. The combined data suggest that chlorination in the presence of light is more surface-selective due to a decreased rate of Cl_2 diffusion through a highly chlorinated product, which is consistent with literature permeability data.[12] DH and DL type surfaces can be prepared using 1 atm of Cl_2 and light (ambient or UV) or dark conditions, respectively. The crude depth-of-reaction calculations indicate that reaction depths are much greater in the dark. Transmission IR spectra at short reaction times support this; samples chlorinated in the dark exhibit more intense C–Cl stretching bands than those of samples chlorinated in light for the same duration.

Chlorinations of PE with Low Cl_2 Concentrations. The differences between the chlorinated products produced at 1 atm of Cl_2 in light and darkness (DH and DL) implicate the rate of Cl_2 diffusion into the film (which changes over the course of the reaction) as the major factor controlling depth of the reaction. To prepare more thinly modified PE samples (SH and SL), we decreased the Cl_2 pressure to lower the diffusion rate. Chlorinations were carried out in a ~100-mL Schlenk tube; the desired chlorine pressure was achieved by injecting the appropriate volume (1 atm) of chlorine into the nitrogen-filled tube with a gas-tight syringe. The effect of chlorine pressure on the rate of reaction was crudely determined by gravimetric analysis of PE samples allowed to react for 5 min with UV irradiation at various chlorine concentrations. The data are plotted in Figure 4. The shape of the curve indicates that the reaction rate depends very strongly on the chlorine concentration at low pressures and less so at higher pressures. We offer no explanation for this behavior, as the chlorine concentration should affect both the diffusion rate (which changes on reaction) and the reaction rate. We used this result, and it should be regarded, only qualitatively; the data are derived from single mass measurements of samples reacted for one

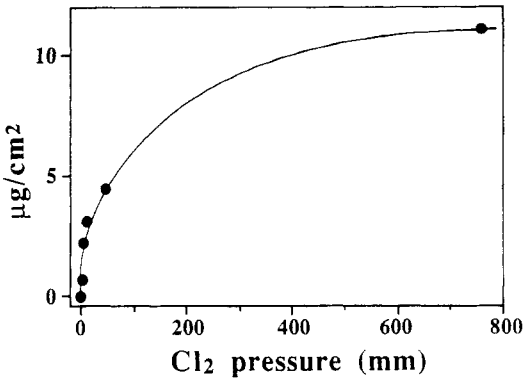

Figure 4. Effect of Cl_2 pressure on the rate of chlorination of PE film. Mass gain upon a 5-min reaction with UV irradiation.

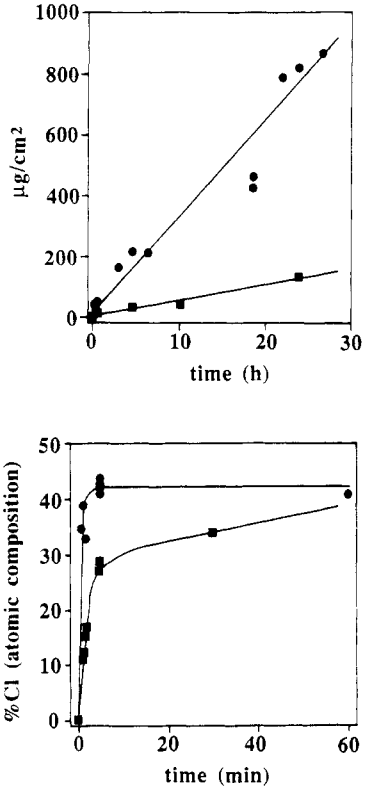

Figure 5. Comparison of the rate of chlorination of PE film at 1 atm (●) and 50 mm (■) of Cl_2 by gravimetric (upper) and XPS (lower) analyses. Note that the time coordinates differ.

length of time.

A series of chlorinations was carried out at 50 mm of Cl_2 in ambient light. Figure 5 shows gravimetric and XPS data for PE samples chlorinated for different time periods at both 50 and 760 mm of Cl_2. The gravimetric data, which monitor the reactions at all depths, indicate that the rate of chlorination at 50 mm is $\sim 1/5$ the rate at 760 mm. The XPS data, which assess the reaction of the outer 10 Å (15° takeoff angle), indicate rate differences as well, but the compositions converge. A sample analyzed after 24 h at 50 mm of Cl_2 was "saturated" ($C_{100}Cl_{109}$) by XPS (survey and C_{1s} region spectra are indistinguishable from those of samples prepared at 1 atm of Cl_2) but gained 134 μg compared to the 790 μg gained by a sample chlorinated for 22 h at 1 atm. This indicates that a more surface-selective reaction occurs at lower pressure. ATR IR spectra indicate this as well. Figure 6 shows ATR IR spectra and XPS spectra of two samples: one was prepared by chlorination at 1 atm of Cl_2 for 30 s; the other was prepared by chlorination at 50 mm of Cl_2 for 30 min. The two samples exhibit close to the same chlorine content by XPS,

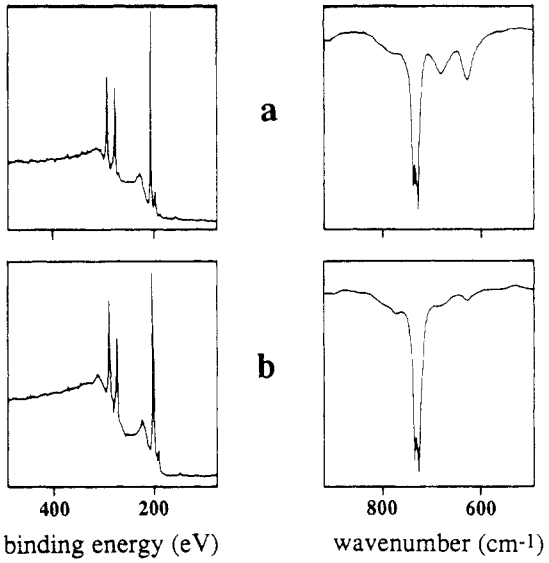

Figure 6. XPS and ATR IR spectra for PE film chlorinated in ambient light at 1 atm of Cl_2 for 30 s (a) and at 50 mm of Cl_2 for 30 min (b).

but the relative intensities of the C–Cl stretching bands in the ATR IR spectra indicate that a much more shallow modification occurs at the lower Cl_2 pressure.

To prepare the target SH and SL surfaces, very low Cl_2 concentrations were needed (Figure 4). An SH surface was prepared with a 5-min reaction at 5 mm of Cl_2 using UV irradiation. The composition of this surface by XPS is $C_{100}Cl_{107}$ (15° takeoff angle) and $C_{100}Cl_{75}$ (75° takeoff angle). Very small C–Cl absorbances which are barely discernable appear in the ATR IR spectrum. The sample gained 2.2 μg/cm² on reaction. A depth estimate of the type described above based on this value is ~100 Å. An SL surface was prepared using 2 mm of Cl_2, a 30-min reaction time, and ambient light. For these conditions the composition was found by XPS to be $C_{100}Cl_{10}$ (15° takeoff angle) and $C_{100}Cl_7$ (75° takeoff angle). No mass gain was detected and no C–Cl stretching bands were observed by ATR IR, indicating a very shallow reaction depth.

Conclusions

In the heterogeneous (gas–solid) chlorination of polyethylene film, the depth of chlorination into the film and the density of chlorine on the polymer chain can independently and simultaneously be controlled by adjusting Cl_2 pressure, photointensity, and reaction time. This was demonstrated through the preparation of four "extreme" modified film samples (SL, SH, DL, and DH).

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