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Surface Fluorination of Polymers in a Glow Discharge Plasma: Photochemistry

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ABSTRACT: The important role of the photon component of a glow discharge plasma is documented for the case of surface fluorination reactions of polymers. Photochemical reactions were carried out with a plasma glow discharge as a source of electromagnetic radiation only; polymer specimens were isolated from all other components of the plasma. Results establish that radiation in the vacuum-ultraviolet range is capable of enhancing the reactivity of polymer surface toward fluorine gas, consistent with what is known about the photochemistry and thermochemistry of the reactants.

Introduction

Glow discharge plasma reactions have been demonstrated to be effective in perfluorinating the surface regions of a variety of polymers.[1-3] A brief discussion of reaction kinetics has also been presented.[4] The mechanism of the gas–solid reaction is not completely understood, however, owing to the very complex nature of the plasma (gas) phase and its interaction with the polymer surface. To gain some insight into this type of reaction, we have investigated the photochemical interaction of plasma radiation with polymer films immersed in a fluorine-containing gas environment. The experiments aimed to establish whether or not photons from the plasma could enhance the fluorination reaction, and if so, to establish the nature of this process.

The electromagnetic radiation present in a glow discharge has sufficient energy to cause photochemical reactions in both the gas and solid phases. Dissociative absorption of radiation by diatomic fluorine gas is one of the many possible events in a plasma and is in this work the process of interest in the gas phase; photoexcitation and photoionization of saturated hydrogen- and fluorine-containing polymers are the important processes that may occur in the solid phase.

The absorption of radiation by fluorine gas has been investigated in the UV–visible (200–800 nm) region[5,6] and in the vacuum-UV (<200 nm) region.[7,8] The key conclusion is that fluorine will dissociatively absorb photons in the continuum between 210 and 450 nm, with a peak at 284.5 nm. However, the extinction coefficient is relatively low compared to other halogens.[9] It is not until below 100 nm that fluorine again absorbs dissociatively, this time to excited fluorine atoms. Examples of photoassisted halogenation reactions discussed in the literature include photochlorination of poly(vinyl chloride)[10] and photofluorination of organic molecules.[11] In these reactions, UV radiation is used to dissociate the halogen molecules, thereby initiating the chain reactions.

The photochemistry of polyethylene, the polymer most heavily studied in this investigation, is another important consideration in our reaction system. Because polyethylene does not contain any chromophores, a relatively large amount of energy is needed for electronic excitation. Partridge[12] and George et al.[13] have investigated the absorption of polyethylene in the vacuum-UV region. Absorption about 185 nm ($\pi \rightarrow \pi^*$) is attributed to unsaturation that is present as an impurity. A region of nonionizing absorption ($\sigma \rightarrow \sigma^*$) occurs at 130 nm, with a transition region between 160 and 130 nm. Photoionization is believed to occur below 120 nm. As fluorine atoms are substituted for hydrogen atoms on the polyethylene chain, the region of photon absorbance shifts to higher energy (shorter wavelength). This is confirmed by valence band X-ray photoelectron spectroscopy, which has been used to study a series of model fluoro polymers.[14]

The product of the interaction of the polymer with the photons is either an excited or an ionized species. An ionized polymer molecule will be readily converted to an excited neutral molecule by charge neutralization with a free electron. The excess energy present will be larger than

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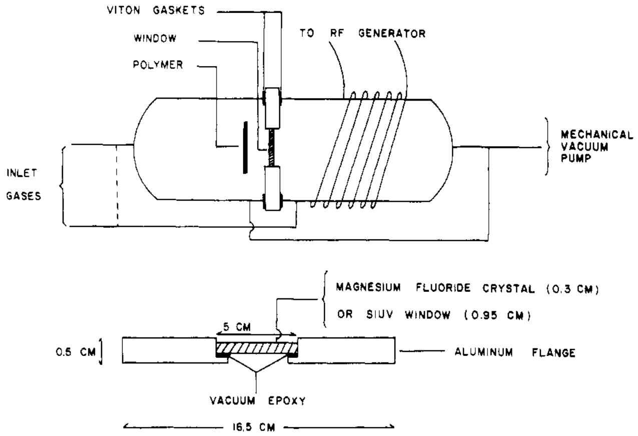

Figure 1. Two-compartment reactor with detail of window assembly.

any bond energy; consequently homolysis to radicals and unimolecular elimination of a small molecule (e.g., H_2) are probable events. The elimination reaction results in the formation of a double bond in the polymer chain. Surface cross-linking is also a result. These events indicate that photons can create reactive sites (radical, ion, and unsaturation) within the polymer phase that are capable of propagating with molecular fluorine.

An important consideration is the penetration depth of vacuum-UV radiation within the condensed polymer phase. This information can be obtained from the polyethylene absorption data discussed earlier.[12] Absorption coefficients (k) have been estimated for each region of the spectrum using the Beer–Lambert law. From these values an effective penetration depth (d) can be calculated, defining d as the depth over which the signal is attenuated to $1/e$ of its original value. The results are as follows: 180–200 nm (unsaturated impurity), $k \approx 1.3 \times 10^3$ cm^{-1}, $d \approx 8$ μm; 130–140 nm (nonionizing absorption), $k \approx 2.0 \times 10^5$ cm^{-1}, $d \approx 50$ nm: <120 nm (photoionization), $k > 2 \times 10^5$ cm^{-1}, $d < 50$ nm. This analysis clearly demonstrates the surface nature of photochemical interactions with polyethylene.

Common radiation sources in the vacuum-UV region are the inert gases and hydrogen.[15] Traditional UV sources lie at wavelengths above this region (i.e., lower energy); an exception is mercury's highest energy strong emission line, which occurs at 184.9 nm. Most optical glasses are opaque in the vacuum-UV. For example, commercial Pyrex and Vycor do not transmit radiation below 300 nm; fused silica and quartz are useful down to 185 nm. Below this wavelength inorganic fluoride salt windows are generally used. In this work magnesium fluoride (~115-nm cutoff) and fused silica (S1UV) (~185 nm) windows were employed in the experiments.

Vacuum-UV radiation generated by a hydrogen glow discharge has been used to cross-link the surface region of polyethylene film.[16,17] It has also been demonstrated that UV radiation is important in the surface cross-linking of ethylene–tetrafluoroethylene copolymers in inert-gas plasmas.[18,19]

Experimental Section

The apparatus employed in this study was a two-piece reactor which isolates the reacting polymer from the glow discharge by a UV-transmitting window (Figure 1). The gaseous composition in each chamber could be varied independently. An inductively coupled radio-frequency (13.56 MHz) power supply was employed to generate the plasma.

The experimental conditions employed throughout this project were as follows: pressure, about 200 Pa (1.5 torr); power input, 50 W; total volumetric flow rate, 50 cm^3 (STP)/min; reaction time, 60 min. Reaction variables included the polymer, the gas composition of the plasma zone and the reaction zone, and the UV-transmitting window.

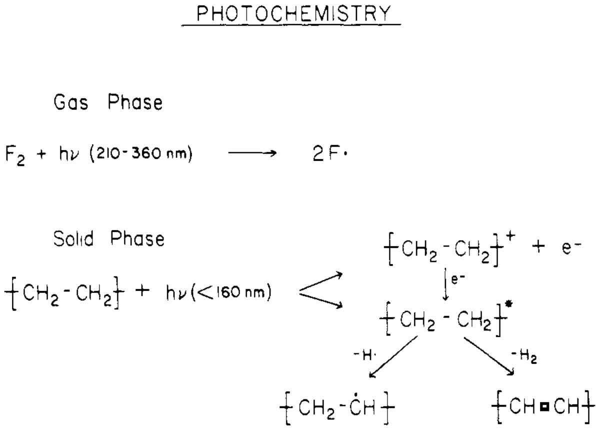

Figure 2. Photochemical reactions appropriate to the solid phase (polymer) and the gas phase.

In a typical experiment, a polymer film was placed vertically in a sample holder parallel to the UV window in the upstream chamber. The system was then evacuated with a mechanical vacuum pump, and the gases were admitted. Next the plasma was ignited and confined to the downstream chamber. After 60 min, the plasma was shut off, the reactor was flushed with an inert gas and evacuated, and finally air was leaked in to bring the system up to atmospheric pressure.

Two different UV-transmitting windows were employed in this work: fused silica (S1UV) (9.5 mm thick) and a magnesium fluoride crystal (MgF_2) (3 mm thick). Their low-wavelength transmission limits are 185 and 115 nm, respectively. The motivation for selecting these materials is based upon the photochemistry of fluorine gas and saturated polymers. As shown in Figure 2, fluorine gas will dissociatively absorb radiation between 210 and 360 nm and below about 100 nm. Polyethylene can be photoexcited/photoionized at wavelengths less than 160 nm. (The nature of this photoexcited/photoionized species is not known; the important result is that it can lead to a variety of other reactive species as shown in Figure 2. For saturated polymers without any chromophores, the dominant photoprocess will probably be photoionization.) Therefore the fused-silica window (transparent down to 185 nm) will only allow the gas-phase photodissociation reaction to occur whereas the MgF_2 crystal (115 nm) will allow both the gas- and solid-phase photoprocesses. Thus these windows should enable us to determine which process, if any, is important.

One cannot neglect absorption of radiation by chromophoric impurities in the polymer.[20] Carbonyl, vinyl, and vinylidene groups are the principal species that must be considered. In general, these all absorb photons above 180 nm so that their contribution to the photoreactions should also be observed with the fused-silica window. For the low-density polyethylene (LDPE), polystyrene (PS), poly(vinylidene fluoride) (PVF_2), and poly(vinyl fluoride) (PVF) films studied in this work, no oxygen signal was detected in the ESCA spectra of the pristine polymers. Also, no oxygen species were observed in the multiple internal reflectance infrared spectrum of LDPE; however, terminal vinylidene end groups were detected.[21] These unsaturated groups have been observed to react with F_2 to form saturated species in elemental (i.e., nonplasma) reactions.

Analysis of the polymer surfaces by X-ray photoelectron spectroscopy (ESCA) was used to determine the extent of fluorination; energy referencing was accomplished by assigning the CH_2 peak to 285 eV regardless of β-substituent chemical shifts. A comparison of the surface facing the window ("front") vs. the opposite surface ("back") provided information on enhanced reactivity due to the photon flux. A curve-fitting software routine was used to estimate the relative concentrations of CF_3, CF_2, CF and CHF, and CH_2 components present in the carbon 1s spectra.[21] The peaks in the ESCA spectra for these various species are located at increasingly higher binding energies as fluorine addition proceeds. Thus CF_3 is found at the extreme left in these spectra and CH_2 is the peak at the extreme right.[2,4,21]

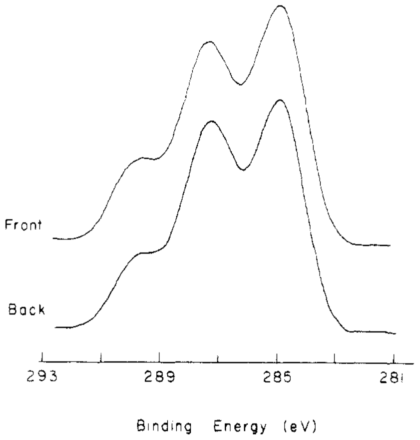

Figure 3. ESCA C_{1s} spectrum of LDPE exposed to 5% F_2/He mixture for 60 min; control experiment for comparison with later figures where UV flux from the plasma was included. The three peaks, left to right, reflect contributions from CF_2, CHF, and CH_2 groups, respectively.

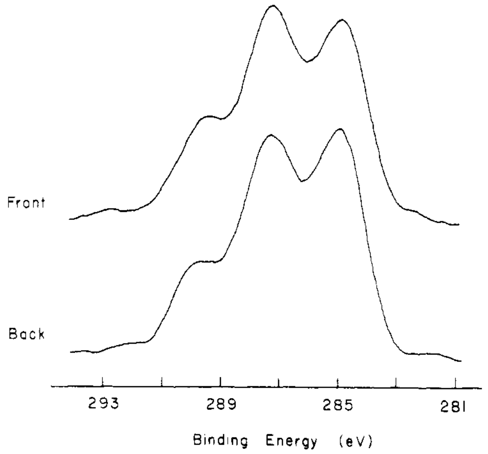

Figure 4. ESCA C_{1s} spectrum of LDPE exposed to 5% F_2/He and UV radiation from a 5% F_2/He plasma source; fused silica was used as the window material in the reactor.

Results

A parametric study involving a variety of reacting (fluorine containing) gases, plasma gases, UV windows, and polymer substrates was conducted. The first set of experiments used a 5% F_2/He premixture, used as received from Matheson Co., as both the reacting and plasma (UV source) gas; LDPE film (0.075 cm thick) was the polymer substrate. This LDPE film was used because ESCA analysis of the untreated polymer showed no sign of oxygen contamination. The motivation for using F_2/He was that this gas mixture has been employed extensively in the previous plasma and elemental fluorination reactions on polyethylene.[1,2,4] With this gas mixture the principal UV and vacuum-UV radiation flux is due to impurity gas emission. H_2O, H_2, O_2, O_3, CO, CO_2, and NO all emit radiation in this region (115–360 nm).[9,15,22] The excited molecule HeF* also emits below 200 nm.[23]

Initially a control experiment was performed without a plasma to verify that both sides of the polymer film would react at the same rate in the absence of any possible UV enhancement. Figure 3 compares the C_{1s} ESCA spectra of both surfaces and establishes that the reaction rate with F_2 is uniform in the absence of plasma (elemental reaction). The next experiment was conducted with a fused-silica (S1UV) window separating the plasma glow and polymer film. A slight increase in the extent of fluorination on the front side is evident in Figure 4. The final experiment in this series employed a MgF_2 window; the ESCA C_{1s} data are shown in Figure 5. A marked increase in conversion (to a perfluorinated product) is achieved on the surface exposed to the UV radiation. Simultaneous surface oxidation to about 5% on an atomic basis[21] was observed on both sides of the LDPE films in all cases. A slightly larger oxygen signal was detected on the irradiated ("front") surface. The nature of the oxygen species is not known; the formation of carbonyl functionalities, which would represent a chromophoric impurity, cannot be discounted.

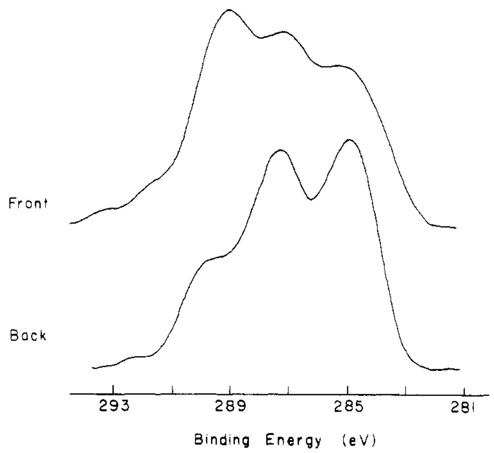

Figure 5. Same experiment as Figure 4, but with MgF_2 replacing fused silica as the window in the reactor. Note the large shift toward a perfluorinated surface for the "front" of the sample, which receives the UV flux. The shoulder above 291 eV in the spectrum of the "front" surface is associated with a small amount of CF_3 species (Table I).

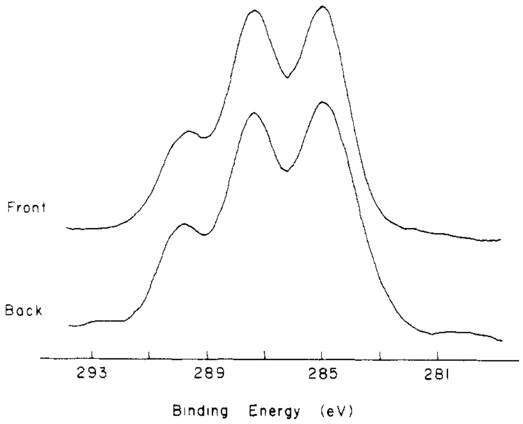

Figure 6. ESCA C_{1s} spectrum of LDPE exposed to 5% F_2/He and UV radiation from a H_2 plasma source; fused-silica window.

These experiments were repeated with 5% F_2/He as the reactive gas and pure hydrogen as the plasma gas. Hydrogen was chosen because its emission spectrum is well-known in the UV and vacuum-UV regions.[15] Hudis and Prescott[16,17] have demonstrated that photons produced in a hydrogen plasma are capable of cross-linking the surface of HDPE. The S1UV and MgF_2 data presented in Figures 6 and 7 for the case of the hydrogen plasma are very similar to the results of Figures 4 and 5 (5% F_2/He plasma). As in the previous experiments, slight oxidation was again observed on both surfaces.

The next series of experiments utilized polystyrene (Dow Tricite) as the reacting polymer. Polystyrene was studied because it contains aromatic groups which are known to absorb radiation strongly in the region near 260 nm. However, as fluorination progresses, aromaticity is lost and the absorbance region decreases in wavelength. The plasma gas and the reaction gas were both 5% F_2/He in

Table I
Percentage (Molar Basis) of CF_3 (3), CF_2 (2), CF (1), and CH_2 (H) Groups within the Surface Region As Determined by ESCA

polymer	reacn gas	plasma gas	window	surface	3	2	1	H
LDPE	5% F_2/He	5% F_2/He	control	front		11.1	42.7	46.2
LDPE	5% F_2/He	5% F_2/He	control	back		10.3	44.5	45.2
LDPE	5% F_2/He	5% F_2/He	S1UV	front		15.4	45.2	39.4
LDPE	5% F_2/He	5% F_2/He	S1UV	back		13.6	45.7	40.7
LDPE	5% F_2/He	5% F_2/He	MgF_2	front	1.9	35.0	31.8	31.3
LDPE	5% F_2/He	5% F_2/He	MgF_2	back		14.5	44.6	40.9
LDPE	5% F_2/He	H_2	S1UV	front		17.7	37.9	44.4
LDPE	5% F_2/He	H_2	S1UV	back		15.2	36.2	48.6
LDPE	5% F_2/He	H_2	MgF_2	front	2.1	34.9	33.6	29.4
LDPE	5% F_2/He	H_2	MgF_2	back		13.1	35.2	51.7
PS	5% F_2/He	5% F_2/He	S1UV	front		24.6	48.6	26.8
PS	5% F_2/He	5% F_2/He	S1UV	back		22.2	49.9	27.9
PS	5% F_2/He	5% F_2/He	MgF_2	front	0.9	44.0	26.3	28.8
PS	5% F_2/He	5% F_2/He	MgF_2	back		21.4	54.4	24.2

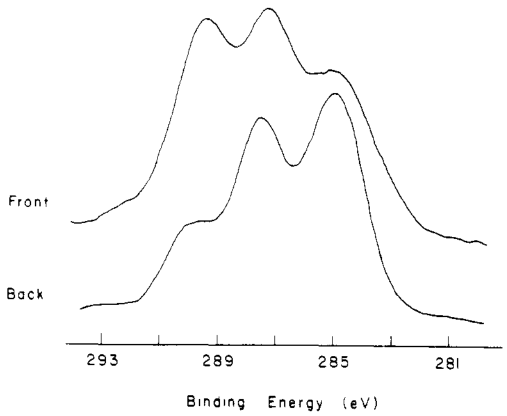

Figure 7. Same as Figure 6, but with MgF_2 replacing fused silica as the window in the reactor.

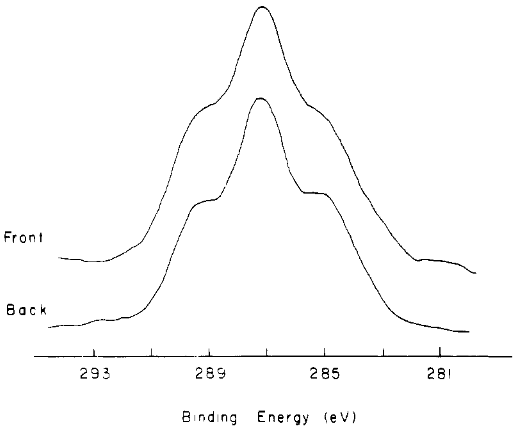

Figure 8. ESCA C_{1s} spectrum of polystyrene exposed to 5% F_2/He and UV radiation from a 5% F_2/He plasma source; fused-silica window.

these experiments. The ESCA C_{1s} spectra of reacted PS are shown in Figures 8 and 9 for experiments with S1UV and MgF_2 windows. The results are consistent with the LDPE samples; the MgF_2 window allows for a significant enhancement in reactivity at the polymer surface. A small amount of oxidation was also observed in these experiments.

The ESCA C_{1s} spectra of the LDPE and PS reactions were deconvoluted[21] into four peaks: CF_3, CF_2, CF/CHF, and CH_2 (includes "β"-shifted and pristine CH_2 peaks). The relative percentage of each species is listed in Table I. Note that CF_3 is only detected in reactions that utilize the MgF_2 window.

The effect of a single and double addition of fluorine to the polyethylene unit on UV-enhanced reactivity was also investigated by using poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVF_2) as model polymers. Both polymers were purchased in powder form from Scientific Polymer Products Co. and solvent cast[21] from *N*,*N*-dimethylformamide and dioxane, respectively. ESCA C_{1s} spectra from experiments utilizing the MgF_2 window are presented in Figure 10 for PVF and Figure 11 for PVF_2. The reacting and plasma gases were both 5% F_2/He in these reactions. The PVF data show a substantial increase in the concentration of CF_3 and CF_2 groups for the UV-irradiated surface. However, only a relatively small increase in the quantity of these groups is noted for the PVF_2 case. These results are consistent with the photochemical model mentioned in the Introduction. As fluorine is added

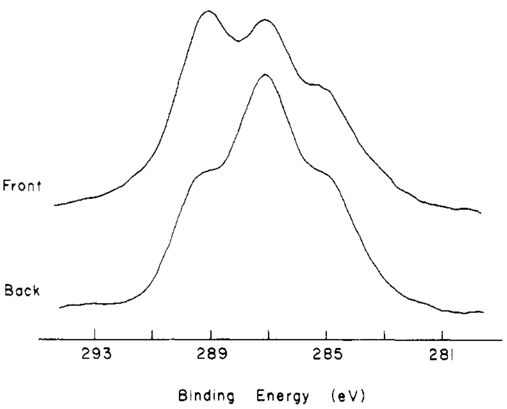

Figure 9. ESCA C_{1s} spectrum of polystyrene after photoassisted reaction; 5% F_2/He plasma source, MgF_2 window.

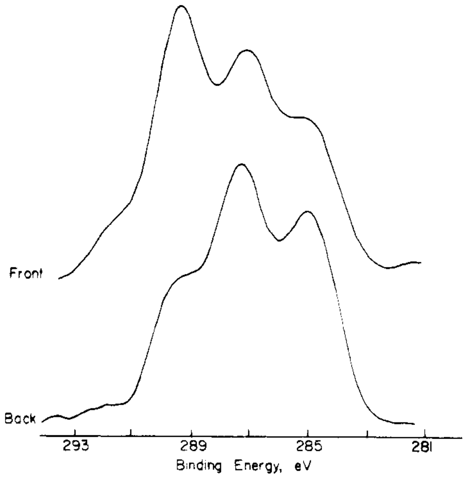

Figure 10. ESCA C_{1s} spectrum of poly(vinyl fluoride) after photoassisted reaction; 5% F_2/He plasma source, MgF_2 window.

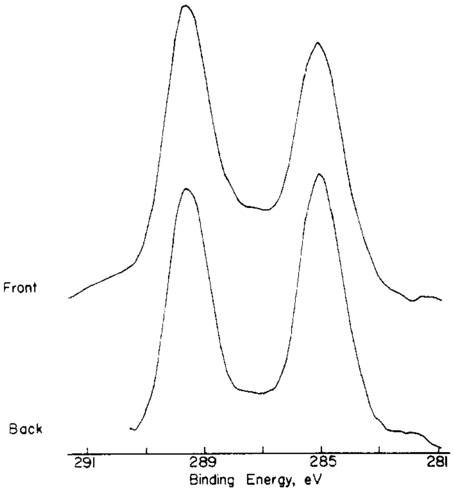

Figure 11. Same as Figure 10, but with poly(vinylidene fluoride) as the polymer substrate.

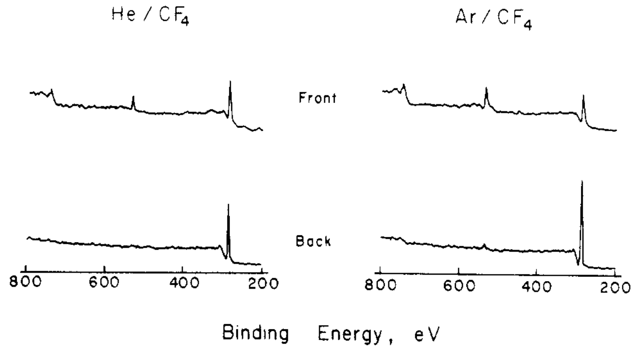

Figure 12. ESCA survey spectra of LDPE after photoassisted reactions using 10% CF_4/He and 10% CF_4/Ar mixtures in place of the 5% F_2/He gas mixture; MgF_2 window.

to the molecule, the region of absorbance should shift to lower wavelength.[14] For the PVF_2 polymer, only the radiation flux near the 115-nm cutoff is effective at photoinitiation within the polymer. Thus, the relative increase in conversion for PVF_2 should be smaller than for PVF or LDPE.

The picture that emerges from the data presented is that radiation below 180 nm is primarily responsible for reaction enhancement. This leads to the conclusion that high-energy photon interactions with the saturated polymer molecules near the surface are more significant than photon absorption by impurities and/or photodissociation of F_2 in the gas phase. Also, as the extent of fluorination increases, it becomes more difficult to induce photoinitiation within the polymer because the absorption limit shifts to shorter wavelengths.

All experiments described to this point have employed F_2 as the fluorinating gas. Additional experiments were performed by utilizing CF_4 and SF_6 as the fluorinating agent. Analysis of the data is somewhat more straightforward with these gases because they do not react in the elemental (nonplasma) mode and no "background" reaction in the absence of plasma needs to be considered. Thus any fluorination on the irradiated polymer surface would indicate a photochemical reaction.

LDPE was the polymer used in these experiments; the MgF_2 window was utilized in all cases. The plasma and reaction gas were chosen to be the same. Figure 12 presents ESCA survey spectra for 10% CF_4/He and 10% CF_4/Ar treatments. In both experiments oxidation is observed to occur preferentially on the irradiated surface. For an experiment utilizing 5% SF_6/He, no fluorination is again observed (Figure 13). An oxygen signal is detected on both sides of the polymer, so no statement can be made about photooxidation. These results can be rationalized with a thermochemical analysis. If a radical species is created by a photoprocess in the polymer phase, will a fluorine-containing molecule react with this site? Since thermochemical data are readily available for the relevant gas-phase species,[24] we will assume that the reaction is occurring exclusively in the gas phase. We take the ethyl radical ($CH_3CH_2\cdot$) to represent the polymeric hydrocarbon radical. If this ethyl radical is in the presence of F_2, CF_4, SF_6, or O_2, will they react? The answer is obtained by calculating the Gibbs free energy change for these reactions, as shown in Figure 14. According to these values, it is thermodynamically possible for F_2, SF_6, and O_2 to react; the CF_4 should not react because equilibrium is strongly shifted to the left. These predictions are in accord with all of the experimental data presented here except for the case of SF_6. Two possible reasons for this are that the reaction may be kinetically limited or the assumptions (gas-phase reaction, primary radical, and low molecular weight organics) may not be valid in this case.

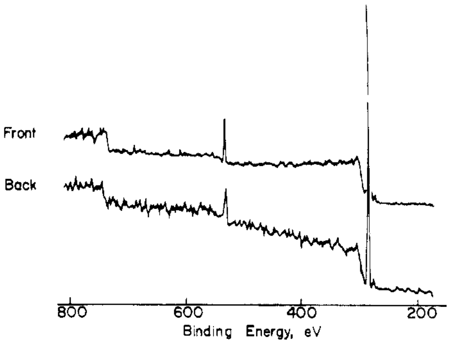

Figure 13. Same as Figure 12, but with 5% SF_6/He gas mixture.

THERMOCHEMISTRY

$\cdot C_2H_5(g) + F_2(g) \rightleftharpoons C_2H_5F(g) + F\cdot(g)$ $\Delta G^\circ_{300} = -67$ kcals/mole

$\cdot C_2H_5(g) + CF_4(g) \rightleftharpoons C_2H_5F(g) + \cdot CF_3(g)$ $\Delta G^\circ_{300} = +20$ kcals/mole

$\cdot C_2H_5(g) + SF_6(g) \rightleftharpoons C_2H_5F(g) + \cdot SF_5(g)$ $\Delta G^\circ_{300} = -15$ kcals/mole

$\cdot C_2H_5(g) + O_2(g) \rightleftharpoons C_2H_5OO\cdot(g)$ $\Delta G^\circ_{300} = -19$ kcals/mole

Figure 14. Thermochemical considerations for several reactions related to the surface modifications under investigation in this work.

Before concluding, two further comments should be made. First, it has been demonstrated[21] that photons in the range of interest (<160 nm) are absorbed within the outermost surface regions of the polymer (<50 nm). That is, the penetration depth of the radiation is much less than the thickness of the polymer (≈0.075 cm), which is consistent with the small perfluorination depths observed in prior work.[1,2,21] Secondly, the possibility of thermal activation, by absorbed radiation selectively heating the irradiated surface, has been discounted in a separate analysis presented elsewhere.[21]

Conclusions

The data presented in this paper establish that fluorination with F_2 and oxidation with O_2 are enhanced at a polymer surface by UV radiation; UV-enhanced reactions with CF_4 and SF_6 did not occur. The experimental results have been shown to be consistent with the photochemistry and thermochemistry of the reactants. Further analysis has supplied evidence which identifies photoexcitation/photoionization of the saturated polymer surface by vacuum-UV radiation as the key processes. The use of photons to activate a polymer surface for reaction appears to be an interesting process. For example, conventional photochlorination of polymers, e.g., photochlorination of polyethylene[25] and of poly(vinyl chloride),[10] employs UV light to dissociate the chlorine molecules and thus initiate a chain reaction. The mechanism of fluorine molecule dissociation appears to be relatively unimportant in the photofluorination reaction, probably because the maximum extinction coefficient for photodissociation of F_2 is an order of magnitude less than for Cl_2.[9]

On the other hand, the UV–polymer photoreactions appear to be an important component of the previously reported[1-4,21] plasma (glow and cage) and surface fluorination reactions, especially since both He and Ar possess strong emission lines below 115 nm. The total flux of vacuum-UV radiation in the plasma reactions may be much larger than in the photochemical experiments reported here. Also, reactive species produced in CF_4 and SF_6 discharges ($F\cdot$, F_2, $\cdot CF_3$, etc.) will participate in the photochemical reactions. Because photodissociation of F_2 was not a primary factor in these UV reactions, this does not imply that atomic fluorine is insignificant in the plasma environments. Electron impact dissociation of F_2 produces a large supply of fluorine atoms.

Acknowledgment. This research was funded by the Division of Engineering of the National Science Foundation. Helpful discussions with Dr. C. E. Schwier are gratefully acknowledged.

Registry No. PS, 9003-53-6; PVF, 24981-14-4; PVF_2, 24937-79-9.

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