Ultraviolet Photoelectron Spectroscopy Study of Synchrotron Radiation-Degraded Polyethylene Ultrathin Films

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The degradation of polyethylene caused by vacuum ultraviolet radiation emitted from a synchrotron was investigated by in situ ultraviolet photoelectron spectroscopy (UPS). Excellent agreement is obtained between the UPS of pristine polymer and the density of states calculated by ab initio molecular orbital method for *n*-decane, five units of an ethylene monomer. The UPS of degraded polymer is analyzed by comparison with molecular orbital calculations of degraded polymer models. The analysis indicates the presence of conjugated double-bond and cross-linked structures in the degraded polymer. The degree of the π conjugation generated upon the photodegradation is discussed.

Introduction

Because of its enormous usage in various industrial applications, the degradation process of polyethylene has been characterized extensively using different irradiation sources. Degradation caused by UV radiation was investigated by means of vibrational spectroscopy and UV−vis absorption spectroscopy,[1−3] and the generation of new chemical bonds in the photodegraded polymer is discussed. Obviously, the UV degradation process of the polymer is an important issue because it directly relates to the chemical and/or physical stability of the polymer under sunlight.

Influence of high-energy particle irradiation on polyethylene also has been investigated with electrons, ions, neutrons, and γ-rays as degradation sources.[4−8] Understanding of effects caused by these high-energy irradiations is valuable not only for academic but also for industrial interest. For example, such knowledge is crucial for evaluating the high-energy particle treatment of the polyethylene film used for prepackaged irradiated foods.[9]

In contrast to numerous publications regarding UV and high-energy particle irradiation, measurement of degradation induced by vacuum ultraviolet (VUV) radiation has not been conducted. The VUV photodegradation has the following unique features compared to those caused by UV and high-energy particles. In general, optical oscillator strengths of organic compounds are the maximum in the VUV energy region. This allows effective ionization and/or excitation of the inner and outer valence electrons of the polyethylene. Therefore, the polymer undergoes degradation very efficiently without help from photocatalysts or reaction-induced molecules such as ozone. Especially, in the energy region of <15 eV, direct photodissociation without ionization occurs with a relatively high yield for *n*-alkanes.[10] This distinguishes from the high-energy radiation chemistry where the secondary processes, after ionization, are most important. In the present work, broadband synchrotron radiation (zero-order light from beamline) was utilized as a VUV radiation source for degradation.

Various experimental techniques have been applied to characterize degradation processes in polyethylene. In addition to vibrational and UV−vis spectroscopies,[1,2,5,6,8] for example, electron paramagnetic resonance (EPR) for estimating free-radical concentration[5,6] and Rutherford backscattering (RBS) for evaluating residual hydrogen density[6] have been employed. Our analytical method of choice here is ultraviolet photoelectron spectroscopy (UPS) that probes the valence electronic structure of the polymer. Since valence electronic states possess rich information about chemical bonding as well as about the structure of a molecule, UPS is a powerful tool in the investigation of the photoinduced reactions. In the present article, UPS spectra of pristine and degraded polymer are analyzed by comparison with model molecular-orbital (MO) calculation results.

Experimental Section

Polyethylene powder (spectrophotometric grade) was purchased from Sigma-Aldrich and used without further purification. The ultrathin film samples were prepared by vacuum deposition on an Au-evaporated Si wafer at room temperature. The deposition rate was ∼0.1 nm/s, and the final film thickness was 10 nm as monitored by a quartz oscillator. This ultrathin film thickness is crucial for preventing sample charging upon photoemission measurements. The sample specimen was transferred to the measurement chamber through the atmosphere.

The photoelectron spectroscopy was performed at the beamline 6B of the Center for Advanced Microstructure and Devices (CAMD) synchrotron radiation facility; VUV radiation is monochromatized by a 3-m toroidal-grating monochromator. The photoelectrons were analyzed by a 50-mm radius hemispherical electron energy analyzer. The total electron energy resolution of the system was 1.5 eV, estimated from the Au Fermi edge. All UPS spectra were recorded at the normal emission with the photon incidence angle of 45° and at the photon energy of 80 eV. The binding energies of spectra presented here are calibrated relative to the Fermi level of the Au substrate.

Broadband synchrotron radiation (zero-order light from the beamline) was utilized for the polymer degradation. Estimated from reflectance of the beamline optical elements, intensity distribution of the zero-order light is between 10 and 150 eV with the maximum peak around 110 eV. No change in UPS

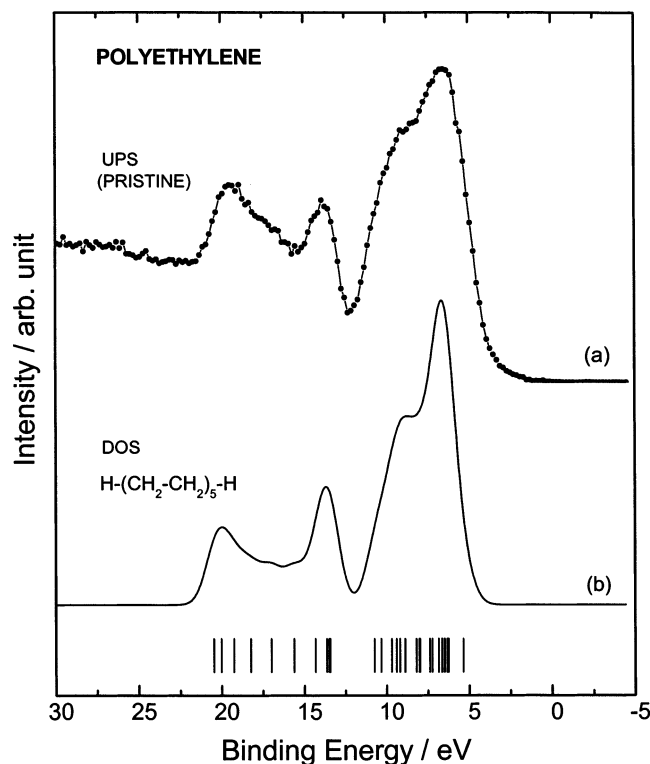* Corresponding author. Fax: +1−225-578-6954. E-mail: eizi@lsu.edu.

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Figure 1. (a) UPS spectrum of polyethylene film measured at $h\nu = 80$ eV. (b) DOS calculated by ab initio MO calculation (Gaussian 94W, 6-31G**) for *n*-decane, five units of polyethylene monomer. Molecular conformation was assumed as all trans in the calculation. Bars indicate the calculated binding energy of molecular orbitals. DOS curve is created from broadening the orbital binding energies by Gaussian with 1.5 eV fwhm. The binding-energy scale for the calculated orbital energy was contracted with a factor of 0.81 and shifted to appropriately align the peaks with the measured ones.

spectra was observed with only the monochromatic 80-eV photon excitation during data acquisition. The pressure at the UPS chamber during measurement was kept in 5×10^{-10} Torr.

Results and Discussions

Pristine Polyethylene ab initio MO Calculations. Theoretical valence band structure of polyethylene was derived through by MO calculations. First, calculations were performed using a semiemperical MO method (MOPAC PM3) with full structure and conformation optimizations. Then, a density of states (DOS) was calculated using an ab initio MO method (Gaussian 94, restricted Hartree−Fock/6-31G**). Preliminary model MO calculations were carried out for 1−6 units of the monomer terminated with hydrogen at the two ends (*n*-alkanes). PM3 calculations resulted in an optimized all-trans conformation. The calculated DOSs indicated very slight differences over the five monomer unit models. Therefore, the five monomer unit model (*n*-decane) was used in the calculations presented here.

The measured UPS spectrum and the calculated DOS for pristine polyethylene are compared in Figure 1. The UPS reveals good agreements with the published X-ray photoelectron spectroscopy (XPS) of polyethylene[11] and the UPS of long-chain alkanes.[12−14] The DOS is also very similar to those previously reported.[14,17] The binding-energy scale for calculated orbital energy was contracted with a factor of 0.81 and shifted to appropriately align the peaks with the measured ones. The DOS spectrum was obtained by convoluting a Gaussian function (full width at half-maximum (fwhm) of 1.5 eV) at each orbital energy. These corrections are standard
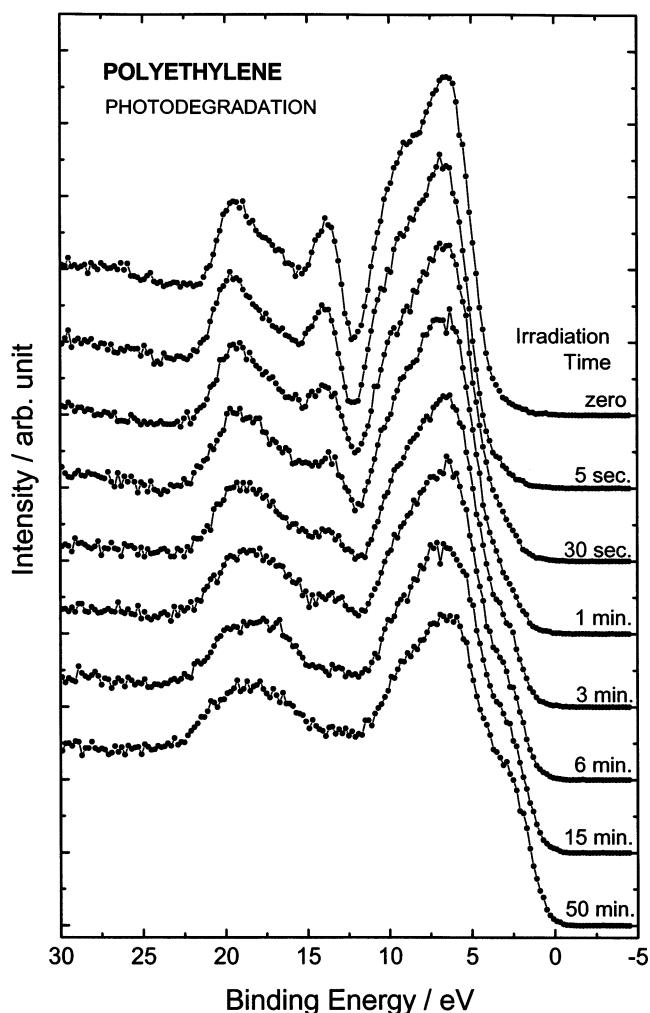

Figure 2. Photodegradation of polyethylene measured by UPS. Zero-order light from the beamline was used to degrade the polymer. UPS spectra were measured at $h\nu = 80$ eV.

procedures when comparing calculated DOS with measured UPS spectra.[15,16] As Figure 1 demonstrates, the DOS agrees quite nicely with the measured UPS, which shows that the electronic structure of polyethylene is well represented by the five-unit model. The major DOS peaks are assigned as follows: the first two peaks located at 5−12 eV mainly involve the orbitals of the C−H and C−C (mainly C 2p) bonds. The characteristic band located at 12−21 eV is associated principally with the carbon 2s orbitals from the polymer main chain. This band shape is a good indication regarding molecular conformation. In case of an all-gauche form, the DOS of this band exhibits a flatter shape.[14]

Photodegradation in Polyethylene. Polyethylene was degraded by the VUV broadband synchrotron radiation (Figure 2). The UPS spectra became broader and less structured upon photodegradation. The C 2s band located at 12−21 eV transformed into a broad single peak, and the intensity of the peak located at 7 eV became slightly smaller. A new peak appeared at the lower binding energy region of ~3 eV, and its intensity increased with increasing the exposure time. Because of the evolution of this new peak, the threshold energy of the degraded polymer moved toward lower binding energy and finally reached the Fermi edge. In general, π molecular orbitals (C=C bond) in organic compounds appear in the lowest binding energy region. Therefore, this new band is assigned to the C=C bonds (an additional argument for this assignment will be given by the MO calculations presented in the next section)
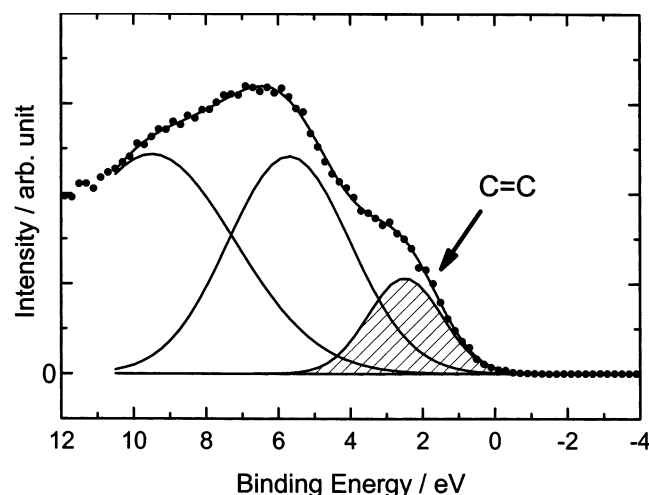
Figure 3. Deconvolution with three Gaussian functions in the low binding energy region of the UPS spectra (the bottom one in Figure 2). Hatched peak corresponds to C=C bonds.

created after dissociation of the C—H bonds in the degraded polymer. Generation of the C=C bonds in the degraded polyethylene has been reported already.[1,5] In the present work, the UPS also confirms the presence of C=C bonds in the VUV photodegraded polymer.

Figure 4 shows the exposure time development of the C=C band, intensity (area), position, and width of the peak. Those values were obtained by deconvoluting the measured UPS spectra (see Figure 3). Significant change and saturation behavior are observed at the beginning and the end of the degradation for all three quantities, respectively. The slow increase of the peak intensity at the late stage of the degradation (Figure 4a) accounts for loss of the hydrogen atoms in the degraded polymer film. As the number of C=C bonds increases, frequency of π-bond conjugation is expected to rise. As π conjugation increases, the threshold binding energy decreases. Therefore, the shift of the peak position to the low binding energy side (Figure 4b) clearly points out development of π conjugation in the degraded polymer. Finally, the increase of the peak width (Figure 4c) suggests coexistence of various lengths of conjugation in the polymer as the degradation proceeds.

Degraded Polyethylene ab initio MO Calculations. Degraded polymer MO calculations that focused on the degree of C=C bond conjugation were performed. The five monomer unit model involving different numbers of conjugated double bonds was simulated systematically. The series of calculated DOSs are presented in Figure 5 together with the measured UPS of the degraded polymer. In the MO calculations, conformation of the model molecule was assumed as all trans. The calculated DOSs clearly confirm that the peak generating at the low binding energy region during the degradation is indeed due to C=C bonds. It is also evident that the energy position of the HOMO shifts to the lower binding energy as the number of conjugated double bonds increases from $n = 1$ to $n = 5$. Since the measured peak position of the C=C bonds in the degraded polymer is ~2.5 eV (from Figure 4b), the conjugation model simulations in Figure 5 suggest that 2—3 conjugated double bonds are developed in the photodegraded polymer.

Although the above conjugated model interprets well the generation of C=C bonds responsible for the low binding energy region of the measured UPS, it does not explain the spectral change observed at the C 2s band (12—23 eV binding-energy region in Figure 2) upon degradation. As seen in Figure 5, the
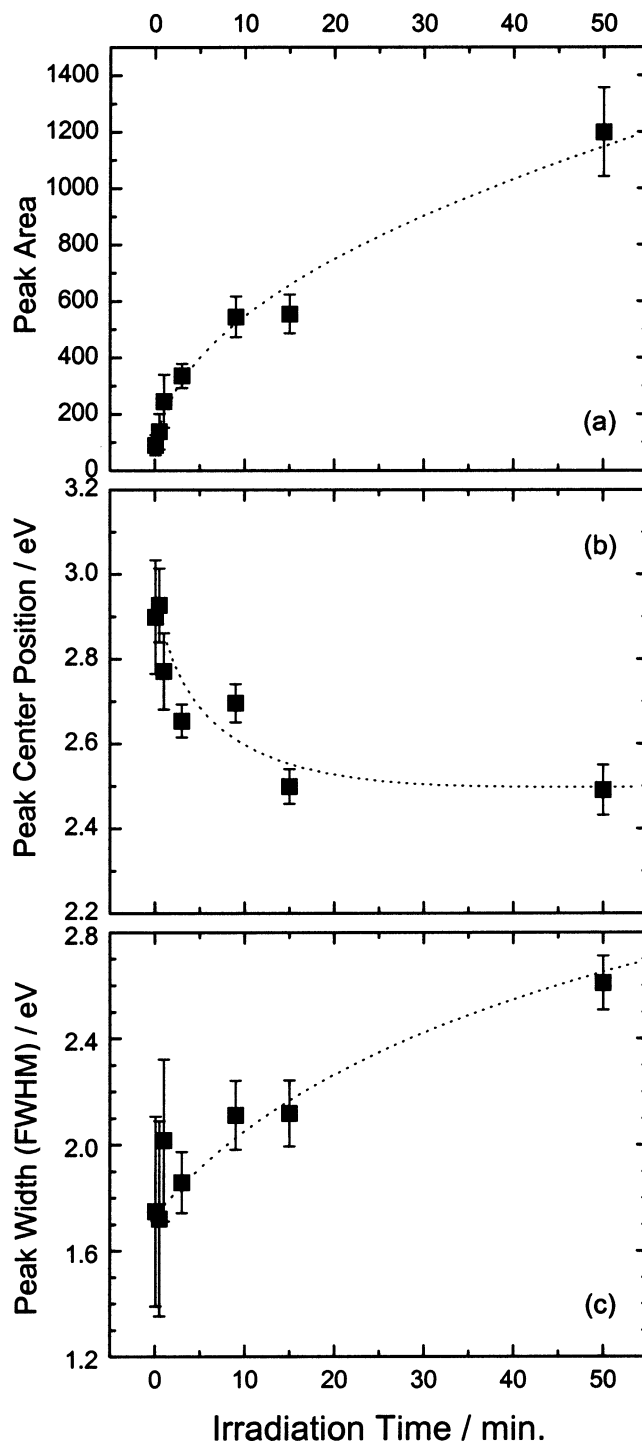

Figure 4. Evolution of the C=C band, (a) peak intensity, (b) peak position, and (c) peak width (fwhm), as a function of the irradiation time.

DOS feature of the C 2s band clearly differs from the unstructured broad shape of the observed band. Therefore, an additional chemical structure must coexist along with the conjugated C=C bonds in the actual polymer. One explanation is cross linking between the polymer chains. A variety of structures can be considered for a cross-linked product. As an example, the calculated DOS for a cross-linked structure involving five-, six-, and eight-member rings is presented in Figure 6. In this model, three chains, each containing seven carbon atoms, are cross linked at multiple locations. Since the distance between the chains becomes closer once cross linkage is established at a single site, multiple linkages are more likely
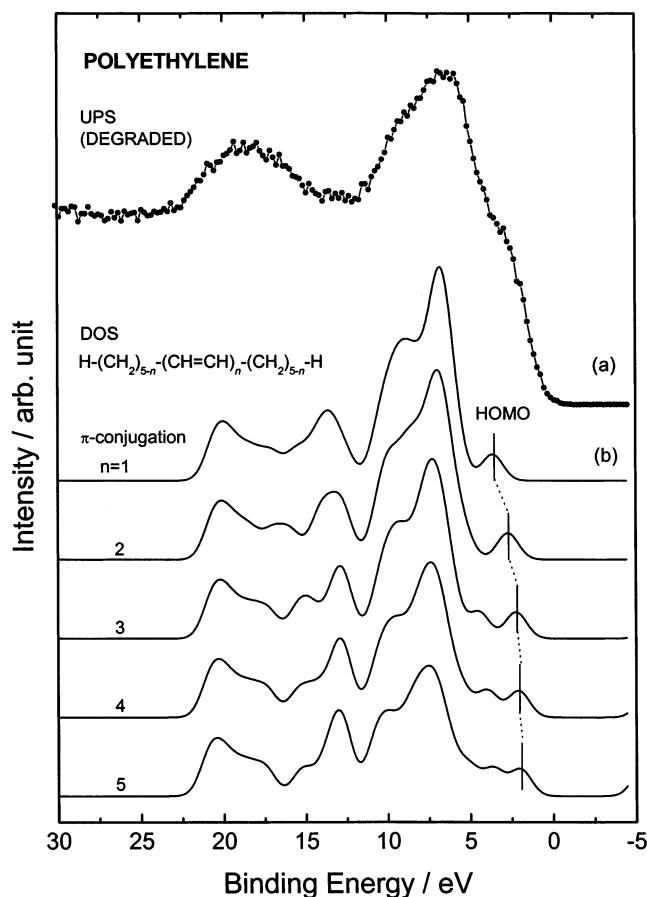
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Figure 5. Ab initio MO calculations for photodegradation. (a) Measured UPS for photodegraded polyethylene (the bottom one in Figure 2) and (b) a series of calculated DOS involving π conjugation. Number of conjugated C=C bonds in the five-monomer unit (denoted by n) was varied systematically. The binding-energy position of the HOMO is indicated by bar. Molecular conformation used in the calculations was the all-trans form. The binding-energy scale of DOS was contracted by 0.81, and DOS peaks were broadened by Gaussians (1.5 eV fwhm).

to occur at other atoms. Such multiple linkage creates various kinds of ring structures that distort carbon-chain angles from pure sp^2 and sp^3 configurations. Thus, cross linking effectively destroys a long-term periodicity of the polymer. This effect is realized clearly at the C 2s band feature of the calculated DOS in Figure 6, where the molecular orbitals are located at the middle area of the whole band instead of at the side areas seen in the DOS for the pristine polyethylene (Figure 1). The C 2s band feature calculated for the cross-linked structure resembles well the observed band in the degraded polymer (Figure 6), thus suggesting a possible involvement of the cross-linking structure in the degraded polymer. Occurrence of the cross linking is considered to be one of the limiting factors responsible for the relatively low degree of conjugation estimated in the degraded polymer.

Conclusions

Degradation of polyethylene induced by VUV irradiation was investigated in situ by UPS. The photoemission spectra of pristine and photodegraded polymer were successfully analyzed by comparing with DOS obtained from ab initio MO calculations. The analysis provided clear evidence for the presence of C=C bond and cross-linked structures in the degraded polymer. It was concluded that 2−3 conjugated double bonds are developed in the degraded polymer. Although the UPS/MO
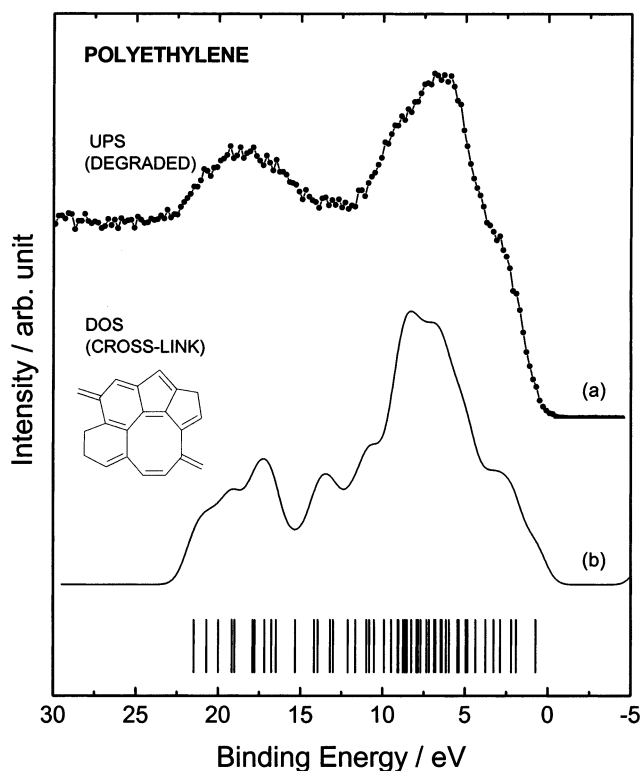

Figure 6. (a) Measured UPS for photodegraded polyethylene (the bottom one in Figure 2). (b) Calculated DOS for a model molecule involving cross-linking structure shown in the figure. The binding-energy scale of DOS was contracted by 0.81 and DOS peaks were broadened by Gaussians (1.5 eV fwhm).

technique is proven to be a very useful analytical tool, as described in this article, the diversity of structures produced in the degradation prevents a more definitive elucidation of the reaction process occurring during photodegradation.

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