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ARTICLE

On the Mechanism of Polyenyl Photoconversion in Irradiated Ultrahigh Molecular Weight Polyethylene

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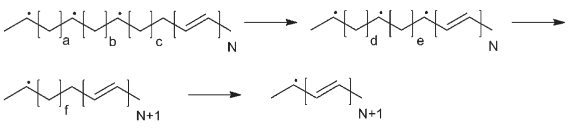
ABSTRACT: The mechanism of polyenyl radical creation upon photoirradiation of ultrahigh molecular weight polyethylene (UHMWPE) containing free radicals is shown to be direct photoconversion from lower to higher order polyenyls. Therefore, the total radical concentration remains unchanged during this process. The rate of photoconversion is identical in the presence and absence of oxygen but is suppressed by hydrogen gas. This demonstrates that the conversion does not occur by a linear alkyl radical addition mechanism wherein alkyl radicals migrate to stable polyene unsaturations and polyenyl radicals, thereby increasing their order, as was previously suggested. Monochromatic photoirradiations show that dienyl radicals are created from diene unsaturations, when photoirradiated at 235 nm, and from allyl radicals, when photoirradiated at 275 nm. Additionally, it is shown that polyene unsaturations are not created during this process, and unlike allyl radicals, polyenyl radicals do not photoconvert to alkyl radicals.

Introduction

The photochemistry of polyethylene is a long studied problem. One of the first studies of the photochemistry of polyethylene containing free radicals was conducted by Ohnishi et al.,[1] wherein they observed that the allyl free radical was converted to the midchain alkyl free radical by ultraviolet light via reaction 1.

(1)

It was noted that this process could be reversed by heating to room temperature, although many of the alkyl radicals decayed in the process. Although not noted, it is clear from their ultraviolet absorption spectra that diene unsaturations were consumed and that dienyl, trienyl, and tetraenyl free radicals were created. Similar results were obtained by Dole et al.,[2] who were also able to assign ultraviolet absorption peaks and molar absorptivities to several higher order polyenes and polyenyls.[3] A reaction scheme involving the linear addition of alkyl radicals, reaction 2, which was initially proposed for the ionizing radiation generation of polyenyl radicals,[4] was suggested as the mechanism for polyenyl photogeneration.[5]

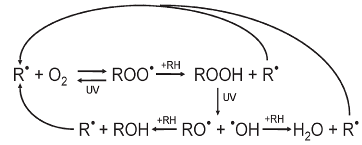


(2)

where $a-f$ are some integers greater than or equal to one. In reaction 2, an alkyl radical migrates to the allylic site of a polyene unsaturation, transforming it to a polyenyl radical. In the next step, another alkyl radical migrates to the polyenyl radical and recombines with it, forming a polyene whose degree of unsaturation has increased by one order. This process can repeat, increasing the degree of unsaturation. It is worthwhile to note that reaction 2 competes with the decay of alkyl radicals via cross-linking and disproportionation. The validity of this mechanism was never verified, and there is reason to question it. Polyenes are transformed into polyenyls via both the intra- and intermolecular migration of alkyl radicals, whereas polyenyls are transformed into polyenes via the intramolecular recombination of radicals. It is known that intermolecular migration is significantly faster than intramolecular migration, even in the crystalline region.[6] Therefore, it is surprising that the radicals should recombine intramolecularly, resulting in an unsaturation, instead of intermolecularly, resulting in a cross-link. It is the purpose of this article to determine the mechanism for polyenyl creation in photoirradiated polyethylene containing free radicals.

Reaction 2 requires an adequate number of alkyl radicals per chain. It is known that oxidation products, such as ketones,[7,8] peroxyl free radicals,[9] and hydroperoxides,[10] decay under ultraviolet light, often resulting in the creation of alkyl radicals and main chain scission. A reaction scheme resulting in a continuous supply of alkyl radicals is shown in Scheme 1. Therefore,

Scheme 1. Reaction Scheme Resulting in a Continuous Supply of Alkyl Radicals upon Photoirradiation in an Oxygen-Rich Environment[a]



[a] Carbon-centered radicals combine with oxygen, forming peroxyl radicals which can then abstract a hydrogen from a nearby chain, producing organic peroxide and an alkyl radical. The peroxide photodecays into an alkoxy and hydroxy radical, both of which can abstract a hydrogen resulting in the creation of two more alkyl radicals. Thus, upon photoirradiation in an oxygen-rich environment, one alkyl radical can produce three alkyl radicals which can then produce even more radicals.

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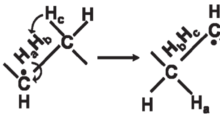
Scheme 2. Reaction Scheme Depicting the Hydrogen Catalysis of Intramolecular Radical Migration



according to reaction 2, the increase in degree of unsaturation should proceed faster in an oxygen-rich environment.

Hydrogen gas is known to increase the rate that alkyl radicals convert to allyl radicals.[11] Cracco et al. suggest that hydrogen catalyzes intramolecular migration along the chain by helping to bridge the 1.93 Å distance between adjacent hydrogen atoms along the chain via a concerted mechanism during which the hydrogen atom is never completely free[12] (Scheme 2).

Thus, hydrogen gas has a marked effect on the *rate* of alkyl decay but has no effect on the *extent* of the decay.[13,14] Since reaction 2 requires intramolecular recombination, one would expect hydrogen gas to catalyze the increase in degree of unsaturation.

Additional insight into the mechanism of polyenyl creation can be gained by photoirradiating at specific wavelengths. For example, it has been calculated[15] that it is energetically favorable for polyenyl radicals to photoconvert to alkyl radicals in an reaction analogous to reaction 1. It is unclear if this photoconversion occurs or if it plays a significant role in the increase in degree of unsaturation.

Experimental Section

Methods. Medical grade UHMWPE (GUR 1050) was microtomed into three 200 μm films. Two films were loaded into a glovebox filled with high purity nitrogen and sealed in J-young resealable EPR tubes. One film was placed in a standard EPR tube, evacuated to ultrahigh vacuum overnight, backfilled to 150 Torr of ultrahigh purity hydrogen, and flame-sealed. All of the films were irradiated with a 7 MeV electron-beam to a dose of 100 kGy. After irradiation, one of the glovebox films was opened to air. While the sealed nitrogen sample contains some oxygen, both from oxygen dissolved in the film and from oxygen in the glovebox environment, the concentration is much lower than that of the air sample. In contrast, due to the extended period in ultrahigh vacuum and purity of the hydrogen gas, the hydrogen sample is virtually oxygen free.

All three films were simultaneously photoirradiated using a 325 W short arc xenon lamp at a distance of 44 cm (Schoeffel Instruments Corp., Westwood, NJ), ensuring even photoirradiation of all three samples. The lamp emits a continuous spectrum from 200 nm to the IR region, and the lamp's output between 300 and 390 nm at 44 cm was measured (Blak-Ray model J221, Upland, CA) to be 5200 ± 340 μW/cm^2. At various time intervals, the films were removed for measurement. EPR measurements were performed while the samples were still in their tubes. Three measurements were averaged for each data point. UV spectra were measured for the air sample in air, while the UV spectra for the nitrogen sample were performed with the film in a nitrogen-filled, quartz cuvette. It was not possible to measure the UV spectra for the hydrogen sample without destroying the hydrogen environment so only a final measurement at the conclusion of photoirradiation was performed. Three measurements were averaged for each data point. In order to investigate the effect of photon flux density, the experiment was repeated in an air and nitrogen environment using a lower power compact short-arc xenon lamp at a distance of 60 cm, reducing the estimated incident light power by a factor of 4.

In order to determine the wavelength dependence of various photoreactions in polyethylene, 200 μm films of UHMWPE were irradiated in a nitrogen environment to a dose of 100 kGy and annealed at 100 °C in a nitrogen environment for 4 h, which removed unstable radicals and prevented subsequent, nonphotoinduced radical decay. The films were then subjected to monochromatic photoirradiation by passing the light from the 325 W xenon lamp through a high intensity monochromator (Bausch & Lomb, Cat. #33-86-27, Rochester, NY). In order to increase signal strength, the monochromator was reduced from double-slit to a single-slit operation. However, even then, the amount of transmitted light was at levels below the detection threshold of the photodetector (< 100 μW/cm^2), and considerably longer photoirradiation times were required. The wavelengths investigated were 235, 258, 275, 285, 310, and 323 nm, corresponding to peak absorbance of diene, allyl, triene, dienyl, tetraene, and trienyl, respectively. Additionally, photoirradiation through a Corning glass filter #3965 was performed to determine the effect of longer wavelengths (> 320 nm). For all samples, a nonphotoirradiated control was also created to verify that all radical changes were photoinduced. EPR and UV–vis spectra were taken at various time intervals. All photoirradiations and measurements were performed in a nitrogen environment.

Table 1. Absorption Maxima and Molar Absorptivities for Various Conjugated Unsaturations and Free Radicals (Numbers with an Asterisk Are Estimations)

	absorption maximum, nm		molar absorptivity, M^{-1} cm^{-1}	
order	unsaturation	free radical	unsaturation	free radical
1	N/A	258	N/A	7 300[3]
2	235	285	25 000[16]	29 000[3]
3	275	323	41 800[16]	46 000*
4	310	359	58 900[17]	63 000*
5	340	396		80 000*

Measurement and Characterization. All EPR measurements were performed with an ESP300 spectrometer (Bruker Biospin, Billerica, MA) using the following instrument parameters: microwave frequency of 9.42 GHz, microwave power of 0.5 mW, frequency modulation of 100 kHz, modulation amplitude of 6.23 G, receiver gain of 50 000, center field at 3350 G, sweep width of 300 G, conversion time of 2.54 ms, and time constant of 2.54 ms. It was verified that the modulation amplitude as well as the ratio of the conversion time to time constant did not distort the signal. While the alkyl radical's signal is slightly power-saturated at 0.5 mW, this power was used for improved signal quality. Thirty scans were added to improve signal-to-noise ratio. Double integrations to determine radical concentrations were performed using the same software that controls the instrument following the integration procedure described in Bruker Technical Note 6.

All UV–vis measurements were made using a Cary-3 spectrophotometer (Varian, Palo Alto, CA) between 200 and 550 nm. A film holder was modified by inserting a piece of aluminized polyethylene containing a slit that was slightly smaller than the PE films being measured, ensuring that light was transmitted only through the films. For measurements in an air environment, PE films of comparable thickness were inserted into both the measurement and reference beam. For measurements in a nitrogen environment, the sample film was loaded into a glovebox, placed in a film holder that was machined to fit into a quartz cuvette, and sealed with a rubber stopper. The reference sample was contained in a similar film holder in a quartz cuvette but was exposed to air. Changes in concentration were calculated by measuring the change in peak height after a linear baseline correction. Since the molar absorptivity for many polyenyl radicals is not known, values were estimated based on the observation that the molar absorptivity increases for the diene, triene, and tetraene compounds[16] by 17 000 M^{-1} cm^{-1} for each degree of unsaturation. It is also known that the molar absorptivity of the dienyl radical is 4000 M^{-1} cm^{-1} greater than diene unsaturation.[3] A list of molar absorptivities for various

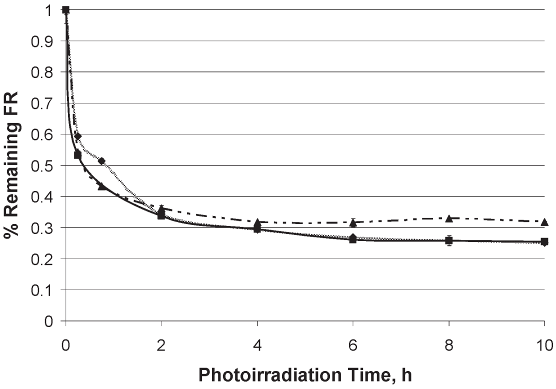


Figure 1. Change in total free radical concentration upon unfiltered photoirradiation at high light fluence in an air (◆), nitrogen (■), and hydrogen (▲) environment. After 2−4 h of photoirradiation, the radical concentration does not significantly change.

conjugated unsaturations and radicals is shown in Table 1. While estimation of molar absorptivity creates uncertainty in the absolute concentration of the radicals, it is worthwhile to note that their relative concentrations are still precise.

Results and Discussion

Effect of Photoirradiation Environment. The decay in the overall concentration of free radicals, as determined by the integration of the EPR spectra, is shown in Figure 1. It is clear that the total free radical concentration does not significantly change from 4 to 10 h of unfiltered photoirradiation. While the overall radical concentration does not change during this time, the types of free radicals present do. The change in concentration of various conjugated species upon increase photoirradiation, as determined by UV spectra peak height, is shown in Figure 2. Overall, the change in free radical types does not depend on oxygen content, but strongly depends on light fluence. After 2 h of photoirradiation at high fluence, the diene unsaturation concentration is sharply reduced while the dienyl and other radical concentrations are increased. After 4 h, the concentration of dienyl radicals begins to decrease and the trienyl concentration peaks. Continued irradiation reduces the concentration of dienyl and trienyl radicals while tetraenyl and pentaenyl radicals continue to increase. A similar pattern is seen at low fluence except that the increases and decreases occur more slowly. Also, higher order free radicals like tetra- and pentaenyl are substantially suppressed. The lack of a significant difference between an oxygen-rich and -poor environment strongly implies that the mechanism for the increase in degree of conjugation does not involve an alkyl intermediate.

A comparison of the final concentration of various conjugated species after 10 h of photoirradiation in different environments can be seen in Figure 3. The concentration of diene unsaturations and dienyl and trienyl radicals is higher and the concentration of tetraenyl and pentaenyl radicals is lower after photoirradiation in hydrogen as compared to other environments. Therefore, the presence of hydrogen gas suppresses, not enhances, the rate of increase in degree of unsaturation. Similar results are seen upon comparison of the evolution of the EPR spectra, as seen in Figure 4. The spectral evolution in hydrogen is similar to, but slower, than the evolution seen in the other environments. This strongly suggests that the mechanism for the increase in degree of conjugation does not involve intramolecular radical recombination.

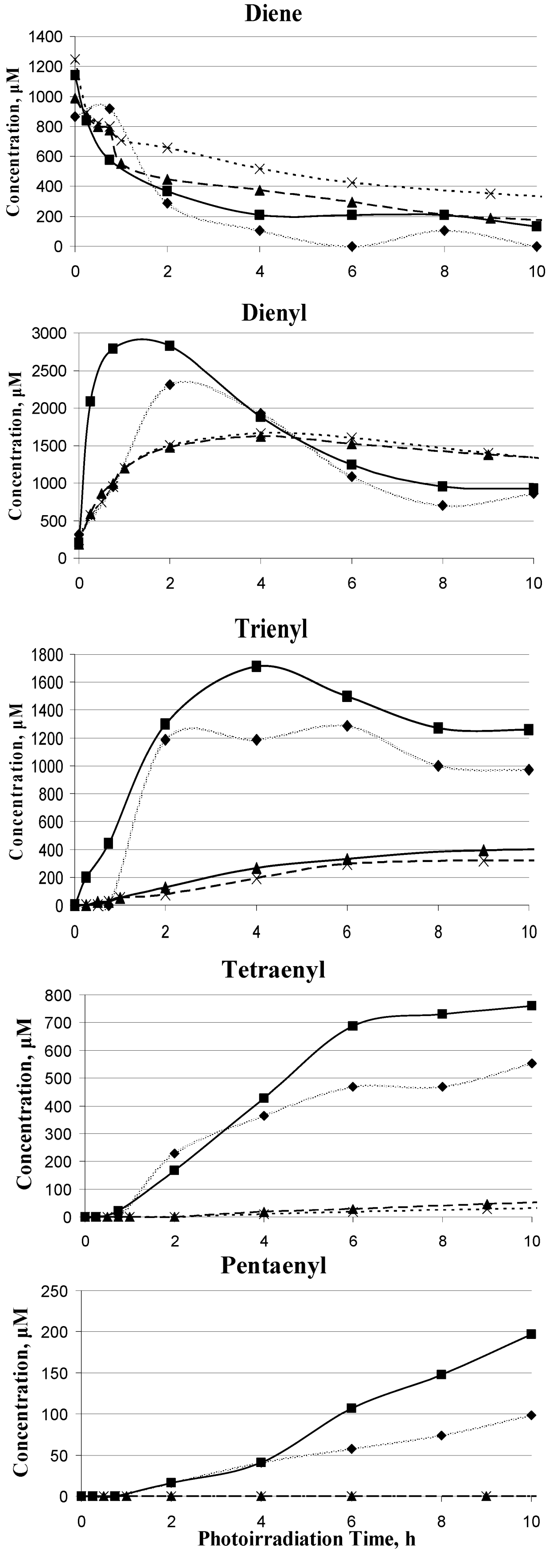


Figure 2. Change in concentration of various conjugated species upon unfiltered photoirradiation at high fluence in an air (◆) and nitrogen (■) environment and at low fluence in an air (▲) and nitrogen (×) environment. Note the difference in scale.

Effect of Photoirradiation Wavelength. In order to better understand the photochemistry of irradiated polyethylene, monochromatic photoirradiations were performed. The change in the UV spectra upon irradiation at 235 nm can be seen in Figure 5. After 68 h of photoirradiation, an approximately equal decrease in the concentration of diene unsaturations and increase in the concentration of dienyl radicals is observed. This implies a direct photoconversion of diene unsaturations to dienyl radicals, presumably via the breaking of the weaker (12 kcal/mol[18]) allylic C−H bond, reaction 3.

(3)

While diene unsaturations are consumed when they are photoconverted into dienyl radicals, it is not the sole source of diene photodecay. It is known that unsaturated dienes react with oxygen when in an excited triplet state.[5] This reaction may be the cause of reduced concentration of diene unsaturations in samples that were photoirradiated in air and, to a lesser extent, in nitrogen (FTIR analysis showed that some photo-oxidation occurred during photoirradiation in the nitrogen environment) (see Figure 3).

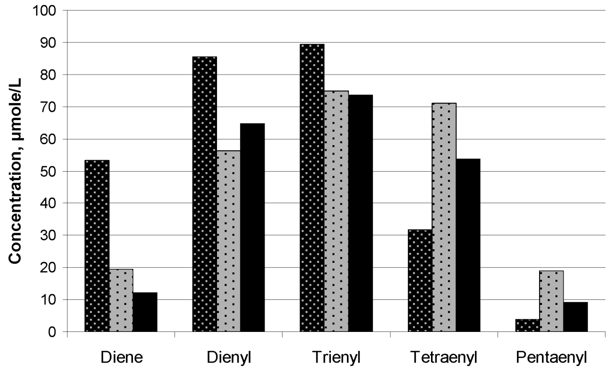


Figure 3. Concentration of various conjugated species in irradiated polyethylene after 10 h of photoirradiation in a hydrogen (shaded bar), nitrogen (dotted gray bar), and air (solid bar) environment. Note that the rate of increase of degree of conjugation is suppressed, not enhanced, in a hydrogen environment.

The change in UV spectra upon photoirradiation at 258 nm is shown in Figure 6. After 23 h of photoirradiation, there is a noticeable decrease in the concentration of allyl radicals and a slight increase in dienyl radicals. After 67 h of photoirradiation, the dienyl radical concentration continues to increase, but the allyl radial concentration does not decrease any further. The decrease in allyl radical occurs through the well-known photoconversion of allyl to alkyl at 258 nm (reaction 1). It is tempting to attribute the increase in dienyl radicals to the migration of the photogenerated alkyl radicals to diene unsaturations. However, it is clear the dienyl radical concentration continues to increase after all allyl radicals photoconvert to alkyl radicals. The continued increase in dienyl radicals cannot be attributed to a delay in the migration of the alkyl radicals to diene unsaturations since, in a similar experiment wherein polyethylene was photoirradiated for 23 h at 258 nm and then allowed to sit at room temperature for a day, no increase in the dienyl radicals is observed. Rather, it appears that the increase in dienyl radicals is a direct photoproduct.

The change in the UV spectra of a nonannealed film of irradiated UHMWPE upon photoirradiation at 275 nm is shown in Figure 7. The concentration of allyl radicals continuously decreases and the concentration of dienyl radicals continuously increases throughout 75 h of photoirradiation. After correction for differences in molar absorptivity,

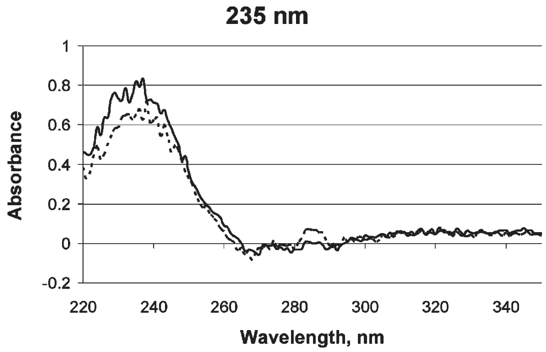


Figure 5. UV spectra before (solid line) and after (dashed line) photoirradiation for 68 h at 235 nm. Note that upon photoirradiation absorbance decreases at 235 nm and increases at 285 nm, corresponding to a decrease of diene unsaturations and an increase of dienyl radicals.

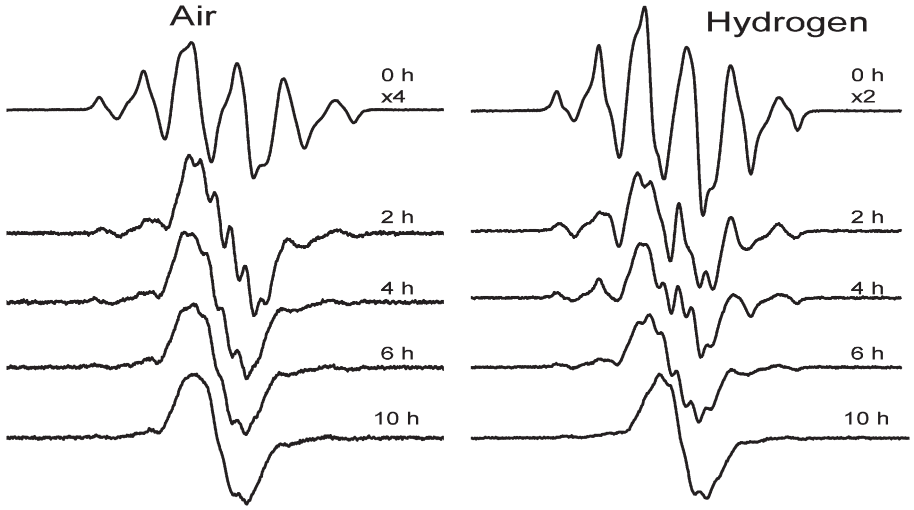


Figure 4. Evolution of the EPR spectra with increasing photoirradiation time in an air and hydrogen environment. The initial spectrum was reduced by either a factor of 2 or 4. The spectral evolution was nearly identical in an air and nitrogen (not shown) environment. The spectral evolution in a hydrogen environment is similar to, but slower than, the evolution in air.

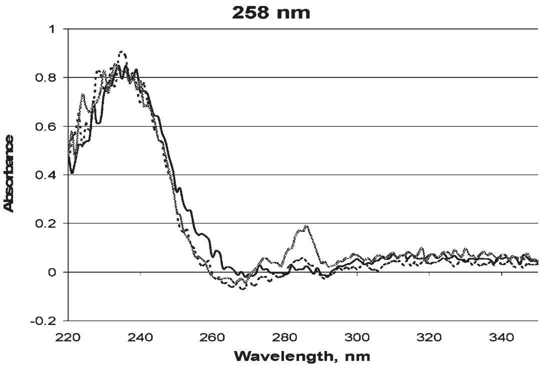


Figure 6. UV spectra before (solid line) and after 23 h (dashed line) and 67 h (faded line) of photoirradiation at 258 nm. A decrease in absorbance at 258 nm, corresponding to a decrease in the concentration of allyl radicals, is observed only after the first 23 h of photoirradiation. A steady increase in absorbance at 285 nm, corresponding to a continuous increase of dienyl radicals, is observed throughout the entire 67 h of photoirradiation. The fact that the increase in dienyl radicals only occurs during photoirradiation implies that it is a direct photoirradiation product.

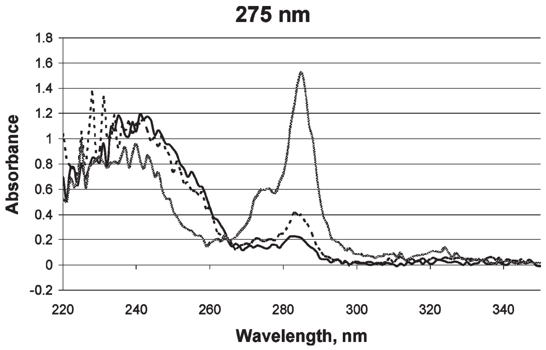


Figure 7. UV spectra before (solid line) and after 25 h (dashed line) and 75 h (faded line) of photoirradiation at 275 nm of a nonannealed irradiated UHMWPE film. Throughout the entire photoirradiation, the allyl radical concentration decreases and the dienyl radical concentration increases by approximately the same amount, suggesting the direct photoconversion of allyl to dienyl radicals.

the change in concentrations are approximately equal, strongly implying a direct photoconversion of allyl to dienyl radicals, presumably via the removal of two allylic hydrogens, reaction 4.

(4)

No change is observed in the spectra after photoirradiation at 285, 310, 323, and greater than 320 nm wavelengths. This demonstrates that, unlike allyl radicals, dienyl and trienyl radicals do not photoconvert to alkyl radicals. It is also evident that longer wavelengths do not play a significant role in the photochemistry of polyenyl radicals. It is somewhat surprising that the photoconversion of dienyl to trienyl radicals is not observed at 310 nm while the photoconversion of allyl to dienyl at 275 nm is observed. This observation is addressed below.

Polyene Unsaturations. From Figure 7, it is clear that the dienyl radical has a shoulder at 275 nm which is usually attributed to the triene unsaturation.[16] Indeed, after 10 h of unfiltered photoirradiation, the UV spectra contains peaks usually attributed to higher order polyenes. Despite having similar molar absorptivities (Table 1), these peaks were significantly smaller than their 1-order-lower polyenyl counterparts. The seeming presence of polyene unsaturations can be misconstrued as evidence for the alkyl addition reaction mechanism (reaction 2) which predicts the presence of polyene unsaturation intermediates. However, upon exposure to air for 50 h all peaks usually attributed to polyene unsaturations, except for the diene unsaturation, are absent. During this time, all peaks attributed to polyenyl radicals also decay. The decay of polyenyl radicals is expected and occurs via the combination with oxygen to form peroxyl radicals. However, the decay of polyene unsaturations is unexpected as unsaturations should be stable upon exposure to air. This effect has been previously observed and attributed to free radical initiated oxidation of the polyene unsaturations.[5] However, a similar experiment wherein photoirradiated polyethylene was annealed at 150 °C for 4 h in a nitrogen environment shows that UV peaks attributed to polyene unsaturations disappear. Further, diene unsaturations do not oxidize upon exposure to air, even when free radicals are present. Therefore, the reduction in polyene unsaturations cannot be attributed to their oxidation. A more plausible explanation is that polyenyl radicals have multiple absorption peaks, some of which coincide with polyene unsaturations. Polyene unsaturations are also known to have multiple absorption peaks, a fact which has been attributed to different C=C stretching.[19] Therefore, it would seem that there is a negligible concentration of higher order polyene unsaturations in photoirradiated polyethylene.

Polyenyl Radical Mechanism. It would seem that the alkyl radical addition scheme, reaction 2, is not the mechanism for the conversion of lower order to higher order polyenyl radicals as the rate of photoconversion was not accelerated in an oxygen-rich or hydrogen environment. Given the above experimental results, the most likely mechanism for the creation of higher order polyenyl radicals is the direct conversion from lower order to higher order via reaction 5.

(5)

The evidence supporting this reaction is (1) it allows for an increase in degree of conjugation without a decrease in the number of free radicals, (2) it does not involve polyene unsaturations, (3) its rate would not be affected by the oxygen content in the photoirradiation environment, (4) it is a direct analogue of the photoconversion of the allyl radical to the dienyl radical observed to occur at 275 nm, and (5) it predicts an increase in conversion rate with increasing light fluence. The fact that higher order polyenyl radical production is severely suppressed at lower light fluences suggests that this is a multiple photon process. This may explain why low power monochromatic photoirradiation at 310 nm does not convert dienyl radicals to trienyl radicals. While it is possible that the suppression of this reaction in a hydrogen environment is due to the back-reaction of reaction 5, this is deemed unlikely since the addition of hydrogen to the unsaturation will destabilize the radical by reducing the number of carbon atoms over which it is delocalized.

Conclusions

The principal finding of this work is that upon photoirradiation polyenyl radicals are directly created in irradiated polyethylene and do not involve alkyl radical or polyene unsaturation intermediates. Dienyl radicals were observed to be directly created from diene unsaturations and allyl radicals via the removal of allylic hydrogens by photoirradiation at 235 and 275 nm, respectively. Higher order polyenyl radicals are presumably created via the removal of allylic hydrogens from lower order polyenyl radicals via a successive photon process. Further experiments are required to determine the quantum efficiency of these photoreactions. It was also determined that, unlike allyl radicals, polyenyl radicals do not photoconvert to alkyl radicals, although it is unclear why. It is also unclear why hydrogen gas suppresses the creation of higher order polyenyl radicals, and further study into the effect of hydrogen gas on radical photochemistry of polyethylene is required.

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