Real-Time Monitoring of Laser Photochemical Reactions of Polyvinylchloride

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ABSTRACT: The formation of conjugated double bonds in polyvinylchloride (PVC) films by ultraviolet (UV) irradiation is analyzed using an *in situ* laser-monitoring technique we have developed to measure changes in transmittance of thin UV-irradiated PVC films. Conjugated polyenes of different lengths are produced by laser irradiation at 193 and 248-nm wavelengths. This technique promises to have broader applications in the study of polymer reaction mechanisms and kinetics. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 59–63, 2000

INTRODUCTION

Considerable work exists concerning the thermal and photochemical dehydrochlorination of PVC.[1,2] Such chemical reactions are initiated via end groups, chain faults, and labile impurities (carbonyls, peroxides, unsaturations, etc.) that arise during polymerization or processing of the polyvinylchloride.[3,4] UV radiation from excimer lasers has been used to study photochemical reactions on polymer surfaces. Under UV irradiation, dehydrochlorination of the PVC proceeds by a zipper reaction that results in conjugated polyenes.[5] As the sequence extends to 8 or more polyenes, absorption extends into the visible range, resulting in PVC discoloration.[6,7] In this article, the formation of conjugated polyenes by UV irradiation of PVC films is investigated. We have developed an *in situ* technique to monitor the UV irradiation-mediated photochemical reactions in PVC. This technique can be used to study other reaction mechanisms and kinetics. Potential ap-

plications for laser irradiation of polymers include localized modification of electrical properties of polymer surfaces, localized surface modification of prostheses to enhance surface properties such as biocompatibility, and investigation of the solar photochemical degradation of PVC, which impacts its cost effectiveness for outdoor applications.

EXPERIMENTAL

In these experiments we used an excimer laser to irradiate thin PVC films, and measured the amount of HCl and the change of transmittance of the PVC films as a result of the formation of conjugated double bonds. Figure 1 shows the PVC photodegradation experimental setup.

Sample Preparation

We used 1185PC polyvinylchloride supplied by Air Products and Chemicals, Inc., which is free of copolymers, stabilizers, and plasticizers. This polymer has a low molecular weight with $M_w = 63,500$ and $M_n = 32,000$. Melting and glass temperatures are $T_m = 176.5°C$ and $T_g = 72°C$,
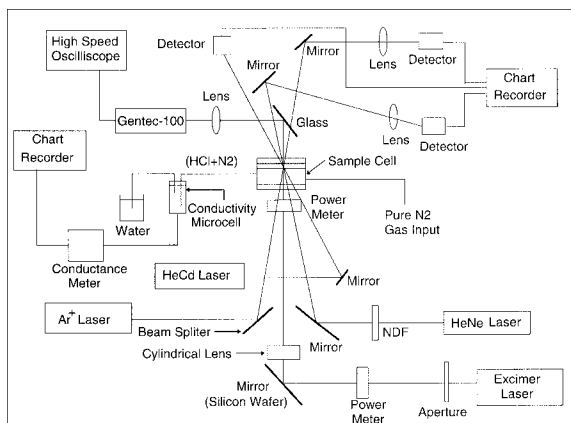

Figure 1 Schematic of the experimental setup.

respectively. A hermetically sealed, 99.9% tetra-hydrofuran (THF, supplied by Aldrich) was used to dissolve the PVC. The THF contained <0.005% water, and was inhibited with <0.025% BHT. Hermetically sealing the THF bottle minimizes the formation of peroxides from exposure to oxygen. Peroxides induce carbonyl formation in PVC.

Polymer films were prepared by dissolving 10 g of PVC in 100 mL of THF, and spin coating the solution onto a quartz or NaCl substrate at 2500–5000 rpm for 10 to 20 s. We used a Headway Research, Inc. model PWM101 spin-coating system. The samples were dried in a vacuum oven in a nitrogen ambient at 55°C for 24 h. The low temperature was used to prevent the formation of polyene structures in the PVC films by thermal degradation. The samples were stored in a desiccator to prevent moisture from being absorbed by the films. A Tencor profilometer was used to measure the film thickness which varied from 1.5 to 8 microns.

Irradiation Conditions

A Lambda Physik LPX210 excimer laser operated at 193 (ArF) and 248 nm (KrF) irradiation wavelengths was used. PVC has a large absorption coefficient at these wavelengths. The absorption depths at 193 and 248 nm are 1.28 and 19 μm, respectively. Pulse durations were 23 ns at 193 nm and 34 ns at 248 nm. We used a rectangular aperture to select the most intense and homogeneous portion of the rectangular excimer laser beam. A cylindrical lens having a focal length of 83 mm at 193 nm and 89 mm at 248 nm was used to defocus the selected part of the beam onto a second aperture positioned close to the substrate

in order to irradiate a rectangular area of the PVC thin film approximately 3 cm^2 in area. To prevent the formation of carbonyl groups, the experiments were performed in a reaction cell under a continuous flow of nitrogen.

Diagnostics

The HCl produced by the dehydrochlorination of the PVC was entrained in the nitrogen flow, and bubbled through water in a conductivity cell. The release of HCl was monitored by measuring changes in the conductance of the water in the conductivity cell.

We also performed *in situ* and *ex situ* measurements to monitor the transmittance of the PVC films. An HP8452A spectrometer with a 2-nm resolution was used to produce spectra of the films at the beginning, during and at the end of each experiment. Samples remained in a nitrogen ambient in the cell throughout the experiments.

As is shown in Figure 1, three different lasers were used to carry out *in situ* measurements of the transmittance of the PVC films: a HeNe laser at 632.8 nm, an Ar$^+$ laser at 488 nm, and a HeCd laser at 325 nm. These lasers were aimed through the same point in the middle of the irradiated region of the PVC film and the transmittances were detected using Si photodiode detectors. The output of the detectors was continuously recorded on a chart recorder. To prevent additional photochemical reactions from the three monitor lasers, low-intensity probe beams were used. In addition to these wavelengths, we have also monitored the transmittance of the 248-nm radiation of the excimer laser. The 193-nm beam was completely absorbed by the PVC film, and its transmittance could not be measured. The transmitted 248-nm radiation was detected using a Gentec-ED100 pyroelectric detector.

EXPERIMENTAL RESULTS

Figure 2 shows the time evolution of the absorbance of a 1.6 μm-thick PVC film at four different wavelengths irradiated by a 248-nm excimer laser. We can distinguish three different regions in this figure that represent the three steps of the dehydrochlorination of PVC: induction, accelerated product formation, and saturation. In the induction stage, the rate of increase of the absorbance is relatively small. The photochemical reactions in the induction phase occur at defect sites
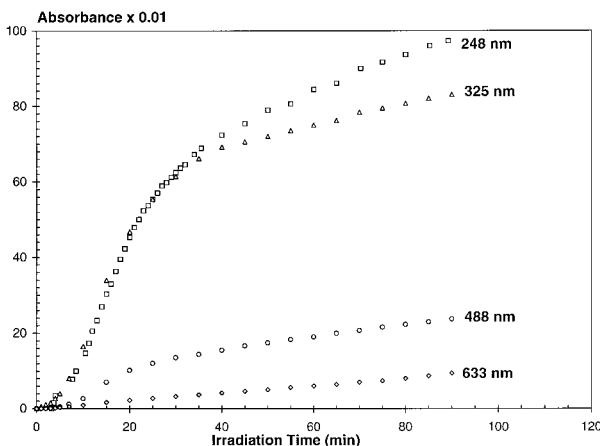
Figure 2 Time evolution of the absorbance of a 1.6-μm PVC film irradiated with a 248 nm, 2 pulse/s excimer laser beam, with a fluence of 21.1 mJ/cm^2. Absorbance is monitored at 248, 325, 488, and 633 nm.

Figure 3 HCl solution conductivity at 193 nm (10 pulse/s, 7.4 mJ/cm^2) and 248 nm (10 pulse/s, 7.0 mJ/cm^2). The irradiated PVC film thickness was 1.95 μm.

in the PVC such as double bonds and carbonyls. As the conjugated polyene structures are formed, the polyene sequences lengthen by a "zip" propagation phenomena with concomitant evolution of HCl. At this stage, the incident photons are increasingly absorbed, leading to an accelerated degradation further enhanced via the autocatalytic effect of the released HCl. The conductance of the water in the conductivity cell increases correspondingly. The saturation phase occurs when the number of CH—CCl bonds capable of undergoing dehydrochlorination decreases and a thin layer of highly absorbing degraded PVC forms.[8] As the saturation phase assumes an increasingly important role, the slope of the transmittance vs. time curve decreases and eventually flattens out.

The conductivity measurements of the evolved HCl for 193 and 248 nm irradiations are shown in Figure 3. Because of the strong absorption at 193 nm, almost no induction period is observed at this wavelength. The small induction time in the conductivity curve, as is shown in Figure 3, results from the dead volume in the HCl collection system. Considering this dead volume, the conductivity measurement results are in reasonably good agreement with the spectroscopic absorbance analysis results.

The formation of conjugated polyenes changes the UV-VIS absorption spectra of the PVC films.[9] Figure 4 shows the absorption spectra for polyenes of different sequence lengths. Most reference spectra are given for polyenes in solution.[7,10–13] Unlike solution polyenes, the polyenes in our ir-
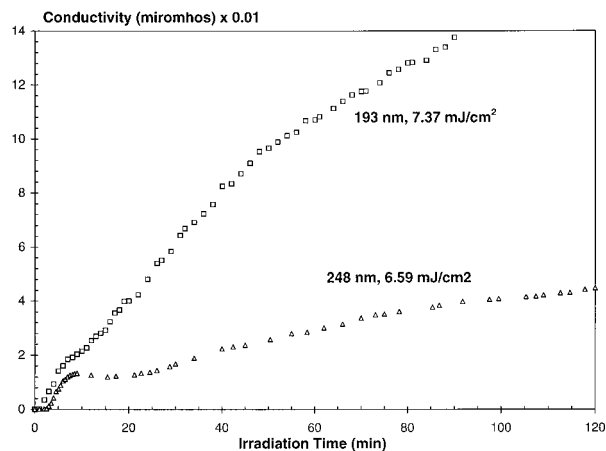
radiated samples are solid, and part of a long chain that contains chlorine atoms. This will change the absorption spectra to some degree, depending on the length of the polyene or the polymer in which the polyene occurs.

Figures 5 and 6 show the UV-VIS spectra for irradiation at 193 and 248 nm wavelengths. As is shown in these figures, there is a marked increase in the absorbance at long wavelengths and, therefore, discoloration of the PVC samples under UV irradiation. The absorption spectrum shifts to longer wavelengths as the length of the conjugated polyene sequence increases. Polyenes with eight or more conjugated double bonds absorb in the visible region.

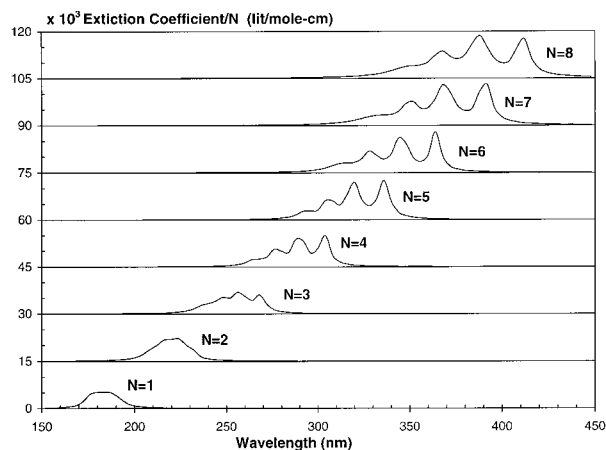When the PVC film is irradiated by either 193 or 248 nm wavelengths, the excitation process is

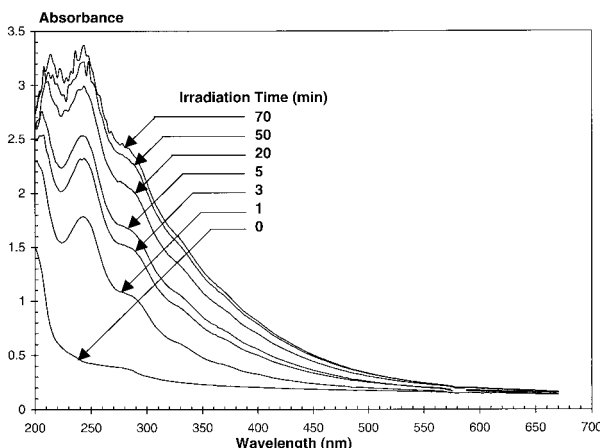**Figure 4** Absorption spectra for polyenes of different lengths.[7,10–13]

Figure 5 UV-VIS spectra of a 5.9 μm-thick PVC film irradiated with a 193 nm, 10 pulse/s, 2.66 mJ/cm^2 excimer laser beam.

initiated at regions of the PVC that contain chromophores. The photochemical reaction occurs only when the incident UV photon has sufficient energy to break the weakest bond in the PVC molecule. Thus, the photochemical reaction depends on the PVC structure as well as the energy of the incident photon. The photon energies for 193 and 248 nm irradiations are 619.2 and 481.9 KJ/mol, respectively.

PVC is an intrinsic absorber at 193 nm, and the photon energy is sufficient to break either the C—Cl or C—H bond.[14] Consequently, there is a high rate of chain initiation during the laser pulse. The possibility of short sequence of polyenes being formed is high, as shown in Figure 5. As shown in the spectra, abundant polyenes are generated with absorption bands between 195 and 245 nm. Most of the polyenes generated absorb at wavelengths less than 400 nm, indicating they contain less than eight conjugated double bonds. A light yellow color is observed after a cumulative total of 112 J/cm^2 of irradiation.

The PVC samples irradiated with 248 nm are more discolored than the ones irradiated with 193 nm. This increase in the discoloration is not due to a higher degree of dehydrochlorination at 248 nm. Rather, the polyenes that are formed by 248 nm irradiation are longer. The UV-VIS spectrum of the 248-nm irradiated PVC shows a broader distribution of polyene sequence lengths than the spectrum of the 193 nm irradiated PVC. Because of the low absorption cross-section of the original PVC sample at 248 nm, the initial dehydrochlorination rate is low. As more conjugated double bonds are formed, the polyene sequences grow

faster because of both the decrease of the activation energy of dehydrochlorination and the increased absorbance.

In the UV-VIS spectra, the absorption maxima of the polyene shifts towards the red, and increases with increasing sequence length. For example, the peaks at 288, 243, and 214 nm in Figures 5 and 6 represent absorption by polyenes having four, three, and two conjugated double bonds ($n = 4$, $n = 3$, $n = 2$), respectively.

A 248-nm photon, in contrast to a 193-nm photon, does not have enough energy to break a C—Cl or C—H bond. It does, however, have sufficient energy to induce the dehydrochlorination of the polyene sequence via the "zipper" reaction. Because the activation energy of polyene dehydrochlorination in the accelerated product formation phase is lower than the activation energy during the induction phase, the accelerated product formation of higher order polyenes is favored at 248 nm, while polyene sequence initiation is favored at 193 nm. Thus, the average length of the polyene sequences for 248 nm irradiation is longer than for 193 nm irradiation. A dark yellow color is observed in the 248-nm irradiated samples after 363 joules/cm^2 of irradiation.

CONCLUSION

The kinetics of the photochemical dehydrochlorination of PVC was investigated using a real-time optical monitoring system and conductivity measurements. Three distinctive stages were observed during dehydrochlorination: induction, accelerated
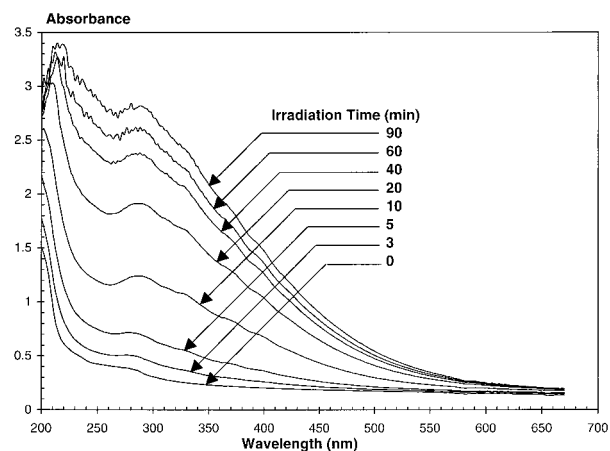

Figure 6 UV-VIS spectra of a 5.9 μm-thick PVC film irradiated with a 248 nm, 10 pulse/s, 6.72 mJ/cm^2 excimer laser beam.

product formation, and saturation. Irradiation at 193 nm has a shorter induction time relative to 248 nm because of the increased absorptivity of higher energy 193 nm photons and consequent increased rate of polyene sequence initiation.

From the UV-VIS spectra, we deduce that the accelerated product formation phase is favored at 248 nm irradiation, while the induction phase is favored at 193 nm. In other words, the longer wavelength radiation tends to form longer polyene sequences and more visible PVC discoloration.

REFERENCES

1. Chatterjee, N.; Basu, S.; Palit, S. K.; Maiti, M. J Polym Sci Part A Polym CHem 1994, 32, 1225.
2. Izumi, Y.; Kawanishi, S.; Suzuki, N.; Maruo, M.; Ichinose, N.; Yamamoto, T. Bull Chem Soc Jpn 1997, 70, 2855.
3. Owen, E. D. Degradation and Stabilisation of PVC; Elsevier Applied Science Publishers; London, 1984.
4. Labana, S. S. ACS Symp. Ser. No. 25; ACS: Washington, DC, 1976, p. 208.
5. Decker, C.; Baladier, M. J Photochem 1981, 15, p. 213.
6. Daniels, V. D.; Rees, N. H. J Polym Sci Polym Chem Ed. 1974, 12, 2115.
7. Sondheimer, F.; Ben Efraim, D. A.; Wolovsky, R. J Am Chem Soc 1961, 83, 1675.
8. Gibb, W. H.; MacCallum, J. R. Eur Polym J 1971, 7, 1231.
9. Philips, R. W.; Volman, D. H. J Am Chem Soc 1969, 91, 3418.
10. Granville, M. F.; Kohler, B. E.; Snow, J. B. J Chem Phys 1981, 75, 3765.
11. Woods, G. F.; Schwartzman, L. H. J Am Chem Soc 1949, 71, 1396.
12. Mebane, A. D. J Am Chem Soc 1952, 74, 5227.
13. Bohlmann, F.; Mannhardt, H. J. Chemi Berichte 1956, 89, 1307.
14. Summers, J. W.; Rabinovitch, E. B. J Vinyl Technol 1983, 5, 91.