Irradiation Effects of Excimer Laser Light on Poly(vinyl chloride) (PVC) Film

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Poly(vinyl chloride) (PVC) film was irradiated with intense monochromatic UV light from ArF, KrF, and XeCl excimer lasers. The detachment of chlorine atoms was observed by X-ray photoelectron spectroscopy, and the formation of polyene structures was observed by optical absorption spectroscopy. The irradiation of ArF and KrF excimer laser light mainly caused the formation of diene and triene structures, respectively. The irradiation of XeCl laser light caused no significant reactions. Upon the consideration of the triplet energies of olefin and diene and the dissociation energy of allylic C–Cl bond, the wavelength dependence was explained by photochemical and photothermal effects of the ArF and KrF lasers, respectively.

Poly(vinyl chloride) (PVC) is one of the most frequently used commercial polymers, which is often used under the conditions of exposed terrestrial sunlight.[1)] However, PVC is quite unstable against sunlight like heat and high-energy radiation, which leads to extensive changes in the polymer structure. There are a large number of papers and reviews on the mechanism and kinetics of the photodegradation of PVC.[1—5)] These studies show that the main reactions caused by irradiation with UV light are dehydrochlorination and the formation of polyene structures. Together with the elimination of hydrochloride, the polymer chain suffers crosslinking, chain scission, and oxidation. More details concerning photodegradation mechanism, however, have not been understood completely, since photochemical, photothermal, and thermal effects were not separated well, because in earlier studies various mercury lamps were used as irradiation sources, and mercury lamps emit a great number of sharp lines in the region of deep UV to IR to which PVC is sensitive. Therefore, it was impossible to identify which line mainly caused the reaction.

A study of photo-induced polymer chemistry by using the monochromatic light sources, such as excimer lasers, is necessary to clarify the effects of the excitation wavelengths. Although studies of laser-irradiation effects of PVC have been few, Shimoyama et al. studied the KrF laser (248 nm) irradiation-induced reaction of chlorinated PVC, and found that the use of KrF laser as a light source is efficient for preparing the π-electron-conjugated polymer.[6)] However, they did not study the effect of irradiation with light of other wavelengths. Kawanishi et al. and Hamada et al. studied the wavelength dependence of laser-irradiation effects on polypropylene and ETFE, respectively.[7,8)] Since pure PVC has no absorption in the >210 nm region, a monochromatic vacuum-UV light source is necessary for selective excitation of the polymer to eliminate its photochemistry. However, such a light source is hardly available, except for the ArF laser (193 nm). To clarify these problems we studied the photochemical reaction of pure PVC induced by intense monochromatic UV light from ArF, and KrF, and XeCl excimer lasers.

Experimental

Preparation of PVC Cast Film. The PVC powder used in this study was purchased from Wako Pure Chemical Industries Ltd., and was dissolved in cyclohexanone at a concentration of 5 wt%. The solution was then transferred onto a flat Pyrex-glass plate and the solvent was slowly evaporated. After more then 48 h, a PVC cast film was washed well (48 h with methanol, 48 h with CS_2, then 48 h with methanol). Then, all of the solvents used in the above procedure were removed from the film in 10^{-1} Pa for more than 2 weeks. All operations of the preparation procedure were performed in the dark in order to prevent any deterioration of the PVC. The absence of solvents was confirmed by an FT-IR measurement. The thickness of the films was 10—30 μm. The obtained PVC films were stored in the dark under a pressure of 10^{-1} Pa in order to prevent degradation, because the films contained neither a stabilizer and anti-oxidants. Before irradiation, the film was cleaned with ethanol using ultrasonic waves for 5 min.

Irradiation of Excimer Laser Light. The PVC film was placed in a glass cell equipped with quartz windows and evacuated to 10^{-4} Pa for more than 10 h. Excimer laser irradiation was carried out with Lumonics Ex-884. ArF, KrF, and XeCl laser light had wavelengths of 193, 248, and 308 nm, respectively. The pulse durations (full width at half maximum; FWHM) were 12—25 ns. The laser was generally operated at a pulse-repetition rate of 1 pulse/s in order to avoid possible effects arising from excessive heating of the sample. The laser-emission intensity was measured with a calorimeter (Scientech 38-4UV). The laser-irradiation intensity of a polymer surface was corrected with the depression value of the light intensity by a quartz window for ArF, KrF, and XeCl lasers. All irradiation was carried out in a vacuum and at ambient temperature. Electron-beam (3 keV, 2 μA) irradiation was also carried out in a vacuum (10^{-7} Pa) at room temperature for a comparison.

Measurement of Spectra. The chemical changes in the bulk of PVC and on the surface of PVC were analyzed by vis-UV absorption spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively. To avoid any reactions with oxygen in the air, the sample irradiated in a vacuum was measured without contacting the air.

The vis-UV absorption spectra were recorded with a Shimadzu UV-2100 spectrophotometer with 0.2 nm resolution. After irradiation, vis-UV differential spectra were obtained by subtracting the spectrum of the non-irradiated sample from that of the irradiated one.

The XPS spectra were obtained with a Shimadzu ESCA 850S using Mg$K\alpha$ 1253.6 eV excitation (8 keV, 15 mA) in a vacuum (10^{-7} Pa). The XPS measurement was carried out on the C_{1s} electron (280—300 eV), O_{1s} electron (526—542 eV) and Cl_{2p} electron (192—210 eV). The atomic ratios, O/C and Cl/C, were calculated from the O_{1s}/C_{1s} ratio and the Cl_{2p}/C_{1s} ratio, respectively, calibrated with the ionization sensitivity factors (C_{1s} 1.00; O_{1s} 2.85; Cl_{2p} 2.36).

Results and Discussion

Figure 1 shows the consumption of Cl atoms on the surface of PVC films irradiated with an electron beam as well as ArF and KrF excimer laser light. Irradiation of XeCl laser light caused no significant change in the atomic ratios. The irradiation conditions were 3 keV, 2 μA for electron, 16.2 mJ cm^{-2} pulse, 5 pps for ArF, and 2.7 mJ cm^{-2} pulse, 5 pps for KrF irradiations. The XPS signal can be correlated with a surface region of about 10 nm. Since PVC has a specific gravity of about 1.4, the project range of 3.0 keV electron is about 290 nm. Therefore, 3.4% of the electron beam energy is absorbed within a surface region of about 10 nm. On the other hand, a PVC film with a thickness of 27 μm had absorbances of 1.46 and 0.023 at wavelengths of 193 and 248 nm, respectively. Thus, PVC with a thickness of 10 nm absorbs 0.124% of ArF laser light and 0.00196% of KrF laser light. As a result of the above-mentioned calculations, this figure indicates the change in the atomic ratios on a surface region of about 10 nm in the cases of an electron beam, ArF and KrF irradiations with absorbed energies of 204, 100, and 0.265 μW cm^{-2}, respectively. The efficiency of Cl atom elimination by ArF and KrF laser irradiation is 6—8 fold higher than that by electron-beam irradiation. This suggests that the irradiation of an excimer laser is more effective than electron-beam irradiation for modifying the surface area of a PVC film.

Figure 2 shows the vis-UV absorption spectra of PVC films non-irradiated and irradiated with ArF and KrF excimer laser light. The irradiation of XeCl laser light caused no significant change in the absorption spectrum. The PVC film before irradiation shows strong absorption at around 200 nm due to the presence of an olefinic moiety within the polymer, whereas almost no absorption is seen at > 220 nm. In other words, the spectrum of non-irradiated film shows that the film includes some extent of double bonds, but no solvents, and that the film absorbs ArF laser light effectively, but KrF excimer laser light ineffectively. The absorption bands at 196, 238, 288, 326, and 367 nm in these spectra are assigned to olefin, diene, triene, tetraene, and pentaene, respectively.[9,10] The disappearance of these peaks after bromination also indicates polyene structures. These spectral changes seem to be different from the former data. While the growth of a broad band at around 500 nm was reported,[1,5,9] the 500 nm band was not observed in the present study. Such a difference

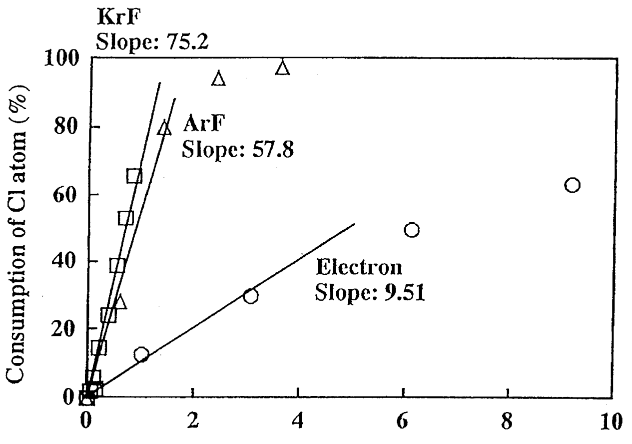

Fig. 1. The consumption of Cl atom on the surface of PVC films irradiated with electron beam (circle), ArF (triangle), and KrF (square) excimer laser lights.

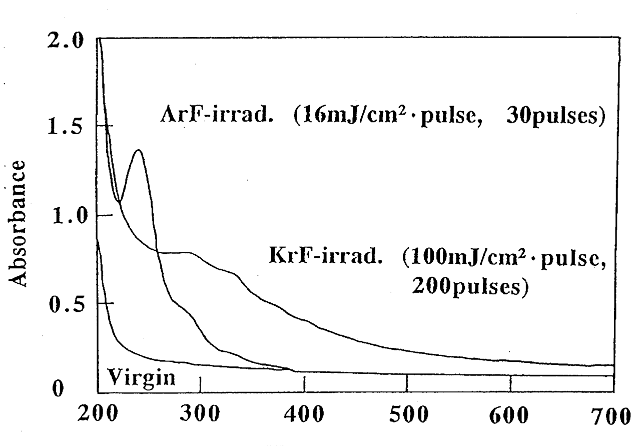

Fig. 2. The vis-UV absorption spectra of PVC films non-irradiated and irradiated with ArF and KrF excimer laser lights.

depends on the quality of the light sources and impurities in the film. Most of the studies on the photochemistry of polymers were performed by using mercury lamps, which emit not monochromatic light, but plural sharp lines. Moreover, most of studies showed that the observed structural changes might be induced by chromophoric impurities, such as residual solvents, carbonyl and hydroperoxide groups.[3)] Thus, the reaction induced by such lamps is a complicated one. On the contrary, in this study, the absence of solvents was confirmed by an FT-IR measurement, and the changes in spectra shown by Fig. 2 were induced by single monochromatic light. The spectral difference between ArF and KrF irradiated films indicates that the species produced by ArF and KrF laser irradiation are different from each other. In other words, we experimentally confirmed that the reaction manners depend on the excitation wavelengths.

Figures 3a and 3b show the results of a wave-form analysis of ArF (a) and KrF (b) irradiated PVC films. The molar absorption coefficients of olefin, diene, triene, tetraene, and pentaene in the PVC films were supposed to be 10000, 21000, 52000, 69600, and 87000, respectively.[11)] A bandwidth (FWHM) of 0.4 eV was used for each polyene. The comparative yield of each component can be obtained by calculating the area of each Gaussian curve. In the case of ArF-irradiated film, the relative yields of olefin, diene, triene, and tetraene were 100 : 23.8 : 3.6 : 0.9, respectively. In the case of KrF-irradiated film, the relative yields of olefin, diene, triene, tetraene, and pentaene were 100 : 9.5 : 3.0 : 1.9 : 0.7, respectively. From these results, ArF laser irradiation mainly formed a diene structure, while KrF laser irradiation formed longer π-conjugations than ArF laser did.

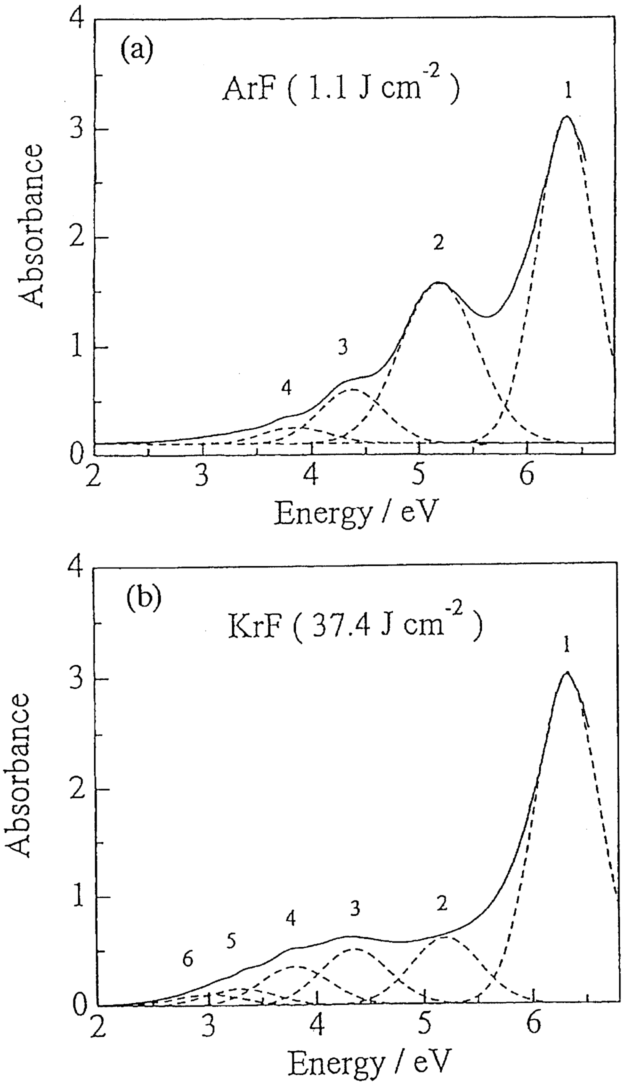

Fig. 3. The result of wave-form analysis of PVC films irradiated with ArF (a) and KrF (b) excimer laser lights.

The changes in the absorbances of these peaks in Fig. 2 are plotted in Figs. 4a and 4b. Although there was a very fast increase in the absorbance of the ArF laser-irradiated film in the region of relatively low irradiation energy, in the region of relatively high irradiation energy the rate of absorbance increase was saturated. On the other hand, there was a much slower increase in the absorbance of the KrF excimer laser-irradiated film in the region of relatively low irradiation energy. To explain these results we propose the following assumption. In the case of ArF excimer-laser irradiation, the light (193 nm) was absorbed effectively by the olefinic site in polymer chain, and hydrochloride was detached from the neighbor monomeric unit. Then, the diene structure was produced mainly and effectively in the polymer chain. Some of absorbed energy was transferred along the polymer chain and an isolated double bond was formed relatively near to another double bond, which was the reaction initiator. However, in the region of relatively high irradiation energy, the absorbance of 193 nm became too large; thus, the ablation-like reaction, which thermochemically destroy the absorption sites and polymer structure, occurred. In the case of KrF excimer-laser irradiation, since most of the light (248 nm) was transmitted, the rate of dehydrochlorination was very low. However, the trace amount of diene, which was initially included in the polymer main chain, absorbed the KrF excimer laser light and triene structure was mainly produced. A certain extent of energy transfer occurred and an isolated olefinic site and diene were produced in the polymer chain. Along with an increase in the irradiated energy, the absorption of KrF laser light and the efficiency of dehydrochlorination increased.

Figure 5 show the intensity dependence of diene formation by ArF irradiation (a) and that of triene formation by KrF irradiation (b). The change in absorbance, which is the ordinate of Fig. 5, was evaluated from the initial slope of the curve of change in absorbance vs. number of pulses such as Fig. 4. The slopes are 0.95 and 1.62 in Figs. 5(a) and 5(b), respectively. Therefore, the formation of diene by ArF irradiation proceeds via one-photon reaction, whereas the formation of triene by KrF irradiation proceeds via a multiphoton reaction. From the viewpoint of the excitation energy, we are supposing the following mechanisms. The ArF laser light is effectively absorbed by the olefin or diene sites in the polymer chain to give rise to its excited state, whereas the KrF laser can excite only diene. Chlorine atoms surrounding

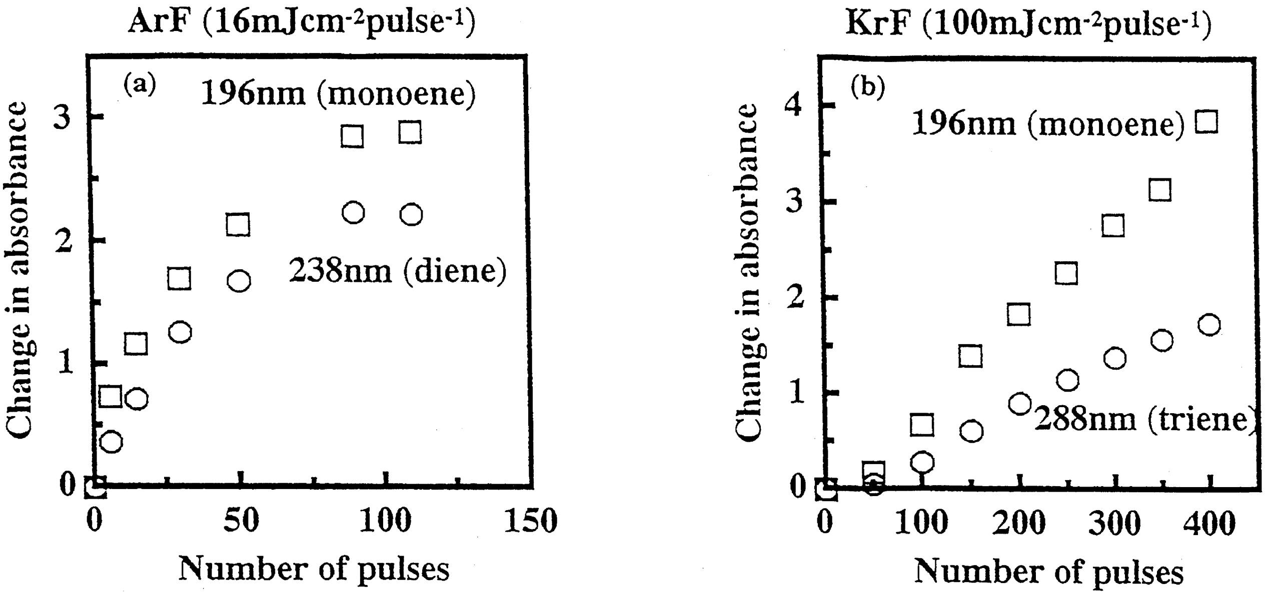

Fig. 4. The change in absorbances of PVC films irradiated with ArF (a) and KrF (b) excimer laser lights.

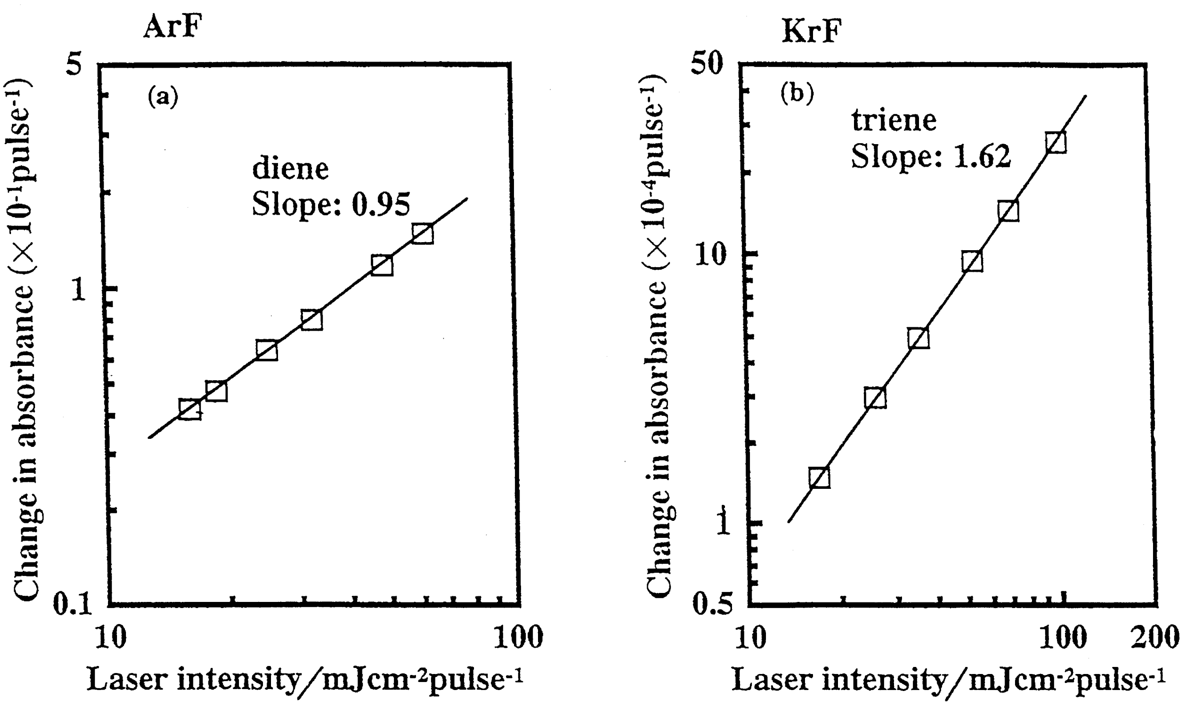

Fig. 5. The laser intensity dependence of diene formation by ArF irradiation (a) and that of triene formation by KrF irradiation (b).

these sites facilitate an intersystem crossing of their singlet to the lowest excited triplet states. These olefinic sites have an allylic Cl atom which undergoes homolytic photochemical dissociation via triplet states. Hydrogen abstraction by a Cl atom produces diene in the polymer chain. Some of absorbed energy may be transferred as thermal energy to form an isolated double bond, which plays the roll of a reaction initiator. The excitation of diene, however, will not lead to bond dissociation from its excited triplet state. The typical triplet energies of aliphatic olefin and diene are ca. 330 and ca. 250 kJ mol^{-1}, and the dissociation energy of the allylic C–Cl bond lies between the two triplet energies (ca. 290 kJ mol^{-1}, supposing similar to that of benzylic C–Cl bond).[12] Upon considering the relationship between the triplet energies and the dissociation energies of the allylic Cl atom for diene and triene, photochemical dehydrochlorination would be limited to diene formation. It was supposed that multiphoton absorption occurred via the T→T* transition with the evolution of heat.[13] Polyene formation in the case of KrF and other stationary state light sources, therefore, can be attributed to the photothermal effect. Less-selective dehydrochlorination was reported for the thermolysis of PVC, giving a polyene structure through a "zipper-like" radical-chain mechanism.[4]

Conclusions

Pure PVC film was irradiated with monochromatic UV light from ArF, KrF, and XeCl excimer lasers. The irradiation of ArF and KrF excimer laser light mainly caused the formation of a diene structure and a triene structure, respectively. It can be concluded from the above results and consideration about the photochemistry of PVC that the reaction, which depends on the excitation wavelengths, arises from the distinction of the absorption sites, and that the absorbance and reaction efficiency are closely related to each other.

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