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Irradiation Effects of Excimer Laser Light on Poly(vinylidene fluoride) (PVdF) Film

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(Received April 2, 1998)

The irradiation effects of intense ultraviolet (UV) light from ArF and KrF excimer lasers on poly(vinylidene fluoride) (PVdF) were studied. The optical absorption spectroscopy made it clear that irradiation with ArF and KrF excimer laser light mainly caused the formation of diene and triene structures, respectively. From the dependence on the laser intensity it was found that ArF and KrF laser-induced reactions proceeded via single-photon and multi-photon processes, respectively. The wavelength dependence was explained by photochemical and photothermal effects of ArF and KrF excimer lasers, respectively. These results indicate that the distinction of the photo-reaction between the two is closely related to the difference in the absorption sites.

Fluoropolymers are well-known for their excellent properties, for example heat resistance and solvent resistance. The surface modification of chemically resistant fluorocarbon polymer films, such as poly(tetrafluoroethylene) (PTFE) and poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), has been widely studied from the view point of industrial applications during the last several decades. However, chemical etching using a wet technique[1)] and radio-frequency plasma processing with oxygen[2)] have some problems, such as low area-selectivity and low durability of the modified layer. On the other hand, the interaction of the excimer laser light with solid organic materials has been extensively studied,[3)] and excimer laser radiation has been shown to be highly effective in modifying the surface of a variety of polymers.[4)] This method using excimer laser light is more efficient for modifying polymer surfaces than several other ones in terms of (a) modification by a dry process in ambient air at room temperature, (b) modification at a short penetration depth, and (c) modification of inert materials. Although most workers in the field of laser chemistry have concentrated their efforts on studying the irradiation effects of excimer laser light on aromatic polymers,[5)] a few studies on the irradiation effects of excimer laser light on aliphatic polymers have been reported;[6—8)] also, the addition or improvement of high functionalities to various aliphatic polymers has been regarded as being important.

During the last several years, the laser-induced modification of fluoropolymer films has been attempted.[9—13)] Although extensive studies have been made on the modification of fluoropolymers, little attention has been paid to the mechanism of their modification. To clarify the mechanism of a laser-induced surface modification, it must be necessary to separate the photochemical, photothermal and thermal effects. Kawanishi et al.[6)] and Hamada et al.[7)] studied the wavelength dependence of laser-irradiation effects on polypropylene (PP) and ethylene–tetrafluoroethylene copolymer (ETFE), respectively. They found that a laser-induced reaction which depends on the excitation wavelengths arises due to the distinction between the photochemical and photothermal effects. In previous papers[8)] we reported on the wavelength-dependence of the laser-induced reaction on poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVdC). The irradiation effects of ArF (193 nm) and KrF (248 nm) excimer laser light on the photo-induced reaction of poly(vinylidene fluoride) (PVdF) film are reported here based on a vis-UV spectroscopy technique.

PVdF has advantages concerning the piezoelectric and pyroelectric properties, which were first reported by Kawai[14)] and Bergman et al.,[15)] respectively. Chemical and physical changes induced in PVdF by ionizing radiation have been extensively reported in elsewhere.[16)]

Experimental

Sample. The PVdF used in this study was 120-μm-thick film with a crystallinity of approximately 50%, purchased from Kureha-Japan. An XPS analysis showed that the sample used in this study was a highly repeating PVdF, having the chemical structure of ($-CH_2-CF_2-$). However, PVdF generally contains 3—6% of inverted monomer units, ($-CH_2-CH_2-$) and ($-CF_2-CF_2-$), as structural defects in an otherwise completely head-to-tail structure.[16)] Before the experiments, the film was cleaned with ethanol using ultrasonic waves for 5 min.

Irradiation of Excimer Laser Light. PVdF film was placed in a glass cell equipped with a quartz window and evacuated to 10^{-4} Pa for more than 12 h. Excimer laser irradiation was carried out with a Lumonics Ex-884. ArF and KrF laser light had wavelengths of 193 and 248 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 5 pulse/s in order to avoid possible effects arising from excessive heating of the sample. The laser emission intensity was measured by using a calorimeter (Scientech 38-4UV). To verify the measured laser intensity, the number of photons was also measured using a potassium tris(oxalato)ferrate(III) actinometer.[17] The laser irradiation intensity of the polymer surface was corrected using the depression value of the light intensity by a quartz window for ArF and KrF lasers. All irradiations were carried out in a vacuum and at ambient temperature.

Measurement of Spectra. The chemical change in the bulk of PVdF film was analyzed by vis-UV absorption spectroscopy. To avoid any reactions with oxygen in air, the sample irradiated in vacuum was measured without contacting to air. The vis-UV absorption spectra were recorded with a Shimadzu UV-2100 spectrophotometer with 0.5 nm resolution. After irradiation, the vis-UV differential spectra were obtained by subtracting the spectrum of the non-irradiated sample from that of the irradiated one.

Results and Discussion

Figure 1 shows the vis-UV absorption spectrum of a non-irradiated PVdF film. Since the PVdF film was turbid in white color due to its polymorphism, in which at least two crystalline phases (α form and β form) and an amorphous part existed, the absorption spectrum in Fig. 1 was estimated by excluding the influence of the reflection of the polymer; $\log(1-R)$ calculated from the reflectivity R was subtracted from the spectrum containing the influence of reflection of the polymer. The absorption spectrum of non-irradiated PVdF may have been due to the imperfect portion of the polymer, such as a small amount of olefin or diene formed during production.

The differential vis-UV absorption spectra between a non-irradiated PVdF film and that irradiated with ArF and KrF excimer laser light are shown in Fig. 2. The influence of the reflectivity of the films on the differential spectra was negligible. The differential spectrum of the film irradiated by an ArF excimer laser had a peak at around 230 nm. In the case of KrF excimer laser irradiation, the differential spectrum had a peak in the wavelength range at around 220 nm and a broad shoulder-peak in the wavelength range of 260—290 nm. Because these absorption peaks and shoulder-peak disappeared after bromination, similar to the result for the brominated PVdF,[18] they were suggested to be attributed to the $\pi\rightarrow\pi^*$ transition of polyene structures. Also, supposing that the $\pi\rightarrow\pi^*$ transition energy of polyene within PVdF is similar to that within ETFE,[7] the absorption bands in the wavelength range of 220—230 and 260—290 nm have been assigned to diene and triene, respectively.[19] Although Kawanishi et al.[6] reported that the absorption band at around 230 nm, which was formed by ArF-irradiation in air, was due to the $n\rightarrow\pi^*$ transition of the –C=O group, the 220—230 nm band observed in this study was not due to the –C=O group, because of the absence of oxygen in the irradiating atmosphere. The spectral difference between ArF and KrF irradiated films indicates that there is a large difference between the irradiation effects of ArF and KrF excimer lasers. The conjugation length of polyene formed by KrF laser irradiation is longer than that of polyene formed by ArF laser irradiation.

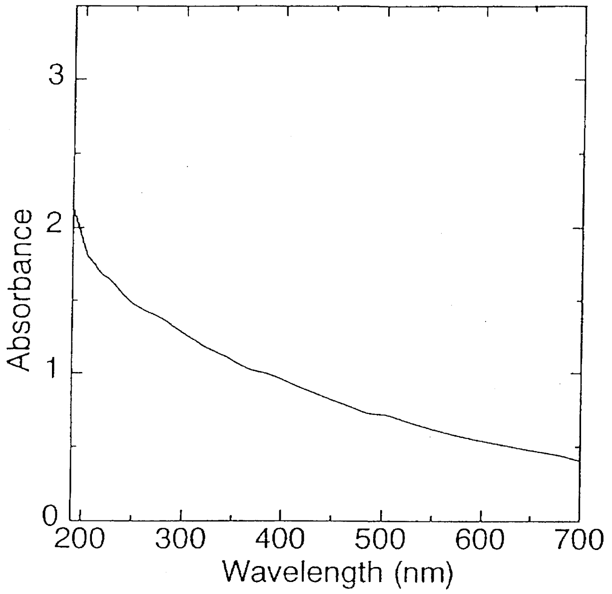

Fig. 1. The vis-UV photo-absorption spectrum of non-irradiated PVdF film.

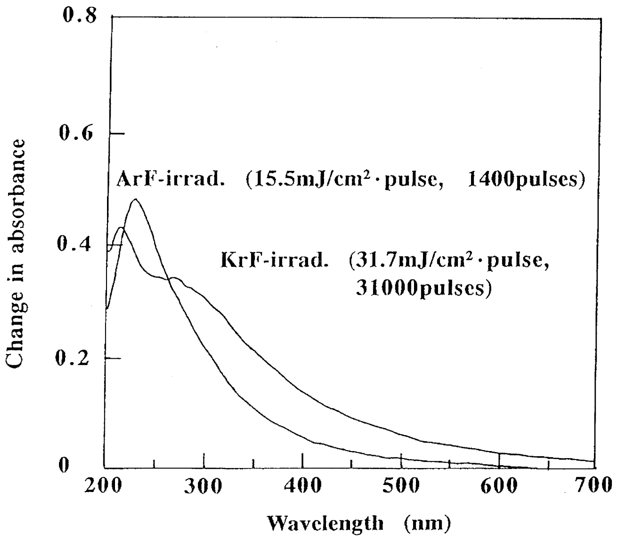

Fig. 2. The differential vis-UV photo-absorption spectra between non-irradiated PVdF film and ArF- and KrF-excimer laser irradiated ones.

A small increase in the absorbance at longer wavelengths (visible region) was also observed in the case of KrF-laser irradiation. This increase is considered to have been due to carbonization due to degradation of the polymer. In fact, the exposed portion of the film became blackened. An amorphous carbon thin film prepared by physical vapor deposition (PVD) exhibited a similar spectrum to the KrF-irradiated PVdF film in the region of 450—700 nm, which also indicated the carbonization of PVdF.

The changes in the absorbances at 230 nm (diene) and 280 nm (triene) vs. number of irradiated laser pulses are plotted in Fig. 3. The formation of polyene structures by the irradiation of PVdF proceeded less efficiently than that by the irradiation of chlorinated polymers.[8] Moreover, although in the cases of the ArF-laser irradiation of PVC and PVdC a tendency of saturation in the rate of absorbance increase was observed,[8] the same tendency was not observed in the case of ArF-laser irradiation of PVdF. Because the bond-dissociation energy of C–H is lower than that of C–F, it can be supposed that, when PVdF is irradiated with UV or ionizing radiations, a hydrogen atom is at first detached from the polymer chain, and then fluorine abstraction by a hydrogen undergoes to form a polyene structure. In fact, in-situ mass analyses using a vacuum chamber for laser irradiation equipped with a quadrupole mass spectrometer showed the evolution of H, H_2, and HF. Therefore, the bond dissociation of C–H actually occurred. Because the bond-dissociation energy of C–C is lower than that of C–H or C–F, the main chain scission must have occurred simultaneously. However, we did not study C–C bond breaking, such as the gel fraction or chromatographic analysis. In this process the zipper-like chain reaction observed in the case of chlorinated polymers can not occur. Therefore, the efficiency of polyene formation in the case of PVdF was much lower than that of a chlorinated polymer system.

Figure 4 shows the intensity dependencies of diene and triene formations due to ArF (a) and KrF (b) irradiation. The change in the absorbance, which is the ordinate of Fig. 4, was evaluated based on the initial slope of the curve of change in the absorbance vs. number of pulses, such as in Fig. 3.

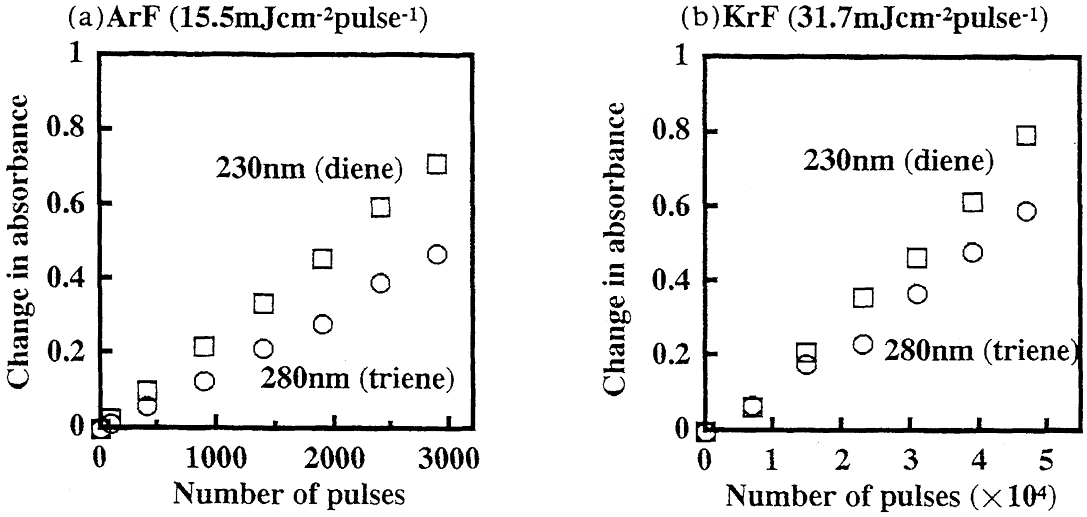

Fig. 3. The change in absorbances of PVdF films irradiated with ArF (a) and KrF (b) excimer laser lights.

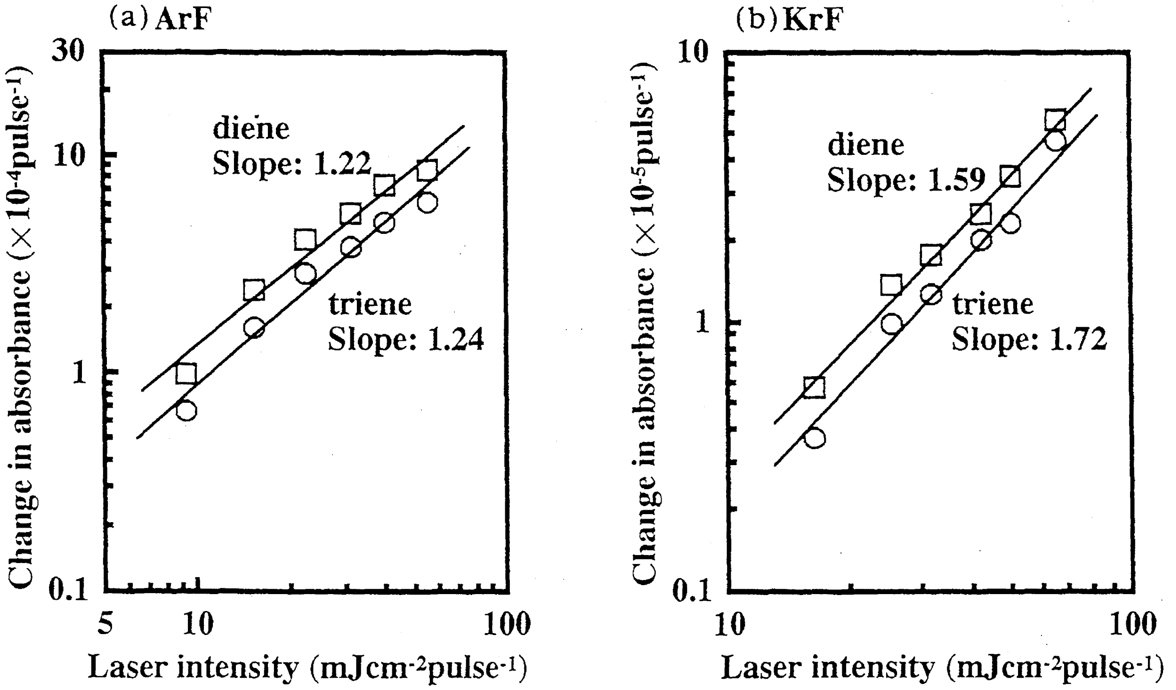

Fig. 4. The excimer laser intensity dependence of diene and triene formations by ArF (a) and KrF (b) excimer laser irradiations.

The slopes in Fig. 4(a) are about 1.2—1.3, whereas those in Fig. 4(b) are 1.59—1.72, respectively.

The relationship between the yield of the product and the irradiated laser-intensity can be expressed as following equation:[20)]

$$N_\mathrm{f} = N_0/n \prod \sigma_i F^n, \tag{1}$$

where N_f is the yield of the product, N_0 the number of the molecules which absorb the laser light and give the product, n the number of photons which contribute to make one product, σ_i the absorption cross section and F the laser intensity. The following expression can be derived from Eq. 1:

$$\log N_\mathrm{f} = n \log F + C, \tag{2}$$

where C corresponds to the Y-intercept in Fig. 4 and n, which is the number of photons that contribute to the reaction, corresponds to the slope in Fig. 4 on a logarithmic scale. Therefore, the formations of diene and triene by ArF irradiation proceed via nearly a single-photon reaction, whereas those by KrF irradiation proceed via a multi-photon reaction.

Although the slope in Fig. 4(a) was not perfectly equal to 1.0, we regarded the formation of diene or triene by irradiating ArF laser as a single-photon reaction based on a consideration of the excitation energy. The ArF laser light is effectively absorbed by the olefinic sites in the polymer chain to give rise to its excited triplet states, whereas the KrF laser can excite only diene. These excited sites facilitate an intersystem crossing of their singlet to the lowest excited triplet states. Because the formed triplet state of olefin has sufficient energy to dissociate the C–H bond, the formation of diene by irradiating ArF laser can proceed via a single-photon process. On the other hand, the triplet states of diene, which were formed by KrF laser-irradiation, can not lead to bond-dissociation. Therefore, the triplet energy will convert to thermal energy. Moreover, because the lifetime of the triplet states is longer than the pulse duration of excimer laser, the $\mathrm{T}\rightarrow\mathrm{T}^*$ transition will occur within the laser-pulse time, and heat evolution will also undergo with the $\mathrm{T}^*\rightarrow\mathrm{T}$ transition. Hence, most of the absorbed energy leads to the evolution of heat. The thermal energy localized by several cycles of the $\mathrm{T}\rightarrow\mathrm{T}^*$ and $\mathrm{T}^*\rightarrow\mathrm{T}$ transition can induce dissociation of the C–H bond. Therefore, the formation of diene by irradiating a KrF laser can be considered to be induced by photothermal effects.

From the above-mentioned discussions, in short, the difference in the radiation effects at 193 nm from those at 248 nm can be classified into whether the laser-induced reaction is a single-photon process or a multi-photon one.

The single-photon reaction in the case of polyene formation by ArF-laser irradiation indicates that this reaction proceeds via a photochemical process without any photothermal effects. Because a zipper-like chain reaction can not occur, the photochemical initiating sites, in other words the absorption sites to form diene and triene, must be olefinic and diene sites, respectively. The absorption spectrum of a non-irradiated film suggests the existence of a small amount of double bonds, such as olefin and diene sites. On the other hand, the multi-photon reaction in the case of polyene formation by KrF-laser irradiation may proceed via a photothermal process in which local photothermal heating occurs via the process of the $\mathrm{T}\rightarrow\mathrm{T}^*$ transition with the evolution of heat.[21)] In this case the photochemical initiating site may be diene and the dissociation of excited diene is limited without the process of the $\mathrm{T}\rightarrow\mathrm{T}^*$ transition with an evolution heat.

Conclusions

In order to elucidate the wavelength dependence of the photochemical reaction of aliphatic polymer, PVdF was irradiated with monochromatic UV light from ArF and KrF excimer lasers. Irradiation with ArF and KrF excimer laser light mainly caused the formation of diene and triene structures, respectively, and it was found that ArF and KrF laser-induced reactions proceeded via single-photon and multi-photon processes, respectively. Upon considering the excited energy of olefin and diene sites, the wavelength dependence was explained by photochemical and photothermal effects of ArF and KrF excimer lasers, respectively.

The authors wish to express their sincere thanks to Dr. Ichinose for his fruitful discussion.

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