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Irradiation Effects of Excimer Laser Light on Vinylidene Chloride–Vinyl Chloride (Saran®) Copolymer Film

Yoshinobu Izumi,* Shunichi Kawanishi,† Noriaki Takagi, Shigeo Honda, and Tadashi Yamamoto

Department of Nuclear Engineering, Graduate School of Engineering, Osaka University,
2-1 Yamada-oka, Suita, Osaka 565-0871

†Office of Light Quantum Research Program, Kansai Establishment, Japan Atomic Energy Research Institute,
25-1 Mii-minami, Neyagawa, Osaka 572-0019

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Vinylidene chloride–vinyl chloride copolymer (Saran® copolymer) film was irradiated with ArF and KrF excimer laser light in a vacuum at ambient temperature. The irradiation of 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 concluded that diene and triene were formed via single-photon and multi-photon processes, respectively. The wavelength dependence was explained by photochemical and photothermal effects for the ArF and KrF lasers, respectively.

There has been considerable interest in the use of intense ultraviolet (UV) light from excimer lasers for modifying polymer surfaces. Since the discovery of the phenomenon of ablative photodecomposition (APD),[1] many reports have appeared dealing with the interaction of excimer laser light with solid organic materials, such as aromatic polymers and biological tissue.[2]

The APD process is useful for the etching of aromatic polymers and biological materials. However, it is not available for modifying aliphatic polymers. The characteristic weak photoabsorption in the UV region of the aliphatic polymers should show a different photoreaction in a polymer matrix of aromatic polymers. Although a few studies concerning the irradiation effects of excimer laser light on aliphatic polymers have been reported, the addition or improvement of high functionalities to various aliphatic polymers is regarded as being important, and is a new application of intense UV light from excimer lasers. Shimoyama et al. studied the KrF laser (248 nm) irradiation-induced reaction of a chlorinated poly(vinyl chloride) (PVC), and found that using the KrF laser is efficient for preparing the π-electron-conjugated polymer.[3] Kawanishi et al.[4] and Hamada et al.[5] studied the wavelength dependence of laser irradiation effects on polypropylene and ETFE, respectively.

We have been interested in the wavelength dependence of laser-irradiation effects on aliphatic polymers. Halogenated polymers undergo dehydrohalogenation and the formation of polyene structures when exposed to light, heat or ionizing radiation. Since the formed polyenes show optical absorption due to the π–π^* transition in the UV region, the reaction of halogenated polymers induced by monochromatic UV light can be an especially attractive subject. In previous papers we reported on the irradiation effects of excimer laser light on poly(vinyl chloride) (PVC) film and its wavelength dependence.[6] The irradiation effects of ArF (193 nm) and KrF (248 nm) excimer laser light on the photodecomposition or degradation of vinylidene chloride–vinyl chloride (Saran®) copolymer film are reported here using the vis-UV spectroscopy technique. Concerning degradation by the thermolysis or radiolysis of poly(vinylidene chloride) (PVdC) and Saran® copolymers, a number of studies have been carried out, and the results summarized elsewhere.[7]

Experimental

Preparation of Saran Copolymer Cast Film. The powder of Saran copolymer, which contained 89% of vinylidene chloride and 11% of vinyl chloride units, used in this study was kindly provided from Dr. T. Tanabe of Asahi Chemical Industry Co., Ltd. The powder was dissolved in cyclohexanone under elevated temperature (≈330 K) with a concentration of 5 wt%. The solution was then transferred onto a flat Pyrex glass plate, and the solvent was slowly evaporated. After more than 48 h, the Saran cast film was well-washed (48 h with methanol, 48 h with CS_2, then 48 h with methanol). Then, all of the solvents used in the above-mentioned 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 film. The absence of solvents was confirmed by FT-IR measurements. The thicknesses of the films were 20—40 μm. The obtained Saran® copolymer 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 nor anti-oxidants. Before irradiation, the film was cleaned with ethanol using ultrasonic waves for 5 min.

Irradiation of Excimer Laser Light. The Saran® copolymer film was placed in a glass cell equipped with a quartz window, and was evacuated to 10^{-4} Pa for more than 10 h. Excimer laser irradiation was carried out with a Lumonics Ex-884. ArF and KrF laser light had wavelengths of 193 nm 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 1 pulse/s in order to avoid any possible effects arising from excessive heating of the sample. The laser-emission intensity was measured with 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.[8] The laser-irradiation intensity of the polymer surface was corrected using the depression value of the light intensity by a quartz window for the ArF and KrF excimer lasers. All irradiation was carried out in a vacuum and at ambient temperature.

Measurement of Spectra. The chemical change in the bulk of Saran copolymer film was analyzed by vis-UV absorption spectroscopy. To avoid any reactions with oxygen in air, the sample irradiated in a 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, vis-UV differential spectra were obtained by substracting the spectrum of the non-irradiated sample from that of the irradiated one.

To comfirm the existence of a polyene structure within the irradiated polymer, bromination was carried out using the following procedure. An irradiated film sample was placed in a screw-cap vial containing 10 ml of 0.2 N Br_2/CCl_4 at 273 K for 20 min. The film was removed from the bromine solution, washed with CCl_4 (three fresh 10 ml portions) and then, likewise, with dichloromethane, and dried under 10^{-1} Pa for 48 h.

Results and Discussion

Figure 1 shows the vis-UV absorption spectrum of non-irradiated Saran® copolymer film. Since the Saran copolymer film was turbid in white color due to its high crystallinity, the absorption spectrum in Fig. 1 was estimated by excluding the influence of reflection of the polymer; $\log(1-R)$ calculated from the reflectivity R from the spectrum containing the influence of reflection of the polymer was then subtracted. The Saran film shows strong absorption around 200 nm due to the presence of an olefinic moiety within the polymer. This indicates that the film absorbs ArF laser light effectively but KrF laser light ineffectively.

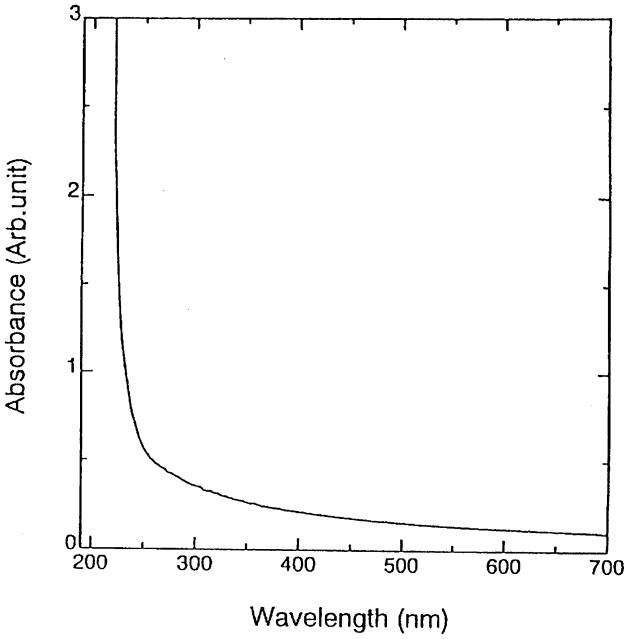

Fig. 1. The vis-UV photo-absorption spectrum of non-irradiated Saran® copolymer film.

The differential vis-UV absorption spectra between non-irradiated Saran® film and that irradiated with ArF and KrF excimer laser light are shown in Fig. 2. The irradiation conditions were 8 mJ cm^{-2} pulse^{-1}, 25 pulses, in vacuum for ArF irradiation, and 25 mJ cm^{-2} pulse^{-1}, 140 pluses, in vacuum for KrF irradiation, respectively. The influence of the reflectivity of the films on the differential spectra was negligible. By irradiating with ArF excimer laser light the differential spectrum had a peak in the wavelength range below 200 nm and a shoulder-peak in the wavelength range of 250—290 nm. In the case of KrF laser irradiation, the differential spectrum had peaks in the wavelength range below 200 nm and at about 290 nm. Because these absorption peaks and shoulder-peak disappeared after bromination, they are assigned to polyene structures. Also supposing that the π–π^* transition energy of polyene within PVdC is similar to that within PVC, the absorption bands at 196, 238, 288 and 326 nm are assigned to olefin, diene, triene, and tetraene, respectively.[6,9,10] 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.

The changes in absorbances at 238 nm (diene) and 288 nm (triene) vs. number of laser pulses are plotted in Fig. 3. The irradiation conditions were 8 mJ cm^{-2} pulse^{-1}, in vacuum for ArF irradiation, and 25 mJ cm^{-2} pulse^{-1}, in vacuum for KrF irradiation, respectively. 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.

From these results, the following process must proceed. In the case of ArF excimer-laser irradiation, the light (193 nm)

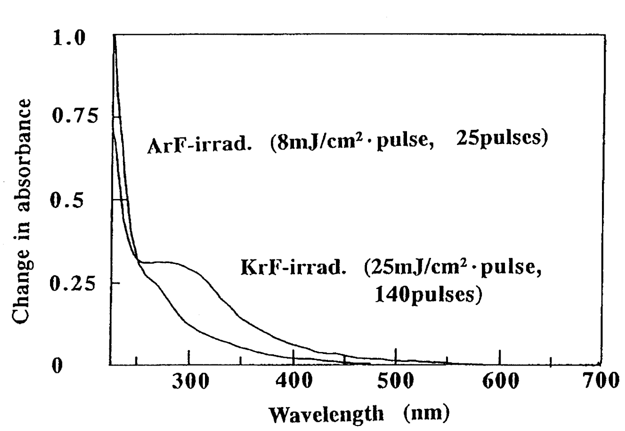

Fig. 2. The differential vis-UV photo-absorption spectra between non-irradiated Saran® film and ArF and KrF excimer laser irradiated one. (The irradiation conditions for ArF and KrF excimer lasers were presented in the figure).

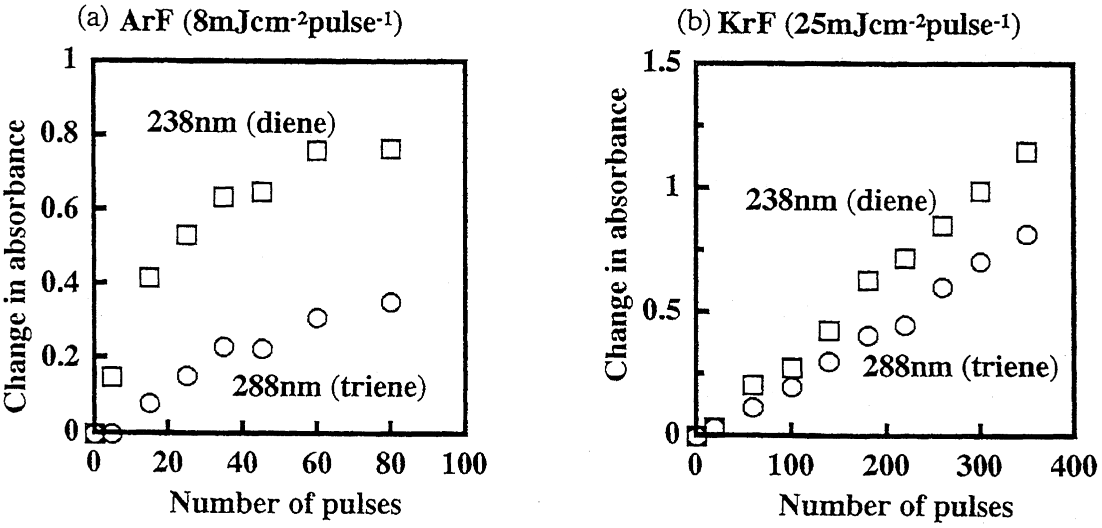

Fig. 3. The change in absorbances of Saran® copolymer films irradiated with ArF; 8 mJ cm^{-2} pulse^{-1} (a) and KrF; 25 mJ cm^{-2} pulse^{-1} (b) excimer laser lights.

was effectively absorbed by the olefinic site in the polymer chain, and hydrochloride was detached from the neighboring monomeric unit. Then, the diene structure was produced mainly and effectively in the polymer chain. Some of the 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 or scattered without absorption, the rate of dehydrochlorination was very low. However, a trace amount of diene, which was initially included within the polymer main chain, absorbed the KrF excimer laser light and the triene structure was mainly produced. A certain extent of energy transfer occurred and isolated olefinic sites or diene sites 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.

In both cases of ArF and KrF laser irradiation, the formed polyene can behave as a new absorption site, and thus the absorption of laser light and the efficiency of dehydrochlorination must increase. For example, the diene site formed by the irradiation of ArF can absorb ArF laser light more effectively. Including both the photochemical and photothermal reaction mechanisms, which are described later, the formed diene site can absorb ArF laser light and give triene. Therefore, the laser-induced reaction in the region of relatively high irradiation energy (large number of pluses) can not be regarded as the same as the reaction of original Saran® copolymer film. In order to estimate the reaction of the original film and to avoid any influence of newly formed absorption sites, it is necessary and important for the following discussions (laser intensity dependence and number of photons which contributes to the reaction) to ignore the behavior of any absorbance change, except for the initial slope in Fig. 3.

Figure 4 shows the intensity dependencies of diene and triene formations by ArF irradiation (a) and that by KrF irradiation (b). The change in absorbance, which is the ordinate of Fig. 4, was evaluated from the initial slope of the curve of change in absorbance vs. number of pulses such as Fig. 3. The slopes in Fig. 4(a) are estimated as about 0.65 and those in Fig. 4(b) are more than unity, respectively.

The relationship between the yield of the product and the irradiated laser-intensity can be expressed by following equation:[11]

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

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

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

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 proceeds via a single-photon reaction, whereas those by KrF irradiation proceed via a multi-photon reaction. We propose the following assumption for the reason why the slopes in Fig. 4(a) are less than unity. By irradiating with excimer laser light, chorine atoms are detached from the polymer chain and abstract hydrogen atoms. This chemical reaction generally proceeds via a "zipper-like" chain mechanism.[12] However, in the case of the high-intensity irradiation, cleavage of the C–H bond may simultaneously proceed. And the eliminated hydrogen atoms play an important role in the termination reaction. Therefore, the higher the irradiation intensity becomes, the lower is the efficiency of the chain reaction, and the less is the yield of final product. Because the observed absorption due to the polyene corresponds not to the yield

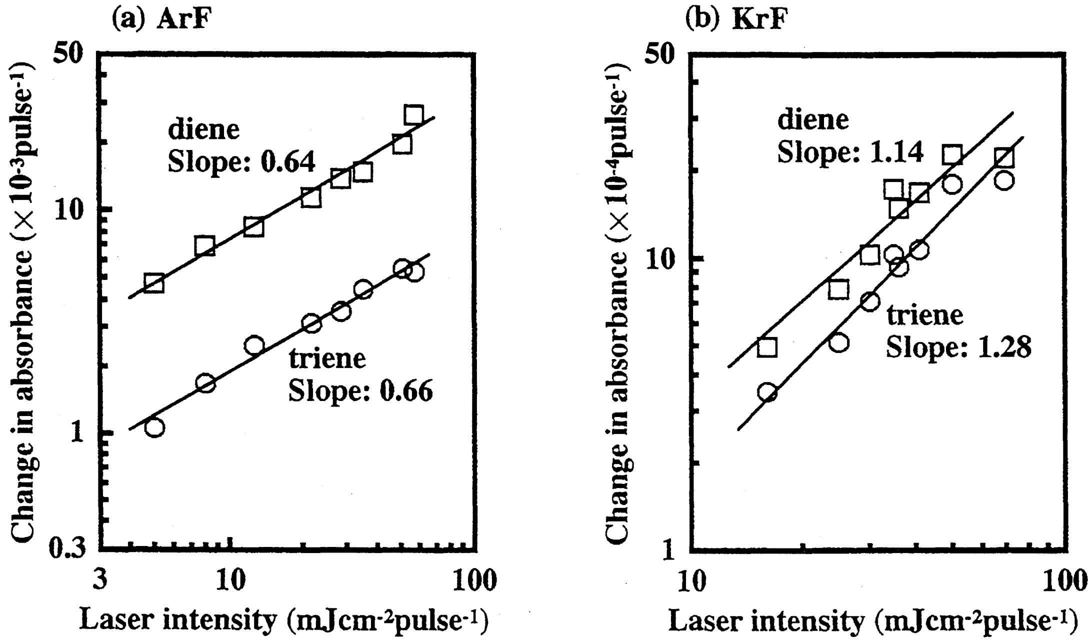

Fig. 4. The excimer laser intensity dependence of diene and triene formations by ArF (a) and KrF (b) irradiation.

of primary reaction, but to the yield of the final product, the slope in Fig. 4(a) on a logarithmic scale is not even unity if the photochemical primary reaction proceeds via a single-photon process.

Next, from the viewpoint of the excitation energy, we are supposing the following mechanisms (the energy diagram possible in the chemical reactions within the chlorinated polymers is shown in Fig. 5). 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 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 the 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 the 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 $\mathrm{kJ\,mol^{-1}}$, and the dissociation energy of the allylic C–Cl bond lies between the two triplet energies (ca. 290 $\mathrm{kJ\,mol^{-1}}$, supposing similar to that of benzylic C–Cl bond).[13] 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 $\mathrm{T}\longrightarrow\mathrm{T}^*$ transition with the evolution of heat.[14] Polyene formation in the case of KrF, therefore, can be attributed to a photothermal effect.

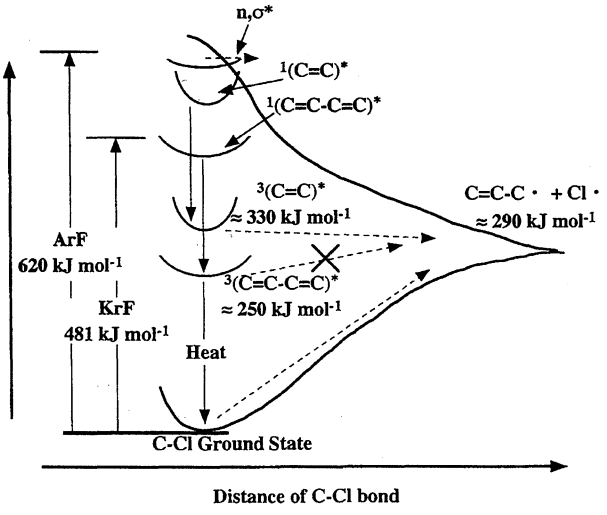

Fig. 5. The possible energy diagram in the chemical reaction within the chlorinated polymers.

On the other hand, the above-mentioned C–Cl bond dissociation can compete with vibrational relaxation. Dlott and his co-worker reported that in a system of large molecules embedded in a solid matrix vibrational cooling can occur within the time scale of 10 ps.[15] However, in this study, the absorption site is not a large monomer, but an olefinic or diene site within the polymer chain, thus a similar vibrational relaxation or cooling to Dlott's case must occur. Because the energy lost by vibrational relaxation does not contribute to the chemical reaction, very rapid and effective vibrational relaxation may make the quantum yield of reaction products low. We have not yet been able to evaluate the quantum yield of polyene formation or dehydrochlorination experimentally. However, we believe that only the energy not deactivated by vibrational cooling contributes to the photochemical or photothermal reaction.

Conclusions

Vinylidene chloride–vinyl chloride copolymer (Saran® copolymer) film was irradiated with monochromatic UV light from ArF and KrF excimer laser light in a vacuum at ambient temperature. The irradiation of ArF and KrF excimer laser light mainly caused the formation of diene and triene structures, respectively. It can be concluded from the above results and a consideration about the photochemistry of chlorinated polymers that the reaction, which depends on the excitation wavelengths, arises from a distinction of the absorption sites, and that the absorbance and reaction efficiently are closely related to each other.

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References

1) Y. Kawamura, K. Toyoda, and S. Namba, *Appl. Phys. Lett.*, **40**, 374 (1982); R. Srinivasan and V. Mayne-Banton, *Appl. Phys. Lett.*, **41**, 576 (1982).

2) R. Srinivasan, *Science*, **234**, 559 (1986); R. Srinivasan and B. Braren, *Chem. Rev.*, **89**, 1303 (1989); S. Lazare and V. Granier, *Laser Chem.*, **10**, 25 (1989).

3) M. Shimoyama, H. Niino, and A. Yabe, *Macromol. Chem.*, **193**, 569 (1992).

4) S. Kawanishi, Y. Shimizu, S. Sugimoto, and N. Suzuki, *Polymer*, **32**, 979 (1991).

5) Y. Hamada, S. Kawanishi, M. Nishii, Y. Shimizu, S. Sugimoto, K. Ema, and T. Yamamoto, *J. Photopolym. Sci. Technol.*, **6**, 385 (1993); Y. Hamada, S. Kawanishi, M. Nishii, S. Sugimoto, and T. Yamamoto, *Jpn. J. Appl. Phys.*, **33**, 4764 (1994).

6) Y. Izumi, M. Maruo, S. Kawanishi, N. Ichinose, and T. Yamamoto, *JAERI-Rev.*, **95-015**, 19 (1995); Y. Izumi, M. Maruo, S. Kawanishi, N. Ichinose, T. Yamamoto, and N. Suzuki, *Technol. Rep. Osaka Univ.*, **46**, 291 (1996); Y. Izumi, S. Kawanishi, N. Suzuki, M. Maruo, N. Ichinose, and T. Yamamoto, *Bull. Chem. Soc. Jpn.*, **70**, 2855 (1997).

7) R. A. Wessling, "Polymer Monographs Vol. 5; Polyvinylidene Chloride," Gordon and Breach Science Publishers, New York (1997), Chap. 9.

8) Y. Izumi, K. Ema, T. Yamamoto, S. Kawanishi, Y. Shimizu, S. Sugimoto, and N. Suzuki, *Rev. Laser Eng.*, **19**, 247 (1991).

9) G. J. Atchison, *J. Appl. Polym. Sci.*, **7**, 1471 (1963).

10) P. Nayler and M. C. Whiting, *J. Chem. Soc.*, **1955**, 3037.

11) S. Speiser, I. Oref, T. Goldstein, and S. Kimel, *Chem. Phys. Lett.*, **11**, 117 (1971), and references therein.

12) D. Braun, "Degradation and Stabilization of Polymers," ed by G. Geuskens, Appl. Sci. Publishers, London (1975), p. 23.

13) S. L. Murov, I. Carmichael, and G. L. Hug, "Handbook of Photochemistry," 2nd ed, Marcel Dekker, New York (1992).

14) H. Fukumura and H. Masuhara, *J. Photopolym. Sci. Technol.*, **5**, 223 (1992).

15) D. D. Dlott, *J. Lumin.*, **45**, 397 (1990); D. D. Dlott, *J. Opt. Soc. Am.*, **B7**, 1638 (1990); H. Kim and D. D. Dlott, *J. Chem. Phys.*, **94**, 8203 (1991).