Title	Excimer Laser-Induced Chemical Reaction and Photochemical Surface Modification of Halogenated Polymers
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Citation	大阪大学, 1999, 博士論文
Version Type	VoR
URL	https://doi.org/10.11501/3155626
rights	
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Excimer Laser-Induced Chemical Reaction and Photochemical Surface Modification of Halogenated Polymers

1998

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A Doctoral Thesis

Excimer Laser-Induced Chemical Reaction and Photochemical Surface Modification of Halogenated Polymers

（　含ハロゲン系高分子のエキシマレーザー
光誘起化学反応及び表面改質　）

1998

Yoshinobu IZUMI

Contents

Chapter 1 General Introduction

1.1 Introductory Remarks

The knowledge of radiation effects on the properties of polymeric materials is inevitable for their application to nuclear energy and space fields, and a great number of works on the radiation chemistry of polymers have been reported.[1] Especially, the radiation-induced oxidative degradation is important for estimation of lifetime of electric cable used in nuclear facilities.[2] The development of radiation-resistant polymers and the elucidation of radiation protection effects are also important for achievement of durable nuclear plants.[3]

For these 40 years, many investigators in the field of radiation chemistry have aimed at obtaining crosslinked polymers with improved physical properties[4] and at modifying the polymer surface by using radiation-induced copolymerization method with various functional monomers.[5] Although there have been a lot of successful reports on the improvement of properties of polymeric materials, it is necessary for obtaining novel functional polymers to use a monochromatic UV light as an irradiation source. The surface modification using a monochromatic UV light is more efficient than radiation-grafting method in terms of (a) modification at a short penetration depth (without any degradations of bulk), (b) comparatively low cost for operation, and (c) selective reaction is expected since UV light generally induces the selective electronic excitation.

On the other hand, the Atomic Energy Commission of Japan published "the long-term plan for nuclear development and application" (Long-Term Plan) in 1987.[6] Especially, the development of nuclear basic technology was considered to be much important in Long-Term Plan. The nuclear basic technology was defined as the technology which was based on the long and/or medium-term needs in the various fields of nuclear science to generate an entirely new technology and had possibility to induce the break-through of nuclear technology. This nuclear basic technology included the following four regions of science, (1) nuclear materials, (2) artificial intelligence for nuclear technology, (3) laser science for nuclear technology, and (4) estimation and decreasing of radiation-risk. The laser science includes laser-induced isotope separation, generation of very short pulse with very high intensity and laser-induced organic chemistry.

In 1988, Osaka Laboratory for Radiation Chemistry, JAERI started the study of laser-induced organic or polymer chemistry as an advanced frontier subject to utilize lasers to chemistry.7) This laboratory had many information obtained from the study of radiation-induced polymer chemistry, and based on the knowledge of radiation chemistry, study of laser-induced polymer chemistry has been done.8) The author collaborated with the laser chemistry group of Osaka Laboratory, JAERI from April 1989 to March 1991 and from April 1993 to March 1996. The author and co-workers had been interested in the effect of excitation wavelength on the photochemistry of polymeric materials. Especially, the UV-induced reaction of halogenated polymers is an attractive subject, because they undergo formation of polyene structures when exposed to light, heat or ionizing radiation and formed polyenes show optical absorption due to π-π^* transition in the UV region. The author studied the irradiation effect of excimer laser light on PVC, Saran copolymer and PVdF.9) Moreover, the author studied the laser-induced surface modification of FEP film.9) The laser actinometry was also studied by the author using potassium ferrioxalato actinometer.9)

1.2 Outline of the Thesis

The present thesis consists of seven chapters including this one and deals with the interaction of excimer laser light with halogenated polymers. Especially, attention is focused on the effect of light source.

In **Chapter 1**, a historical background of laser-induced polymer chemistry and the reason why the author started the study of laser-induced polymer chemistry represented in this thesis are described.

In **Chapter 2**, the applicability of potassium tris(oxalato)ferrate (III) to actinometry of ArF, KrF and XeF excimer laser light is described. This substance in 0.1 N H_2SO_4 has been widely used for actinometry of stationary mercury lamps. Although the quantum yields of Fe^{2+} by irradiation of excimer laser was different from those by irradiation of stationary lamps, this actinometer is satisfactorily usable as an actinometer for excimer lasers.

In **Chapter 3**, the irradiation effects of electron beam and ArF, KrF and XeCl excimer laser light on poly(vinyl chloride) (PVC) film are described. The irradiation of ArF and KrF excimer laser light was more effective than electron-beam irradiation for modifying the surface area of a PVC film. The author discussed the wavelength dependence based on the triplet energies of olefin and diene and the dissociation energy of allylic C-Cl bond. Photochemical and photothermal effects and the photo-absorption sites are important factor of wavelength-dependent reaction of PVC.

In **Chapter 4**, the irradiation effects of ArF and KrF excimer laser light on vinylidene chloride-vinyl chloride (Saran) copolymer film are described. The author proposed a possible energy diagram concerning a laser-induced chemical reaction of chlorinated polymers. Photochemical and photothermal effects and the photo-absorption sites are important factor of wavelength-dependent reaction of Saran copolymer.

In **Chapter 5**, the irradiation effects of ArF and KrF excimer laser light on poly(vinylidene fluoride) (PVdF) film are described. Fluorinated polymer showed the wavelength-dependent reaction which was similar to those observed in the chlorinated polymer system.

Chapter 6 is concerned with the photochemical surface modification of fluoropolymer. Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) was irradiated by various kinds of UV light in contact with triethylamine (TEA), and both hydrophilic and oleophilic functionarities were obtained. The mechanism of this modification was discussed based on the effects of light source, polarity of solvent and presence of additives. This modification method using photoreaction is very useful for synthesizing hydrophilic and oleophilic surface on the inactive fluoropolymers.

The conclusions drawn from the present study are summarized in **Chapter 7**.

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9) See following chapters (Chap. 2-6) in this thesis.

(note) The following papers are closely related to this chapter.

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Chapter 2

Application of Potassium Tris(oxalato)ferrate (III) to Actinometry of Excimer Laser Light

Abstract

Actinometry of intense UV light from ArF, KrF and XeF excimer laser has been studied with a ferrioxalate chemical actinometer. The relation between the number of photons per pulse (N) and the absorbance change per pulse (ΔA) at 510 nm could be expressed by using a first-order function; $N = a\ \Delta A - b$. (a, b: numerical constants characterized by a laser-wavelength). The experimental errors in this method were 4.8, 5.2, and 1.6% for ArF, KrF and XeF excimer lasers, respectively. The results prove that the ferrioxalate chemical actinometer is satisfactorily usable as an actinometer for excimer lasers.

2.1 Introduction

In recent years, lasers are finding extensive applications in spectroscopy, instrumentation engineering, communication engineering, medical science and chemical processes such as micro-processing, chemical synthesis and isotope separation. The measurement of laser power becomes important along with the diversity of laser applications.1) The methodology of laser dosimetry includes calorimetry, photoelectrical technique using photoelectric devices, photochemical measurement using photo-sensitive materials etc. Among them, calorimetric measurement is most frequently used technique for laser power measurement, because it is most stable in wide region of wavelength and highly accurate system. However, the photo-sensor plate is very sensitive to high-intensity laser radiations such as excimer lasers. Therefore the reliability of measured value by using calorimeter might sometimes be problem, when the calorimeter is frequently used and the sensor plate is degraded. Moreover, calorimetric method can not directly evaluate the laser power which is transmitted through window materials but the laser power before transmitting or scattering with the window materials. Therefore, the development and establishment of actinometric method for direct measurement of photons which are incident into the reaction cell or vessel are strongly expected.

On the other hand, potassium ferrioxalate and uranyl ferrioxalate chemical actinometers have been widely used for actinometry of mercury lamps.2) These methods can evaluate the number of photons incident through the window materials. Especially, potassium ferrioxalate is the most widely used actinometer for actinometry of mercury lamps because of its excellent properties such as high-sensitivity, high-reproducibility, high-reliability, simplicity for operation.

The photoreduction of aqueous potassium tris(oxalato)ferrate (III) solution has been studied extensively,2-6) and the absolute quantum yields for Fe^{2+} formation at a number of wavelengths (the common mercury lines) have been determined. This substance in 0.1N H_2SO_4 was developed and tested as an actinometer by Parker and his co-worker.3-5)

On exposure to light with wavelength less than about 550 nm the solution of the ferrioxalate ion undergoes decomposition according to the reaction formula (here in shortened form),

$$[Fe^{3+}(C_2O_4)_3]^{3-} \xrightarrow{hv} [Fe^{2+}(C_2O_4)_2]^{2-} + 2CO_2. \qquad (1)$$

This complex is very sensitive to blue and UV lights and the quantum yield for Fe^{2+} formation is larger than unity for the wavelength less than 440 nm. The effects of various conditions such as dissolved oxygen,4) irradiation temperature5) and variations in complex or acid concentration5) upon the quantum yield were studied and found this system very stable. Moreover, the effect of the light intensity was also studied2,5) using high-pressure mercury lamp and xenon flash discharge tube, and no variation of quantum yield with light intensity was observed between $5\text{x}10^{-11}$ and $2\text{x}10^{-4}$mol(photon)$cm^{-2}s^{-1}$.

However, the photochemical reaction of potassium ferrioxalate induced by more intense UV light is not known.2,7) The photoreduction induced by the N_2 laser light with relatively low pulse energy was studied.8) However, the studies on the photochemical reaction induced by the intense UV light from rare gas halide excimer laser are not found. In this chapter, the photoreduction of potassium ferrioxalate induced by excimer laser irradiation is studied and the applicability of potassium ferrioxalate to actinometry of excimer laser lights is discussed.

2.2 Experimental

2.2.1 Preparation of Aqueous Solution of Potassium Tris(oxalato)ferrate (III)

Potassium tris(oxalato) ferrate (III) trihydrate ($K_3[Fe(C_2O_4)_3]3H_2O$), which was the raw material for the present experiments, was synthesized from Iron (III) ammonium sulfate 12-water and recrystallized for purification. This compound was dissolved in 0.1N sulfuric acid. The standard solution was 6.0 mM in Fe^{3+} concentration. For experiment upon the effect of initial Fe^{3+} concentration, it was varied between 1.0 and 24.0 mM. All operations of the preparation procedure were performed in total darkness or in the presence of weak red illumination in order to prevent the deterioration of potassium ferrioxalate (crystalline or solution).

2.2.2 Irradiation of excimer laser light

The solution of potassium ferrioxalate (70.0 ml) was placed in a Pyrex cylindrical vessel (volume: 91.5 ml, diameter: 35.5 mm, length: 70.0 mm) equipped with synthetic quartz window for the incidence of excimer laser beam and well-bubbled with the atmospheric gas (N_2, O_2 or CO_2) for saturation . The appearance of the irradiation vessel is shown in **Fig. 2. 1**. Then the solution was stirred magnetically (500 rpm), and irradiated with the ArF (193 nm), KrF (248 nm) or XeF (350 nm) excimer laser (Lumonics Hyper EX-460, frequency: 1 Hz, pulse duration (FWHM): 12-15 nsec, beam shape: 8 x 33 mm) at room temperature. The absorbances of this solution (1.0 mM in concentration, 10 mm in optical pathlength) at 193 nm, 248 nm and 350 nm were more than 5.0, more than 5.0 and about 1.0, respectively. Therefore, almost 100 % of photons must have been absorbed within the 70 mm layer of solution. In fact, the laser power passing through the 70 mm solution layer was monitored and estimated to be negligible. During the irradiation, the O_2 or CO_2 saturated solution was bubbled in a similar manner as before irradiation, while the vessel containing with the N_2 saturated solution was sealed off.

2.2.3 Calorimetry of Excimer Laser Pulse

The laser intensity (the pulse energy) was measured with two calorimeters (Scientech model 38-4UV5 and Ophir model FL 100A-EX). The variances of ArF, KrF and XeF laser pulse energy were 2.8 %, 2.8 % and 1.0 %, respectively. Calibration of calorimeter was done by using internal electric heater. The measured values by using two different calorimeters almost agreed (< 0.8 %), and they coincided with calibrated value by Joule's heat from internal electric heater. Therefore, the author confirmed that the calorimeters used in this study were very reliable and that measured laser power was accurate to within 1.0 %. The diminution fractions of the intensity by passing through the synthetic quartz window were previously determined as 74%, 83% and 89% for ArF, KrF and XeF excimer laser, respectively.

The number of photons (N_{photon}) transmitted through the synthetic quartz window was represented by the following relation,

$$N_{photon} = (\lambda E / 198.6) \times 10^{15}, \qquad (2)$$

where λ [nm] was the laser wavelength, E [mJ] was the laser energy transmitted through the synthetic quartz window.

2.2.4 Quantitative Analysis of Fe (II)

After irradiation, 1.0 ml acetate buffer (30.0 ml 1.0 M CH_3COONa in 18.0 ml 0.5 M H_2SO_4 + 2.0 ml distilled water) and 0.5 ml of 0.1 % 1,10-phenantroline solution were added into 1.0 ml of the irradiated ferrioxalate solution to give the photometric measuring volume of 20.0 ml. After standing of 30 minutes, the optical density at 510 nm (A) in a layer of 10 mm was determined by spectrophotometer (Shimadzu UV-2100) and compared with the optical density of an unirradiated control. The net value was used to calculate the number of photolytically formed Fe^{2+} according to the following relation,

$$N_{Fe(II)} = (N_A V_2 V_3 A / \varepsilon V_1) \times 10^{-3}, \qquad (3)$$

where $N_{Fe(II)}$ was the number of formed Fe^{2+}, V_1 was the volume of the ferrioxalate solution removed to determine Fe^{2+} (= 1.0 ml), V_2 was the volume of irradiated ferrioxalate solution (= 70.0 ml), V_3 was the volume of the photometric measuring solution (= 20.0 ml), N_A was Avogadro's constant, and A was the optical density (net value) of the measuring solution at 510 nm.

The quantum yield for Fe^{2+} formation ($F_{Fe(II)}$) can be calculated according to the following equation,

$$F_{Fe(II)} = N_{Fe(II)} / N_{photon}. \qquad (4)$$

2.3. Results and Discussion

2.3.1 Relationship Between the Number of Photons and Change in Absorbance

Figure 2. 2 shows the relations between the number of absorbed photons and the change in absorbance arisen from Fe^{2+} formation under N_2 atmosphere for ArF, KrF and XeF excimer laser irradiations, respectively. In any cases of irradiation wavelength, the photolytically formed Fe^{2+} increased proportionally with increase of irradiated laser pulse number, and the linearities were very good in the present experimental region of number of photons ($< 2.05 \times 10^{19}$, $< 2.51 \times 10^{19}$ and 1.74×10^{19} for ArF, KrF and XeF irradiations, respectively). This suggests that the ferrioxalate chemical actinometer is applicable to the actinometry for intense UV lights from rare gas halide excimer lasers.

2.3.2 Relationship Between the Number of Photons per Pulse and Change in Absorbance per Pulse

In order to elucidate the relation between the number of photons per pulse and change in absorbance per pulse at 510 nm, the ferrioxalate actinometer solution which was saturated with nitrogen was irradiated by ArF, KrF or XeF excimer laser light and change in absorbance per pulse was measured. **Figures 2. 3, 2. 4** and **2. 5** show the relation between the number of photons per pulse (N) and change in absorbance per pulse at 510 nm (ΔA) for ArF, KrF and XeF laser-irradiated cases, respectively. (**Figures 2. 6** also show the quantum yields for Fe^{2+} production by ArF, KrF and XeF-irradiations calculated from data obtained in **Fig. 2. 3**, **2. 4** and **2. 5**, respectively.) In the cases of relatively low pulse energy irradiation, the quantum yield of Fe^{2+} production was about the same as the case of UV lamp-irradiation; $\Phi =$

1.25 for 253.7 nm, and $\Phi = 1.18$ for 365 nm which were previously reported.3) For example, the quantum yields of Fe^{2+} production were 1.33 and 1.24 for KrF (45.7 mJ / pulse) and XeF (44.6 mJ / pulse) irradiations, respectively. These results indicate that the reduction of Fe^{3+} cation induced by excimer laser with relatively low pulse energy can be proceeded via similar mechanisms to the case induced by a stationary lamp.

On the other hand, in any cases, the quantum yield for Fe^{2+} formation decreased with increase of laser pulse energy (i.e. from 0.857 to 0.660 for ArF, from 1.33 to 0.898 for KrF, and from 1.24 to 1.08 for XeF excimer laser). Such a decrease of the quantum yield for Fe^{2+} formation can be induced by multi-photon absorption of tris(oxalato) ferrate (III) ion, re-absorption of excimer laser light by an excited tris(oxalato) ferrate (III) ion, and deactivation of excited tris(oxalato) ferrate (III) ion by the interaction between plural excited tris(oxalato) ferrate (III) ions.

Although the quantum efficiency of Fe^{2+} formation decreased along with an increase of pulse energy, in each case, change in absorbance per pulse linearly increased with increase of laser intensity. The relations between the number of photons per pulse (N) and change in absorbance per pulse at 510 nm (ΔA) can be expressed by the following equations,

ArF; $N = 1.30 \times 10^{20} \Delta A - 3.18 \times 10^{16}$ (5)
($5.39 \times 10^{16} - 2.30 \times 10^{17}$ photons/pulse)

KrF; $N = 8.62 \times 10^{19} \Delta A - 3.51 \times 10^{16}$ (6)
($5.71 \times 10^{16} - 5.24 \times 10^{17}$ photons/pulse)

XeF; $N = 7.10 \times 10^{19} \Delta A - 1.17 \times 10^{16}$. (7)
($8.35 \times 10^{16} - 4.19 \times 10^{17}$ photons/pulse)

The standard deviations, which included the fluctuations of laser-emission, in this method were 4.8, 5.2 and 1.6 % for ArF, KrF and XeF excimer lasers, respectively. These results indicate that the actinometry of excimer lasers using potassium tris(oxalato) ferrate (III) is very reliable and excellent method with high accuracy.

2.3.3 Effect of Dissolved Oxygen

The actinometry using potassium tris(oxalato) ferrate (III) is based on the photo-reduction yield of Fe^{3+} as shown Eq (1). Therefore, in the presence of dissolved oxygen in ferrioxalate solution, the photo-produced Fe^{2+} may oxidized to Fe^{3+} and the observed photo-reduction efficiency decrease. Because such a decrease of photo-produced Fe^{2+} yield seriously affects on the reliability of this actinometry, it is very important to elucidate the effect of dissolved oxygen on the photo-reduction reaction of potassium tris(oxalato) ferrate (III). **Figures 2. 7, 2. 8** and **2. 9** show the relation between the number of photons per pulse (N) and change in absorbance per pulse at 510 nm (ΔA) for O_2-bubbled (50 ml/min) solutions irradiated by ArF, KrF and XeF lasers, respectively. (The results obtained in N_2-saturated solutions that were previously shown in **Figs. 2. 3, 2. 4** and **2. 5** are also represented with dotted lines in same figures.)

Comparing to N_2-saturated cases, the change in absorbance per pulse at 510 nm was decreased by the presence of dissolved oxygen, in all cases of ArF, KrF and XeF excimer laser irradiation; i. e. the efficiencies of Fe^{2+} formation in the cases of ArF, KrF and XeF irradiation under the condition of O_2-saturation decreased about 66 - 71 %, 79 - 91 % and 89 - 97 % of those in the cases of ArF, KrF and XeF irradiation under the condition of N_2-saturation, respectively.

The author proposes the following mechanisms for the reason why above-mentioned decrease of photo-reduction yields occurred. Dissolved oxygen can be ozonized by irradiation of UV light as shown in the following equations,[9]

$$O_2 \xrightarrow{h\nu} 2O \tag{8}$$

$$O + O_2 \longrightarrow O_3. \tag{9}$$

The intense UV light such as excimer laser light will more effectively ozonize the dissolved oxygen. On the other hand, Fe^{2+} cation dissolved in aqueous solution is easily oxidized by ozone,[10)]

$$Fe^{2+} + O_3 \longrightarrow Fe^{3+} + O_3^- \tag{10}$$

$$O_3^- + Fe^{2+} + H_2O \longrightarrow O_2 + Fe^{3+} + 2OH^-. \tag{11}$$

Therefore, based on these mechanisms, the decrease of photo-produced Fe^{2+} is due to the oxidation by ozone. Also, the order of reduction of Fe^{2+} formation, ArF > KrF > XeF, corresponds to the degree of photo-absorption by dissolved oxygen.[11)]

These results indicate that it is necessary for actinometry of intense UV-excimer laser light by using potassium tris(oxalato) ferrate (III) not to irradiate under the atmosphere including oxygen.

2.3.4 Effect of the Initial Concentration of Fe(III)

When the laser-irradiation effects of various matters are studied, various kinds of irradiation cells can be used. In order to proceed the actinometry appropriately, it is important to prepare the actinometer solution with suitable photo-absorptivity comparing to the absorptivity of the matter, which is to be tested. The absorptivity of actinometer solution can be varied by changing the concentration of potassium tris(oxalato) ferrate (III). The effect of the initial concentration of potassium tris(oxalato) ferrate (III) upon the photo-reduction efficiency by the irradiation with KrF-excimer laser was tested, and the results were shown in **Fig. 2. 10.**

From this figure, it is obvious that the absorbance change per pulse at 510 nm (ΔA) was not affected by the variation of initial concentration of Fe^{3+} (from 1.0 mM to 24.0 mM). Therefore, the initial concentration of potassium tris(oxalato) ferrate (III) can be varied in the range from 1.0 mM to 24.0 mM depending on the irradiation cell (for example optical path length).

2.4. Conclusions

Actinometry of intense UV light from ArF, KrF and XeF excimer laser was studied with a ferrioxalate chemical actinometer. The relations between the number of photons per pulse (N) and change in absorbance per pulse at 510 nm (ΔA) can be expressed by the following equations,

ArF; $N = 1.30 \times 10^{20}\,\Delta A - 3.18 \times 10^{16}$ (5)
(5.39×10^{16} - 2.30×10^{17} photons/pulse)
KrF; $N = 8.62 \times 10^{19}\,\Delta A - 3.51 \times 10^{16}$ (6)
(5.71×10^{16} - 5.24×10^{17} photons/pulse)
XeF; $N = 7.10 \times 10^{19}\,\Delta A - 1.17 \times 10^{16}$. (7)
(8.35×10^{16} - 4.19×10^{17} photons/pulse)

The standard deviations, which included the fluctuations of laser-emission, in this method were 4.8, 5.2 and 1.6 % for ArF, KrF and XeF excimer lasers, respectively. These results prove that the ferrioxalate chemical actinometer is satisfactorily usable as an actinometer for excimer lasers. Incidentally, it is necessary for this actinometry to remove the dissolved oxygen in order to prevent the oxidation of photo-produced Fe^{2+}.

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(note) This chapter is extracted from following paper.
"Actinometry of an Excimer Laser with a Ferrioxalate Chemical Actinometer", Y. IZUMI, K. EMA, T. YAMAMOTO, S. KAWANISHI, Y. SHIMIZU, S. SUGIMOTO and N. SUZUKI, *Rev. Laser Eng.*, **19** (3), 247-253 (1991), *in Japanese*.

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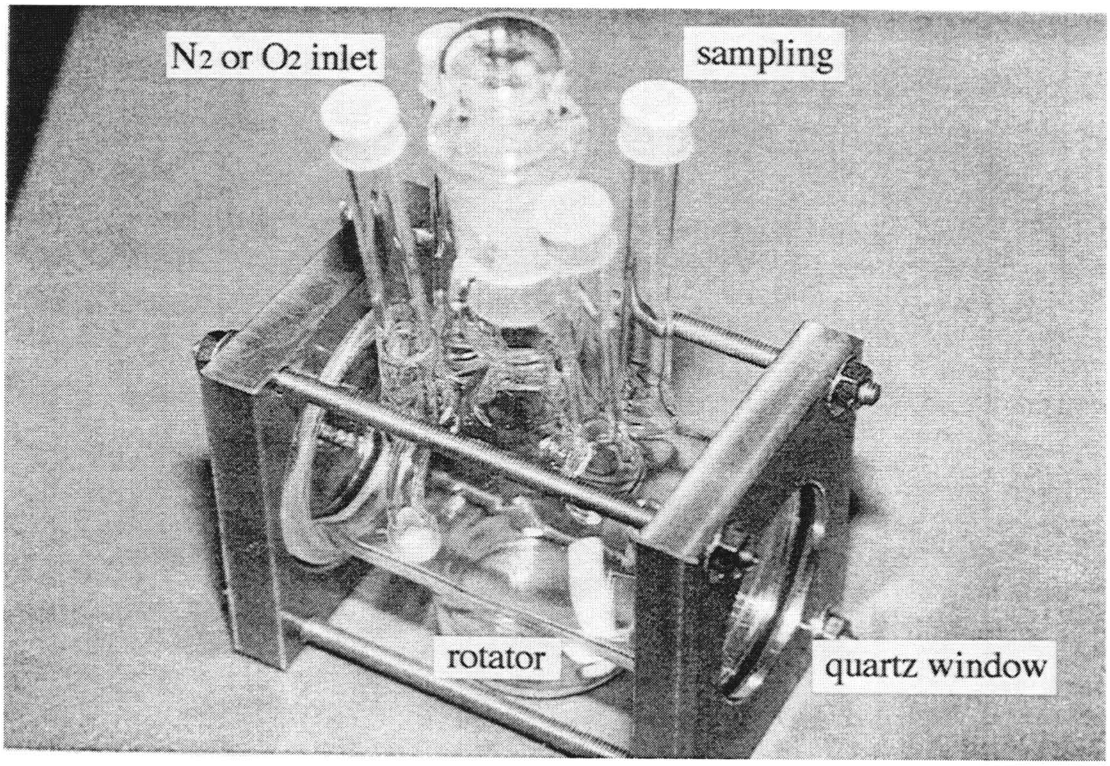

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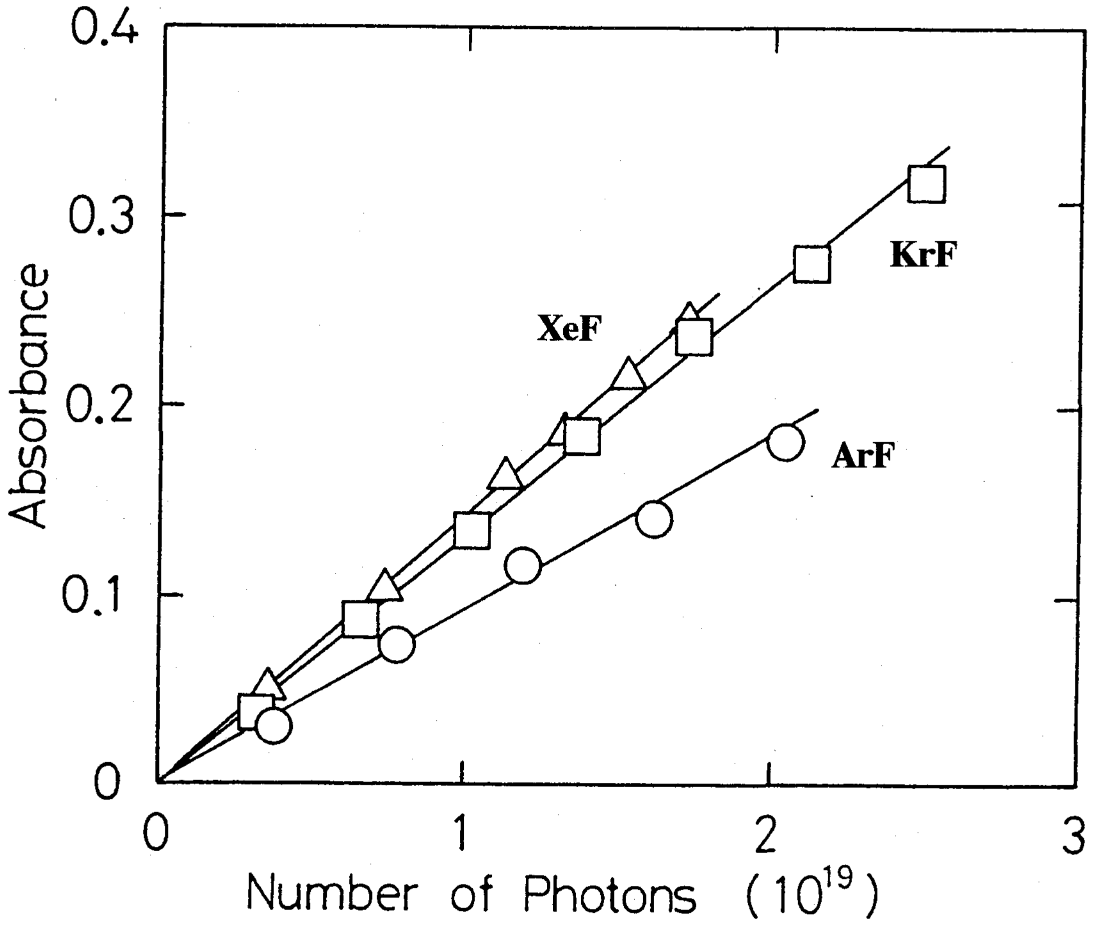

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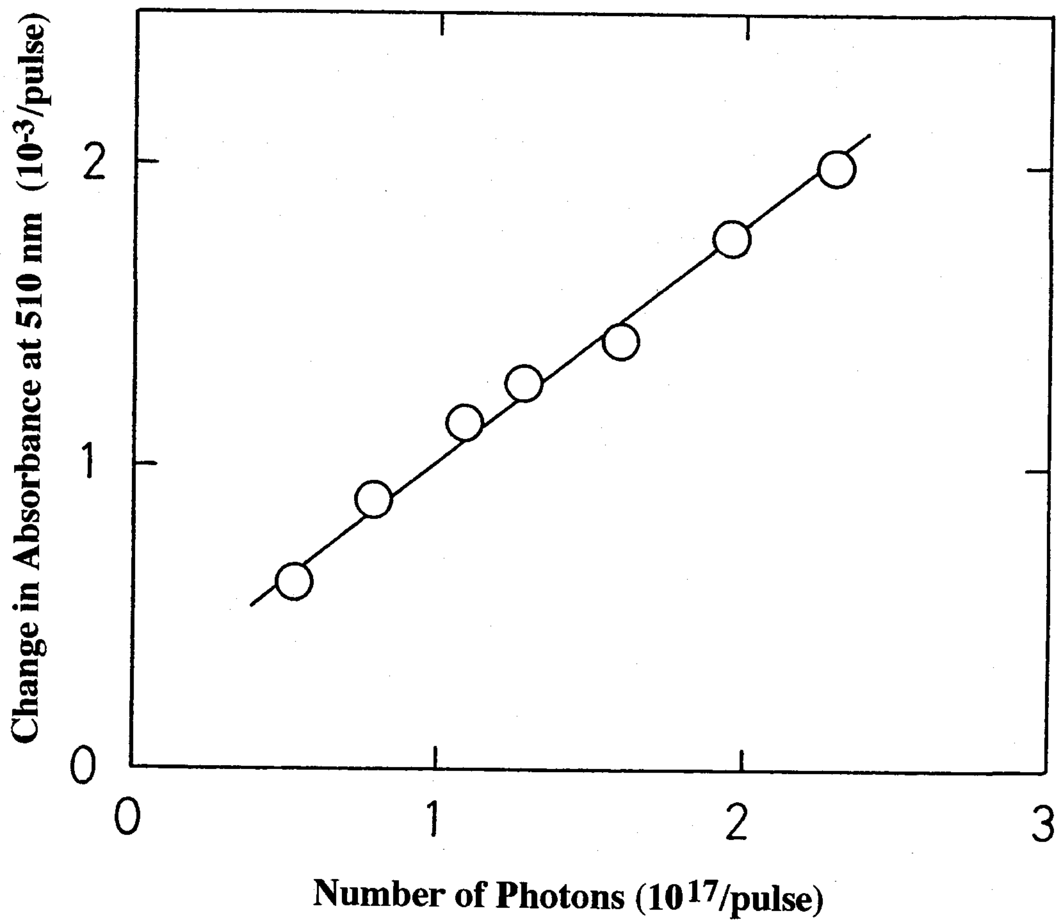

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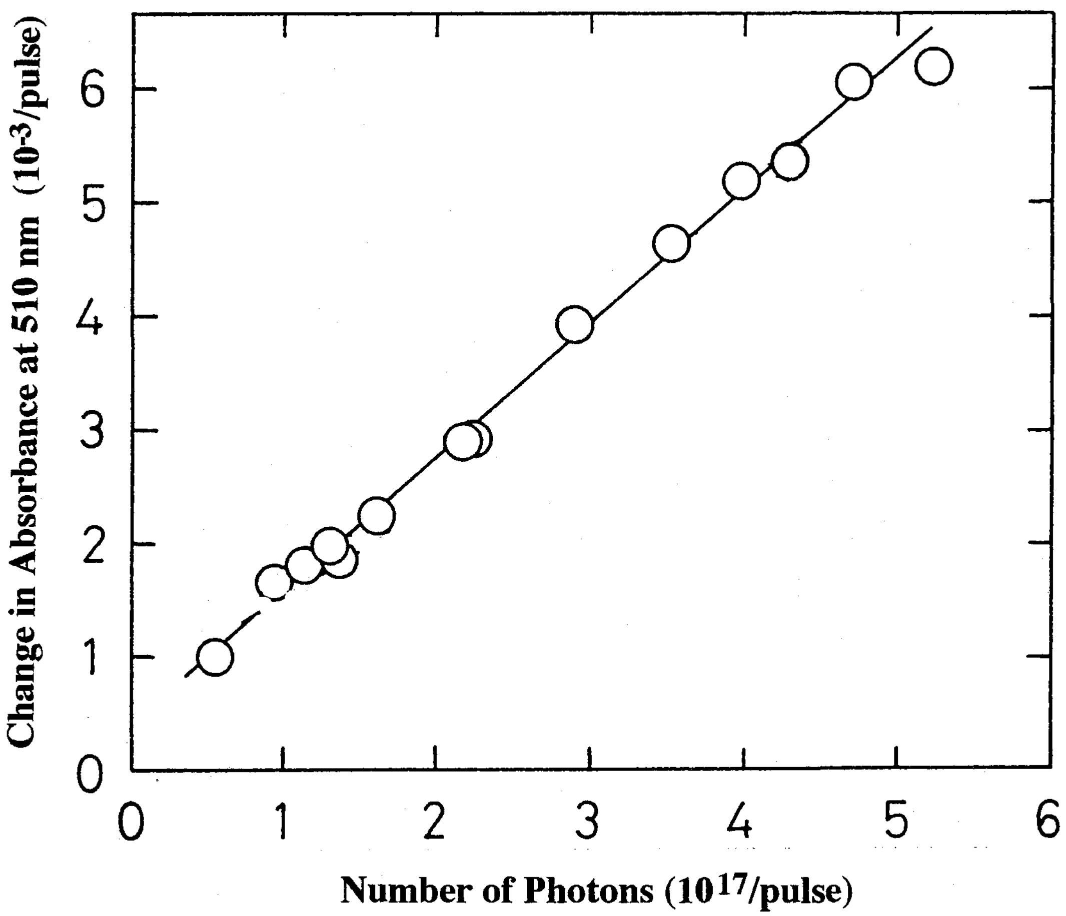

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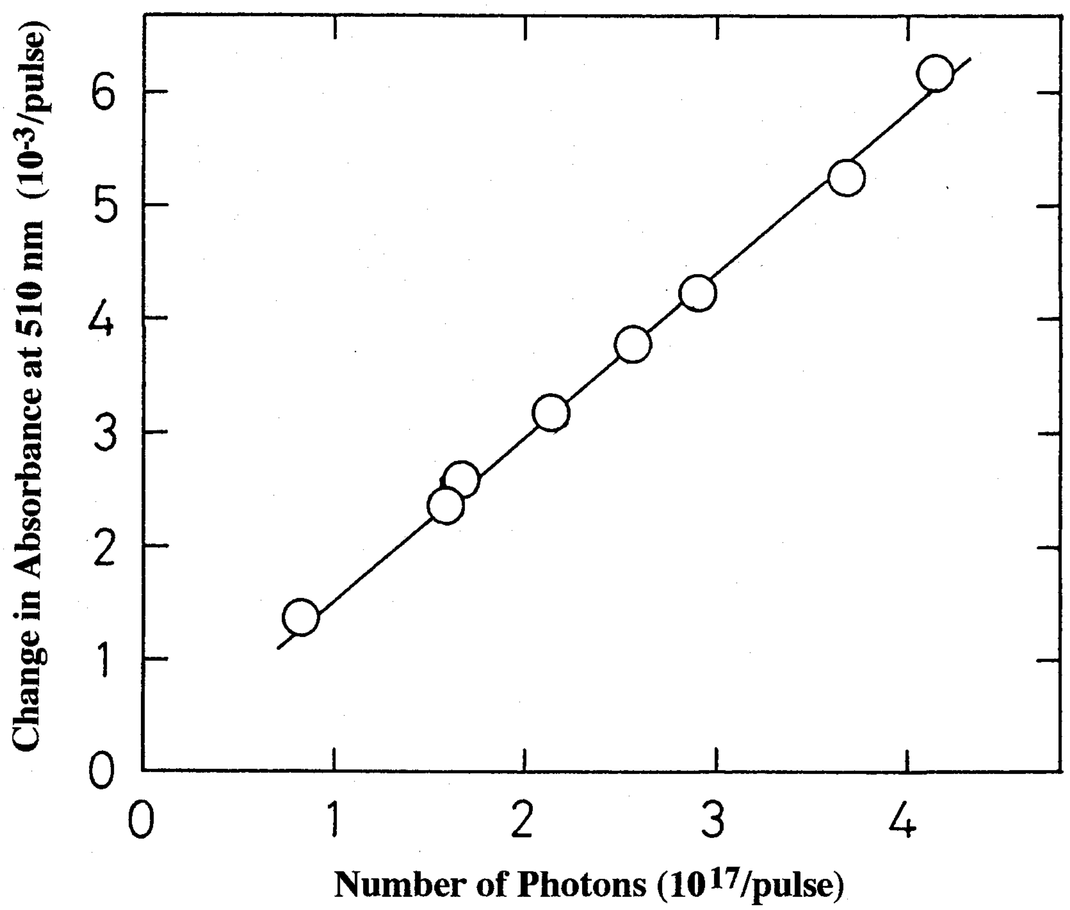

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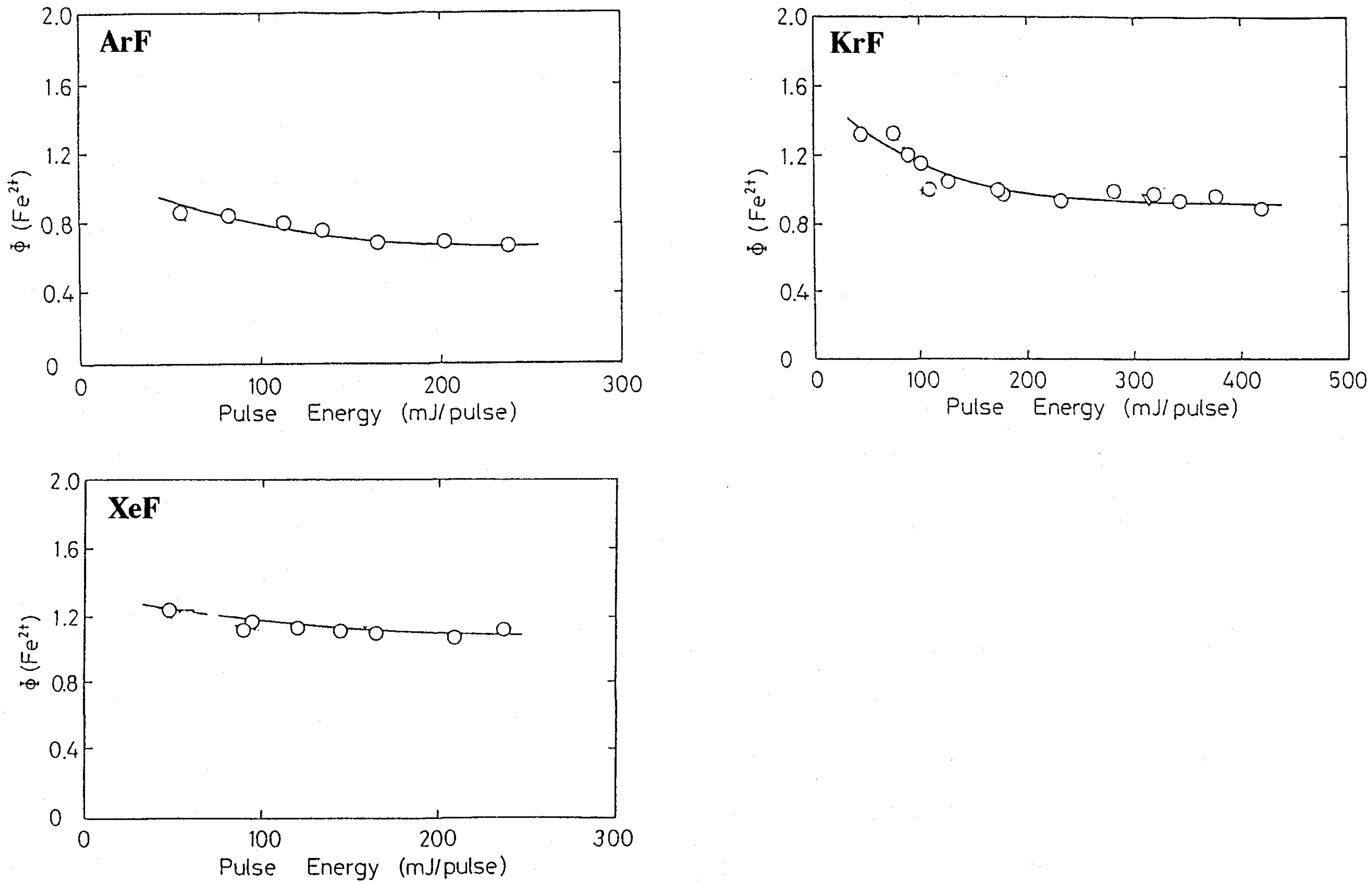

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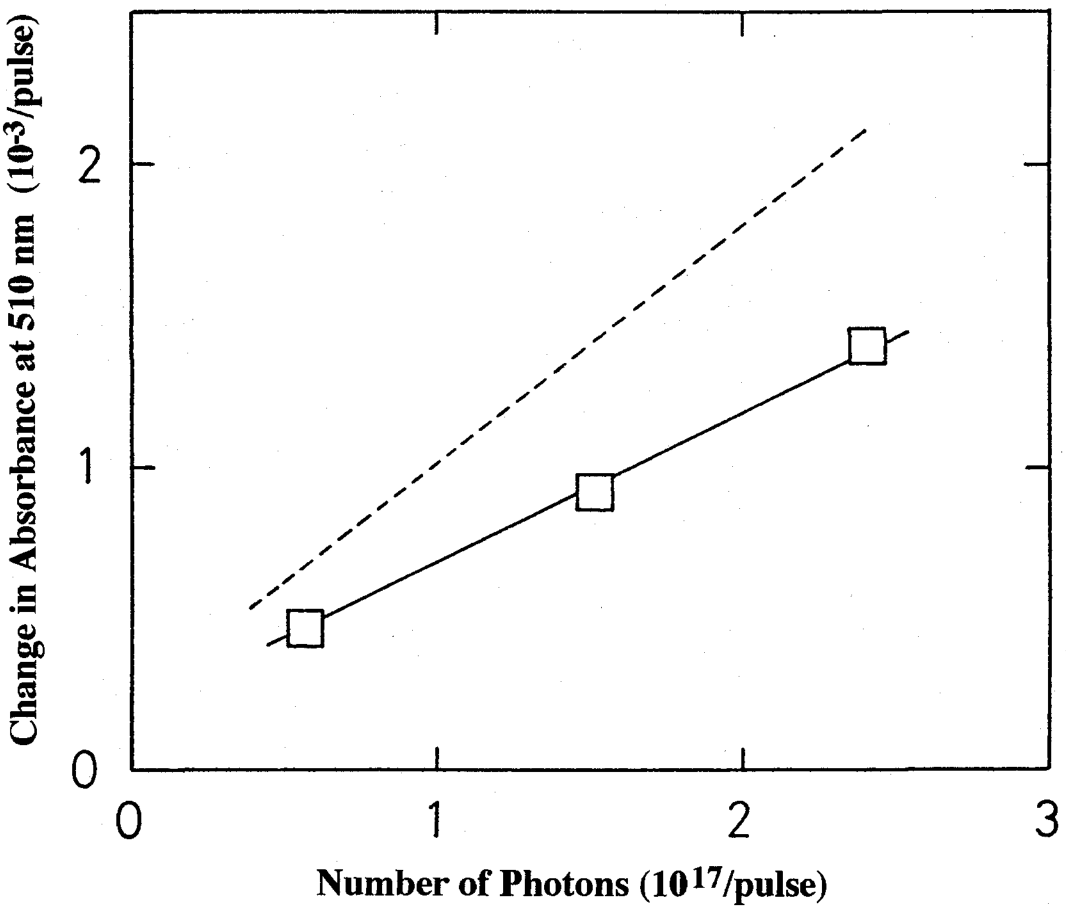

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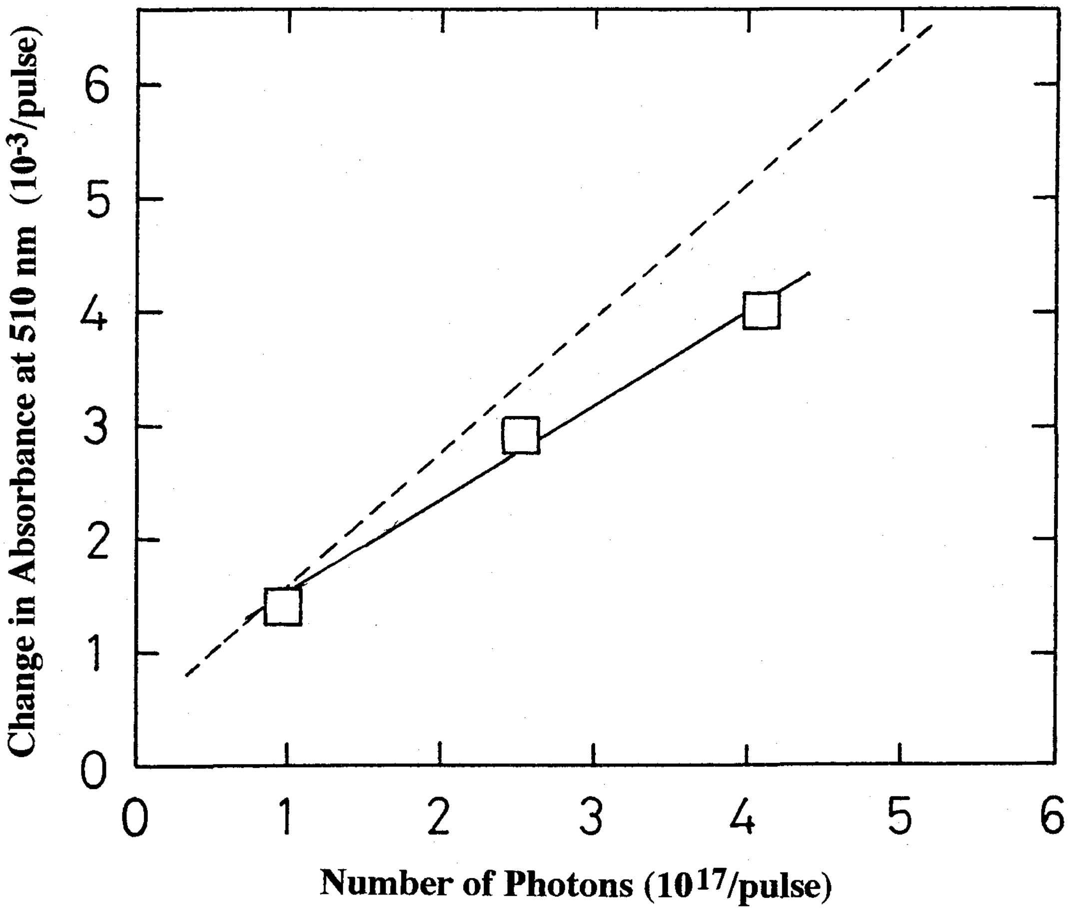

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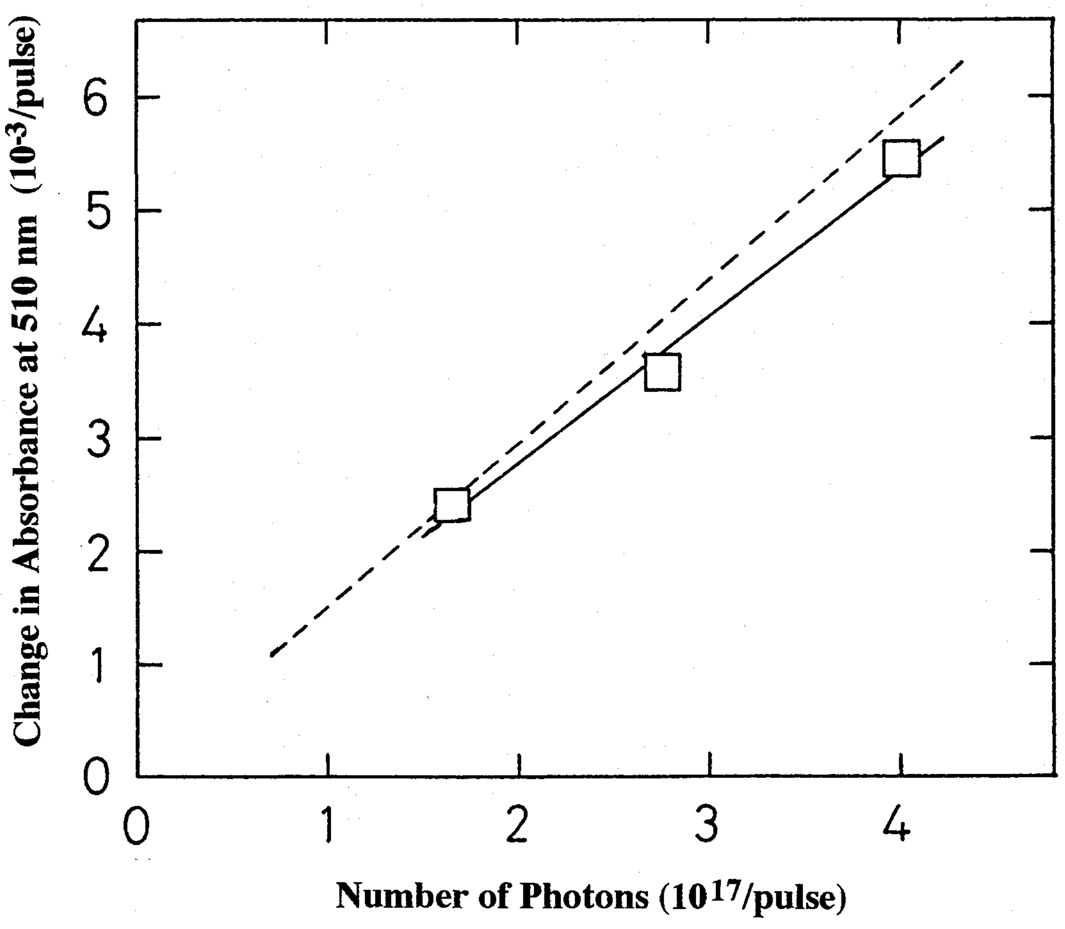

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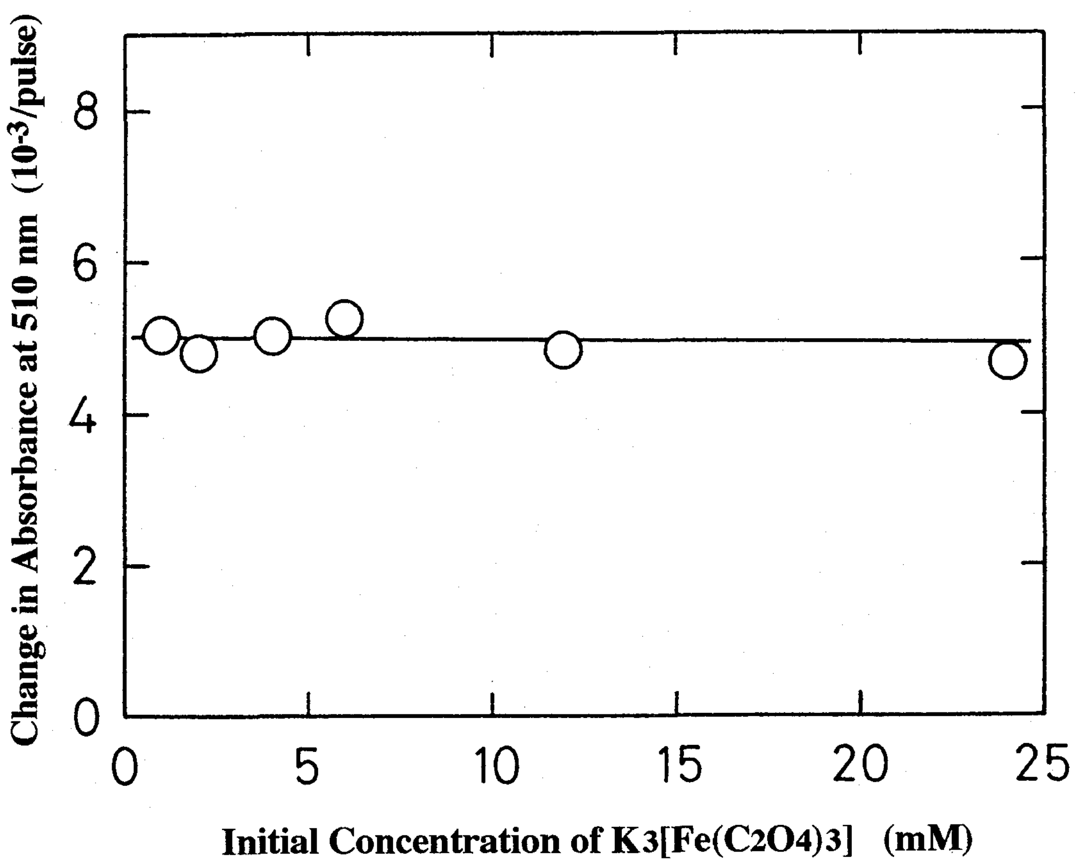

Fig. 2. 10 Relation between the change in absorbance per pulse and the initial concentration of $K_3[Fe(C_2O_4)_3]$ in KrF-irradiation. N_2-saturated. 4.17 x 10^{17} photons/pulse.

Chapter 3
Irradiation Effects of Excimer Laser Light on Poly(vinyl chloride) (PVC) Film

Abstract

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.

3.1 Introduction

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.$^{1\text{-}5)}$ 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, the photochemical reaction of pure PVC induced by intense monochromatic UV light from ArF, KrF and XeCl excimer lasers are studied in this chapter.

3.2 Experimental

3.2.1 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 than 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.

3.2.2 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 nm, 248 nm 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.

3.2.3 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 MgKα 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).

3.3 Results and Discussion

Figure 3. 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 nm 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 μW / cm^2, 100 μW / cm^2 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 3. 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 nm, 238 nm, 288 nm, 326 nm 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 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. 3. 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, the author experimentally confirmed that the reaction manners depend on the excitation wavelengths.

Figures 3. 3 (a) and **3. 3 (b)** 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, respectively11). 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.

The changes in the absorbances of these peaks in **Fig. 3. 2** are plotted in **Figs. 3. 4 (a)** and **3. 4 (b)**. 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 the author proposes 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 neighboring 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.

Figures 3. 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. 3. 5**, was evaluated from the initial slope of the curve of change in absorbance vs. number of pulses such as **Fig. 3. 4**. The slopes are 0.95 and 1.62 in **Figs. 3. 5 (a)** and **3. 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 multi-photon reaction. From the viewpoint of the excitation energy, the author is 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 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 ≈ 330 and ≈250 kJ mol^{-1}, and the dissociation energy of the allylic C-Cl bond lies between the two triplet energies (≈ 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 multi-photon 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)

3. 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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(note) This chapter is extracted from following papers.

"Excitation Wavelength Effect on Laser-Induced Dehydrochlorination of Poly(vinyl chloride) (PVC) Film", Y. IZUMI, M. MARUO, S. KAWANISHI, N. ICHINOSE and T. YAMAMOTO, *JAERI-Rev.*, **95-015**, 19-21 (1995).

"Formation of Polyene Structures in a Poly(vinyl chloride) Film by Irradiation of Monochromatic Lights from ArF and KrF Excimer Lasers", Y. IZUMI, M. MARUO, S. KAWANISHI, N. ICHINOSE, T. YAMAMOTO and N. SUZUKI, *Technol. Rep. Osaka Univ.*, **46**, 291-295 (1996).

"Irradiation Effects of Excimer Laser Light on Poly(vinyl chloride) (PVC) Film", Y. IZUMI, S. KAWANISHI, N. SUZUKI, M. MARUO, N. ICHINOSE and T. YAMAMOTO, *Bull. Chem. Soc. Jpn.*, **70** (11), 2855-2859 (1997).

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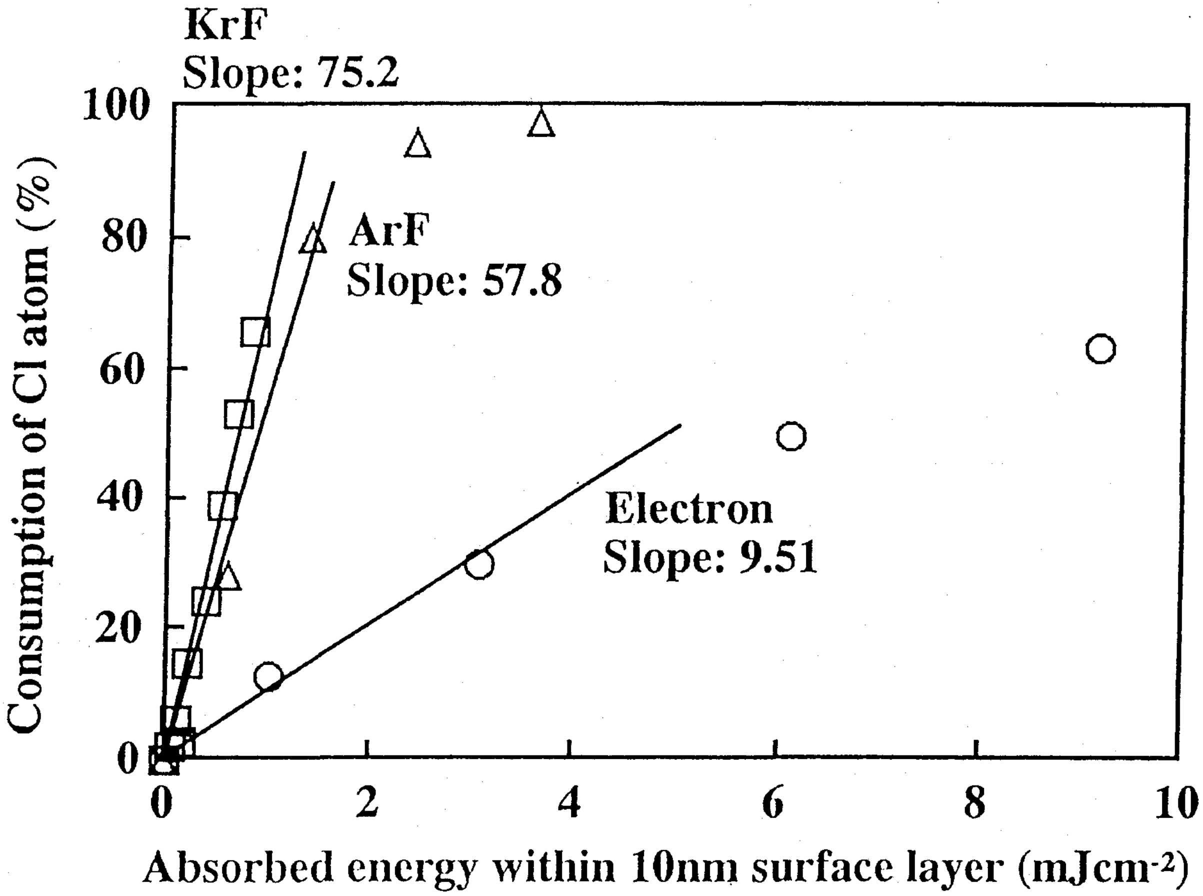
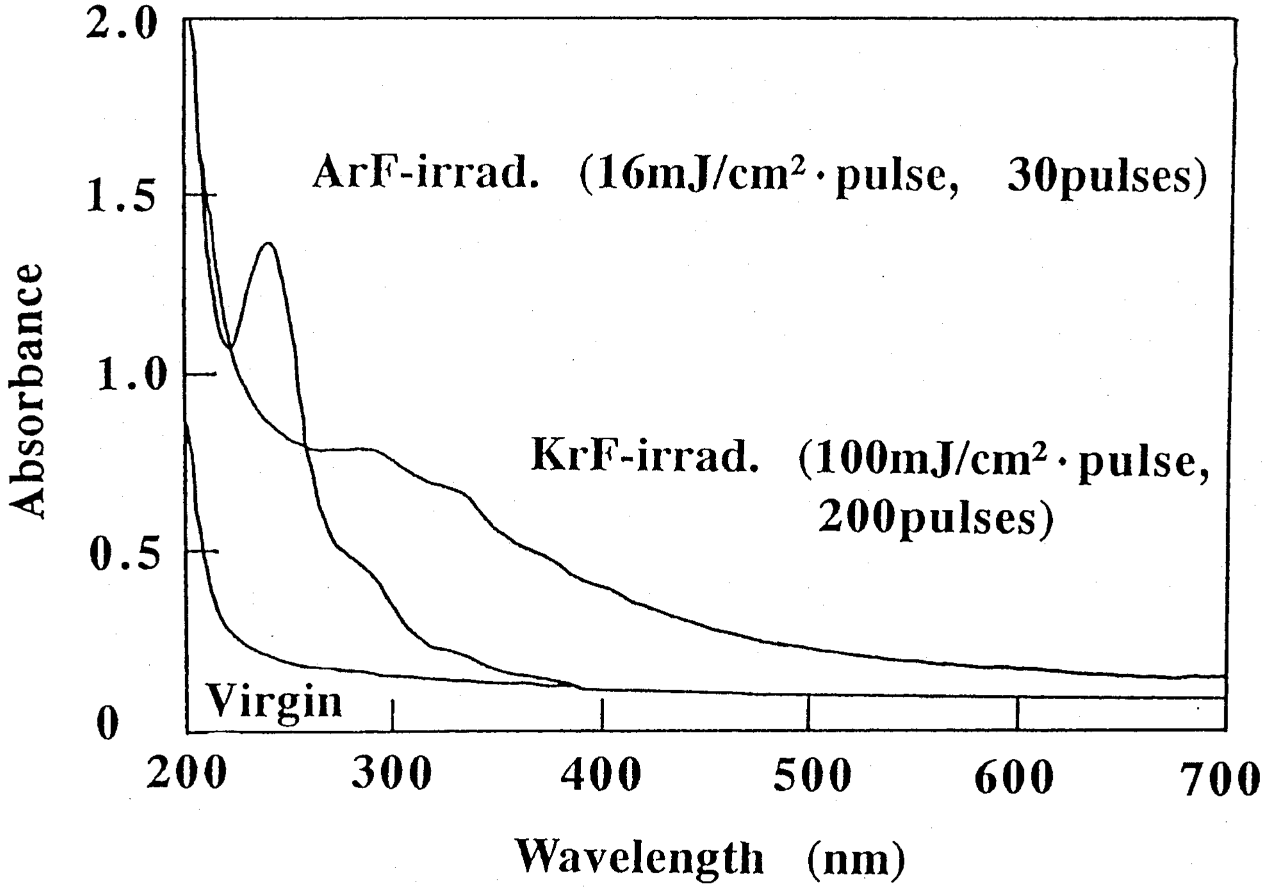


Fig. 3. 1 The consumption of Cl atom on the surface of PVC films irradiated with electron beam (circle), ArF (triangle) and KrF(square) excimer laser lights.



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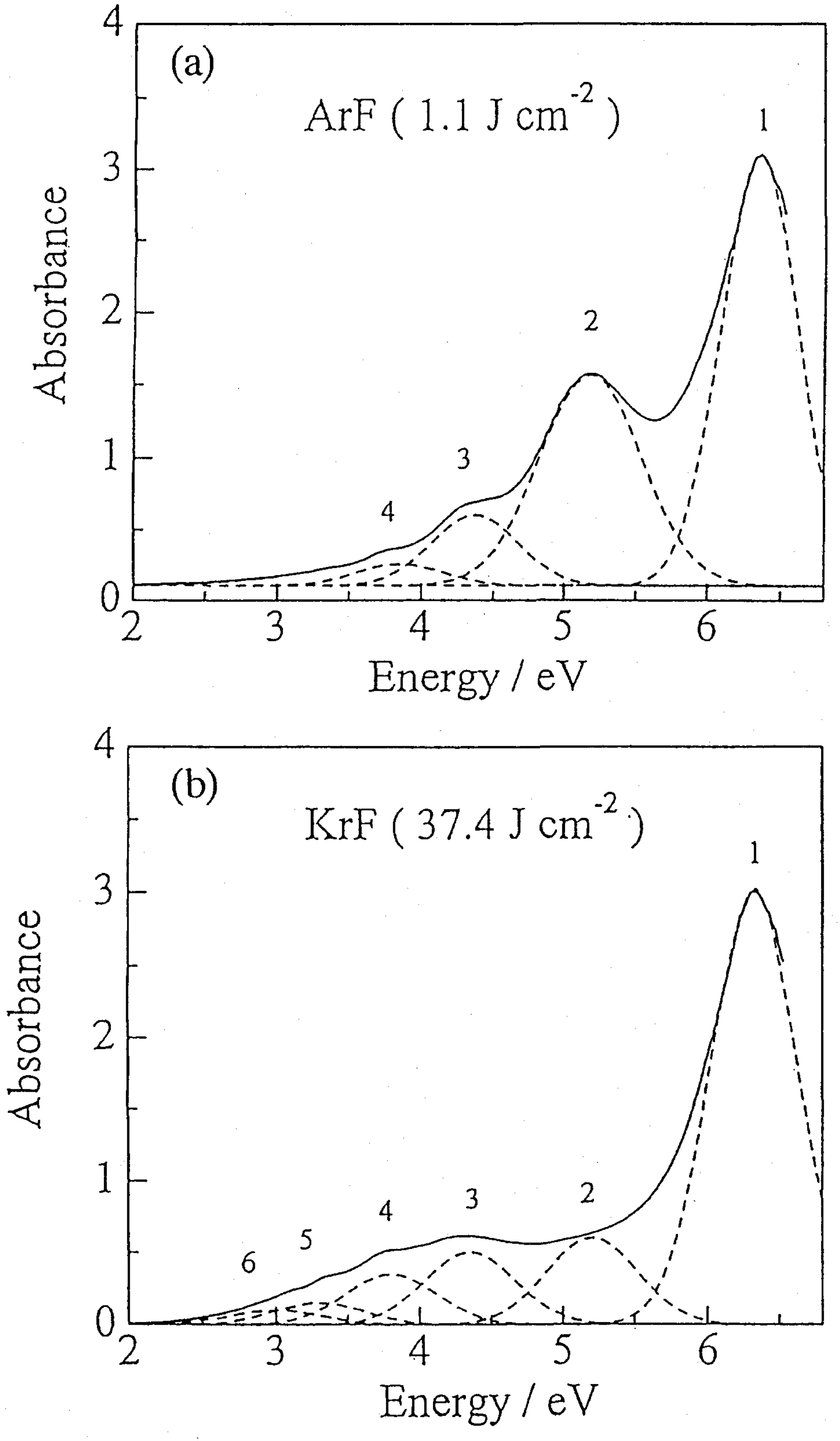

Fig. 3. 3 The result of wave-form analysis of PVC films irradiated with ArF (a) and KrF (b) excimer laser lights.

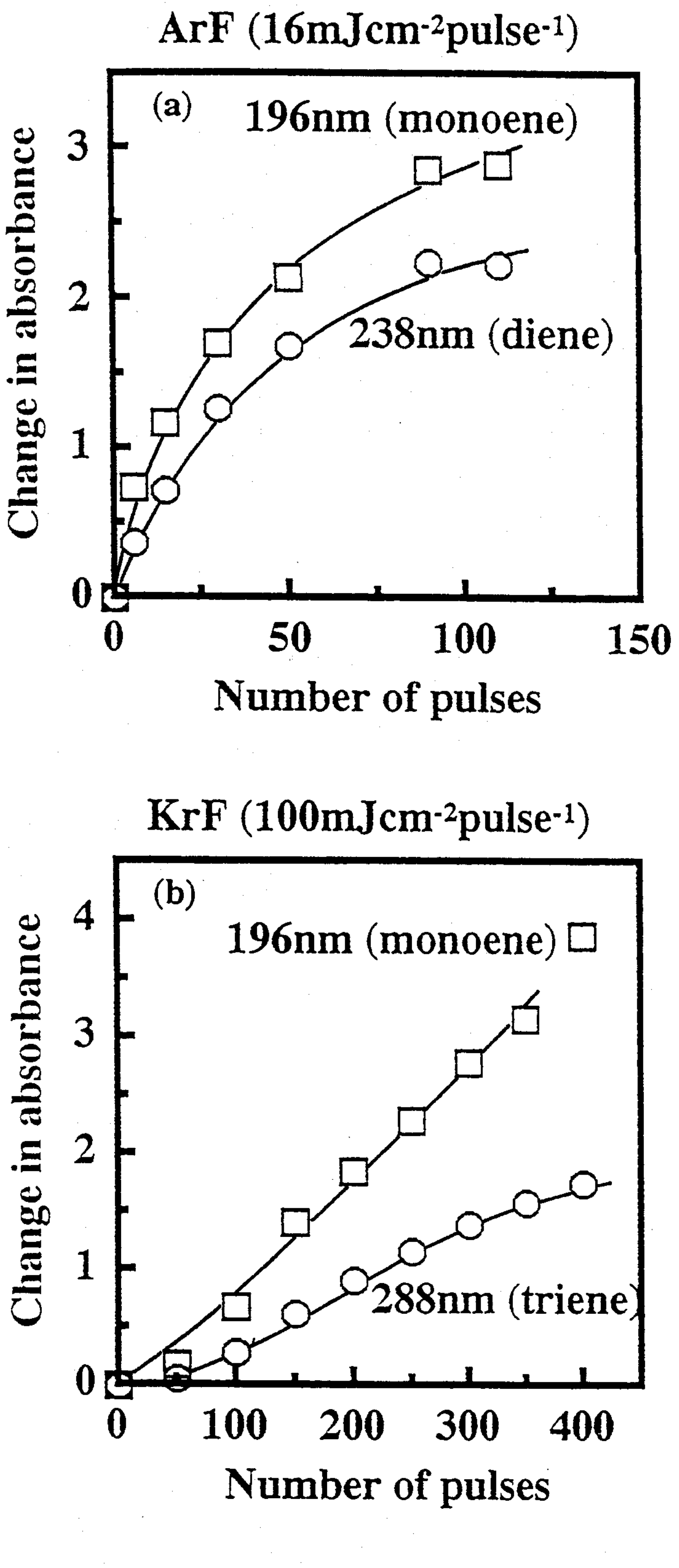

Fig. 3. 4 The change in absorbances of PVC films irradiated with ArF (a) and KrF (b) excimer laser lights.

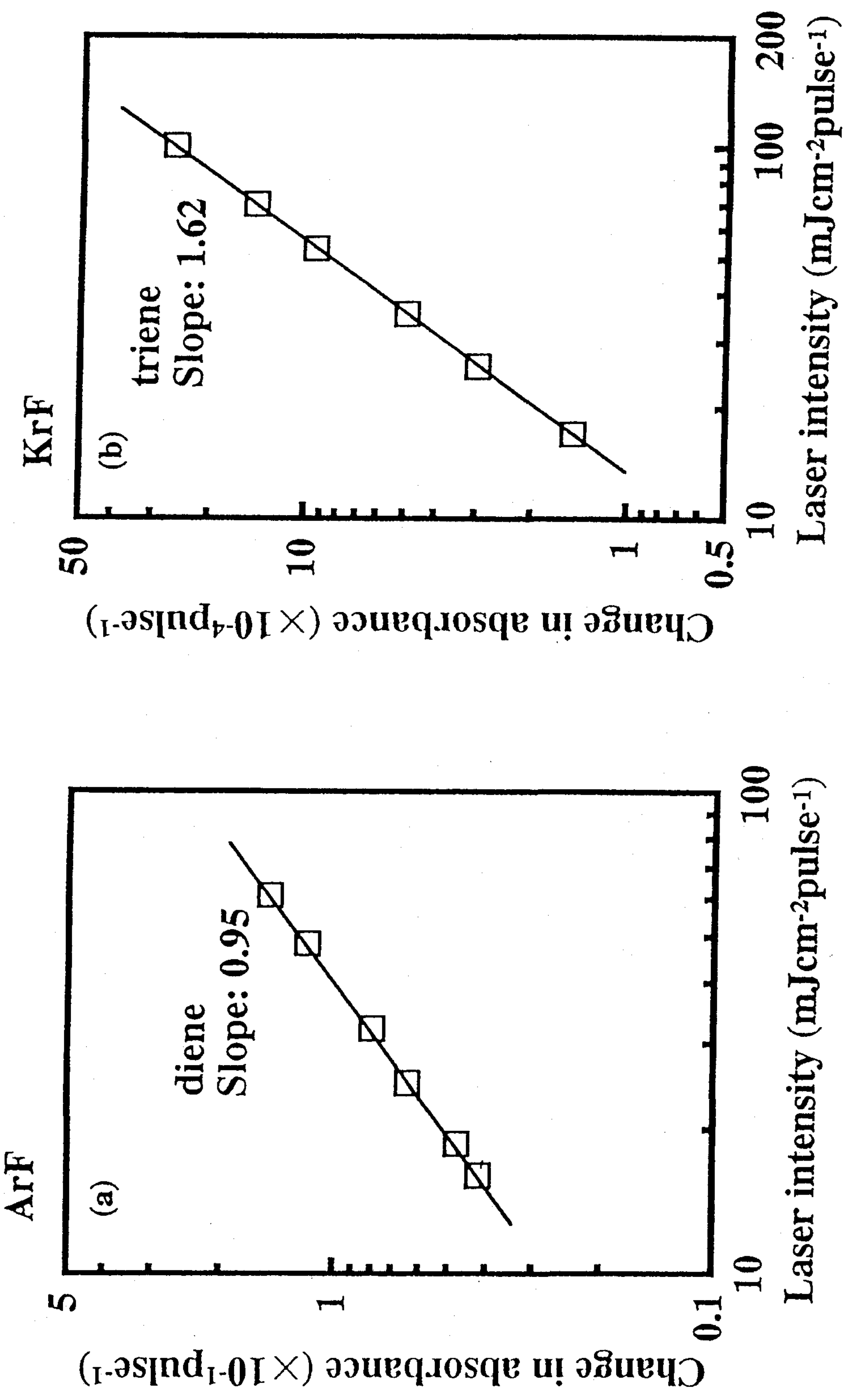

Fig. 3. 5 The laser intensity dependence of diene formation by ArF irradiation (a) and that of triene formation by KrF irradiation (b).

Chapter 4

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

Abstract

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.

4.1 Introduction

There has been considerable interest in the use of intense ultraviolet (UV) light from excimer lasers for modifying the polymer surfaces. Since the discovery of the phenomenon of ablative photodecomposition (APD),1) many reports have appeared dealing with interaction of the 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 the use of KrF laser is efficient for preparation of the π-electron-conjugated polymer.3) Kawanishi *et al.*4) and Hamada *et al.*5) studied wavelength dependence of laser irradiation effects on polypropylene and ETFE, respectively.

The author has 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 π-π^* transition in the UV region, the reaction of halogenated polymers induced by monochromatic UV light can be an especially attractive subject. In **Chapter 3**, the author described 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 the 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 in elsewhere.⁷⁾

4 .2 Experimental

4.2.1 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 the flat Pyrex glass plate, and the solvent was slowly evaporated. After more than 48 h, 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.

4.2.2 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 irradiations were carried out in a vacuum and at ambient temperature.

4.2.3 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 subtracting the spectrum of the non-irradiated sample from that of the irradiated one.

To confirm 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 M 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.

4.3 Results and Discussion

Figure 4. 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. 4. 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.

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. 4. 2**. The irradiation conditions were 8 mJcm^{-2}pulse^{-1}, 25 pulses, in vacuum for ArF irradiation, and 25 mJcm^{-2}pulse^{-1}, 140 pulses, 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 nm, 238 nm, 288 nm 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. 4. 3**. The irradiation conditions were 8 mJcm^{-2}pulse^{-1}, in vacuum for ArF irradiation, and 25 mJcm^{-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) 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 an 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, diene site formed by 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 pulses) can not be regarded as 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 absorbance change, except for initial slope in **Fig. 4. 3**.

Figure 4. 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. 4**, was evaluated from the initial slope of the curve of

change in absorbance vs. number of pulses such as **Fig. 4. 3**. The slopes in **Fig. 4. 4 (a)** are estimated as about 0.65 and those in **Fig. 4. 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]

$$Nf = N_0 / n \Pi \sigma i F^n, \tag{1}$$

where Nf 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, σi is the absorption cross section, and F is the laser intensity. The following expression can be derived from Eq. (1), namely:

$$\log Nf = n \log F + C, \tag{2}$$

where C corresponds to the Y-intercept in **Fig. 4. 4** and n, which is the number of photons that contribute to the reaction, corresponds to the slope in **Fig. 4. 4** on a logarithmic scale. Therefore, the formations of diene and triene by ArF irradiation proceeds via single-photon reaction, whereas those by KrF irradiation proceeds via a multi-photon reaction. The author proposes the following assumption for the reason why the slopes in **Fig. 4. 4 (a)** are less than unity. By irradiating with excimer laser light, chlorine 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 of primary reaction, but to the yield of the final product, the slope in **Fig. 4. 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, the author is supposing the following mechanisms (the energy diagram possible in the chemical reactions within the chlorinated polymers is shown in **Fig. 4. 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 diene, however, will not lead to bond dissociation from its excited triplet state. The typical triplet energies of aliphatic olefin and diene are ≈ 330 and ≈250 kJ mol^{-1}, and the dissociation energy of the allylic C-Cl bond lies between the two triplet energies (≈ 290 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 multi-photon absorption occurred via the T -> T* transition with the evolution of heat.14) Polyene formation in the case of KrF, therefore, can be attributed to a photothermal effect.

On the other hand, above-mentioned C-Cl bond dissociation can compete with vibrational relaxation. Dlott and his co-worker reported that in the 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, absorption site is not 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. The author has not yet been able to evaluate the quantum yield of polyene formation or dehydrochlorination experimentally. However, I believe that only the energy not deactivated by vibrational cooling contributes to the photochemical or photothermal reaction.

4.4 Conclusions

Vinylidene chloride - vinyl chloride copolymer (Saran copolymer) film was irradiated with monochromatic UV light from ArF and KrF excimer laser 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 efficiency are closely related to each other.

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(note) This chapter has been published as following paper.

"Irradiation Effects of Excimer Laser Light on Vinylidene Chloride - Vinyl Chloride (Saran) Copolymer Film", Y. IZUMI, S. KAWANISHI, N. TAKAGI, S. HONDA and T. YAMAMOTO, *Bull. Chem. Soc. Jpn.*, **71** (10), 2459-2463 (1998).

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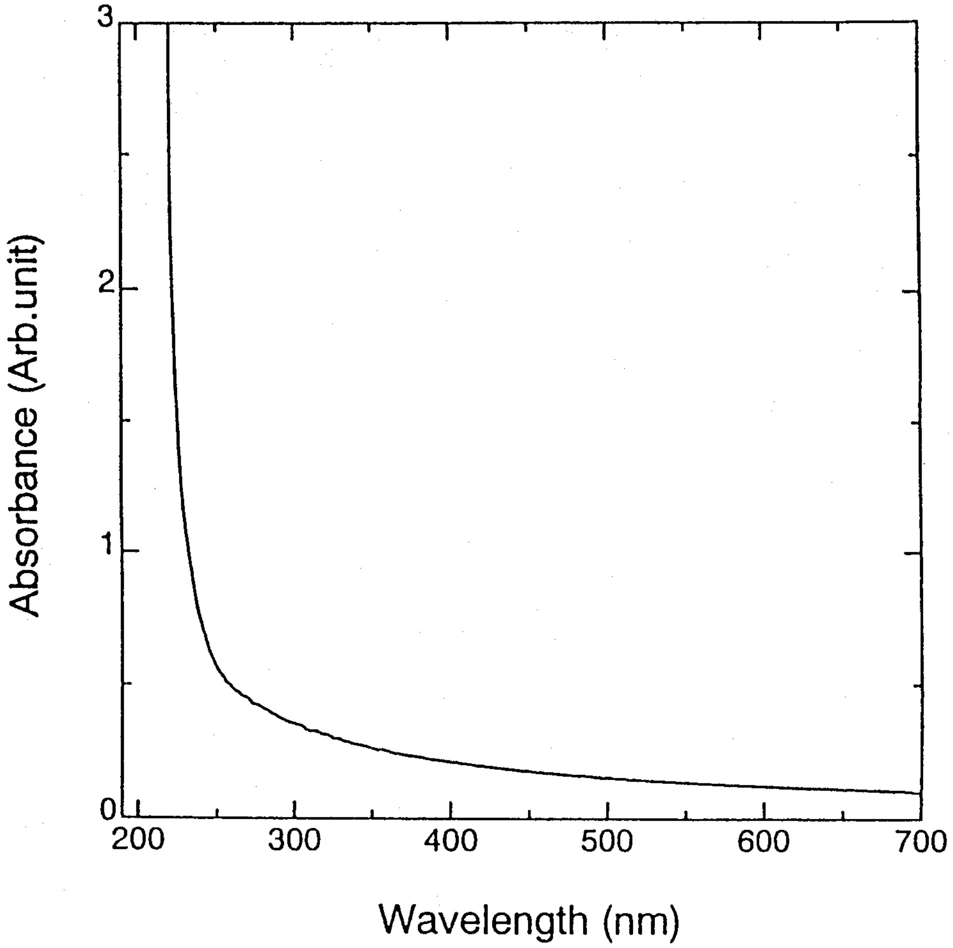
Fig. 4. 2 The differential vis-UV photo-absorption spectra between non-irradiated Saran film and ArF and KrF excimer laser irradiated one. (The irradiation conditions for ArF and KrF excimer lasers were presented in the figure)

Fig. 4. 3 The change in absorbances of Saran copolymer films irradiated with ArF; 8 mJcm^{-2}pulse^{-1} (a) and KrF; 25 mJcm^{-2}pulse^{-1} (b) excimer laser lights.

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

Fig. 4. 5 The possible energy diagram in the chemical reaction within the chlorinated polymers.



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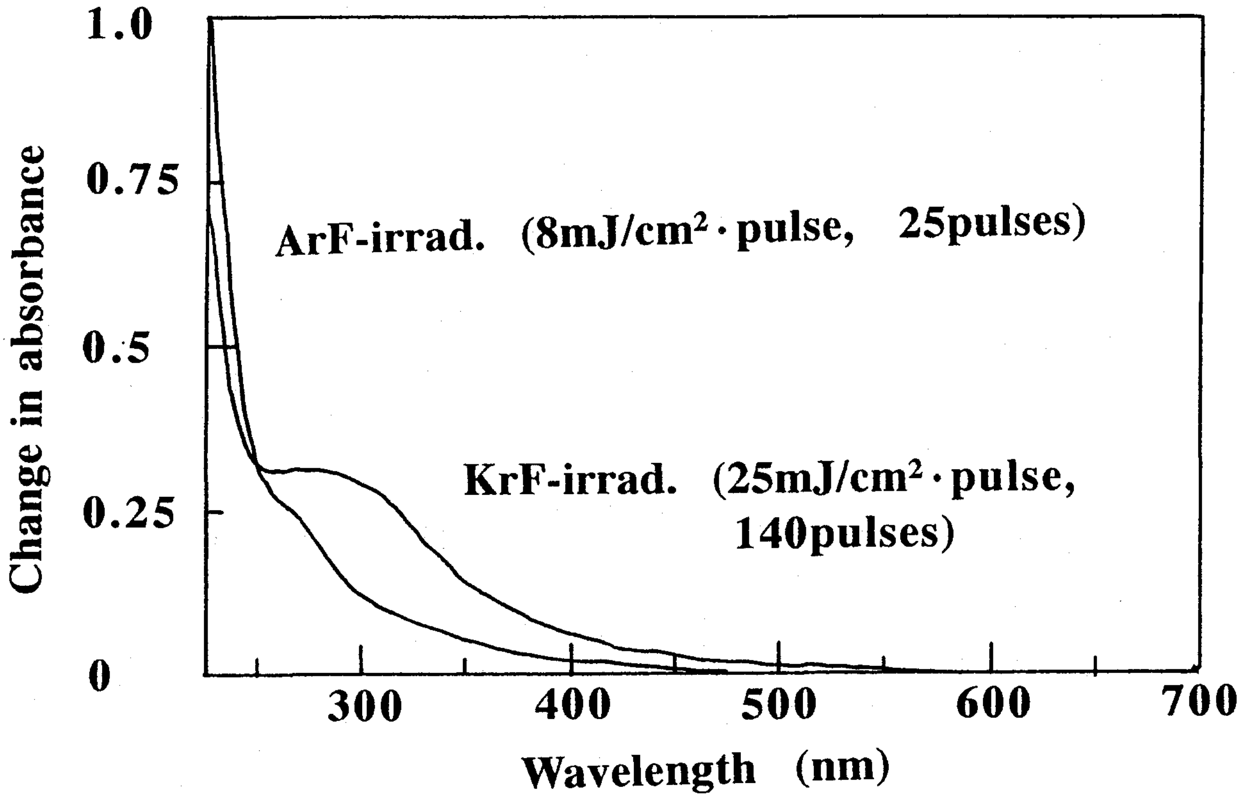
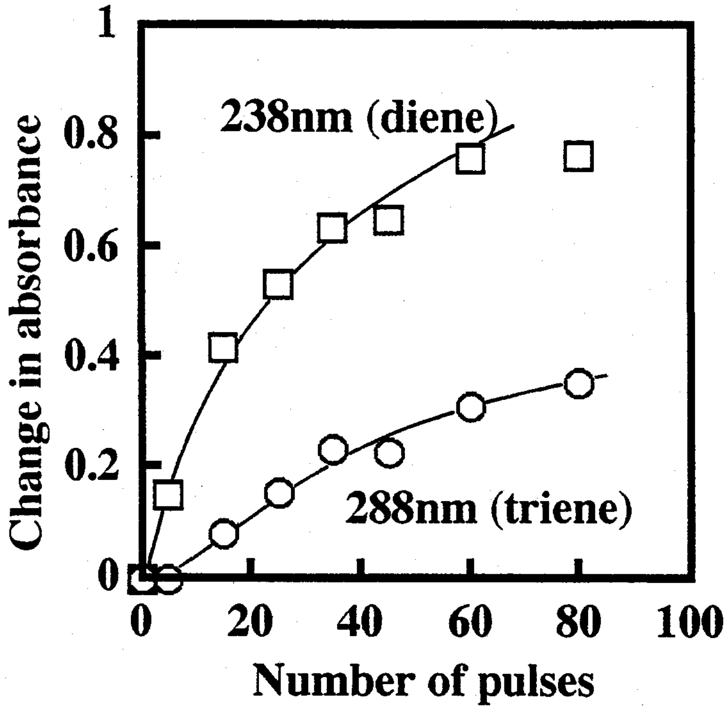


Fig. 4. 2 The differential vis-UV photo-absorption spectra between non-irradiated Saran film and ArF and KrF excimer laser irradiated one. (The irradiation conditions for ArF and KrF excimer lasers were presented in the figure)

(a) ArF (8mJcm^{-2}pulse^{-1})



(b) KrF (25mJcm^{-2}pulse^{-1})

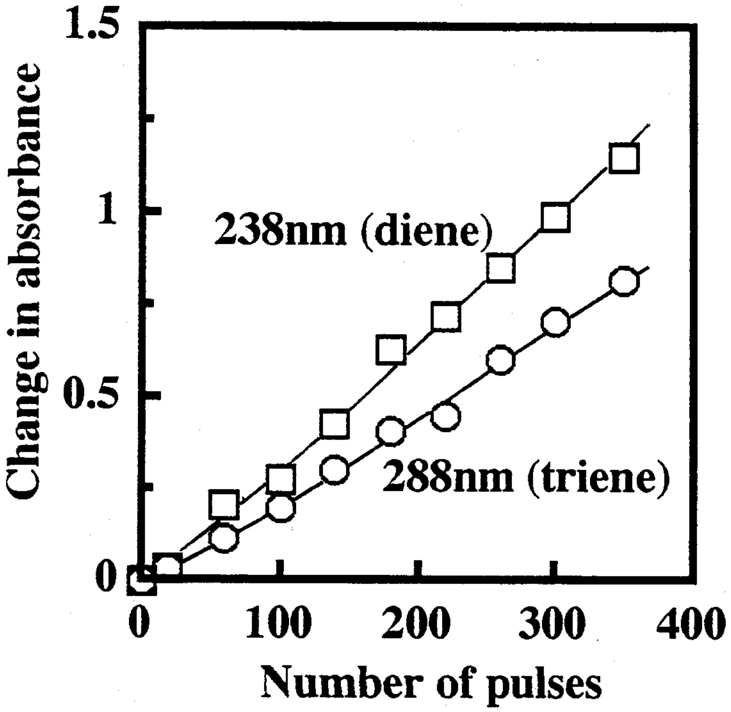


Fig. 4. 3 The change in absorbances of Saran copolymer films irradiated with ArF; 8 mJcm^{-2}pulse^{-1} (a) and KrF; 25 mJcm^{-2}pulse^{-1} (b) excimer laser lights.

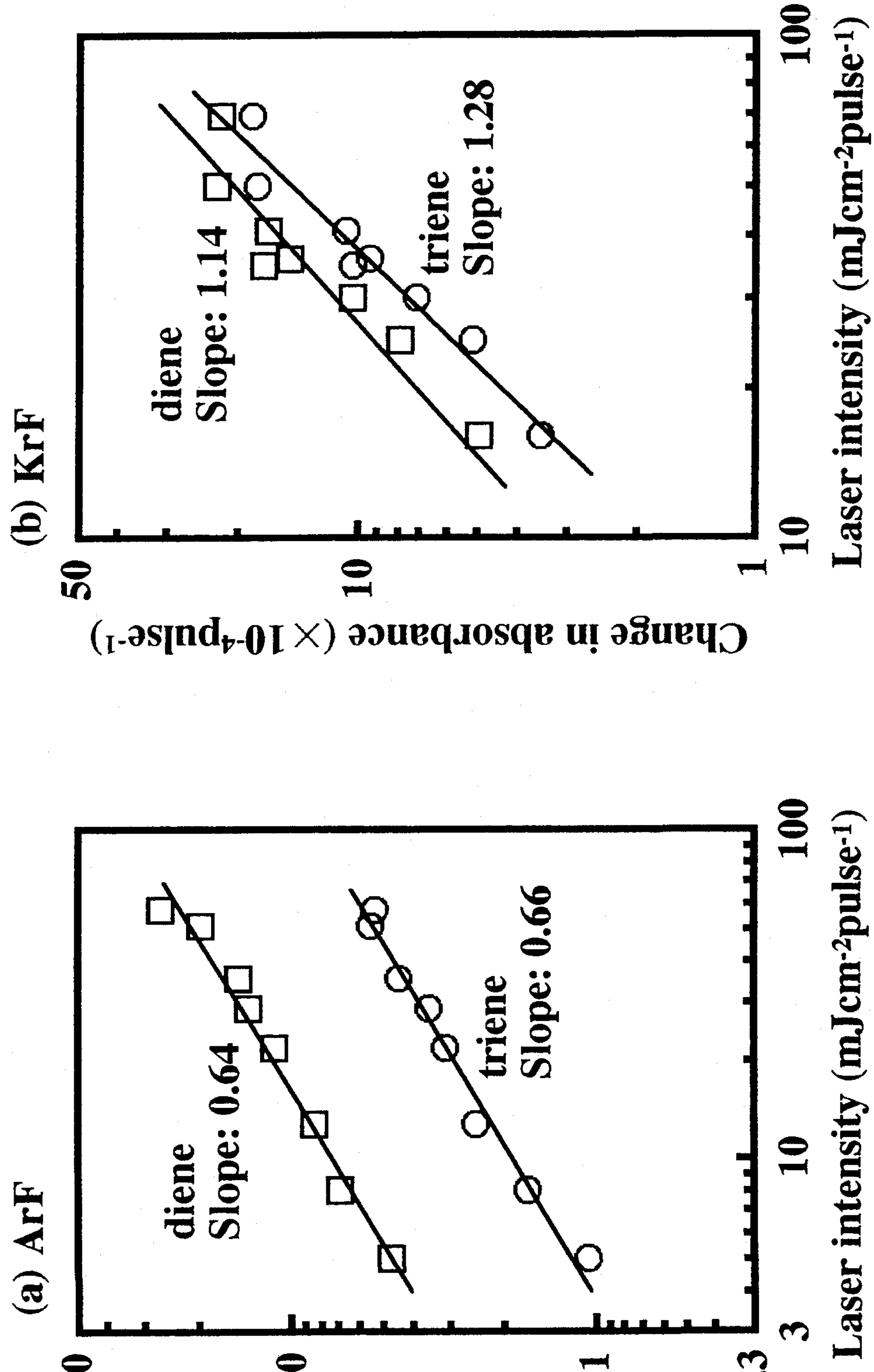


Fig. 4. 4 The excimer laser intensity dependence of diene and triene formations by ArF (a) and KrF (b) irradiation.

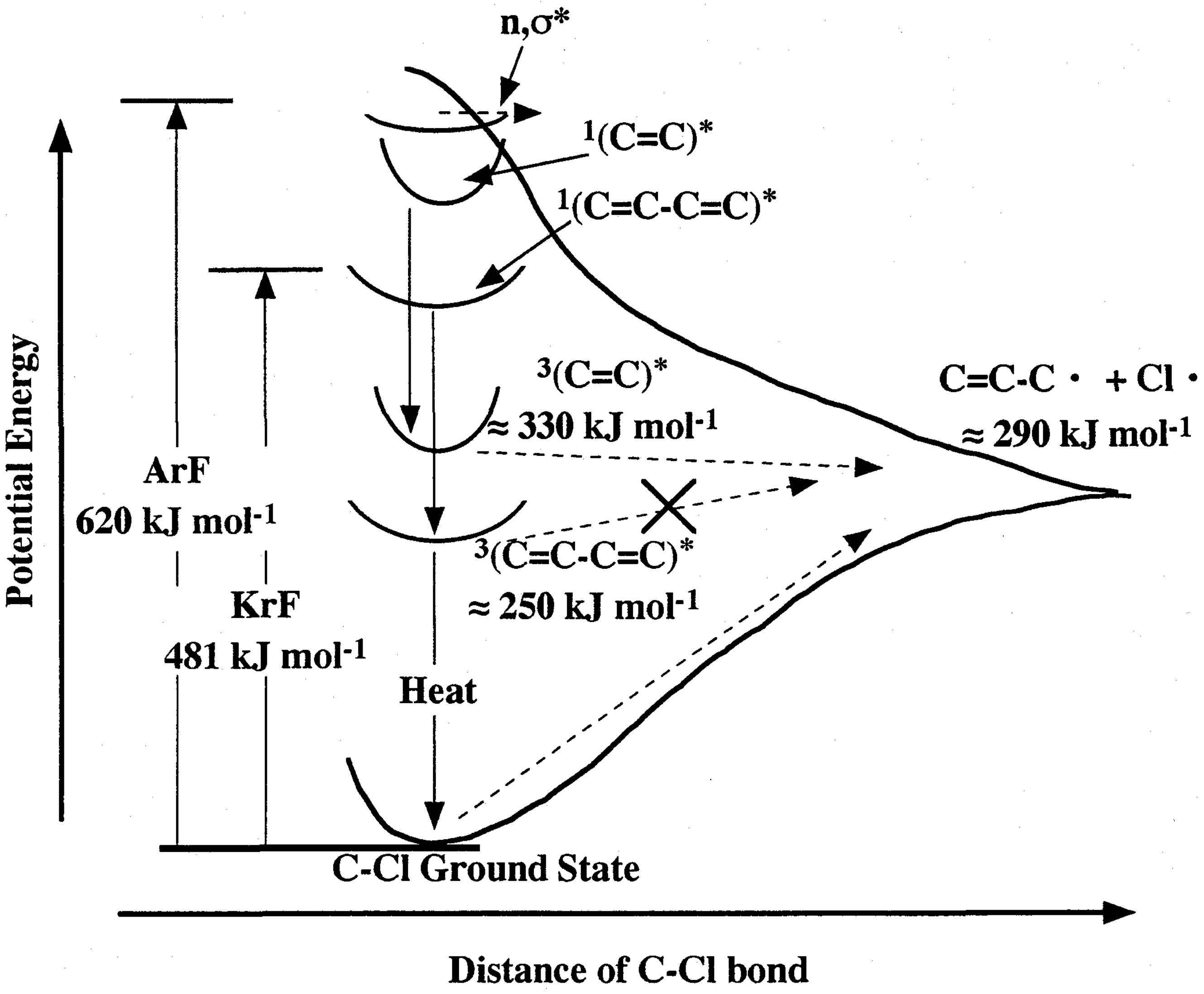


Fig. 4. 5 The possible energy diagram in the chemical reaction within the chlorinated polymers.

Chapter 5

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

Abstract

The irradiation effects of intense ultraviolet (UV) light from ArF and KrF excimer lasers on poly(vinylidene fluoride) (PVdF) film 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.

5.1 Introduction

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 technique1) and the radio-frequency plasma processing with oxygen2) 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 studied extensively,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 the previous chapters,8) the author 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 Kawai14) and Bergman *et al.*,15) respectively. Chemical and physical changes induced in PVdF by ionizing radiation have been extensively reported in elsewhere.16)

5.2 Experimental

5.2.1 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.

5.2.2 Irradiation of Excimer Laser Light

The 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 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 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.

5.2.3 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.

5.3 Results and Discussion

Figure 5. 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. 5. 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. 5. 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 of the brominated PVdF,[18] they were suggested to be attributed to the π -> π* transition of polyene structures. Also, supposing that the π -> π* transition energy of polyene within PVdF is similar to that within ETFE,7) the absorption bands in the wavelength range of 220 - 230 nm 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 -> π* 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.

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 the 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 carbonization of PVdF.

The changes in absorbances at 230 nm (diene) and 280 nm (triene) vs. number of irradiated laser pulses are plotted in **Fig. 5. 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, the author 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 5. 4 shows the intensity dependencies of diene and triene formations due to ArF (a) and KrF (b) irradiation. The change in absorbance, which is the ordinate of **Fig. 5. 4**, was evaluated based on the initial slope of the curve of change in absorbance vs. number of pulses, such as **Fig. 5. 3**. The slopes in **Fig. 5. 4 (a)** are about 1.2 - 1.3, whereas those in **Fig. 5. 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)]

$$Nf = N_0 / n \Pi \sigma i F^n, \qquad (1)$$

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

$$\log Nf = n \log F + C, \qquad (2)$$

where C corresponds to the Y-intercept in **Fig. 5. 4** and n, which is the number of photons that contribute to the reaction, corresponds to the slope in **Fig. 5. 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. 5. 4 (a)** was not perfectly equal to 1.0, the author 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 life time of the triplet states is longer than the pulse duration of excimer laser, the T -> T* transition will occur within the laser-pulse time, and heat evolution will also undergo with the T* -> T transition. Hence, most of the absorbed energy leads to the evolution of heat. The thermal energy localized by several cycles of the T -> T* and T* -> T transition can induce the dissociation of 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 T -> 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 T -> T* transition with an evolution of heat.

5.4 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. The 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.

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19) Although the UV absorption spectra of the model compounds, CH_3-CF=CH-CF=CH-CF_3 and CH_3-CF=CH-CF=CH-CF=CH-CF_3, for diene and triene structures in PVdF have not been reported, 1,3-butadiene, 2,4-hexadiene, hexafluoro-1,3-butadiene and 1,3,5-hexadiene have absorption peaks at 217 nm, 227 nm, 202 nm and 247 - 268 nm, respectively, which were described in "CRC Spectral Data and

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(note) This chapter has been published as following paper.

"Irradiation Effects of Excimer Laser Lights on Poly(vinylidene fluoride) (PVdF) Film", Y. IZUMI, S. KAWANISHI, S. HARA, D. YOSHIKAWA and T. YAMAMOTO, *Bull. Chem. Soc. Jpn.*, **71** (11), 2721-2725 (1998).

List of Figures in Chapter 5

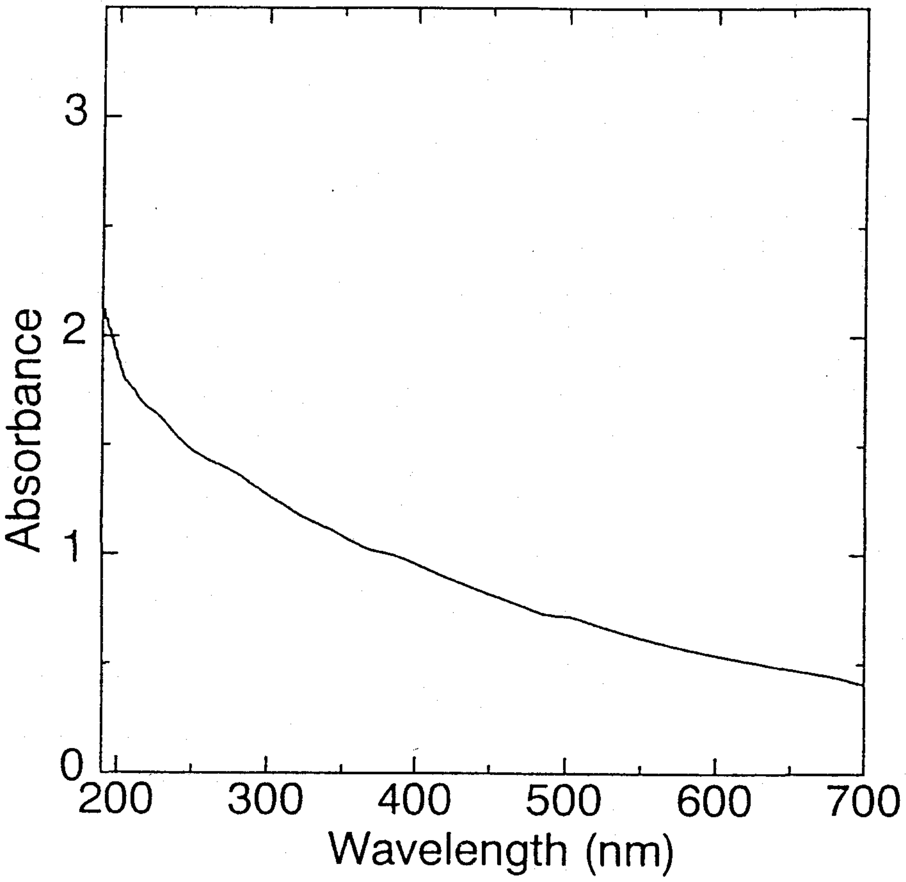

Fig. 5. 1 The vis-UV photo-absorption spectrum of non-irradiated PVdF film.

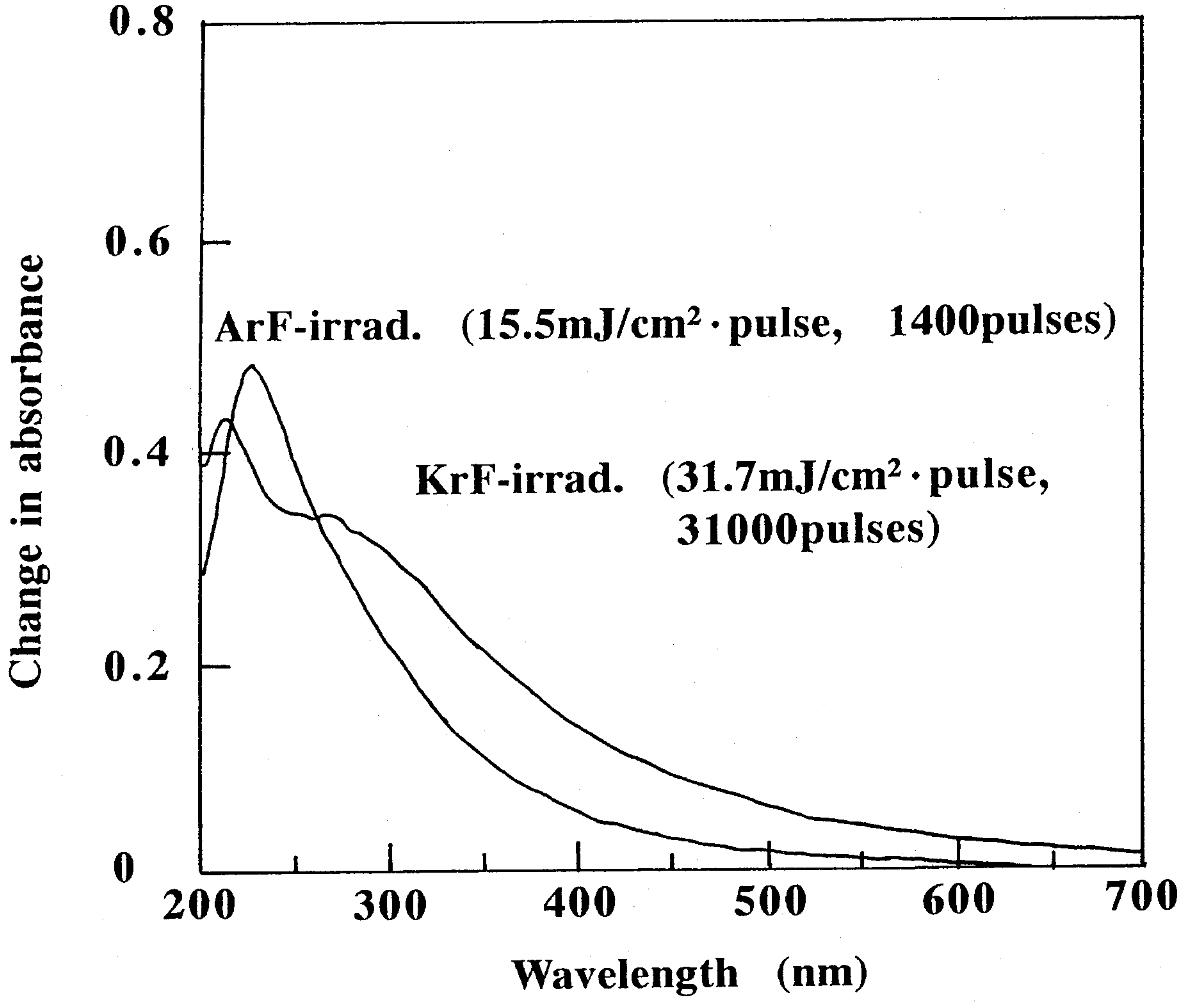

Fig. 5. 2 The differential vis-UV photo-absorption spectra between non-irradiated PVdF film and ArF- and KrF-excimer laser irradiated ones.

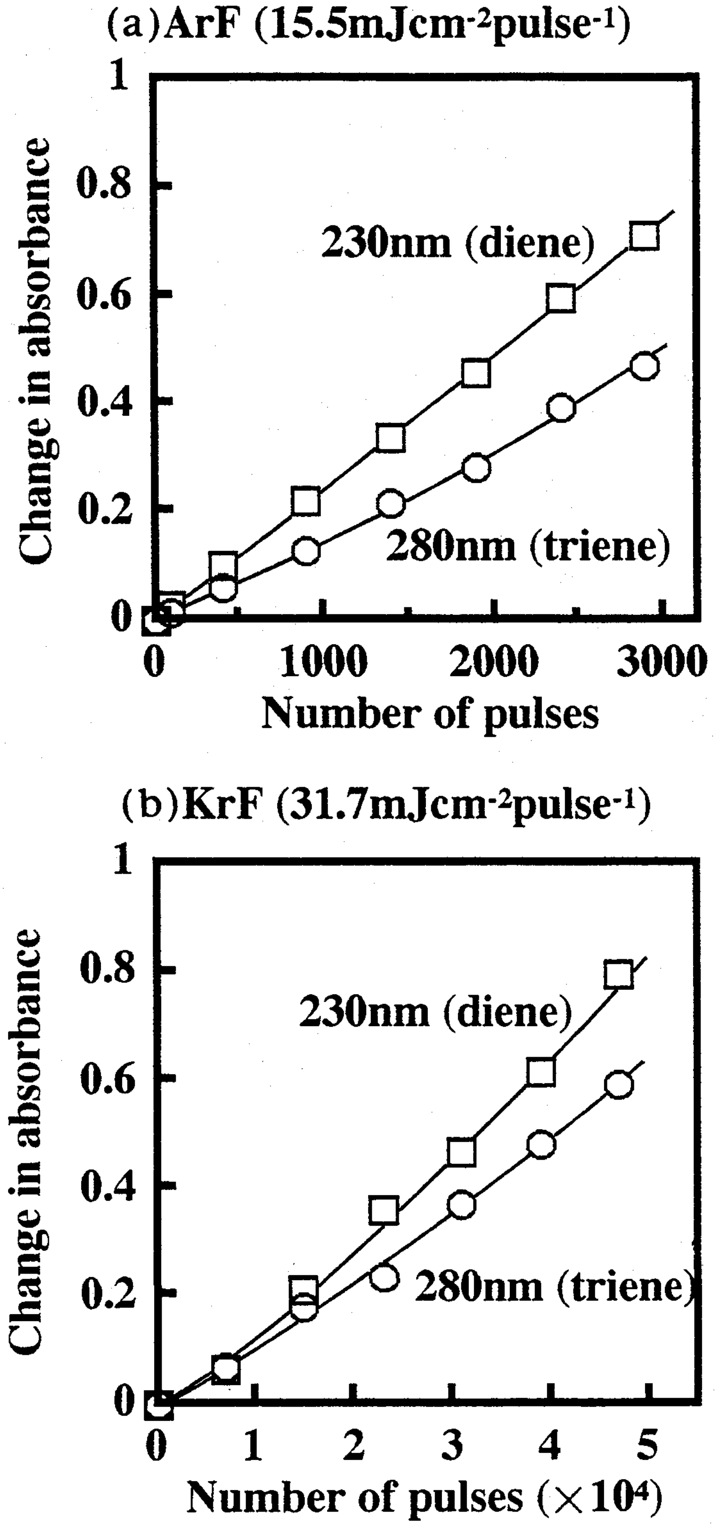

Fig. 5. 3 The change in absorbances of PVdF films irradiated with ArF (a) and KrF (b) excimer laser lights.

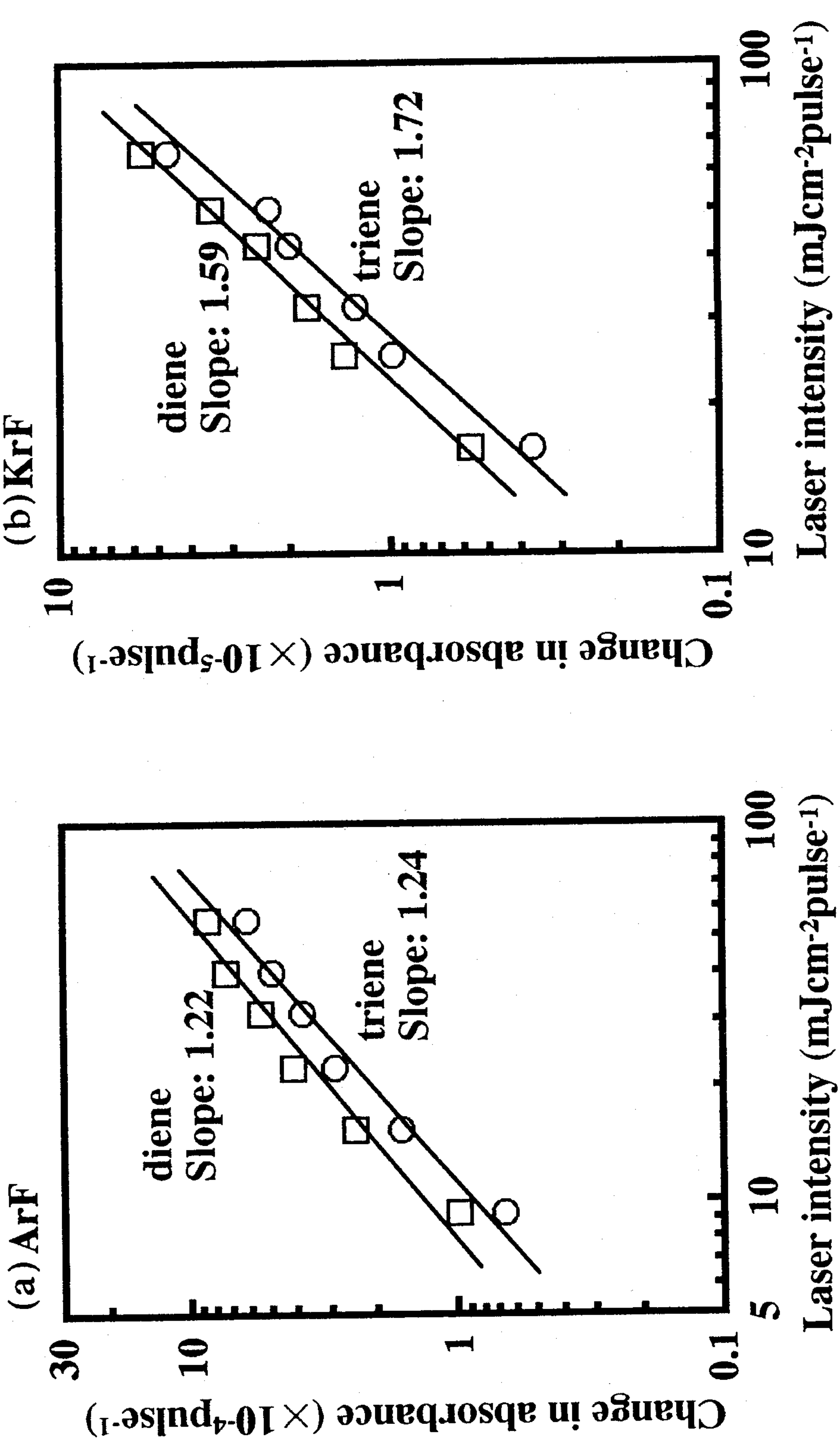

Fig. 5. 4 The excimer laser intensity dependence of diene and triene formations by ArF (a) and KrF (b) excimer laser irradiations.

Chapter 6
Photochemical Surface Modification of Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) Film with Triethylamine (TEA)

Abstract

Thin film of poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) reacted with triethylamine (TEA) upon UV-irradiation to give hydrophilic and oleophilic surface through complicated defluorination reactions such as introduction of diethylaminoethyl group and formation of unsaturated bonds. Solvent and additive effects on the photoreaction strongly suggested the involvement of an electron transfer process from TEA to FEP.

6.1 Introduction

Fluoropolymers are well-known for their excellent properties, for example heat resistance and solvent resistance. The surface modification of chemically resistant fluorocarbon polymer is an important process in their fabrication especially in adhesion since raw material strongly refuses adhesives, ink or other chemicals. In general, treatment with alkali metal in liquid ammonia or with oxygen plasma is performed to modify the surface.1) However, these methods have some problems, such as low-area selectivity and low durability of the modified layer. On the other hand, several attempts with laser irradiation have been reported for physical and chemical surface modification of fluoropolymers, which will be advantageous from the viewpoints of convenient and short-time operation, and spatial control.2-4) For the chemical reactions with vapor3) and solution,4) introduction of some chemical functionality and defluorination were observed.

In **Chapter 5**, the author reported the interaction of excimer laser light with poly(vinylidene fluoride) (PVdF) film, and described the wavelength-dependent photoreaction.5) The author will describe here a photochemical reaction of poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) with triethylamine (TEA) giving hydrophilic and oleophilic surface.

6.2 Experimental

6.2.1 Materials

Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) film, 100 μm-thick, supplied from Gunze, Japan was used as sample for irradiation after cleaning with acetone using ultrasonic waves for more than 5 min. The optical absorption spectrum of non-irradiated FEP film is shown in **Fig. 6.1**, and the XPS spectra are shown in **Fig. 6.2**. Triethylamine (TEA) (Wako Chemical, guaranteed reagent grade (GR)) was used as solute without further purification. The absorption spectrum of TEA dissolved in acetonitrile is shown in **Fig. 6.3**. Acetonitrile, cyclohexane and 1,4-dioxane were also used as solvent without further purification. Carbon tetrachloride, dimethyl terephthalate (DMTP) and naphthalene were used as additives without further purification. All chemicals, other than TEA, were purchased from Nacalai and GR grade.

6.2.2 Irradiation of Excimer Laser Light and Other Stationary Light

An FEP film (4 x 4 cm^2, 100 μm thickness) was placed on a cell equipped with quartz windows for the incidence of UV light in contact with a nitrogen-purged acetonitrile solution of TEA (10 mM) and was irradiated with KrF excimer laser (248 nm; 35 mJ $cm^{-2}pulse^{-1}$, 10 pps), XeCl excimer laser (308 nm; 45 mJ $cm^{-2}pulse^{-1}$, 10 pps) or super low-pressure mercury lamp through the film to excite the solution at interface.

A KrF excimer laser irradiation was carried out with a Lumonics Ex-884, and a XeCl excimer laser irradiation was carried out with a Lumonics Hyper Ex-460. The pulse durations were 12 - 25 ns and 8 - 12 ns for KrF and XeCl excimer lasers, respectively. Pulse repetition rate was 10 pulse per second (pps). The 30-W and 60-W super low-pressure mercury lamps were used as stationary light source. The 30-W lamp emitted 185 nm UV-radiation. The 60-W lamp emitted UV-radiations with wavelengths of 185 and 254 nm. An water layer with 30 mm-thick was used as optical filter in order to remove 185 nm UV-radiation.

6.2.3 Analysis

The irradiated surface was analyzed by measuring contact angles with water (θ_W) and with hexadecane (θ_{HD}). The qualitative analysis of the functional group attached to the surface was carried out by using contact angles with buffer solutions (pH = 10.02, 9.18, 6.86, 4.01 and 1.68).

The irradiated surface was also analyzed by X-ray photoelectron spectroscopy (XPS) using Mg K_α 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), F_{1s} electron (680 - 700 eV) and N_{1s} electron (392 - 410 eV). The atomic ratios (F/C, N/C and O/C) were calculated from the F_{1s}/C_{1s}, N_{1s}/C_{1s} and

O_{1s}/C_{1s} ratios, respectively, calibrated based on the ionization sensitivity factors (C_{1s} 1.00; O_{1s} 2.85; F_{1s} 4.84; N_{1s} 1.77).

The chemical change in the bulk of FEP film was analyzed by vis-UV optical absorption spectroscopy . The vis-UV absorption spectra were recorded with a Shimadzu UV-2100 spectrophotometer with a slit-width of 2.0 nm and wavelength ranging 190 - 700 nm.

6.3 Results and Discussion

6.3.1 KrF Laser-Induced Reaction Between FEP and TEA

Figure 6.4 shows changes in the contact angle of the FEP film with water (θ_W) and those with hexadecane (θ_{HD}) droplets with laser shot number. Non-irradiated film had θ_W and θ_{HD} value of 107 and 47 deg, respectively. The contact angles with both water and hexadecane gradually decreased along with an increase of laser shot number (< 6000 shot), which indicated that the irradiated surface gradually became both hydrophilic and oleophilic. After 6000 shot, the contact angle with water increased probably because of decomposition of hydrophilic functionalities.

Figure 6.5 shows the result of the contact angle titration[6) of an FEP film irradiated with KrF laser in contact with aqueous and acetonitrile solutions of TEA. In the case of irradiation in contact with acetonitrile solution, an sigmoidal behavior with pH showing an abrupt increase from pH = 6 to pH = 7 was observed to suggest the introduction of basic diethylaminoethyl group to the surface. This group will show high hydrophilicity in an acidic media through protonation to give quaternary ammonium salt. On the other hand, the contact angle of a film irradiated in water was almost independent of pH.

The XPS spectra of KrF laser-irradiated FEP film surface are shown in **Fig. 6.6**. In C_{1s} spectrum, photoelectron peak at a binding energy of 293 eV was strongly reduced by irradiation. Since this peak was attributed to the $-CF_2-$ carbon, fluorine atom was detached from FEP film surface by irradiation. From the F_{1s} photoelectron spectrum, F/C ratio = 0.29 was obtained for the KrF-irradiated FEP surface, which was much lower than F/C = 2.11 in non-irradiated FEP. Moreover, O_{1s} and N_{1s} photoelectron spectra indicated the introduction of oxygen and nitrogen by the irradiation (O/C = 0.08, N/C = 0.06). Therefore, the detachment of fluorine atom, introduction of amino functional group and simultaneous oxygenation or hydrolysis of surface must be induced by irradiation with KrF excimer laser in contact with TEA. Though source of oxygen is not clear at present, it may be derived from oxygenation or hydrolysis of the introduced functionalities.

The film irradiated in acetonitrile solution colored yellow to light brown, while that irradiated in water were less colored. The vis-UV absorption spectrum of the film irradiated in acetonitrile solution (**Fig. 6.7**) showed broad absorption from 200 to 600 nm. This broad absorption was decreased by treatment with bromine vapor to indicate the presence of conjugated olefinic bondings. Therefore, the formation of conjugated double bonds must simultaneously occur with introduction of amino functional group after the detachment of fluorine atom.

Since similar irradiation in the absence of TEA little affected the contact angles and atomic ratios, the changes described above are attributed to a photochemical reaction between FEP and TEA.

6.3.2 Effect of Solvent

KrF laser-induced surface modification of FEP film with TEA dissolved in various solvents was tested and the results were summarized in **Table 6.1**. The preference of polar solvent for the present reaction suggests the involvement of ionic intermediates. The author considers this photoreaction as the involvement of an electron transfer process from TEA to FEP, where two mechanisms can be considered: direct electron transfer and photoionization of TEA followed by capture of solvated electron (e_s^-) by FEP. Use of water, however, was ineffective probably owing to rapid protonation to quench the excited singlet state of TEA giving $(CH_3CH_2)_3NH^+ \cdots OH^-$.[7,8]

6.3.3 Effect of Light Source

Table 6.2 indicated the light source effect on the photoreaction in acetonitrile solution, which was monitored by the contact angle and XPS measurements. TEA showed two broad absorption bands ranging from 220 to 260 nm (S_1-S_0 transition) and from 210 to 190 nm (S_2-S_0 transition) in cyclohexane solution, which were not clearly observed in acetonitrile solution (**Fig. 6. 3**). Upon direct excitation at 185 nm and 254 nm with a supper low-pressure Hg lamp, similar results were obtained as observed with KrF excimer laser. Since the stationary light emitted from supper low-pressure Hg lamp has photon-intensity of about 1 Wcm^{-2}, multi-photon reaction did not occur. Therefore, the photoreaction between TEA and FEP was considered to be a single-photon process via S_1-S_0 or S_2-S_0 transition. On the other hand, irradiation at 308 nm with XeCl excimer laser (45 mJ cm^{-2}pulse^{-1}, 6000 shot) did not induce the reaction to rule out non-resonant two-photonic excitation, though two-photon energy at 308 nm is enough for excitation of TEA.

6.3.4 Effect of Additives

In the above-described sections concerning effects of solvents and light source, it was strongly suggested that the photoreaction between TEA and FEP induced by UV-irradiation was ionic, especially electron transfer, reaction via excitation of TEA. Effect of additives was also studied in order to obtain the more detail information about mechanisms. TEA is electron-donating regent, and its excited state can be quenched by electron-acceptor via electron transfer reaction. Therefore, the excited state of TEA is quenched by acetonitrile to give rise to radical anion of acetonitrile and TEA cation radical.[9] In the presence of electron-accepting additive, for example oxygen, dimethyl terephthalate (DMTP) and carbon tetrachloride (CCl_4), the electron transfer from acetonitrile anion radical to FEP may be inhibited.

As shown in **Table 6.3**, CCl_4 effectively reduced the photoreaction between TEA and FEP induced by UV-irradiation. Since electron attachment by CCl_4 causes the rapid dissociation of its intermediate to form CCl_3 and Cl^-, this electron transfer is irreversible process. Therefore, this effective inhibition of photoreaction must be due to irreversible electron transfer from acetonitrile anion radical to CCl_4, which is dissociative electron attachment by CCl_4. On the other hand, the addition of oxygen was not effective to the reduction of the photoreaction between TEA and FEP induced by UV-irradiation. The concentration of dissolved oxygen was not so high enough to induce the electron transfer from acetonitrile to oxygen. In the presence of DMTP, most of laser-photon is absorbed by DMTP to form DMTP excited state. Formed DMTP excited state may be quenched by electron transfer from TEA to give rise DMTP anion radical and TEA cation radical. In this case, the photoreaction between TEA and FEP occurred. This reaction can be considered as the result of electron transfer from DMTP anion radical to FEP.

The photoreaction between TEA and FEP can be induced by UV-light having more long-wavelength, such as XeCl laser, if sensitizing reaction such as observed in DMTP-added case is used. As shown in **Table 6.2**, the irradiation at 308 nm with XeCl excimer laser (45 mJ $cm^{-2}pulse^{-1}$, 6000 shot) did not induce the reaction to rule out non-resonant two-photonic excitation, though two-photon energy at 308 nm is enough for excitation of TEA. But irradiation with XeCl excimer laser in the presence of naphthalene (Np) induced the considerable reaction. In this case, reaction initiator can be photo-excited Np. The photoreaction sensitized by Np can proceed via following reactions, namely,

$$Np^* + TEA \longrightarrow Np^{-\cdot} + TEA^{+\cdot},$$
$$Np^{-\cdot} + FEP \longrightarrow Np + FEP^{-\cdot},$$
$$TEA^{+\cdot} + FEP^{-\cdot} \longrightarrow FEP(+\text{ adduct TEA}), \quad (1)$$

or,

$$Np^{**} \longrightarrow Np^{+\cdot} + e^-,$$
$$e^- + \text{acetonitrile} \longrightarrow e_s^-,$$
$$Np^{+\cdot} + TEA \longrightarrow Np + TEA^{+\cdot},$$
$$FEP + e_s^- \longrightarrow FEP^{-\cdot},$$
$$TEA^{+\cdot} + FEP^{-\cdot} \longrightarrow FEP(+\text{ adduct TEA}). \quad (2)$$

6.3.5 The mechanisms of Surface Modification of FEP with TEA

From the above-described sections, the photo-induced surface modification of FEP film can be the result of the following reactions between FEP and TEA dissolved in acetonitrile (MeCN),

$$\mathrm{TEA} \xrightarrow{h\nu} \mathrm{TEA}^{*}, \tag{3}$$

$$\mathrm{TEA}^{*} + n\cdot\mathrm{MeCN} \longrightarrow \mathrm{TEA}^{+\cdot} + (\mathrm{MeCN})_{n}^{-\cdot}\ (e_{s}^{-}), \tag{4}$$

$$(\mathrm{MeCN})_{n}^{-\cdot} + \mathrm{FEP} \longrightarrow n\cdot\mathrm{MeCN} + \mathrm{FEP}^{-\cdot}, \tag{5}$$

$$\mathrm{TEA}^{+\cdot} + \mathrm{FEP}^{-\cdot} \longrightarrow \mathrm{FEP}(+\ \mathrm{adduct\ TEA}). \tag{6}$$

These reactions can be induced by KrF excimer laser and stationary 185 or 254 nm light. Since the initiator of these reactions is photoexcited TEA, XeCl laser having a wavelength of 308 nm, where TEA has no absorption, can not induce this surface modification. In the presence of sensitizing additives such as Np and DMTP, reactions (1) or (2) can proceed and successive photo-induced surface modification is induced.

6.4 Conclusions

Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) film was irradiated with KrF or XeCl excimer laser or super low-pressure mercury lamp (185 or 254 nm) in contact with various solutions of TEA. FEP reacted with TEA upon UV-irradiation, except 308 nm, to give hydrophilic and oleophilic surface through complicated defluorination reactions such as introduction of diethylaminoethyl group and formation of unsaturated bonds. Solvent and additive effects on the photoreaction strongly suggested the involvement of an electron transfer process from TEA to FEP. Moreover, sensitizing photoreaction was observed in the presence of DMTP or Np. In these cases, initiator of photoreaction is sensitizer molecule and the mechanism is different from the shorter wavelength case. This modification method using photoreaction is very useful for synthesizing hydrophilic and oleophilic surface on the inactive fluoropolymers.

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(note) This chapter has been partly published as following paper.

"Photochemical Surface Modification of Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) Film with Triethylamine", N. ICHINOSE, M. MARUO, S. KAWANISHI, Y. IZUMI and T. YAMAMOTO, *Chem. Lett.*, **1995**, 943-944 (1995).

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Table 6. 1 KrF laser-induced surface modification of FEP film with TEA in various solvents.[a]

Solvent (ε)[b]	θ_W[c]	θ_{HD}[d]	F/C[e]	N/C[e]	O/C[e]
Before irradiation	107	47	2.11	0.00	0.02
cyclohexane (2.02)	90	20	1.47	0.02	0.08
1,4-Dioxane (2.20)	59	< 5	0.22	0.04	0.24
Acetonitrile (35.94)	58	< 5	0.29	0.06	0.08
Water (80.16)	76	16	1.49	0.02	0.08

[a] [TEA] = 10 mM; KrF laser: 35 mJ $cm^{-2}pulse^{-1}$, 10 Hz, 6000 shots, irradiated under N_2 atmosphere.

[b] Dielectric constant.

[c] Contact angle with water droplet.

[d] Contact angle with hexadecane droplet.

[e] Measured by XPS.

Table 6. 2 Light source effect on the surface modification of FEP film with TEA in acetonitrile.[a]

Wavelength /nm	θ_W[b]	θ_{HD}[c]	F/C[d]	N/C[d]	O/C[d]
Before irradiation	107	47	2.11	0.00	0.02
185 [e]	66	< 5	0.04	0.12	0.06
248 [f]	58	< 5	0.29	0.06	0.08
254 [g]	65	6	0.47	0.07	0.15
308 [h]	107	48	2.12	0.00	0.01
	76 [i]	7 [i]	0.34 [i]	0.05 [i]	0.16 [i]

[a] [TEA] = 10 mM, irradiated under N_2 atmosphere.
[b] Contact angle with water droplet.
[c] Contact angle with hexadecane droplet.
[d] Measured by XPS.
[e] 30-W super low-pressure Hg lamp, 2h.
[f] KrF laser: 35 mJ $cm^{-2}pulse^{-1}$, 10 Hz, 6000 shots.
[g] 60-W super low-pressure Hg lamp with 30 mm thick water filter, 2h.
[h] XeCl laser: 45 mJ $cm^{-2}pulse^{-1}$, 10 Hz, 6000 shots.
[i] In the presence of naphthalene (Np); [Np] = 5 mM.

Table 6. 3 Effect of additives on the surface modification of FEP film with TEA in acetonitrile.[a]

Additive	(mM)	θ_W[b]	θ_{HD}[c]	F/C[d]	N/C[d]	O/C[d]
none		58	< 5	0.29	0.06	0.08
O_2	(1.27)	62	< 5	0.04	0.10	0.14
DMTP [e]	(1.0)	65	< 5	0.10	0.08	0.20
DMTP [e]	(10)	78	< 5	0.07	0.08	0.15
CCl_4 [f]	(100)	96	30	1.47	0.04	0.06

[a] [TEA] = 10 mM; KrF laser: 35 mJ $cm^{-2}pulse^{-1}$, 10 Hz, 6000 shots, irradiated under N_2 atmosphere (except for the case of O_2-addition).

[b] Contact angle with water droplet.

[c] Contact angle with hexadecane droplet.

[d] Measured by XPS.

[e] Dimethyl terephthalate.

[f] Carbon tetrachloride.

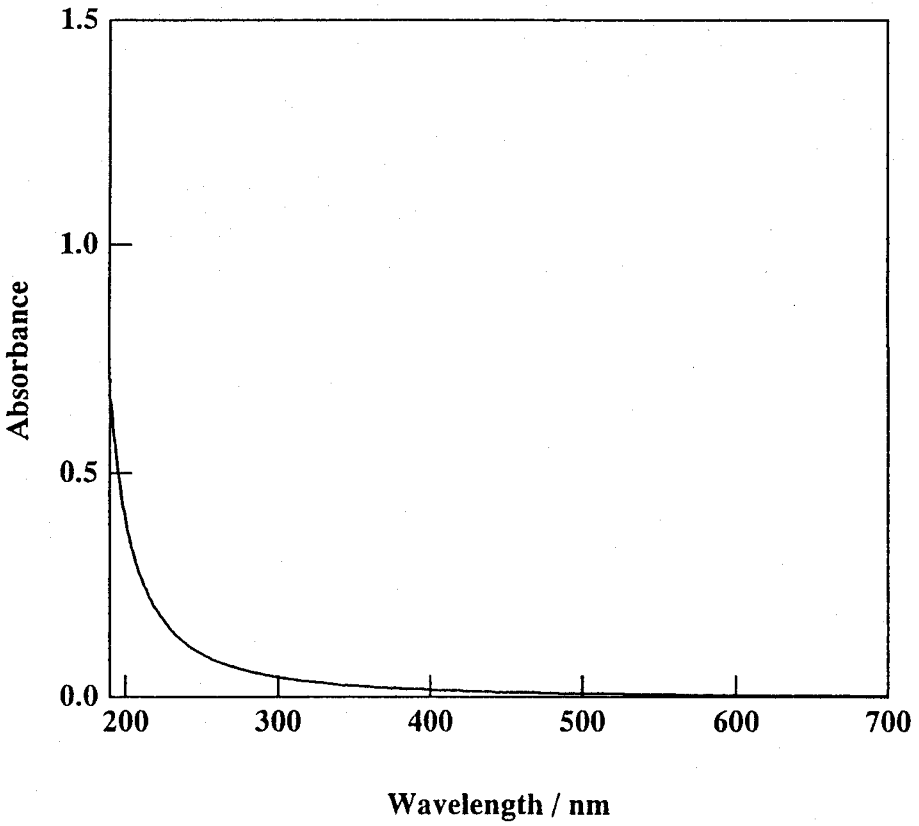


Fig. 6. 1 Optical absorption spectrum of FEP film.

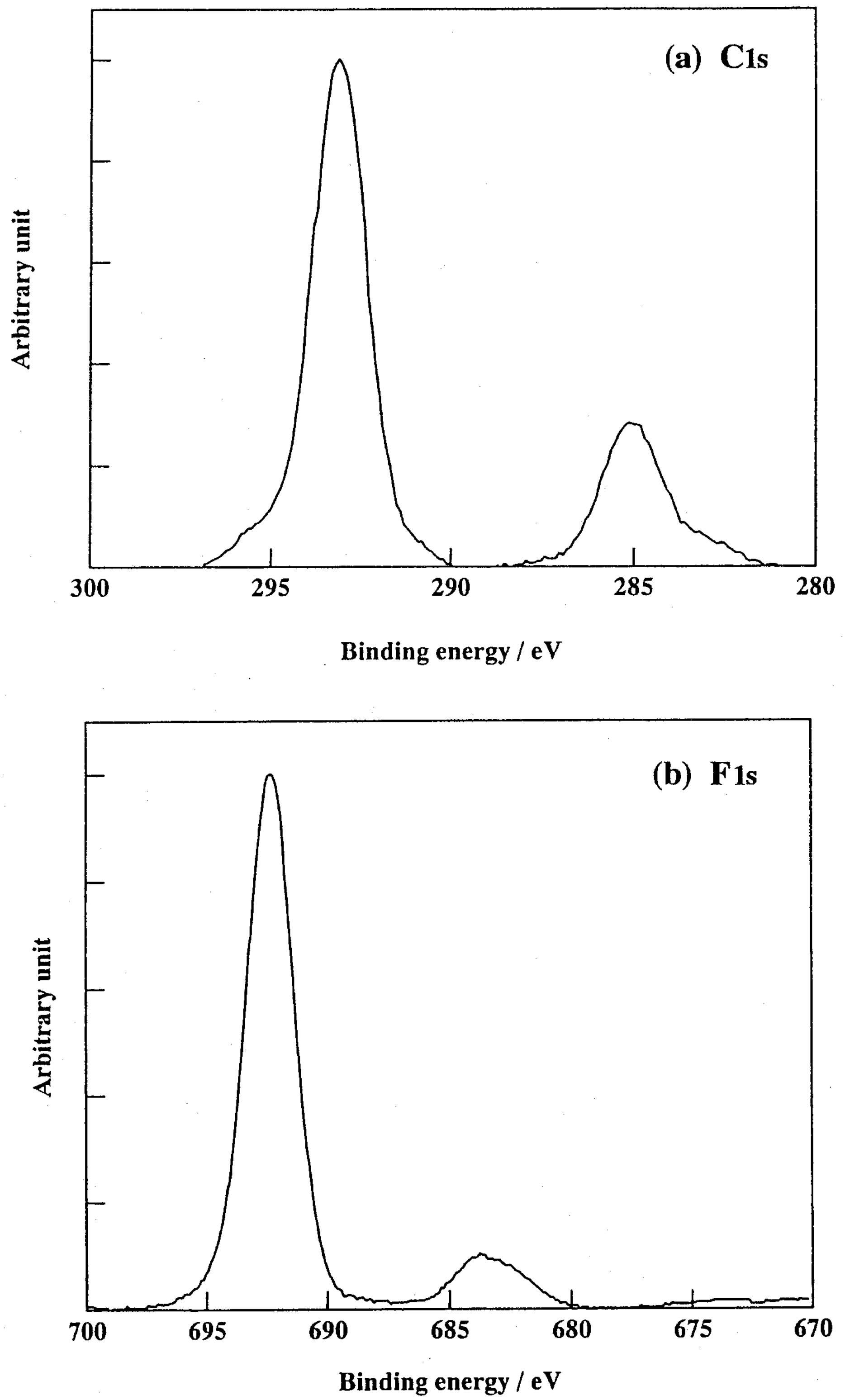
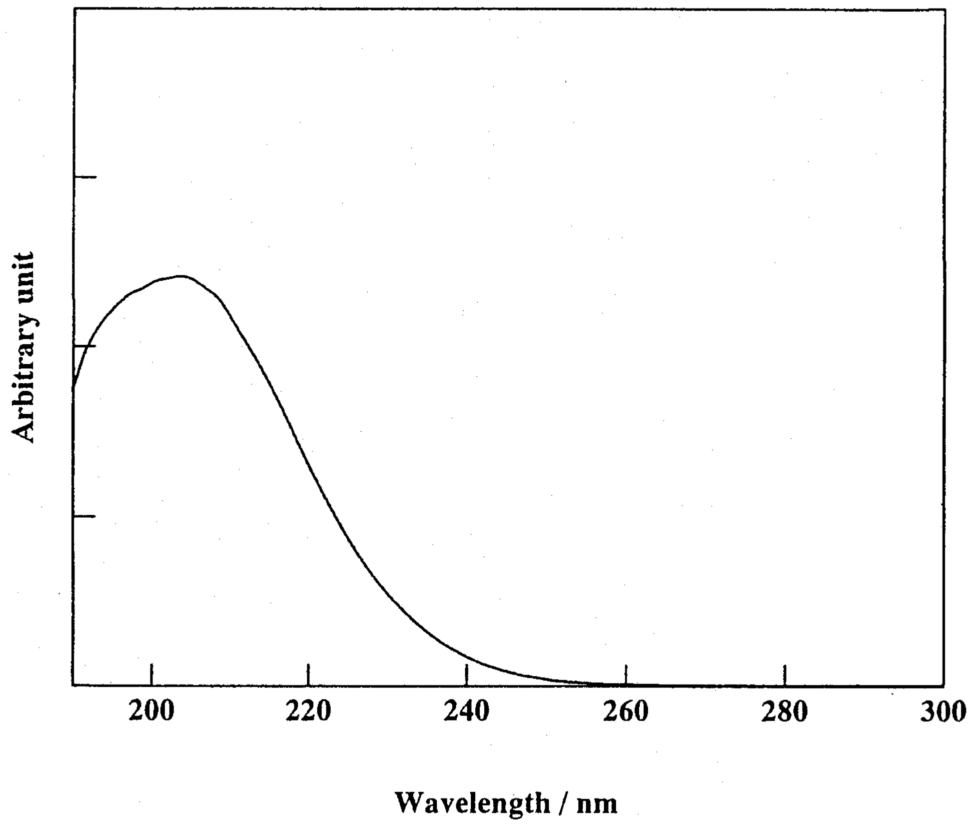


Fig. 6. 2 C1s (a) and F1s (b) XPS spectra of non-irradiated FEP film.



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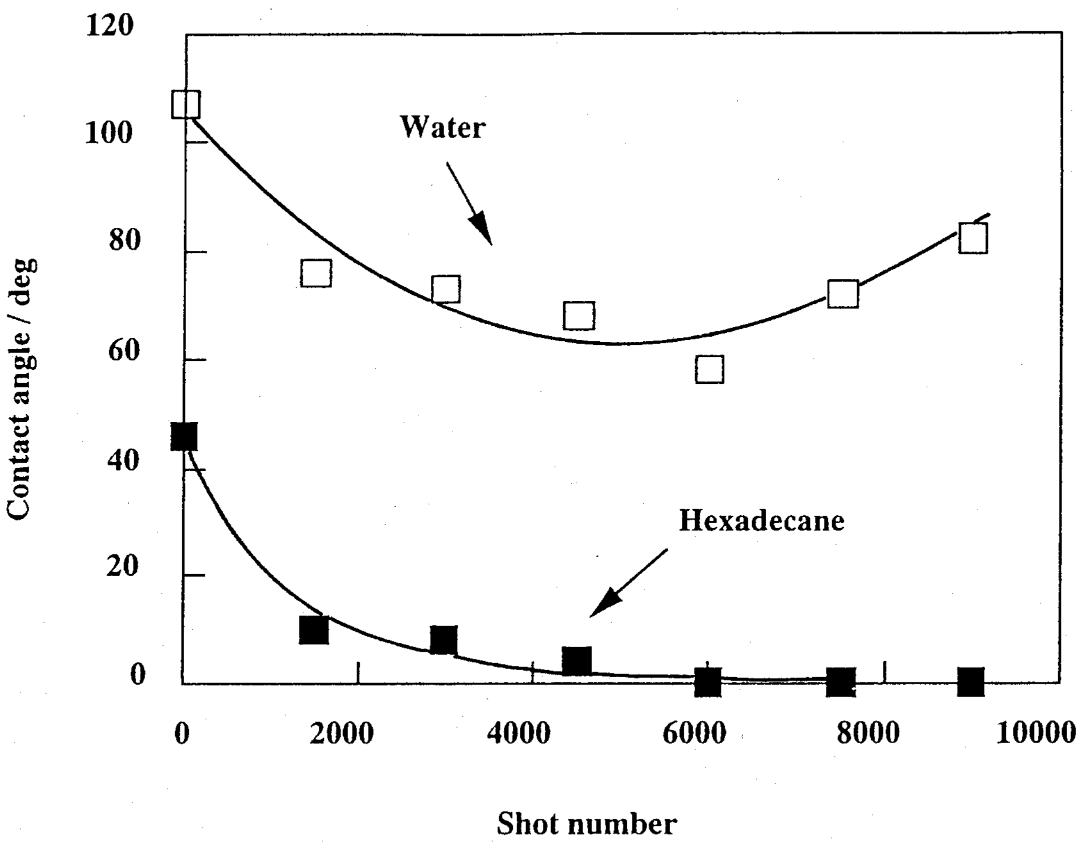

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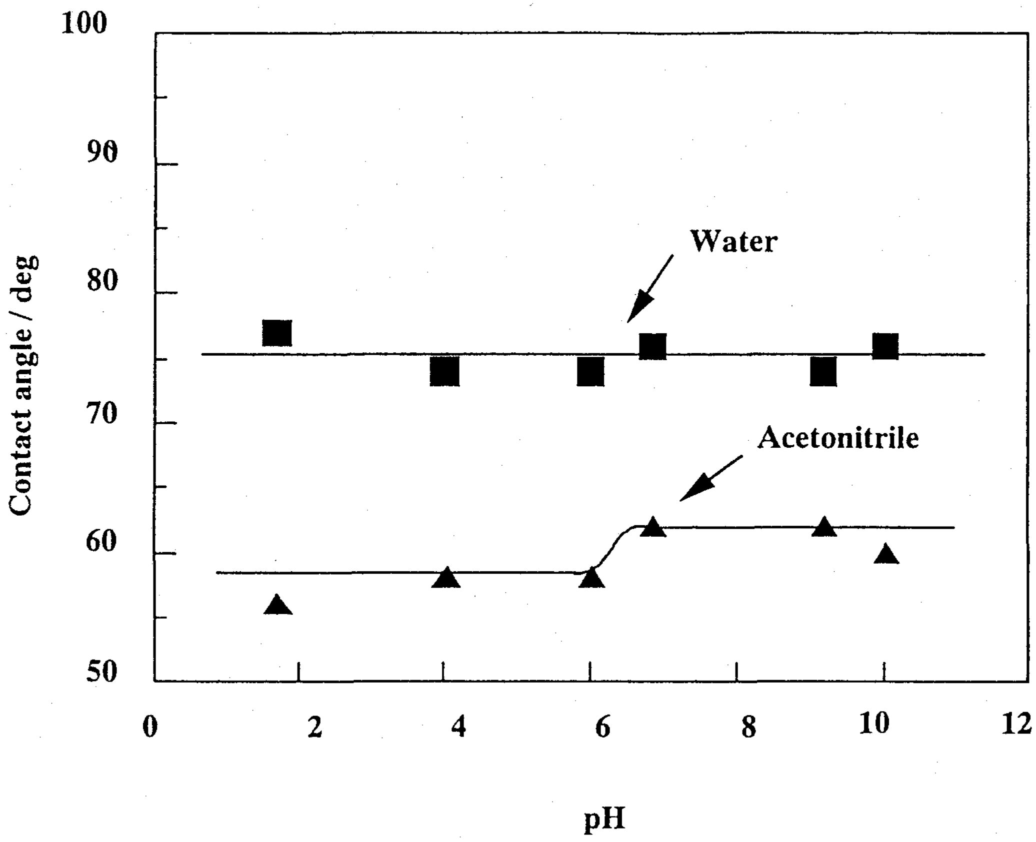

Fig. 6. 5 Contact angle titration of an FEP film irradiated with KrF laser in contact with aqueous and acetonitrile solutions of TEA: [TEA] = 10 mM, KrF laser 35 $mJcm^{-2}pulse^{-1}$, 6000 shots.

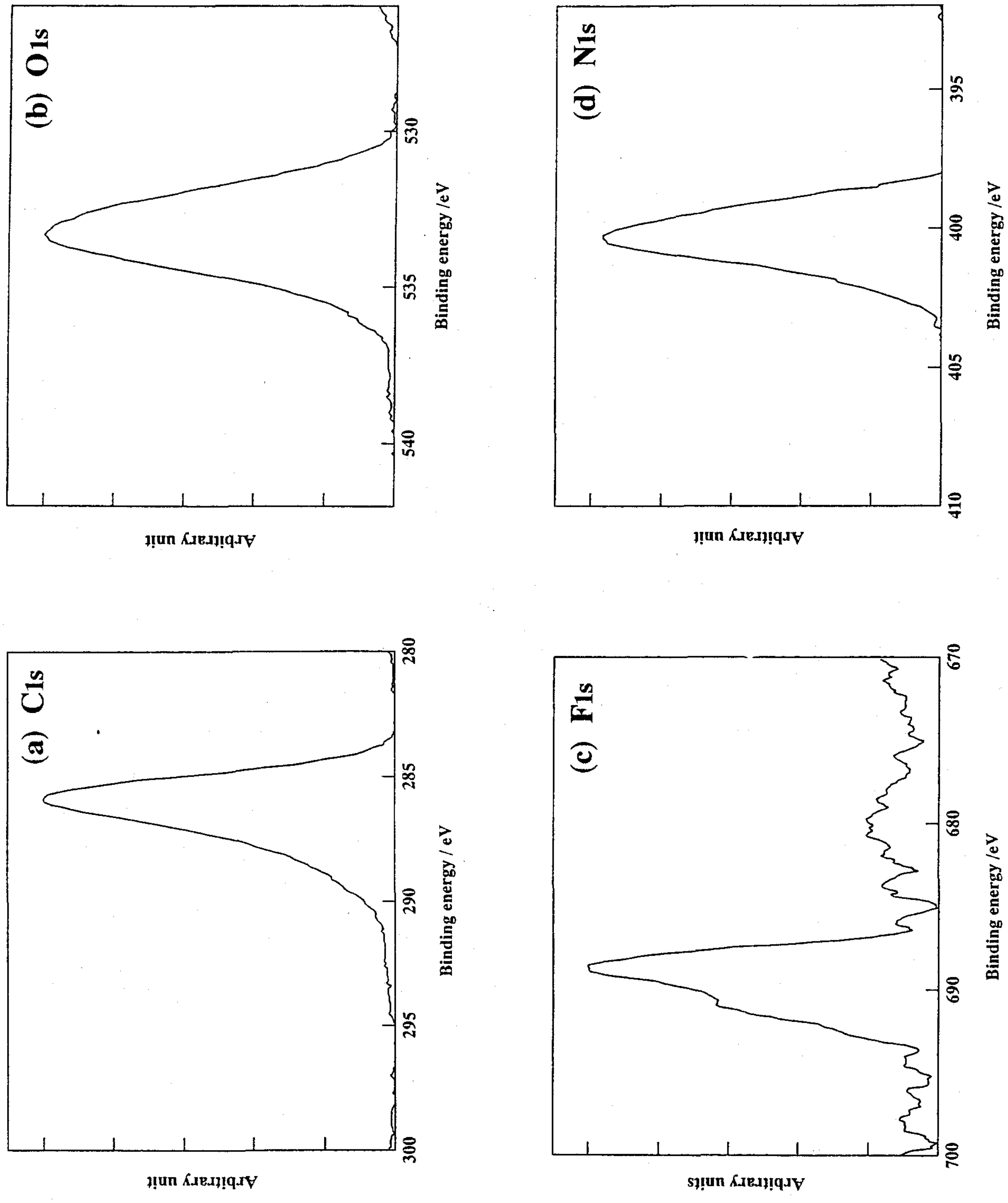

Fig. 6. 6 C1s (a), O1s (b), F1s (c) and N1s (d) XPS spectra of KrF laser-irradiated FEP film: 35 mJcm^{-2}pulse^{-1}, 6000 shots.

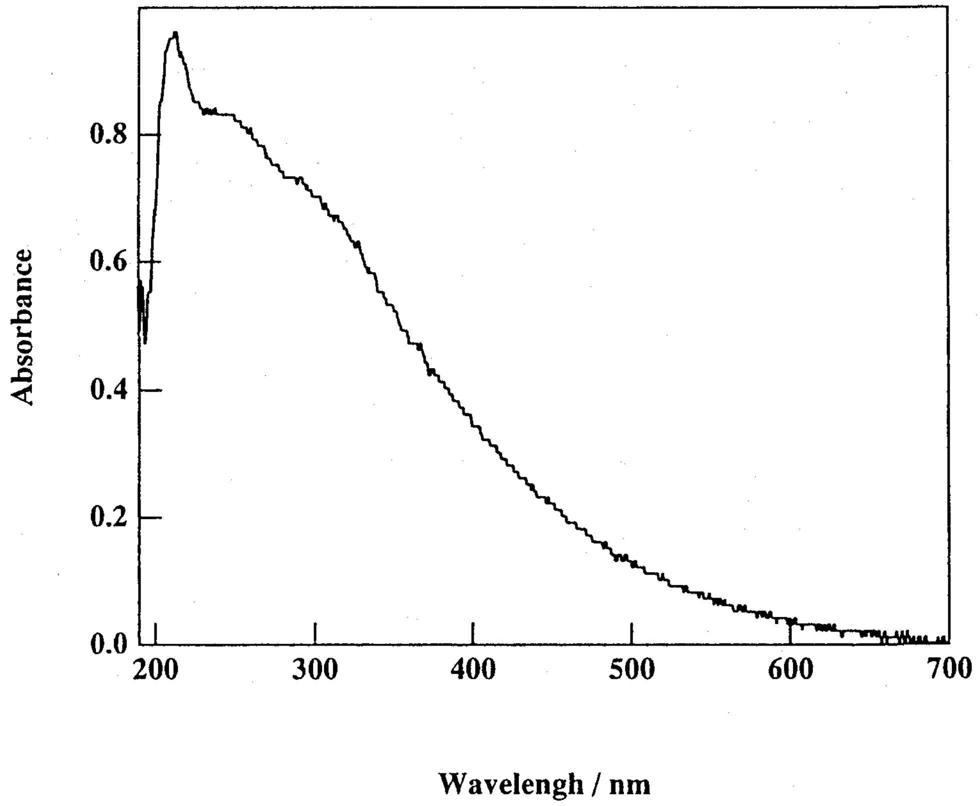

Fig. 6. 7 Optical absorption spectrum of FEP film treated with laser-modification in 10 mM TEA / acetonitrile solution: 35 mJcm^{-2}pulse^{-1}, 6000 shots.

Chapter 7 Summary

In this thesis, the interactions of excimer laser light with halogenated polymers were described. Especially, effects of excitation wavelength upon the formation of polyene structures within the halogenated polymer films such as PVC, Saran copolymer and PVdF were discussed based on the photochemical and photothermal processes and the photo-absorption sites.

In **Chapter 1**, a historical background of laser-induced polymer chemistry was reviewed. According to "the long-term plan for nuclear development and application", which was published by the Atomic Energy Commission of Japan in 1987, the laser-induced polymer chemistry is one of the most important fields of science, and it has been expected to generate an entirely new technology and to induce the break-through of nuclear technology.

In **Chapter 2**, the applicability of potassium tris(oxalato)ferrate (III) to actinometry of ArF, KrF and XeF excimer laser light was described. This substance in 0.1 N H_2SO_4 has been widely used for actinometry of stationary mercury lamps. In order to evaluate the amount of photon which are incident into the reaction cell or vessel, the methodology for actinometry of excimer laser was established. Although the quantum yields of Fe^{2+} by irradiation of excimer laser was different from those by irradiation of stationary lamps, this actinometer is satisfactorily usable as an actinometer for excimer lasers. Effect of dissolved oxygen was also discussed.

In **Chapter 3**, the irradiation effects of electron beam and ArF, KrF and XeCl excimer laser light on poly(vinyl chloride) (PVC) film were described. The irradiation of ArF and KrF excimer laser light was more effective than electron-beam irradiation for modifying the surface area of a PVC film. The irradiation of ArF and KrF excimer laser light mainly caused the formation of diene and triene structures, respectively, while the irradiation of XeCl laser light caused no significant reactions. The observed wavelength-dependent reaction was discussed based on the triplet energies of olefin and diene and the dissociation energy of allylic C-Cl bond. In conclusion, photochemical and photothermal effects and the photo-absorption sites were one of the most important factors of wavelength-dependent reaction of PVC.

In **Chapter 4**, the irradiation effects of ArF and KrF excimer laser light on vinylidene chloride-vinyl chloride (Saran) copolymer film were described. Similarly to the case of PVC, the irradiation of ArF and KrF excimer laser light mainly caused the formation of diene and triene structures, respectively. The author proposed the possible energy diagram concerning a laser-induced chemical reaction of chlorinated polymers.

In **Chapter 5**, the irradiation effects of ArF and KrF excimer laser light on poly(vinylidene fluoride) (PVdF) film were described. Fluorinated polymer showed the wavelength-dependent reaction which was similar to those observed in the chlorinated polymer systems.

Based on the conclusions of **Chapters 3 - 5**, the author believes that polyene structures, whose π-conjugation length is controlled, can be synthesized on the surface of halogenated polymers. This method can be expected as one of the applications to the development of newly functional polymeric materials.

Chapter 6 was concerned with the photochemical surface modification of fluoropolymer. Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) film was irradiated with various kinds of UV light, such as KrF and XeCl excimer lasers and 185-nm and 254-nm stationary lamps, in contact with TEA, and both hydrophilic and oleophilic functionalities were obtained. The mechanism of this modification was discussed based on the effects of light source, polarity of solvent and presence of additives. This modification method using photoreaction is very useful for synthesizing hydrophilic and oleophilic surface on the chemically inactive fluoropolymers.

Acknowledgments

The author would like to express his deep gratitude to Professor Dr. Tadashi Yamamoto for his continuous encouragement and precious guidance. The author would like to express his deep gratitude to Professor Dr. Masahiro Katsura and Professor Dr. Shinsuke Yamanaka for their valuable discussions and suggestions. The author deeply indebted to Professor Dr. Seiichi Tagawa, the Institute of Scientific and Industrial Research, Osaka University for his kind and helpful advises and constructive criticism.

The work of this thesis was performed under the collaboration between Department of Nuclear Engineering, Osaka University and Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute. The author greatly indebted to Dr. Nobutake Suzuki and Dr. Shunichi Kawanishi for their continuous encouragement, close collaboration throughout this work and valuable discussions. The author also indebted to Dr. Yuichi Shimizu, Dr. Shunichi Sugimoto and Dr. Nobuyuki Ichinose for their close collaboration and valuable discussions. The author also indebted to Dr. Kazushige Nishizawa and Dr. Kimiko Ema for their helpful advises and suggestions. The author greatly acknowledges to the students of Nuclear Chemical Engineering Laboratory (Yamamoto Labo.), Department of Nuclear Engineering, especially Mr. Yuji Hamada, Mr. Masaharu Maruo, Mr. Shinji Hara, Mr. Shigeo Honda, Mr. Daishi Yoshikawa, Mr. Noriaki Takagi, for their collaborations and various supports.

The author would like to thank his parents, Mr. Toshihiko Izumi and Ms. Michika Izumi, and sister, Ms. Noriko Makino, for their warm encouragement and support. Finally, the author would like to thank his wife, Ms. Kimiko Izumi, and daughter, Ms. Momoka Izumi for their hearty encouragement.

Osaka
1998

Yoshinobu Izumi

Research Activities by the Author

List of Publications

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1) "Effect of Molecular Orientation on the Radiolysis of Polyethylene in the Presence of Oxygen",
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Technol. Rep. Osaka Univ., **48**, 309-316 (1998).

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* The present doctoral thesis is including the works described in these seven published papers.