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FOR RADIATION CHEMISTRY
JAPAN ATOMIC ENERGY RESEARCH INSTITUTE
(No.29)
April 1,1995-March 31,1996**

March 1997

Advanced Photon Research Center

**日本原子力研究所
Japan Atomic Energy Research Institute**

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Annual Report of the Osaka Laboratory for Radiation Chemistry
Japan Atomic Energy Research Institute
(No. 29)

April 1, 1995 - March 31, 1996

Advanced Photon Research Center

Kansai Research Establishment
Japan Atomic Energy Research Institute
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(Received February 5, 1997)

The annual research activities of the Osaka Laboratory for Radiation Chemistry, JAERI, during the fiscal year 1995, are reported.

The research activities were conducted under two research programs: the study on laser-induced organic chemical reactions and the study on basic radiation technology for functional materials. Detailed description of the activities are presented as reviews on the following subjects: laser-induced chemical transformation, laser-induced reaction of polymer surface, photochemical separation of stable isotopes, microprocessing by radiation-induced polymerization, preparation of fine metal particles by gamma-ray irradiation, and electron beam dosimetry. The operation report of the irradiation facility is also included.

In October 1995, the Osaka Laboratory was dissolved into the Kansai Research Establishment which was newly inaugurated to promote advanced photon research. Therefore, this is the final issue of the annual report of the Osaka Laboratory for Radiation Chemistry.

Keywords: Excimer Laser, Electron Beam, Gamma-Ray, Photochemical Reaction, Polymer Modification, Polymerization, Dosimetry

平成7年度大阪支所年報 (No. 29)
1995年4月1日～1996年3月31日

日本原子力研究所関西研究所
光量子科学センター

(1997年2月5日受理)

本報告書は、大阪支所において、平成7年度に行われた研究活動をまとめたものである。主な研究題目は、レーザー有機化学反応の研究と放射線加工技術の基礎研究であり、本報告書では以下の研究活動について詳細に述べる。レーザー光による物質変換、レーザー光による高分子の表面化学反応、放射線重合による微細加工、放射線による金属微粒子の合成、線量測定および照射施設の運転・管理。光量子科学を推進するため、大阪支所を発展改組し、平成7年10月に関西研究所が設立された。大阪支所年報は本号が最後の報告書となる。

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I. Introduction

The annual research activities of the Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, during the fiscal year 1995, are reported.

The research activities were conducted under the following two research programs: 1) The Study on Laser-Induced Organic Chemical Reactions and 2) The Study on Basic Radiation Technology for Functional Materials, with the support of Operation and Maintenance Group of the radiation facilities. The total number of people working in the laboratory was 27 including visiting research collaborators from industrial companies and student research assistants from universities. JAERI funded expenditures during the period amounted to ca. 36 million yen, excluding personnel expenses.

The study on laser-induced organic chemical reactions was initiated in 1988 as an advanced frontier subject to utilize lasers to chemistry. Under this program, three research subjects were studied in this fiscal year: (1) laser-induced chemical transformation, (2) laser-induced surface photoreaction of polymers, and (3) photochemical separation of stable isotopes. Concerning the research program of the basic study on radiation technology for functional materials, three research subjects were studied: (1) microprocessing by radiation-induced polymerization, (2) preparation of fine metal particles by gamma-ray irradiation, and (3) low energy electron beam dosimetry. Cooperative research programs with universities (6 groups) and joint research programs with industrial companies (4 groups) were conducted under our research subjects.

In the operation and maintenance of the irradiation facilities, the cobalt gamma-ray source and two electron accelerators of 800 keV and 2 MeV were operated without any serious trouble for irradiation. Irradiation service has been extended to request from researchers outside of the laboratory since April 1991. In this fiscal year, ca.10% of the beam time was used for this purpose.

A training program which is offered for researchers from universities and industries has been held once a year since 1968. This seven-day program includes lectures and instruction on radiation chemistry of polymers, to which laser chemistry has been added as a new subject since last year. We accepted 10 trainees this year.

Detailed description of each activity is given in Chapter 2. A list of publications including patent applications is given in Chapter 3. Cooperative and joint programs are summarized in Chapter 4.

In October 1995, JAERI inaugurated the Kansai Research Establishment by integrating the Osaka Laboratory and Department of Synchrotron Radiation Facilities Project to promote advanced photon research which includes research on advanced lasers such as x-ray lasers as well as research through the utilization of the large synchrotron

radiation facility (SPring-8). With this reorganization, the current activities of the Osaka Laboratory were terminated by the end of March 1996. Therefore, this is the final issue of the annual report of Osaka Laboratory for Radiation Chemistry.

Masafumi Nakano

Director of the Osaka Laboratory for Radiation Chemistry

(October, 1992 - September, 1995)

Present address: Kansai Research Establishment

II. Current Research Activities

1. Study for the Optical Resolution of Tartaric Acid with Circularly Polarized Laser Beam

Y. Shimizu and S. Kawanishi

Optical resolution of racemic mixtures is of great importance in preparation of optically active compounds. In the last report,¹ we have demonstrated a possibility of the optical resolution of racemic tartaric acid (DL-TA) by a photochemical procedure using a circularly polarized light (CPL) from XeF excimer laser (351 nm) of a high intensity. Thereafter further works have been performed for the quantitative analysis of the laser-induced optical resolution. In this annual report we describe more quantitative results of the aqueous solution of DL-TA irradiated with right (r)-CPL from an XeF laser.

The experimental apparatus and method were mostly the same as those used in the previous report.¹ The irradiation with a focused r-CPL was carried out for N₂-saturated aqueous solutions of DL-TA (6.67×10^{-1} and 10^{-3} M) at room temperature. A calorimeter (Sciencetech 38-4UV5) which was used for the measurements of laser fluence was placed behind the reaction vessel to determine precisely the photon energy absorbed by the solution during the irradiation. The initial fluence of the CPL was about $1.6 \text{ J cm}^{-2} \text{ pulse}^{-1}$. Each sample was analyzed by HPLC (Shimadzu LC-6A) equipped with a chiral column (SUMICHIRAL OA-5000).

Figure 1 shows the change in the relative concentration of L-TA in the course of the irradiation of the DL-TA solution. As shown in Figure 1, the concentration of L-TA decreased with increasing absorbed energy. A decrease in the concentration of ca. 13.9% was observed at the dose of about $1 \times 10^4 \text{ J}$.² On the contrary, the concentration of D-TA was almost constant throughout the irradiation as shown in Figure 2. Thus it was clearly indicated that D-TA can be optically enriched by the irradiation of racemic tartaric acid with a high-intensity CPL from an XeF laser. Further works will be focused on the elucidation of mechanism of the optical resolution and will be reported elsewhere.

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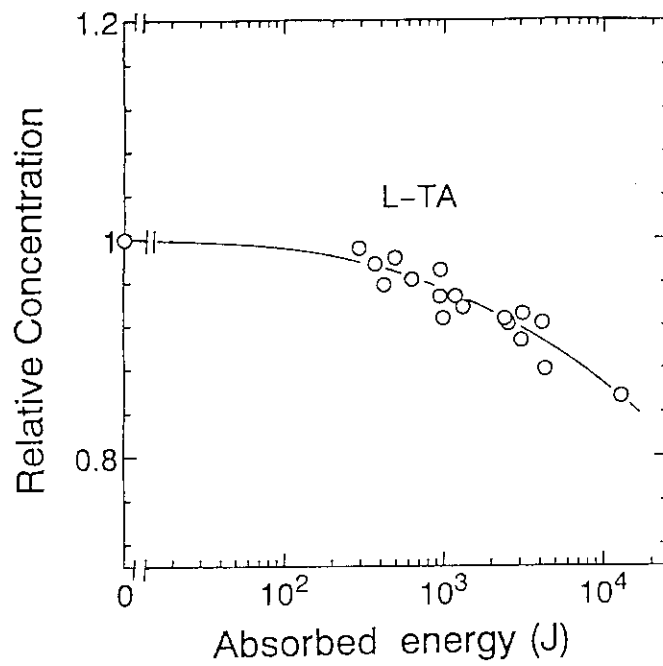


Figure 1. The change in the relative concentration of L-TA in the course of irradiation of racemic tartaric acid with a focused r-CPL.

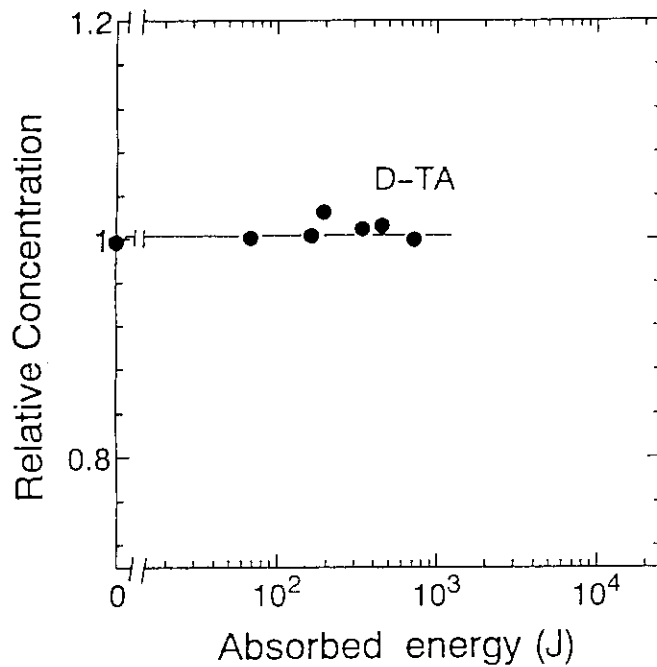


Figure 2. The change in the relative concentration of D-TA in the course of irradiation of racemic tartaric acid with a focused r-CPL.

2. A Study on the Photochemistry of Poly(4-trimethylsilylmethylstyrene) Film upon KrF Laser Irradiation

N. Ichinose and S. Kawanishi

Recently, a number of fields in science and technology have searched lithographic approaches to make minute devices and tools such as microsensors.¹ Chemical properties at the surface play an important role in the processes of lithographic approach. As well as control of solubility of the resist layer, control of surface functionality is also a subject for the recent approaches. We have studied the surface photochemistry of the title polymer, poly(4-trimethylsilylmethylstyrene) (PTMSMS), as a lithographic material.^{2,3} The polymer unit has a photochemically reactive C-Si bond which gives radical species leading to various reactions.

Thin films (0.8-1.5 μm) of PTMSMS were prepared by spin-coating on quartz plates (29-mm diameter, 1 mm thick) from a toluene solution. The polymer films were irradiated in air at 254 nm with a low-pressure Hg lamp or at 248 nm with KrF laser and were analyzed by X-ray photoelectron spectroscopy (XPS), ATR-FT-IR, or contact angle measurement. Photoirradiation of thin films of polystyrene (PS) and poly(4-methylstyrene) (P4MS) was also studied for comparison. When the polymer films were irradiated at 254 nm, the surface became hydrophilic through photooxygenation. The hydrophilicity was monitored by the contact angle of the surface with water droplet. The contact angle of the films decreased with irradiation time. As compared with the irradiation of PTMSMS, the surfaces of PS film became less hydrophilic. Analysis of the surface composition by XPS showed an increase of the O/C ratio for all the polymers and a decrease of the Si/C for PTMSMS suggesting the cleavage of the C-Si bond followed by oxygenation. Carboxylic group was produced by the oxygenation, which was assigned on the basis of a qualitative analysis by the contact angle titration,⁴ dye adsorption, and ATR-FT-IR. The contact angles of the irradiated surface with buffer solutions of various pH's showed a pH-dependence characteristic to the surface bearing carboxylic functionality as shown in Figure 1. In contrast, an irradiated PS film did not show such a pH-dependence. These results also strongly support the C-Si bond cleavage. Basic or cationic dyes such as rhodamine 6G was adsorbed selectively onto the irradiated surface of PTMSMS (Figure 2), whereas anionic or acidic dyes were not. This must be due to the presence of acidic and anionic functional groups at the surface. Presence of -OH group on the irradiated PTMSMS film was demonstrated by ATR-FT-IR measurement.²

The PTMSMS films became insoluble by the irradiation, whereas PS or P4MS films, on the other hand, became soluble even in a poor solvent (ethanol-benzene: 6/1 v/v). These results can be attributed to the formation of a cross-linked structure for PTMSMS and a reduction of molecular weights by the oxidative degradation for PS and P4MS. Micro-patterning of the negative and positive images of these polymers were carried out by irradiation of KrF laser light ($15 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$) through a photomask (Figure 3). Higher spatial resolution was obtained with KrF laser than that with Hg lamp. This must be due to the high directivity of the laser beam.²

Excited state of the polymers can be considered to be the same as alkylbenzenes and trimethylsilylmethylbenzene. These molecules undergo photochemical cleavage of benzylic C-H or C-Si bond to give benzyl-type radicals.^{4,5} However, the cleavage of C-H bond on the main chain will compete with the cleavage of C-H or C-Si bond of 4-substituents of the benzene ring. The two-types of the benzylic radicals at the surface of the film would be attacked by molecular oxygen in air, which lead to the formation of carboxylic group and degradation of the main chain (Scheme 1). The radicals formed inside the film can couple each other to form cross-linking network because of the low concentration of oxygen.

The radicals formed at the surface may couple each other when they are formed in a high concentration. The surface concentration of carboxylic groups can be estimated by the dye adsorption, assuming 1 : 1 adsorption to the acid group. The surface concentration of the acid is given by $\text{OD}/1000\epsilon$ (mol cm^{-2}), where OD is the absorbance of the film stained by the dye and ϵ is the molar extinction coefficient ($\epsilon = 1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for rhodamine 6G). We have estimated the degree of the radical coupling competing with the formation of acid groups upon KrF laser irradiation with various laser intensities ($1\text{-}60 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$) which generates the radicals in a variety of the surface concentrations. The surface concentrations of the acid groups formed per pulse ($\text{molecules cm}^{-2} \text{ pulse}^{-1}$) were plotted against the laser intensity (I , $\text{mJ cm}^{-2} \text{ pulse}^{-1}$) as shown in Figure 4.³ The formation of acid groups is proportional to the laser intensity at low intensities indicating that the reaction is a one-photon process. However, the slope of the plot gradually decreased with increasing the laser intensity and became negative at $\approx 30 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$. This laser power dependence of the acid group formation is fitted with a quadratic equation eq 1.

$$[\text{carboxylic acid group}] = AI - BI^2 \quad (\text{molecules cm}^{-2} \text{ pulse}^{-1}) \quad (1)$$

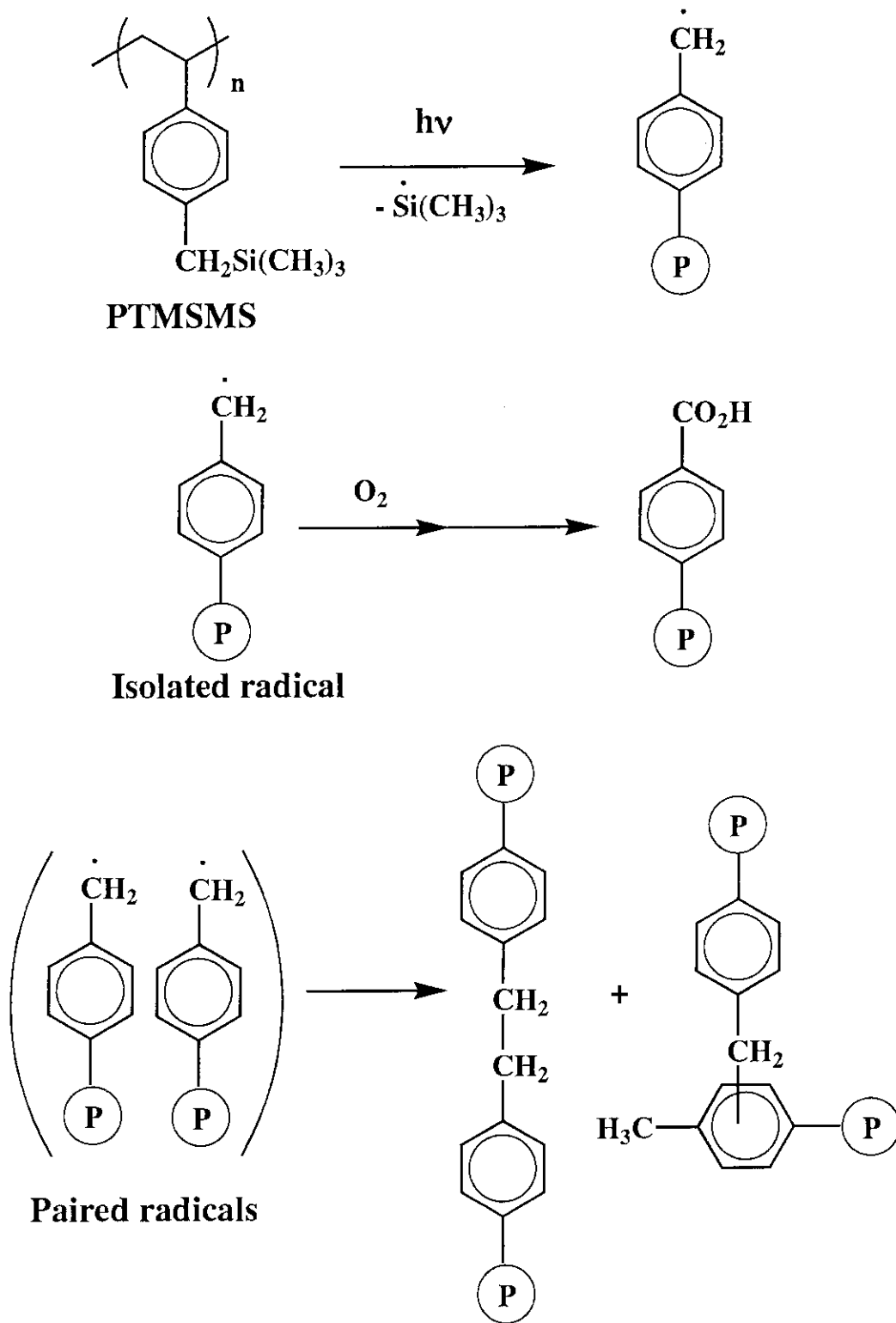
where A and B are constants ($A = 3.55 \times 10^{10} \text{ molecules mJ}^{-1}$ and $B = 6.2 \times 10^8 \text{ molecules mJ}^{-2} \text{ cm}^2 \text{ pulse}$ for Figure 4). The second term was attributed to the coupling of the radicals since radical formation is a one-photonic process and two photons are, therefore, required for radical pair formation from a pair of 4-trimethylsilylmethylphenyl

group. The contribution of the other two-photon processes such as singlet-singlet (S-S) or triplet-triplet (T-T) annihilation or two-photon ionization to the laser power dependence can be ruled out because these processes will produce an excited state with two photons. From the two parameters, the selectivity of oxygenation to coupling process can be estimated by $1 - AI/B = 1 - 0.017I$. This means the oxygenation is favorable at lower laser intensities. On the other hand, the selectivity for the cross-linking given by $0.017I$ means that the use of laser as a light source is favorable for the negative image formation as shown in Figure 3.³ As a conclusion, the irradiation of the cross-linkable polymer with properly intensive excimer laser pulses affords the negative pattern in a short time with a good spatial resolution as compared to that with a Hg lamp.

The authors thank Dr. Toshiyuki Tamai, Dr. Isao Hashida (Osaka Municipal Technical Research Institute), Prof. Hiroo Inoue, and Prof. Kazuhiko Mizuno (Osaka Prefecture University) for their kind help in the present work.

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Scheme 1

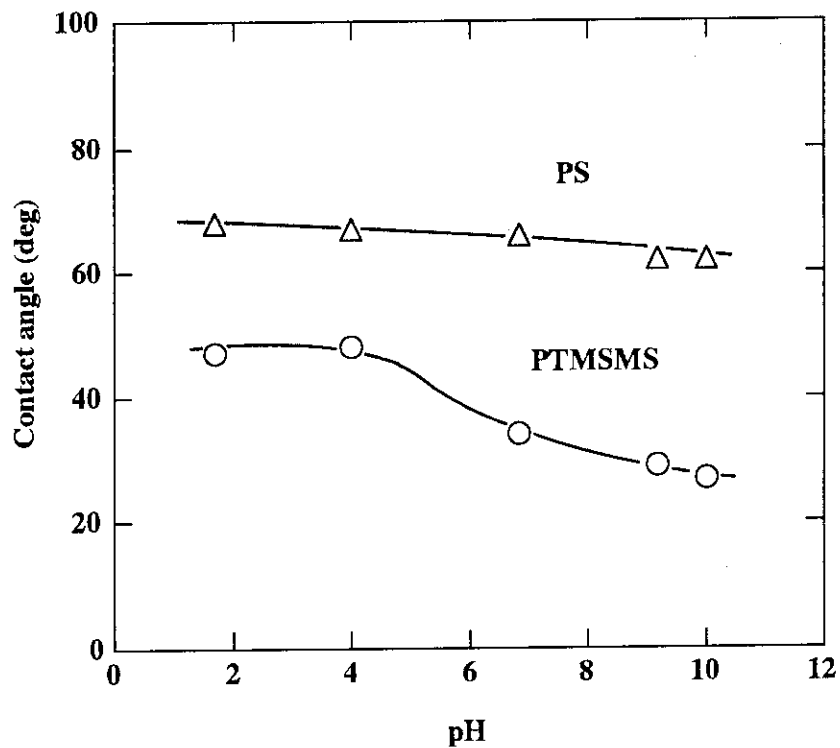


Figure 1. The pH-dependence of the contact angle of the irradiated PTMSMS and polystyrene (PS) films with buffer droplets: 60-W low-pressure Hg lamp.

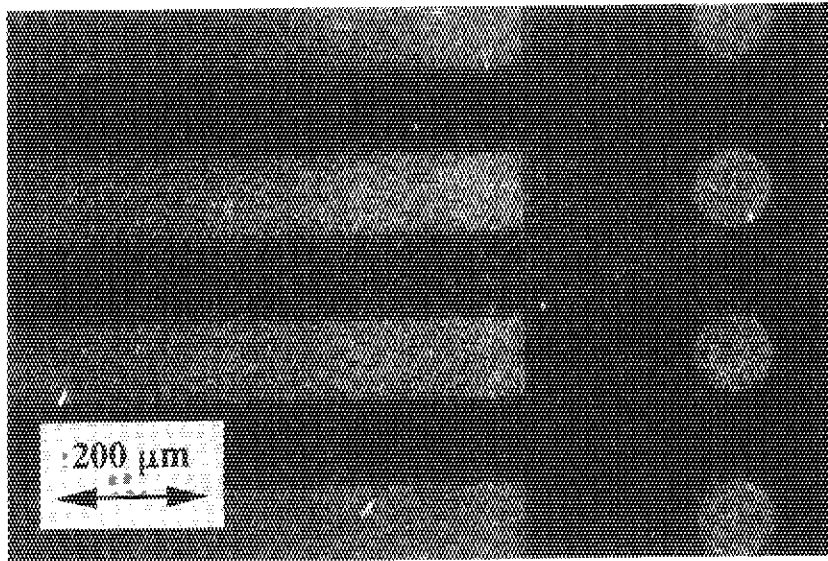


Figure 2. A fluorescence micrograph of an image of photomask formed on a PTMSMS film which was irradiated with KrF laser and stained with Rh6G.

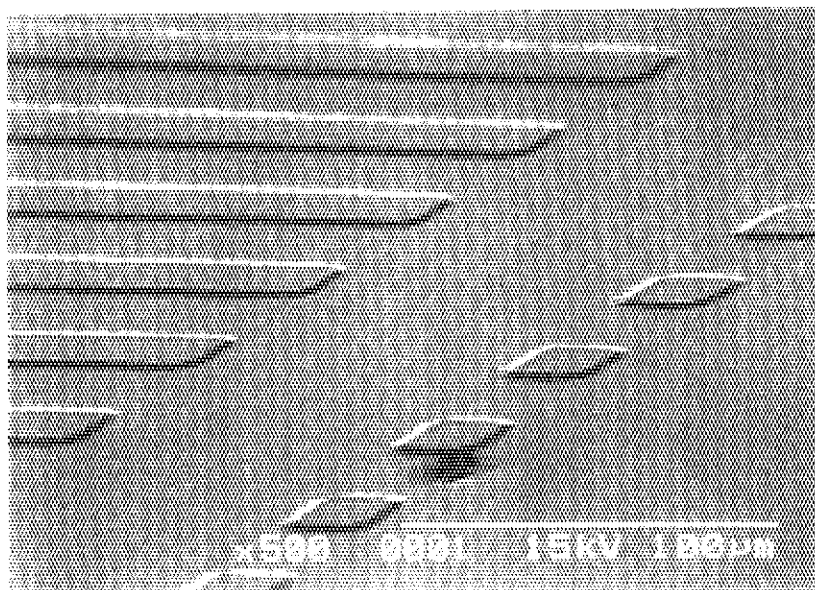


Figure 3. An SEM image of a negative pattern of a PTMSMS film irradiated with KrF laser through a photomask.

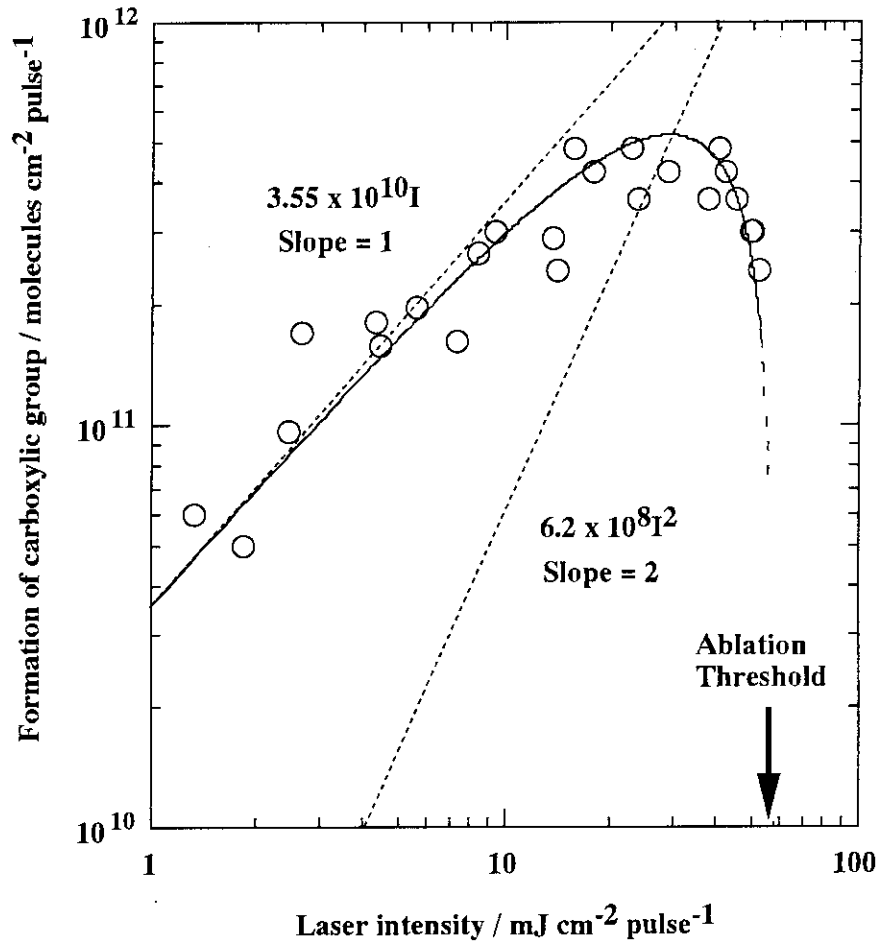


Figure 4. The laser power dependence of the formation of carboxylic group on the PTMSMS films irradiated with KrF laser.

3. KrF Laser-Induced Graft Reaction of Poly(acrylic acid) (PAA) onto Tetrafluoroethylene-Perfluoroalkyl Vinyl Ether Copolymer (PFA) Film

A. Okada, N. Ichinose, and S. Kawanishi*

Recently, laser-induced surface photoreactions of fluoropolymer have been proposed by several groups including us.^{1,2} In the previous papers,^{3,4} we reported that excimer laser irradiation of tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) in water dissolving various gasses or ammonia made the surface wettable. We now report to proceed surface modification of PFA by KrF laser irradiation with poly(acrylic acid) (PAA) aqueous solution through a novel graft reaction of PAA.⁵

A PFA film (0.1 mm thickness) prepared by extrusion processing was washed with ethyl alcohol with supersonication and was air-dried at room temperature before irradiation. PAA (M_w : 2000 and 150000) were used as received and dissolved in distilled water. The PFA film placed in contact with the PAA solution was irradiated with KrF laser (wavelength: 248 nm, frequency: 40 Hz). After the irradiation, the film was washed thoroughly with water and ethyl alcohol. Surface wettability was estimated by the contact angle of the PFA film with a water droplet. Surface composition of the PFA film was analyzed by X-ray photoelectron spectroscopy (XPS) to obtain atomic ratios and C1s spectra. Rhodamine 6G (Rh6G) was adsorbed onto the irradiated surface from its aqueous solutions (1×10^{-5} mol dm^{-3}).⁶ Surface morphology was examined by scanning electron microscopy (SEM).

The PFA films in contact with an 1 wt% solution of high and low molecular weight PAA were irradiated with 10000 pulses at a fluence of $22 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$. The surfaces of the films became hydrophilic as judged by changes in the contact angle from 106° to $40\text{-}60^\circ$ before and after the irradiation. With PAA solutions whose concentrations were greater than 3 wt%, however, a considerable gelation in liquid phase occurred, but the surface was less wettable. On the other hand, the irradiation with solutions whose concentrations were smaller than 0.5 wt% was less effective than that with solution of 1 wt% throughout the present study. Figure 1 shows changes in the contact angles of the PFA film as a function of the irradiation energy with various laser fluences. Though the

* Shiga Laboratory, Gunze Ltd.

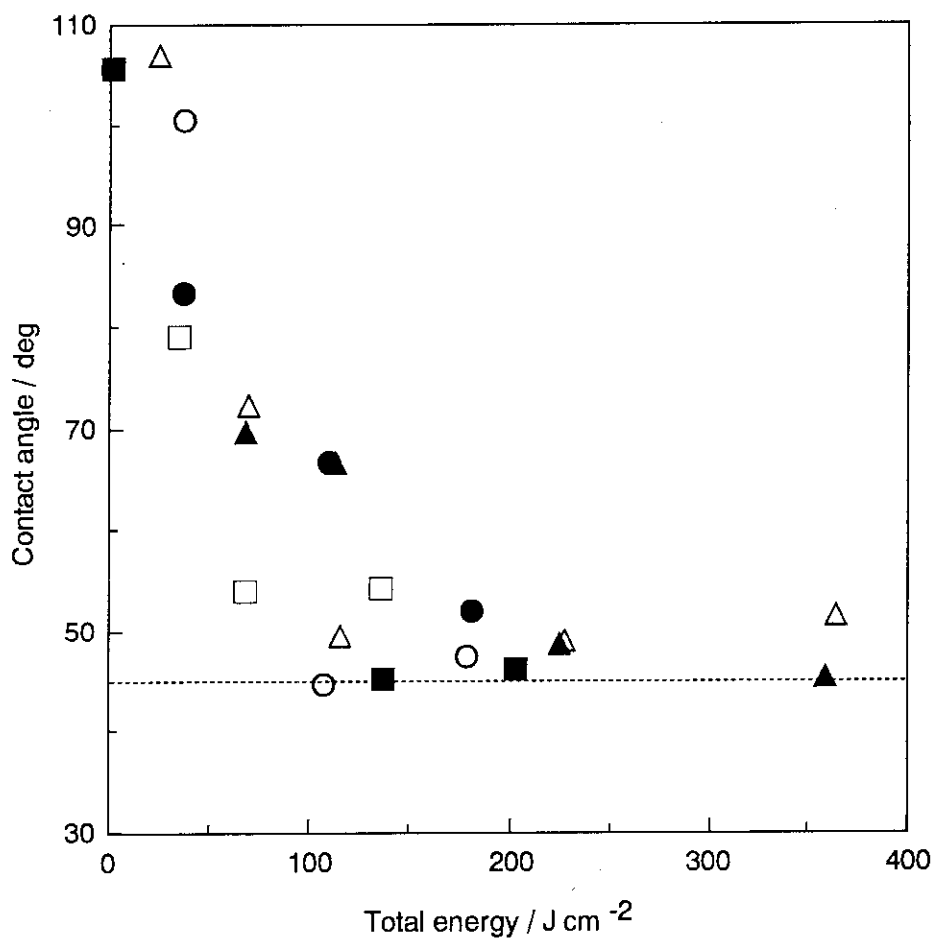


Figure 1. Plot of contact angle on the PFA films irradiated with 1.0 wt% PAA solutions vs. total laser energy with several laser fluences and molecular weights: (closed triangle), $22.4 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, $M_w = 150000$; (closed circle), $36.3 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, $M_w = 150000$; (closed square), $67.6 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, $M_w = 150000$; (open triangle), $22.6 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, $M_w = 2000$; (open circle), $35.6 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, $M_w = 2000$; (open square), $67.4 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, $M_w = 2000$.

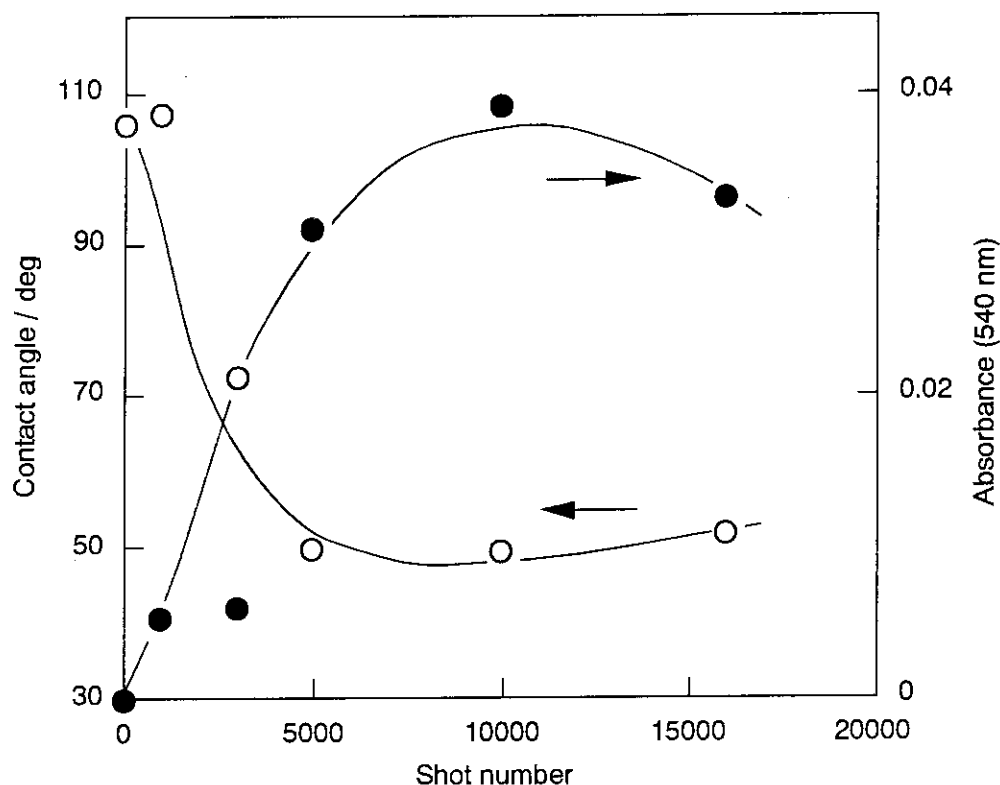


Figure 2. Plot of the contact angle of the irradiated PFA films with water droplet (open circle) and absorption at 540 nm based on the adsorption of Rh6G (closed circle) vs. shot number of KrF laser pulse ($22.6 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$).

decrease of contact angle with total energy was observed for each fluence, the contact angle was leveled off at $45 - 50^\circ$ in the range of the irradiation energy of $> 100 \text{ J cm}^{-2}$. With the laser pulses of $> 150 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, ablation of PFA or its reacted layer took place to result in damage of the surface. There seems to be little fluence dependence in the wettability, which is rather governed by the total energy than by the fluence.

The contact angle was not changed by the KrF laser irradiation with water which did not contain PAA.³ The wettability was not affected by washing with 0.5 N NaOH followed by those with 0.5 N HCl and water to rule out simple adsorption of PAA. No morphological change in the irradiated PFA surface was observed with SEM ($\times 10000$). The surface was smooth, which rules out contribution of surface roughness induced by laser ablation on the wettability. Therefore, the surface wettability was attributed to a photochemical reaction between PFA and PAA. The surface was stained well with a basic dye such as Rh6G and not with acidic dyes such as sulforhodamine. The absorbance (A) at 540 nm based on Rh6G adsorbed on the surface increased with shot

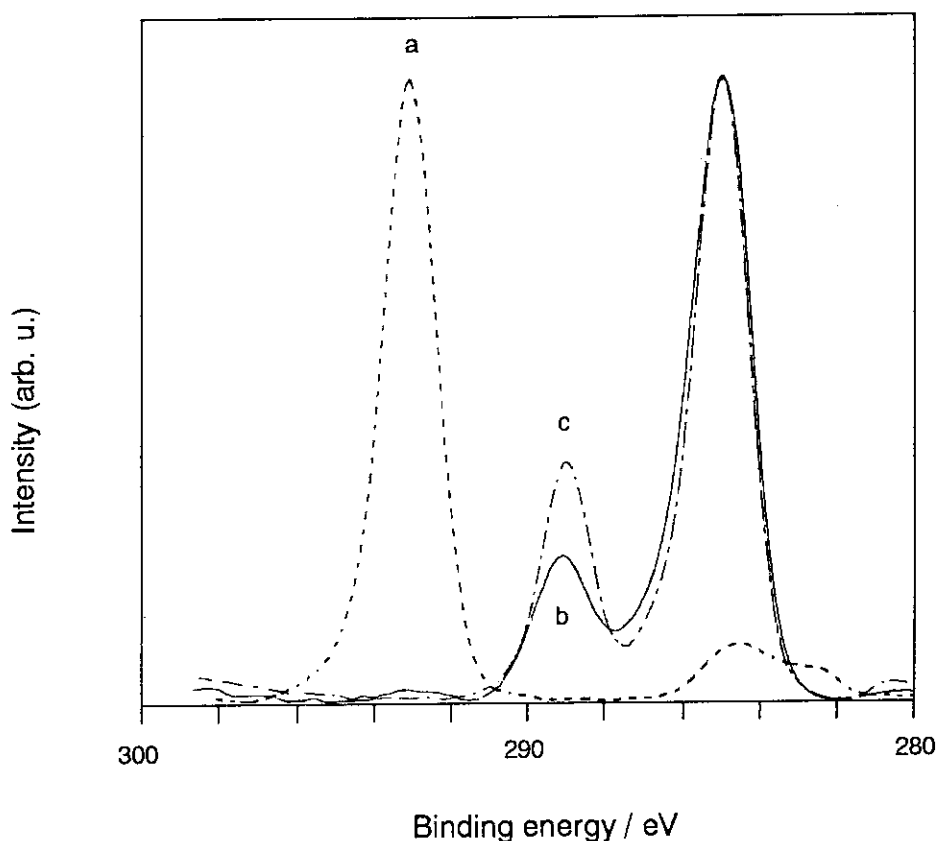


Figure 3. Normalized XPS C1s spectra of PFA film (a) before and (b) after irradiation ($22.6 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 16000 pulses) in contact with a 1.0 wt% low molecular weight PAA solution, and (c) that of PAA cast film.

number as shown in Figure 2. These results suggested introduction of carboxylic group which was induced by a photochemical reaction between PAA and the PFA surface.

Figure 3 shows a C1s XPS spectra of the PFA film before and after the irradiation together with that of PAA. A large peak of a PFA film before irradiation assigned to $-\text{CF}_2-$ (293.0 eV) was decreased after the irradiation, and growth of two new peaks was observed at 285.0 and 289.2 eV which can be assigned to methylene or methine and carboxylic groups, respectively. Since the spectrum after the irradiation resembled that of PAA, the origin of the carboxylic group at the surface was attributable to a photochemical grafting of PAA chain onto the PFA surface in a form of thin layer or sparse cluster. The results for contact angle and dye adsorption also seemed to be in accordance with thin or sparse coverage. Elemental analysis of the surface by XPS indicated considerable loss of fluorine (F/C ratio from 2.18 to 0.07) and increase of oxygen (O/C ratio from 0.004 to

0.384) by irradiation (KrF laser: $22.6 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 16000 pulses, 1.0 wt% low molecular weight PAA solution).

The present reaction is a new approach for grafting PAA without the use of acrylic acid monomer and will modify the surface without damages in bulk. Various functional groups can be introduced onto the surface through the present reaction of copolymers of acrylic acid to enhance affinity to various organic chemicals such as inks or adhesives for instance. Detailed work with simple carboxylic acids concerning the mechanistic feature of the present alkylation will be reported elsewhere.⁷

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4. XeCl Laser Irradiation of Fluoropolymer Films Coated with Sodium Anthraquinone-2-sulfonate As an Ultraviolet Absorbent for Improvement of Adhesion Property

T. Nagase, M. Nishii, S. Sugimoto,** and S. Kawanishi*

Though fluoropolymer is an organic material with excellent properties such as thermal stability and chemical inertness, there is a difficulty in adhesion without chemical/physical treatment because of its extremely low surface energy. Several group including us have recently attempted to improve adhesion property of fluoropolymers by excimer laser irradiation.¹⁻⁵ Since fluoropolymers have no absorption band in an ultraviolet region of > 200 nm, we have studied the effect of aromatic ultraviolet absorbents of polymers and small molecules such as Ekonol,² sodium benzoate,⁴ and sodium anthraquinone-2-sulfonate (SAQS)⁵ in forms of a blend or a coating on the irradiation with KrF laser (248 nm). Here we report the effect of SAQS coating as an ultraviolet absorbent upon the XeCl laser (308 nm) irradiation. Since the photon energy of XeCl laser is smaller than that of KrF laser, less damage of optical components is expected and the use of XeCl laser as a light source will be favorable in the practical purpose.

Thin films (100 μm) of tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) were used as samples. A surfactant bearing perfluoroalkyl group was added to an aqueous solution of SAQS in order to obtain a good coating on the PFA film by reducing the surface tension of the solution. The solution was coated uniformly on the film surface with an applicator (25 μm thickness). After air drying, the film was irradiated with XeCl laser (fluence 200 - 500 mJ cm^{-2} pulse⁻¹; frequency 40 Hz, number of pulses 2-16) in an ambient condition. The adhesive strength of the irradiated film was evaluated as the 180°-peel strength of the sample adhered on a stainless steel plate with an epoxy resin adhesive.

Figure 1 the shows plots of the 180°-peel strength of the PFA films irradiated at 210 and 440 mJ cm^{-2} pulse⁻¹ versus total laser energy. The adhesive strength of a PFA film coated with SAQS was remarkably increased from 0.01 to 1.2 kgf cm^{-1} by the irradiation (fluence 440 mJ cm^{-2} pulse⁻¹, 2 pulses), whereas the similar irradiation of a film without the coating had almost no effect. The peel strength is constant with the irradiation energy for the pulses of a fluence of 440 mJ cm^{-2} pulse⁻¹. However, the

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irradiation of a coated PFA film at a fluence of $210 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ had a little effect on the adhesive strength of the film even with the increase of the total laser energy. Though a similar effect was observed with the KrF laser at a fluence of $\geq 50 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, much higher fluences of $> 440 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ were required with XeCl laser. The difference in the action of the two lasers may be attributed to a difference in the molar extinction coefficient (ϵ) of SAQS at the two wavelengths ($\epsilon_{248} = 35000 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$, $\epsilon_{308} = 3200 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$). Though the irradiation of PFA films coated with SAQS with XeCl laser was less effective than that with KrF laser, the use of an absorber with high molar extinction coefficient will improve the present surface modification.

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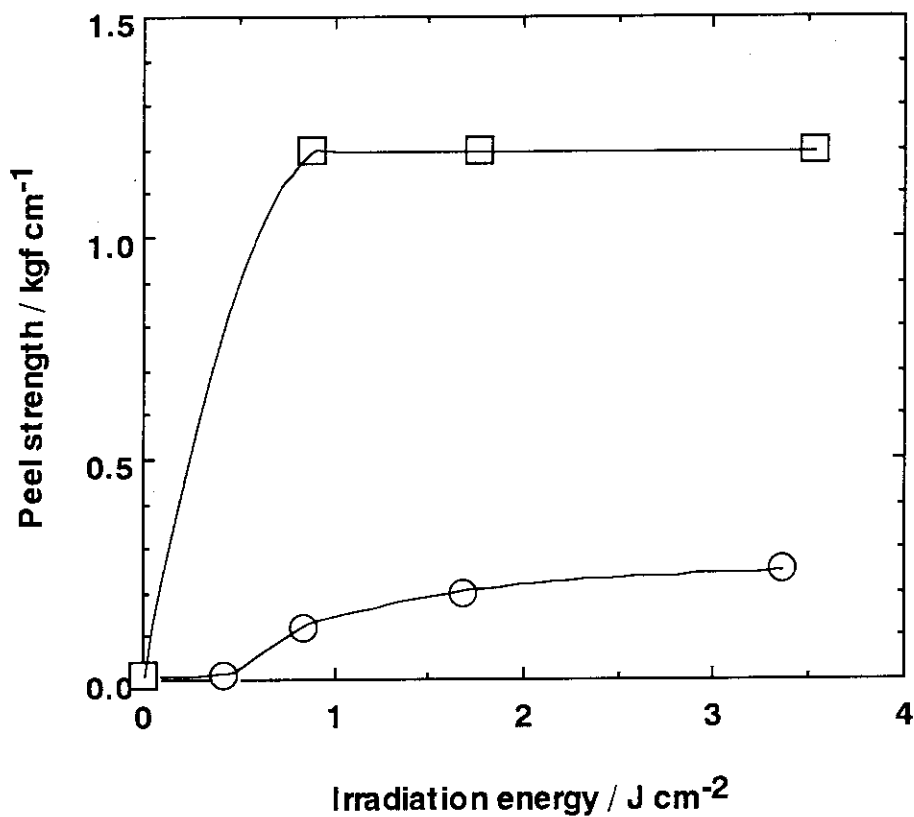


Figure 1. A plot of the peel strength vs. total irradiation energy at fluences of (circle) 210 and (square) 440 mJ cm⁻² pulse⁻¹ in the course of the XeCl laser irradiation of the PFA films coated with sodium anthraquinone-2-sulfonate (SAQS).

5. Improvement of Filterability of PTFE Membrane by Excimer Laser Irradiation

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Filter cartridges composed of all fluoro-resin are widely used to filtrate various chemicals in the semiconductor manufacturing industry. As highly circuits are integrated from year to year, smaller pore size of the filters has been required. However, the smaller pore size makes the filtration of chemicals with high surface tension such as buffered aqueous solutions of hydrogen fluoride more difficult because of the low surface tension of PTFE filter membranes. For this reason, we have attempted to make the PTFE membranes wettable. As reported previously, the wettability of the PTFE membranes can be improved by the irradiation with KrF laser after the impregnation of the membranes in an aqueous solution of hydrogen peroxide. In the present work, the filterability of filter cartridge of the laser-treated PTFE membrane and elution of metals have been studied.

The PTFE membranes (pore size: 0.1 μm ; 45 μm thick) were purchased from Japan Goretex. The membranes were impregnated in an aqueous solution of hydrogen peroxide and were irradiated with KrF laser at room temperature. The treated membranes were washed thoroughly with pure water and were dried. The wettability of the membranes was evaluated by a method with the standard solutions prepared according to JIS K-6768 specification having various wettability indices. The standard solutions were dropped onto the membrane in an ascending order of the surface tension of the solutions. The wettability index of a membrane was determined as a maximum surface tension of the solutions which penetrate into the membranes. The wettability index of PTFE membranes was increased by the irradiation with KrF laser (fluence: 200 mJ cm^{-2} pulse $^{-1}$; total energy 1 J cm^{-2}) from < 31 to 32 dyn cm^{-1} .

Table 1 shows the results of an analysis by atomic absorption spectrometry of metals eluted in a 30% aqueous solution of hydrochloric acid from the membranes after 3-day immersion at room temperature. The metal elution from the membranes was low and was unchanged by the treatment. No morphological changes were observed by electron microscopy. An analysis of the treated membranes by X-ray photoelectron spectroscopy revealed that only a thin surface layer was modified by the present treatment

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method. It is noteworthy that the present method can improve the surface wettability without losing the excellent properties such as thermal and chemical resistivity of the original membrane.

Figure 1. shows the plots of flux of an aqueous solution containing ammonia and hydrogen peroxide ($\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 13$ v/v) from the cartridges with the treated and untreated membranes as a function of the effective filtering area at a differential pressure of 0.2 kgf cm^{-2} at 25°C . Each cartridge was impregnated with ethanol before applying the flow of the ammonia-hydrogen peroxide solution. The flux from the cartridge with the treated membrane was noticeably greater than that with the untreated membrane. Though the flux of the solution from the cartridge with the untreated membrane was not restored and decreased by 30% owing to a sticking of bubbles to the membrane when the solution was applied again after letting the solution flow out to expose the membrane to air. On the other hand, the flow from the cartridge with the treated membrane was not affected by the exposure to air. From these results, it has been demonstrated that the treated membrane is suitable for filtration of various chemicals which readily bubbles.

Since the present modification method can afford hydrophilicity to any part porous PTFE membranes in any extent, various applications of the filter systems with the treated membranes such as medical and electronic equipments can be expected.

Table 1. Elution of metal from PTFE membranes in 30% HCl aqueous solution

Membrane	Metal / ng per 1cm^2 of membrane									
	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Ni	Zn
Untreated	N.D.	N.D.	N.D.	N.D.	1.1	N.D.	N.D.	1.3	N.D.	0.6
Treated	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5
Limit of detection	0.4	0.5	0.5	0.5	0.5	0.1	0.1	0.2	0.3	0.1

N.D.: Not detected.

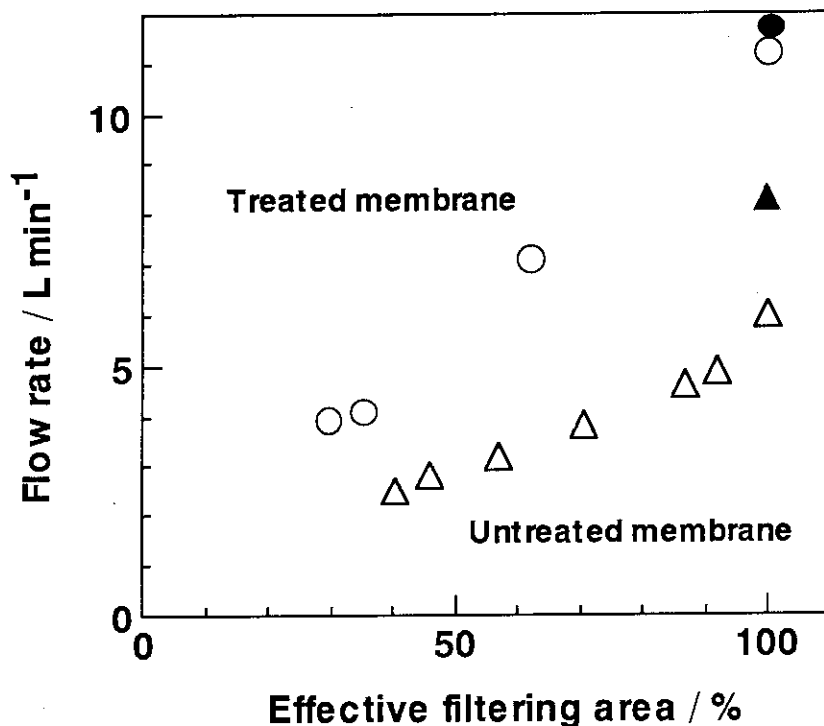


Figure 1. The flux of an aqueous solution containing ammonia and hydrogen peroxide ($\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 13$ v/v) at a differential pressure of 0.2 kgf cm^{-2} through the PTFE membranes irradiated (circle) and unirradiated (triangle) with KrF laser. The membranes were exposed to air to examine the effect of the bubbles at the membrane surface on the flow rate (see text). Closed circle and triangle indicate the membranes without exposure to air.

6. Separation of Silicon Isotopes by Infrared Multiple-Photon Decomposition Method II. Separation of ^{28}Si

*S. Sugimoto, *S. Kawanishi, A. Isomura, ** T. Ikawa, ** and S. Arai***

Silicon is one of the abundant elements which compose the crust of the earth and it contains 27.7% of silicon as silica and its derivatives. Natural silicon contains three stable isotopes in a ratio (natural abundance ratio) of $^{28}\text{Si} : ^{29}\text{Si} : ^{30}\text{Si} = 92.23 : 4.67 : 3.10$. It is possible to isolate small amounts of a silicon isotope by use of large-sized mass analyzer. On the other hand, Arai et al. have studied the separation of the silicon isotopes by means of the infrared multiple-photon decomposition (IRMPD) method using a TEA CO_2 laser.¹ We have also tried to demonstrate that IRMPD is the advantageous method to separate a large amount of silicon isotopes. We have focussed on the enrichment of ^{28}Si the most abundant isotope of silicon by applying the same method.

The purified hexafluorodisilane (Si_2F_6) was introduced into a cylindrical irradiation vessel (100 mm ϕ x 950 mm; 5.1 L) made of Pyrex glass with NaCl windows (50 mm ϕ , 5 mm thickness) at the both ends. Infrared laser beam (10P(8) line, wavelength 10.476 μm) from pulsed CO_2 laser was introduced through the window to irradiate Si_2F_6 at 1Hz. The wavelength of 10P(8) line was selected because of its closeness to that of an absorption peak due to ^{30}Si -F vibration. It is expected that a multiphoton absorption at this wavelength causes a selective decomposition of Si_2F_6 which contains ^{30}Si isotope to enrich ^{28}Si and ^{29}Si in remainder Si_2F_6 . After the irradiation, the reaction mixture was separated into two fractions A (a gaseous component) and B (a condensed component) by cooling at the Dry Ice-ethanol temperature. Each fraction was analyzed by GC-MS (DB-1 capillary column). The fraction A was assigned to SiF_4 . The fraction B was assigned to Si_2F_6 mainly $^{28}\text{Si}_2\text{F}_6$ and small amount of $^{28}\text{Si}^{29}\text{SiF}_6$ and $^{29}\text{Si}_2\text{F}_6$ which remained unchanged through the irradiation. Any compounds which contain ^{30}Si isotope could not be detected in fraction B under the conditions. It means that only Si_2F_6 that contains ^{30}Si is selectively decomposed to form SiF_4 by the 10P(8) line irradiation of CO_2 laser. The isotope of ^{28}Si in the fraction B is enriched by the irradiation.

The ratios of $^{28}\text{Si}_2\text{F}_6$ and $^{28}\text{Si}^{29}\text{SiF}_6$ isotopic isomers in the remained Si_2F_6 of fraction B were dependent both on the charging pressure of starting material Si_2F_6 and on the fluence of the CO_2 laser. The selectivity of ^{28}Si isotope is then defined by the ratio of $^{28}\text{Si}_2\text{F}_6$ in fraction B. The selectivities of the isotope after the irradiation with 2500

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pulses at various fluences of the CO₂ laser are shown in Figure 1 as functions of the charging pressure of Si₂F₆. The selectivity of ²⁸Si isotope at a laser fluence of 2.2 J cm⁻² pulse⁻¹ was 97.7% at 5 Torr and 100% at ≤ 3 Torr and the rest was unreacted ²⁹Si. At a fluence of 1.6 J cm⁻² pulse⁻¹, the charging pressure of ≤ 1 Torr was required to obtain the 100% selectivity of ²⁸Si. The irradiation at a fluence of 0.6 J cm⁻² pulse⁻¹ did not afford the 100% selectivity of ²⁸Si at any pressure. These results indicate that Si₂F₆ molecules containing ²⁹Si as well as ³⁰Si is also decomposed by the irradiation at a high fluence.

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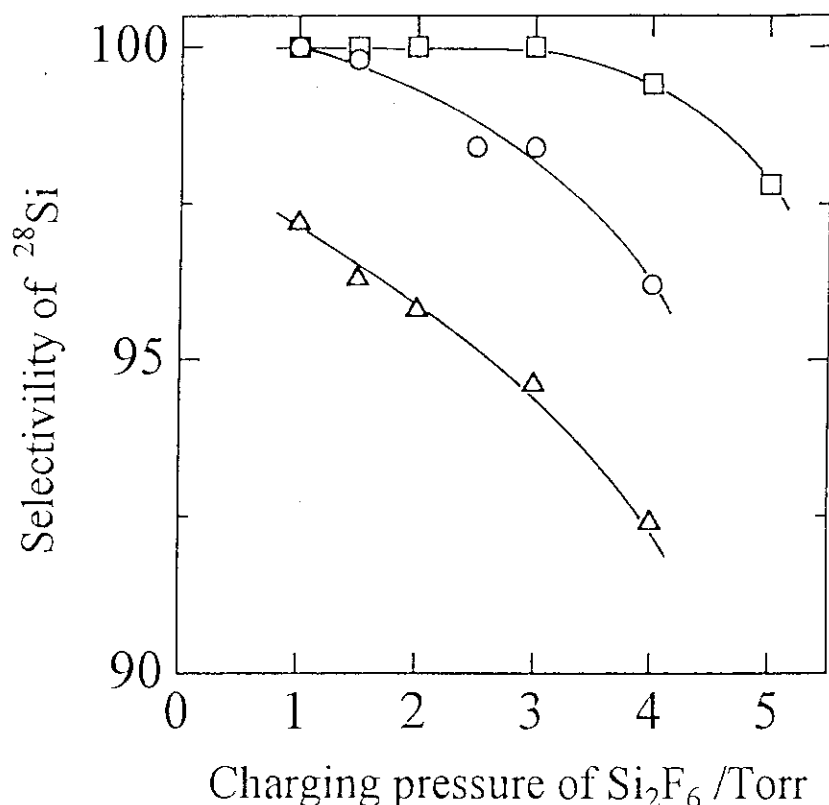


Figure 1. The charging pressure dependence of the selectivity of ²⁸Si isotope in the fraction B obtained by the IRMPD of Si₂F₆ at 10.476 μm (10P(8)) with 2500 pulses of the fluences of 0.6 (triangle), 1.6 (circle), and 2.2 J cm⁻² pulse⁻¹ (square).

7. The Effect of Excimer Laser Beam Irradiation on F⁻ Uptake in Enamel

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We previously reported that the substitution of carbonate ion (CO₃²⁻) in enamel crystals by fluoride (F⁻) was accelerated by excimer laser beam irradiation.^{1,2} In this study, the F⁻ uptake in extracted tooth enamel induced by a simultaneous action of 2%-NaF solution and KrF laser was examined.

The sample were prepared by cutting buccolingual enamel (extracted healthy bilateral molars) into 4 plates (approximately 7.0 x 4.5 mm²) and polishing by 100 μm from the surface. The samples were submitted to the treatment with a 40 μL portion of a 2% NaF solution under KrF laser irradiation (248 nm; 70 mJ cm⁻² pulse⁻¹; 2000 shot (Irradiation A), 4000 shot (Irradiation B)). Samples treated with the NaF solution under dark (Single), KrF irradiation alone, and those without any treatment were prepared as control samples. After washing with 1-M KOH solution for 1 day, CaF₂ was eliminated from the enamel which had been treated with the NaF solution. The morphology of the enamel surfaces was examined by scanning electron microscopy (SEM) (JEOL, JSM-5300). Formation of fluoroapatite (FAp) on the surface of enamel was estimated with a micro-X-ray diffractometer (Rigaku, RINT 1200). For an acid-resistance test, the enamel surfaces were decalcified by attaching a cellulose acetate film (Φ: 3 mm) containing 2 mL of 0.1-M lactic acid buffer solution (pH 4.0) for 1min, and were treated by wet calcification. The amount of eluted Ca²⁺ was analyzed with an ICP emission spectrometer (Shimadzu, ICPS-50).

Figure 1 shows X-ray diffraction patterns (2θ: 49-54°) of the samples treated with NaF (I) and treated with NaF and Irradiation B (II). The former showed a peak at a angle corresponding to a (213) plane, which would be due to the weakness of X-ray source. On the other hand, the latter exhibited a marked peak corresponding to a (004) plane in addition to the (213) plane.

Figure 2 shows the results of the acid-resistance test for the sample groups of Single-treatment (NaF) and combined treatment (NaF and Irradiation A or B). These results indicate a higher acid resistance of the latter than the former owing to the laser irradiation.

Figure 3a shows the SEM images of the enamel surfaces after the single-treatment

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(group I) and the combined treatment (group II). A rough trace due to laser ablation was observed for the sample of the combined treatment. Though the surface of the single treatment was smooth, scars were observed after the decalcification with a buffer solution of lactic acid (0.1 M, pH 4.0) for 1 min (Figure 3b). The decalcification also afforded a few scars on the sample of the combined treatment.

Though the action of NaF caused a small amount of F^- uptake, which was washed out with an aqueous solution of KOH (1 M), remarkable F^- uptake into the crystals of the enamel surface was observed by the combined treatment of NaF and the laser irradiation.³ This could be attributed to a photochemical reaction induced by KrF laser as observed in Figure 1. We also observed the effect of the irradiation on the Ca elution. The elution of Ca compared with those of the single treatment was suppressed by 12.2% and 22.7% by the irradiation with 2000 and 4000 pulses of KrF laser light (Irradiation A and B). The availability of the combined treatment was also strongly supported by the SEM observation in Figure 3.

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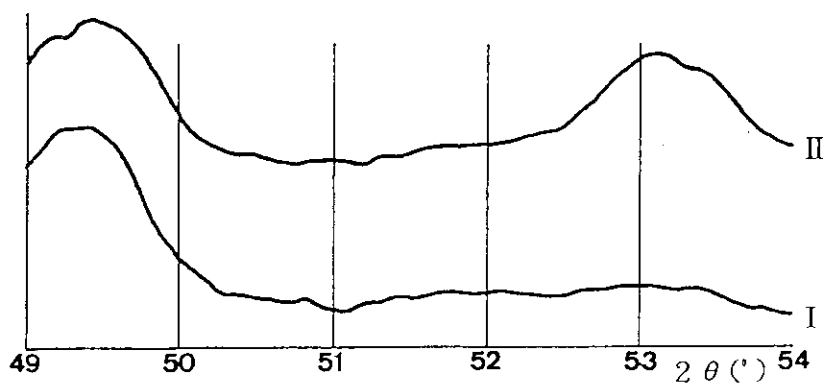


Figure 1. A peak profile (2θ : 49-54°) of micro-X-ray diffraction from the enamel surface. I: action of the 2% NaF aqueous solution and II: action of the 2% NaF aqueous solution and Irradiation B.

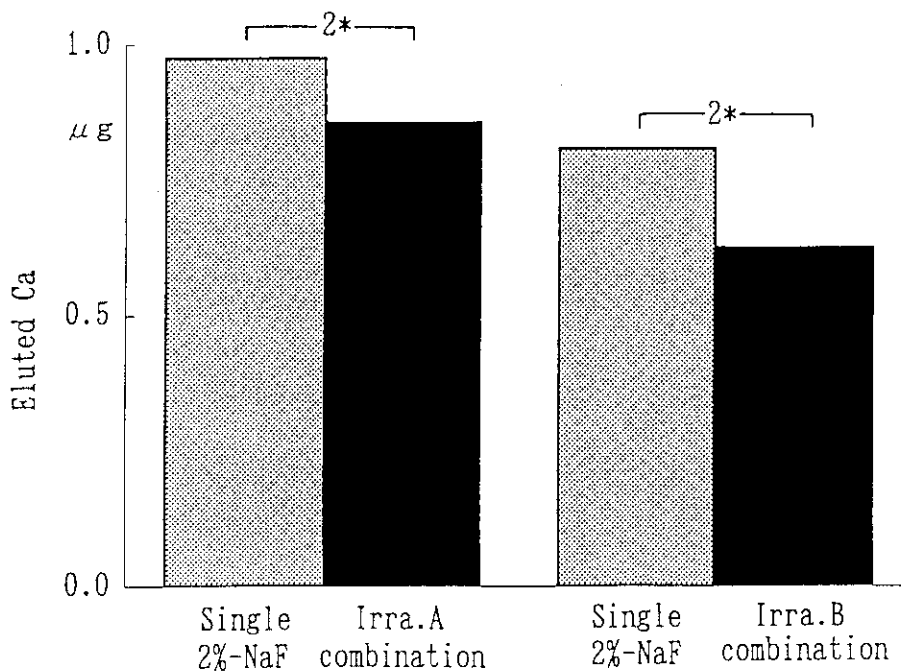


Figure 2. The results of the acid resistance test of the enamel surfaces (see text). 2*: $p < 0.01/t$ test.

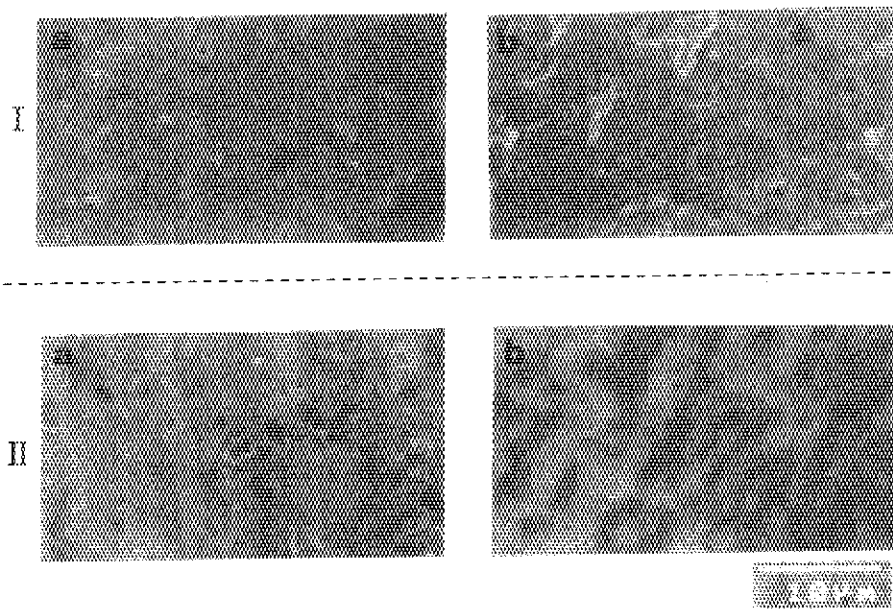


Figure 3. a) The SEM images of the enamel surfaces after the single-treatment (group I) and the combined treatment (group II).
b) Those after the decalcification with a buffer solution of lactic acid (0.1 M, pH 4.0) for 1 min.

8. Electron Beam-Induced Polymerization of Epoxyacrylate Film

Y. Nakase, H. Murakami, and I. Kaetsu**

Various functional polymers have been developed to satisfy the requirements of microelectronic devices. There is a strong demand for stable and adhesive organic materials for microlithography, electrode- or insulator-printing, microsensing, etc. Several studies have been reported on ultraviolet- (UV-) or electron beam- (EB-) induced polymerization of bisphenol A epoxy resin containing an initiator in a form of spin-casted films of several micrometer to ca. 1 mm thickness.¹⁻³ In the previous paper,⁴ we have reported an EB-induced polymerization of epoxyacrylate oligomer without an initiator under nitrogen gas stream. In this report, we describe some physical properties of the polymerized films and an attempt for their functionalization.

Thin films of an epoxy acrylate oligomer (Arakawa Kagaku Kogyo Co. Ltd) were prepared on silicon wafers by spin coating from neat liquid, or from its acetone solution for thickness control if necessary. The films were irradiated under nitrogen stream with a Van de Graaf accelerator (1.5 MeV). The energy deposited in the film was estimated by CTA-film dosimeter. The thickness of the film was determined from the absorbance of a band of -CH₂- group at 2940 cm⁻¹. The polymerization rates were estimated from the decreasing rate of the absorbance of a band of vinylic =CH₂ group at 1636 cm⁻¹. No polymerization took place when the sample was irradiated in air at room temperature, nor heated in air.

Figure 1 shows the chemical structure and the infrared absorption spectra of the oligomer. The absorption intensity at 1636 cm⁻¹ decrease with increasing dose, but that at 2940 cm⁻¹ remained almost unchanged. This result indicates the decrease of =CH₂ group by polymerization.

Figure 2 shows a relationship between the irradiation time and the conversion in the polymerization obtained for the samples of 17 μm thickness. The films with a conversion of < 40% are soluble in ethanol, but not for those over 40%.

Figure 3 shows a relationship between the conversion and the contact angle of the films with water or Vicker's hardness of the samples prepared by electron beam irradiation. The initial increase of the contact angle seems to depend on the conversion up to about 40%, and the contact angle becomes almost constant at about 45° at the conversion of > 40%. The value of 45° is lower than that of commercial poly(methyl methacrylate) plate (about 60°). The hardness of the sample increased almost linearly

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with the increase of the conversion. These results indicate that the surface characteristics change with the increase of conversion up to 40%, but not over 40%, and the cross-linking reaction may take place in the sample by further irradiation judging from the linear increase of hardness.

This high hydrophilicity of the sample must be suitable for biological material. For this reason, we examined the adsorption and desorption of water in the sample with the aid of a diatomaceous earth (DAE) due to its high porous character. The DAE with 150 wt% water and the epoxyacrylate oligomer (4 : 6 by weight) were mixed homogeneously to cast on a polyester film with the thickness of about 200 μm . After the electron beam irradiation of 4.8 kGy at room temperature, the 200- μm film was immersed in water. The maximum water absorption was about 250 mg per 1 g of the dry film as shown in Figure 4. When the sample was kept under the condition of RH 85% and 15 °C, the amount of water absorbed decreased with time to reach an equilibrium value after about 1 h. On the other hand, the sample dried at 80 °C in vacuum was kept under the same condition, then the amount of water absorbed in the sample increased with time to reach about 10 mg/g film after 1 h. The absorption and desorption of water can take place depending on the relative humidity of the ambient condition.

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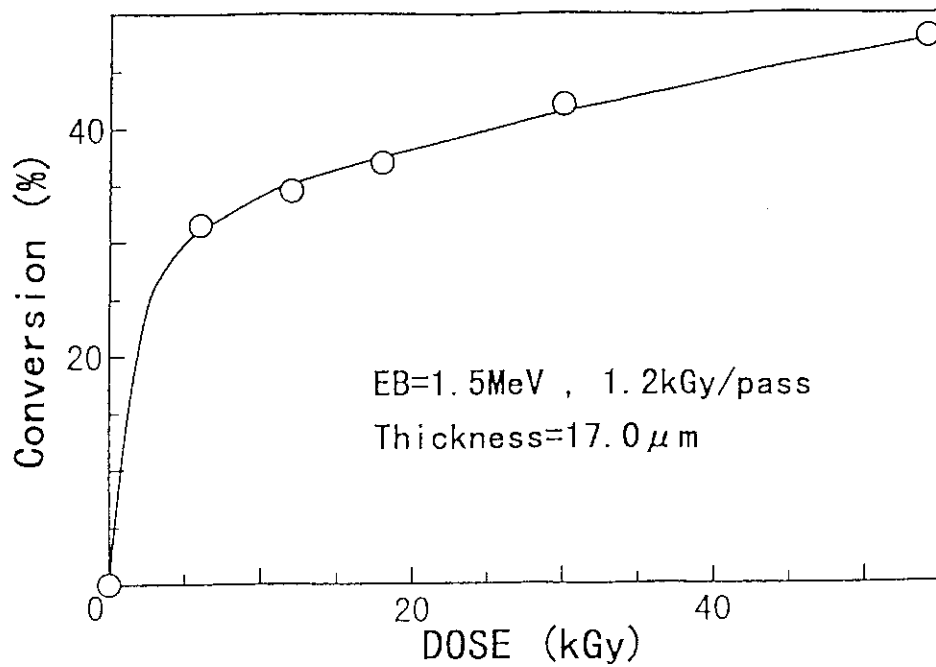


Figure 2. A relationship between doses and conversion in the polymerization by electron beam (1.5 MeV, 1.2 kGy/pass) irradiation. The sample thickness is ca. 17 μm.

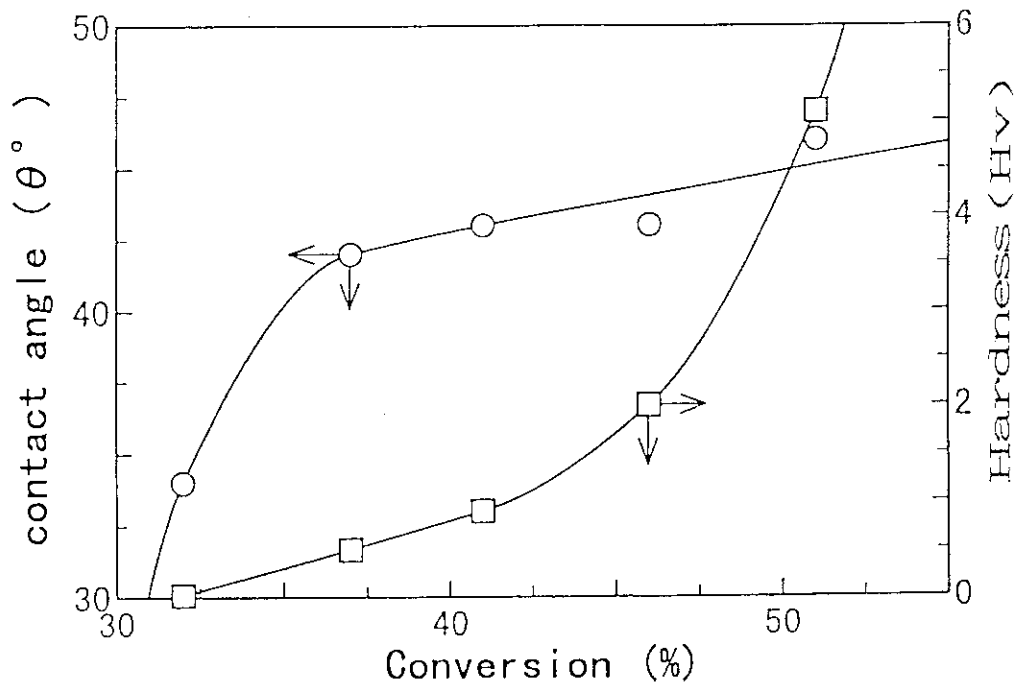


Figure 3. A relationship between conversion and contact angle of water, or Vicker's hardness (Hv) of the same sample as indicated in Figure 2.

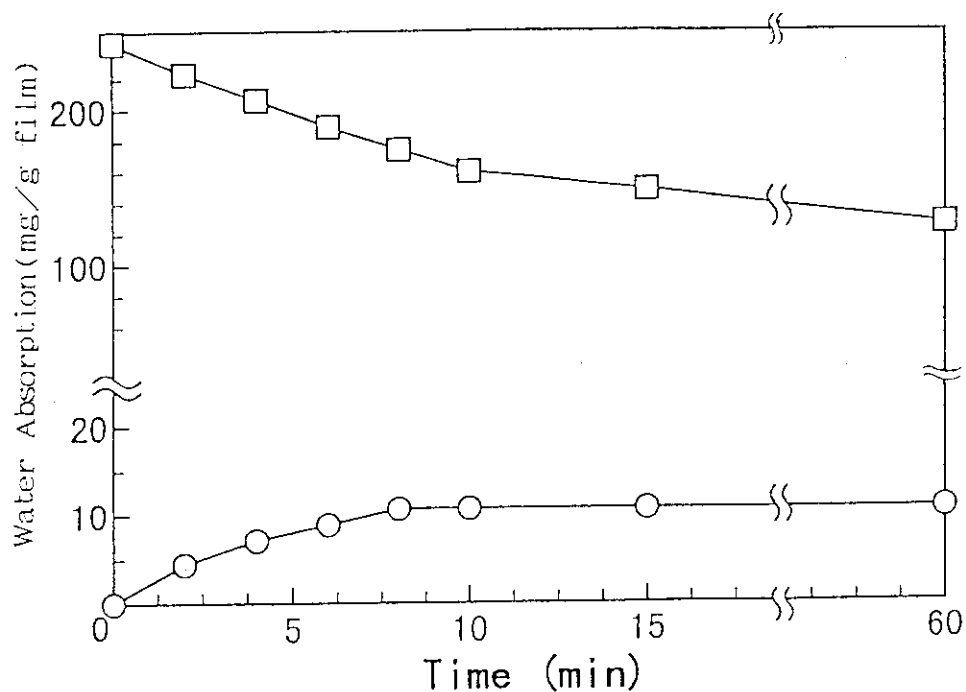


Figure 4. Change of water absorption per 1 g film with time under the condition of RH 85% and 15 °C. The samples are a composite of diatomaceous earth and epoxyacrylate (4 : 6 by weight), where diatomaceous earth contains 150 wt% water. The samples (200 μm thick) covered by a polymer film was irradiated at 4.8 kGy (1.2 kGy/pass x 4 pass) at room temperature.

9. Formation of Fine Particles from Aqueous Solution of Silver Ion by γ -Ray Irradiation (II)

Y. Nakase, K. Ushiroda, and I. Kaetsu**

Many studies have been carried out on the radiation-induced formation of metal clusters from aqueous solution of metal ions, mostly noble metals. Their efforts were concentrated on reaction mechanisms of cluster formation,^{1,2} where they used a surface active reagent that stabilizes metal cluster formed. We are intending to prepare functional materials having catalytic activities for solid-gas heterogeneous reactions. In the previous papers,^{3,4} we have reported that silver ions was reduced to form fine metal particles by the irradiation at pH = 0.43 in solutions of palladium and silver ions, and at pH = 7 in the absence of palladium ion. The present study has been carried out in order to obtain some information on the radiation-induced formation of silver metal particles in solutions of silver ions at pH > 4.

The solutions with nitrogen gas bubbling were irradiated by ⁶⁰Co γ -rays and transferred to a cuvette for the colorimetric determination of silver ion using a UV spectrophotometer and a reagents (supplied by Hach Chemicals), or to a quartz tubing for dynamic light scattering (DLS) measurement within 3 min after irradiation.³

Figure 1 shows the reduction rate of silver ion measured by colorimetry and the diameter of the particles as a function of pH indicating that the higher the pH, the higher the reduction rate of silver ion and the larger diameter of the particles formed by irradiation. The high reduction rate can be explained by the standard electrochemical potentials of hydrogen and silver as mentioned in the previous paper.³ The equilibrium electrochemical potential of silver aggregates ($E(\text{Ag}^+/\text{Ag}_n^0)$) can be expressed by the standard electrochemical potential (E_0) as follows: assuming the corrosion of silver metal occurs when 10^{-6} molar silver ion is formed in the solution,³

$$E(\text{Ag}^+/\text{Ag}_n^0) = E_0(\text{Ag}^+/\text{Ag}_n^0) - 0.355$$

$$E(\text{H}^+/\text{H}_2^0) = E_0(\text{H}^+/\text{H}_2^0) - 0.059\text{pH}$$

where $E(\text{H}^+/\text{H}_2^0)$ and $E_0(\text{H}^+/\text{H}_2^0)$ are the equilibrium and the standard electrochemical potentials, respectively. When $E(\text{Ag}^+/\text{Ag}_n^0)$ is larger than $E(\text{H}^+/\text{H}_2^0)$, the silver aggregates cannot be reoxidized to dissolve into the solution. Then,

$$E_0(\text{Ag}^+/\text{Ag}_n^0) > 0.355 - 0.059\text{pH} \text{ for } E_0(\text{H}^+/\text{H}_2^0) = 0$$

Depending on the pH of the solution, solid silver must have a suitable number of n. For example, the aggregation numbers of $n \geq 8$ (pH = 4), ≥ 7 (pH = 7), and ≥ 5 (pH =

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9) has been reported.² It can be noticed that silver aggregates tend to have a small number of n at a high pH. We, however, observed the formation of large silver aggregates at a large pH as shown in Figure 1. It is, therefore, supposed that small silver aggregates easily coagurate to form large particles.

Reducing species such as hydrated electron and hydrogen atom are produced upon radiolysis of aqueous solutions as well as the same amount of oxidizing $\cdot\text{OH}$ radical. The former species reduce the silver ion to form solid particles whereas the latter oxidize the particles formed to dissolve.⁵ In order to obtain the solid particles efficiently, ethanol was used to scavenge the $\cdot\text{OH}$ radicals.

Figure 2 shows a relationship between reduction percents of silver ion and doses irradiated at three dose rates. The conversion of silver ion was obtained by the colorimetric measurements. The reduction of silver ion was completed with a small dose upon the irradiation at a high dose rate. Figure 3 shows a dose rate dependence of the reduction percents and that of the diameter of the particles at an early stage of the irradiation (840 kGy). It is clear that the higher the dose rate, the more efficient the reduction of silver ion and the smaller the particle size. When the reduction was completed large particles were obtained at a high dose rate compared to a low dose rate as shown in Figure 4. Since the large particle size observed at the initial stage was not observed at the end of reduction, it is suggested that the particles of the diameter larger than 200 nm precipitate through a mutual coaguration in the case of the low dose rate of 0.84 kGy/h owing to a slow formation of the particles as compared to the coaguration rate.

It is safely concluded that the size of the silver particles formed by the present radiation reduction can be controlled both by dose rate and by pH of solution.

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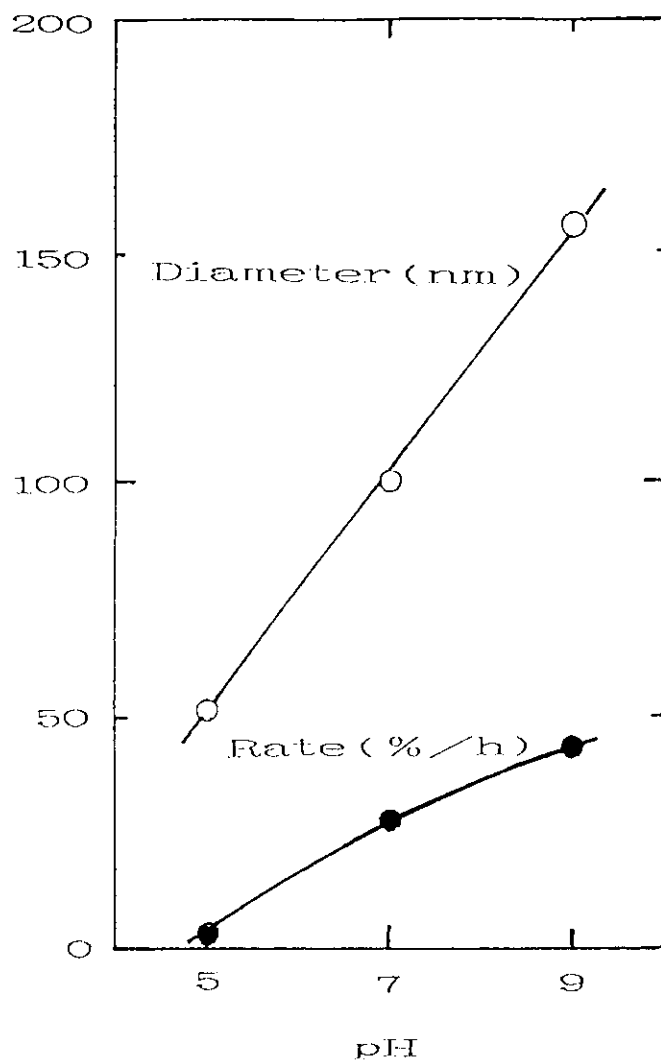


Figure 1. The reduction rate of silver ion measured by colorimetry and the diameter of the particles measured by DLS as a function of pH. $[\text{AgClO}_4] = 0.5 \text{ mM}$, dose rate = $8.4 \text{ kGy/h} \times 1 \text{ h}$ under a nitrogen gas stream.

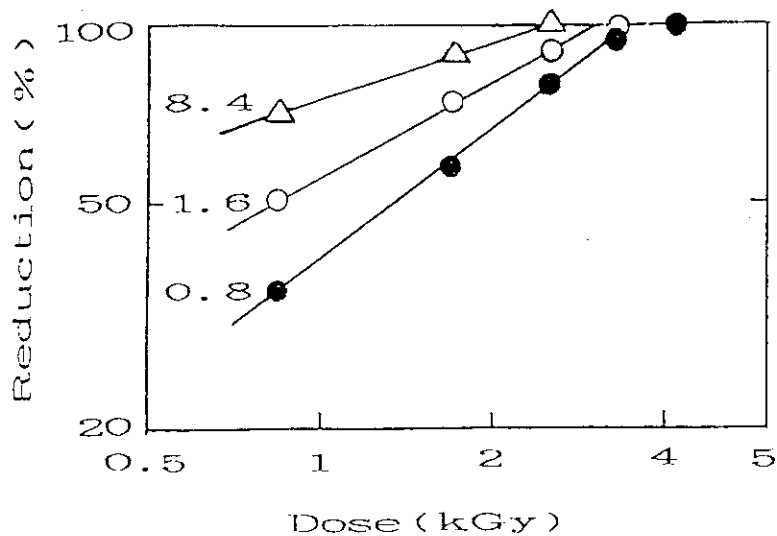


Figure 2. Reduction of silver ion measured by colorimetry as a function of irradiation doses with various dose rates. Dose rates (kGy/h) are indicated in the figure. $[AgClO_4] = 0.5 \text{ mM}$, $[EtOH] = 7 \text{ mM}$, $pH = 9$.

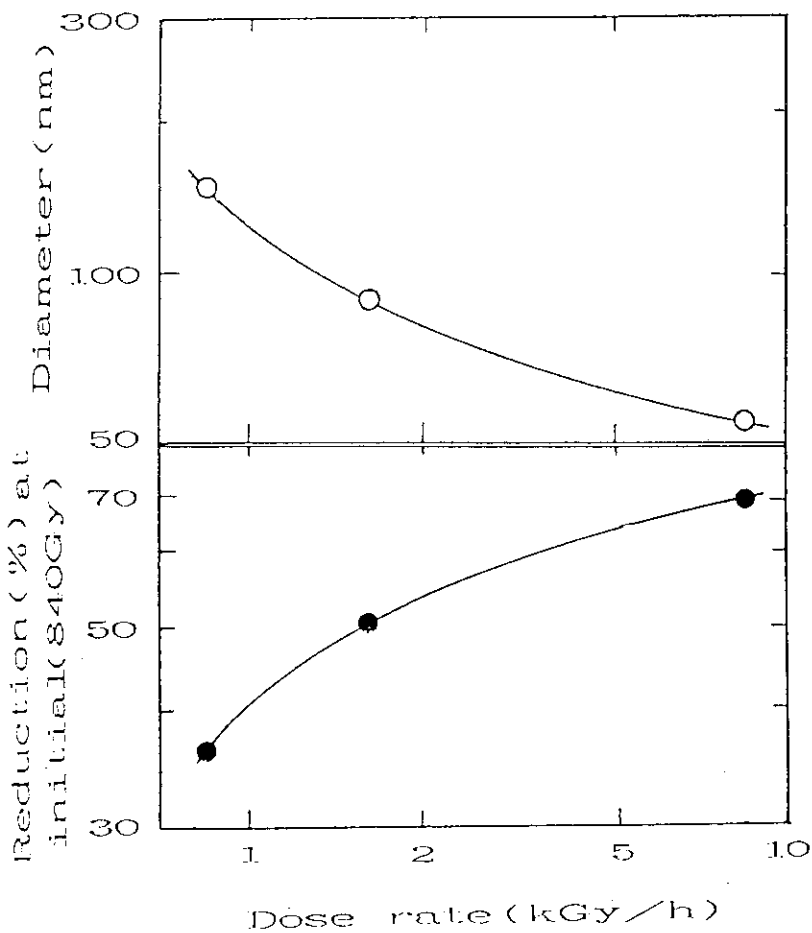


Figure 3. Reduction of silver ion at an initial stage of irradiation and the diameter of particles obtained as a function of dose rates, taken from Figure 2.

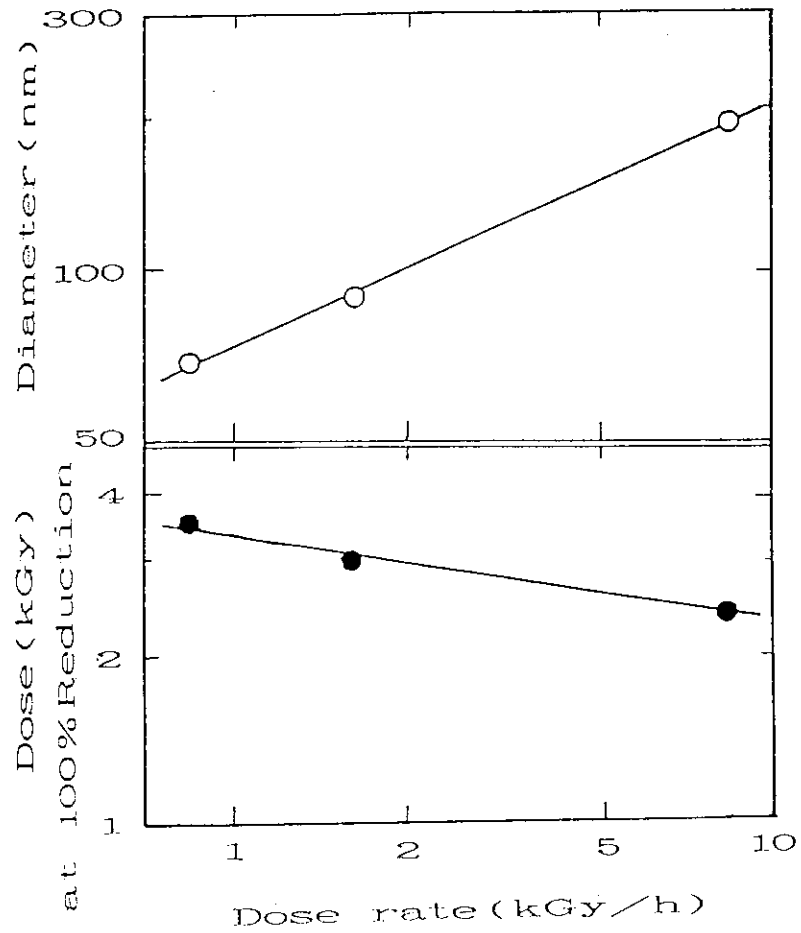


Figure 4. Doses at the 100% reduction of silver ion and the diameter of particles obtained as a function of dose rates, taken from Figure 2.

10. Charge Accumulation of Grafted Open-Cell Type Polyethylene Foam by Electron Beams

N. Kotani and Y. Nakase*

Positive or negative charging-up takes place within polymeric materials, when they are bombarded by electron beams. Charged electrets are widely used in industry such as microphone, electric recording devices, filters, and so on. The charging-up can be controlled by applying a bias through an external electrode. Though electron injection produce a negative charge in general, samples can be charged positively by electron irradiation by hole generations, when a negative bias is applied to the samples through a rear electrode attached to them.¹ It is difficult, however, to understand the mechanisms for charge build-up and decay, since the number of electrons emitted from a bombarded surface (secondary electrons) is influenced by several factors such as an incident beam current, energy distribution of elastically and inelastically backscattered electrons. In addition, the number of emitted electrons is larger than that of primarily injected electrons. We have studied the charging and decay behavior of open-cell type polyethylene foam (OPCELL) irradiated by electron beams for its new applications. In previous paper,² we have reported the charge accumulation of the open-cell type polyethylene foam by electron beams. In the present paper, we describe the results of the foam modified by grafting of a F-containing acrylate monomer.

The OPCELL has apparent density of 0.029 g/cm^3 , and contains cells of 0.5 mm of average radius. Grafting was carried using a preirradiation technique. The sample of foams were placed into a polyethylene film bag, which was sealed off after replacing air inside with nitrogen. The foams were irradiated with an electron beam from a Van de Graaff (1.5 MeV, 100 kGy at a dose rate of 5 kGy/pass). After irradiation, foams were transferred into a glass ampule, which was filled with an air-free methanol solution of trifluoroethyl methacrylate (10 wt%) containing Mohr's salt as an inhibitor of homopolymerization. The ampule was placed in a water bath at a desired temperature for 3 h. The graft percent was 8% at 60 °C and 16% at 70 °C. This grafted foam (45 x 45 x 5 mm³) were placed on an aluminum plate electrode and a sample surface was suppressed roughly to obtain a good contact with a rear electrode made of aluminum foil applying a 0 volt (earth) potential. Irradiation for charge-up was carried out in air with an electron beam (1.5 MeV, 10 kGy at a dose rate of 0.5 kGy/pass). The dosimetry was performed with a 125 μm thick cellulose triacetate (CTA) film dosimeter. The irradiated sample

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were stored in air without support, otherwise noticed. Surface voltage at the irradiated side of the grafted sample was measured in air without support by a SIMCO EVL-3R electrostatic locator. Charges retained in the foam were measured by a Faraday cup under an ambient condition.

Figure 1 shows the relationship between the applied voltage (V_a) on an aluminum plate electrode and the charge density (ρ) of the grafted sample. When a positive voltage was applied on the electrode, a negative charge on the sample was observed immediately after the irradiation of 10 kGy. Charge densities increase with the increase of applied voltage up to 2 kV for OPCELL of 5-mm thickness, and become almost constant over 2 kV. It is noticed that the higher the graft percent, the higher the charge density, particularly at lower applied voltage below 2 kV. Such an increase of was not observed in the case of ethyl methacrylate grafting.

Figure 2 shows the decay curve of the surface voltage for the grafted foam stored in air without support after the irradiation with applying voltage of ± 5 kV on the rear electrode. The positive surface voltage (V_s) was observed for the samples immediately after the irradiation with applying a negative voltage. The positive V_s decreased to 0 V within 0.5 h of storing time after irradiation, and changed its polarity into negative after leaving longer time in air without support. The polarity change suggests that the holes in the grafted sample irradiated with negative applied voltages are removed during the storage in air to show the negative surface voltages. It has been reported before that the retained charge on polypropylene film is very stable for long period when they are stored in contact with a relatively thick PMMA plate.³ We have also examined the stability of the charge on OPCELL stored in contact with aluminum plate after the irradiation of 10 kGy. The decay curves are shown in Figure 3. The retained charges on the sample were quite stable for a week at least and no polarity change was observed. The similar results were also observed in the case of the grafted OPCELL.

It is suggested that the grafted OPCELL can be used as an electret under a specific condition such as the storage in contact with an aluminum plate at a temperature lower than 70 °C.

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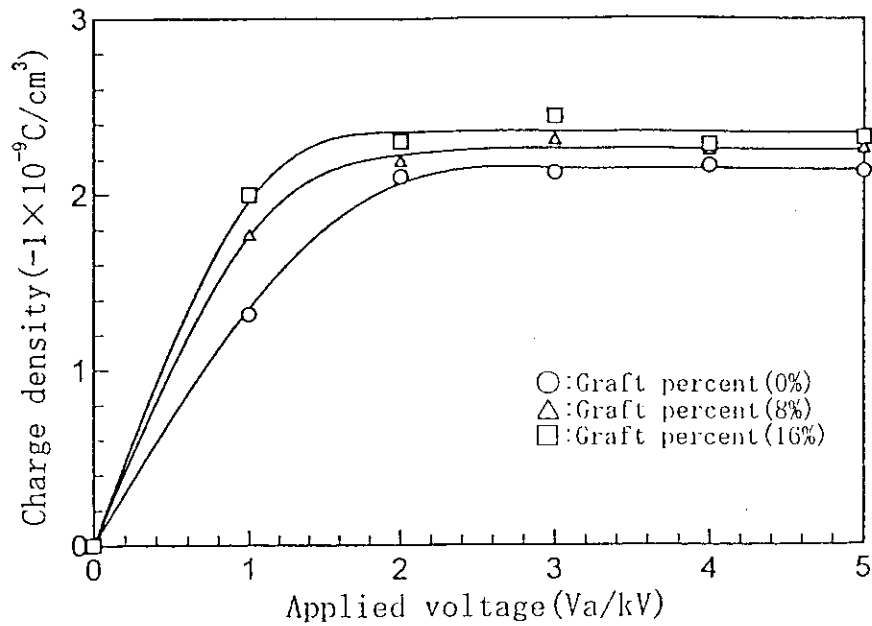


Figure 1. Relationship between applied voltage on an electrode and initial charge density for grafted OPCELL irradiated by electron beams (1.5 MeV, 0.5 kGy/pass x 20 pass) in air. Graft percents were indicated in the figure.

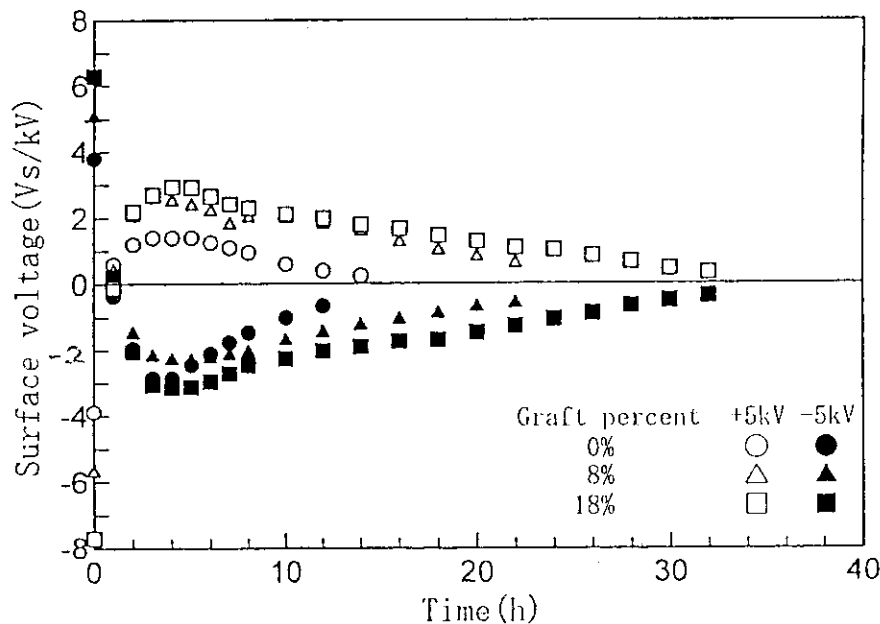


Figure 2. Decay curves of surface voltage for grafted OPCELL stored in air without support after irradiation by electron beam (1.5 MeV, 0.5 kGy/pass x 20 pass) with the applied voltage of 5 kV (open circles, triangles, and squares) and -5 kV (closed circles, triangles, and squares).

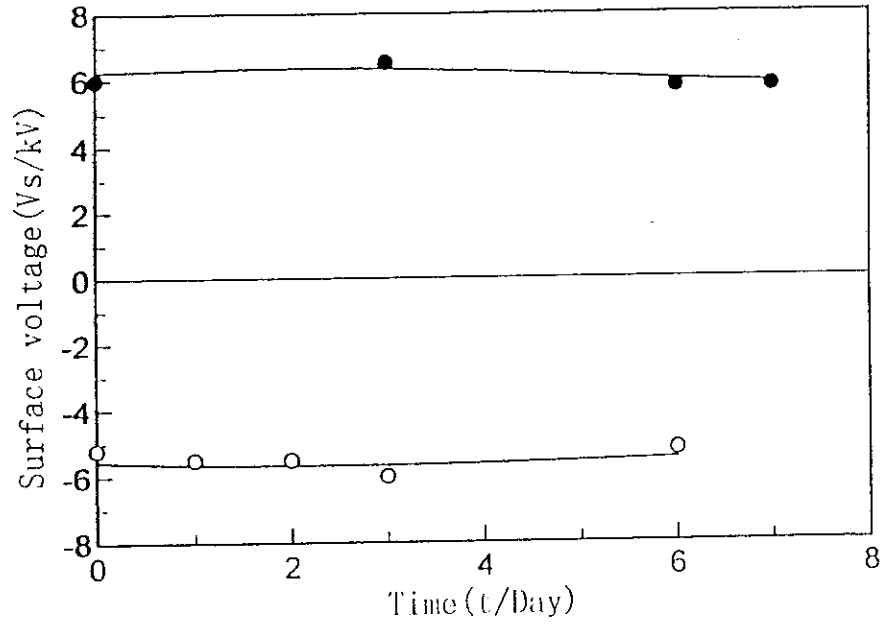


Figure 3. Decay curves of surface voltage for OPCELL stored on an aluminum plate after irradiation by electron beam (1.5 MeV, 0.5 kGy/pass x 20 pass) with the applied voltage of 5 kV (open circle) and -5 kV (closed circle).

11. Monte Carlo Calculation of the Behavior of 300 keV Electrons from Accelerators

T. Kijima, Y. Nakase, and K. Nakato

Monte Carlo methods to calculate dose distributions by electrons have been developed, and there are some codes released for public use, for example, ETRAN¹ for plane-parallel slab absorbers, ITS² based on the ETRAN model, i. e. TIGER for one-dimensional multilayers, CYTRAN for axisymmetric cylinders and ACCEPT for combinatorial geometry, and EGS4³ for arbitrary geometry. These codes mentioned are so large that we have to use a computer system with a large memory for running them. Murata et al. developed a simple Monte Carlo method based on a single scattering model to solve the problems in electron probe microanalysis and scanning electron microscopy.^{4,5} This model is easy to set up and flexible to physical and electromagnetic boundary conditions. We have developed a Monte Carlo code⁶ to calculate absorbed dose with the simple model based on the algorithm of Murata's group. The code can be adapted easily to an arbitrary number of target layers. In this paper, we describe an outline of the code and the results obtained for energy spectra and angular distributions of electrons at the sample surface and absorbed dose in a sample under irradiation by 300 keV electrons. The computed absorbed doses are compared with the experimental results obtained with a cellulose triacetate (CTA) film dosimeter.

Figure 1 shows distributions of incident directions calculated for 300 keV electrons at the surface of CTA layer exactly under the beam center and at distances of 10 and 20 cm from the beam center in the static irradiation. In order to clarify angular distributions of electrons incident on the CTA surface at the beam center (0 cm) and at distances of 5, 10, 20 cm from the beam center, the numbers of electrons as a function of angle of incidence are shown in Figure 2. Due to the multiple scattering of electrons in Ti and air layers, the angles of incidence of electrons at the surface are broadly distributed over 0° to 90°. The angular distribution becomes symmetrical with increasing distance from the beam center. The most probable and mean angles of incidence become closer with increasing distance, and are nearly equal at distances larger than about 10 cm from the beam center.

When samples travel back and forth on the conveyer, i. e. in dynamic irradiation, the angular distribution of incident electrons is given by the sum of distributions at different distances, and hence the incident direction of electrons becomes almost symmetric around the vertical axis as imagined from Figure 2. Figure 3 shows the angular distributions of incident electrons at surface of the CTA layer calculated by taking

backscattering into account. The broken curve shows the relative electron density per unit solid angle, and the solid curve shows the electron density per unit polar angle. The latter density was obtained by multiplying the former by $\sin \theta_0$, where θ_0 is the angle of incidence. The maximum of the electron density per unit solid angle is observed at the incident angle of 0° whereas the maximum of the electron density per unit polar angle is seen at an incident angle between 30 and 40° .

The validity of our calculation code was examined by comparison with the experiment on the absorbed dose in CTA. Figure 4 shows the calculated and experimental depth-dose distributions in the layer of a CTA film of $114 \mu\text{m}$ thickness, placed on each of the different backing materials (CTA, Al, Fe, Sn, and Pb). The calculated results show good agreement with experimental data in all the cases. For comparison, the calculated depth-dose distributions in the Ti window, the air layer and the backing materials are shown also in Figure 4.

Figure 5 shows calculated and experimental depth-dose distributions in one to seven layers of CTA film on the aluminum backing. The change in the surface absorbed dose caused by backscattered electrons decreases with increasing number of CTA layers. Thus, it has been confirmed that our simple code is useful for dose evaluation at the initial electron energy of 300 keV . Studies on the factors influencing depth-dose distributions by this code are in progress.

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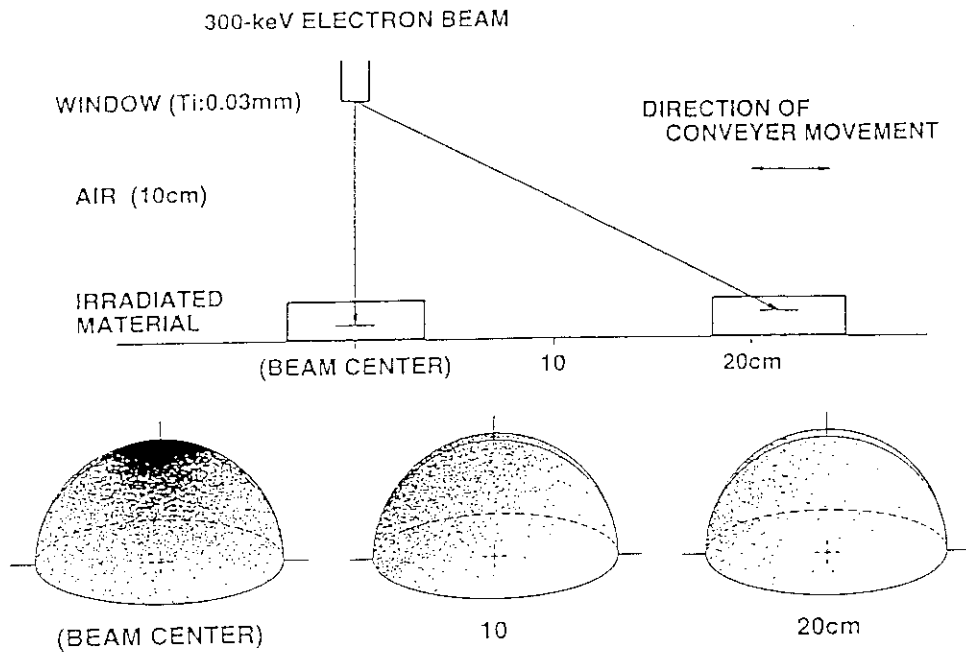


Figure 1. Calculated distributions of the incident directions of electrons at the surface of a semi-infinite CTA layer exactly under the beam center and 10 and 20 cm from the beam center.

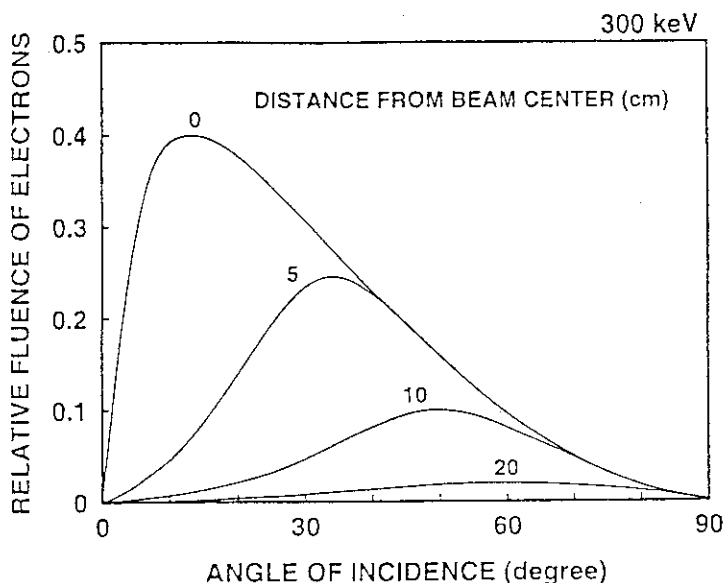


Figure 2. Calculated angular distributions of electrons incident on the surface of a semi-infinite CTA layer for static irradiation. The distance from the beam center shown are measured perpendicular to the beam-scanning direction. Before entering the CTA layer, the electrons of 300 keV passed through a 30 μm Ti window and a 10 cm air gap.

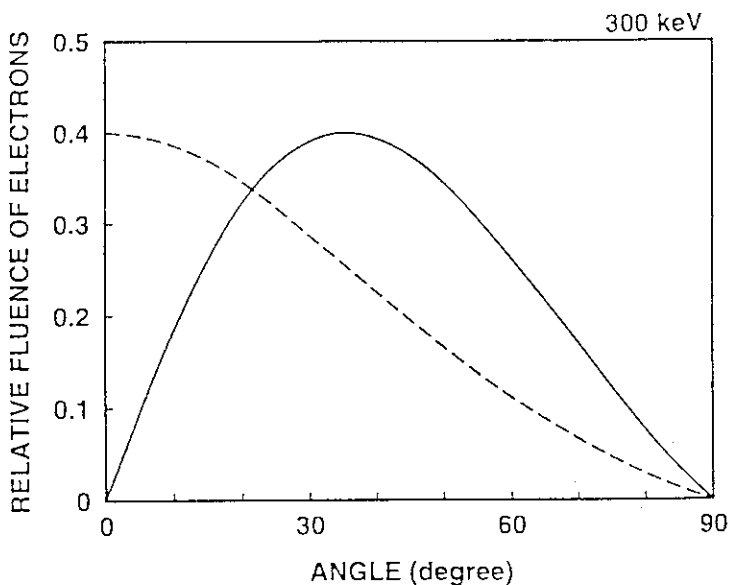


Figure 3. Calculated angular distributions of incident electrons at the surface of a semi-infinite CTA layer. The broken curve shows the relative electron density per unit solid angle, and the solid angle shows electron density per unit polar angle.

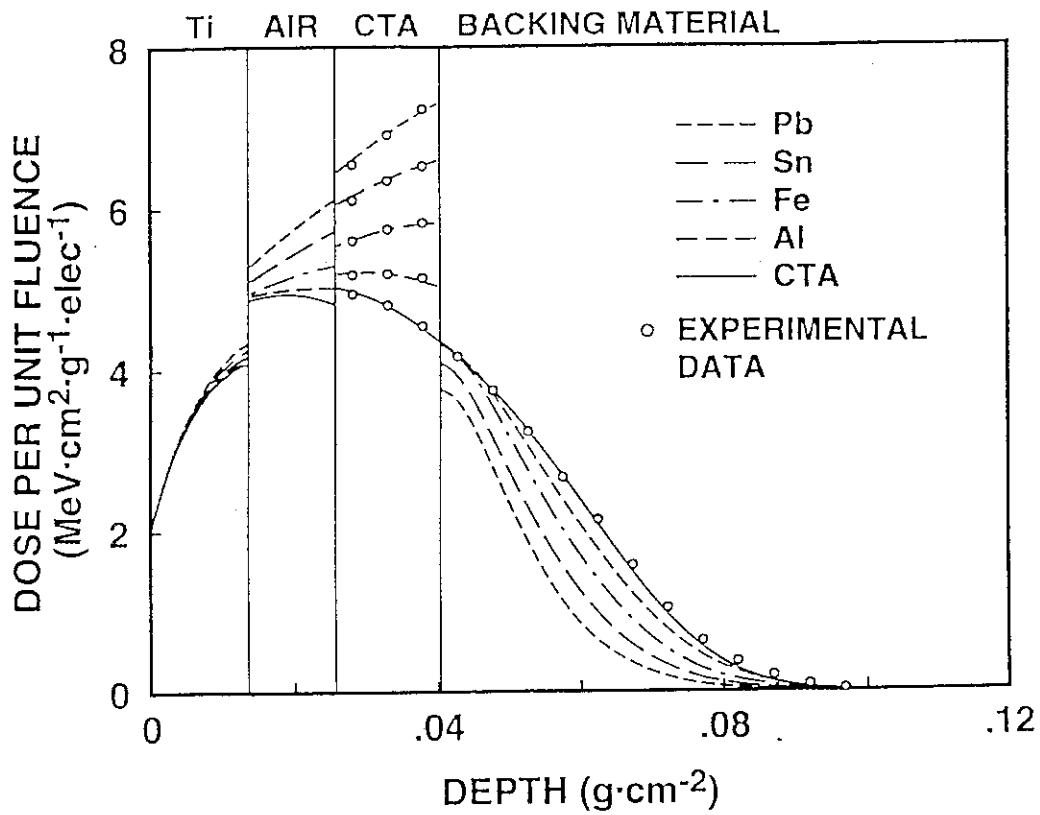


Figure 4. Comparison of calculated (lines) and experimental (circles) depth-dose distributions in the CTA film of $114\ \mu\text{m}$ thickness upon dynamic irradiation on various backing materials of effectively semi-infinite thickness.

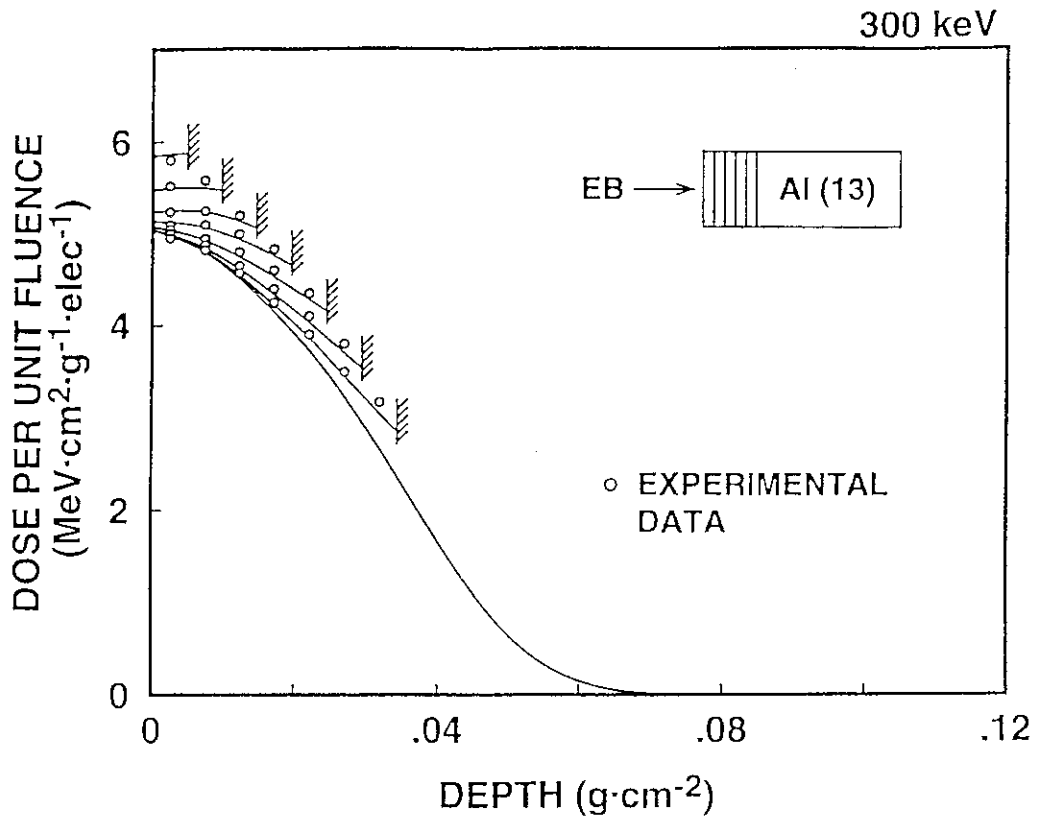


Figure 5. Comparison of calculated (lines) and experimental (circles) depth-dose distributions in one to seven layers of CTA films upon dynamic irradiation on an Al layer of effectively semi-infinite thickness.

12. Measurement of Absolute Photo-emission Intensity (N_2 $C^3\Pi_u \rightarrow B^3\Pi_g$) by 0.6MeV Electron Irradiation of N_2

K. Nakato, I. Fujita, J. Suzuki*, and T. Kijima*

Studies on photo-emission from gas under irradiation of high energy electron beam are important to understand the role of excited species in radiation chemical reactions. Information on the quenching and energy transfer has been obtained from relative intensities and lifetimes of emissions from gases of various pressures or mixing ratios, which were measured by stationary state spectroscopy¹⁻⁴ and by time-resolved spectroscopy, respectively. A few studies have been reported, however, on the measurement of absolute emission intensity,⁵ which gives information on the contribution of the excited states to radiation chemical reactions as compared with that of ionic species. In this study, measurement of absolute intensity of photo-emission was attempted. Nitrogen was chosen as a sample gas, because the emission of N_2 , $C^3\Pi_u \rightarrow B^3\Pi_g$ (0,0) band (337.1nm) is very intense, and therefore would be a standard for future calibration of intensities for other gases of radiation chemical interest, such as CO_2 , CO , NH_3 . Photo-emission study would also provide means of measurement of spatial distribution of excited species.

A schematic diagram of the apparatus is shown in Figure 1. An electron beam (0.6 MeV, 30 μA) entered the irradiation vessel through an aluminum foil (0.1 mm). The beam was approximately uniform at the distance of 12 cm from the aluminum window. A GaAsP photodiode detector (Hamamatsu G2119) was placed at the distance of 37.9 cm from the center of the vessel, and an aperture of 2 cm x 2 cm was placed in order to limit the view from the photodiode. The sensitivity of the photodiode was 0.07 A/W at 337 nm, and was calibrated by means of a UV-meter (Minolta UM-1). An interference filter with the center wavelength of 337 nm and the half width of 20 nm was used for detecting the relevant band emission. The photo-emission intensity was proportional to the beam current up to 50 μA .

Figure 2 shows an emission spectrum in the wavelength region of 300 - 450 nm obtained by electron beam irradiation of N_2 gas at 760 Torr. In this wavelength region, the most prominent band system was the second positive system (N_2 , $C^3\Pi_u \rightarrow B^3\Pi_g$), whereas the first negative system (N_2^+ , $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) were seen weakly. In the present study, intensity of the (0,0) band of the $C \rightarrow B$ system at 337.1 nm was measured as a function of pressure.

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Figure 3 shows the emission intensity measured with the photodiode as a function of the pressure of nitrogen gas. Leveling-off of the intensity is seen as the pressure increases. In our previous papers,¹⁻⁴ similar leveling-off has been reported for CO₂, NH₃, and CO, and the self-quenching mechanism has been proposed. The present data can also be explained by a similar self-quenching mechanism.

Figure 4 shows the reciprocal of the emission intensity as a function of the reciprocal of the pressure. The linear relationship shown in the figure may indicate that the simple mechanism similar to those described in the previous papers can explain the relationship.

At the limit of low pressure, the intensity (I) is proportional to the pressure (P) as follows:

$$I/P = 3.5 \times 10^{-9} \text{ W/atm} \quad (1)$$

Here we assume that the light is emitted to all the direction uniformly. Considering the solid angle from the light emitting source viewing the detector, the emission intensity for all the direction becomes $6.3 \times 10^{-5} \text{ W/atm}$. The volume of light source from which the light reaches the detector was roughly estimated to be 115 cm^3 . The beam current density was measured to be $2.3 \times 10^{-7} \text{ A/cm}^2$. From these values, the intensity per unit volume per unit pressure per unit current density is calculated as

$$2.4 \text{ W}/(\text{atm cm}^3 \text{ A/cm}^2) \quad (2)$$

Though the emission intensity without quenching is given by the above calculation, the actual intensity was not proportional to the gas pressure. The intensity per unit volume per unit current density (absolute intensity) at 1 atm was

$$0.27 \text{ W}/(\text{cm}^3 \text{ A/cm}^2) \quad (3)$$

The values in this scale are given on the right hand axis in Figure 3.

In order to estimate the absorbed energy in the present apparatus, a cellulose triacetate (CTA) film was put at the center of the irradiation vessel filled with nitrogen gas at 1 atm, and was irradiated with an electron beam of $30 \mu\text{A}$. From the absorbance of the CTA film, the absorbed energy was obtained to be 247 Gy/sec . The energy which would be absorbed by nitrogen gas per unit pressure per unit volume per unit current density was roughly estimated to be

$$1.3 \times 10^3 \text{ W}/(\text{atm cm}^3 \text{ A/cm}^2) \quad (4)$$

By comparing (4) with (2), it turned out that about 0.2 % of energy among the absorbed energy was emitted as photons. The total emission intensity including the other bands (such as (0,1) band) of the C \rightarrow B band system was estimated to be $4.8 \text{ W}/(\text{atm cm}^3 \text{ A/cm}^2)$. Considering that the energy of the C³Π state is 11.05 eV, the energy used in the excitation to the C³Π state is about 1.1 % of the absorbed energy. This value is comparable to literature value, 0.6 eV per absorbed energy of 100 eV.⁵

It is expected that the absolute intensity in the present research for N₂ can be used as a standard for the emission intensities of other gases, and it is useful for investigating the role of the excited species in gas phase reactions by electron beam irradiation.

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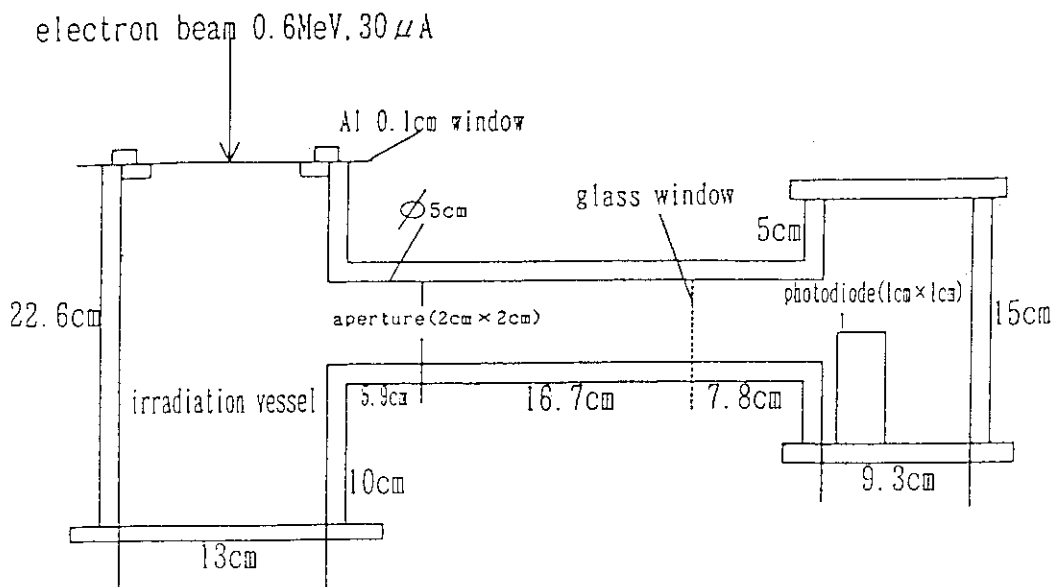


Figure 1. Schematic diagram of the apparatus.

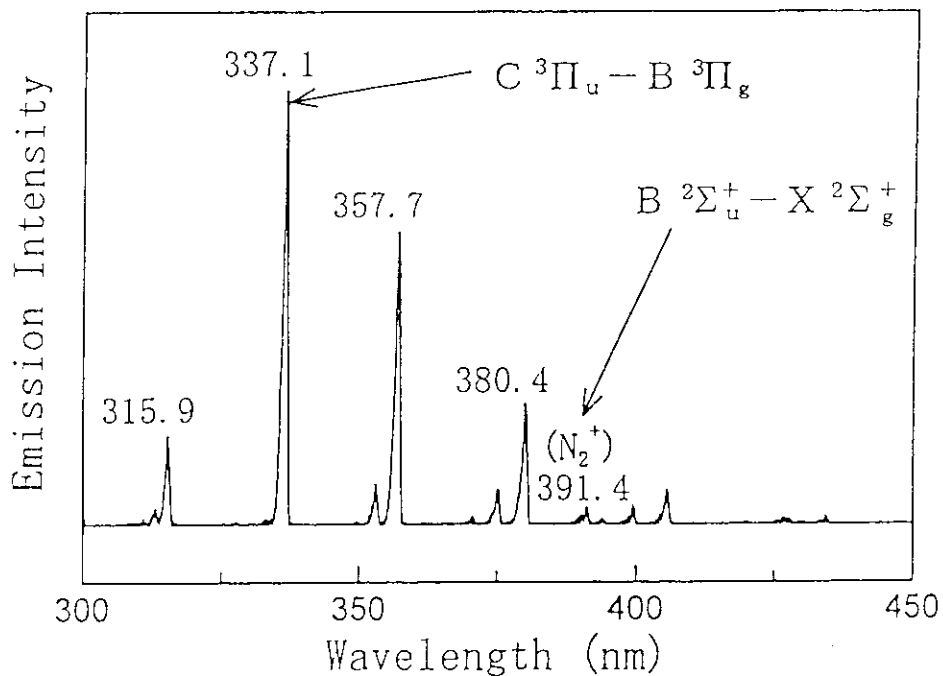


Figure 2. Emission spectrum obtained by electron beam irradiation of N_2 . Pressure of N_2 : 760 Torr (760 Torr = 1 atm).

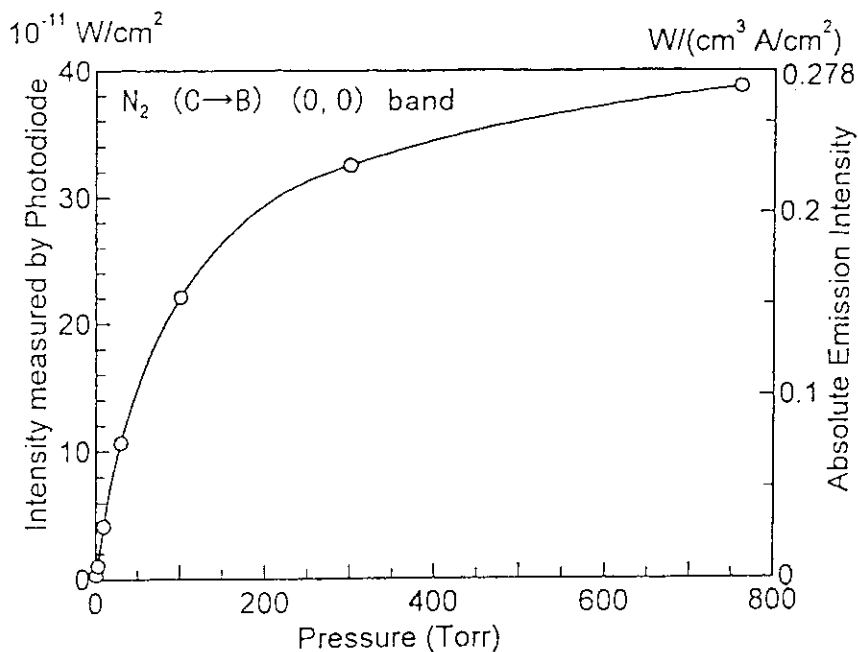


Figure 3. Emission intensity at 337 nm wavelength as a function of pressure of N_2 . Abscissa axis: Pressure on N_2 . Left hand axis: Emission intensity measured by photodiode. Right hand axis: Considering the solid angle from light emitting source viewing photodiode, absolute intensity per unit volume per unit current density.

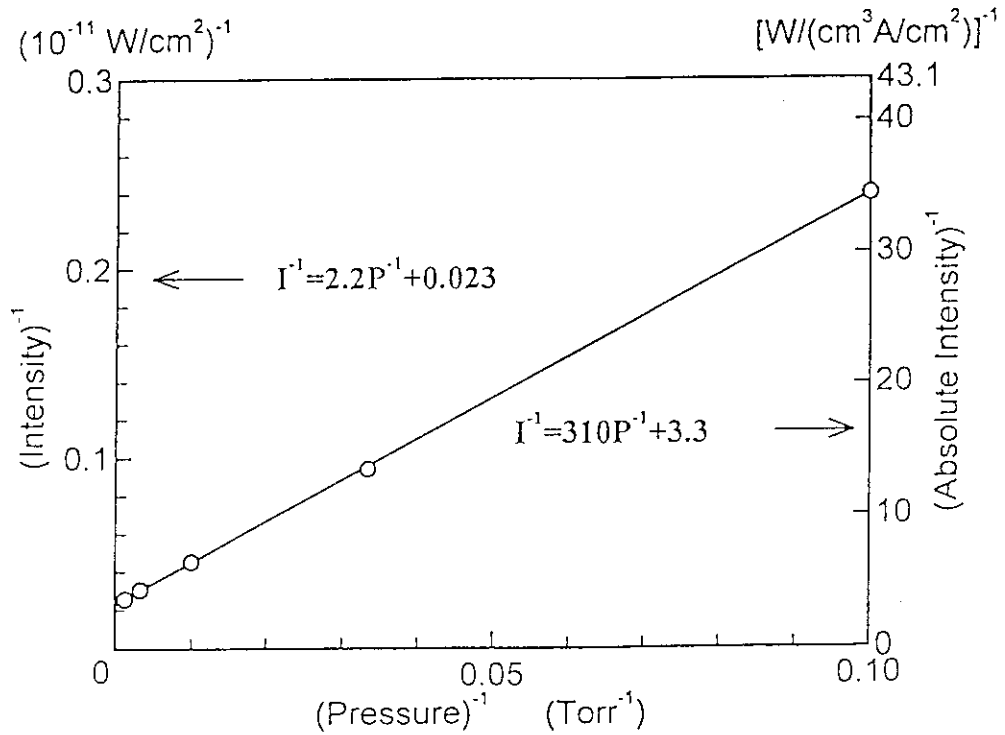


Figure 4. Reciprocal intensity vs. reciprocal pressure. Abscissa axis: Reciprocal pressure of N₂. Left hand axis: Reciprocal emission intensity measured by photodiode. Right hand axis: Considering the solid angle from light emitting source viewing photodiode, reciprocal intensity per unit volume per unit current density.

13. Operation and Maintenance of Irradiation Facilities

K.Nakato

The irradiation facilities in our laboratory were operated for researches performed in the laboratory and for those in cooperation with universities or industries. The facilities were also operated for irradiation service to industrial companies and universities. By the routine maintenance works, operation of the Van de Graff accelerator (No.1 accelerator), the accelerator of a rectified transformer type (No.2 accelerator), and the cobalt-60 (^{60}Co) irradiation equipment were carried out without any major trouble throughout the current year. The annual operation of the facilities is listed in Table 1.

Table 1 Utilization and operation of the facilities during fiscal 1995

	Van de Graff accelerator (No.1 Accelerator)	Accelerator of rectified transformer type (No.2 Accelerator)	^{60}Co irradiation equipment
Operation time	(hour:min) 121:48	(hour:min) 22:12	(hour:min) 1080:52
Number of experiments			
JAERI	321	25	214
Universities	4	1	0
Industries	3	4	9
Research organizations	0	0	0
Total	328	30	223

III. List of Publications

1. Published Papers

"Photoinduced 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.

"Micropatterning of Organosilane Thin Layers on Glass Surface by Laser Irradiation for Patterned Immobilization of Polyaminopolymers"

N. Ichinose, *Macromol. Reports*, **A33 (suppl.)**, 33 (1996).

"A Novel KrF Laser-Induced Graft Reaction of Poly(acrylic acid) onto Tetrafluoroethylene-Perfluoroalkyl Vinyl Ether Copolymer Film"

A. Okada, N. Ichinose, and S. Kawanishi, *Polymer*, **37**, 2281 (1996).

"Excimer Laser-Induced Surface Modification of Fluoropolymers with Liquid Water"

N. Ichinose, and S. Kawanishi, *Macromolecules*, **29**, 4155 (1996).

"An Efficient Enantiomeric Enrichment of Tartaric Acid Using a Highly Intense Circularly Polarized Light"

Y. Shimizu and S. Kawanishi, *Chem. Commun.*, **1996**, 819.

"Laser-Induced Enantiodifferentiating Reaction of Tartaric Acid Using High-Intensity Circularly Polarized Light"

Y. Shimizu and S. Kawanishi, *Chem. Commun.*, **1996**, 1333.

"A New and Direct Synthesis of Lactic Acid from Acrylic Acid Using an Excimer Laser with High Intensity"

Y. Shimizu, and S. Kawanishi, *Chem. Lett.*, **1996**, 935.

"U.v.-Irradiation of Thin Films of Polystyrene Derivatives: Formation of Carboxylic Group and Crossing from 4-Trymethylsilylmethyl Substituent"

T. Tamai, I. Hashida, N. Ichinose, S. Kawanishi, H. Inoue, and K. Mizuno, *Polymer*, **37**, 5525 (1996).

"Laser-Induced Chemical Modification of the Surface of Fluoropolymers"

S. Kawanishi and N. Ichinose, *Rev. Laser Eng.*, **24**, 780 (1996).

"Possibilities of Photochemical Processes Using Excimer Lasers (I):

Organic Synthesis with Laser"

N. Suzuki and Y. Shimizu, *Hoshasen Kagaku (Radiat. Sci. Jpn)*, **39**, 291 (1996).

"Possibilities of Photochemical Processes Using Excimer Lasers (I):

Surface Modification of Polymeric Materials"

N. Suzuki and S. Kawanishi, *Hoshasen Kagaku (Radiat. Sci. Jpn)*, **39**, 337 (1996).

"Monte Carlo Calculations on the Passage of Electron through Thin Films Irradiated by 300 keV Electrons"

T. Kijima, M. Kotera, H. Suga and Y. Nakase, *IEICE Trans. Electron.*, **E78-C**, 557 (1995).

"Monte Carlo Calculations of the Behavior of 300 keV Electrons from Accelerators"

T. Kijima and Y. Nakase, *Radiat. Meas.*, **26**, 159 (1996).

"Studies on the Dose Evaluation of Low-Energy Electrons"

T. Kijima and Y. Nakase, *JAERI-Research*, in press.

2. Oral Presentations

"Surface Photoreaction of Fluoropolymers with Aliphatic Carboxylic Acids"

N. Ichinose and S. Kawanishi, *44th Annual Meeting of Polymer Society of Japan*, (Yokohama).

"Photoreaction of Fluoropolymer Surface with Aliphatic Amines"

M. Maruo, N. Ichinose, and S. Kawanishi, *44th Annual Meeting of Polymer Society of Japan*, (Yokohama).

"Laser-Induced Formation of Carboxylic Group at the Surface of Poly(4-trimethylsilyl-methylstyrene) Film"

N. Ichinose, S. Kawanishi, T. Tamai, I. Hashida, K. Mizuno, H. Inoue, *44th Symposium on Polymer Science of Japan*, (Suita).

"Photochemical Alkylation of Fluoropolymer Surface"

N. Ichinose and S. Kawanishi, *Symposium on Photochemistry 1995*, (Fukuoka).

"Laser-Induced Photoreaction of Poly(4-trimethylsilylmethylstyrene) Film Giving Wettable Surface "

T. Tamai, N. Ichinose, S. Kawanishi, I. Hashida, K. Mizuno, H. Inoue, *Symposium on Photochemistry 1995*, (Fukuoka).

"Formation of Carboxylic Group and Cross-Linking upon Laser Irradiation of Poly(4-trimethylsilylmethylstyrene)"

T. Tamai, N. Ichinose, S. Kawanishi, I. Hashida, K. Mizuno, H. Inoue, *6th Symposium on Organo Silicon Material Chemistry*, (Fuji-yoshida).

"Photooxygenation of Aryldisilanes via Photoinduced Electron Transfer"

T. Tamai, K. Mizuno, I. Hashida, H. Inoue, N. Ichinose, S. Kawanishi, *1995 International Chemical Congress of Pacific Basin Societies*, (Honolulu).

"Photochemical Reactivity of Fluoropolymer Surface"

N. Ichinose and S. Kawanishi, *Workshop on Polymer Surface 1995-1*, (Tokyo).

"Photochemical Reactions of Fluoropolymers and Application to Surface Modification"

N. Ichinose, *Workshop on Polymer Surface 1995-2*, (Hamamatsu).

"Photochemical Sulfonation of Fluoropolymer Surface"

N. Ichinose and S. Kawanishi, *70th Annual Meeting of the Chemical Society of Japan*, (Tokyo).

"Depth-Dose Distributions at an Absorber Irradiated by Low-Energy Electrons"

T. Kijima, H. Suga and Y. Nakase, *1995 Autumn Meeting of the Institute of Electronics, Information and Communication Engineers*, (Tokyo).

3. Patent Applications

"Process for Hydrophilizing a Porous Material Made of Fluorine Resin"

M. Nishi, S. Kawanishi, S. Sugimoto, T. Tanaka, and M. Sano, *US Patent*, application, 08/435,975.

"Method of Imparting Organic Functional Groups to the Surface of Fluoropolymers by Irradiation of Carboxylic Acids with Ultraviolet Light"

N. Ichinose, S. Kawanishi, S. Sugimoto, and A. Okada,
US Patent, application, 08/550,812.

"Method for Introduction of Organic Functional Groups on Fluoropolymer Surface by UV Irradiation with Carboxylic Acids"

N. Ichinose, S. Kawanishi, A. Okada, and S. Sugimoto,
Jpn. Kokai Tokkyo Koho, 08-27293 (940715).

IV. List of Cooperative and Joint Research Programs

"Effect of Laser Beam Irradiation on Polymer Materials (III)"

Faculty of Engineering, Osaka University

"Infrared Multiphoton Decomposition of Fluoroorganic Compounds (III)"

Material Science and Technology, Kyoto Institute of Technology

"Effects of Irradiation on Oral-Related Materials (II)"

Department of Preventive Dentistry, Ohu University

"Surface Modification of Fluoropolymers by Laser Irradiation (II)"

Kurabo Industries, Ltd.

"Improvement of Vital Affinity on Fluoropolymers (II)"

Gunze Ltd.

"Distribution of Trapped Electrons in Organic Thin Layer"

Osaka Institute of Technology

"Studies on the Electron Irradiation-Induced Damage of Thin Films"

Faculty of Engineering, Himeji Institute of Technology

"Studies on the Biomaterial with Fine Powders Modified by Irradiation"

Faculty of Science and Technology, Kinki University

"Studies on the Electron Charging of Thin Insulators"

Sanwa Kakou Co. Ltd.

"Studies on the Radiation-Induced Curing of Fine Particles"

Kaginushi Kogyo Co. Ltd.

V. List of Personnel

Dr. Masafumi Nakano, Director

Prof. Hiroshi Masuhara, Invited Researcher from Osaka University

OFFICE OF ADMINISTRATION

Mr. Teruo Yagi, Administrative Manager

Ms. Junko Kobayashi

Ms. Atsuko Hayashi

Ms. Harumi Ogata [1]

STUDY ON LASER-INDUCED ORGANIC CHEMICAL REACTIONS

Dr. Shunichi Kawanishi, Group Leader, Principal Scientist

Mr. Yuichi Shimizu, Senior Scientist

Dr. Masanobu Nishii, Research Scientist

Dr. Nobuyuki Ichinose, Research Scientist

Mr. Shun'ichi Sugimoto [2]

Mr. Tomohiro Nagase [3]

Mr. Tadaharu Tanaka [3]

Mr. Atsushi Okada [4]

Mr. Takashi Ikawa [5]

Mr. Koji Hatanaka [6]

Mr. Akihiro Isomura [7]

Mr. Masaharu Maruo [8]

Mr. Shuhei Sasaki [9]

STUDY ON BASIC RADIATION TECHNOLOGY FOR FUNCTIONAL MATERIALS

Dr. Yoshiaki Nakase, Group Leader, Senior Scientist

Mr. Nobuyoshi Kotani [10]

Mr. Tetsu Kaginushi [11]

Ms. Liu Li [12]

Mr. Atsushi Nakamune [13]

Mr. Kazushi Ushiroda [13]

OPERATION AND MAINTENANCE OF IRRADIATION FACILITIES

Mr. Kiyori Nakato, General Manager

Mr. Toshiyuki Kijima [14]

- [1] Office Assistant
- [2] Cooperative Staff from Radiation Application Development Association
- [3] Research Collaborator from Kurabo Industries, Ltd.
- [4] Research Collaborator from Gunze Industries, Ltd.
- [5] Fellow of Advanced Science from Kyoto Institute of Technology
- [6] Fellow of Advanced Science from Osaka University
- [7] Student Research Assistant from Kyoto Institute of Technology
- [8] Student Research Assistant from Osaka University
- [9] Student Research Assistant from Osaka Electro-Communication University
- [10] Research Collaborator from Sanwa Kako, Ltd.
- [11] Research Collaborator from Kaginushi Kogyo, Ltd.
- [12] Fellow of Advanced Science from Himeji Institute of Technology
- [13] Student Research Assistant from Kinki University
- [14] Technical and Research Assistant