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OSAKA LABORATORY FOR RADIATION CHEMISTRY  
JAPAN ATOMIC ENERGY RESEARCH INSTITUTE  
(No. 22)

April 1, 1988 - March 31, 1989

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Osaka Laboratory for Radiation Chemistry

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. 22)

April 1, 1988 - March 31, 1989

Osaka Laboratory for Radiation Chemistry  
Takasaki Radiation Chemistry Research Establishment  
Japan Atomic Energy Research Institute  
Mii-minami-machi, Neyagawa-shi, Osaka-fu

(Received February 27, 1991)

This report describes research activities of Osaka Laboratory for Radiation Chemistry, JAERI during one year period from April 1, 1988 through March 31, 1989. The latest report, for 1987, is JAERI-M 90-054.

Detailed descriptions of the activities are presented in the following subjects : (i) studies on laser-induced organic chemical reactions and (ii) studies on radiation chemistry of high polymers and radiation dosimetry.

Previous reports in this series are :

Annual report of the Japanese Association for Radiation Research on Polymers (JARRP), Vol. 1 (1958/1959) through Vol. 8 (1966).  
Fundamental Studies in the Osaka Laboratory for Radiation Chemistry (Annual Report) No. 1, JAERI 5018 (1967); No. 2, JAERI 5022(1968); No. 3, JAERI 5026 (1969); No. 4, JAERI 5027 (1970), No. 5, JAERI 5028 (1971); No. 6, JAERI 5029 (1972); No. 7, JAERI 5029; No. 7, JAERI 5030 (1973).  
Annual Report of the Osaka Laboratory for Radiation Chemistry, No. 8, JAERI-M 6260 (1974); No. 9, JAERI-M 6702 (1975); No. 10, JAERI-M 7355 (1976); No. 11, JAERI-M 7949 (1977); No. 12, JAERI-M 8569 (1978); No. 13, JAERI-M 9214 (1979); No. 14, JAERI-M 9856 (1980); No. 15, JAERI-M 82-192 (1981); No. 16, JAERI-M 83-199 (1982); No. 17, JAERI-M 84-239 (1983);

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大阪支所

(1991年2月27日受理)

本報告書は、大阪支所において昭和63年度に行われた研究活動を述べたものである。主な研究題目は、レーザー有機化学反応の研究、電子線照射による重合反応の研究、ポリマーの改質、光化学反応による有機化合物の合成に関する研究および線量測定の基礎研究等である。

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(1970); No. 5, JAERI 5028 (1971); No. 6, JAERI 5029 (1972); No. 7, JAERI  
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-M 82-192 (1981); No. 16, JAERI-M 83-199 (1982); No. 17, JAERI-M  
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## I. INTRODUCTION

Osaka Laboratory was founded in 1958 as a laboratory of the Japanese Association for Radiation Research on Polymers (JARRP), which was organized and sponsored by some fifty companies interested in radiation chemistry of polymers. The JARRP was merged with Japan Atomic Energy Research Institute (JAERI) on June 1, 1967, and the laboratory has been operated as Osaka Laboratory for Radiation Chemistry, Takasaki Radiation Chemistry Establishment, JAERI. The research activities of Osaka Laboratory have been oriented towards the fundamental research on applied radiation chemistry, and have been carried out under two main subjects.

One is the study on laser-induced organic chemical reactions which was initiated this year. Fundamental studies are in progress using the intense ultraviolet light from an excimer laser source to obtain valuable fine chemicals from simple compounds such as methane and methanol. Creative studies are also initiated to obtain chemically active functional surfaces by modifying polymer surface by laser beam irradiation.

It was found that methyl formate was produced with high quantum yield and high selectivity from methyl alcohol containing small amounts of hydrogen peroxide and oxygen by laser beam irradiation.

Irradiation of laser beam and irradiation of electron beam on propylene and ethylene-tetrafluoroethylene copolymer resulted in carbonization and unsaturated bond formation, and the mechanisms of the degradation of the polymer surface were discussed on the basis of the energy absorption of laser beam of different wavelength and electron beam.

The other main subject of research is radiation chemistry of high polymers, stress having been laid on radiation modification of surface layer of the polymer, some of which have been carried out under collaboration with industrial companies in Osaka-Kyoto area and vicinity.

The hydrophilic properties of acrylic acid grafted polyethylene foam material prepared in the previous year were investigated and it was found that the foam has excellent hydrophilic properties almost equivalent to those of PVA foam.

In order to develop thin and uniform resist coating technique used in semiconductor device production technology, polymerization of thin multilayers of calcium salt of long aliphatic carboxylic acids prepared by Langmuir-Blodgett technique has been carried out, and it was found that uniform polymer LB films as thin as 50nm were obtained.

Krypton ion beam generated by a low energy ion generator was irradiated on polymer films such as polyester, or cellulose triacetate, and optical density change induced by the ion bombardment was investigated. It was found that PET film is more sensitive than the other.

Intensities of optical emissions from excited states of NH fragment from helium-ammonia gas mixture by electron beam irradiation has been measured and the results are discussed in relation to the energy transfer between the species in the system.

January 22nd, 1991

Dr. Motoyoshi Hatada, Director  
Osaka Laboratory for Radiation Chemistry  
Japan Atomic Energy Research Institute



## II. RECENT RESEARCH ACTIVITIES

## 1. Photoinduced Synthesis of Formic Acid and Methyl Formate from Methanol Containing Hydrogen Peroxide

The direct transformation of methanol into more valuable compounds is very important from a point of view of effective utilization of organic resources. As reported already,<sup>1, 2)</sup> we found that ethylene glycol is selectively synthesized by UV irradiation of nitrogen-saturated methanol containing hydrogen peroxide. The direct synthesis of methyl formate from methanol has been investigated using supported copper or metal carbide such as WC catalysts,<sup>3, 4)</sup> but the lifetime of the catalysts is very short and reaction temperature is high. Also, formic acid is produced by two steps process, that is-the hydrolysis of methyl formate. We report here a method for the photoinduced direct and selective synthesis of formic acid and methyl formate from methanol containing H<sub>2</sub>O<sub>2</sub> with O<sub>2</sub>.

The reaction was carried out in an inner light source typed Pyrex glass reaction vessel (500 ml). Methanol (225 ml; 5.6 mol) was placed in a vessel and bubbled with O<sub>2</sub>. The O<sub>2</sub>-saturated methanol was stirred magnetically (500 rpm), and irradiated with a 120 W low pressure mercury lamp (Eikosya EL-J-120, mainly 253.7 nm). Aqueous 30 % hydrogen peroxide (1~8 ml h<sup>-1</sup>, 0.01~0.10 mol h<sup>-1</sup>) was added to methanol with a micro feeder at the same time with irradiation. The methanol solutions were kept at 25°C. The quantity of light (3.38 X 10<sup>18</sup> photons s<sup>-1</sup>) from the low-pressure mercury lamp was determined using a ferrioxalate actinometer (0.006 mol dm<sup>-3</sup>)<sup>5)</sup> under the same conditions as the reaction. Products were analyzed by gas chromatographs (Shimadzu GC-7A: Porapak Q column: Porapak N column, and GC-3BT: Molecular sieve 5A column). Formic acid was analyzed by ion chromatography (Yokogawa IC-100: SAX1-205 column).

When the O<sub>2</sub>-saturated methanol was irradiated with UV light in the presence of H<sub>2</sub>O<sub>2</sub>, formic acid methyl formate were produced as major products and ethylene glycol, ethanol

and acetaldehyde were produced as minor products. Figure 1 shows the concentrations of main products as a function of irradiation time. The concentrations of formic acid and methyl formate increased with irradiation time. The concentrations of formic acid, methyl formate and ethylene glycol were 192.2, 98.2 and 1.4 mmol, respectively, on irradiation for 7 h.

Figure 2 shows the effect of  $O_2$  flow rate on formic acid and methyl formate formations. The concentrations of formic acid and methyl formate increased steeply with  $O_2$  flow rate up to  $20 \text{ ml min}^{-1}$  and gradually above it. This result indicates that the  $O_2$  flow rate above  $20 \text{ ml min}^{-1}$  is desirable for effective formation of formic acid and methyl formate.

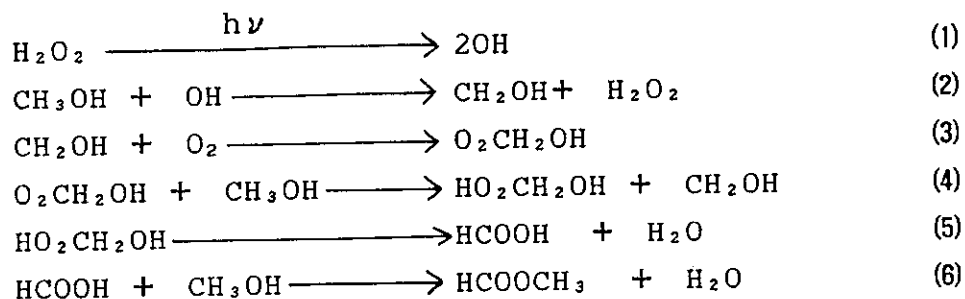
Figure 3 shows the effect of  $H_2O_2$  feeding rate on formic acid and methyl formate formations. The concentrations of formic acid and methyl formate increased with  $H_2O_2$  feeding rate and became the maximum at  $5 \text{ ml h}^{-1}$  of  $H_2O_2$  feeding rate.

Table 1 shows the effect of  $H_2O_2$  feeding rate on the quantum yields  $\Phi$  of formic acid and methyl formate formations, and the combined selectivity. The quantum yields of formic acid and methyl formate formations increased with  $H_2O_2$  feeding rate and become the maximum ( $\Phi = 1.36$  and  $0.69$  for formic acid and methyl formate, respectively) at  $5 \text{ ml h}^{-1}$  of  $H_2O_2$  feeding rate. The combined selectivity of formic acid and methyl formate formations was 99.1 % at  $100 \text{ ml min}^{-1}$  of  $O_2$  flow rate and  $5 \text{ ml h}^{-1}$  of  $H_2O_2$  feeding rate. These results indicate that formic acid and methyl formate are directly and selectively synthesized by UV irradiation of the  $O_2$ -saturated methanol containing  $H_2O_2$ .

It is well known that  $H_2O_2$  is easily decomposed by UV light irradiation to form hydroxyl radical.<sup>6)</sup> The effect of thiocyanate ion, which is an efficient scavenger of hydroxyl radical,<sup>7)</sup> on formic acid and methyl formate formations has been examined, in order to elucidate an initi-

ating species of formic acid and methyl formation. The formations of formic acid and methyl formate were almost perfectly suppressed by the addition of 0.02 mmol of potassium thiocyanate. This indicates that hydroxyl radical is an initiating species of formic acid and methyl formate formations. The sum of quantum yields of formic acid ( $\Phi = 1.36$ ) and methyl formate ( $\Phi = 0.69$ ) formations was more than 2. This suggests that a chain reaction occurs in this system. It is known that in the presence of  $O_2$ , the hydroxymethyl radical, which is formed by the abstraction of  $\alpha$ -hydrogen atom of methanol,<sup>8)</sup> reacts rapidly with  $O_2$  to form hydroxymethyldioxy radical.<sup>9)</sup> It is also known that the hydroxymethyldioxy radical abstracts hydrogen atom from methanol to form hydroperoxy-hydroxy-methane which is decomposed photochemically to formic acid and water.<sup>10)</sup> The formation of formaldehyde was hardly observed. When formic acid was added to methanol, the formation of methyl formate was observed even without irradiation.

It can be presumed from these facts that formic acid is synthesized through the reactions (1)-(5) and methyl formate through the reactions (5) and (6).



Scheme 1

It should be noted as a new method for direct and selective synthesis of formic acid and methyl formate by UV irradiation of methanol containing  $H_2O_2$  with  $O_2$ .

(Y. Shimizu, S. Sugimoto, S. Kawanishi, and N. Suzuki)

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Table 1 Effect of feeding rate of hydrogen peroxide on the quantum yields  $\phi$  of formic acid and methyl formate formations and the combined selectivity.<sup>a</sup>

H <sub>2</sub> O <sub>2</sub> feeding rate <sup>b</sup> ml h <sup>-1</sup>	$\phi$ <sup>c</sup>		combined selectivity <sup>c</sup> %
	HCOOH	HCOOCH <sub>3</sub>	
0	0.32	0.06	95.9
1	0.91	0.47	98.7
2	1.00	0.58	98.8
4		0.66	
5	1.36	0.69	99.1
8	1.16	0.45	98.9

<sup>a</sup> Low pressure mercury lamp (120 W), CH<sub>3</sub>OH: 225 ml, Temperature: 25°C, O<sub>2</sub> flow rate: 100 ml min<sup>-1</sup>.

<sup>b</sup> Aqueous 30 % H<sub>2</sub>O<sub>2</sub>.

<sup>c</sup> Irradiation time: 7 h.

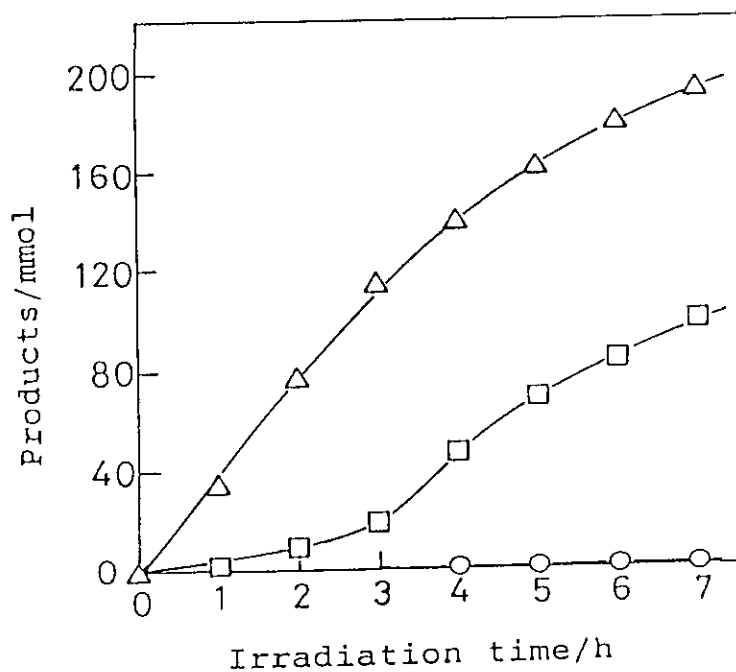


Fig. 1 Concentration of main organic products as a function of irradiation time.  $\triangle$ : Formic acid,  $\square$ : Methyl formate,  $\circ$ : Ethylene glycol.  $\text{H}_2\text{O}_2$  feeding rate:  $5\text{ ml h}^{-1}$ ,  $\text{O}_2$  flow rate:  $100\text{ ml min}^{-1}$ .

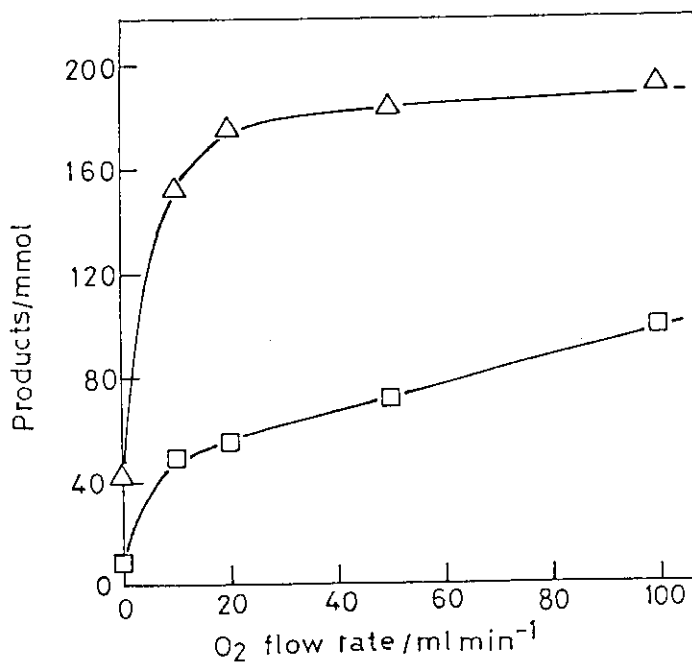


Fig. 2 Effect of  $\text{O}_2$  flow rate on formic acid and methyl formate formations.  $\triangle$ : Formic acid,  $\square$ : Methyl formate.  $\text{CH}_3\text{OH}$ :  $225\text{ ml}$ ,  $\text{H}_2\text{O}_2$  feeding rate:  $5\text{ ml h}^{-1}$ , Irradiation time:  $7\text{ h}$ , Irradiation temp.  $25^\circ\text{C}$ .

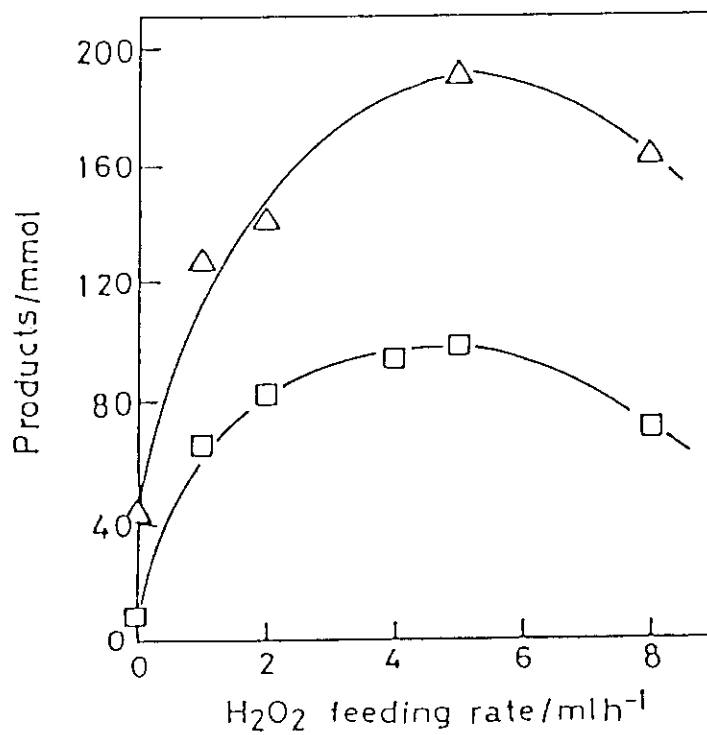


Fig. 3 Effect of H<sub>2</sub>O<sub>2</sub> feeding rate on formic acid and methyl formate formations.  $\Delta$ : Formic acid,  $\square$ : Methyl formate. CH<sub>3</sub>OH: 225 ml, Irradiation time: 7h, Irradiation temp. 25°C.

## 2. Laser and Electron Beam Irradiation Effects on Polypropylene and Ethylene-Tetrafluoroethylene Copolymer

There have been a considerable interest recently in the use of intense ultraviolet radiations from excimer laser for advanced modification of polymer surface to improve adhesion or to provide functionalities. The laser ablation processing is useful for the etching of the aromatic polymers and the biological materials, however, is not available for modification of aliphatic polymers. The characteristic weak photoabsorption in the UV region of the aliphatic polymers should show the different photoreaction in the polymer matrix of the the laser ablation for aromatic polymers. The commercially merit of the aliphatic polymers is to be produced at a low cost. Addition of high functionalities to these polymer materials is regarded as important and new application of intense UV radiation from excimer laser.

Commercially available polymer films of PP (25  $\mu\text{m}$  thick) and ETFE (50  $\mu\text{m}$  thick) were used for samples. The laser used for irradiation was a Lumonics model HE-460 excimer laser emitted 0.1-0.5 J pulses at 193 nm (ArF) and 248 nm (KrF) of wavelengths. It was generally operated at 1 Hz to avoid heating effect on the polymer. The fluence of the laser beam was measured by a Gen-Tech Joule meter (Model ED-500). Laser irradiation was carried out in air at room temperature. Electron beam irradiation was carried out at room temperature with a van de Graaff type accelerator operated at 1.5 MV of accelerated voltage and 50  $\mu\text{A}$  of beam current. The absorbed dose of each sample was  $10^5$  Gy ( $=10^5$  J/kg).

UV-V spectra of PP films are shown in Figure 1. When the PP film was irradiated with KrF laser (spectrum a), the absorbance was enhanced in the wavelength range of 190 to



400 nm as compared with that of the non-irradiated film (spectrum b). In contrast with this case, with ArF laser irradiation (spectrum c) the absorbance decreased in the range of 190 to 240 nm.

Differential UV-V spectra between non-irradiated and irradiated PP films are shown in Figure 2. Quantities of absorbed energy into the polymer films for irradiation with electron beam, KrF laser (15 pulses) and ArF laser (15 pulses) radiation were  $10^5$ ,  $1.7 \times 10^5$  and  $3.9 \times 10^5$  J/kg, respectively. By irradiation with KrF laser (spectrum a) and electron beam (spectrum b) the differential spectra had peaks in the wavelength range below 190 nm, and at about 210 nm and 250 nm. On the other hand, in the case of ArF excimer laser irradiation (spectrum c) the considerable decrease in absorbance was clearly observed in the wavelength below about 240 nm. These results indicate that there is a large difference between irradiation effects of KrF and ArF laser radiation; KrF laser irradiation induces the formation of new absorption bands and ArF laser irradiation decomposes a component contained in the polymer. Irradiation effect of electron beam is similar to that of KrF laser radiation. Results of IR measurements indicate that the -C-C- bonds in PP polymer chains is transformed into -C=C- bonds by irradiation with KrF laser and electron beam and the oxidation of the polymer matrix chains is induced alone by irradiation with electron beam. From the results of emission measurement, the decrease of the UV-V absorption component by ArF laser irradiation is considered to be attributable to the decomposition of the antioxidant contained in the polymer.

As shown in Figure 3, the absorption spectrum of non-irradiated PP film in the wavelength of 190 to 400 nm consists of two components. One is due to the imperfections of the polymer such as -C=C- bond which introduced through the production process of the polymer. The other is due to

the antioxidant. In Figure 3, spectrum b is ascribed to the portion of the imperfections of the polymer and the estimated spectrum c approximately corresponds to the absorption one of the additive contained in PP polymer as an antioxidant.

Since the wavelength of KrF laser radiation, 248 nm, differs from that of the absorption bands of the antioxidant, the radiation energy is largely absorbed into the imperfect portion of the polymer. So that, the polymer is predominantly degraded by KrF laser irradiation without the decomposition of the antioxidant and the increase in UV-V absorbance due to the formation of  $-C=O$  and  $-C=C-$  groups is observed.

On the other hand, as the absorption spectrum of the antioxidant possesses peaks at 198 and 230 nm, ArF laser radiation, 193 nm, can be largely absorbed into the antioxidant. It is therefore presumed that the selective decomposition is induced by the photon energy directly absorbed into the antioxidant.

For irradiation with electron beam, since the energy absorbed into materials is proportional to the the electron density of the materials, the degradation of the polymer precedes the decomposition of the antioxidant whose concentrations are less than about 0.5%.

UV-V absorption spectra of ETFE films irradiated with KrF laser (100 pulses) are shown in Figure 4. The absorption spectrum of non-irradiated ETFE may be due to the imperfect portion of the polymer formed through a production process. A large increase in absorbance for ETFE irradiated with KrF laser was observed in the wavelength range longer than 190 nm.

Figure 5 shows the UV-V differential spectra between non-irradiated and irradiated ETFE. Quantities of absorbed energy for irradiation with KrF laser (100 pulses), ArF laser (100 pulses) and electron beam were  $3.7 \times 10^5$ ,  $6.1 \times 10^5$

and  $10^5$  J/kg, respectively. In these cases, the absorption band whose peak centered at about 230 nm newly appeared. For irradiation with KrF laser (spectrum a), in addition to the 230 nm-peak absorption band a large increase in the absorbance broadened to the longer wavelength was observed. Such a remarkable increase in the absorbance is considered to be attributable to a carbonization due to the degradation of the polymer. In fact, the exposed portion of the films blackened. On the other hand, ArF laser irradiation gave the formation of only the 230 nm-absorption band. Furthermore, electron beam irradiation (spectrum c) increased the absorption band spread in shorter wavelength than 200 nm, with overlapping 230 nm-absorption band.

It is clarified from the results of the IR measurements that the observed UV-V absorption bands below 200 nm and at 230 nm by irradiation with ArF and electron beam are corresponding to  $\pi \rightarrow \pi^*$  absorption of  $-C=C-$  group and  $n \rightarrow \pi^*$  of  $-C=O$  one, respectively. These results indicate that irradiation with ArF laser and electron beam degrades the polymer with the formation of  $-C=C-$  and  $-C=O$  groups and KrF laser irradiation induces much larger degradation of the polymer with a carbonization.

By irradiation with KrF, ArF laser and electron beam,  $-C=O$  group is formed in the polymer matrix and the 230 nm-peak absorption band appeared. Since the wavelength of KrF laser radiation, 248 nm, is close to the peak wavelength of the 230 nm-absorption band, the photon can be efficiently absorbed into the polymer to induce directly the degradation of the polymer matrix. In contrast with this case, the wavelength of ArF laser radiation, 193 nm, has no component of this absorption band, so that, a photon energy is absorbed into only the imperfect portion of the polymer. The absorbed energy induces only the oxidation and increases the intensity of the 230 nm-absorption band. On the other hand, energy of electron beam is absorbed by the polymer

matrix through Compton scattering process and the quantities of absorbed energy are proportional to the electron density of materials. Therefore, the chemical reactions induced by electron beam irradiation occur in the polymer matrix at random.

For only KrF laser irradiation, much larger degradation of the polymer compared with irradiation with ArF laser and electron beam occurs through a selective excitation of the absorption band formed in advance by the irradiation.

(S. Kawanishi, Y. Shimizu, S. Sugimoto and N. Suzuki)

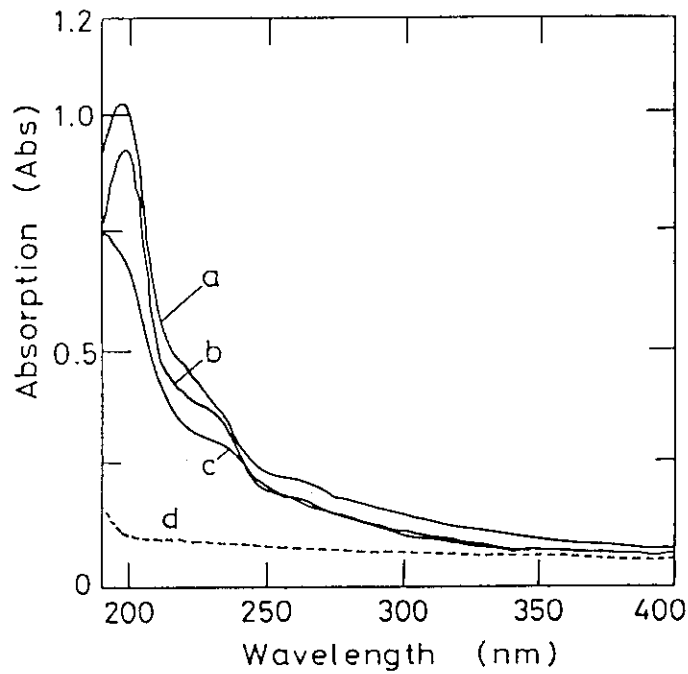


Fig. 1 UV-V absorption spectra of PP. a: KrF laser irradiation 15 pulses, b: non-irradiated sample, c: ArF laser irradiation 15 pulses, d: plot of  $\log(1-R)$ , where R is the reflectivity of non-irradiated PP film.

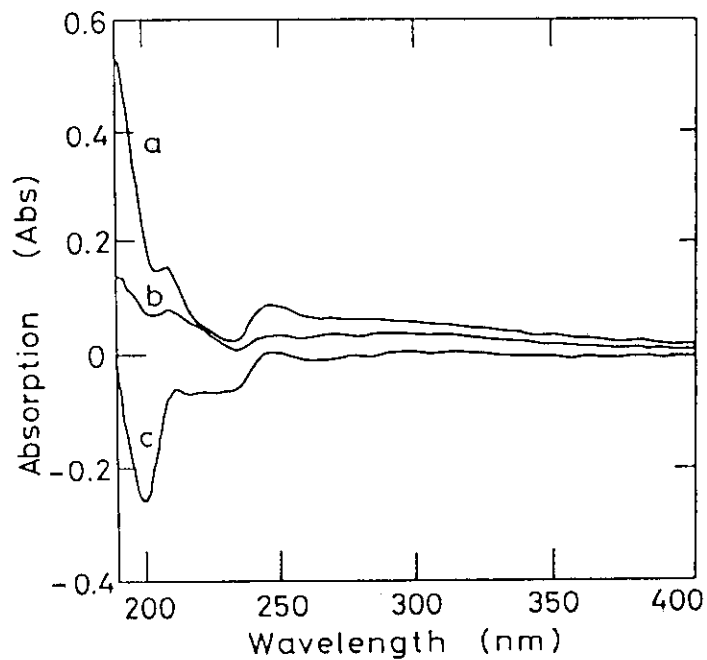


Fig. 2 UV-V differential spectra between non-irradiated and irradiated PP. a: KrF laser irradiation  $1.7 \times 10^5$  J/kg, b: 1.5 MeV electron beam irradiation  $10^5$  J/kg, c: ArF laser irradiation  $3.9 \times 10^5$  J/kg.

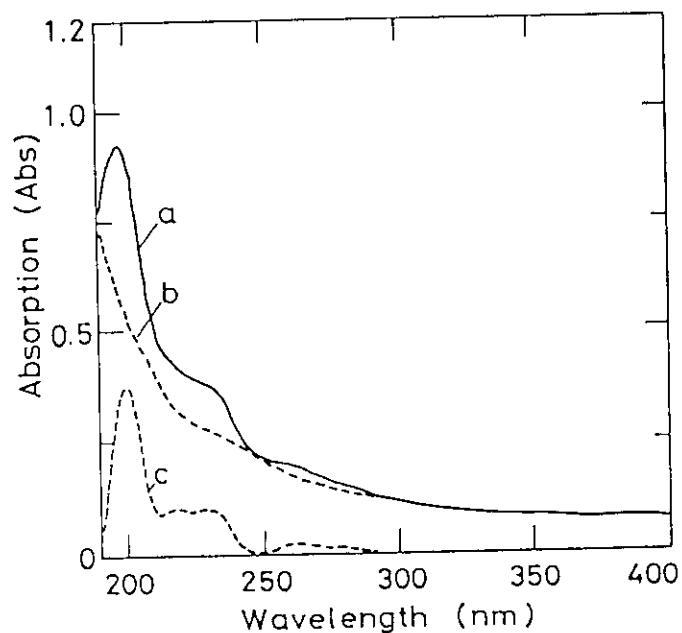


Fig. 3 Measured and evaluated spectra of non-irradiated PP.  
 a: measured spectrum, b: evaluated spectrum by subtraction  
 the spectrum c from the measured spectrum a, c: evaluated  
 spectrum due to the antioxidant estimated by the decrease  
 component in Figure 2 (spectrum c).

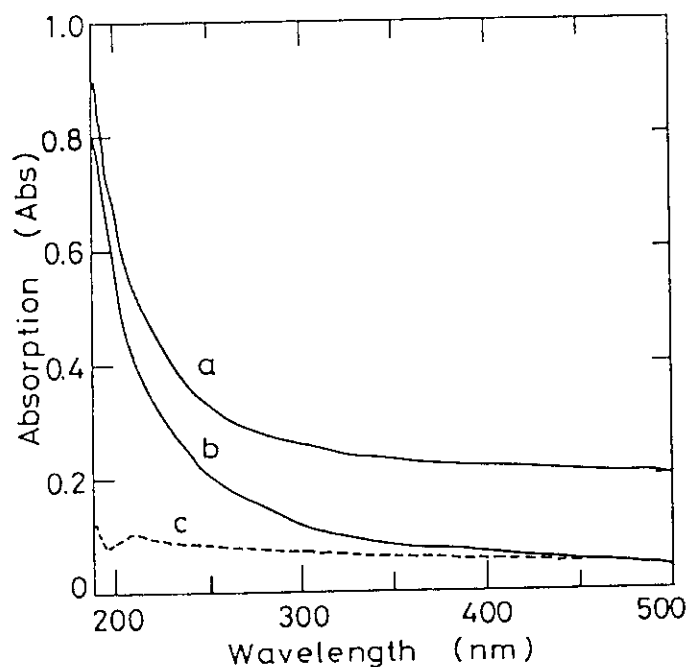


Fig. 4 UV-V absorption spectra of non-irradiated and KrF laser 100  
 Pulses irradiated ETFE. a: non-irradiated, b: 100 pulses  
 irradiated, c: plot of  $\log(1-R)$ , where R is reflectivity  
 of non-irradiated ETFE film.

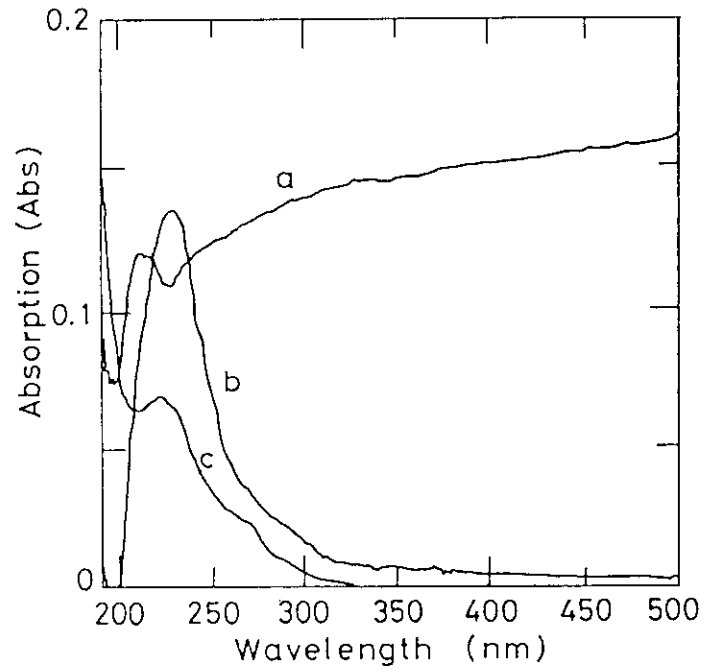


Fig. 5 UV-V differential spectra between non-irradiated and irradiated ETFE. a: KrF laser irradiation  $3.7 \times 10^5$  J/kg, b: ArF laser irradiation  $6.1 \times 10^5$  J/kg, c: 1.5 MeV electron beam irradiation  $10^5$  J/kg.

### 3. Irradiation of Krypton Ions to Polymer Films

In order to investigate dose evaluation method, polymer films were irradiated with  $Kr^+$  by low energy ion generator (LEIG).

In the previous paper(1), the Kr-concentration after the  $Kr^+$ -irradiation to the film can be estimated from optical density measurements.

Figure 1 shows the schematics of a Faraday cup and the  $Kr^+$  beam irradiation area. The Faraday cup was constructed with 41 small Al-electrodes of 0.5mm diameter.

Ti-mask took a role to suppress the secondary electrons from the irradiating surface.

Figure 2 shows the effects of suppression voltage on the current density at two electrodes(No. 15 & 20) of the Faraday cup. By applying negative voltage on Ti-mask over 10 V, current density decreased remarkably.

Transparent PET and CTA films colored to metallic dark brown with the ion-irradiation. The optical density of irradiated PET and CTA films was measured carefully at the corresponding position to be able to compare properly with measured current.

Figure 3 shows the relationship between dose( $Kr^+$ -current density) and optical density increase by irradiation of PET(A) and CTA(B), where current density was measured by the Faraday cup, and optical density by UV spectrometer at 340nm in PET and at 280nm in CTA

The slopes of the plots in Figure 3A and B were calculated as 0.22 and 0.17 for PET and CTA, respectively.

These values suggest that PET film is more sensitive to ion-irradiation than the case of CTA, thus more suitable for dose estimation than CTA film.

(Y.Nakase)

#### Reference

- 1) a) Y.Nakase, JAERI-M 89-151, 1989
- b) Y.Nakase, JAERI-M 90-054, 1990



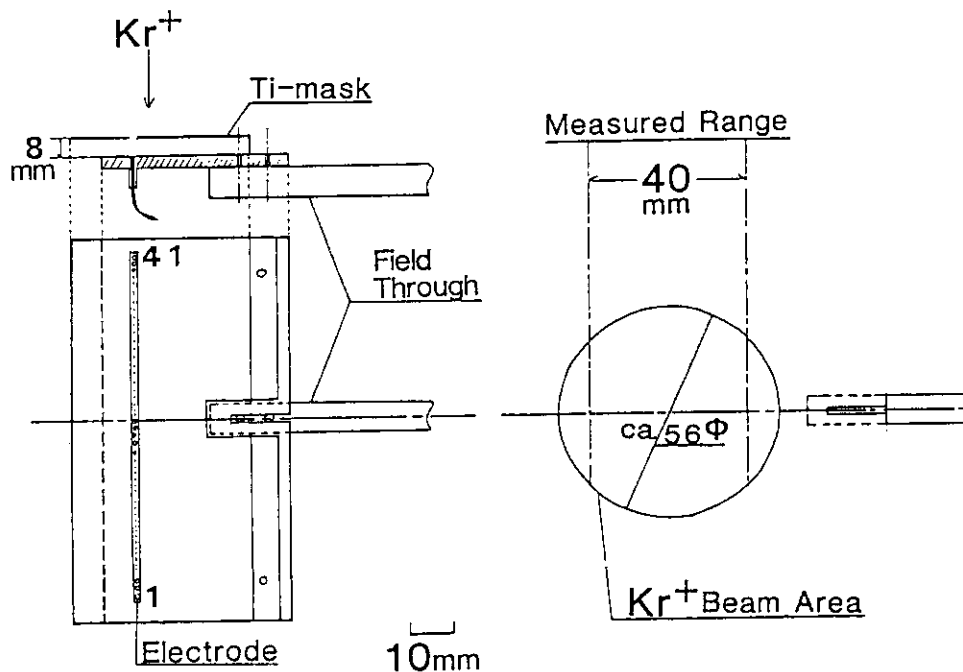


Fig. 1 Small electrode Faraday cup device.

Electrode : Al (0.5mm diameter)

Ti-mask : Secondary electron suppression electrode,  
(0.1mm thick)

A : Schematic diagram of the Cup.

B : Beam irradiation area.

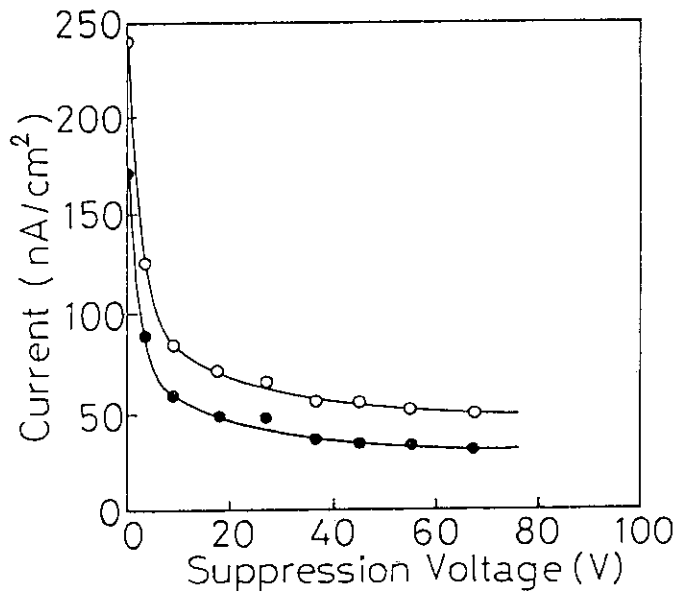


Fig. 2 Effect of suppression voltage.

Kr<sup>+</sup> : 35keV, total current of 100 μA (56mm dia).

Suppression voltage : Dry batteries (1.5V and 9V)

● : Electrode No.15, and ○ : No.20.

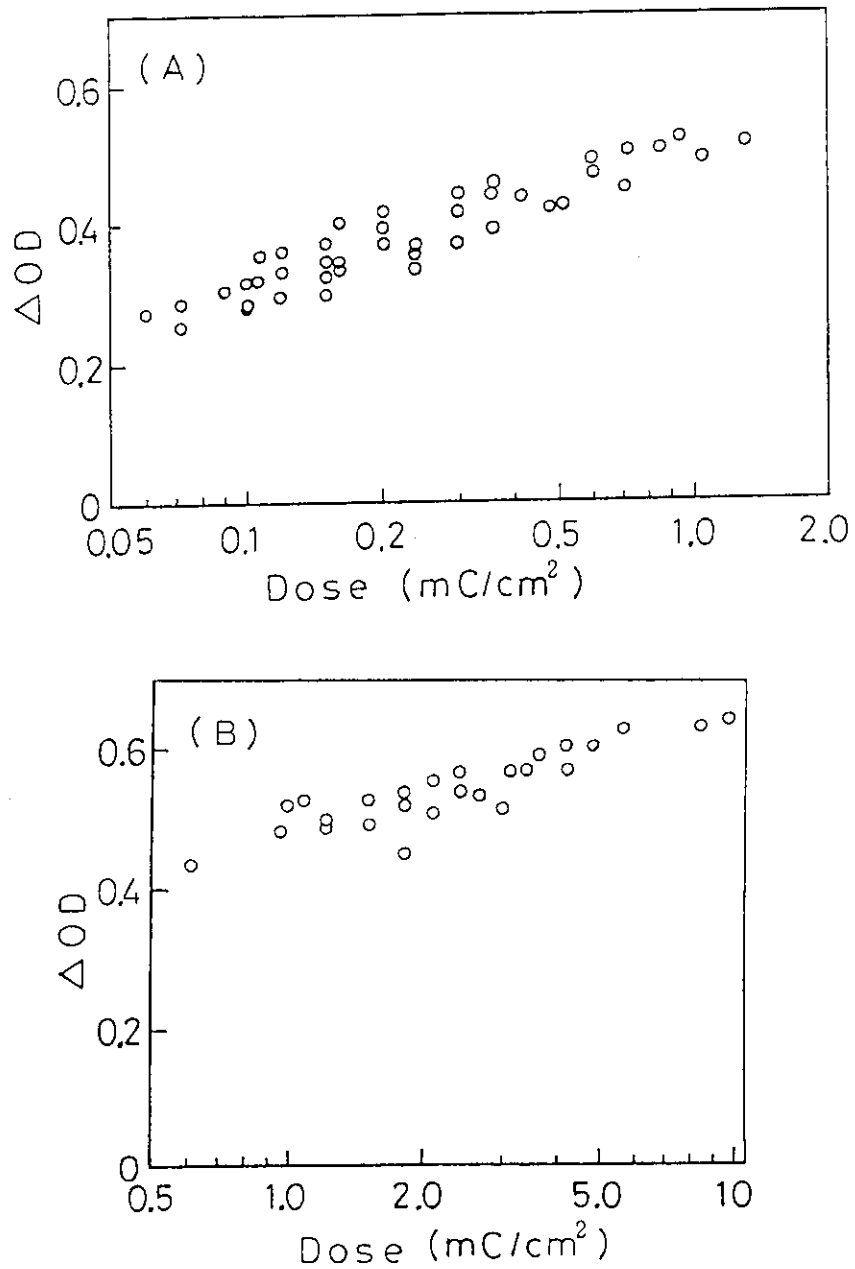


Fig. 3 Relationship between optical density of  $Kr^+$  irradiated films and  $Kr^+$  dose (current density).

$Kr^+$  : 35keV, no suppression voltage applied.

Dose : Current density ( $\mu A/cm^2$ ) x Time (s)

A : PET film (25 $\mu m$  thick), optical density at 340nm.

B : CTA film (125 $\mu m$  thick), optical density at 280nm.

#### 4. Hydrophilic Properties of Acrylic Acid Grafted Polyethylene Foam of Open Cell Type

In a previous annual report, we reported that grafting of acrylic acid onto polyethylene foam of open cell type is successfully performed by preirradiation technique using monomer solution containing Mohr's salt as inhibitor by careful removal of air from the cells of the polyethylene foam and that antistatic property was improved. In this report, we describe some results of hydrophilic properties such as dyeability, hygroscopicity, and wicking behavior, and tensile property of the acrylic acid-grafted foam thus prepared. The foam grafted with acrylic acid was immersed in 1 % aqueous solution of sodium bicarbonate for 2 hrs at 80 °C to convert the grafted acid to sodium salt.

The original polyethylene foam cannot be dyed at all, but it turns to be dyeable with cationic dyes when carboxylic groups are introduced to polyethylene chains. Homogeneous but poor dyeability was obtained by 2 % grafting when the grafted foam was dyed with Sevron Brilliant Red B by the method mentioned in a former report<sup>3)</sup>, but for satisfactorily deep dyeability, grafting of more than 20 % graft percent was necessary.

In Fig. 1, moisture regain of the grafted foam is plotted as a function of graft percent when the grafted foam was equilibrated with moisture at 66 % and 93 % relative humidities. The broken line indicates the moisture regain calculated from the graft percent provided that the moisture regain of the grafted foam be equal to sum of the value of each component multiplied by weight fraction of the component. In the atmosphere of low relative humidity (at 66 %), the observed moisture regain of the grafted foam agreed well with the calculated value, but at high relative humidity, the observed value was lower than the calculated one in the whole range of graft percent. The result means that at low relative humidity, the complete equilibrium of moisture exists between foam and atmosphere, but at high relative humidity, some entanglement of polyethylene chains and polyacrylic acid(PAA) chains may restrict the movement of chain segments

of the latter to inhibit hydration of some fraction of carboxylic groups in the PAA chains, thus giving lower moisture regain than the calculated value.

The moisture regain of the grafted substance is determined by the amount of carboxylic group in the substance which is linearly related to the amount of grafted PAA chains, and is independent of the form of the substance whatever it may be a film, fiber or others. But the data obtained for foam show that the moisture regain is a little higher than that obtained for fiber<sup>4)</sup> probably due to a capillary condensation effect.

The moisture regain of grafted foam in which the carboxylic groups were converted to sodium salt is also plotted as a function of graft percent by filled circles in Fig. 2. It is noted from the figure that the moisture regain of grafted foam converted to sodium salt is about several times higher than that of free acid of the same graft percent.

Wicking tests were carried out to know the initial rate of water absorption by following three methods. The same tests were also carried out for commercially available PVA foam for reference purpose. Specimens used in the tests were immersed in water and then squeezed out water before use.

The first test is to measure the time required for disappearance of water droplet to be absorbed in the foam after the water droplet of 0.03 ml was delivered on the foam surface from a Pasteur pipette kept 2 cm above the surface. The droplet on the original foam kept its shape even after 3 minutes, but a droplet on the 4 % grafted surface disappeared quickly within a second. This indicates that the grafting of graft percent as small as 4 %, the initial rate of water absorption is large as that observed for PVA foam which is appeared on market as water absorbing foam.

The second test of wicking is to measure time required for 1 cm vertical migration of water front after the piece of foam came in contact vertically with water surface. No migration of water front was observed for the original foam, but the time required for 1 cm migration was only 2 - 3 seconds for 4 % grafted foam, 1.5 seconds for 10 % grafted foam and 1 sec for 40 % grafted foam which is equal to

that obtained for PVA foam.

The third test of wicking is to measure the migration distance of water front during first 5 sec and 10 sec after the foam came in contact on water surface. The results are shown in Fig. 3. Again, the original foam showed no water front migration, but 2.5 cm migration after 5 sec and 3 cm after 10 sec were observed for 10 % grafted foam, and these values did not change when the graft percent increased further. These values are the same as those observed for PVA foam.

All these wicking tests by three methods mentioned above agree in that large improvement in hydrophilic properties was obtained by small graft percent, and further increase of graft percent was not necessary. This indicates that the properties of the surface are mainly determined by the functional groups on the surface, and thus sufficient improvement is attained by small graft percent if the surface concentration of the functional group is high.

We have examined whether the radiation-grafting causes deterioration of the tensile properties. Tensile length and elongation were measured by an Autograph DES-500 (Shimadzu Works Co., Ltd.) at 20 °C and 60 % relative humidity. Sample length and crosshead speed were 40 mm and 500 mm/min, respectively. In Fig. 4 and 5, tensile strength and elongation of the foam are plotted as a function of graft percent, respectively. The tensile strength seems to increase with increasing graft percent. Elongation decreased with increasing graft percent (Fig. 5) probably due to formation of hydrogen bonding network between carboxylic groups of PAA chains.

(K. Kaji, I. Yoshizawa, C. Kohara, K. Komai, and M. Hatada)

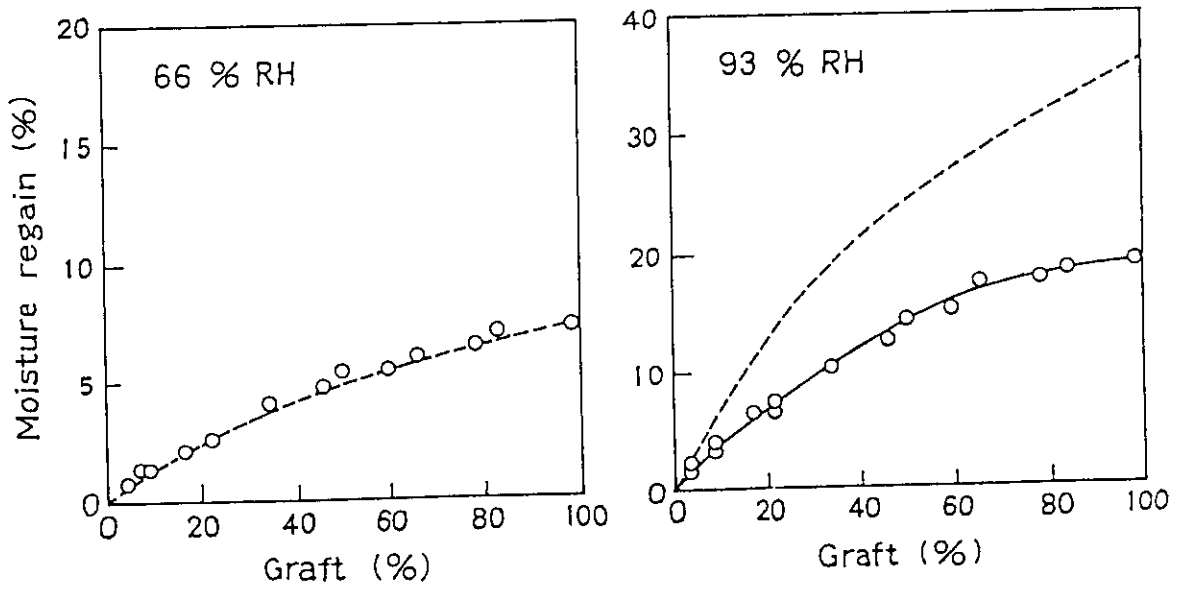


Fig. 1 Moisture regain of acrylic acid grafted foam ;  
 Broken line shows values calculated from the moisture regain  
 of polyethylene and that of poly (acrylic acid).

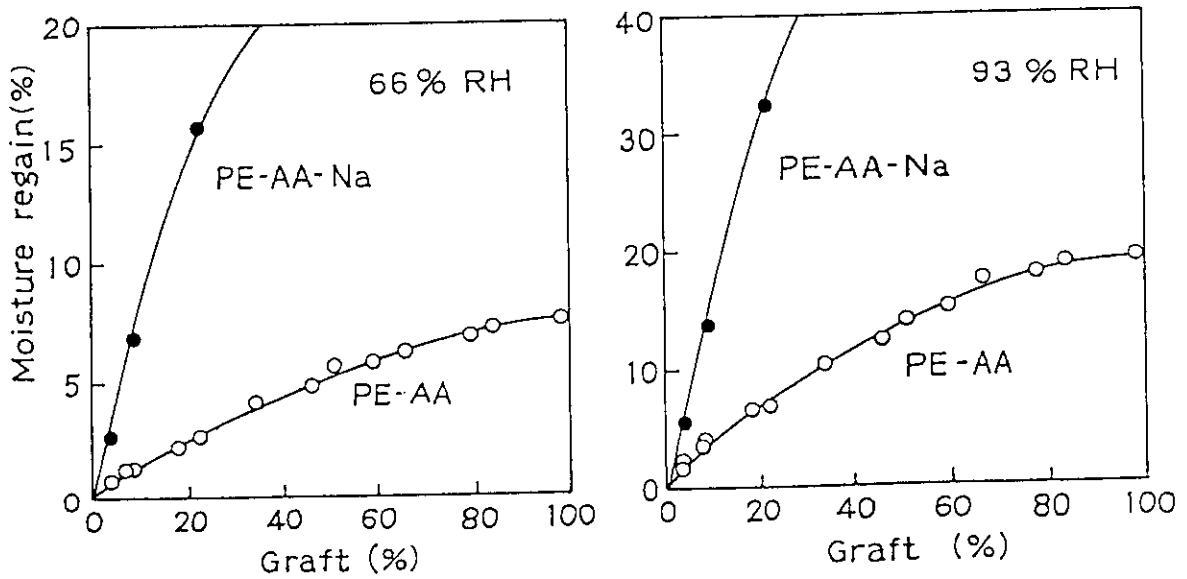


Fig. 2 Moisture regain of grafted foam as a function of  
 graft percent : (○) Acid, (●) Na-salt.

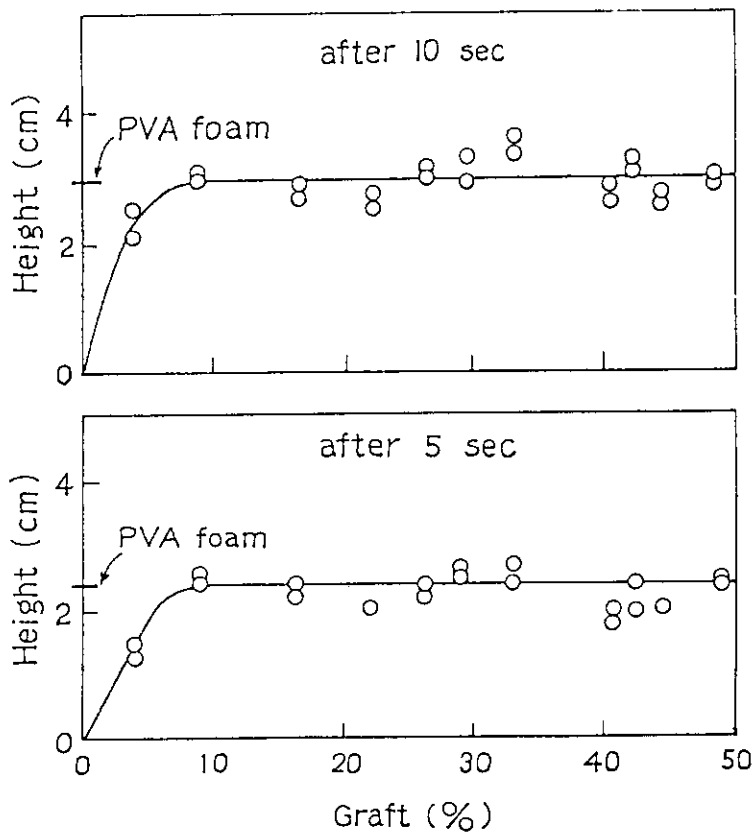


Fig. 3 Vertical migration of water front in grafted foam ; dash on the ordinate indicates the data obtained for PVA foam.

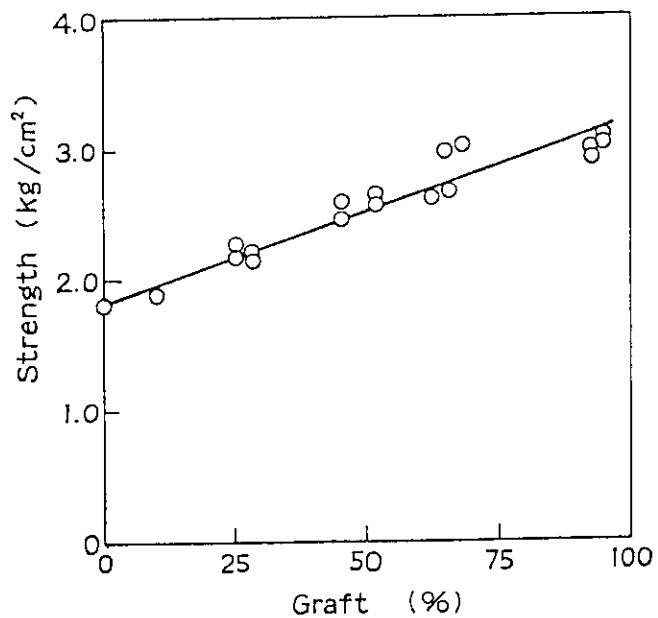


Fig. 4 Strength of grafted foam as a function of graft percent.

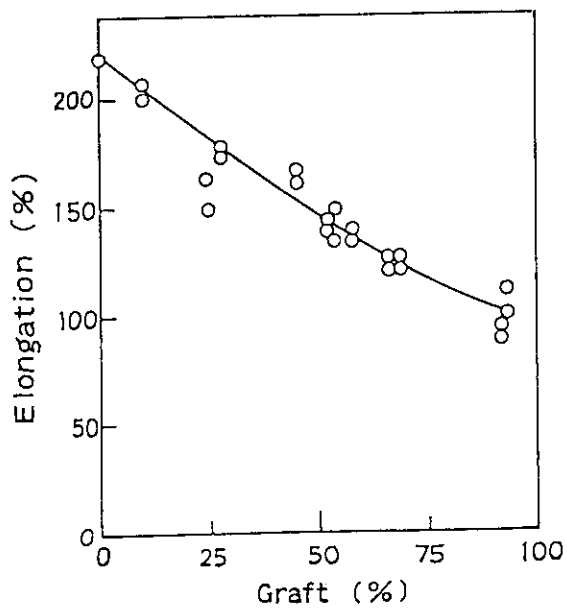


Fig. 5 Elongation of grafted foam as a function of graft percent.



## 5. Electron Beam Irradiation of LB Films of Calcium Salts of Arachidic Acid, $\omega$ -Tricosenoic Acid and $\omega$ -Tricocynoic Acid

In the previous annual report, we reported that Langmuir-Blodgett(LB) films of  $\omega$ -tricosenoic acid(TSA) and  $\omega$ -tricocynoic acid (TCA) can be polymerized by irradiation of high energy electron beam to give the polymer LB films.<sup>1)</sup> In this study, LB films of calcium salt of  $\omega$ -tricosenoic acid(TSA) and  $\omega$ -tricocynoic acid (TCA) were irradiated with electron beams and the reactivity of the films has been studied comparatively to those obtained with the LB films of the corresponding free acids. The radiation effects on LB films of calcium salt of arachidic acid (ADA) was also studied.

The method of preparation of the LB films and irradiation procedure were the same to those described in the previous report except that the monolayers of these acids were spread on aqueous solution of calcium chloride ( $1.6 \times 10^{-4}$  mole/l) in stead of pure water. Monolayer substance (ca. 0.1 mg) was spread on the water from chloroform solution (100 mg/l). The LB films were built-up in a silicon wafer covered with oxide layer. The velocity of up- and down-movement of the substrate during building-up was 12 mm/min. During the building-up, the surface pressures were kept constant at 41, 41, and 46 mN/m for Ca-ADA, Ca-TSA, and Ca-TCA monolayers, respectively, which give the molecular area of 20  $\text{\AA}^2$ /molecule for these monolayers. An LB film of Y-type of 25 layers was built-up.

Irradiation was carried out with an electron beam from a Nissin High Voltage accelerator of a transformer type (300 kV, 50  $\mu\text{A}$ ) in nitrogen atmosphere on a cold plate cooled by running water. The dose rates were 0.02 Mrad/sec at 50  $\mu\text{A}$  and 0.2 Mrad/sec at 500  $\mu\text{A}$  and temperature of the sample during irradiation was below 30  $^{\circ}\text{C}$ .

The infrared spectra of the LB films before and after irradiation were taken on a Shimadzu FTIR-4000 spectrophotometer. Solubility tests were carried out by dipping the films into ethanol for 10min at 20  $^{\circ}\text{C}$ .

The changes of IR spectrum during irradiation observed for Ca-

ADA, Ca-TSA, and Ca-TCA LB films are shown in Figs. 1, 2, and 3, respectively. The spectra of films measured before irradiation were similar to those observed for films of corresponding free acids except that bands due to wagging vibrations of methylene group in hydrocarbon chain appearing at 1350 to 1190  $\text{cm}^{-1}$  are weaker in the former. This indicates that the hydrocarbon chains of calcium salts are more tightly packed than those of free acids and thus in less movable state.

As shown in Fig. 1 from A through D, it was observed for the Ca-ADA LB films that the intensities of absorption bands due to C-H stretching vibrations of methyl group ( $\nu_a$ :2960,  $\nu_s$ :2860  $\text{cm}^{-1}$ ), those of methylene group ( $\nu_a$ :2920,  $\nu_s$ :2850), and scissoring vibrations ( $\delta$ :1470) decreased with increasing dose, indicating that the methylene group in the ADA LB film was destroyed by the irradiation. Similar decrease of absorption intensities was also found for  $\text{CO}_2^-$  stretching vibrations ( $\nu_a$ :1580,  $\nu_s$ :1430). The progression bands due to methylene wagging and twist vibrations ( $\omega$ ,  $\delta$ :1350 - 1190) became weaker as the dose increased, but were still recognized at 200 Mrad irradiation, indicating that the cross-linking between hydrocarbon chain of the LB layers occurred by the irradiation and disturbed the mobility of vibration of hydrocarbon chains.

From the change of the IR spectrum of Ca-TSA LB films during irradiation shown in Fig. 2A through D, the intensities of absorption bands due to C-H stretching vibrations ( $\nu_a$ :2920,  $\nu_s$ :2850) of methylene group and bands due to  $\text{CO}_2^-$  stretching vibrations ( $\nu_a$ :1580,  $\nu_s$ :1430). The progression bands due to methylene wagging and twist vibrations ( $\omega$ ,  $\delta$ :1350 - 1190) became weaker as the dose increased, but were still recognized at 200 Mrad irradiation, indicating that the cross-linking between hydrocarbon chain of the LB layers occurred by the irradiation and disturbed the mobility of vibration of hydrocarbon chains.

From the change of the IR spectrum of Ca-TSA LB films during irradiation shown in Fig. 2A through D, the intensities of absorption bands due to C-H stretching vibrations ( $\nu_a$ :2920,  $\nu_s$ :2850) of methylene group and bands due to  $\text{CO}_2^-$  stretching vibrations ( $\nu_a$ :1580,  $\nu_s$

:1430), decreased with increasing dose, as was observed in the Ca-ADA LB films. The intensity of the bands due to C=C stretching vibration ( $\nu$ :1650), bands due to =CH<sub>2</sub> scissoring vibration ( $\delta$ :920), and progressive bands due to wagging and twist vibrations of methylene group ( $\omega$ ,  $\delta$ :1350 - 1190) also decreased during irradiation, but the rate of disappearance of the bands was higher than that of the other bands and they disappeared completely by 200 Mrad irradiation. This indicates that the double bond reacted to polymerize by irradiation or to react with hydrogen which had split off from the adjacent hydrocarbon chain during the irradiation.

Similar results were obtained for Ca-TCA LB films, as shown in Fig. 3 A through D. Similar decrease with dose was observed for the intensities of bands due to CH<sub>2</sub> stretching vibration, and bands due to C=O stretching vibrations. The intensity of C≡C stretching band ( $\nu$ :3300) and progressive bands due to -CH<sub>2</sub>- wagging and twist vibrations decreased more quickly than the other bands, indicating that the C≡C group is the most reactive.

The reactivities of CH<sub>2</sub> and unsaturated groups are compared with those of corresponding free acids in Fig. 2 a through c, where it is noted that the bands due to -CH<sub>2</sub>- group in the free acids disappeared more rapidly during irradiation. The unsaturated group of the free acids are more sensitive to radiation than those of corresponding calcium salts. This may account for the rigid structure of LB film of calcium salts.

(K. Ogawa, T. Tamura, M. Hatada, and T. Ishihara)

1) K. Ogawa, H. Tamura, M. Hatada, and T. Ishihara, Annual Report, JAERI-M90-054(1990).

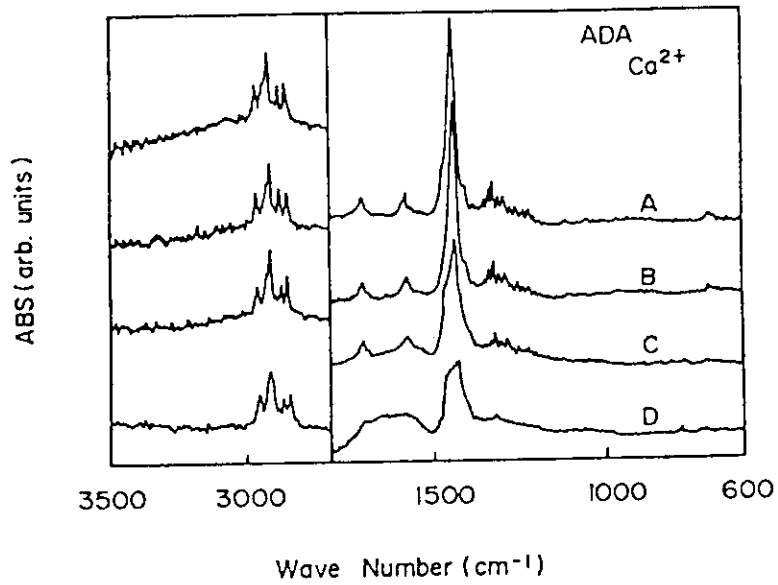


Fig. 1 Change of IR absorption spectrum of Ca-ADA LB film under electron beam irradiation ; (A) 0, (B) 2 Mrad, (C) 20 Mrad, and (D) 200Mrad.

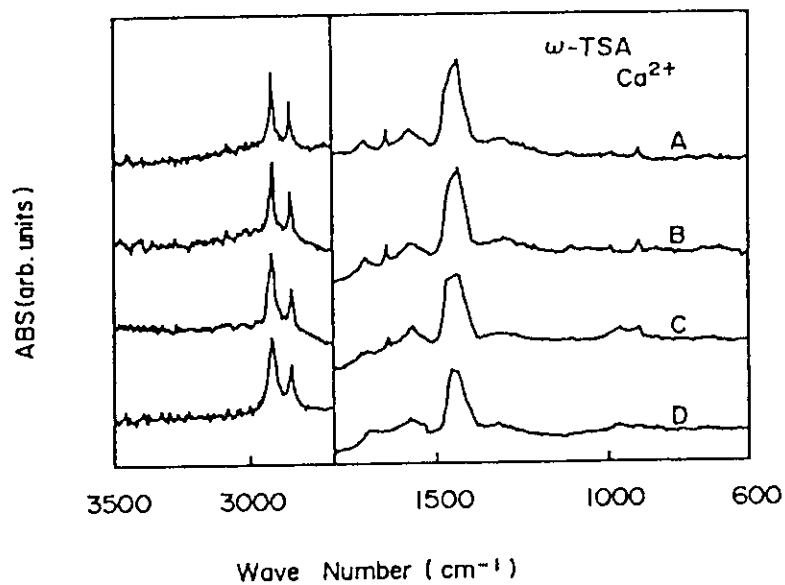


Fig. 2 Change of IR absorption spectrum of Ca-TSA LB film under electron beam irradiation ; (A) 0, (B) 2 Mrad, (C) 20 Mrad, and (D) 200Mrad.

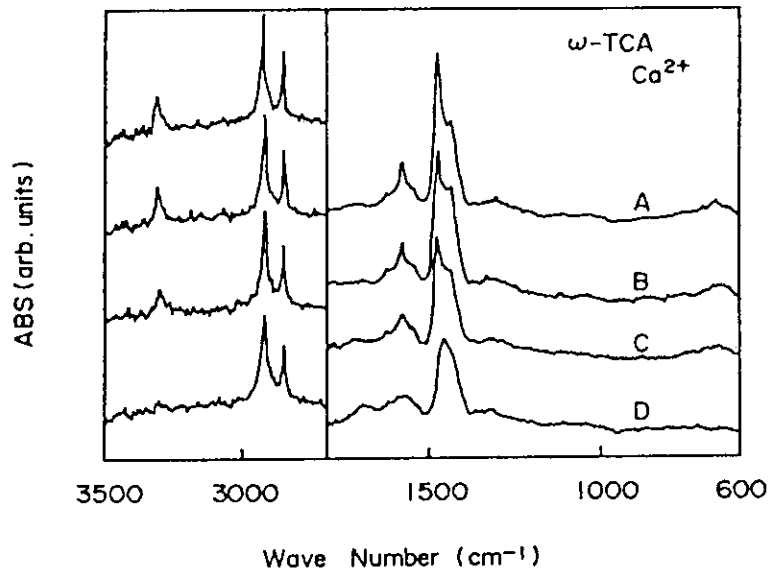


Fig. 3 Change of IR absorption spectrum of Ca-TCA LB film under electron beam irradiation ; (A) 0, (B) 2 Mrad, (C) 20 Mrad, and (D) 200Mrad.

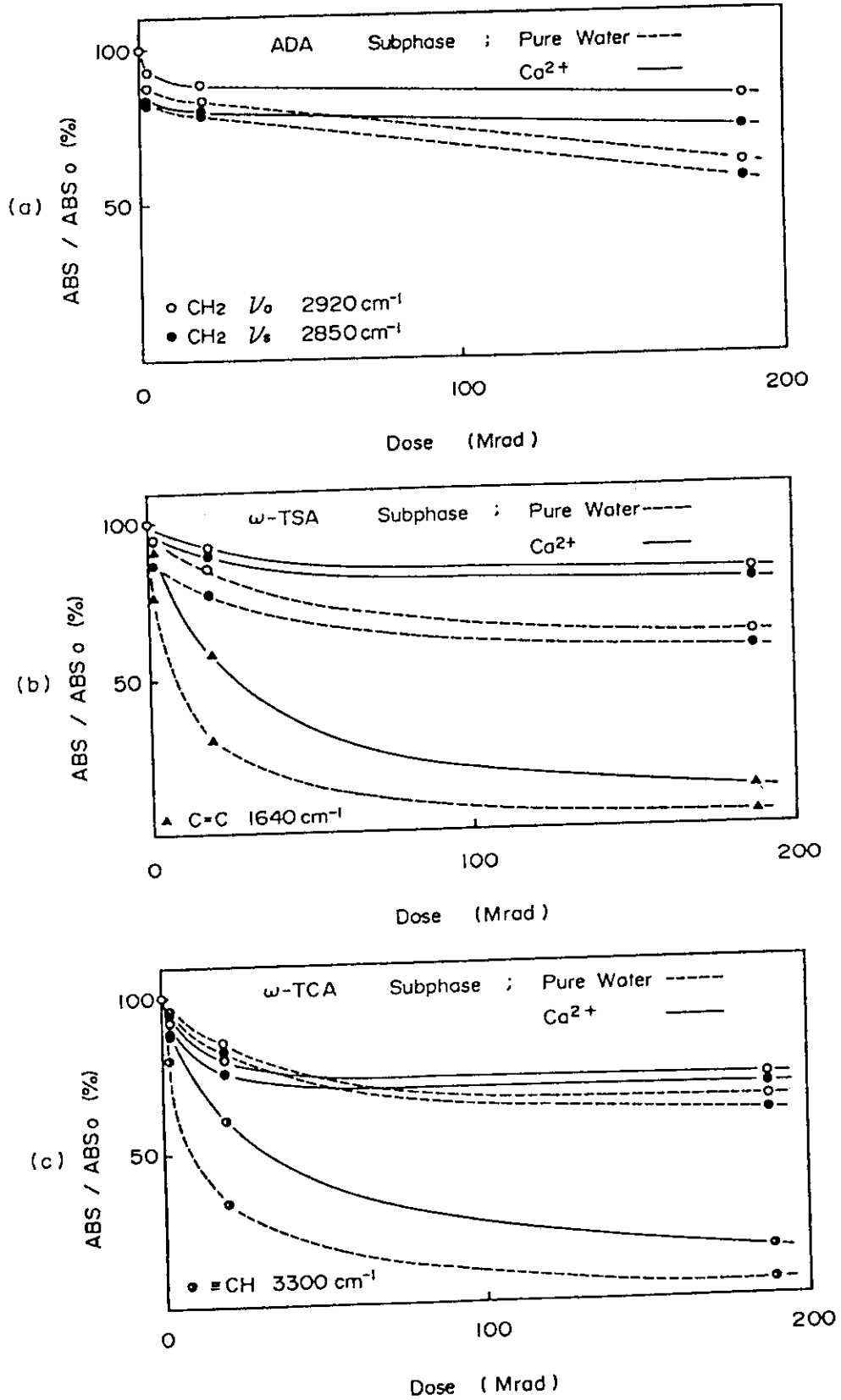


Fig. 4 Relative absorption as a function of dose ; (a) Ca-ADA and ADA, (b) Ca-TSA and TSA, and (c) Ca-TCA and TCA.

## 6. Emissions from the Excited NH Fragment Formed by Electron Impact of Ammonia-Helium Gas Mixture

A gas mixture of helium-ammonia was irradiated with an electron beam (0.6 MeV, 10  $\mu$ A) from a Van de Graaff accelerator and emission intensities from the excited NH fragments were measured as a function of pressure and composition of the mixture, and with the presence of additives, and the results are discussed in relation to the energy transfer between the species in the system which is important for the radiation chemistry of binary gas mixture.

Figures 1(a) and 2(b) show the emission spectra obtained by the irradiation of He-Ammonia mixture at partial pressure of ammonia of 0.057 Torr and 0.95 Torr, respectively, while the pressure of helium was constant at 770 Torr. Two emission bands, one due to the  $c^1\Pi - a^1\Delta$  transition of NH radical in singlet state and the other  $A^3\Pi - X^3\Sigma$  transition of NH radical in triplet state, were observed in both spectra (these bands are abbreviated as NH(c-a) and NH(A-X), respectively, and the fragments in these states are indicated by NH(c), NH(a), NH(A), and NH(X), respectively). It is noticed that the intensities of both bands decreased, and especially, the intensity of the singlet bands decreased more compared to that of the triplet bands when the ammonia partial pressure was increased. The intensities increased with increasing partial pressure of ammonia, reached maxima at 0.06 Torr, and then decreased with pressure monotonously. The result indicates that both intermediates (singlet and triplet) came from the common source and the singlet species is more favorable to be quenched by collision with ammonia molecule than the triplet species.

When the total pressure was increased while the pressure ratio of ammonia to helium was kept constant at 0.000247, the intensities of the both bands increased with increasing pressure with levelling-off tendency, and the curve for the singlet bands levelled-off at lower pressure than the other. The results indicate that the both species are formed by energy transfer to ammonia from helium which was pri-

marily excited by the radiation, and again, the singlet species quenched with ammonia molecules more favorably than the triplet one.

The following assumptions are made to write a series of reactions which fit to the above experimental results:

- 1) There are many possible excited helium or ionized helium which are concerned in the formation of excited NH, but we do not distinguish them.
- 2) Deactivation of the excited helium atom may occur either bimolecularly or unimolecularly, but only the former is considered to occur. However, this does not affect the conclusion.
- 3) The NH radical excited to c state deactivates to A state by collision induced intersystem crossing as reported by Rohrer et al.<sup>6)</sup>
- 4) The quenching rate of NH\* by helium atom is small compared with that by NH<sub>3</sub>, and therefore, only the quenching by ammonia molecule is considered in the scheme.

The reaction scheme is shown in Table 1. At the steady state condition at higher concentration of ammonia, the concentration of NH(c) is approximately given by

$$[\text{NH}(c)]^{-1} = \text{const} \times [\text{NH}_3] \quad (1)$$

where B is a constant. Similar equation is obtained for steady state concentration of NH(A). Reciprocals of the emission intensities of the NH(c-a) and NH(A-X) are plotted as a function of concentration of ammonia in Fig. 2, where both plots lie on straight lines at higher ammonia concentration region above 0.8 Torr.

In the case where total gas pressure was varied while ratio of the concentration of ammonia to that of helium was kept constant at 0.000247, one obtains the following equation:

$$[\text{NH}(c)] = \text{const} \times (k_I + k_Q) + k_R / [\text{NH}_3] \quad (2)$$

The plot of experimental data according to eq. (2) is shown in Fig. 3, where the intercept gives the ratio  $(k_I + k_Q)/k_R = 9.3 \text{ Torr}^{-1}$ . By use of the data  $k_R = 1/\tau_R = (440\text{ns})^{-1} = 2.3 \times 10^6 \text{ sec}^{-1}$ ,  $(k_I + k_Q)$



is obtained to be  $2.1 \times 10^7 \text{ Torr}^{-1} \text{ sec}^{-1} = 6.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  which is in reasonably good agreement with the literature values ( $9.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ); ( $4.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ) (Haak et al., 1984).

Under low pressures, NH(c) is reported to be observed in highly rotationally excited levels with rotational temperatures of 1500K, 1690K, and 3200K, depending on the method of excitation and gas pressure (Sameda et al., 1988; Sekiya et al., 1987; Tokue et al., 1980). The rotational distribution of the NH(c) bands at atmospheric pressure agrees well with the simulated spectrum assuming the Boltzmann distribution at 300K. This indicates that most of the NH radicals exist in stationary state during electron beam irradiation have been completely relaxed to the room temperature by collisional relaxation with helium atoms. Decrease of the gas pressure resulted the decrease of the emission intensities of both bands and the rotational distribution of the NH(c) radical seems to change to the one that populated toward higher levels indicating that the decreasing number of collisional relaxation of rotational levels. On the other hand, the spectrum of the NH(A) bands slightly changed by the decrease of the total pressure. This suggests that the rotational relaxation of NH(A) by collision with helium atom is less favorable than that of NH(c).

The emission intensity of NH(c-a) is measured as a function of partial pressure of different additives. The emission intensity decreased linearly with increasing amount of nitrogen, while for methane, oxygen, and ethylene, large decrease of the emission intensity was observed in the region of small partial pressure of additives, but the decrease became smaller as the pressure of additives increased. When sulfur hexafluoride was added to the system, more complex sigmoid change was observed. Similar changes of emission intensities were observed for NH(A-X) band system. No data could be obtained for the case where nitrogen was added in the system, because the measurement of emission intensity of NH(A-X) bands was difficult because of overlapping of very strong N<sub>2</sub> (0,0) emission. The result that both NH(A-X) and NH(c-a) emission intensities show similar dependence to the additives may indicate that the additives compete with ammonia for

a common precursor, possibly, excited helium atom (reaction 8 in Table 1).

Quenching of NH(c) and NH(A) by different gases are reported by three authors(Kawasaki et al., 1973; Sasaki et al., 1986; Hofzumahaus et al., 1985), and quenching rate constant of NH(c) with N<sub>2</sub> is reported to be small(Kawasaki et al., 1973) thus supporting the importance of reaction (8) mentioned above.

( K. Matsuda, I. Fujita, T. Kijima, H. Yamamoto, and M. Hatada)

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Table 1 Reaction Scheme

Number	Reactant	Product	Rate Constant	Type of Reaction
1	He + e	He*	B	Energy absorption
2	He* + He	He + He	$k_{D2}$	Deactivation
3	He* + NH <sub>3</sub>	NH(c) + H <sub>2</sub> or 2H	${}^1k_0$	Energy transfer
		NH(A) + H <sub>2</sub> or 2H	${}^3k_0$	and dissociation
4	NH(c) + NH <sub>3</sub>	NH(A) + NH <sub>3</sub>	${}^1k_0$	Intersystem crossing
		NH(X) + NH <sub>3</sub>	${}^1k_Q$	Quenching
		NH(a) + NH <sub>3</sub>		
5	NH(c)	NH(a) + hν	${}^1k_R$	Radiation emission
6	NH(A) + NH <sub>3</sub>	NH(X) + NH <sub>3</sub>	${}^3k_Q$	Quenching
7	NH(A)	NH(X) + hν	${}^3k_R$	Radiation emission
8	He* + Additive	He + Additive		Deactivation

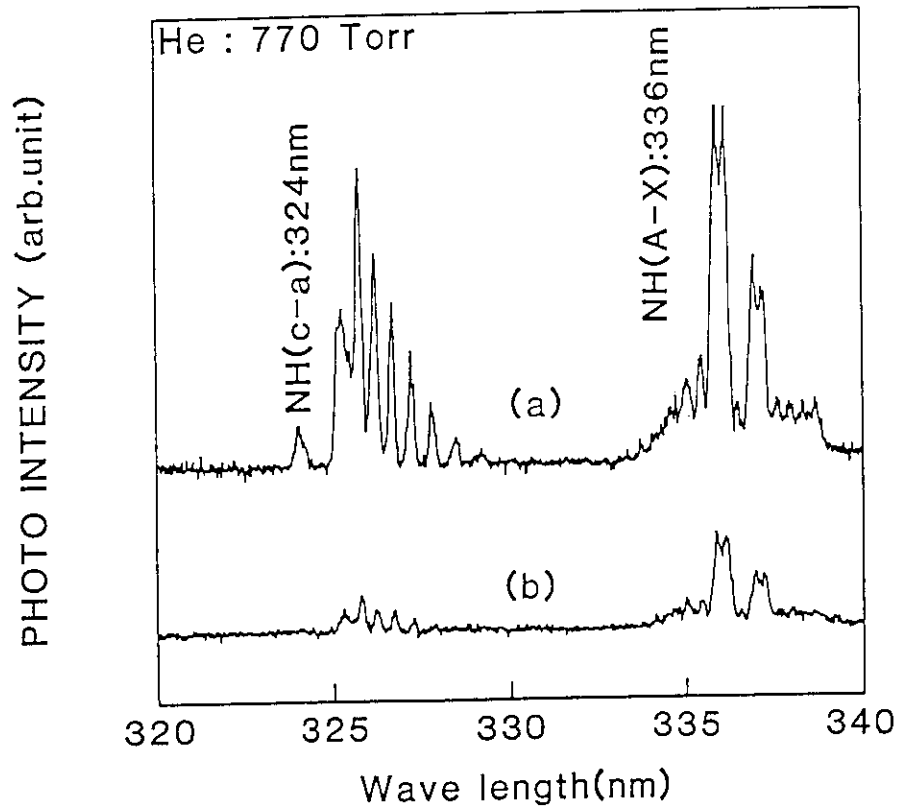


Fig. 1 Emission spectra of NH (c-a) and NH (A-X) under electron impact ; pressure of helium, 770 Torr ; partial pressure of ammonia, 0.057 Torr(a) and 0.95 Torr(b).

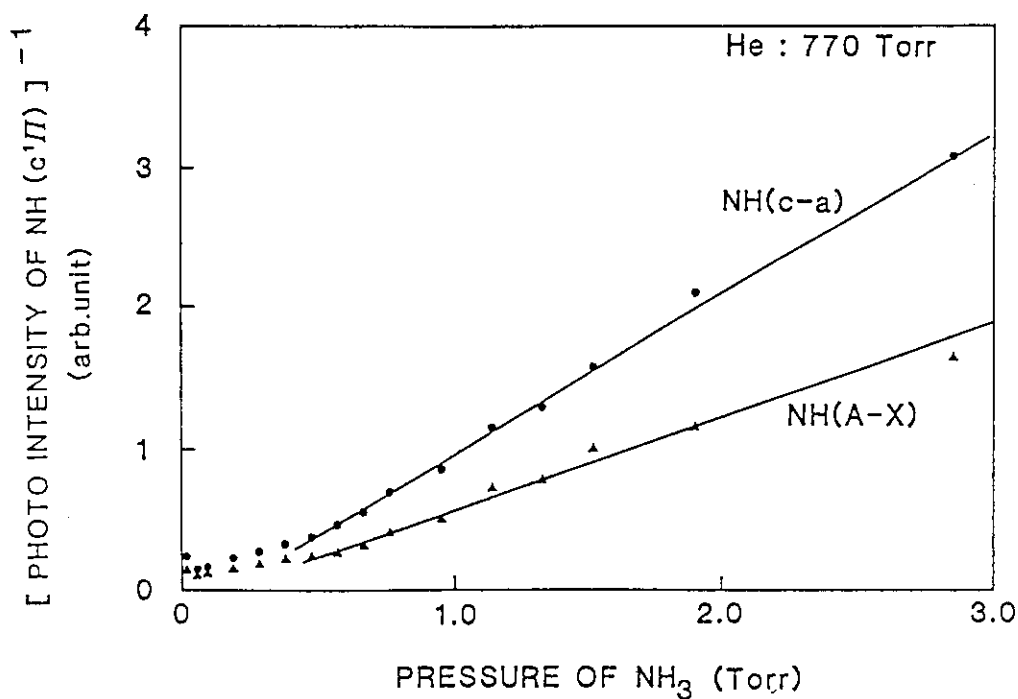


Fig. 2 Reciprocals of emission intensities NH(c-a) and NH(A-X) as a function of NH<sub>3</sub> pressure.

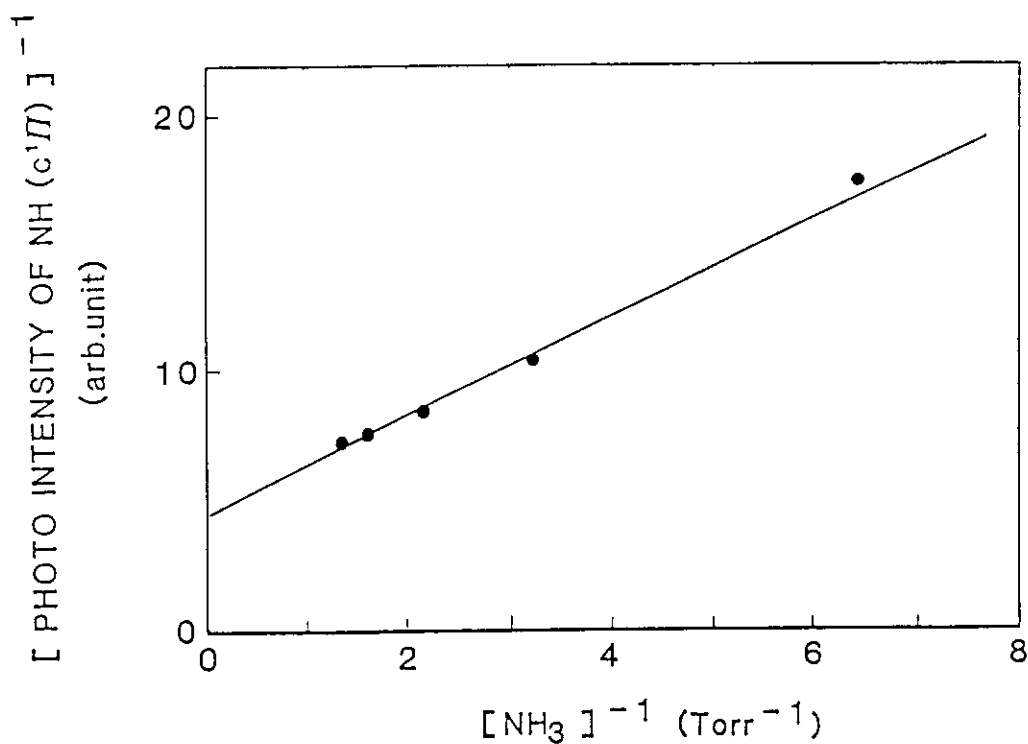


Fig. 3 Reciprocal of emission intensity of NH(c-a) as a function of reciprocal of [NH<sub>3</sub>]

## III. LIST OF PUBLICATIONS

## 1. Published Papers

- 1....Ka. Hayashi, J. Takezaki, T. Okada, and I. Sakurada, "Radiation-Induced Polymerization of Methyl Methacrylate and Alkyl Acrylates at High Dose Rate", *J. Appl. Polym. Sci.*, 36, 295(1988).
- 2....S. Sugimoto, S. Nagai, and M. Hatada, "Fischer-Tropsch Reaction on Iron Catalysts Prepared by Electron Beam Implantation on Kapton Film", *Appl. Surface Sci.*, 35, 388 (1988-89).
- 3....K. Ogawa, H. Tamura, M. Hatada, and T. Ishihara, "Spectroscopic Evaluation on Photosensitive Langmuir-Blodgett Films Using Multichannel Spectrophotometer", *Jpn. J. Appl. Phys.*, 27, 1492(1988).
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- 5....K. Ogawa, H. Tamura, M. Hatada, and T. Ishihara, "Study of Photo-reaction Processes of PDA Langmuir Films", *Langmuir*, 4, 903 (1988).
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- 11...Y. Shimizu, S. Sugimoto, and N. Suzuki, "Photoinduced Selective Synthesis of Ethylene Glycol from Methanol in the Presence of Hydrogen Peroxide", Chem. Lett., 333(1988).
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#### Reviews

- 14...K. Sumita, H. Yamaoka, T. Kakuta, Y. Shouno, T. Nakamura, Y. Nakase, and J. Furuta, "Radiation Hardened Equipment and Material Data Base" J. Nucl. Soc. Japan, 30, 370(1988).
- 15...S. Nagai, K. Matsuda, "Plastic Dosimeter", Development and Application of Solid Radiation Dosemeter (1988).

#### Patent Applications

- 16...K. Kaji, M. Hatada, I. Yoshizawa, and K. Komai, "Modification of Polyolefin Foam of Open Cell Type", Japan Kokai 63-172496.
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- 18...S. Sugimoto, Y. Shimizu, and N. Suzuki, "Preparation of Methyl Formate", Japan Kokai, 63-148467.

## 2. Oral Presentations

- 1....T. Okada, T. Asano, M. Hatada, J. Takezaki, and K. Ochi, "Electron Beam Curing of Epoxy Resin in the Presence of Cyclic Ethers", The 34th Symposium on Polymer Science (Kobe), Jul. 8, 1988.
- 2....Y. Shimizu, S. Sugimoto, and N. Suzuki, "Photochemical Reaction of Methanol with Hydrogen Peroxide", The 56th Annual Meeting (Spring) of the Chemical Society of Japan (Tokyo), Apr., 1988.
- 3....S. Sugimoto and M. Hatada, "Fischer-Tropsch Catalytic Activity of electron Beam Implanted Solid Surface from Iron Pentacarbonyl Silane-Argon Mixture", The 41st Discussion Meeting on Colloid and Surface Science (Sendai), Sep. 30, 1988.
- 4....Y. Shimizu, S. Sugimoto, S. Kawanishi, and N. Suzuki, "Photochemical Reaction of Methanol with Hydrogen Peroxide (II) Selective Synthesis of Methyl Formate", The 57th Annual Meeting (Fall) of the Chemical Society of Japan (Sendai), Sep. 30, 1988.
- 5....T. Okada, T. Asano, J. Takezaki, M. Hatada, and K. Ochi, "Electron-Beam Curing of Epoxy Oligomer in the Presence of Tetrahydrofuran", International Meeting on Ultra-violet and Electron Beam Curing(Tokyo), Oct. 30, 1988.
- 6....K. Matsuda, T. Kijima, "300 keV Electron Depth Dose Distribution in Multilayer Slab Absorbers", International Meeting on Ultra-violet and Electron Beam Curing(Tokyo), Oct. 30, 1988.
- 7....H. Tamura, K. Ueda, K. Ogawa, and M. Hatada, "Preparation of Multilayer films with Adsorption Method", The 33rd Annual Meeting of Japanese Society of Applied Physics, Sep. 30, 1988.
- 8....T. Yamamoto, Y. Doi, M. Nishii, and M. Hatada, "Radiation-Induced Cross-linking of Poly(methyl acrylate) Emulsion Particles", The 5th Discussion Meeting on Polymer Microsphere (Tokyo), Nov. 18, 1988.

## Invited Lecture

- 9....K. Kaji, "Surface Modification of Polyethylene Foam by Radiation Grafting ", The 40th Western Regional Meeting of Organization of Epikote Industries (Neyagawa), May 19, 1988.



#### IV. EXTERNAL RELATIONS

A training program for scientists and engineers in industries and government organizations was held in the laboratory as one of the courses offered by the Radio-isotope and reactor school, JAERI in Tokyo. This one week program starting Oct. 22 included lectures and laboratory experiments concerned with the radiation chemistry of polymers from basic subjects to recent application in industries. We welcomed 20 trainees this year.

Some studies in this laboratory were conducted under the cooperative agreements with Professors in Kyoto, Osaka and vicinity area:

- Prof. Y. Tsuji, Kinki University
- Prof. H. Saito, Naruto College of Education
- Prof. T. Okada, Ohita University
- Prof. K. Hatada, Osaka University
- Prof. Y. Ikada, Kyoto University

Four joint research programmes have continued this year with industrial companies listed below:

- Matsushita Electric Industries, Ltd.
- Showa High Polymer Co., Ltd.
- Seiren Co., Ltd.
- Sanwa Kako Co., Ltd.

A sponsored investigation was made under a contract with the Mitsubishi Electric Corporation.

