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(NO. 21)

April 1, 1987 - March 31, 1988

March 1990

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. 21)
# April 1, 1987 - March 31, 1988

Osaka Laboratory for Radiation Chemistry
Takasaki Radiation Chemistry Research Establishment
Japan Atomic Energy Research Institute
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(Received February 19, 1990)

This report describes research activities of Osaka Laboratory for Radiation Chemistry, JAERI during one year period from April 1, 1987 through March 31, 1988. The latest report, for 1986, is JAERI-M 88-272.

Detailed descriptions of the activities are presented in the following subjects: (i) studies on surface phenomena under electron and ion irradiations 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 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); No. 18, JAERI-M 86-051(1984); No. 19, JAERI-M 87-046(1985); No. 20, JAERI-M 88-272(1986).

Keywords: Electron Beam Irradiation, Gamma-Irradiation, Radiation Induced Reaction, Polymerization, Grafting, Polymer Modification, Radiation Chemistry, Epoxy Resin, Polyester Fiber, Krypton Ion, Fischer-Tropsch Reaction, Ethylene Glycol, Methanol, Hydrogen Peroxide, Cellulose Triacetate Film, Dosimetry

# 昭和62年度日本原子力研究所大阪支所年報（No.21）
1987年4月1日－1988年3月31日

日本原子力研究所高崎研究所
大阪支所

（1990年2月19日受理）

本報告書は，大阪支所において昭和62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，電子イオン照射下の界面現象に関する基礎研究，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。

日本放射線高分子研究協会年報，Vol.1（1958／1959）－Vol.8（1966）.

日本原子力研究所大阪支所における放射線化学の基礎研究，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 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）；No.18，JAERI－M 86－051（1984）；No.19，JAERI－M 87－046（1985）；No.20，JAERI－M 88－272（1986）.

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## CONTENTS

III. LIST OF PUBLICATIONS

# 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 mergerd 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 radiation chemistry at interface which was initiated in 1983 in an attempt to elucidate chemical reaction at interface under radiation including ions. Adsorption and desorption of gases at solid surface under electron- and ion-impact were the main interest of this subject, since they will help understand the phenomena occurred on the first wall surface of present-day and future nuclear fusion reactors. Most of the study has continued in the Takasaki Radiation Chemistry Establishment.

Study to prepare catalytic surface by electron beam doping technique has continued using a mixture of iron pentacarbonyl and argon as doping gas, and it was found that more homogeneous distribution of iron aggregates was obtained by addition of silane in the doping gas.

Krypton ion beam generated by the low energy ion generator which was installed in the previous year was irradiated on polymer films such as Kapton, polyester, or cellulose triacetate, and chemical change induced by the ion bombardment was investigated by RBS and change of UV and IR spectra.

As a survey experiment for study on organic chemical reactions induced by laser beam, illumination of methanol containing hydrogen peroxide with a low pressure mercury arc has been carried out, and it was found that ethylene glycol was obtained with high selectivity and high quantum yield.

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 colaboration with industrial companies in Osaka-Kyoto area and vicinity.

Grafting of acrylic acid onto polyethylene foam material has continued in order to give hydrophillic properties to the foam, and it was found that a foam of excellent hydrophilic properties was obtained by grafting of low degrees.

A study has been carried out on dynamic mechanical properties of electron-beam cured bisphenol A type epoxy resins prepared by the method developed in the previous year and it was found that the epoxy resins thus cured are of highly cross-linking density.

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

The study has been carried out in order to evaluate the dose absorbed in a thin layer substance when it was exposed to an electron beam, and different depth-dose curves in the extremely thin layer were obtained depending on backing material, indicating that the backscattering from the backing materials is important for precise dosimetry of the film substance.

January 22nd, 1990

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

# II. RECENT RESEARCH ACTIVITIES

## 1. Catalytic Activity of Iron Doped Kapton Film by Electron Beam Irradiation of Iron Pentacarbonyl-Silane-Argon Gas Mixture

In the previous reports, we described that Kapton film or a-silicon surface showed catalytic activity for Fischer-Tropsch reaction when the surface was doped with iron using electron beam doping technique using doping gas containing argon and iron pentacarbonyl. This year, the studies have continued on Kapton surface doped with iron using the doping gas added with silane which will react to form silicone fine particles during irradiation and the fine particles thus formed is expected to prevent iron from aggregation and to help deposited iron in more dispersed state.

Experimental procedures are the same as those described in the previous report. Argon containing small amount of iron pentacarbonyl and silane was irradiated in an irradiation vessel which contains a slip of Kapton film or a silicon plate with an electron beam (0.8 MeV, 2 mA) for 3,600 sec. The iron deposited solid surface was examined by an SEM.

The iron deposited solid was transferred to a catalytic reaction vessel, and hydrogen-carbon monoxide gas mixture was circulated through the vessel. Concentrations of hydrocarbon products accumulated in the circulating gas were analyzed by gaschromatographic method at a certain time interval.

In Fig. 1, yields of hydrocarbon products are plotted as a function of reaction time, the reaction temperature being changed from 254 to 304 °C by 4 steps during the course of the reaction. The reaction products were first detected at 268 °C, and the yields of the products increased linearly with time. The rate of product formation increased with increasing temperature. It is noted that unsaturated compounds were produced more favorably than corresponding saturated compounds.

Distributions of hydrocarbon products formed on the Kapton film surface implanted with iron with or without silane are compared in Table 1. It is noted that the surface implanted with silane shows higher activity than the one implanted without silane for all hydrocarbon products and shows higher selectivity toward olefin product(about 4 times as high as the latter).

Change of product distribution with reaction time is shown in Table 2. Selectivity toward methane increased with increasing reaction time. The selectivity toward ethylene decreased with time, but still the yield of ethylene is larger than that of ethane.

In Fig. 2, the catalytic activity is plotted as a function of irradiation time for electron beam doping. The activity to form methane, ethylene and propylene decreased with irradiation time,but the activity to form ethane did not change with the irradiation time, and distribution of hydrocarbon products becomes similar to that observed for the surface implanted without silane. The reason for this may be that the prolonged irradiation results in aggregation of iron particles.

The catalytic activity is plotted as a function of accelerating voltage during electron beam doping in Fig. 3, where it is evident that the activity toward methane decreased with acceleration voltage, but those toward other hydrocarbon products did not depend on the acceleration voltage.

In Fig. 4, secondary electron micrographs of Kapton surface implanted from doping gas with and without silane are shown in Fig. 4 a and b, respectively. The size of the particles is not uniform for both cases, but it is recognized that average size of the former is larger than the latter. The difference found between the two may be one of the reasons that the both surfaces gave different distribution of hydrocarbon products.

Similar experiment was carried out on a-silicon surface using doping gas containing silane, and the result is shown in Table 3. The activity and selectivity of the hydrocarbon products are close to those observed for Kapton film implanted with silane.

Preliminary test was carried out on a silicon surface which had been irradiated with 35 kV krypton ion for 90 min through 5 μm thick iron foil which was in contact on the a-silicon surface. The activity was almost the same as those observed for the surface implanted with iron under the presence of silane, but the selectivity toward ethylene found in this test was the highest among those found in a series of the experiments (Table 4). This may indicate that the accelerated krypton ion (35 kV) has enough energy to displace iron atom from lattice to inject it on a-silicon surface and chemical active surface can be obtained by this technique.

(S. Sugimoto and M. Hatada)

Table 1 Distribution of hydrocarbon products formed on the Kapton film surface implanted with iron with or without the presence silane

| | $CH_4$ | $C_2H_4$ | $C_4H_6$ | $C_3H_6$ | $C_2H_4/C_2H_6$ |
|---|---|---|---|---|---|
| 5%$SiH_4$-Ar | 0.0290*<br>(58.6)** | 0.0084<br>(17.0) | 0.0007<br>(1.4) | 0.0062<br>(12.5) | 12.2 |
| Ar | 0.0045<br>(77.3) | 0.0003<br>(6.0) | 0.0001<br>(2.1) | 0.0002<br>(3.1) | 2.9 |

* μmol/l reactant/10cm²Kapton/min.

** Hydrocarbon content(%).

Irradiation Condition : 0.8MV,2mA,1,800sec,gas flow rate 30ml/min.

F·T reaction condition: CO:$H_2$=1:4, 750Torr, 284℃ .

Table 2 Change of hydrocarbon product distribution with reaction time on the ion implanted Kapton film

| | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_2H_4/C_2H_6$ |
|---|---|---|---|---|---|
| 1 | 0.0297*<br>(53.1)** | 0.0103<br>(18.5) | 0.0008<br>(1.5) | 0.0058<br>(10.5) | 12.0 |
| 2 | 0.0420<br>(58.7) | 0.0131<br>(18.3) | 0.0013<br>(1.8) | 0.0066<br>(9.3) | 10.2 |
| 3 | 0.0437<br>(59.3) | 0.0134<br>(18.2) | 0.0016<br>(2.1) | 0.0068<br>(9.2) | 8.5 |
| 4 | 0.0439<br>(58.5) | 0.0139<br>(18.6) | 0.0019<br>(2.6) | 0.0066<br>(8.8) | 7.2 |
| 5 | 0.0478<br>(60.1) | 0.0141<br>(17.7) | 0.0019<br>(2.4) | 0.0066<br>(8.3) | 7.4 |

* μmol/l reactant/10cm²Kapton/min.

** Hydrocarbon content (%).

Irradiation condition : 0.8MV, 2mA, 3,600sec, gas flow rate 30ml/min.

F·T reaction codition : CO:$H_2$=1:4, 750Torr, 304℃.

Table 3 Distribution of hydrocarbon products formed on the silicone plate implanted with iron

| | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_2H_4/C_2H_6$ |
|---|---|---|---|---|---|
| 5%$SiH_4$-Ar | 0.0115*<br>(66.2)** | 0.0023<br>(13.4) | 0.0003<br>(1.5) | 0.0012<br>(7.3) | 8.7 |

* $\mu$mol/l reactant/10cm$^2$Kapton/min.

** Hydrocarbon content (%).

Irradiation condition : 0.8MV, 2mA, 1,800sec. gas
flow rate 30ml/min.

F・T reaction condition : CO:$H_2$=1:4, 750Torr, 305℃.

Table 4 Catalytic activity of silicone surface implanted with iron by the irradiation of 35 kV Krypton ion through 5 μm iron foil attached on the silicone surface

| | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_2H_4/C_2H_6$ |
|---|---|---|---|---|---|
| 5μIron foil | 0.0177*<br>(63.4)** | 0.0047<br>(16.7) | 0.0002<br>(0.7) | 0.0021<br>(7.5) | 23.4 |

* $\mu$mol/l reactant/10cm$^2$Kapton/min.

** Hydrocarbon content (%).

Irradiation condition : 35kV, $Kr^+$ ion, 90min.

F・T reaction condition : CO:$H_2$=1:4, 750Torr, 305℃.

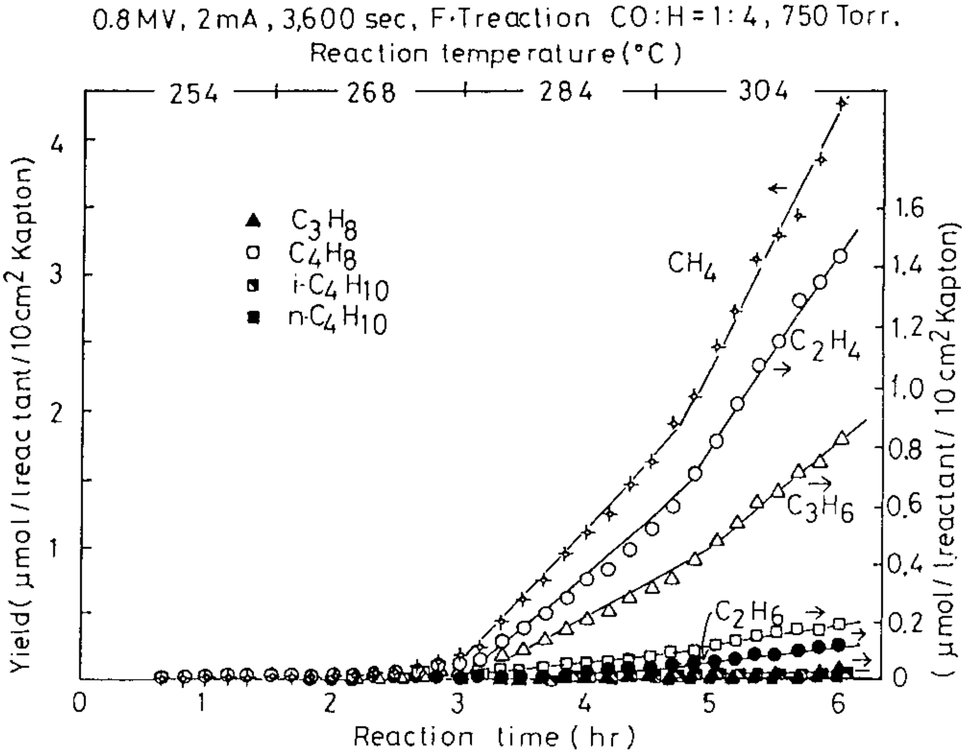


Fig. 1 Yields of hydrocarbon products formed on the Kapton film surface implanted with iron plotted as a function of reaction time.

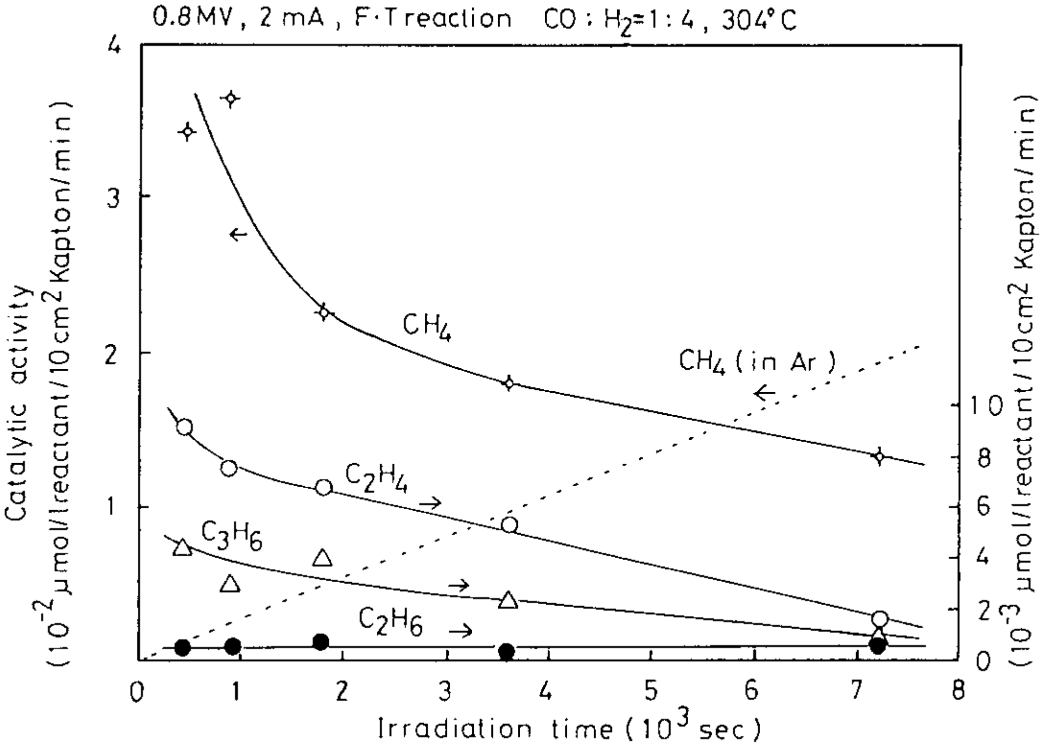


Fig. 2 Catalytic activity plotted as a function of irradiation time during electron beam doping.

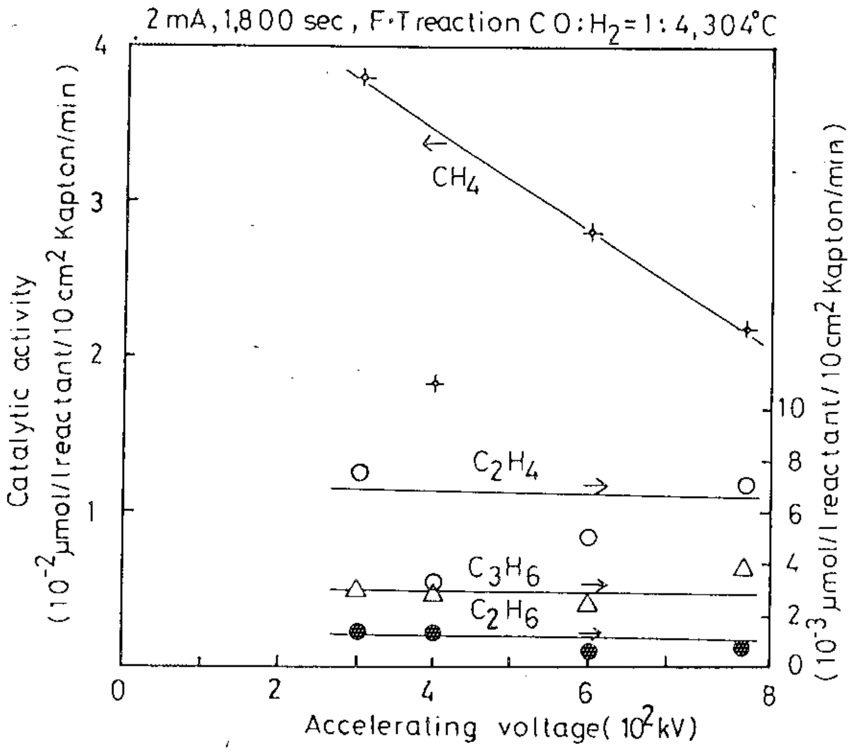
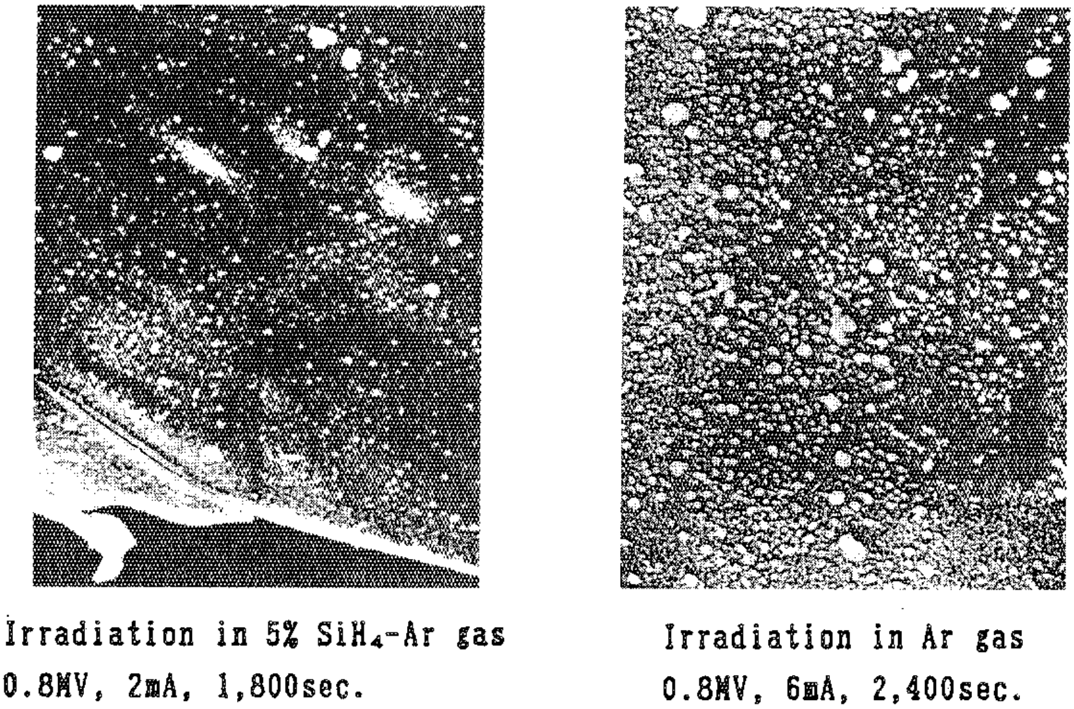


Fig. 3 catalytic activity plotted as a function of accelerating voltage during electron beam doping.


**Irradiation in 5% SiH₄-Ar gas**
**0.8MV, 2mA, 1,800sec.**

**Irradiation in Ar gas**
**0.8MV, 6mA, 2,400sec.**

Fig. 4 SEM photograph of Kapton surface implanted from doping gas with or without presence of silane.

## 2. Irradiation of Krypton Ion into Polymer Films

The importance of the dose evaluation was reported previously in the study of surface modification of polymer films by ion-irradiation, and carbonization of the sample surface also took place due to the loss of nitrogen and oxygen in the experiment of Kapton film by $Kr^+$-irradiation(1).

In order to evaluate the dose of irradiated $Kr^+$ at this carbonizing region, the dosimetry films, such as cellulose triacetate(CTA) and polyethylene terephthalate(PET) tape, were used here.

Ion-irradiation apparatus characterized as low energy ion generator(LEIG) is constructed newly for this investigation, where ion energy is less than 35 keV, and has no special mass-filteration device.

Figure 1 shows the block diagram of LEIG, composed of power supply, vacuum system with ion generator and instrumentation. Two ion guns with accerelation(ion-extraction) voltage up to 35 keV are prepared, one for the solid ionization material(LEIG-I) and the other for the gas(LEIG-II). Another ion gun with accerelation voltage up to 5 keV is also set-in for surface-sputtering of the sample. Sputtered fragments are analyzed by the quadrupole mass spectrometer up to 200 amu.

The $Kr^+$ beam intesity is electrically measured by Faraday cup, by the Ti-foil plane target(shutter), and also by calorimetry, where temperature change of the sample surface during and after $Kr^+$-irradiation is measured through the $CaF_2$ window by IR thermometer at 7.9 ± 0.15 μm wave length.

Figure 2 shows the surface temperature of the sample and its simulation counting with the in-put energy by $Kr^+$, the energy loss into the sample by heat conduction, and the energy loss by radiation from the sample surface. Appropriate values from the references are taken as thermal conduction, emissivity and heat capacity.

There is remarkable difference between the experimental and simulation data, which may indicate the presence of extra heat loss from the surface during $Kr^+$-irradiation.

In order to clarify this descrepancy, the mass spectroscopy of sputtered materials is performed during $Kr^+$-irradiation.

Figure 3(A) shows the partial pressure of mass atoms numbering with 1 amu(H), 12 amu(C), and 16 amu(O), indicating the maximum at the beginning of irradiation(less than 30s), followed by monotonous decrease in each mass numbers. This result shows the occurrence of chemical bond dissociation such as C-C, C-O, C-H, which causes the deviation of experimental data from the simulation, shown in Figure 1. It became clear now that the bond cleavage energy makes a large temperature drop at the surface of the ion-irradiated sample.

Figure 3(B) shows the partial pressure of the mass atoms numbering with 1 amu(H), 12 amu(C), 16 amu(O), and 84 amu(Kr), by $Ar^+$-irradiation of the $Kr^+$-irradiated PET sample. At the beginning of $Ar^+$-sputtering, partial pressure of Kr atoms released increases and gives a maximum, indicating the storage of Kr atoms at the surface layer of PET sample. The delayed appearance of partial pressure maxima of C, H, and O suggest the occurrence of the carbonization at the surface of the sample during $Kr^+$-irradiation.

Rutherford Backscattering Spectroscopy(RBS) is performed by $He^{++}$(2.275MeV) at 100° of grazing detector angle, and the depth profile of Kr atoms in PET sample is analyzed to give the maximum concentration of Kr atoms at about 50 nm depth from the surface. $Kr^+$-irradiated PET and CTA films contain Kr atoms within 150 nm depth, and the surface coloured metallic brown.

The transmission of light is examined in both samples of PET and CTA irradiated by $Kr^+$(35 keV), and the doses were estimated as $43.3\mu A/cm^2 \times 120s(=5.2mC)$, and $75\mu A/cm^2 \times 60s(=4.5mC)$, respectively.

Figure 4(A) shows the relationship between optical density(OD) and wave length at the several positions of $Kr^+$-irradiated CTA, indicating no special absorption behavior except the total increase of OD.

Figure 4(B) shows also the similar relationship in the sample of PET, compared to CTA.

Figure 4(A&B) show only the OD change in the range of 270~340nm in CTA, and 310~420nm in PET, but the similar result is obtained in the range of visible light(350~800nm) in both samples. It may be possible to evaluate the dose from the increase of OD, at 280nm in CTA and at 340nm in PET.

Figure 5 shows the relationship between OD-increase of $Kr^+$-irradiated PET and atomic concentration of Kr in relation to C concentration, obtained from the analysis of RBS data as mentioned above.

Roughly speaking from a small number of experimental data , the Kr-concentration increase with the increase of OD, or with the dose of $Kr^+$-irradiation.

(Y.Nakase and M.Nishii)

1) Y.Nakase, JAERI-M 88-071, 1988.3.

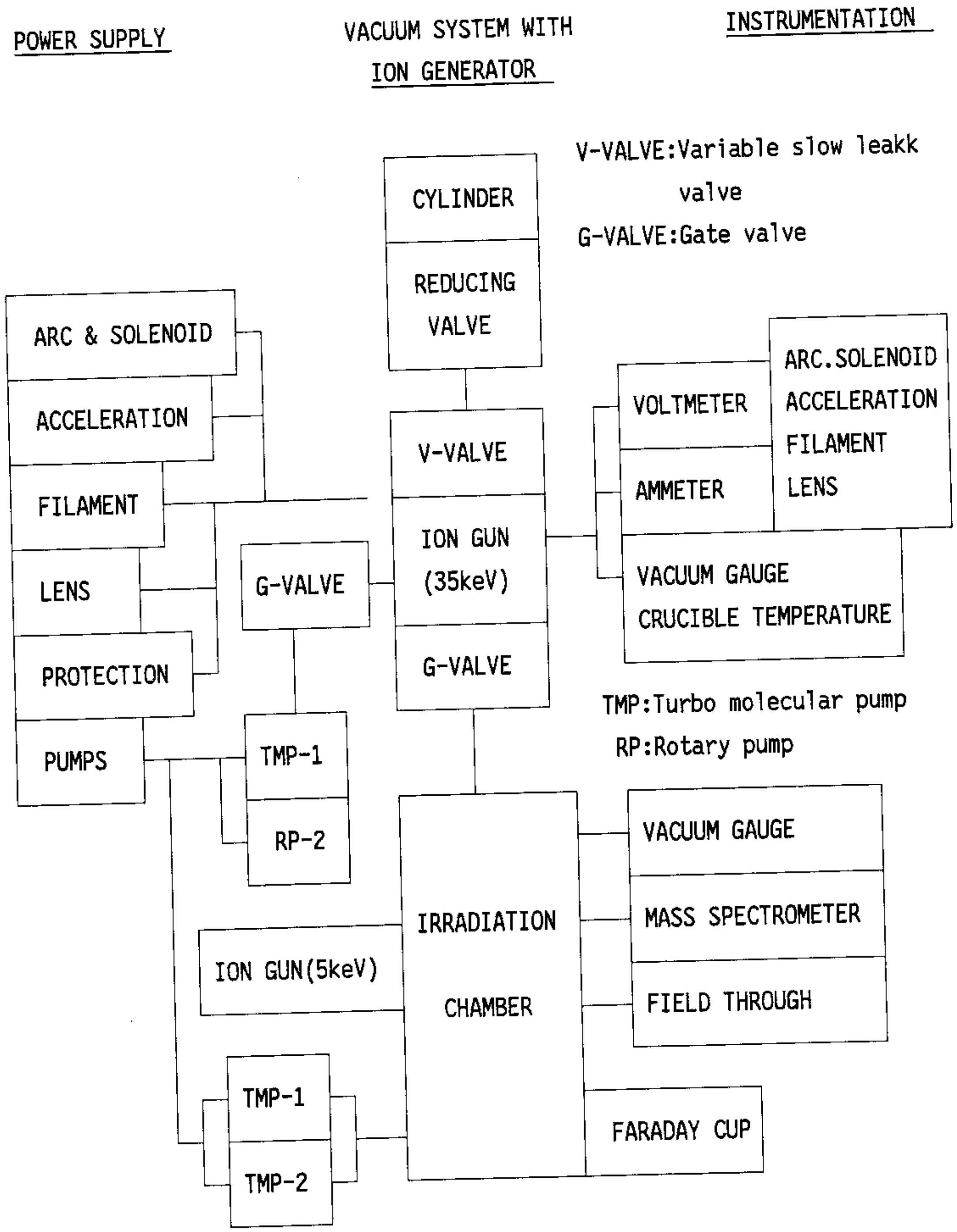


Fig. 1 Block diagram of low energy ion generator (LEIG) apparatus.

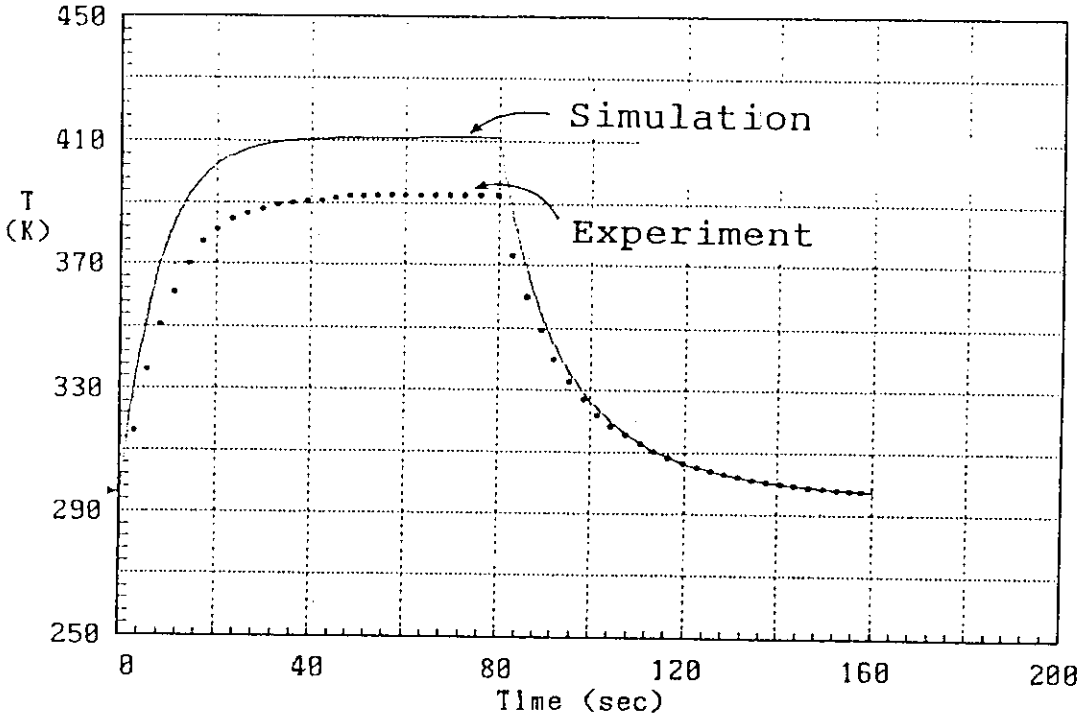


Fig. 2 Temperature change of polyethylene terephthalate film surface during $Kr^+$-irradiation.
Simulation: simulated data.
Experiment: data obtained by IR thermometer.

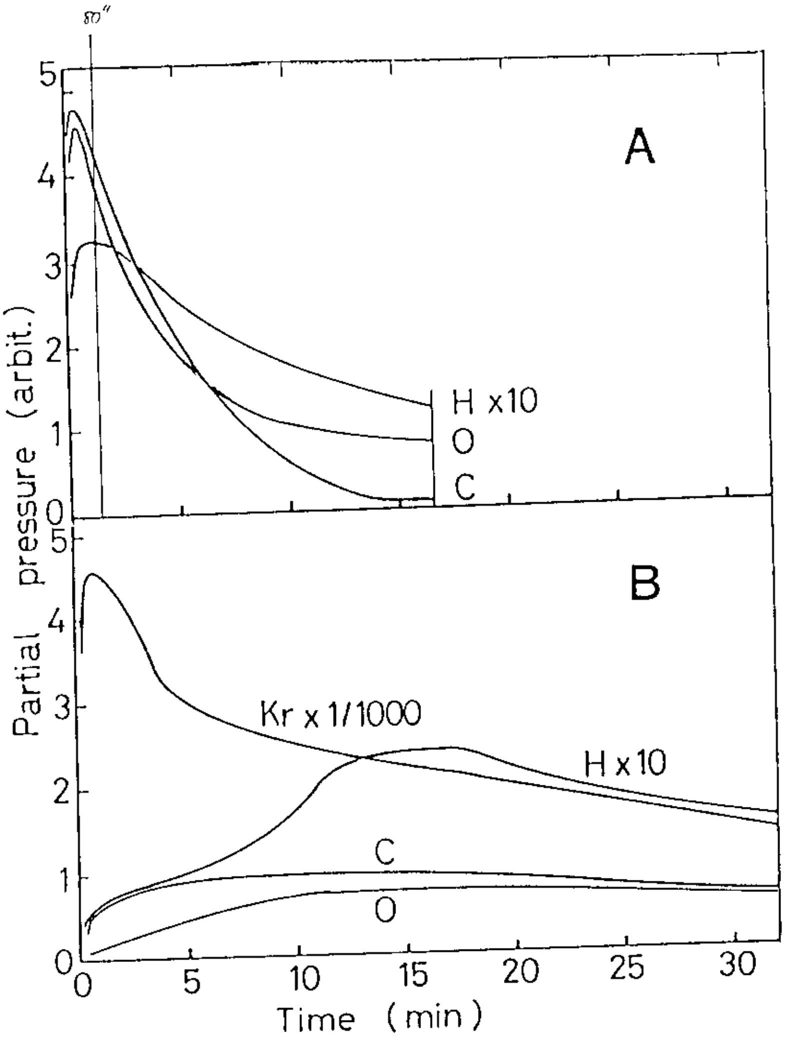


Fig. 3 Partial pressure of sputtered fragments in PET film.

A:During Kr$^{+}$ (35keV, 0.41μA/cm$^{2}$×1000s)-irradiation of the original.

B:During Ar$^{+}$ (35keV, 3.8μA/cm$^{2}$×2400s)-irradiation of the Kr$^{+}$-irradiated.

H:1 amu, C:12 amu, O:16 amu, and Kr:84 amu.

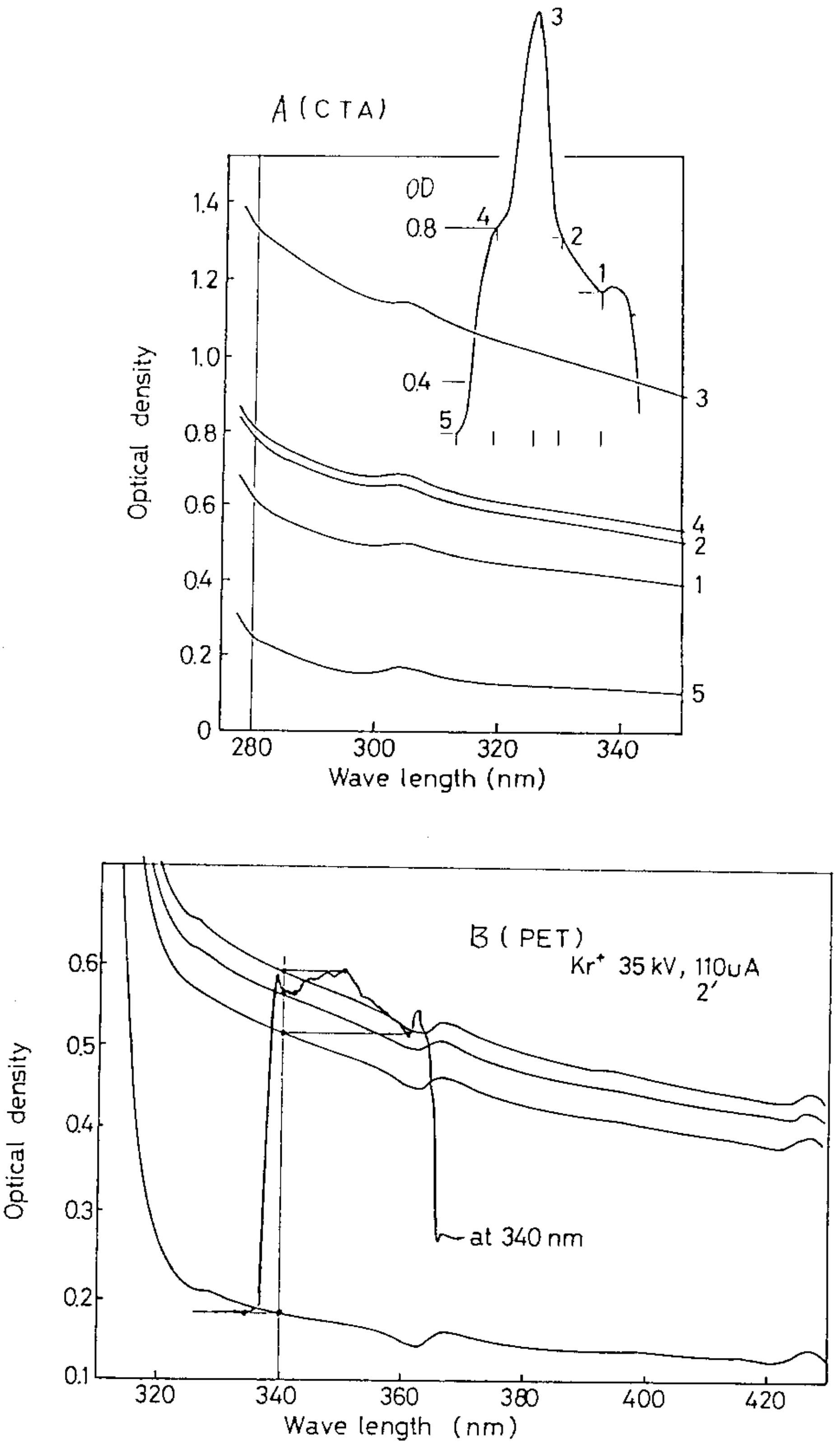


Fig. 4 Relationship between optical density of $Kr^+$ (35keV)-irradiated films and wave length.
A:CTA film(125μm t) irradiated($Kr^+$,75μA/$cm^2$×60s)
B:PET film(25μm) irradiated($Kr^+$,43.3μA/$cm^2$×120s)

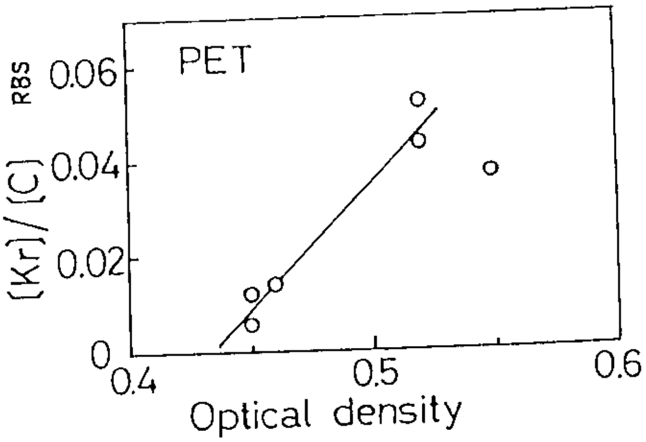


Fig. 5 Relationship between optical density and Kr atom concentration in relation to C atom concentration([Kr]/[C]) determined from RBS data. Sample:$Kr^{+}$-irradiated PET.

# 3.Photoinduced Synthesis of Ethylene Glycol from Methanol in the Presence of Hydrogen Peroxide

Ethylene glycol, present-day produced from ethylene by two steps method, is very important as a raw material of the industrial production of polyester synthetic fiber and polyester resin, and also as antifreezing agent and so on. The direct synthesis of ethylene glycol from methanol, other than petrochemicals, has been investigated in the presence of organic peroxides such as di-t-butyl peroxide,[1,2] but the selectivity for the ethylene glycol formation is not satisfactory. On the other hand, photochemical reaction of methanol using rhodium complex gave high selectivity for ethylene glycol formation,[3] however, very expensive photocatalyst is required for the acceleration of this reaction. We report here a method for the photoinduced selective synthesis of ethylene glycol from methanol in the presence of hydrogen peroxide.

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 well-bubbled with nitrogen (99.9%) in order to remove oxygen. The $N_2$-saturated methanol was stirred magnetically (500 rpm), and irradiated with a 120 W low pressure mercury lamp (Eikosha EL-J-120, mainly 253.7 nm). Aqueous 30% hydrogen peroxide (1 ∿ 8 $ml \cdot h^{-1}$, 0.01 ∿ 0.10 $mol \cdot h^{-1}$) 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 ($3.38 \times 10^{18}$ $photons \cdot s^{-1}$) from the low-pressure mercury lamp was determined using a ferrioxalate actinometer ($0.006\ mol \cdot dm^{-3}$)[4] under the same conditions as the reaction. Products were analyzed by gas chromatographs (Shimadzu GC-7A: Porapak Q column, GC-4C: Porapak N column, and GC-3BT: Molecular sieve 5A column).

When methanol in the presence of hydrogen peroxide was irradiated, ethylene glycol was produced as a major product and methyl formate, ethanol, acetaldehyde, formaldehyde, formic acid, hydrogen, carbon dioxide, carbon monoxide and methane as minor products.

Figure 1 shows the concentrations of main organic products as a function of irradiation time in the case of 5 $ml \cdot h^{-1}$ of $H_2O_2$ feed rate. The concentration of ethylene glycol increased with irradiation time and was much large compared with other products. For example, when methanol was irradiated for 7 h, the concentration of ethylene glycol was 102.1 mmol and those of other products were less than about 7 mmol. On the other hand, when methanol alone was irradiated in the absence of $H_2O_2$, organic products were hardly produced even in the case of 7 h irradiation.

Figure 2 shows the effect of $H_2O_2$ feed rate on the amount of formed ethylene glycol and the selectivity. The concentration of ethylene glycol increased with $H_2O_2$ feed rate, and become the maximum at 5 $ml \cdot h^{-1}$ of $H_2O_2$ feed rate. The selectivity of ethylene glycol formation decreased from 97.8% at 1 $ml \cdot h^{-1}$ of $H_2O_2$ feed rate to 79.5% at 8 $ml \cdot h^{-1}$. When the concentration of formed ethylene glycol gave the maximum value, the selectivity was ca. 90.9%. Thus the concentration of ethylene glycol and the selectivity were affected markedly by $H_2O_2$ feed rate. It was found from these results that ethylene glycol is selectively synthesized when methanol was irradiated with u. v. light in the presence of $H_2O_2$.

Table 1 shows the effect of $H_2O_2$ feed rate on the quantum yield $\Phi$ of ethylene glycol formation. The quantum yield of etylene glycol formation increased with $H_2O_2$ feed rate and become the maximum ($\Phi = 0.73$) at 5 $ml \cdot h^{-1}$ of feed rate.

It is well known that $H_2O_2$ is easily decomposed by u. v. light irradiation to form hydroxyl radical.5) The effect of thiocyanate ion, which is an efficient scavenger of hydroxyl radical,6) on ethylene glycol formation has been examined, in order to elucidate an initiating species of ethylene glycol formation. Ethylene glycol formation was almost perfectly suppressed by the addition of 0.02 mmol of thiocyanate ion. It is concluded from these facts that hydroxyl radical is an initiating species of ethylene glycol formation.

It is also known that hydroxyl radical reacts rapidly with methanol to form hydroxymethyl radical,$^{7)}$ which is rapidly dimerized to form ethylene glycol in the absence of oxygen.$^{8)}$ Therefore, it can be considered that the ethylene glycol formation proceeds efficiently through the quick dimerization of hydroxymethyl radicals formed by the abstraction of α-position hydrogen of methanol by hydroxyl radical as follows.

$$H_2O_2 \xrightarrow{h\nu} 2\cdot OH \qquad (1)$$

$$CH_3OH + \cdot OH \longrightarrow \cdot CH_2OH + H_2O \qquad (2)$$

$$2\cdot CH_2OH \longrightarrow (CH_2OH)_2 \qquad (3)$$

Scheme 1.

The decrease in ethylene glycol formation in higher $H_2O_2$ feed rate may be mainly attributed to the scavenzing of hydroxyl radical by $H_2O_2$.$^{9)}$

It should be noted as a new method for direct synthesis of ethylene glycol from methanol that ethylene glycol is selectively synthesized by u. v. light irradiation of methanol in the presence of $H_2O_2$.

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

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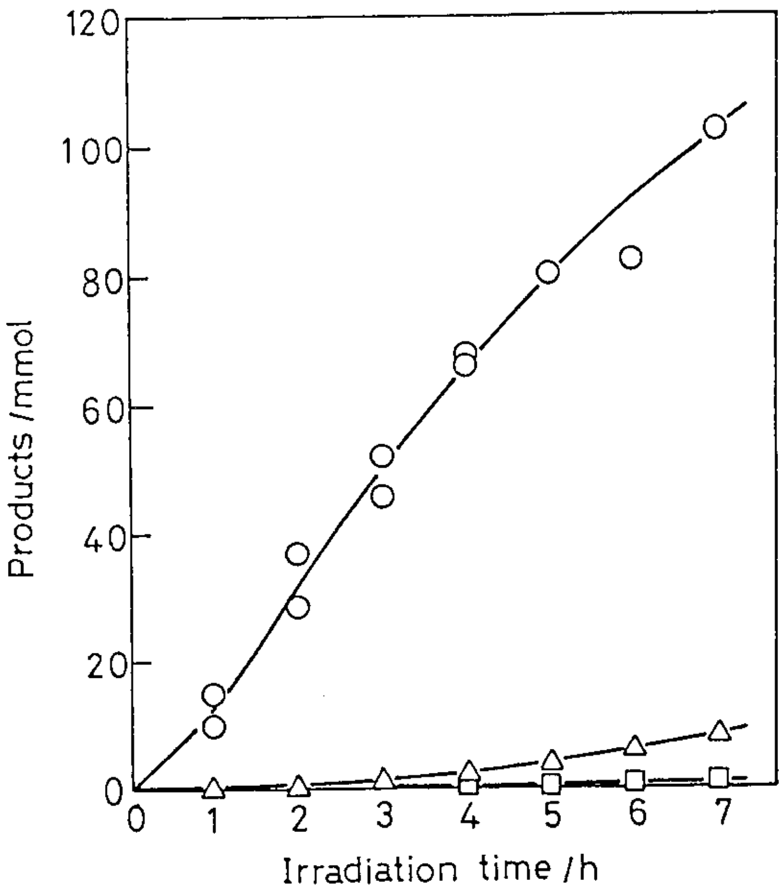

Fig. 1 Main organic product yield as a function of irradiation time for the u. v. light irradiation of methanol in the presence of hydrogen peroxide at 25°C. $CH_3OH$: 225 ml, $H_2O_2$ : aqueous 30% $H_2O_2$, $H_2O_2$ feed rate: 5 $ml \cdot h^{-1}$. (○) Ethylene glycol, (△) Methyl formate, (□) Ethanol

Table 1 Effect of feed rate of hydrogen peroxide on the yield and the selectivity for ethylene glycol.[a]

| $H_2O_2$ feed rate[b] mℓ $h^{-1}$ | Φ[c] | selectivity[c] % |
|---|---|---|
| 1 | 0.35 | 97.8 |
| 2 | 0.50 | 97.4 |
| 3 | 0.71 | 94.4 |
| 5 | 0.73 | 90.9 |
| 6 | 0.68 | 86.3 |
| 8 | 0.62 | 79.5 |

[a] Low pressure mercury lamp(120W), $CH_3OH$: 225 mℓ, Temperature: 25 ℃.

[b] Aqueous 30% $H_2O_2$.

[c] Irradiation time: 7 h.

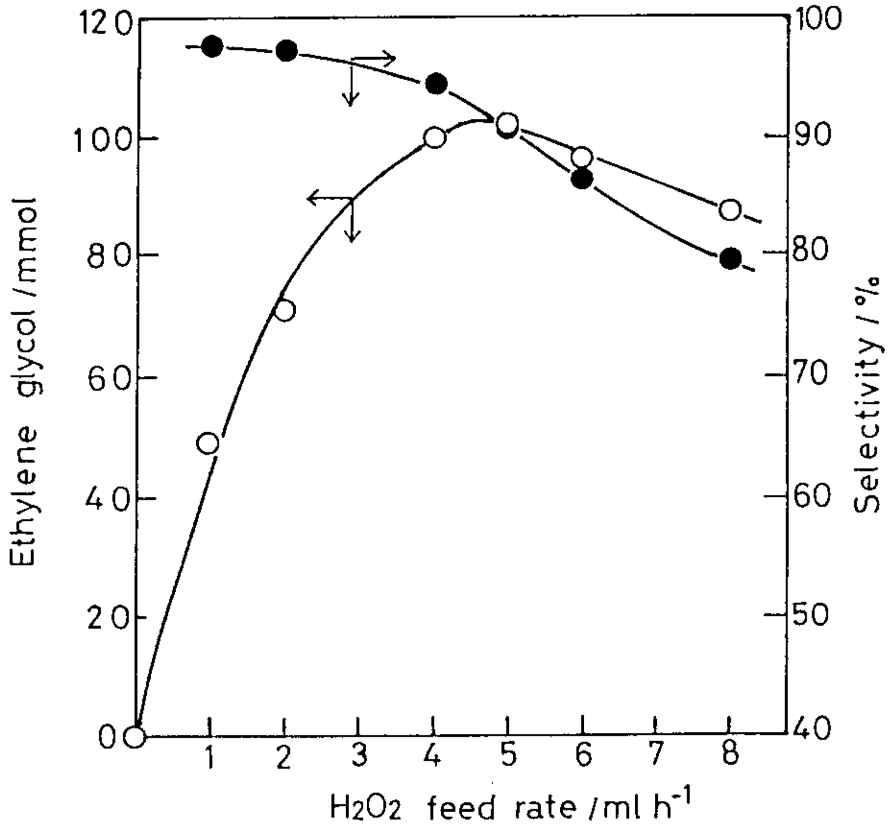

Fig. 2 Effect of $H_2O_2$ feed rate on the amount of formed ethylene glycol and the selectivity.

## 4. Dynamic Mechanical Properties of Electron Cured Epoxy Resins

Studies have been carried out on dynamic mechanical properties as a function of gel content during electron beam curing of bisphenol A epoxy oligomers. Samples were prepared by the method described in the previous report 1). Epikote 828 casted in an aluminum frame was irradiated on a conveyer traveling under the irradiation window of a Van de Graaff electron accelerator. The traveling velocity of the sample was 0.48 m/min. The gel contents were 69, 81, 91, 95, and 98% at dose of 2, 5, 7.5, 10, and 15 Mrad, respectively. IR examination of the sample revealed that the amounts of ether and hydroxy groups increased with increasing dose. The content of epoxy group, which was 43 % before irradiation, decreased with increasing dose, but it was 26.5 % even after 42.5 Mrad irradiation.

Dynamic mechanical properties were measured with a free oscillation torsion pendulum (Rhesca 110AD). The frequency of the oscillation was adjusted to be within the range of 0.05-0.5Hz. The temperature range between -160 °C and 250 °C was studied. The samples were heated at a rate of 0.7 °C/min.

In Fig. 1, the shear modulus and tan $\delta$ are plotted as a function of temperature for samples obtained at four different doses. The shear modulus at 25 °C and that at 40 °C above glass transition temperature were determined from the curves in Fig. 1(upper curves) and designated as $G_{25^\circ C}$ and $G_{Tg+40\ C}$, respectively. The Tg can be determined from large peaks appeared between 103 and 107 °C in the tan and temperature curves. The small peak appeared at a temperature around -75 °C is assigned as $\beta$ relaxation peak, which is correlated to movement of bisphenol skeleton or of hydroxy ether chain. The latter assignment seems to be supported in the recent studies 2). These dynamic mechanical data of the specimens cured at different doses along with gel fractions are summarized in Table 1.

The shear modulus at glassy state, $G_{25^\circ C}$, for the samples cured at 10 Mrad, was 1.4 X $10^{10}$ dyn/$cm^2$ and decreased with increasing dose to 1.1 X $10^{10}$ dyn/$cm^2$ at 42.5 Mrad.

Shear modulus in rubbery state, $G_{Tg+40\,^{\circ}C}$ of the sample obtained by curing at lower doses increased with increasing temperature as predicted by rubber elasticity theory. The shear modulus in the rubber state was the highest for the specimen cured with 10 Mrad. The samples cured with lower doses contain non-network structures and unreacted epoxy groups. Therefore, molecular segments which are not included in the network structure reacts as cross-linking reagent to increase the density of cross-linking when the temperature increased during the dynamic mechanical measurement. On the other-hand, the samples cured with large dose, e.g., 42.5 Mrad, little or no cross-linking proceeded during the dynamic mechanical measurement. Since scission of molecular chain of epoxy oligomer occurs simultaneously with cross-linking during irradiation, the shear modulii at room temperature and at rubbery state decrease with increasing dose. This was supported by the fact that the glass transition temperature decreased with increasing dose. The temperature at which beta peak appears also slightly decreased with dose.

Effect of heat treatment after electron beam irradiation is described below. The result of measurement of dynamic mechanical properties are shown in Fig. 2 for the sample containing 1 % initiator which was irradiated with electron beam and for the same sample but with heat-treatment at 130 °C for 0.5 hours in air after irradiation. The results of the same measurement on the sample containing 8 % initiator are shown in Fig. 3. From both measurements, it is evident that electron irradiation without further treatment can not cure the sample completely, and heat-treatment after the electron beam irradiation is necessary for complete curing. The electron irradiated samples without further heat-treatment contains oligomer that is not included in the network structure and is thermally cured during measurements of dynamic mechanical properties. These samples show complex temperature dependence on shear modulus and loss factor. The dynamic mechanical characteristic values obtained from the curves in Figs. 2 and 3 are also summarized in Table 1. When one compares the data obtained for heat-treated sample containing 8 % initiator to that containing 1 %, the former showed higher glass transition temperature and higher shear modulus in glassy and rubbery states than the latter. This indicates that the sample containing 8 % initiator cured in higher degree or almost completely.

It is known that the network of epoxy resins thermally cured using tertiary amines as catalyst is exclusively composed of ether bond. The curing was carried out on Epikote 828 containing 10 phr 2,4,6-tris(dimethylaminomethyl)phenol at 80 °C for 2 hrs followed by additional heating at 180 °C for 6 hrs. The $G_{25\,^\circ C}$, $G_{Tg+40\,^\circ C}$, and Tg are reported to be $10.5 \times 10^{10}$ dyn/cm$^2$, $1.2 \times 10^{8}$, and 124 °C 3). The comparison of these values with the corresponding values listed in Table 1 reveals that the electron beam cured resins and those with further cured thermally showed the shear modulus in rubber state and Tg which are similar to or considerably higher than those obtained for catalytic cured resins. This indicates that heat-treatment after irradiation at room temperature is effective method to obtain the cured sample of high cross-linking density.

Shimpo, et al.4) reported that cured resins obtained by UV irradiation at 100 °C in the presence of UVE-1014 initiator showed Tg of 186 °C and its shear modulus at rubber state was extremely higher than that obtained for cured resins by conventional catalytic thermal method. Therefore, it is expected that the electron irradiation at high temperature gives cured resins of high cross-linking density.

(K. Ochi, T. Okada, and J. Takezaki)

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Table 1 Dynamic mechanical data of EB-cured epoxy resins

| initiator | Dose | H.T.* | Gel | $G_{25°C}$ | $G_{Tg+40°C}$ | β-peak | $T_g$ |
|---|---|---|---|---|---|---|---|
| % | Mrad | °C, h | % | x $10^{10}$ dyne/$cm^2$ | x $10^{8}$ dyne/$cm^2$ | °C | °C |
| 3.9 | 10 | -- | 95 | 1.4 | 2.7 | -76 | 107 |
| 3.9 | 15 | -- | 98 | 1.3 | 2.4 | -75 | 105 |
| 3.9 | 35 | -- | 99 | 1.1 | 2.3 | -75 | 103 |
| 3.9 | 42.5 | -- | 100 | 1.0 | 2.0 | -72 | 103 |
| 1.0 | 6 | -- | 86 | 1.2 | 4.6 | -86 | - |
| 1.0 | 6 | 130, 0.5 | 98 | 1.1 | 3.1 | -79 | 121 |
| 8.0 | 6 | -- | 92 | 1.35 | 2.5 | -86 | - |
| 8.0 | 6 | 130, 0.5 | 98 | 1.2 | 4.0 | -79 | 153 |

H.T.*: Heattreatment after EB-irradiation

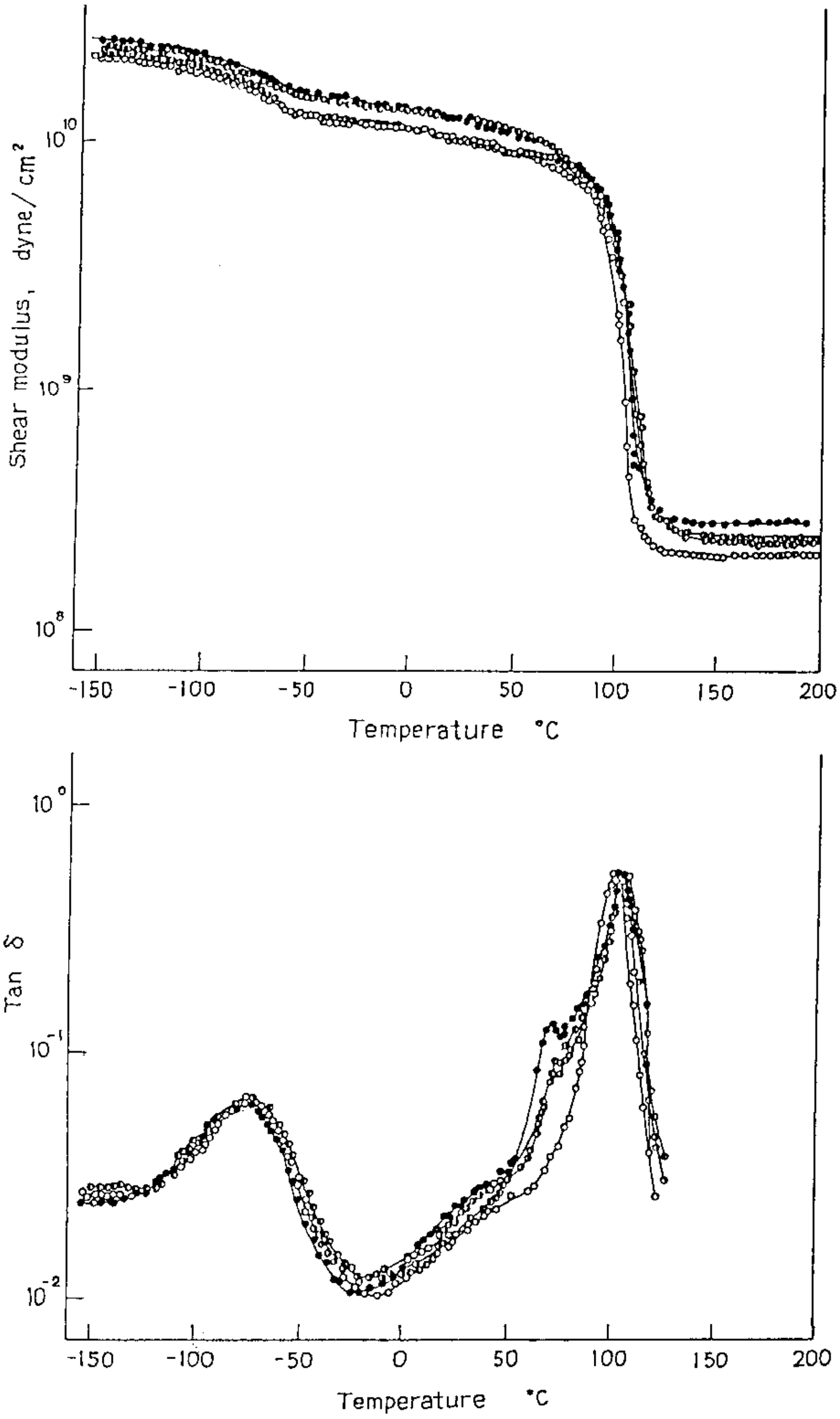

Fig. 1 Dynamic mechanical properties of EB-cured epoxy oligomer. Initiator: UVE-1014 3.9 %, Irradiation dose: (●), 10 Mrad; (◑), 15 Mrad; (◐), 35 Mrad; (○), 42.5 Mrad.

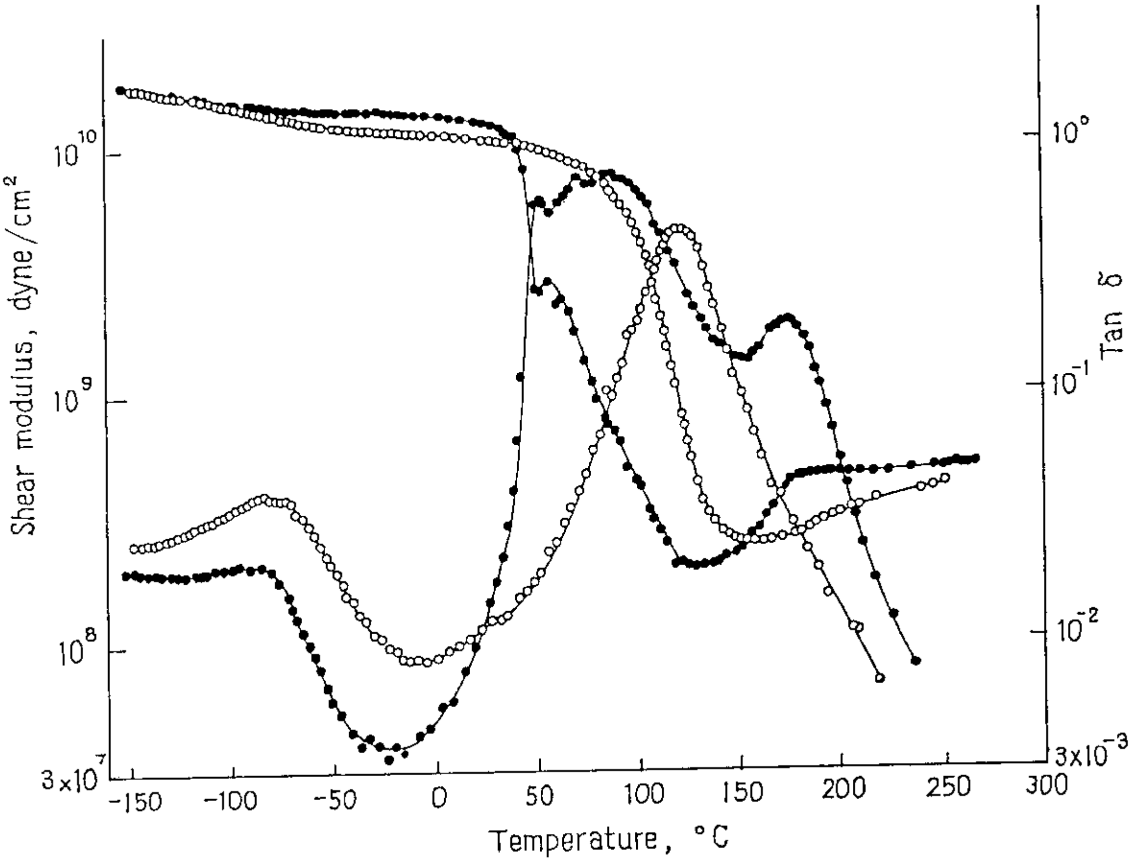

Fig.2 Effect of heat-treatment on the dynamic mechanical properties of EB-cured epoxy oligomer.
Initiator: UVE-1014 1 %, dose 6 Mrad. (●), without heat-treatment; (○), heat-treated at 130°C and for 0.5 h.

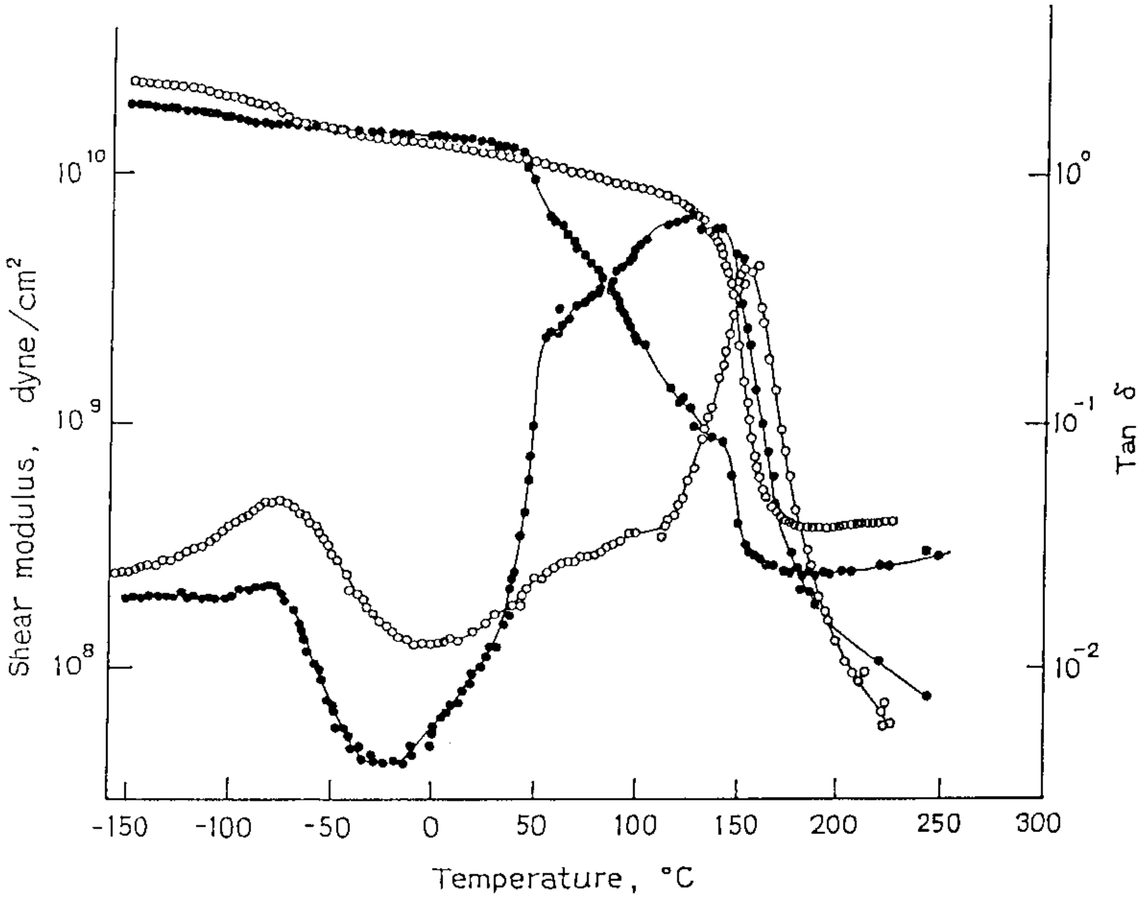

Fig.3 Effect of heat-treatment on the dynamic mechanical properties of EB-treated epoxy oligomer.
Initiator: UVE-1014 8 %, dose 6 Mrad. (●), without heat-treatment; (○), heat-treated at 130°C and for 0.5 h.

## 5. Distribution of Graft Poly(Methacrylic Acid) in Polyester Fiber

In our former studies on radiation-induced grafting on polyethylene[1-5] and poly(ethylene telephthalate) [6,7], we reported that depth distribution of grafted functional group is an important factor which governs properties of grafted surface. Studies have been carried out in an attempt to reveal the radial distribution of concentration of functional group of grafted polyester fiber at near surface region up to 1 μm below the surface by etching method. Surface of the grafted polyester fiber is hydrolyzed by alkali-treatment successively, and dyability of the etched surface at every hydrolysis step was examined by spectrophotometry. This method developed for this purpose has advantages in that the functional group concentration distribution near surface can be obtained precisely by selecting the etching conditions, and that the method can be applied to obtain polyester fiber having functional groups at high surface concentration, which is also the purpose of the present studies.

Fabric woven by polyester(PET)mono-filament (diameter 45 μm) is washed with water containing non-ionic detergent and then dried for 3 minutes at 110 or 130 ° C (samples are abbreviated as PET-110 and PET-170). Commercially available methacrylic acid and ethylene dichloride(EDC) were of first grade and specially pure grade, respectively, and were used as received.

The washed PET fabric was cut to a rectangular sheet, and immersed in EDC-methanol solution at certain temperatures and for certain time, and then the swelling degree was calculated using following equation:

$$\text{swelling degree(vol\%)} = \frac{d_{PET} \times w_{solv}}{d_{solv} \times w_{PET}} \times 100$$

where $d_{PET}$ and $d_{solv}$ are densities of PET and solvent, respectively, and $w_{PET}$ and $w_{solv}$ are weights of PET and solvent, respectively. Pre-swollen PET with EDC was immersed in methacrylic acid at 20 °C for 60 min, and then irradiated with electron beams from a Van de

Graaff (1.5 MeV, 50 μA, dose rate 0.9 kGy/s) in nitrogen atmosphere (dose, 60kGy). The irradiated PET fabric was washed with 10% aqueous solution of sodium bicarbonate at 85 °C for 20 min. to extract homopolymer, washed with water, dried in vacuum, weighed, and then the graft percent was calculated by the following equation:

$$\text{graft \%} = \frac{w - w_o}{w_o} \times 100$$

where w and $w_o$ are weight of grafted and the starting PET, respectively.

Alkali-treatment was carried out on the grafted PET fabric with 1 % sodium carbonate aqueous solution, the amount being equal to 200 times as much of the weight of the PET sample. The time of the treatment was 15, 30, 45, and 60 min at 90 °C. Relative amount of weight loss by the treatment was determined on the alkali-treated PET sample after washing with water, drying in air, and then drying in vacuum.

Cationic dye, Rodamine B was used for dyeing the Grafted PET and the alkali-treated PET. The following dyeing conditions were used; dyeing solution : solution containing 1 % owf Rodamine B and 0.5 ml/l 80% acetic acid; solution ratio : 1 : 200; dyeing temperature : 90 °C ; dyeing time: 30 min. The PET after dyeing was dried after washing with water.

Dyability was evaluated by (1) visual inspection and (2) by calculating Kubelka-Munk function K/S using reflectance at the wavelength giving maximum absorption (at 520 mμ) using an automatic recording spectrophotometer.

Pre-swelling treatment was carried out at 20 °C and 40 °C for 60 min using 10, 20, 30, and 40 % EDC-methanol swelling solutions. In Fig. 1, degree of swelling are plotted as a function of EDC concentration in the swelling solution. It is clear from the figure that the degree of swelling is larger at higher concentration of EDC in the swelling solution, at higher temperature of swelling treatment, and for the sample heat-treated at lower temperature. Since it was revealed that PET-110 swollen at 20 °C and PET-170 swollen at 40 °C show similar degree of swelling, PET-110 swollen at 20 °C and PET-170 swollen at 40 °C using the swelling solutions mentioned above are used as the samples to be grafted.

The results of grafting on the samples after pre-swelling treatment are shown in Table 1, where it is evident that the degrees of grafting for both PET-110 and PET-170 did not depend on the degree of pre-swelling. Comparison of grafting between PET-110 and -170 reveals that the degree of grafting depends on the pre-heat treatment. The reason why the pre-swelling does not affect the degree of grafting is that the degree of grafting levels off because monomer was consumed shortly after the grafting was initiated. We will consider this problem elsewhere.

In advance to investigate the effect of alkali-treatment on the grafted PET, it is important to know the effect of pre-swelling treatment on anti-alkali property of the PET.

The weight losses of PET-110 and PET-170 after alkali-treatment are shown in Table 2 and 3, respectively. As mentioned previously, the pre-swelling temperatures were 20 and 40 °C for PET-110 and PET-170,respectively, in order to carry out the grafting for the sample of the same degree of swelling.

It is evident from the tables, the weight losses after 1 h alkali-treatment on starting PET without pre-swelling treatment were extremely small as 0.12 % and 0.06 %, respectively, whereas the weight loss becomes larger as the EDC content in the swelling solution becomes higher for the swollen PET fabric. However, even the largest weight losses for the swollen PET-110 and -170 were 0.29 % and 0.15 %, respectively, and were slightly larger than those obtained for the original PET samples. Thus, the anti-alkali property of the PET was not lost by the pre-swelling treatment by EDC-methanol solution.

The weight losses of the grafted PET samples after alkali-treatment are shown in Table 4 (PET-110) and Table 5(PET-170), in which it is evident that the large weight loss was observed for the grafted samples, and the weight loss increased with increasing time of the alkali-treatment.

It is reported that grafting of hydrophilic monomers on PET results in decrease of anti-alkali property and weight loss results by alkali treatment[8,9]. The weight loss is caused by the hydrolysis of the polyester, and this is enhanced by the alkali-accessible structure of the fiber which is resulted by the grafting of the hydrophilic monomer. It is surprising, however, that alkali-hydrolysis occurred for the sample of only 1 % degree of grafting.

Dyability of alkali-treated PET fabric to cationic dye was investigated by (1) visual inspection and (2) spectrophotometric method. Original PET is not dyed at all with cationic dye, but the grafted PET having -COOH group of poly(methacrylic acid), most of which was converted to -COONa by alkali-treatment, can be dyed with cationic dye. Thus, relative amount of grafted methacrylic acid can be determined by measuring dyability.

Visual inspection of dyed samples in Tables 4 and 5 indicated that the sample of degree of grafting of several % can be dyed only at contamination level. But after alkali-treatment, these samples can be dyed clearly even at these low degree of grafting.

In order to evaluate the dyability semi-quantitatively, dyed density (K/S) was calculated using Kubelka-Munk function from reflectance obtained 520 mμ. The K/S value obtained for the alkali-treated grafted PET is shown in the last column in Tables 4 and 5. The K/S value for the original PET is 0. For the sample of the K/S value higher than 10 gives clearly dyed impression by the visual inspection. As shown in Tables 4 and 5, the K/S value for PET of any degree of grafting was very low when no alkali-treatment was carried out ( at 0 weight loss), but increased with increasing weight loss. However, the K/S value decreased when weight loss increased further by excess alkali-treatment. This was already confirmed by the visual inspection which was mentioned earlier.

In Figs. 2 and 3, the K/S value is plotted as a function of weight loss after alkali-treatment for PET-110 and PET-170, respectively. These plots lie on convex curves having a maximum.

Assuming that the weight loss occurred uniformly from the filament surface, the weight loss, W, is approximately given by

$$W=2\pi r_0 l \rho$$

where $r_0$ is radius of the filament, l, the depth from the surface, $\rho$, average density of the filament at near surface, and $l \ll r_0$. Thus, W on the abscissa is regarded approximately as l.

The curves convex upward in Figs. 2 and 3 indicate that the K/S value increases sharply at small weight loss and then decreased with increasing weight loss reaching the center of the filament. The area below the curves may correspond to the degree of grafting, but the correlation between the two does not always good. However, the area becomes large as the pre-swelling condition becomes severe, indicating that the surface structure of PET is modified by the pre-swelling treatment.

All these experimental results indicate that the concentration of grafted poly(methacrylic acid) becomes maximum at certain depth below the surface. The depth at which the concentration becomes maximum is estimated to be 0.2 - 0.3 μm for PET-110 and 0.05 - 0.1 μm for PET-170 filament ($2r_0$ =45 um, density=1.4). This depth dimension is too small to be studied even by an X-ray micro-analysis.

As mentioned above, the concentration of grafted methacrylic acid is low at surface and becomes maximum below the surface at near surface region. This means that the polyester filament of high surface concentration of functional group can be obtained even at extremely low degree of grafting by removing the surface area by etching and exposing the layer of maximum degree of grafting. As a fact, the grafted PET given in Table 1 is not dyed by cationic dye, but can be clearly dyed even for the sample of less than 1 % degree of grafting after alkali-treatment resulting proper weight loss.

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Table 1 Grafting of methacrylic acid onto polyester fabric by mutual irradiation method with electrons from V. D. G. accelerator; dose rate: 0.9 kGy/s; dose: 60 kGy

1) PET-110

| Sample No. | Condition of pre-swelling* | | Graft |
|---|---|---|---|
| | Concn. of EDC (%) | Degree of swelling (%) | (%) |
| 1 | non treatment | 0.0 | 4.1 |
| 2 | 10.0 | 1.6 | 4.0 |
| 3 | 20.0 | 3.8 | 5.1 |
| 4 | 30.0 | 10.7 | 3.7 |
| 5 | 40.0 | 15.1 | 4.5 |

2) PET-170

| Sample No. | Concn. of EDC (%) | Degree of swelling (%) | Graft (%) |
|---|---|---|---|
| 6 | non treatment | 0.0 | 1.4 |
| 7 | 10.0 | 0.8 | 0.4 |
| 8 | 20.0 | 6.1 | 2.0 |
| 9 | 30.0 | 11.9 | 1.6 |
| 10 | 40.0 | 19.5 | 1.1 |

* PET was pre-swollen with EDC-MeOH soln. for 60 min at 20°C and 40°C for PET-110 and for PET-170, respectively.

Table 2 Weight loss by alkali treatment for starting PET-110 pre-swollen with EDC

Condition of alkali treatment: 1% $Na_2CO_3$ aq. soln., 85°C

| Pre-swelling* | | | Alkali treatment | |
|---|---|---|---|---|
| Concn. of EDC (%) | temp (℃) | Degree of swelling (%) | time (min) | wt. loss (%) |
| non-treatment | | 0 | 30 | 0 |
| non-treatment | | 0 | 60 | 0.12 |
| 10 | 20 | 1.6 | 30 | 0.06 |
| 10 | 20 | 1.6 | 60 | 0.17 |
| 20 | 20 | 3.8 | 30 | — |
| 20 | 20 | 3.8 | 60 | — |
| 30 | 20 | 10.7 | 30 | 0.18 |
| 30 | 20 | 10.7 | 60 | 0.29 |
| 40 | 20 | 15.1 | 30 | 0.23 |
| 40 | 20 | 15.1 | 60 | 0.29 |

* swelling time: 60 min

Table 3 Weight loss by alkali treatment for starting PET-170 pre-swollen with EDC

Condition of alkali treatment: 1% $Na_2CO_3$ aq. soln., 85°C

| Pre-swelling* | | | Alkali treatment | |
|---|---|---|---|---|
| Concn. of EDC (%) | temp (°C) | Degree of swelling (%) | time (min) | wt. loss (%) |
| non-treatment | | 0 | 30 | 0 |
| non-treatment | | 0 | 60 | 0.06 |
| 10 | 40 | 0.8 | 30 | 0.0 |
| 10 | 40 | 0.8 | 60 | 0.04 |
| 20 | 40 | 6.1 | 30 | 0.0 |
| 20 | 40 | 6.1 | 60 | 0.10 |
| 30 | 40 | 11.9 | 30 | — |
| 30 | 40 | 11.9 | 60 | — |
| 40 | 40 | 19.5 | 30 | 0.10 |
| 40 | 40 | 19.5 | 60 | 0.15 |

* swelling time: 60 min

Table 4 Change of dyeability of graft PET-110 by alkali treatment

| Sample No. | Condition of pre-swelling1) | | Graft | Alkali treatment2) | | |
|---|---|---|---|---|---|---|
| | Concn. of EDC (%) | Degree of swelling (%) | (%) | Time (min) | Wt. loss (%) | K/S |
| 1 | non-treatment | 0 | 4.1 | 0 | 0 | 1.52 |
| | | | | 15 | 1.02 | 7.07 |
| | | | | 30 | 1.75 | 17.43 |
| | | | | 45 | 3.17 | 13.45 |
| | | | | 60 | 4.61 | 6.73 |
| 2 | 10 | 1.6 | 4.0 | 0 | 0 | 1.18 |
| | | | | 15 | 0.98 | 8.92 |
| | | | | 30 | 1.75 | 16.71 |
| | | | | 45 | 3.62 | 19.80 |
| | | | | 60 | 6.56 | 6.42 |
| 3 | 20 | 3.8 | 5.1 | 0 | 0 | 6.11 |
| | | | | 15 | 0.81 | 10.01 |
| | | | | 30 | 2.05 | 21.89 |
| | | | | 45 | — | — |
| | | | | 60 | 6.31 | 6.08 |
| 4 | 30 | 10.7 | 3.7 | 0 | 0 | 1.31 |
| | | | | 15 | 1.33 | 31.67 |
| | | | | 30 | 2.20 | 32.91 |
| | | | | 45 | 4.59 | 20.28 |
| | | | | 60 | 6.13 | 16.33 |
| 5 | 40 | 15.1 | 4.5 | 0 | 0 | 1.28 |
| | | | | 15 | 1.03 | 51.33 |
| | | | | 30 | 2.07 | 52.24 |
| | | | | 15 | 4.13 | 12.34 |
| | | | | 60 | 5.99 | 10.73 |

*1) PET was pre-swollen with EDC-MeOH soln. at 20°C for 60 min.
*2) Graft PET was treated with 1 % $Na_2CO_3$ aq. soln. at 90°C.

Table 5 Change of dyeability of graft PET-170 by alkali treatment

| Sample No. | Condition of pre-swelling 1) | | Graft | Alkali treatment 2) | | |
|---|---|---|---|---|---|---|
| | Concn.of EDC (%) | Degree of swelling (%) | (%) | Time (min) | Wt.loss (%) | K/S |
| 6 | non-treatment | 0 | 1.4 | 0 | 0 | 1.71 |
| | | | | 15 | 0.23 | 5.15 |
| | | | | 30 | 1.37 | 12.99 |
| | | | | 45 | 2.30 | 8.97 |
| | | | | 60 | 4.20 | 3.05 |
| 7 | 10 | 0.8 | 0.4 | 0 | 0 | 1.42 |
| | | | | 15 | 0.11 | 9.51 |
| | | | | 30 | 0.35 | 13.57 |
| | | | | 45 | 1.14 | 10.59 |
| | | | | 60 | 3.15 | 2.52 |
| 8 | 20 | 6.1 | 2.0 | 0 | 0 | 1.73 |
| | | | | 15 | 0.17 | 18.88 |
| | | | | 30 | 0.59 | 14.12 |
| | | | | 45 | 1.65 | 5.63 |
| | | | | 60 | 4.28 | 2.95 |
| 9 | 30 | 11.9 | 1.6 | 0 | 0 | 1.88 |
| | | | | 15 | 0.28 | 26.20 |
| | | | | 30 | 0.41 | 28.12 |
| | | | | 45 | 1.61 | 15.49 |
| | | | | 60 | 3.93 | 3.71 |
| 10 | 40 | 19.5 | 1.1 | 0 | 0 | 1.81 |
| | | | | 15 | 0.58 | 37.62 |
| | | | | 30 | 0.92 | 30.25 |
| | | | | 45 | 1.58 | 17.96 |
| | | | | 60 | 3.31 | 6.25 |

*1) PET was pre-swollen with EDC-MeOH soln. at 40°C for 60 min.
*2) Graft PET was treated with 1 % $Na_2CO_3$ aq. soln. at 90°C.

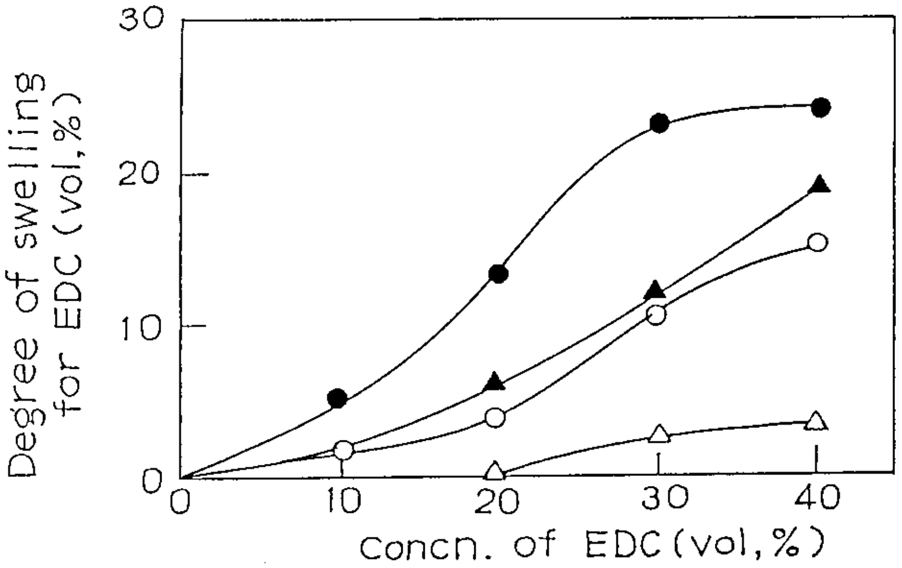

Fig.1 Degree of swelling in EDC of PET fabric; Sample: PET-110 (○,●), PET-170(△,▲);Swelling temp.: 20°C (○,△), 40°C (●, ▲); swelling time: 60 min.

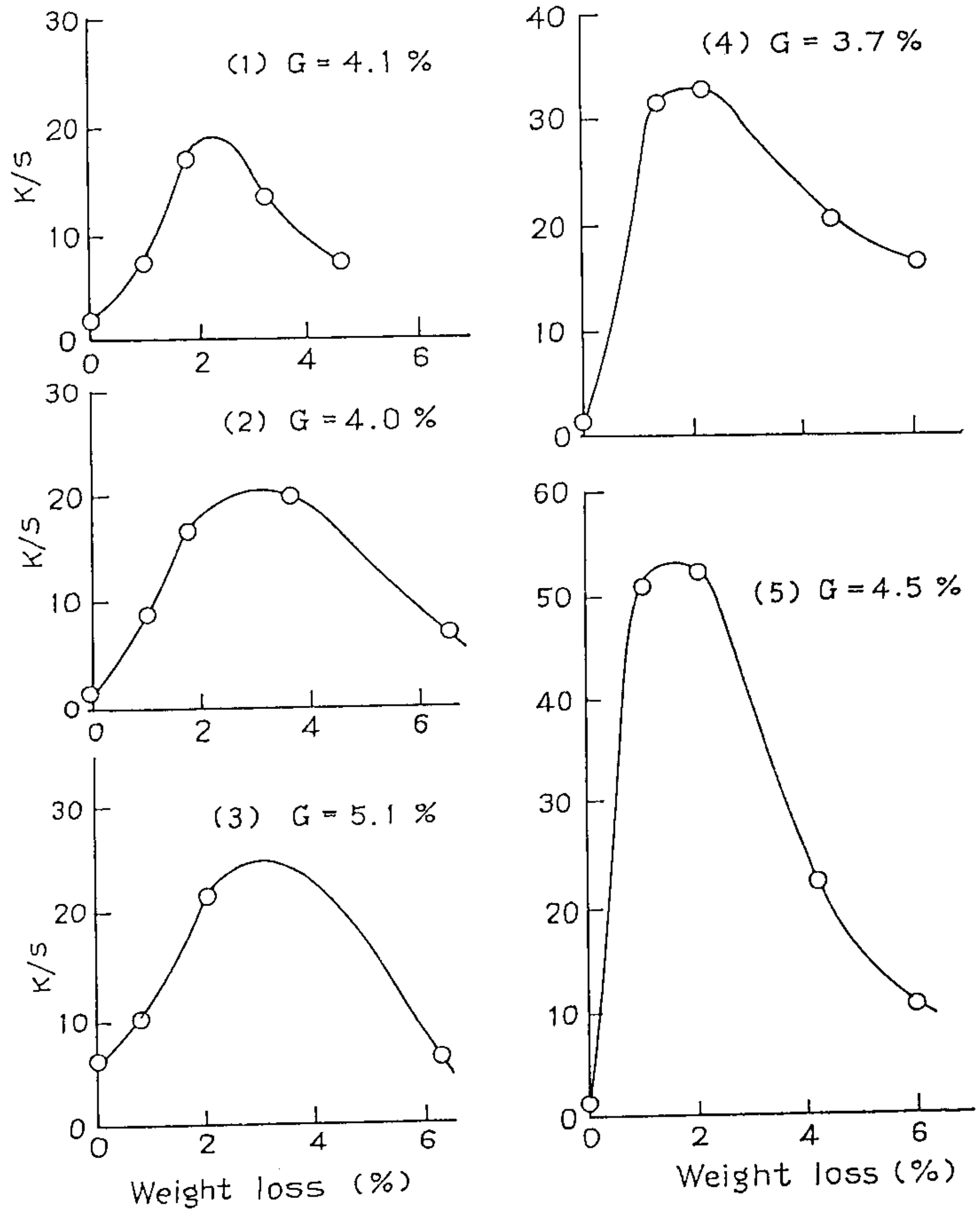

Fig.2 Relation of color intensity(K/S) and weight loss by alkali treatment for graft PET-110.

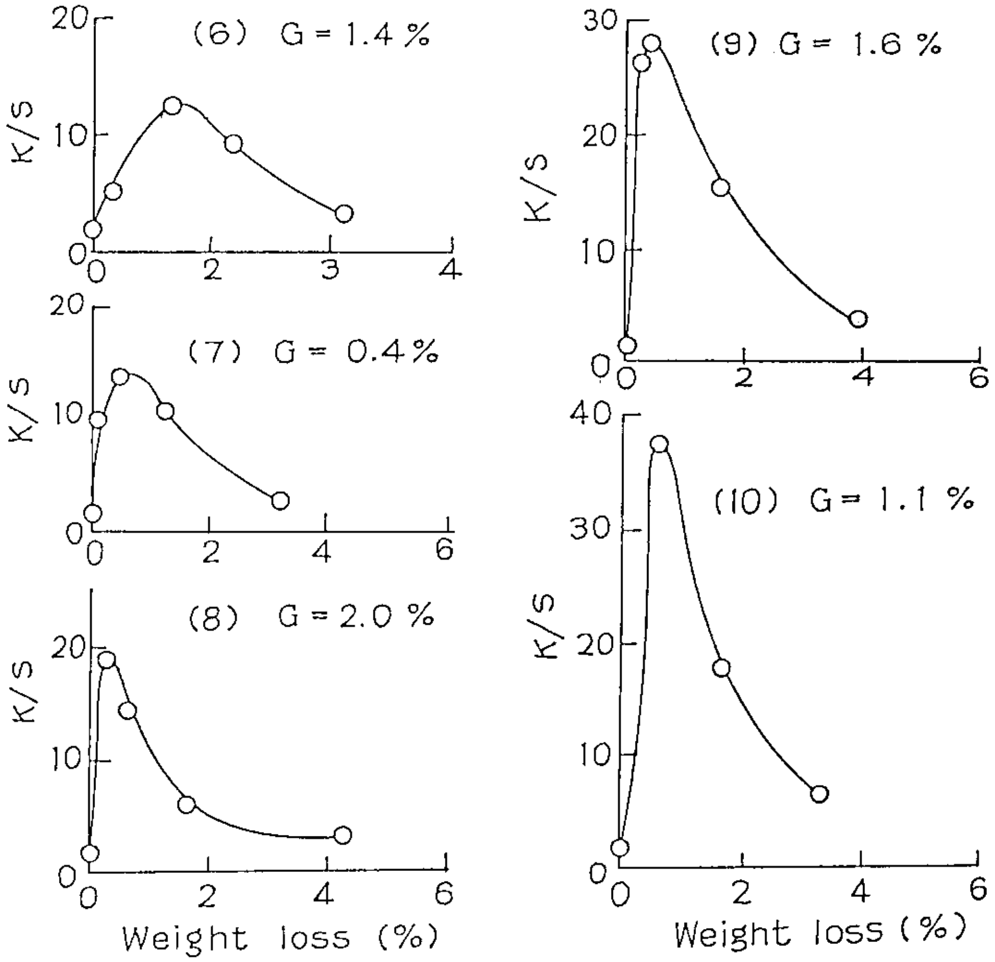

Fig.3 Relation of color intensity(K/S) and weight loss by alkali treatment for graft PET-170.

## 6. Electron Beam Irradiation of LB Films of Saturated and Unsaturated Acids

In former reports[1,2,3], we reported that Langmuir-Blodgett(LB) films of monomers can be polymerized by irradiation of high energy electron beam to give the polymer LB films which are further cross-linked by additional irradiation[1]. The monomers used in these studies were the ones which have an unsaturated bond in polar group. In this study, LB films 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 monomers having unsaturated bond in the polar end. The radiation effects on LB films of arachidic acid (ADA) was also studied.

The film 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 51, 48, and 45 mN/m for ADA, TSA, and TCA monolayers, respectively, which give the molecular area of 20 $A^2$/molecule for these monolayers. 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 µA) in nitrogen atmosphere on a cold plate cooled by running water. The dose rates were 0.02 Mrad/sec at 50 µA and 0.2 Mrad/sec at 500 µA and temperature of the sample during irradiation was below 30 °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 °C.

The changes of IR spectrum during irradiation observed for ADA, TSA, and TCA LB films are shown in Figs. 1, 2, and 3, respectively.

As shown in Fig. 1 from A through D, it was observed for the

ADA LB films that the intensities of absorption bands due to C-H stretching vibrations of methyl group ( $\nu$a:2960, $\nu$s:2860 $cm^{-1}$) , 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 C=O and C-O stretching vibrations ( $\nu$:1720, $\nu$ :1445). The progression bands due to methylene wagging and twist vibrations ( $\omega$ , $\gamma$ :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 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 C=O and C-O stretching vibrations ( $\nu$ :1720 and $\nu$ :1445, respectively), decreased with increasing dose, as was observed in the ADA LB films. The intensity of the bands due to C=C stretching vibration ( $\nu$ :1650), bands due to $=CH_2$ scissoring vibration ( $\delta$ :920), and progression bands due to wagging and twist vibrations of methylene group ( $\omega$, $\gamma$ :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 TCA LB films, as shown in Fig. 3 A through D. Similar decrease with dose was observed for the intensities of bands due to $CH_2$ stretching vibration, and bands due to C=O and C-O stretching vibrations. The intensity of C≡C stretching band ( $\nu$ :3300) and progressive bands due to $-CH_2-$ wagging and twist vibrations decreased more quickly than the other bands, indicating that the C≡C group is the most reactive.

TSA and TCA LB films turned insoluble to ethanol by 20 Mrad irradiation, indicating that the polymerization took place above this dose, but no evidence for polymerization was obtained for ADA LB films.

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

1) M. Hatada, M. Nishii, and K. Hirota, JAERI 5030, 26(1975).
2) M. Hatada and M. Nishii, J. Polym. Sci., Polym. Chem. Ed.,15, 927(1977).
3) M. Nishii and M. Hatada, JAERI 5030, 33(1975).

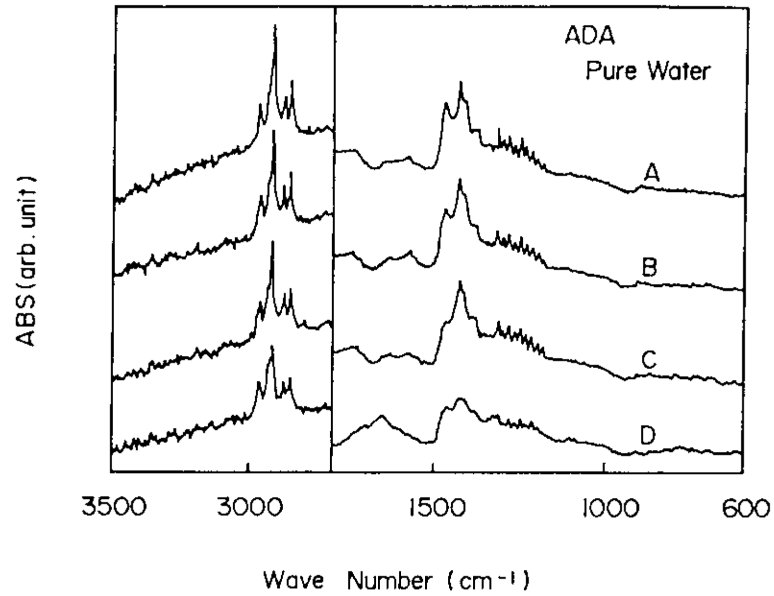

Fig. 1 Change of IR absorption spectrum of ADA LB film under electron beam irradiation; (A) 0, (B) 2 Mrad, (C) 20 Mrad, and (D) 200Mrad.

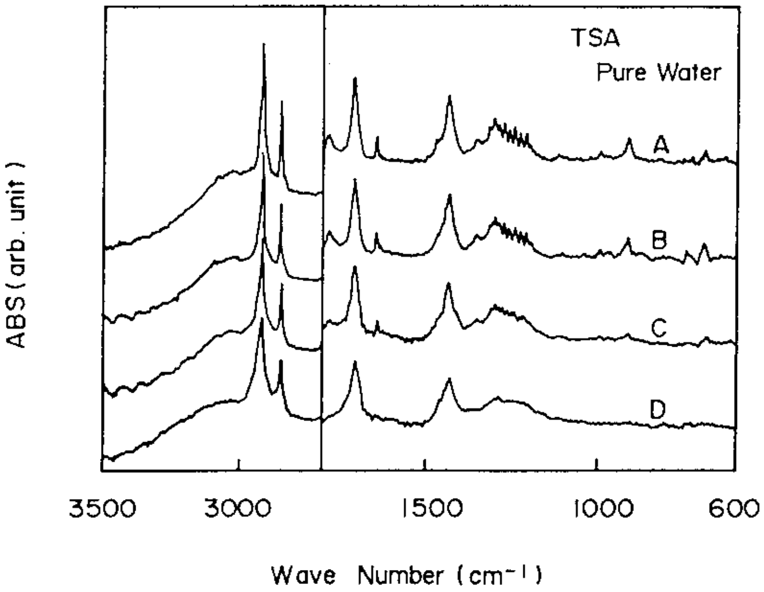

Fig. 2 Change of IR absorption spectrum of TSA LB film under electron beam irradiation; (A) 0, (B) 2 Mrad, (C) 20 Mrad, and (D) 200Mrad.

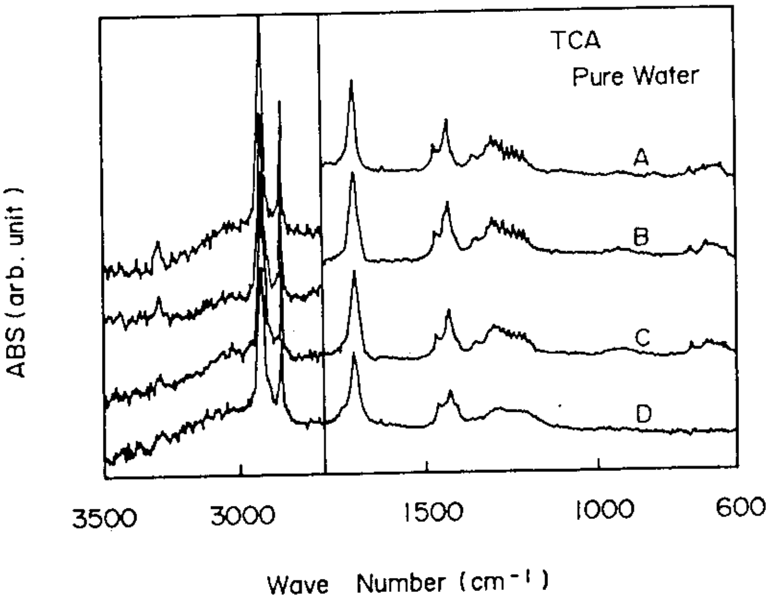

Fig. 3 Change of IR absorption spectrum of TCA LB film under electron beam irradiation; (A) 0, (B) 2 Mrad, (C) 20 Mrad, and (D) 200Mrad.

## 7. EB Dosimetry Using Thin Multi-layer Films

In the last annual report, we reported that contribution from backscattering energy from the substrate becomes important for dose measurement of thin layer substance, the thickness of which is small compared to the range of incident electrons.

This year, we have measured the depth dose distribution in three layers of air, a CTA dosimeter(cellulose triacetate multi-layer) and substrate upon which the CTA dosemeter is exposed to 300 keV electrons which come out through an irradiation window of titanium of 30 μm thick. The results were compared with curves calculated by a computation code EDMULT which was developed by Tabata, et al.

The experimental set up is the same as reported in the previous report. A stack of thin films of CTA dosemeter(thickness, 38 μm) was irradiated on a conveyer which travelled under the irradiation window perpendicular toward the direction of beam scanning.

Experimental result for a three-layer substance composed of Ti(the irradiation window, 30 μm thick), air (exists between the irradiation window and the CTA film stack, 10 cm thick), and the CTA film stack is shown in Fig. 1 along with the calculated curve. The difference between the calculated and the experimental may come from the fact that electrons impinged into Ti window with various angles from the normal to the surface in the experiment, whereas the calculation considers the only electrons that hit the surface perpendicularly.

Since EDMULT can calculate the energy dissipation in composite composed of upto three layers, we have to make assmptions of two types in order to calculate the energy dissipation in composite composed of four layers (Ti, air, CTA, and semi-infinite CTA backing material: assumption(1) is that the composite be composed of Ti, air, and semi-infinite CTA as in Fig. 2, and the other assumption(2) is a mixed layer of Ti and air, CTA thin layers and CTA semi-infinite backing layer. The results of the two calculations are shown in Fig. 3, where it is evident that the agreement between the calculations based on the two assumptions is quite satisfactory. The calculation based on assumption (2) is carried out for other backing materials.

Figure 4 summarizes both experimental and calculated energy dissipation in CTA thin layer on different backing materials from CTA to Pb. The calculated energy dissipation in the CTA thin layer agrees well with the experimental data, but the appearance of the energy dissipiation curve obtained by the calculation does not agree with the experimental curve; the calculation predicts that the energy dissipation becomes smaller as the depth increases, whereas the experimental data indicates opposite behavior. It is also noted that the energy dissipation in CTA increases as the atomic number of backing material increases. (K. Matsuda and T. Kijima)

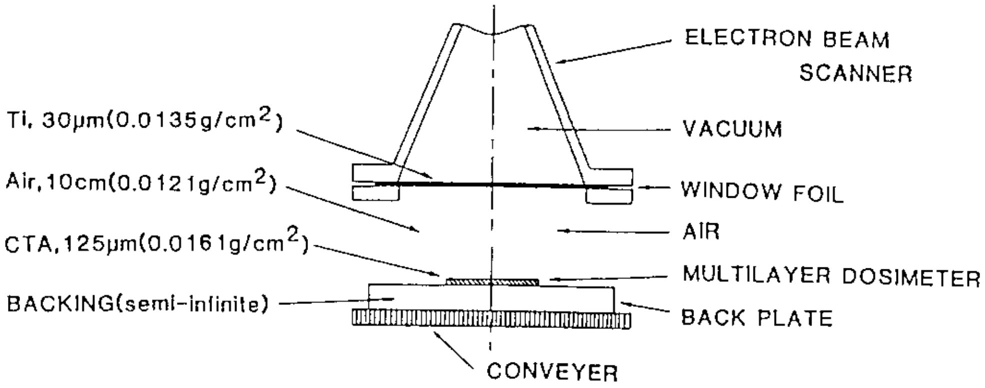

Fig. 1 Experimental set up for energy dissipation measurement of electrons on various semi-infinite backing materials.

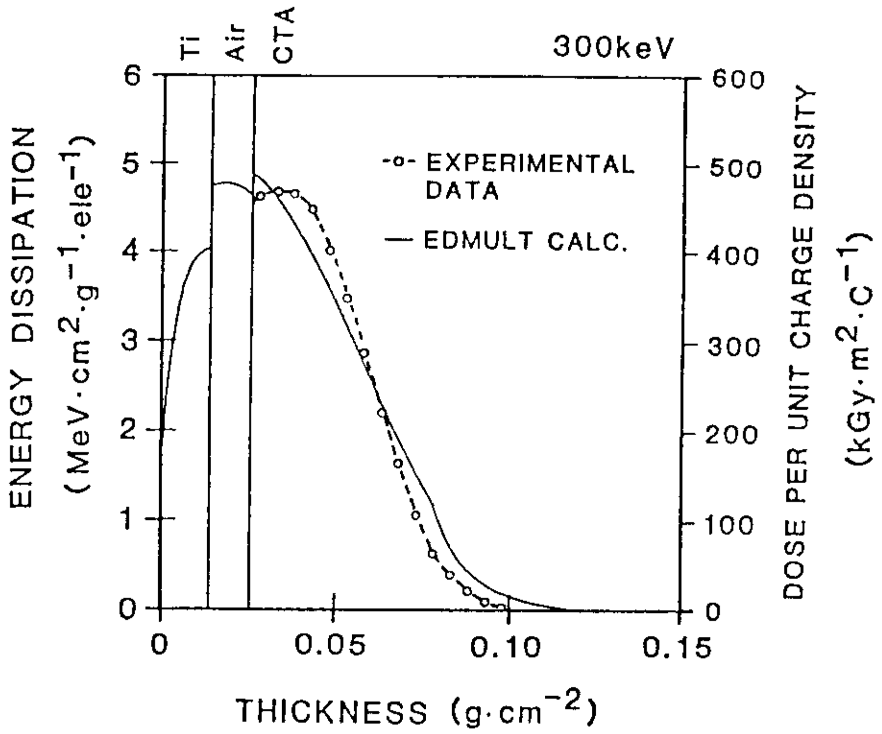

Fig. 2 Comparison of experimental depth dose distribution in a semi-infinite CTA slab for 300 keV electrons with EDMULT calculation.

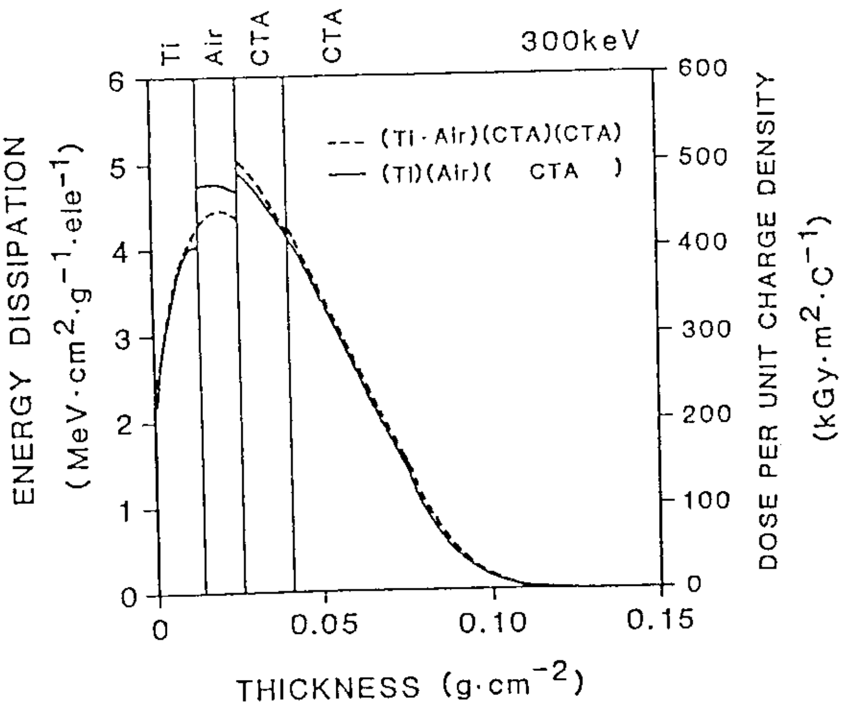

Fig. 3 Two EDMULT calculations for four layer composite with three layer approximations: (---) Ti+Air, CTA, CTA semi-infinite; (——) Ti, Air, CTA semi-infinite.

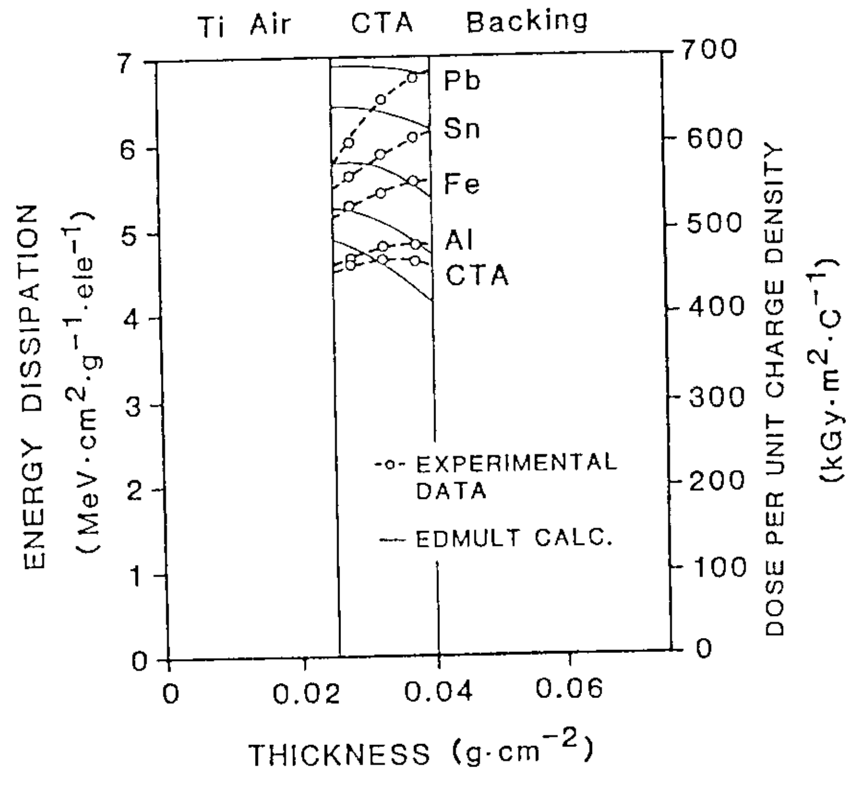

Fig. 4 Comparison of experimental depth dose distributions with EDMULT cal. for 300 keV electrons in a thin CTA slab on various semi-infinite backing layers.

# III. LIST OF PUBLICATIONS

## 1. Published Papers

1....K. Kaji, "Distribution of Poly(Acrylic Acid) in Polyethylene Film", J. Appl. polym. Sci.,32, 4405(1986).

2....S. Sugimoto and M. Nishii, "Radiation-Induced Chemical Reactions of Carbon Monoxide and Hydrogen Mixture. 5. Increase in Product Yields due to the Methane Addition", Radiat. Phys. Chem.,29, 295(1987)

3....K. Ogawa, H. Tamura, M. Hatada, and T. Ishihara, "Spectroscopic Evaluation and Photo-reaction Process of Photo-sensitive Dye Langmuir Films Using Multi-channel Spectrophotometer", Thin Solid Films,159,91-100(1987).

4....K. Ogawa, H. Tamura, M. Hatada, and T. Ishihara, "Study of Langmuir Blodgett Film for KrF Excimer Laser Resist", Langmuir, 4, 195(1988).

5....T. Okada, T. Asano, J. Takezaki, M. Hatada, and K. Ochi, "Electron Beam Curing of bisphenol A Epoxy Resins" Koubunshi Ronbunshu, 44, 761 (1987).

### Reviews

6....K. Kaji, "Improvement of Hydrophilic Properties of Polyester Fiber" Koubunshi Kakou, 37, 425 (1987).

7....Y. Nakase, "Studies on Radiation hardness at JAERI", Research Survey Report of the Osaka Nuclear Science Association (1987).

8....Y. Nakase, "Radiation Hardness Data at EPRI", Survey Report of the Osaka Nuclear Science Association, (1987).

9....Y. Nakase, "Explanation of Qualification Testing Evaluation and Nuclear Plant Aging Research Progaram", Survey Report of the Osaka Nuclear Science Association, (1987).

## Patent Applications

10...J. Takezaki and T. Okada, "electron Beam Curing of Epoxy Resins", Japan Kokai 62-125822.

11...K. Kaji and Y. Kanaya, "Surface Active Polyester Fiber", Japan Kokai, 63-22314.

12...Y. Shimizu, S. Sugimoto, and N. Suzuki,"Preparation of Ethyleneglycole", Japan Kokai, 62-306967.

## 2. Oral Presentations

1....T. Okada, T. Asano, M. Hatada, J. Takezaki, and K. Ochi, "Electron Beam Curing of Epoxy Resin Containing Tetrahydrofurane", The 33rd Symposium on Polymer Science (Kobe), Jul. 10, 1987.

2....Y. Nakase, "Surface Structure of $Kr^+$-irradiated Kapton Film", The 55th Annual Meeting (Fall) of the Chemical Society of Japan (Fukuoka), Oct. 16, 1987.

3....S. Sugimoto and M. Hatada, "Catalytic Reaction of Fe-implanted Amorphus Silicon by Electron Beam Doping", The 55th Annual Meeting (Fall) of the Chemical Society of Japan (Fukuoka), Oct. 17,1987.

4....S. Sugimoto and M. Hatada, "Reactivity of Fe-Implanted Solid Surface by Electron Beam Doping", The 40th Discussion Meeting on Colloid and Surface Science (Kyoto), Sep. 27, 1987.

5....K. Hatada, T. Kitayama, K. Ute, T. Shinozaki, T. Sasaki, and M. Hatada,"Effect of Gamma-Ray Irradiation on Tacticity of PMMA", Central Regional Meeting of Chemical Society of Japan (Nagano), Oct. 1, 1987.

6....T. Okada, T. Asano, J. Takezaki, M. Hatada, and K. Ochi, "Electron-Beam Curing of Epoxy Oligomer in the Presence of Cyclic Compounds", Kyushu-Shikoku Regional Meeting of Chemical Society of Japan (Nagasaki), Jul. 17, 1987.

7....I. Yoshizawa, F. Murakami, K. Kaji, and M. Hatada,"Surface Modification of Polyethylene Foam of Open Cell Type by Radiation-Induced Grafting Technique", The 18th Japan Conference on Radiation and Isotopes (Tokyo), Nov. 25, 1987.

8....K. Ogawa, H. Tamura, M. Hatada, and T. Ishihara, "Study on Photo-

Reaction Process of Pentacosa-diynoic Acid Langmuir Films", The 3rd International Meeting on LB Films(Goettingen), Jul. 26th, 1987.

9....K. Matsushima,T. Haraoka, Y. Shimizu, and S. Nagai,"Formation of the Low Members of Hydrocarbons via Radiation Chemical Reaction of Methane", The 31st International Congress of Pure and Applied Chemistry (Sophia), Jun. 22, 1987.

## Reviews and Invited Lectures

10....K. Kaji, "Radiation Grafting onto Polyethylene", New Techno Forum of Adhesion Society of Japan(Neyagawa), Jul. 9, 1987.

11...M. Hatada, "Polymerization of Langmuir-Blodgett Films by Electron Beam Irradiation", New Techno Forum of Adhesion Society of Japan (Neyagawa), Jul. 9, 1987.

12...Y. Nakase, K. Sumita, H. Yamaoka, Y. Shouno, T. Kakuta, T. Nakamura, and J. Furuta, "Data Base Research on Radiation Hardened Materials and Equipment", Research Committee on Electric Insulation Materials, Electric Engineering Society of Japan(Osaka), Dec. 15,1987.

## 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 polyers from tis basic subjects to recent application in industries. We welcomed 20 trainees this year.

Some studies in this labaoratory were conducted under the co-operative agreements with Profesors in Kyoto, Osaka and vicinity area:

Prof. Y. Tsuji, Kinki University
Prof. H. Saito, Naruto College of Education
Prof. S. Ohnishi,Kyoto University
Prof. I. Oshiyama, Kyoto University of Industrial Technology
Prof. T. Okada, Ohita Unioversity
Prof. K. Hatada, Osaka University
Prof. Y. Ikada, Kyoto University

Four joint research programms have continued this year with inductrial companmies listed below:

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

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

# V. LIST OF SCIENTISTS
(Apr. 1, 1987-Mar. 31, 1988)

## [1] Staff Members

| | |
|---|---|
| Motoyoshi HATADA | Dr., physical chemist, Director |
| Seizo OKAMURA | Professor emeritus,<br>Kyoto University, Advisor |
| Nobutake Suzuki | Dr., physical chemist |
| Yoshiaki NAKASE | Dr., polymer chmeist |
| Kanako KAJI | Dr., polymer chemist |
| Koji MATSUDA | Physicist |
| Shun'ichi SUGIMOTO | Physical chmeist |
| Jun'ichi TAKEZAKI | Physical chemist |
| Masanobu NISHII | Dr., Polymer chemist |
| Yuuichi SHIMIZU | Physical chemist |

## [2] Visiting Researchers

| | |
|---|---|
| Kuniaki KOMAI | Organic chemist, Sanwa Kako Co., Ltd. |
| Kastuhiko OIKAWA | Physical chemist, Gunze Co., Ltd. |