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ANNUAL REPORT OF THE

OSAKA LABORATORY FOR RADIATION CHEMISTRY

JAPAN ATOMIC ENERGY RESEARCH INSTITUTE

(No. 8)

(April 1, 1974 - March 31, 1975)

October 1975

Osaka Laboratory for Radiation Chemistry

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Japan Atomic Energy Research Institute

JAERI-M 6260

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April 1, 1974 - March 31, 1975
(Received September 20, 1975)

This report describes research activities in Osaka Laboratory for Radiation Chemistry, JAERI during the one year period from April 1, 1974 through March 31, 1975.

The major research field covers the following subjects: studies related to reactions of carbon monoxide and hydrogen; polymerization studies under the irradiation of high dose rate electron beams; modification of polymers; fundamental studies on polymerization, degradation, crosslinking, and grafting.

NOTICE

JAERI - M 6260

昭和49年度日本原子力研究所大阪研究所年報

日本原子力研究所 大阪研究所

　本報告は、大阪研究所において昭和49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、一酸化炭素と水素の反応ならびにそれに関連した研究、高線量率電子線照射による重合反応の研究、ポリマーの改質および上記の研究と関連して重合反応、高分子分解、架橋ならびにグラフト重合に関する基礎的研究などである。

お 知 ら せ

　本報告は、昭和50年5月、JAERI　5030　として発行された大阪研究所年報（No.8）の継続である。
本年度より年報には原報はのせないこととし、そのかわり、1年間の研究活動を若干詳しく記載することとした。以後、大阪研究所年報はJAERI－Mレポートとして刊行され、本号はJAERI－M 6260 である。

CONTENTS

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. JARRP merged with the Japan Atomic Energy Research Institute (JAERI) on June 1, 1967, and the laboratory changed its name from Osaka Laboratory, JARRP to Osaka Laboratory for Radiation Chemistry, JAERI. The research activities of Osaka Laboratory have been oriented towards the fundamental researches on radiation chemistry.

The results of the research activities of the Laboratory were published in the Annual Reports of JARRP which consisted essentially of original papers written in Japanese. The Annual Report started in 1958 had been published without change until Vol. 8. However it had to change its name and appearance a little when JARRP was merged with JAERI; the Annual Report was included in "JAERI Report", and the first issue was published as "JAERI 5018" in December 1968.

Meanwhile we have discussed the problem, whether it is really desirable to publish our original papers on radiation chemistry mostly in "JAERI Report", and come to conclusion to continue our Annual Report without original papers. The present Annual Report is our first trial of the idea, and published as a volume of JAERI-M report. It contains no original paper but presents outlines of the current research activity (April 1, 1974 - March 31, 1975) in some detail. Those investigations

which have appeared in the journals and have been presented at professional society meetings in the above indicated period are given in the list of publications on page 78 and in the list of oral presentations on page 80, respectively.

Another change is that the whole content is written in English; we believe this is a welcome change to foreign readers, because they can get direct information not only about our completed works but also about those which have been just begun or is in progress.

In the fiscal year of 1974 (April 1, 1974 - March 31, 1975) emphasis was laid on two projects; one is "Effect of radiation on the reaction of carbon monoxide with hydrogen", and the other "Radiation-induced chemical reactions under high dose rate electron beams".

Chemical synthesis from CO, CO_2, H_2 and H_2O is an essentially important problem concerning raw materials for chemical synthesis, since the beginning of the 20th century hundreds of papers have appeared on the reaction of CO with H_2. Lind for the first time reported in 1925 reaction of CO or CO_2 with H_2O by alpha rays of Rn-222. Pichler carried out experiments of radiation-induced reaction of CO with H_2 in the presence of iron and ruthenium catalysts. We have begun our experiments in the absence of catalyst, though from the practical point of view the presence of some catalyst seems to be desirable to lead the reaction to a certain final product.

Most of the fundamental researches on radiation chemistry are carried out with gamma rays of Co-60, where the highest dose rate is some 10^3 rad/sec. Recently the number of experi-

ments has increased in which an electron accelerator is employed, and the highest dose rate is in this case generally about 10^5 rad/sec. It was intended to perform radiation chemical reaction at a dose rate two orders of magnitude higher than that of the conventional accelerator. It is expected that the rate of creation of radicals or ions increases to hundred times and the chance of reactions between two radicals may increase to ten thousand times. An accelerator which delivers electron beams of 25 mA and 800 keV was completed two years ago, however we had to wait until we get agreements of inhabitants in the neighbourhood of the laboratory to operate the new accelerator. Therefore detailed preliminary experiments were carried out with a Van de Graaff accelerator and some details of the experiments are found in the text. We got inhabitants' full agreement on May 30 of this year. The new accelerator is now in full operation, and we expect that we can report our activity with the new facility in the next Annual Report.

August 31, 1975

Prof. Ichiro Sakurada, Head

Osaka Laboratory for Radiation Chemistry

Japan Atomic Energy Research Institute

II. RECENT RESEARCH ACTIVITIES

[1] Effect of Radiation on the Reaction of Carbon Monoxide
with Hydrogen

T. Sugiura, S. Sugimoto, and M. Nishii

There are hundreds of works for the reaction of carbon monoxide with hydrogen. The present study is undertaken to investigate the effect of radiation on the reaction. As the first step of the project, a study on homogeneous gas phase reaction of carbon monoxide with hydrogen is performed in the absence of catalyst at room temperature under static condition by the use of a Van de Graaff electron beam accelerator.

A 6 liter reaction vessel is made of stainless steel; two pyrex tubes are connected to the vessel, one for evacuation and sample inlet and the other for a vacuum guage head. For penetration of electron beams, a titanium window of 30 micron thickness, 23 cm long and 8 cm wide, is situated at the upper side of the vessel using polyimide gasket. Under such a condition no reaction takes place without radiation at room temperature.

After irradiation, the content of the vessel is pumped out to collect the reaction products in three successive traps, one with dry ice-methanol and the others with liquid nitrogen. A mass spectrometer is used for the analysis. Reaction in $CO-D_2$ system is also studied for the identification of the products.

When CO/H_2 is 1/6 in pressure, main products are

formaldehyde, methanol, acetaldehyde, formic acid, glyoxal, acetic acid, trioxane and carbon suboxide together with carbon dioxide and water which are not our concern at the moment. Their yields vary as a function of irradiation time as shown in Fig. 1. The yields of acetic acid, acetaldehyde and methanol
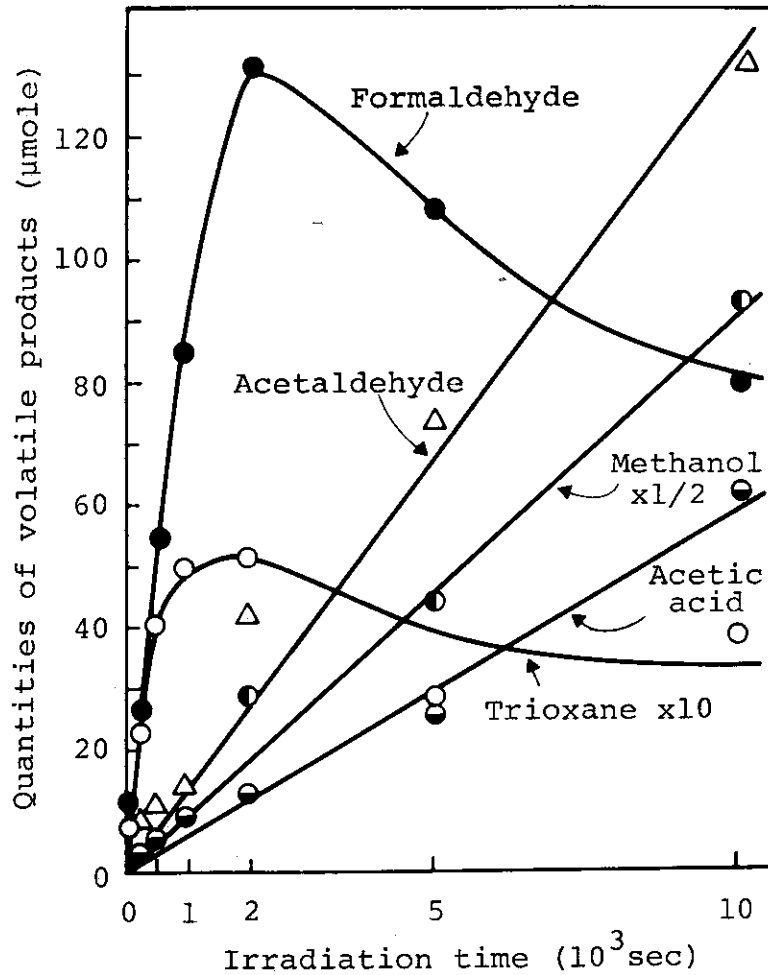
Fig. 1. Variation of the main product yields as a function of irradiation time. Total pressure, 600 torr, $CO/H_2 = 1/6$; irradiation, 800 keV, 100 μA.

increase linearly with time. On the other hand, formaldehyde and trioxane show rapid increase of their yields at the initial stage, then maxima and finally tend to level off. From the initial slopes of the products in Fig. 1, the following

- 5 -

values are obtained.

Table 1. Initial G values of the main products

Product	CH_2O	CH_3OH	CH_3CHO	HCOOH	$(CHO)_2$	CH_3COOH	Trioxane
G value	1.5	0.42	0.32	0.12	0.14	0.11	0.13

After 5,000 or 10,000 second irradiation, the vessel wall
is found to be coated with very thin layer of involatile,
sticky compound. This is insoluble in nonpolar solvent as
benzene, n-hexane and carbon tetrachloride, but soluble in
polar solvent as methanol, ethanol and tetrahydrofuran and
partly soluble in water. The IR spectroscopy shows the pres-
ence of $-CH_2-$, alcohlic -OH, ester or aldehyde $>C=O$, and
-C-O-C- bondings. This may be due to the polymerization of
formaldehyde and trioxane on vessel wall.

The effect of composition of the reactant gases is studied
changing the CO content from 5 to 80 % but keeping the total
pressure at 600 torr. In Fig. 2, the product yields per
fixed absorbed energy which is equal to that when 14.7 % CO
mixture is irradiated for 1,000 seconds are given as a function
of gas composition. In CO rich region, main products are
acetaldehyde and carbon dioxide, though the latter is not
shown in the figure. Methanol yield increases monotonously
with the increase of hydrogen content. Acetic acid gives a
maximum yield at approximately 50 % composition, while
formaldehyde and trioxane give maxima at 14.7 % CO content.
These complicated variations indicate that those yields of

individual product are influenced by numerous concurrent re-
actions.
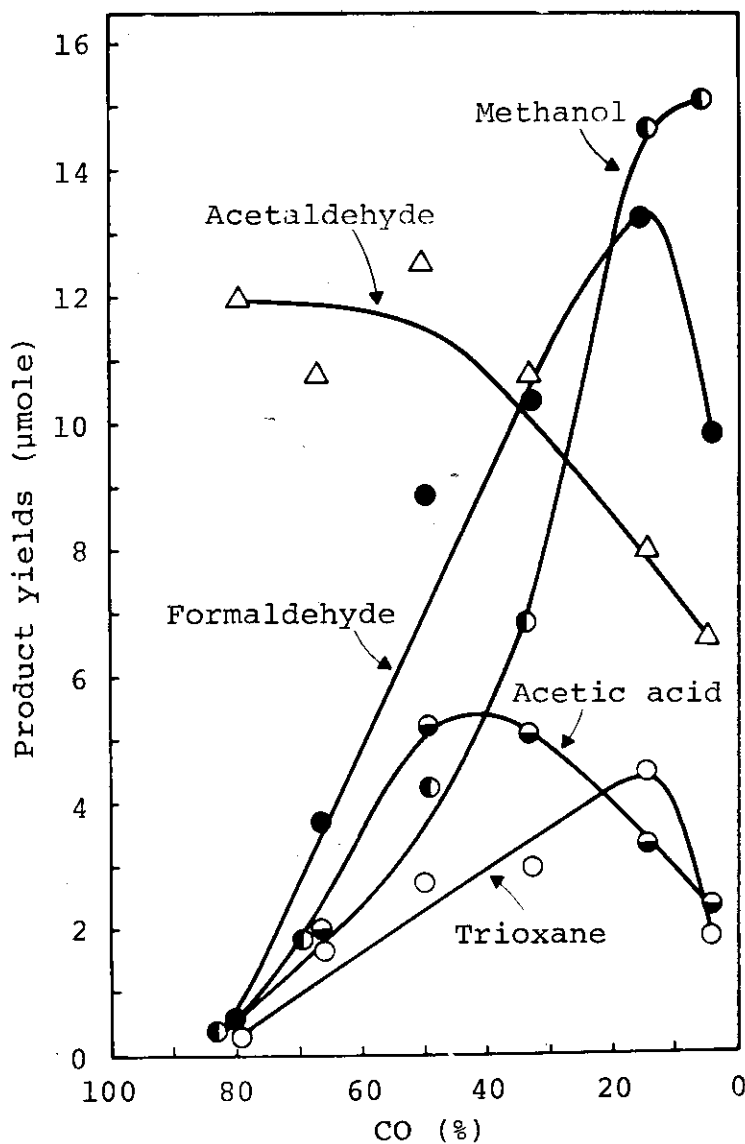
Fig. 2.   Variation of the main product yields as a function
of CO content.

Solid products are always obtained regardless of the gas
composition.   At 80 % CO content, the product is studied in
some detail.   It is yellow, sticky compound and soluble in
methanol, ethanol and water.   It dissolves into water with
slight bubbles and the resultant solution shows relatively
strong acidity.   The IR spectra give strong absorptions of

acidic $>C=O$. On heat decomposition in vacuum, it yields carbon dioxide, carbon monoxide, hydrogen, water and acetic acid with carbon black residue. Therefore, this is considered to be the product of the polymerization of carbon suboxide on the vessel wall.

Quantitative discussion as to the formation mechanism of the each product can not be made at the moment. However, we tentatively propose a cluster ion as $(CO)_m(H_2)_n CO^+$ or $(CO)_m(H_2)_n CHO^+$ which is responsible to the formation of tri-oxane in its neutralization decomposition.

[2]   Dosimetry of Electron Beams in Gases

Y. Nakai, K. Matsuda, and T. Takagaki

1.   Estimation of Effective Electron Energy in a Reaction

Vessel

Gas phase dosimetry is generally performed by chemical

dosimeter as N_2O or ethylene. The energy absorption in N_2O

can be converted to that in the gas under investigation by

multiplying their stopping power ratio. There is a problem

that the stopping power depends on the energy of incident

electron. When some gas is irradiated in a metal reactor by

high energy electron beams, the electrons which actually

interact with the gas molecule have a broad distribution of

kinetic energy because of backscattered secondary electrons

from the reactor wall. Therefore, it is important to estimate

average energy of electrons in gas.

Here, we consider two gases, for instance, CO and H_2.

The ratio of ionization yield of these gases is given by,

$$\frac{I(H_2)}{I(CO)} = \frac{S(H_2)}{S(CO)} \cdot \frac{W(CO)}{W(H_2)} .$$

I, S and W mean ionization yield, stopping power per molecule

and W value for ionization, respectively. Stopping powers for

CO and H_2 were already calculated by Berger et al.[1] W values

for CO and H_2 are known to be 32.3[2] and 36.3[3] eV, respective-

ly. From these values, $I(H_2)/I(CO)$ can be calculated as a

function of electron energy as shown in Fig. 1. The $I(H_2)/$

$I(CO)$ ratio increases with decreasing the electron energy.

Ionization yield of gas is easily determined experimentally in an ionization chamber. For 1.5 MeV electron beams, the ratio of ion current, $I(H_2)/I(CO)$ is 0.1465, which is in a fair agreement with the calculated value in Fig. 1, 0.1451.
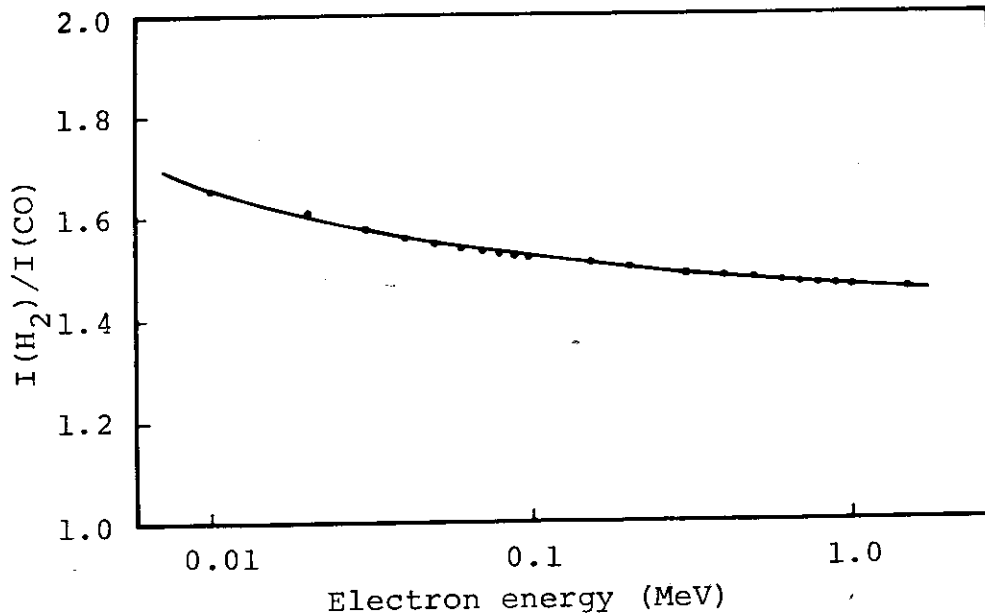
Fig. 1. Relative ionization current of H_2 compared to that of CO as a function of electron energy.

Next, the lower electrode of the chamber is replaced with a stainless steel block of 5 mm thickness and ionization current measurements are carried out by 1.5 MeV electron beams. The ratio obtained is 0.1586, which corresponds to the ratio at electron energy of ca. 25 keV from Fig. 1.

This method is reasonably simple and is available for the rough estimation of effective electron energy in a metal tube or a reactor where incident electron energy changes greatly by the backscattering from the wall material.

1) M.J. Berger and S.M. Seltzer, NASA Report, SP-3012 (1964).
2) G.G. Meisels, J. Chem. Phys., 41, 51 (1964).
3) W.P. Jesse and J. Sadaukis, Phys. Rev., 107, 766 (1957).

2. Measurement of W-Values for Carbon Monoxide-Hydrogen Mixtures

In the study of the chemical reaction in carbon monoxide and hydrogen mixtures under irradiation of high energy electron beams, the estimation of the total absorbed energy is essential for the quantitative discussions. Ionization measurement is the most suitable method for the present purpose.

The energy absorbed in a gas, E is given by,

$$E = W \cdot I, \qquad (1)$$

when one obtains the total number of ion pairs, I. Here, W denotes the average energy spent by a charged particle to give an ion pair in the gas. In binary system, the W value at partial pressure of $P(CO)$ or $1-P(H_2)$, $W[P(CO)]$ is given by the following formula when the ionization yields of the gas and pure hydrogen, $I[P(CO)]$ and $I[H_2]$ are determined experimentally.

$$W[P(CO)] = W[H_2] \cdot \frac{P(CO) \cdot S(CO) + P(H_2) \cdot S(H_2)}{I[P(CO)]} \cdot \frac{I[H_2]}{S[H_2]} \qquad (2)$$

S means, the stopping power of the gas, which was calculated by Berger et al[1]. $W[H_2]$ was determined to be 36.3 eV by Jesse[2].

The reciprocals of W values are plotted in Fig. 1 as a function of Z.

$$Z = \frac{S(CO) \cdot P(CO)}{S(CO) \cdot P(CO) + S(H_2) \cdot P(H_2)} \qquad (3)$$

The solid, straight line means the expected relationship when

there is no interaction between CO and H_2 gases under irradiation.

The deviation of the results from the solid line can be explained in terms of Penning Ionization and energy dependence of the stopping power. The first effect is that the excited hydrogen molecule gives rise to ionization of carbon monoxide through energy transfer between two molecules. The possibility
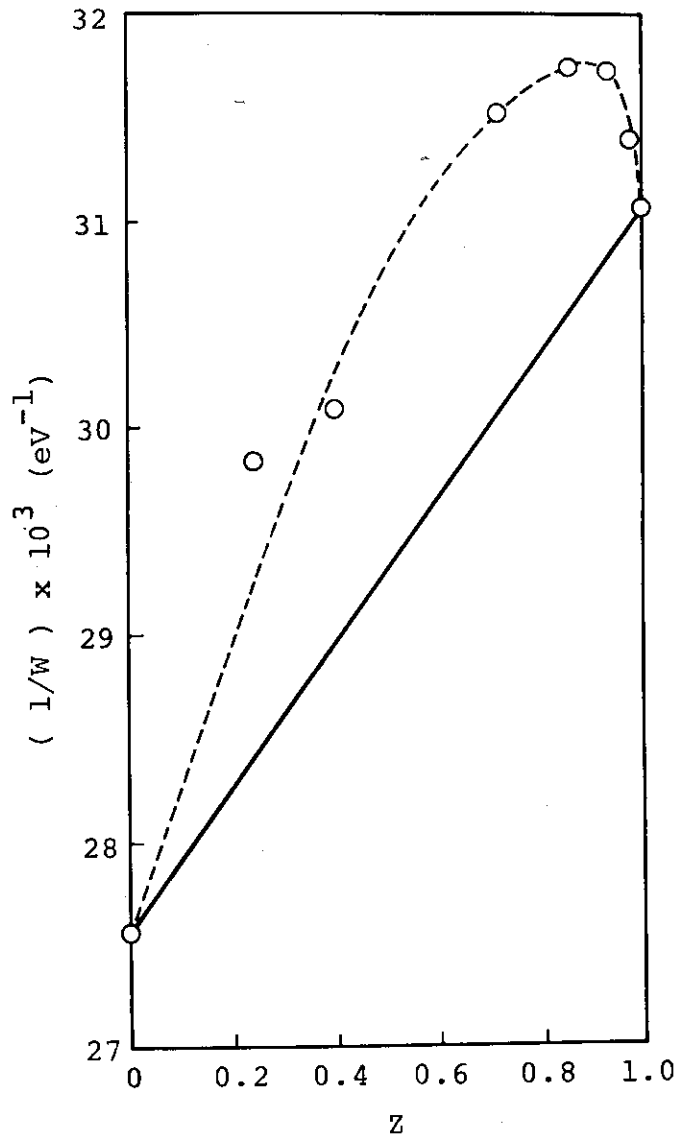
Fig. 1. Reciprocal of W-value as function of Z for $CO-H_2$ mixture. Incident electron energy, 1.5 MeV; total pressure, 746 torr.

of the second effect means that it is not correct to use the stopping power at the incident electron energy if the ionization by secondary electrons is significant.

1) M.J. Berger and S.M. Seltzer, NASA Report, SP-3012 (1964).

2) W.P. Jesse and J. Sadaukis, Phys. Rev., 107, 766 (1957).

[3]   Radiation-Induced Polymerization of Multilayers

M. Hatada and M. Nishii

1.   Octadecyl Methacrylate Multilayer

The radiation-induced polymerization of monomers in a
form of monolayer was investigated in an attempt to establish
radiation chemistry on polymer in two dimensional system. It
has been concluded that the monolayer of vinyl monomers having
long aliphatic chain is polymerized to give a sheet-like polymer
when irradiated at a nitrogen-water interface using electron
beams from a Van de Graaff[1]. By use of an automatic surface
balance of Langmuir type which was designed for constant
surface pressure condition, the rate of polymerization of
octadecyl acrylate (ODA) monolayer was found to depend on the
surface pressure at which the irradiation was carried out and
to show a maximum at 15 dyn/cm where the monomer molecules in
the monolayer took the most suitable configuration for poly-
merization[2].

Knowledge on properties and structure of the surface
polymerized polymer is necessary for understanding the poly-
merization in two dimensional system, but the polymer monolayer
on water surface is not mechanically strong enough to be lifted
up from the water surface for measurements on its properties.
The amount of monolayer substance is also too small to allow
analysis using physical chemical methods familiar in polymer
chemistry. Another difficulty which does not encounter in
ordinary three dimensional system is that intermediates

radiation-chemically produced in water phase contribute to the monolayer polymerization. In order to get rid of these difficulties, we extend the work to the monomer multilayer which can be built-up from the monolayer on solid surface by Langmuir-Blodgett technique. The studies on ODA and vinyl stearate (VST) multilayers have revealed that the polymerization of the monomer multilayers by irradiation provides the exclusive method to prepare thin polymer film having regular layer structure[3,4]. As a part of the program, this study is carried out on octadecyl methacrylate (ODMA) multilayers.

The ODMA multilayers are prepared on aluminum plated glass plates from an ODMA monolayer spread at an air-water interface using Langmuir-Blodgett technique in which the monolayer substance is transferred to the solid surface on repeated cycles of down or/and up trips of the plates through the monolayer.

Using electron beams from a Van de Graaff accelerator (dose rate, 5×10^5 rad/sec), the multilayers are irradiated in nitrogen atmosphere on a copper plate, the lower side of which is cooled by water held at 10°C. The temperature of the specimen during irradiation is 16°C or lower as measured by a thermocouple.

The irradiation effects are examined by X-ray diffraction curves and infrared spectra using multiple reflection technique which designed for the present purpose. A pair of multilayers is set face to face at a distance of 3 mm in a cassette through which the infrared light is multi-reflected.

The ODMA multilayer prepared is of 130 layers and of an X type which is formed when the deposition of the film

material occurs only on every downward trip provided that no
overturning of the molecule occurs. The multilayer is not
stable forming denderite within 1 hr unless the multilayer is
polymerized by irradiation within this period of time.
Multilayers of two types and of the combination of the two are
formed as seen in the X-ray patterns, one showing a layer
spacing of 23.8 A (type I) and the other, 31.1 A (type II).

The changes of X-ray patterns by irradiation observed for
the ODMA multilayers of type I and type II are shown in Figs.
1 and 2, respectively, in which it is clear that the intensi-
ties of the reflection due to the monomer layer structure
decrease and a series of new reflections appear upon irradi-
ation, and its intensities increase when the irradiation con-
tinues further.
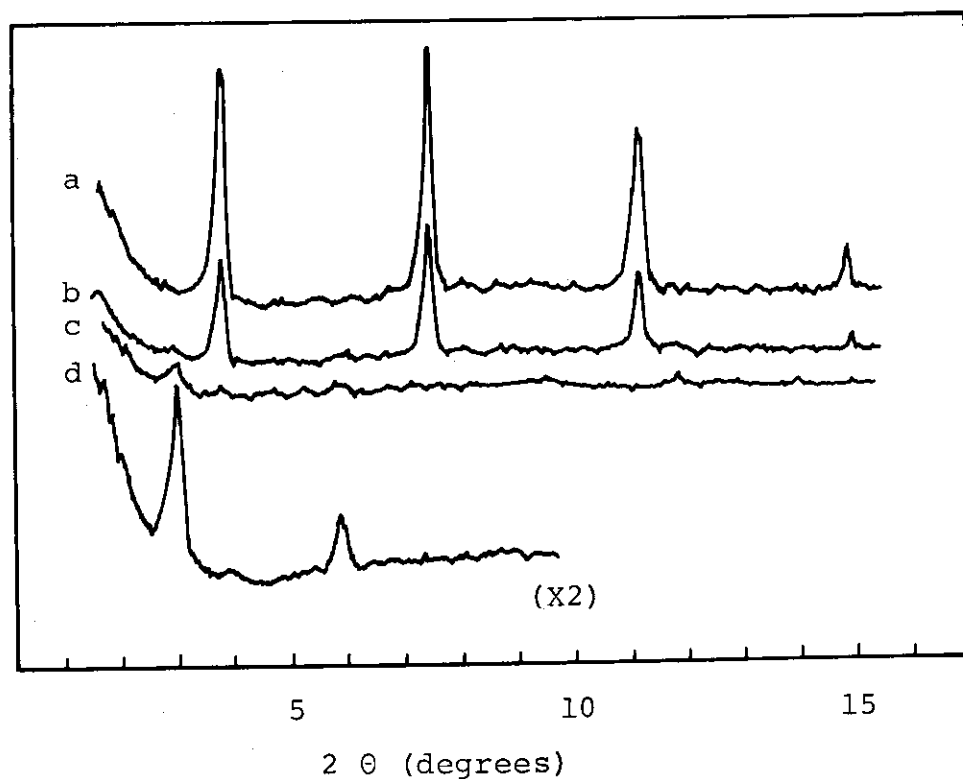
Fig. 1. Change in X-ray diffraction curve during irradiation
for ODMA multilayer of type I: a, 0; b, 3.75;
c, 6.25; d, 35 Mrad.
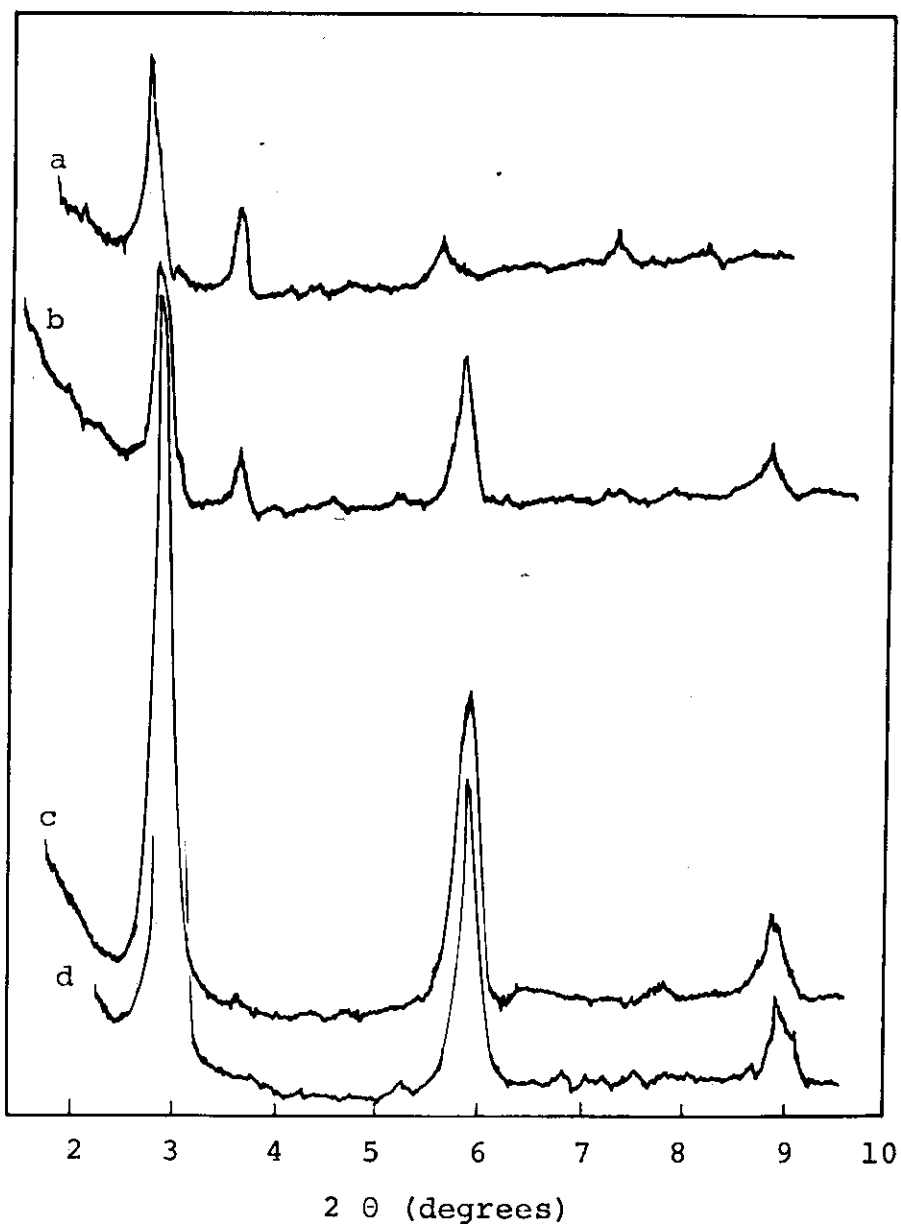
Fig. 2. Change in X-ray diffraction curve during irradiation
for ODMA multilayer of type II: a, 0; b, 1; c, 10;
d, 25 Mrad.

The change of the infrared spectra of the ODMA multilayer
upon irradiation is shown in Fig. 3 (a) through (d). The
bands due to vinyl group observed in the spectrum of the un-
irradiated multilayer (a) decrease as the dose increases, and
disappear by the irradiation above 2 Mrad. The multilayer
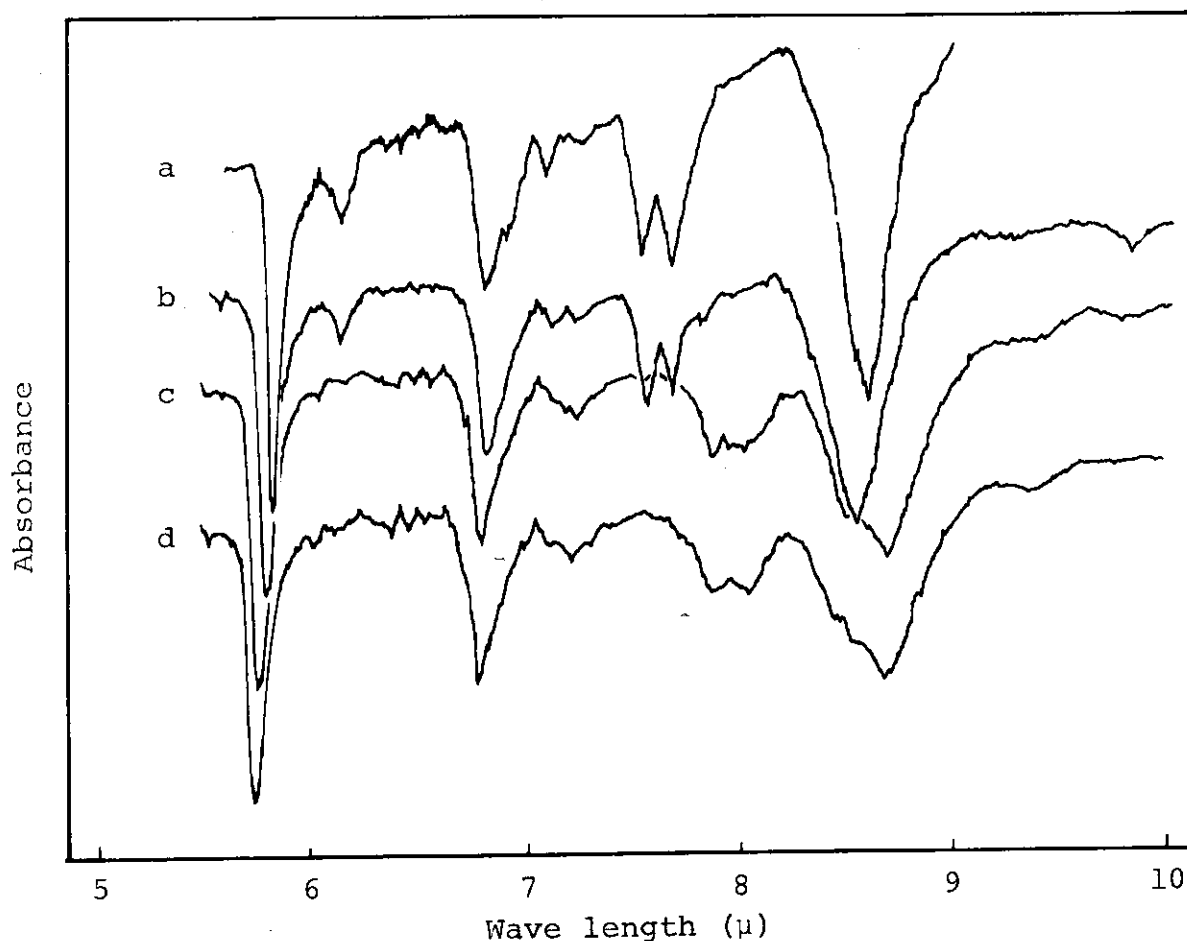
Fig. 3. Change in infrared spectrum during irradiation.
Dose: a, 0; b, 2.5; c, 10; d, 35 Mrad.

turns insoluble in a solvent of the monomer but still soluble in a solvent for polymer even after extensive irradiation above 25 Mrad. This may indicate that the poly(ODMA) thus produced is not cross-linked by the irradiation, being contrasted to the previous finding[3] on ODA that ODA is cross-linked by the irradiation above 2 Mrad.

The results mentioned above lead to a conclusion that the ODMA multilayer is polymerized by electron beam irradiation to form thin polymer film having regular layer structure. The polymer film obtained here may be considered to be of comb-like structure in which side chains stick out one side of the main

chain from the X type structure of the monomer multilayer. The layer structure of the polymer is destroyed by heating the multilayer above 40°C and does not recover when it is cooled to room temperature.

No indication of polymerization is obtained when the irradiation is carried out in air.

1) M. Hatada, M. Nishii, and K. Hirota, J. Colloid and Interface Sci., 45, 502 (1973).

2) M. Hatada, M. Nishii, and K. Hirota, Macromolecules, 8, 19 (1975).

3) M. Hatada, M. Nishii, and K. Hirota, JAERI, 5030, 26 (1975).

4) M. Nishii, and M. Hatada, JAERI 5030, 23 (1975).

2. Mixed Multilayers of Octadecyl Acrylate and Vinyl Stearate

The radiation-induced polymerization of multilayers is extended to mixtures of octadecyl acrylate (ODA) and vinyl stearate (VST). The purposes of the present study are to prepare stable thin polymer film having regular layer structure and to investigate copolymerization reaction of monomers restricted in two dimensional layer. ODA and VST are selected since they are considered to be a position isomer (Fig. 1)
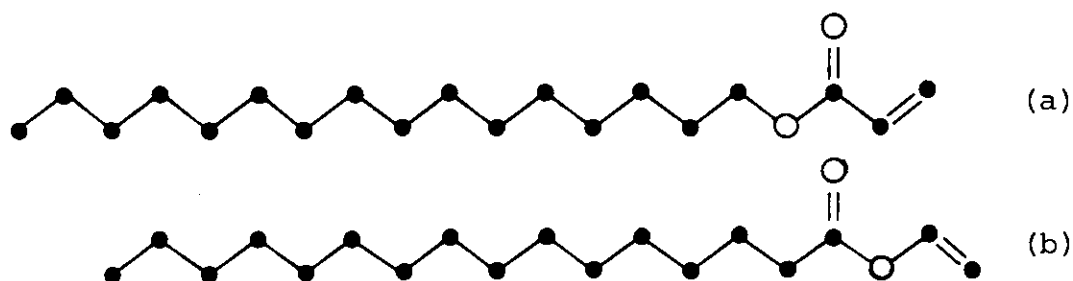
Fig. 1. Schematic representation of ODA (a) and VST (b).

with each other and the behavior of their multilayers to radiation was found to be different[1,2].

The multilayers are prepared by Langmuir-Blodgett technique from mixed monolayers of ODA and VST of different compositions. The methods of irradiation and examination of the irradiation effects are the same as those described in the previous section.

The type of the monolayer deposition changes from X type for pure ODA monolayer to Y type for pure VST monolayer in a way that the number of Y type deposition increases with increasing VST content in the monolayer.

All the multilayers thus obtained have X type structure irrespective of the type of deposition as seen from X-ray diffraction curves of the multilayers. The layer spacing of the unirradiated multilayer decreases with increasing VST content of the multilayer, as shown in Fig. 2, to a limiting value at 80% VST content, while the intensities of the reflection decrease and another set of reflections appears. The spacing of the latter decreases when the VST concentration is increased further. This fact indicates that the VST dissolves in ODA to form a solid solution up to 80 % VST content, but phase separation occurs at this content resulting in the presence of the two series of reflections. The layer spacing decreases or increases upon irradiation depending on the VST content of the multilayer and the relation between the spacing and VST content of the multilayer lies on a smooth curve (Fig. 2c) after 15 Mrad irradiation. The intensities of the reflections decrease on irradiation but increase when the irradiation continues further above 1 Mrad.
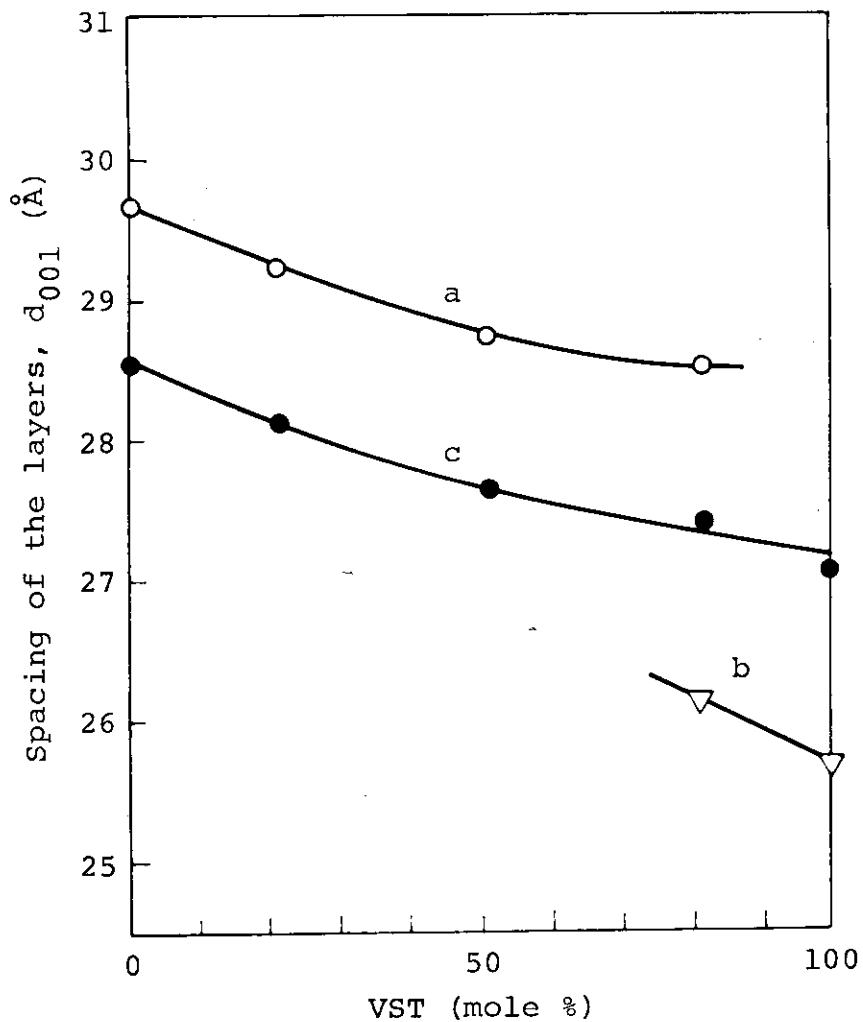
Fig. 2. Spacing of ODA-VST mixed multilayers (d_{001}) at various monomer compositions. Dose: a and b, 0; c, 15 Mrad.

The infrared spectra of the mixed multilayers are explained as simple addition of the spectrum of each component, indicating that there is no particular interaction between ODA and VST. The comparison of the infrared spectra of the mixed multilayer (ODA : VST = 1 : 1) before and after irradiation (2.1 Mrad) (Fig. 3) reveals that by the irradiation the bands due to vinyl group disappear and carbonyl bands of ODA and VST appeared at different wave numbers, 1725 and 1760 cm^{-1}, come to one wave number, 1735 cm^{-1}, and complex bands appear at 1350

- 1200 cm^{-1} region, which are assigned to wagging motion of straight aliphatic methylene chains.
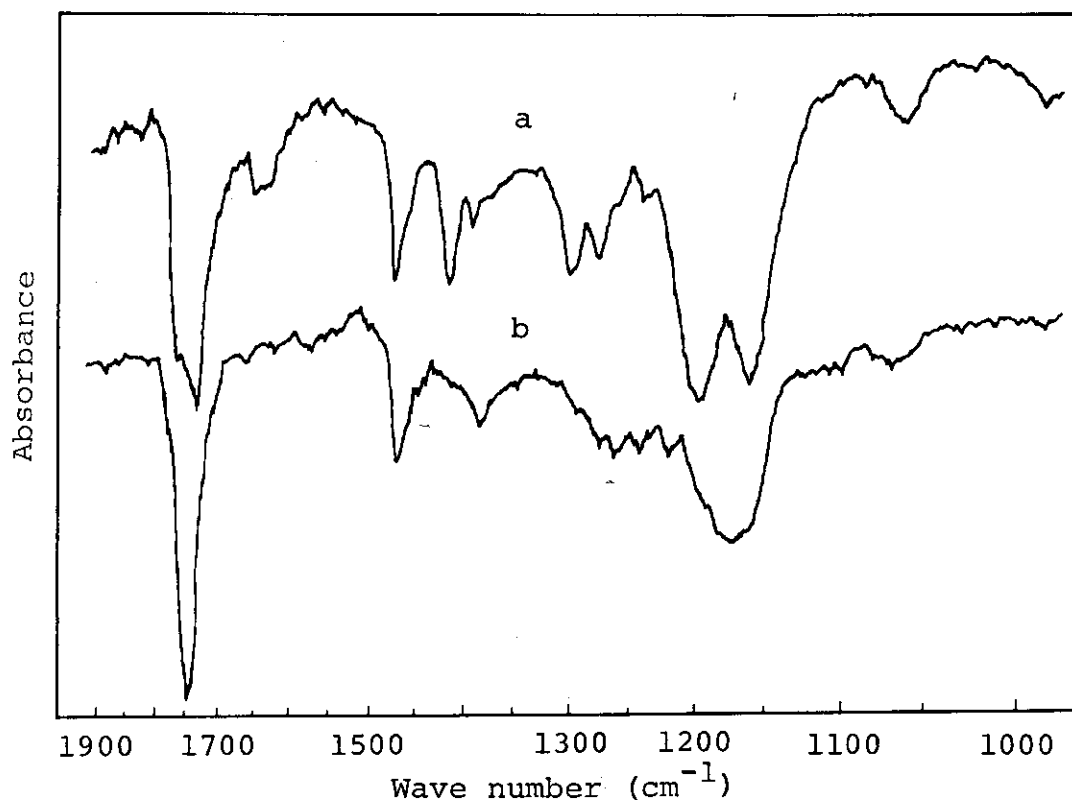
Fig. 3.   Infrared spectra of the mixed multilayer: a, 0;
b, 2.1 Mrad irradiation

These results indicate that both ODA and VST polymerize to form well oriented polymer multilayers. However, the question whether copolymerization of ODA and VST occurs in the multilayer remains for future study. The rate of polymerization is found to lie on an intermediate value between those for ODA and VST multilayers.

1) M. Hatada, M. Nishii, and K. Hirota, JAERI, 5030, 26 (1975).
2) M. Nishii, and M. Hatada, JAERI, 5030, 33 (1975).

[4]   Radiation-Induced Emulsion Polymerization

H. Kamiyama

1.   Spectroscopic Study on Water-Polymer Interaction at the
     Particle Surface of Polymer Emulsion

Polymer emulsion prepared by electron beam irradiation is
semi-transparent and composed of fine polymer particles of 20
- 35 nm in diameter. As a first step of the investigation of
the emulsion, an IR spectroscopic study on polymer-water inter-
action at the emulsion surface was carried out.

The 1.9 µm band in near infrared region, a combination
band of OH stretching and deformation vibrations, is used for
the present differential spectroscopic study. This absorption
band is found to increase its strength with the decrease of
the degree of hydrogen bonding.

The difference spectra of water in polystyrene emulsion
and film relative to pure water are different from that of
aqueous solution of sodium dodecyl sulfate (SDS), the emulsi-
fier. The spectra of polystyrene films show a blue shift from
the normal water spectrum to the opposite direction from those
of polyvinyl alcohol and cuprophane films of hydrophilic
character (Fig. 1). However the blue shift is observed in
considerably hydrophobic film as cellulose acetate. These
results indicate that a substantial part of the particle
surface remains uncovered by emulsifier and has a direct
contact with water.
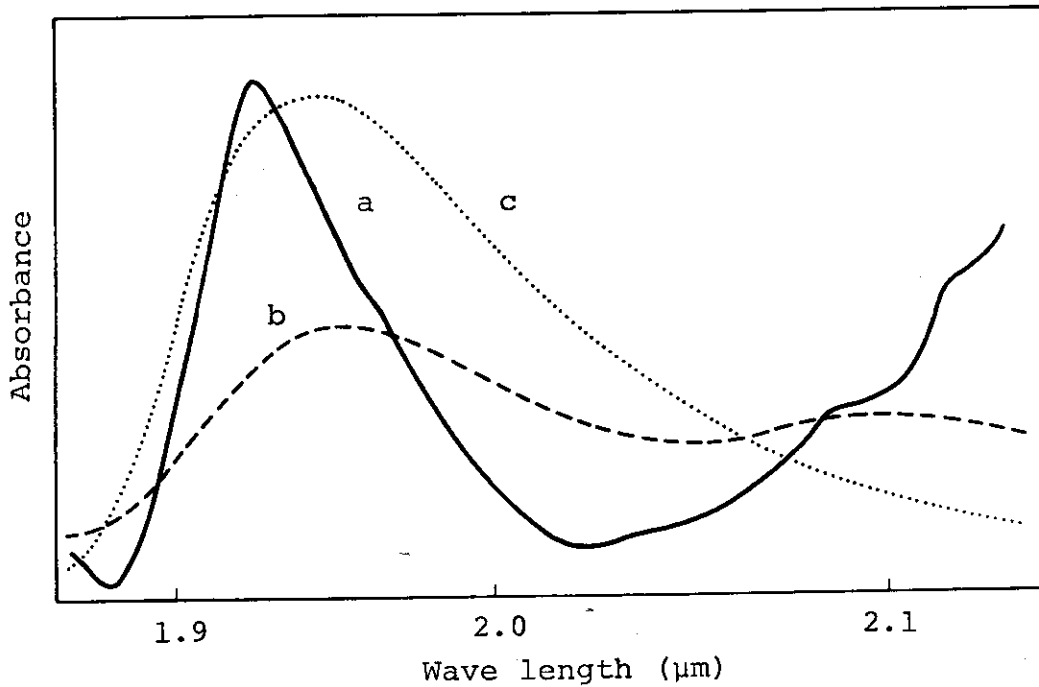
Fig. 1. 1.9 μm band of water at 25°C: a, in 2 mm polystyrene
film prepared from its emulsion (full line); b, in
60 μm polyvinyl alcohol film (broken line); c, in
100 μm pure water (dotted line).

2. High Dose Rate Polymerization of Vinyl Acetate in Aqueous Solution

Studies on radiation-induced emulsion polymerization at
high dose rate have been continued under employment of several
vinyl monomers as vinyl acetate and its higher homologues,
methyl and ethyl acrylates and styrene. Characteristics of
such a type of emulsion polymerization are as follows; the
levelling off of the reaction rate at high dose rate and
transparency of the emulsion. To investigate effect of the
particle number on the levelling off of the reaction rate,
polymerization of vinyl acetate in aqueous solution containing
1 % sodium dodecyl sulfate (SDS) is studied.

The dose rate exponent of the polymerization rate changes from 0.75 to 0.30 at a dose rate of ca. 2×10^3 rad/sec. Such a variation of the dose rate dependence is commonly observed in all the three aqueous systems of different SDS concentrations and also in emulsion polymerization as shown in Fig. 1.
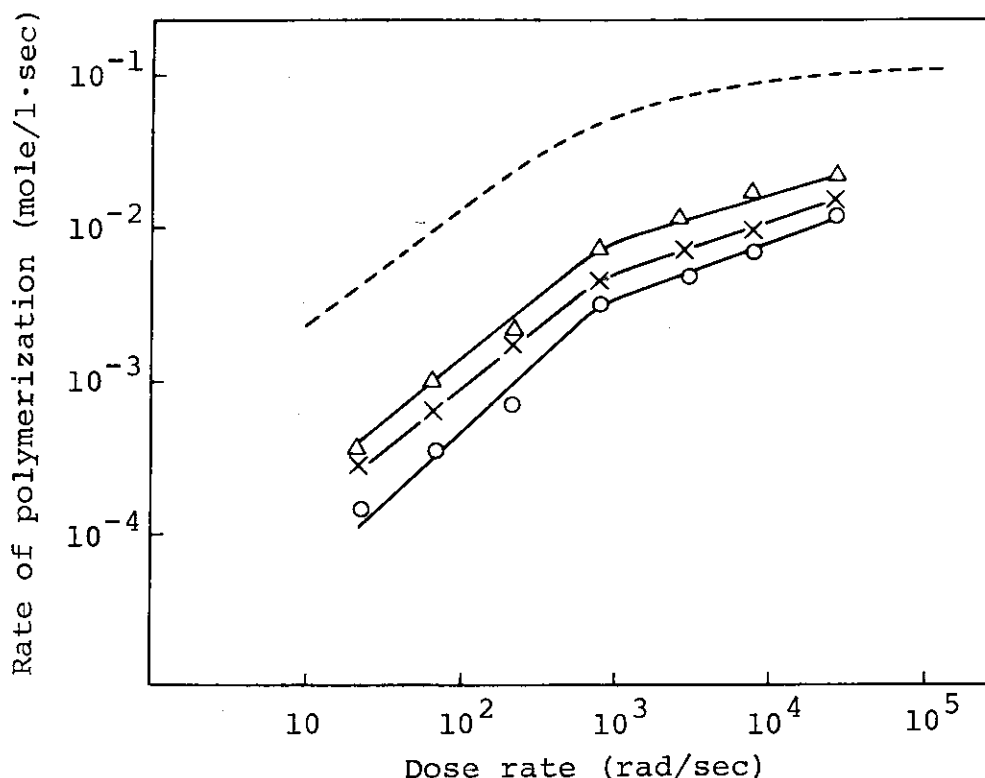
Fig. 1.   Dose rate dependence of the rate of polymerization of vinyl acetate in its aqueous solutions containing 0.5 % (Δ), 1.0 % ($\times$) and 2.0 % ($\circ$) sodium dodecyl sulfate.   Dashed line shows the dependence in emulsion polymerization of 20 % monomer system.

The turbidity of the emulsion remains unchanged untill the polymer conversion reaches to a certain value and then it starts to increase rapidly at a fixed rate, which is shown in Fig. 2. Both the inflection point of the turbidity and the rate of turbidity increase increase with the SDS concentration, but they are almost independent of the dose rate.   This means that

the formation of polymer particles is affected neither by the dose rate nor by the rate of polymerization. However such conditions as polymer content and emulsifier concentration have an effect on the particle size.
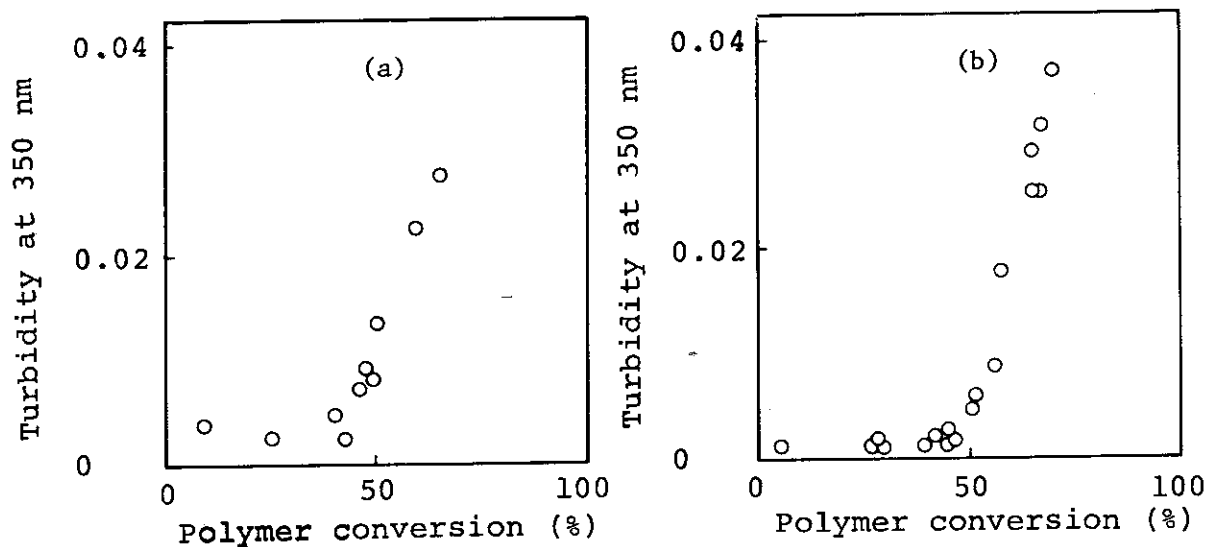
Fig. 2.   Turbidity change with conversion to polymer in polymerization of 2.5 % aqueous solution of vinyl acetate containing 1 % of SDS. Dose rate: a, 22.3;   b, 28,000 rad/sec.

It may be regarded that the particle formation process is similar in both the emulsion and solution polymerization since there is practically no difference in the dose rate dependences of the reaction rate.

[5]   Radiation-Induced Crosslinking and Degradation of

Polyacrylamide

I. Sakurada, T. Okada, and A. Tsuchiya

Polyacrylamide (PAAm) is irradiated at room temperature

with γ-rays in air and vaccum, sol fraction is determined, and

the G-values for the crosslinking and scission are calculated

with the Charlesby-Pinner equation to find the following

values.

Air irrad.   G(c.l.) 0.68   G(sci.) 1.89

Vacuum irrad.   "   0.68   "   1.16

When aqueous solution of PAAm of higher molecular weight

($M = 3 \times 10^6$) is irradiated in the absence of air, even 0.1 %

solution shows viscosity increase due to crosslinking, so the

experiments are carried out with solutions whose concentration

is lower than 0.05 %, and the scission of the polymer molecules

is followed viscometrically. The number of scissions is inde-

pendent of the dose rate, polymer concentration and degree of

polymerization. It is remarkable that the number of scissions

per 1,000 bonds per 1 Mrad is found to be 58; the G value of

scission is 790. Such an enormously high value of scission

is presumably due to indirect effect of water.

Polyacrylic acid (PAA) is also water soluble and the vis-

cosity drop by the irradiation has already been measured[1];

calculation of the number and G-value of scissions of PAA is

carried out based on the curves to compare with those of PAAm

and the following values are obtained: Number of scissions

per 1,000 bonds of PAA in 0.1 % aqueous solution by 1 Mrad

irradiation is 9.4 (in air) and 5.7 (in the absence of air);

G-value for scission 127 (in air) and 70 (in the absence of

air). It is true that PAA has also a very high G-value of

scission, however the value is about an order of magnitude

smaller compared with that of PAAm.

A simple scheme of the reaction which can explain essential

feature of the degradation of PAAm or PAA is as follows.

Direct scission of a polymer molecule by radiation into

two polymer molecules

$$P \xrightarrow{k_1} P_n + P_m \qquad (1)$$
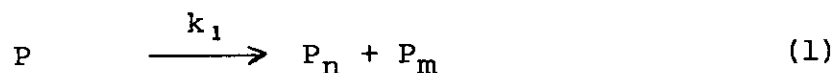
Radiation induced scission of water into an active species

$$H_2O \xrightarrow{k_2} A \qquad (2)$$

A may be $H\cdot$, $\cdot OH$, H_2, H_2O_2 etc.; the nature of A will not be

discussed here. It is only assumed that A induces indirect

scission of the polymer molecule.

$$A + P \xrightarrow{k_3} P_n + P_m \qquad (3)$$
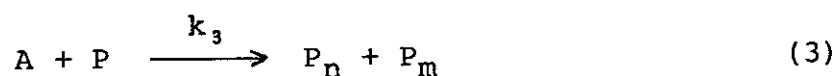
A's disappear not only by the reaction with polymer mole-

cules but also by the mutual reaction.

$$A + A \xrightarrow{k_4} B \qquad (4)$$

B is a stable molecule which can not react with P to de-

grade it.

If a stationary state is assumed, we can write as follows,

where R means radiation dose,

$$\frac{d[A]}{dR} = k_2[H_2O] - k_3[A][P] - k_4[A]^2 = 0 . \tag{5}$$

Here it is further assumed that the second term of the right hand side of equation (5) is much smaller than the third term, then we get the following equation as the condition of the stationary state.

$$[A] = (k_2/k_4)^{1/2} [H_2O]^{1/2} \tag{6}$$

The rate of scission is as follows.

$$\frac{dS}{dR} = k_1[P] + k_3[A][P] \tag{7}$$

S means severed bond in mole per unit volume and R dose in Mrad. Concentration of polymer, i.e. [P] is expressed in basic mole per unit volume.

Putting eq. (6) into (7), the following relation is obtained.

$$\frac{dS}{dR} = k_1[P] + k_3(k_2/k_4)^{1/2} [H_2O]^{1/2} [P] \tag{8}$$

Now we have to modify eq. (8), because we obtain by molecular weight change of polymer not the amount of severed bond in mole per unit volume but number of scissions of bonds per unit number of bonds. If we denote number of scissions per 1,000 bonds with s, we get

$$S = \frac{dS}{dR} \cdot \frac{1,000}{[P]}$$

$$= 1,000\{k_1 + k_2(k_2/k_4)^{1/2}[H_2O]^{1/2}\} . \tag{9}$$

The first term in the bracket which corresponds to direct scission is much smaller than the second one, so it can be neglected when it is concerned with very dilute solution. It is true that more detailed scheme is necessary, however, eq. (9) agrees satisfactory with the experimental results, that the number of scission is independent of the dose rate, degree of polymerization and concentration of polymer.

1) I. Sakurada and Y. Ikada, Bull.,Inst. Chem. Res., Kyoto Univ. <u>41</u>, 114, (1963).

[6]   Polymerization of Vinyl Monomers by Electron Beams

I. Sakurada, T. Okada, J. Takezaki, and

K. Hayashi

1.   Simultaneous Occurence of Radical and

Cationic Polymerization of Styrene

It was already shown in the case of polymerization of
moderately dried styrene (water content = 3.2×10^{-3} mole/l)
that weight fraction of polymers produced by ionic mechanism
increased by increasing dose rate[1]. When irradiation is
carried out by γ-rays at a dose rate of 4.7×10 rad/sec the
most part of the product consists of polymer produced by
radical mechanism, on the other hand by electron beam irradi-
ation at a dose rate of 1.2×10^5 rad/sec the main part is
produced by ionic mechanism.

For the kinetic analysis of the polymerization rate R_p,
it is assumed that initiation-radicals and -ions are created
independently from each other, and the rate of creation of
both the species is proportional to the dose rate. For the
simplification it is also assumed that the growing radicals
terminate by mutual reaction and growing ions by reaction
with water which is contained in styrene as an impurity.

The total rate of polymerization (R_p) may be written as
a sum of radical (R_r) and ionic polymerization rate (R_i).

$$R_p = R_r + R_i = B_r \, I^{1/2} + B_i \, [X]^{-1} \, I \qquad (1)$$

where I and [X] mean dose rate and water content respectively

and B_r and B_i are constants which contain G-values for radical and ion formation and rate constants of radical and ionic polymerization. The above equation may be rewritten as

$$\frac{R_p}{I^{1/2}} = B_r + B_i \frac{[I]^{1/2}}{[X]} \qquad . \qquad (2)$$

From the experimental value of R_p at various dose rates I and water content [X], which is kept constant at 3.2×10^{-3} mole/l we can find easily B_r and B_i, consequently R_r and R_i by graphical representation of equation (2). Thus we can calculate contribution of ionic or radical polymerization in the reaction. Table 1 shows the calculation results together with experimental results of contribution of ionic polymerization, which correspond to weight fraction of polymer formation inhibited by an addition of ammonia.

Table 1. Radiation-Induced Polymerization of Moderately Dried Styrene at Various Dose Rate, $[H_2O] = 3.2 \times 10^{-3}$ mole/l

Dose rate, I (rad/sec)	1.2×10^5	6.2×10^3	3.4×10^2	4.7×10
R_p (mole/l-sec)	3.22×10^{-2}	6.35×10^{-4}	8.2×10^{-5}	1.0×10^{-5}
Ionic calc.	95	82	52	29
Polym. % exp.	95	76	50	(4)

Agreement of the calculated and experimental values is sufficient except a case of the lowest dose rate where experimental error for ionic polymerization is very large. The agreement is a strong support for the proposed mechanism of

simultaneous occurence of radical and ionic mechanism. The

mechanism predicts that the contribution of both the mechanism

is independent of the dose rate when we evaluate it not in

weight as in Table 1 but in number of polymer molecules.

For the purpose of obtaining more information about mo-

lecular weight distribution and number average molecular weight

of the products gel permeation chromatography is carried out.

Fig. 1 shows the molecular weight distribution curve of polymer

obtained at 1.2 x 10^5 rad/sec as an example. The curve has a

large peak at molecular weight of about 32,000, small peaks

corresponding to dimer and trimer and a shoulder. Obviously

the large peak is due to ionic and the shoulder to radical

polymerization. Under appropriate assumptions based on other

curves, especially those for products obtained in the presence

of ammonia or water, the contribution of the two mechanisms and

the number average molecular weight of the two kinds of polymers
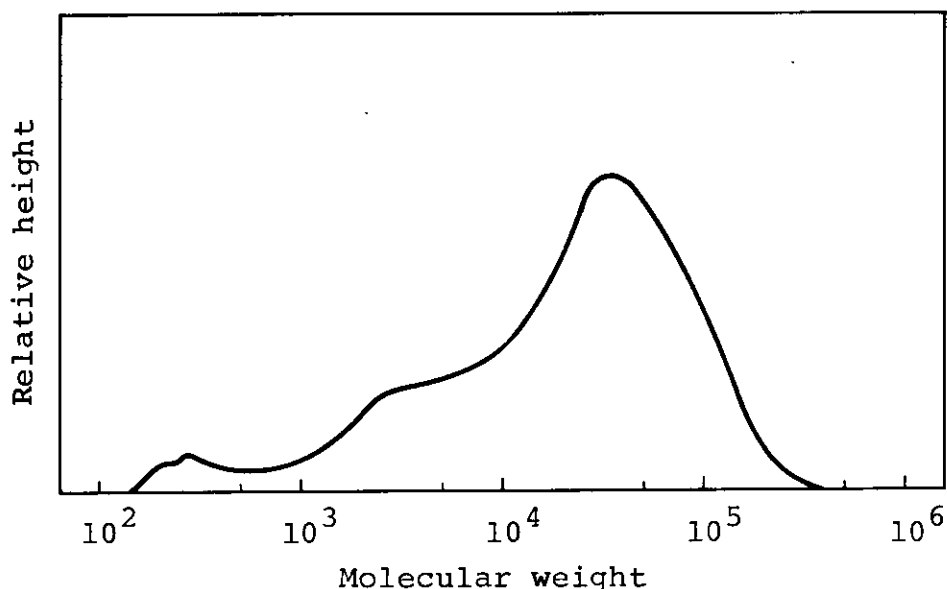
Fig. 1. GPC chromatogram of polystyrene obtained by
irradiation of electron beams at 1.2x10^5 rad/sec.
Water content of styrene; 3.0x10^{-3} mole/1.

are estimated. The weight contribution of each mechanism agrees fairly well with values shown in Table 1. With help of number average molecular weight, numbers of the two kinds of molecules obtained at four different dose rates are calculated and it is found that always about 25 % of the total number of polymer molecules are formed by ionic mechanism independent of the dose rate.

1) J. Takezaki, T. Okada, and I. Sakurada, JAERI, 5029, 66, 73 (1974).

2. Polymerization of Methyl Methacrylate

Methyl methacrylate is known to polymerize via radical or anionic mechanism by conventional means of initiation. Several investigators have carried out radiation-induced Polymerization of this monomer using γ-rays and come to the conclusion that the reaction proceeds via free radical mechanism. In continuation of studies on polymerization of styrene, methyl methacrylate is taken up because little information is available on the polymerization of this monomer initiated by high dose rate electron beams from an accelerator.

Methyl methacrylate which is purified by a conventional method and has a water content of 4×10^{-3} mole/l is employed for the experiment, and irradiated as a thin layer of 1 mm thickness in a flat reaction cell at room temperature. Irradiations are performed over a wide range of dose rate from 4×10 to 2.4×10^5 rad/sec. Polymer is recovered by pumping out residual monomer under vacuum.

Rate of polymerization is followed by a gravimetric method and it is found that the square root relationship for the dose rate dependence of the polymerization rate holds over the whole dose rate range investigated. Molecular weight distribution curves of polymers prepared at different dose rate are obtained by gel permeation chromatography and shown in Fig. 1.
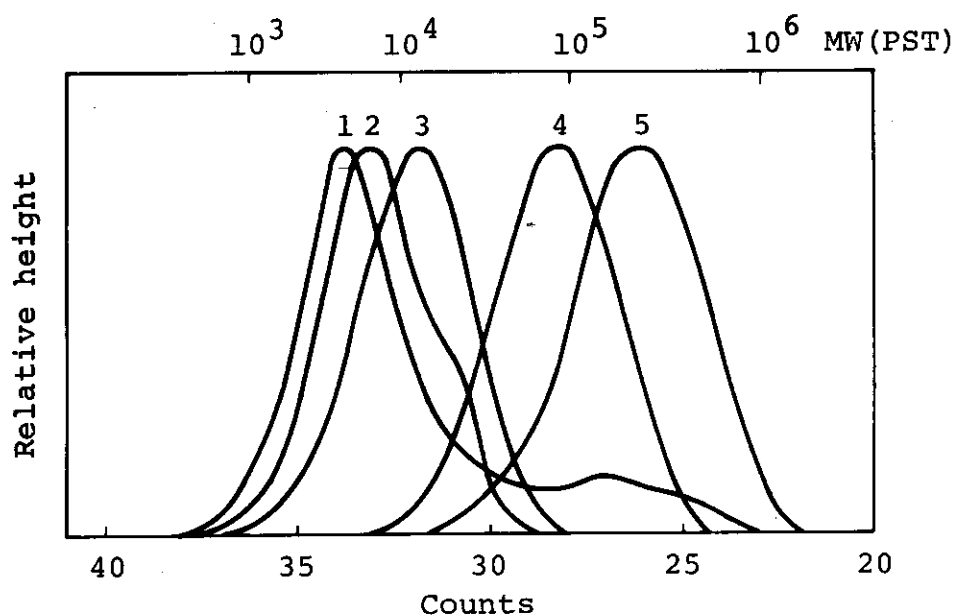
Fig. 1. GPC chromatogram of PMMA, effect of dose rate on the molecular weight distribution. $[H_2O]=1.4 \times 10^{-3}$ mole/l. Dose rate: 1, 2.4×10^5; 2, 4.0×10^4; 3, 6.0×10^3; 4, 3.7×10^2; 5, 2.4×10 rad/sec.

Curves of polymers prepared at dose rates lower than 6.0 x 10^3 rad/sec are unimodal, while the curve of polymer prepared at 4.0 x 10^4 rad/sec has a weak shoulder at the higher molecular weight side of the peak, and that of polymer prepared at 2.4 x 10^5 rad/sec has two distinct peaks; one of which is large and the other small. Apparently the large one is the same peak as in other curves and the small one is new and observed only in the polymerization at high dose rate.

The small peak shifts to lower molecular weight and the

average molecular weight decreases with increasing conversion. This may be due to degradation induced by radiation.

Number average molecular weights of polymers in the initial stage of polymerization at different dose rates show that the inverse square root relationship of molecular weight and dose rate holds up to 4×10^4 rad/sec. The experimental value of molecular weight at 2.4×10^5 rad/sec is somewhat greater than the value expected from the inverse square root relationship. This result of the kinetic analysis also suggests that some other polymerization mechanism becomes remarkable at the highest dose rate studied.

To get more information on the polymerization mechanism effect of additives on the polymerization of methyl methacrylate is studied. As inhibitor for specific polymerization mechanism N_2O, water or acetic acid is added to the monomer and irradiated at different dose rate up to 2.4×10^5 rad/sec. Neither the rate of polymerization nor the shape of molecular weight distribution is markedly affected by the addition of the additives. However, when DPPH is added to the monomer, it is observed that the polymerization is retarded. The retardation decreases with increasing dose rate and at 2.4×10^5 rad/sec the effect of DPPH on the rate of polymerization is very small. On the other hand the effect of DPPH on the shape of the molecular weight distribution curve is rather large and the small peak disappears.

It is now intended to employ much higher dose rate for the polymerization to get more information.

3. Polymerization of Alkyl Acrylates

Alkyl acrylates and methacrylates are of technical interest for their wide use in paint, coating and plastic material and their relatively high rates of polymerization especially in lower alkyl acrylates. As a part of a series of works on the polymerization at high dose rate, polymerizations of methyl, ethyl and n-butyl acrylates (MA, EA and BA, respectively) are carried out and experiments with methyl methacrylate (MMA) are also performed for the direct comparison to the acrylates.

Monomers are dried by calcium hydride and degassed in vacuum. 1.5 MeV electron beams from Van de Graaff accelerator are irradiated to the monomer of 1 mm thickness through 0.1 mm stainless steel plate soldered to a stainless steel block. All the irradiations are made at room temperature, ca. 17°C. Polymers are recovered by pumping out the residual monomer in a vacuum oven.

In Fig. 1, dose rate-polymer conversion relationships at low dose rate region by γ-rays are given for the comparative purpose. MA and EA polymerize much more easily than BA and MMA. The rapid rise of R_p attributed to "gel effect" is observed in all the monomers, particularly in MA and EA.

Results by electron irradiation are shown in Fig. 2. MA and EA polymerize much more easily than BA and MMA, again. However, in all cases, the acceleration of R_p due to gel effect is less clear. This is explained by the following reasons. First, at higher dose rate polymerization, a growing
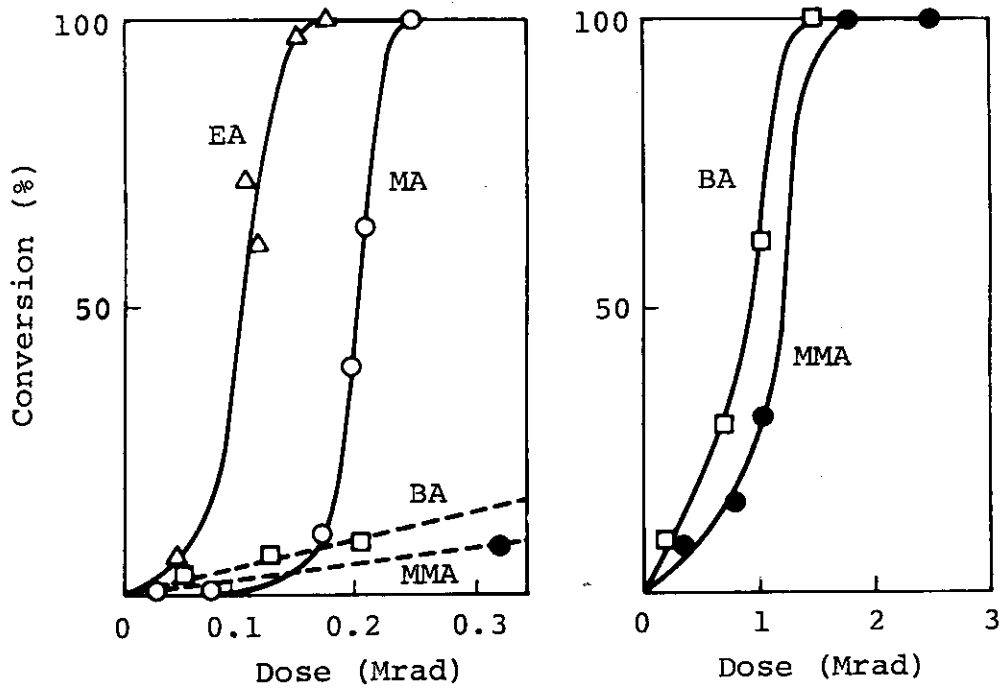
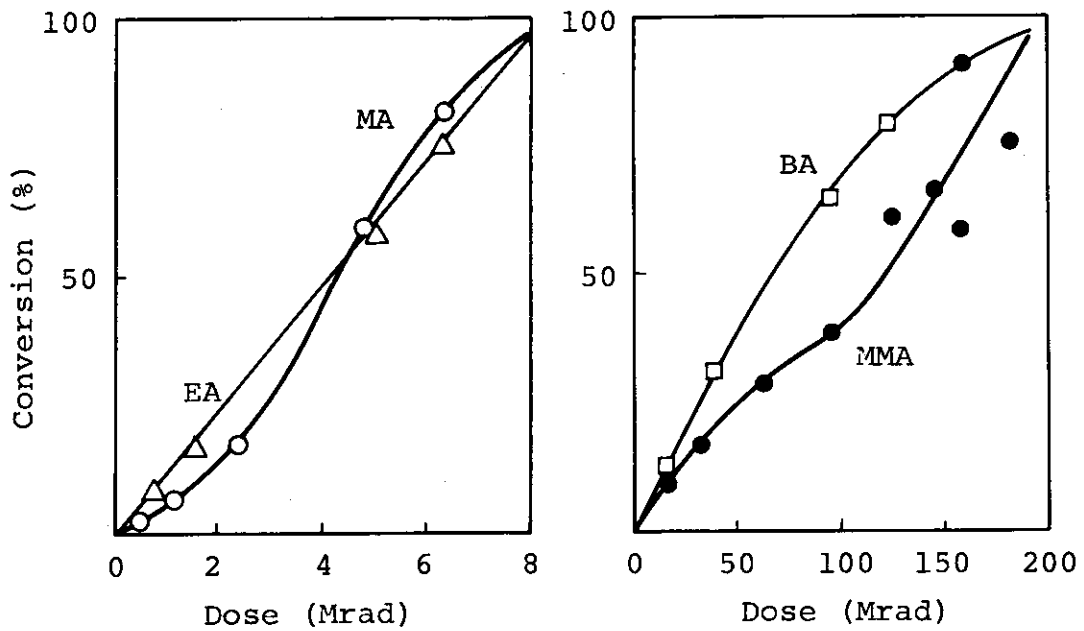Fig. 1. Polymerization by γ-rays at the dose rate of 83 rad/sec.

Fig. 2. Polymerization by electron beams at the dose rate of
1.6 x 10⁵ rad/sec.

radical finds less difficulty to recombine with other radical
even in fairly viscous system because of high radical concen-

tration. Second, the diffusion of polymer radical must be
easier in higher dose rate case for the smaller increase of
bulk viscosity arisen from the lower MW of the polymer formed.

R_p and molecular weight (MW) by electron beam irradiation
are summarized in Table 1. As polymer becomes gel at high
conversion of MA and EA, MW's are compared at approximately
10 % conversion. MW's are tentatively evaluated from GPC
chart calibrated by standard polystyrenes without further
calibration. In most of all cases we studied, bimodal MW
distributions are obtained at high dose rate irradiation.
The high MW fraction is separated by an appropriate method on
GPC chart and MW's are calculated separately. MW's are still
substantially large in MA and EA polymers.

Table 1. R_p and MW at the dose rate of 1.6×10^5 rad/sec

	R_p (mole/1-sec)	high MW fraction (%)	$10^{-4}\overline{M}_n$	$10^{-4}\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
Methyl Acrylate	1.2×10^{-1}	1-2	4.4	9.1	2.1
			109	130	1.2
Ethyl Acrylate	1.7×10^{-1}	8	6.5	15	2.2
			130	155	1.2
n-Butyl Acrylate	8.8×10^{-3}	24	0.27	0.79	2.9
			23	42	1.8
Methyl Methacrylate	8.8×10^{-3}	17	0.18	0.44	2.4
			13	25	1.9

The dose rate dependences of R_p at initial stage and MW
are also studied. In the discussion below, only the $\overline{M}_n$ of the
main fraction is taken into account. In MMA, $R_p \propto I^{0.45}$ and

$MW \propto I^{-0.48}$ are obtained in a fair agreement with $R_p \propto I^{0.5}$ and $MW \propto I^{-0.5}$ which is expected from the steady state kinetics. However, the acrylates do not follow these relations. The dose rate exponents of MW are -0.62 for BA, -0.27 for EA and -0.44 for MA. Dose rate dependence of R_p is less meaningful for their very low initial R_p's at low dose rate region.

We have studied as to the high MW fraction in PMMA in some detail. It appears at high dose rate prominently to about 10 - 25 % of the total polymer. The MW drastically reduces with the increase of polymer yield probably due to the degradation and at higher conversion than 50 % conversion, it is incorporated into the tail of the main fraction whose peak MW in GPC remains almost invariant during the whole course of the polymerization. Further drying of the monomer enhances the R_p by 20 % but the fraction of high MW polymer does not change. Copolymerization with acrylonitrile gives a puzzling result that copolymer compositions of the two fractions differ only slightly and lie in between the radical and anionic composition curves.

[7] Estimation of the Purity of Graft Copolymers by Thin-Layer Chromatography[1]

F. Horii, Y. Ikada, and I. Sakurada

It has recently been reported that thin-layer chromatography (TLC) makes it possible to characterize polymers with respect to the differences in composition, monomer arrangement, steric isomerism, and molecular weight. Therefore TLC is applied to the graft copolymers isolated from various grafting reaction products and the purity is evaluated by comparing the chromatogram of the graft copolymer sample with that of graft copolymer-homopolymer mixtures of given mixing ratios.

The graft copolymers are produced by radiation grafting in the following combinations: poly (vinyl alcohol)-styrene, poly (vinyl alcohol)-methyl methacrylate, cellulose-styrene, nylon-styrene, and poly (ethylene terephthalate) (PET)-styrene. Prior to the chromatographic development the homopolymers are removed as rigorously as possible by extraction or selective precipitation. The hydroxyl groups in the three former graft copolymers are completely acetylated to obtain poly (vinyl acetate) (PVAC)-g-polystyrene (PS), PVAC-g-poly (methyl methacrylate) (PMMA), and cellulose triacetate (CTA)-g-PS. The characterization study proves that all the graft copolymers have one branch per molecule on the average, the number-average molecular weight of the branches being 1×10^5. The homopolymers used are the mother backbone polymers or those formed during the grafting.

The TLC substrate is silica gel precoated on 5 x 20 cm

or 20 x 20 cm glass plates (Merck A. G., Darmstadt, Germany).
The thickness of the thin layer is 0.25 mm. The gel layer is
developed with methanol followed by activating at 110°C for 1
hr just prior to use. From 4 to 40 µg of the polymers is
deposited as a band of 5 cm length parallel to the developing
direction by using a microsyringe. This bandlike deposition
is made because about 40 µg is necessary to detect amounts as
small as < 1 % homopolymers occluded in the sample, and such
a large amount of polymer normally can not be developed when
deposited as a tiny spot. The developers are listed in Table
1, together with solvents used for preparing sample stock
solutions and indicators for staining of chromatograms.

The adsorption and desorption of polymers on the chromato-
graphic gel are strongly dependent on the polarity of solvent
and polymer as well as the activity of stationary gel layer.
In general, a mixture of polymers with different polarities
is readily separated in such a fashion, as the less polar
polymer is developed while the more polar one remains at the
spotted point on the plate. On the contrary, it is impossible
to develop the more polar polymer alone, as the separation
proceeds by an adsorption-desorption mechanism. Chromato-
graphy which proceeds through a selective elution mechanism
is required in order to develop only the more polar polymer.
The developer to be used for such chromatography must be a
solvent for the more polar polymer but a nonsolvent for the
less polar one and, of course, must be capable of developing
the former. Besides these difficulties, the continuous
development method is often required to gel a satisfactory
separation.

Table 1.

Experimental Conditions of Thin Layer Chromatography for Graft Copolymers

Sample	Homopolymer corresponding to the backbone			Homopolymer corresponding to the branch	
	Spotting solvent	Developer	Indicator	Developer	Indicator
CTA-g-PS	$CHCl_3$	$CH_2Cl_2/CH_3OH(1:1)$	10% $HClO_4$ aq. soln.	$CHCl_3$	10% $HClO_4$ aq. soln.
PVAC-g-PS	$CHCl_3$	CH_3OH/H_2O (9:1)[a]	10% $HClO_4$ aq. soln.	$CHCl_3$	10% $HClO_4$ aq. soln.
PVAC-g-PMMA	$CHCl_3$	CH_3OH/H_2O (9:1)[a]	0.05N I_2 aq. soln.	MEK/CCl_4(8:2)	0.05N I_2 aq. soln.
Nylon-g-PS	$HCOOH/CHCl_3$(2:8)	$HCOOH$[a]	0.05N I_2 aq. soln.	$CHCl_3$	10% $HClO_4$ aq. soln.
PET-g-PS	Phenol/CH_3OH(95:5)	Phenol/H_2O(75:25)	H_2O-CH_3OH soln. of Kayalon Fast Brown R[b]	$CHCl_3$	H_2O-CH_3OH soln. of Kayalon Fast Brown R[b]

a : Continuous development.

b : Manufactured by Nippon Kayaku Co., Ltd.

Typical chromatograms of PVAC-g-PS graft copolymers are
demonstrated in Figs. 1 and 2. The TLC is always carried out
not only for the graft copolymer sample, but for mixtures of
known quantities of sample and homopolymer to evaluate quanti-
tatively the amount of the homopolymer contaminating the
starting graft copolymer sample. Fig. 3 shows the scanning

$$\frac{PS}{PVAC-g-PS}$$

4/0
4/40
0.4/40

0.2/40
0/40
PVAC 40
(μg)

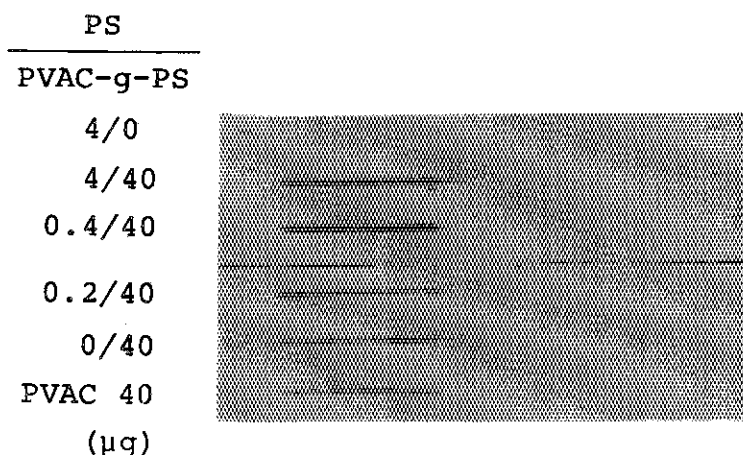Fig. 1. Thin-layer chromatograms of the PS homopolymer,
the PVAC homopolymer, the isolated PVAC-g-PS, and
mixtures of PS and PVAC-g-PS with different mixing
ratios. Developer: chloroform.

$$\frac{PVAC}{PVAC-g-PS}$$

4/0
4/40
0.4/40

0.2/40
0/40

(μg)
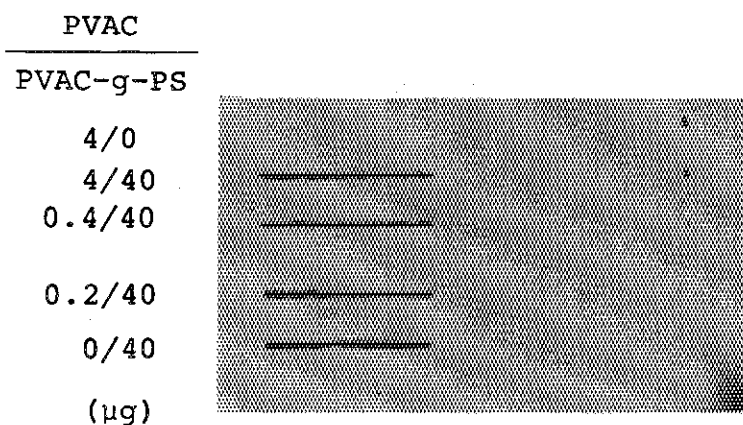
Fig. 2. Thin-layer chromatograms of the PVAC homopolymer,
the isolated PVAC-g-PS with different mixing ratios.
Developer: methanol-water (9 : 1) mixture.
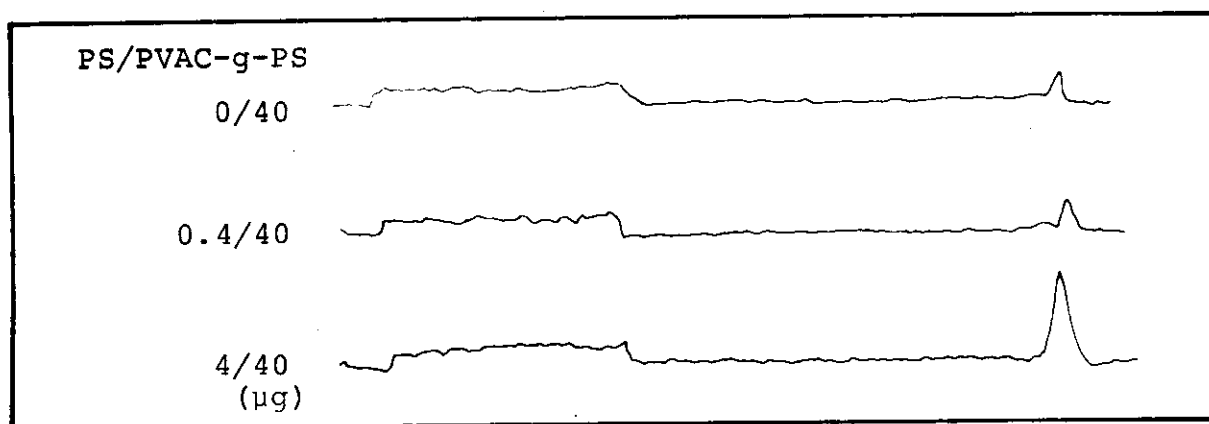
Fig. 3. Scanning spectrodensitometric traces for PS in the
chromatograms of the mixtures of PS and PVAC-g-PS
(corresponding to Fig. 1).

spectrodensitometric traces with the reflected light at 256 nm

for PS in the developments of mixtures of PS and PVAC-g-PS.

It seems highly possible that the graft copolymer is not at

all developed, the corresponding homopolymer alone being

developed. Comparison of the staining degrees of the developed

polymers reveals the purity of the PVAC-g-PS to be about 95 -

98 %. CTA-g-PS, nylon-g-PS, and PET-g-PS give similar, clear

chromatograms. The purity of the two former graft copolymers

is evaluated as about 95 - 99 %, and the two latter are found

to be, in some cases, contaminated with their homopolymers to

the extent of about 10 %.

In conclusion, we can easily detect by the TLC method

homopolymers contaminating graft copolymers, even by so small

amounts as 0.5 - 1.0 %, though in some cases the development

with selective solvents should be continued carefully for   ·

more than 10 hr. This success in polymer characterization by

the TLC method suggests that the grafting product would be

separated in a preparative scale also with the help of a
similar chromatographic technique. In fact, the pure graft
copolymer could be effectively isolated from its reaction
product by a column adsorption chromatography with the silica
gel.

1) F. Horii, Y. Ikada, and I. Sakurada, J. Polym. Sci.,
   Polymer Chem. Ed., 13, 755 (1975).

[8] Modification of Polymers

I. Sakurada, M. Gotoda, T. Okada, K. Kaji,

and A. Tsuchiya

1. Radiation-Induced Grafting of Acrylonitrile onto

Polyvinylidene Chloride Fiber

As a continuation of studies of grafting of acrylonitrile

onto polyvinyl chloride fiber, experiments are undertaken to

graft acrylonitrile onto polyvinylidene chloride fiber for the

purpose of modifying properties without serious loss of flame-

retardance of the original fiber.

The grafting takes place smoothly when a suitable swelling

agent such as dimethyl formamide is used as a medium for the

immersion grafting of acrylonitrile by a simultaneous irra-

diation technique. In most cases 1 : 1 mixture of dimethyl

formamide and acrylonitrile is employed for the reaction

without an addition of ferrous salt, because this is insoluble

in the monomer mixture. In spite of the absence of an in-

hibitor outside of the fiber, degree of grafting higher than

100 % can easily be achieved and graft fiber separated from

the mixture.

Some properties of the graft fibers are measured. It is

known that the density of polyvinylidene chloride fiber is

about 1.70, which is the highest value among common organic

fibers; the value becomes lower by the grafting and the fiber

of 100 % graft shows a value of 1.40 which is similar to that

of polyester. The initial Young's modulus of the fibers

increases with grafting. A fiber with 33 % graft has a value

of 239 kg/mm^2, which is 2.5 times greater that of the original

fiber.

Tenacity of the fibers decreases with increasing degree

of grafting; the original fiber has a value of 1.78 g/d, which

changes to 0.96 g/d at 33 % graft. Such a drop of the tenacity

is always the case when a fiber is grafted and the tensile

strength is expressed in tenacity, i.e. in g/d, because not the

length but the cross section of the single fibers increases by

the grafting, and the weight increase by the grafting is only

a dead load for the fiber unless the fiber is drawn after the

grafting for the orientation of the grafted polymer.

Flame-retardance of the fibers is studied in some detail.

The fiber is exposed to flame of 0.16 cm in length for 1

second to see whether the specimen fibers are self-extinguish-

ing or not and the results are shown in Table 1 together with

Table 1. Flame Retardance of Acrylonitrile Graft
Polyvinylidene Chloride Filaments

Apparent graft (%)	Cl content (%)	Flame retardance
0	75.2	s.e.
12.9	66.6	s.e.
36.0	55.3	s.e.
54.0	48.8	s.e.
73.6	43.3	s.e.*
110.0	35.7	n.s.e.

s.e., self-extinguishing; n.s.e., not self-extinguishing.
*, extinguished 3 seconds after removal of flame.

other observations. Graft fibers are self-extinguishing so
long as the graft % is less than 73.6 % (Cl content is greater
than 43.3 %). Table 2 shows similar experimental results with
acrylonitrile graft polyvinyl chloride fabrics. The threshold
graft % is in this case much lower than the former case and
has a value of about 36 % which corresponds to a Cl content of
about 42 %. It seems that 42 - 43 % Cl content is the common
threshold for the self-extinguishing of polyvinylidene and
polyvinyl chloride fibers grafted with acrylonitrile and tested
under the condition employed in the present experiments.

Table 2. Flame Retardance of AN Graft PVC Fabrics

Apparent Graft (%)	Cl cont. (%)	Weight (mg/cm^2)	Flame Retardance	Burning rate (cm/min)
0	56.8	5.6	s.e.	-
11.5	50.9	20.5	s.e.	-
35.9	41.7	21.8	s.e.	-
60.6	35.4	23	n.s.e.	24
90.2	29.8	25	n.s.e.	36
PAN	0	-	n.s.e.	40

2. Radiation-Induced Grafting of Acrylic acid onto
    Polyvinyl Chloride fiber

Polyvinyl chloride fiber is flame-retardant but it has
a serious disadvantage that the softening temperature is low,
so that it shows a remarkable heat-shrinkage at about 70°C.
It was already reported, that heat-resistance was improved

by radiation-induced grafting of acrylonitrile[1]. However, to obtain sufficient heat-resistance at least 100 % grafting of acrylonitrile is desirable and this percent graft results in a drop of flame-retardance so that the fiber is no more self-extinguishing as shown in Table 2 of the preceding work. We are now engaged in a work to graft acrylic acid to poly-vinyl chloride fiber to obtain fiber which shows higher softening temperature than the original fiber without serious damage to its flame-retardance.

The grafting of acrylic acid is carried out in a mixture of acrylic acid, ethylene dichloride and water containing a small amount of Mohr's salt (60 : 20 : 20, by volume) with irradiation of γ-rays at 23°C. Ethylene dichloride is used as a swelling agent to polyvinyl chloride fiber and Mohr's salt is added to the monomer solution to suppress useless formation of acrylic acid homopolymer outside of the fibers. Undrawn and drawn polyvinyl chloride fibers are immersed in a slacked or stretched states in the monomer mixture at room temperature and irradiated with γ-rays at a dose rate between 5.5×10^3 and 2.6×10^5 rad/hr.

According to the experiments it is not difficult to obtain fibers of 38% graft at a dose rate of 2.6×10^5 rad/hr. in five minutes.

Impregnation grafting also is carried out using electron beams from a Van de Graaff accelerator. A typical example is as follows. In a case of about 40 % pick up of the monomer solution 20 % graft is obtained by irradiation of 0.2 Mrad at a dose rate of 0.1 Mrad/sec, which corresponds to some 80 %

monomer utilization for the grafting.

Acrylic acid graft polyvinyl chloride fibers have high heat-shrinkage temperature, especially when acrylic acid is converted to calcium salt (see Fig. 1). Flame retardence is much less damaged by the grafting of acrylic acid and fibers of some 100 % graft are still self-extinguishing as the original fiber.
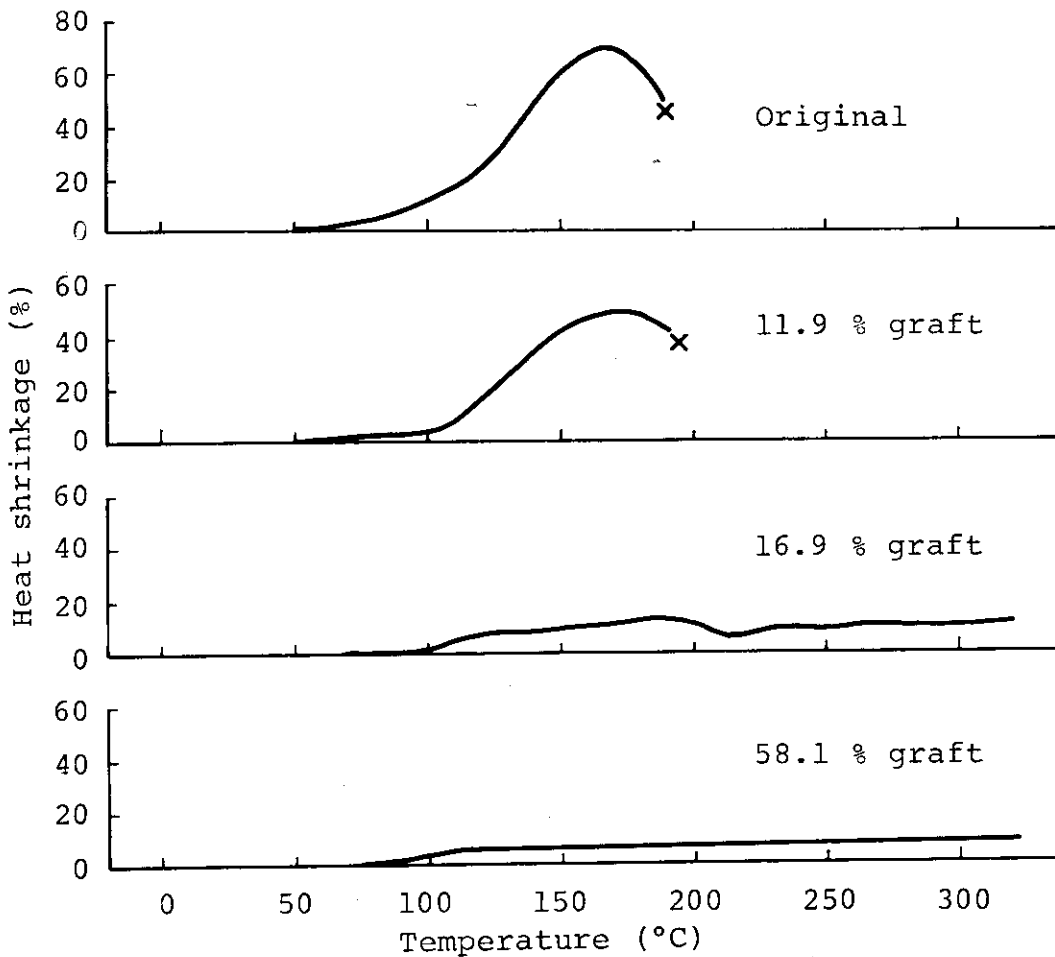

Fig. 1. Heat Shrinkage of AA-Ca graft PVC fibers.

1) T. Okada and I. Sakurada, Annual Report of the Japanese Association for Radiation Research on Polymers, 6, 57 (1965).

3. Surface Modification of Polyester Film by Radiation-Induced Chlorination

Experiments on the surface modification of polyester film by radiation-induced chlorination are carried out to enhance adhesive performance of the film.

A polyester film, a commercially available one (polyethylene terephthalate, "Lumilar", 0.096 mm thickness) is employed and irradiated in chlorine gas with γ-rays at room temperature. Weight increase of the fiber by the reaction is regarded to be due to the chlorination and the Cl-content of the film is calculated.

Chlorination curve at a dose rate of 3.0×10^4 rad/hr is shown in Fig. 1. By irradiation of 0.5 Mrad, Cl-content shows a value of 1 %, but further irradiation has almost no effect
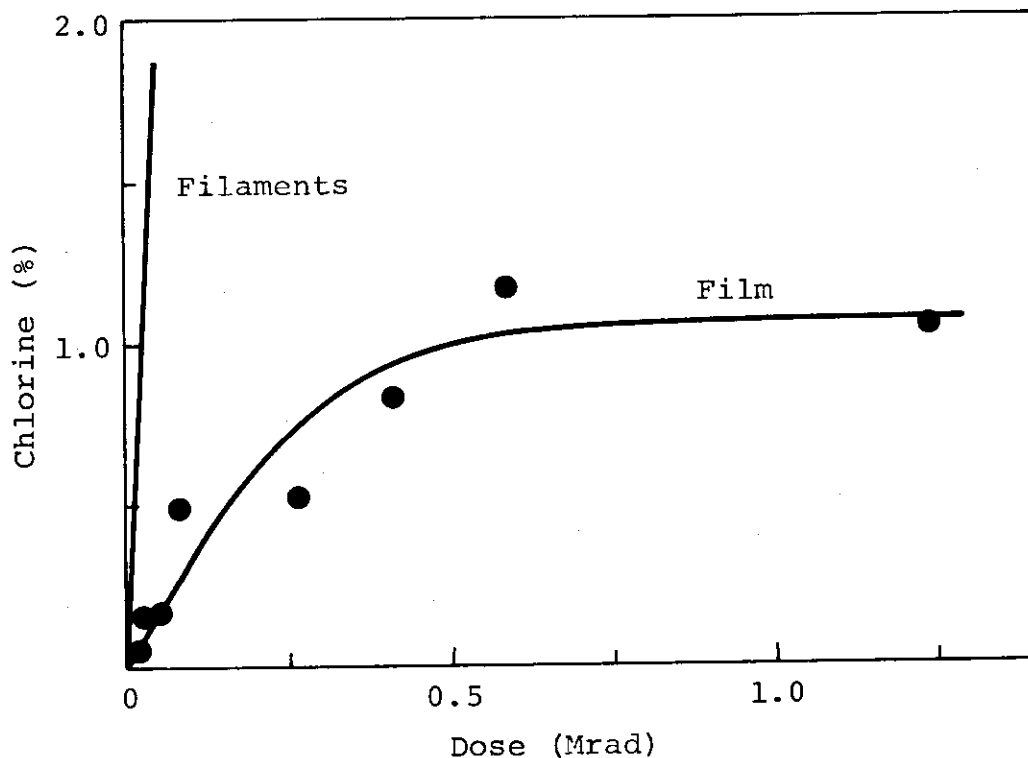

Fig. 1. Radiation-induced chlorination of polyester film at 3.0×10^4 rad/hr at 28°C.

to enhance the Cl-content. Fig. 1 shows a chlorination curve

of polyester filament (2 denier x 30) also. Rate of chlori-

nation of the filament is much higher than that of the film

and seems to suggest that the chlorination takes place mainly

on the surface.

Effect of Cl-content on the contact angle of a water

droplet on the film is studied and shown in Fig. 2. As the

Fig. 2. Contact angle of chlorinated polyester film.
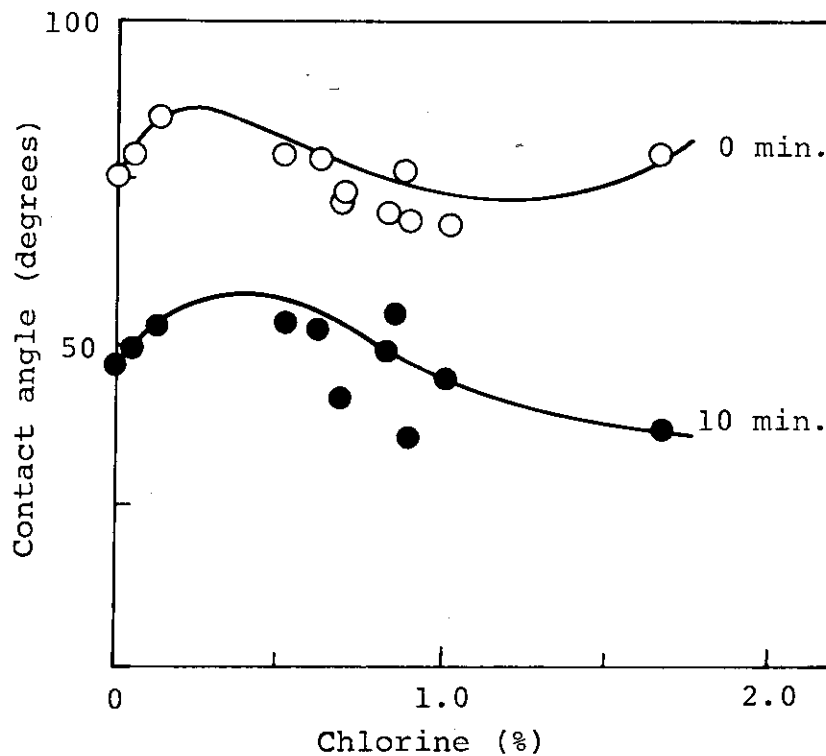
angle changes with time Fig. 2 shows the extrapolated value of

contact angle at time zero and that after ten minutes of con-

tact. In both cases curves show maxima at a Cl-content of

about 0.3 %.

Adhesion test of chlorinated film is also carried out

using a commercial epoxy type adhesive ("Sumikadyne"). Two

pieces of film of the same Cl-content are bonded by curing

20 minutes at 140°C, and peel force is measured. As seen in
Fig. 3, peel force shows a very sharp maximum at such a low
Cl-content as 0.1 %. Peel force increases from 43 g/cm of
the original film to 330 g/cm at the maximum and then decreases
with increasing Cl-content. At the maximum peel force, not
the bond but the film itself is broken by the test.
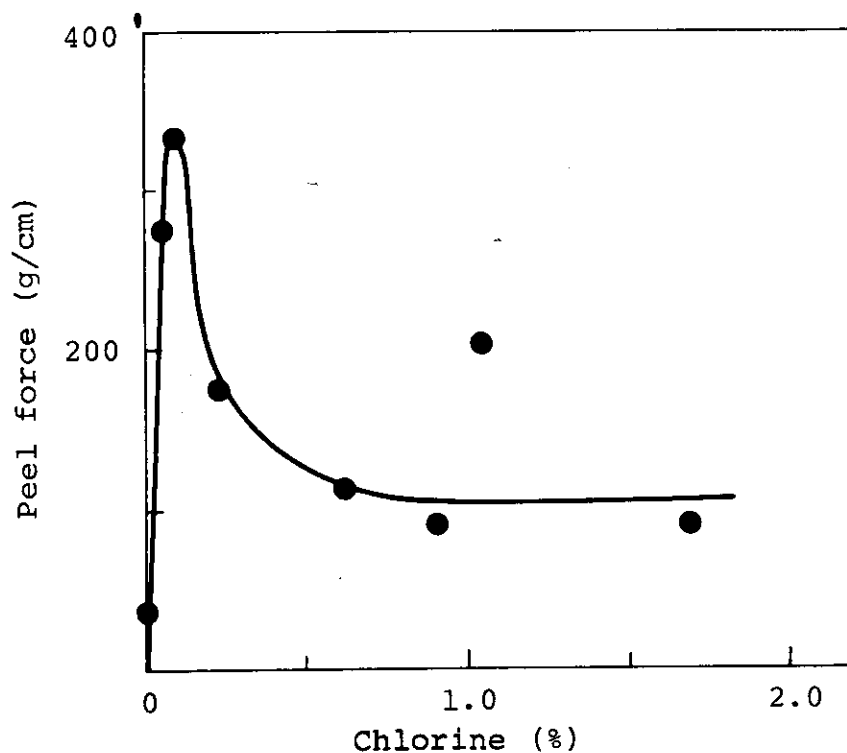
Fig. 3. Effect of chlorination of adhesion improvement of
polyester film. Adhesive; "Sumikadyne A019-HE"
(epoxy type).

ATR infrared spectra are taken and the appearance of new
bands between 900 and 1100 cm^{-1} is observed inspite of the
small Cl-content such as 1.0 or 1.8 %. New bands between 1700
and 1800 cm^{-1} seem to suggest that the formation of some
oxygen containing groups which contribute to wetting and bond-
ing is also likely.

4. Radiation-Induced Chlorination of Polyester Fiber

For the purpose of making polyester fiber flame retardant experiments are undertaken to introduce chlorine atom in the polyester (polyethylene terephthalate) structure by radiation-induced chlorination.

Filament of fabric of polyester is placed in a glass reaction vessel in which chlorine gas is filled to about atmospheric pressure and irradiated with γ-rays at room temperature for the chlorination. Typical results are shown in Fig. 1. Weight increase by the reaction is regarded to be due to chlorination and the chlorine content of the fiber is calculated.

After irradiation of 20 hours chlorine contents are 4.6 and 5.0 % for the fabric and filament respectively. By
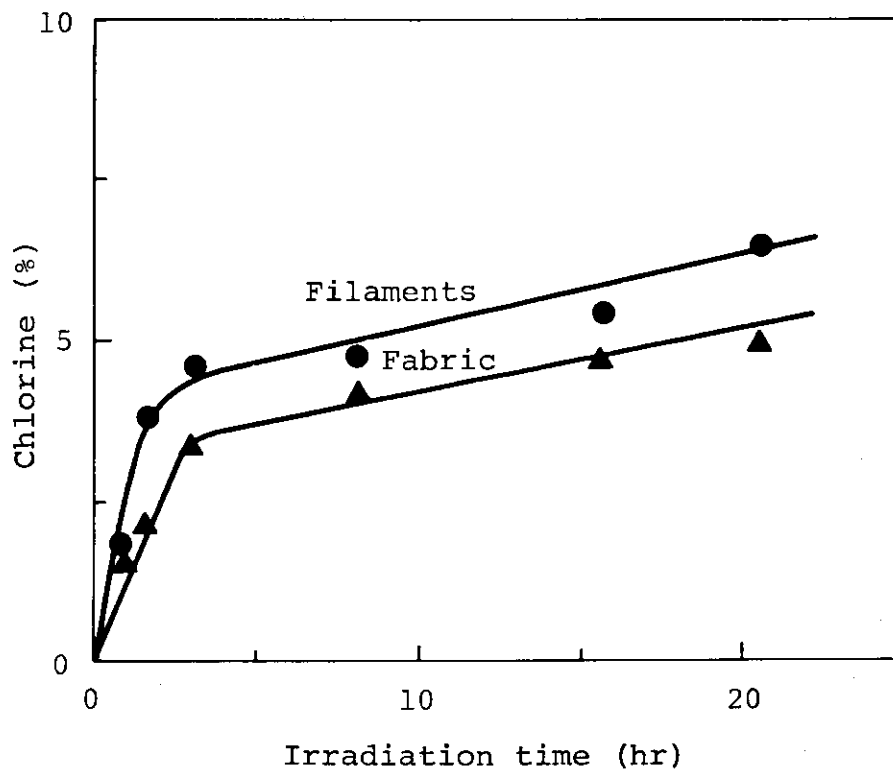

Fig. 1. Radiation-induced chlorination of polyester filaments and fabric at 5.6 x 10^4 rad/hr at 28°C.

further irradiation the chlorine content increases only a little. The initial G-value for the filament is calculated to be 3.8 x 10^4. When polyester is impregnated with a suitable swelling agent and subjected to chlorination, the reaction proceeds more smoothly.

Tenacity of fibers shows a little decrease by the chlorination; 4.9 g/d of the original fiber drops to 3.5 g/d when chlorinated to 13.7 %. Although flame retardance of the fiber is much improved by the chlorination, thermal stability of the chlorinated fiber tested by thermogravimetric analysis is inferior to that of the original fiber. Further studies are being continued.

5. Abrasion of Polyethyleneglycol Dimethacrylate Graft Polyester Fabrics

Polyester fabrics are made hydrophilic by surface-grafting polyethyleneglycol dimethacrylate (PEGMA) whose degree of polymerization is 14. As already reported, grafting of PEGMA proceeds readily by irradiation of electron beams from a Van de Graaff accelerator and the PEGMA graft polyester fabrics exhibit satisfactory water absorption- and antistatic-characteristics. PEGMA can not penetrate into the inside of polyester fibers because of its high molecular weight and most part of PEGMA is deposited and held on the surface of the fibers as insoluble polymer due to crosslinking. Therefore it is unexpected that the water-absorption and antistatic properties of the graft polyester fabrics are fast to repeated

laundrying. In connection with the fastness to laundrying, abrasion tests are performed on the PEGMA grafted fabric with a Custom-type abrasion machine and the water absorption is measured after certain cycle of abrasion. Table 1 shows effects of abrasion on the strength-loss and wicking time for 9.6% graft polyester fabric. Wicking time means the time

Table 1. Effect of Abrasion on the Strength Loss and the Water Absorption Rate (Wicking Time) of PEGMA Graft Polyester Fabric (9.6% graft)

Abrasion cycles	Breaking load (kg)	Strength loss (%)	Wicking time (sec)
0	43.0	0	15.0
4,000	46.7	0	10.0
12,000	32.7	24	12.5
30,000	5.8	87	15.0

required for a water droplet to be absorbed in the fabric and is a measure of water-absorption rate. Wicking time for the original fabric is above 1800 sec and more hydrophilic fiber requires less time for the wicking. As seen from the table strength loss reaches a value of about 87 % after 30,000 cycles of abrasion while the graft fabric still retains water-absorption power of the fiber before abrasion.

Scanning electron microscopic observation of fabrics before and after the abrasion reveals that PEGMA polymer on the surface of fibers is not peeled off by abrasion but still held in crushed and flattened form on the surface.

6. Combustion and Smoking of Composites of Wood-Vinylidene Chloride Copolymer[1]

Wood plastic composites (WPC) of small polymer loading (30 - 40 %) having excellent fire retardency as well as excellent dimensional and thermal stabilities were prepared by γ-ray irradiation of wood impregnated with vinylidene chloride (VDC) with or without triallylphosphate (TAP) and acrylonitrile (AN)[2].

Detailed examinations are undertaken on inflammability and smoking for WPC of beach sapwood loaded with two monomer systems comparatively; one, VDC alone, and the other, mixture of VDC, TAP, and AN (5 : 4 : 1).

The method of preparation of WPC is the same as that described previously[2]. Differential thermal analysis (DTA) is carried out for specimens in air stream. The combustion tests are carried out for specimen of 1 g using a thermal balance. Simultaneous measurements are made on combustion temperature, temperature of atmosphere during combustion, and optical density change of atmosphere caused by smoke evolved from the specimen. Analyses of the combustion exhaust for CO, CO_2, and HCl are also made.

The activation energy of combustion and specific smoke evolution are measured for different polymer loadings for VDC-WPC and VDC/AN/TAP-WPC. The comparisons of the results indicate that the higher combustion resistance is obtained by smaller polymer loading using the monomer mixture and

the smoke evolution is smaller in the two systems than ex-
pected.

The improvement of fire retardency in WPC containing the
monomer mixture is illustrated by DTA diagrams in Fig. 1.
Untreated wood gives two exothermic peaks at 310° and 410°C,
which have been assigned as due to oxidation reactions of
cellulose in a cell wall and of lignin which exists between
cells, respectively (Fig. 1a). The peak at 410°C disappears
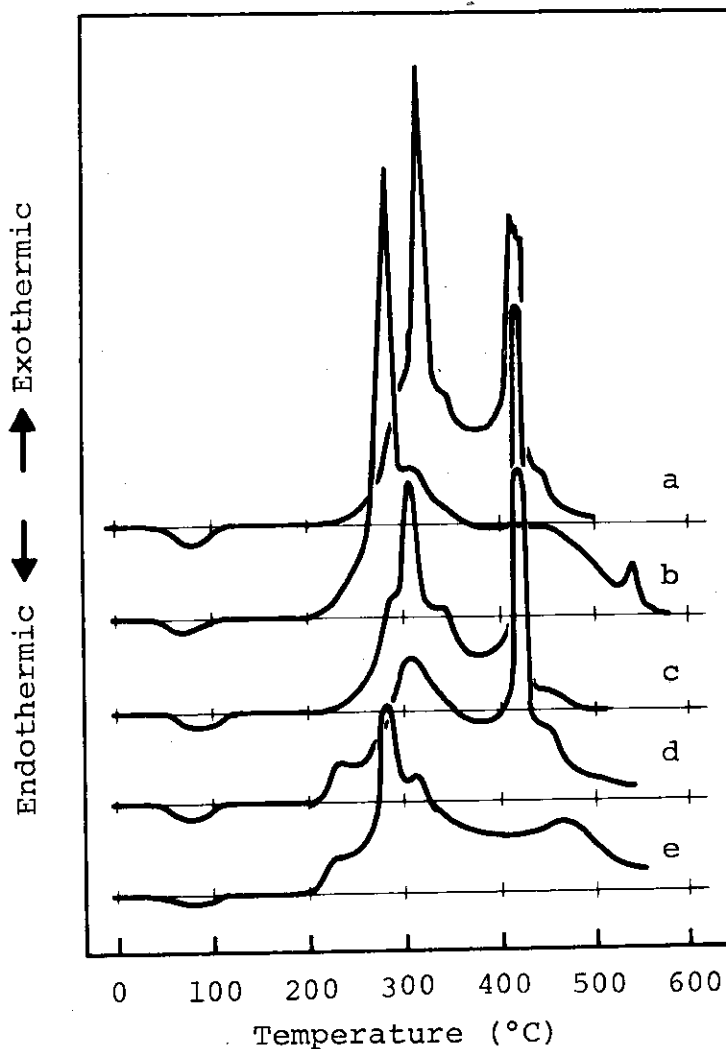with small shift of the peak at 310°C to lower temperature

Fig. 1. DTA diagrams for wood and WPC: a, untreated wood;
b, AN-WPC (19 %); c, MMA-WPC (14 %); d, VDC-WPC
(28 %); e, VDC/AN/TAP-WPC (19 %).

when AN is loaded in the wood (Fig. lb). This is explained

by that the PAN loaded in the wood protects the lignin part

away from oxygen, but gives a little modification in the

cellulose in a cell. The addition of MMA affects the cell

wall a little (Fig. lc), but drastic effect on cell part is

obtained by the addition of VDC, diminishing most of the

exothermic peak at 310°C (Fig. ld). The results of the ex-

periment undertaken in an attempt to diminish both exothermic

peaks by simultaneous addition of both AN and VDC are suc-

cessful (Fig. le).

The heat of evolution in the gas phase decreases and

then increases with increasing amount of polymer loading.

The similar tendency is also observed for the combustion

efficiency. These are explained by two competing factors;

one is endothermic decomposition reaction to release HCl, and

the other, the combustion of polymer having high heat of com-

bustion.

1) T. Handa, A. Takahashi, M. Gotoda, N. Ebihara,
   M. Saito, and Y. Ikeda, Proc. 18th Japan Congr. on
   Materials Res., 182 (1975).
2) M. Gotoda and N. Takeshita, JAERI, 5030, 72 (1971).

[9] Preparation of Crosslinked Poly(vinyl Alcohol)

Membranes by Radiation Technique

Y. Ikada, T. Mita, F. Horii, and M. Hatada

Application of hydrophilic polymers highly swollen with water or hydrogels as biomedical membrane is currently an important problem. Since poly (vinyl alcohol) (PVAL) seemed to be promising for this specific applications, a series of investigations on membrane is taken up choosing PVAL as a starting material for preparing membranes. According to the previous works[1] crosslinking of PVAL takes place readily when it is irradiated in the presence of water.

In the present work the irradiation of PVAL is carried out for aqueous solutions and water-swollen films. Prior to irradiation dry PVAL films are swollen with water at room temperature to equilibrium. The degree of swelling (DS), defined as gram of water in the swollen film per gram of the dried film, is 1.00 for the film without heat treatment and 0.221 for the film with heat treatment. Aqueous solutions and the water-swollen films are placed on a glass plate and then covered with a glass plate of 0.125 cm thickness. Mylar films are used as spacer in the case of aqueous solutions. This procedure is always performed without excluding the atmospheric oxygen. Irradiation is carried out with a Van de Graaff accelerator at a dose rate of 1.0×10^5 rads/sec under forced cooling with a fan. If the swollen film is not covered with glass plate, no gel is formed regardless of the radiation dose.

The irradiated, gelled solutions and swollen films are immersed in boiling water for an hour to extract any sol part and to "melt" residual crystallites. The resulting PVAL membranes are stored in plenty of water at room temperature and subjected to measurements of DS and permeability of water. The thickness of the wet membrane is calculated from the DS and the surface area under the assumption of additivity of water and polymer densities.

Fig. 1 gives Charlesby-Pinner plot for the irradiation of PVAL film without heat treatment in a water-swollen state.

$$S + \sqrt{S} = p_0/q_0 + 1/q_0 \overline{P}_n(0) R$$

Where p_0 is the ratio of main chain scissions per unit dose
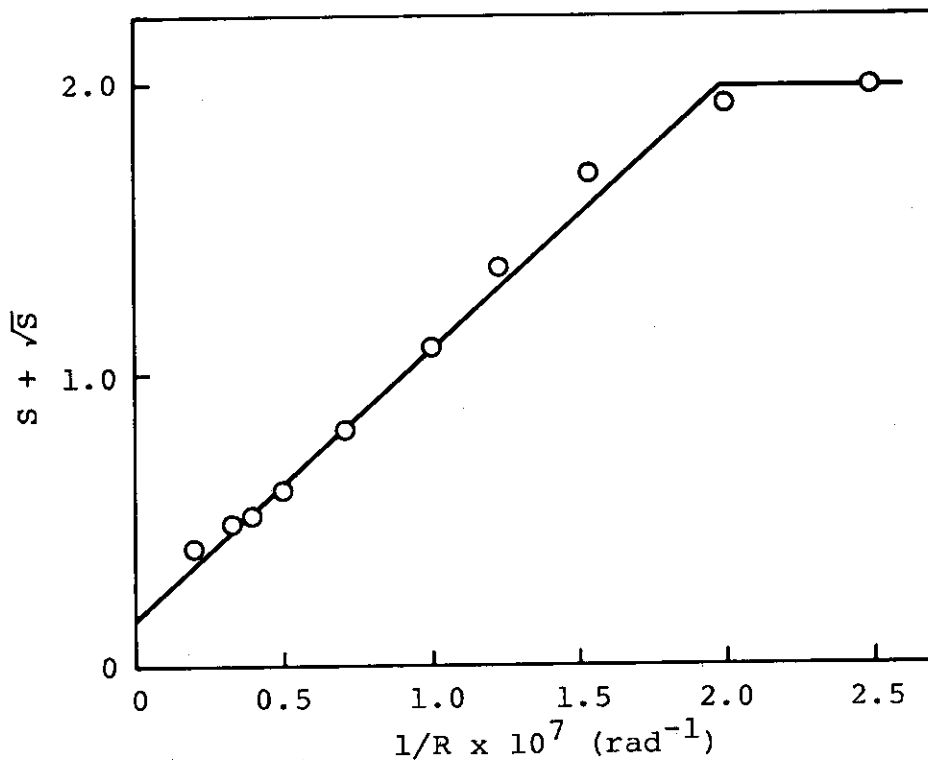

Fig. 1. Charlesby-Pinner plot for PVAL films without heat-
treatment irradiated in a water-swollen state
(DS$_0$ = 1.00) at a dose rate of 1.0 x 10^5 rad/sec.

to chain units and q_o is the proportion of chain units cross-linked per unit dose. In the present case p_o/q_o is found to be 0.16 and hence the ratio of main chain scissions to cross-linkage formation is 0.32.

It is apparent from Fig. 2, where DS of membranes obtained are given, that as the polymer concentration at the irradiation increases, DS of the membrane becomes higher, if compared at a fixed dose. Even when a water-swollen film is irradiated to 100 Mrads, no coloration is observed. The membranes which are produced by irradiation of aqueous
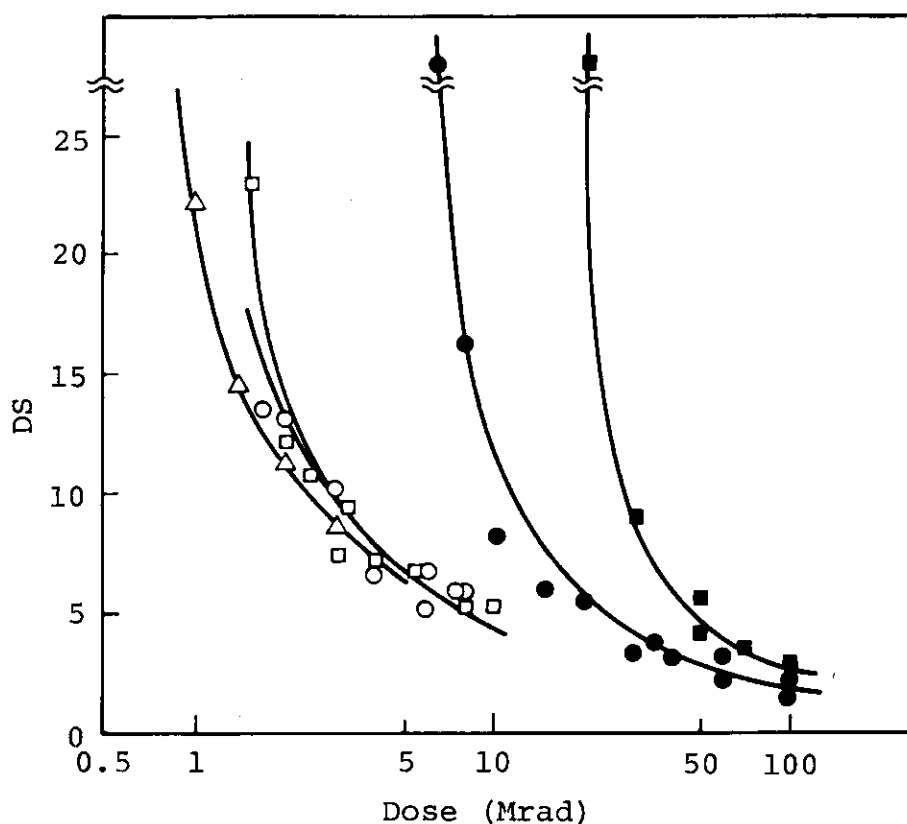

Fig. 2. Degree of swelling (DS) of PVAL membranes obtained by irradiation of PVAL aq. solutions and water-swollen films. PVAL concentration at irradiation; aq. soln., 4 % ($\triangle$), 8 % ($\circ$), 11 % ($\square$); water-swollen film, 50 % (DS = 1.00) ($\bullet$), 82 % (DS = 0.221) ($\blacksquare$).

solutions are somewhat fragile. The DS in water of the
membrane boiled with n-propanol-water (25 - 75) mixture is
the same as that of the membrane boiled with water. Since
the mixed solvent has much better solvency than water, the
result provides an evidence that the membrane has no appreci-
able amount of crystallite. It is also found that the swell-
ing recovers almost to the initial state even though the wet
membrane is once dried. The DS of the dried membrane without
reboiling is lower than that of the membranes before drying,
especially for those obtained at low doses.

The dose for incipient gelation, that is, the critical
dose at which DS of membrane becomes infinite is plotted in
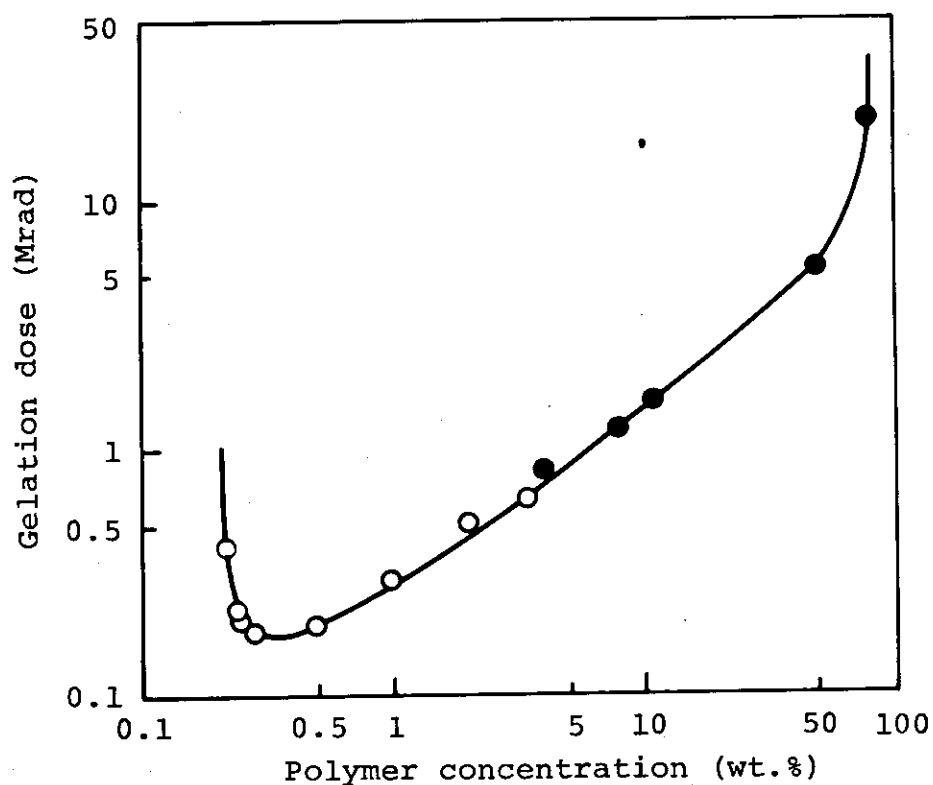Fig. 3 against the PVAL concentration at irradiation, together

Fig. 3. Dependence of gelation on polymer concentration
(degree of polymerization of PVAL = 1,100 - 1,700).

with that found in the previous work[1] (gamma-ray irradiation of deaerated aqueous solution of PVAL with $\overline{P}_v$ of 1,500). The markedly high gelation dose found for the water-swollen film is understandable, because all the data fall on the same curve. It is well known that no network is formed when a dry PVAL film is irradiated at room temperature.

For measurement of permeability of water the membrane is mounted between two cell elements with the use of two sheets of Millipore Filter as support. Each cell department has a capillary. The effective area of membrane is 10.0 cm^2 and the volume of each cell is 10 ml. Both cells are filled with distilled water till to the top of the capillaries and put in a thermostat kept at 30.0°C. Pressures from a nitrogen cylinder are given through one capillary and the meniscus change of the capillary is followed with a cathetometer.

Only typical results on water flux J are given in Fig. 4. The friction coefficient per mole of monomer unit to water, f, is calculated from the data in Fig. 4 according to Peterlin, Yasuda and Olf[2]. The f-value is found to be strongly dependent on the water content of the membranes, w. Therefore we get f_o by extrapolating $(1 - w)$ to zero. This value is 2.6 x 10^{-10} g/sec. The f-value determined from viscosities of dilute aqueous solution is 7.7 x 10^{-10} g/sec and that from the diffusion constant in PVAL aqueous solutions is 11.3 x 10^{-10} g/sec.

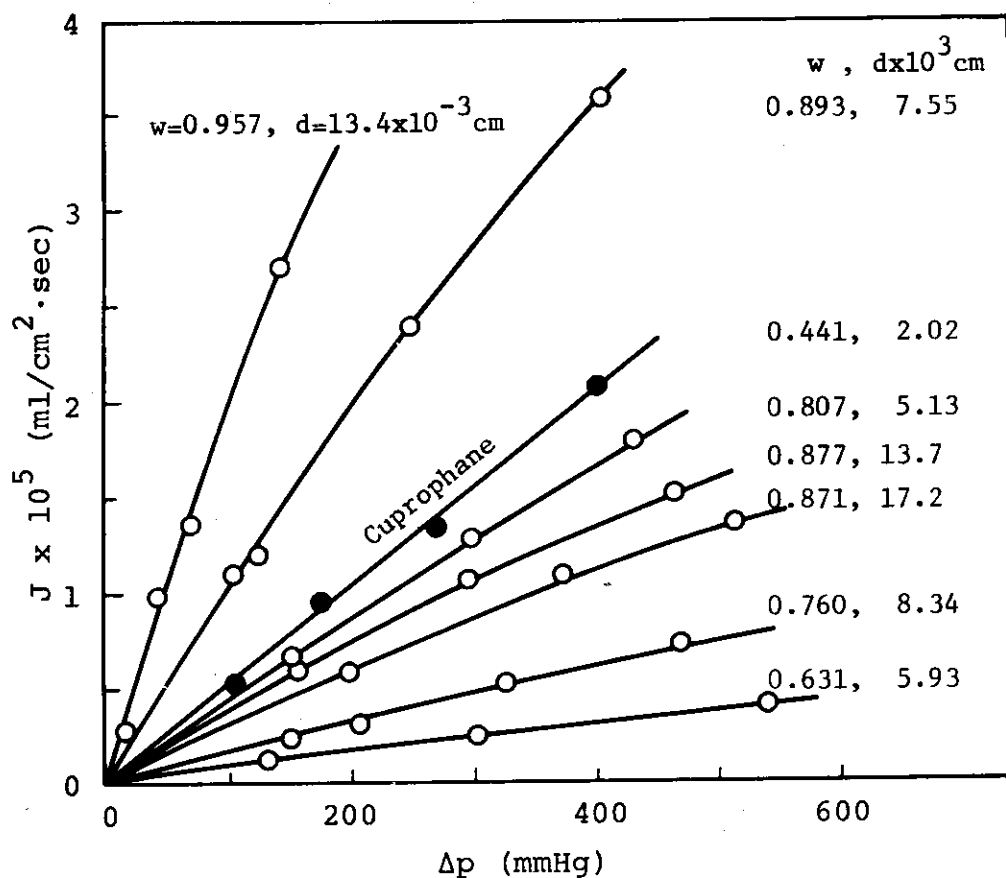Fig. 4. Flux of water at 30°C through PVAL membranes and
         cuprophane [water content (w) and thickness (d)
         of swollen membranes were given in figure].

The measurement of tensile properties of the membranes
is currently in progress.

1) I. Sakurada and Y. Ikada, Bull. Inst. Chem. Res., Kyoto
   Univ., 44, 66 (1966).
2) A. Peterlin, H. Yasuda, and H. G. Olf, J. Appl. Polym.
   Sci., 16, 865 (1972).

[10]   Comparative Studies on the Curing by Electron Beam and
       Ultraviolet Irradiations of Epoxyacrylate

J. Kumanotani, T. Koshio, M. Gotoda, and

T. Yagi

Studies have been carried out on the electron beam curing
and its industrial application of mixtures of vinyl monomers
and reactive prepolymers such as diallylphthalate and epoxy-
acrylate prepolymers[1].

Experiments are now carried out in an attempt to examine
the curing behavior of bisphenol A type epoxyacrylate using
electron beam (EB) and ultraviolet (UV) radiations compara-
tively.

The monomer is prepared from bisphenol A glycidyl ether
and acrylic acid in the presence of an inhibitor.

A monomer specimen of 10 x 30 mm and 0.2 - 0.3 mm thick
sandwitched in between two polyester films is irradiated with
electron beams from a Van de Graaff accelerator (1.5 MeV, 0.7
Mrad/sec). The irradiation is carried out on a conveyor belt
which carries the specimen back and forth horizontally under
the irradiation window. The dose absorbed by the specimen
during one trip is 0.5 Mrad.

Ultraviolet irradiation is carried out using two high
pressure mercury arcs: a model USH-500 (500 W) arc and a
model H-1000 (1 kW) arc. The temperature of the specimen
during the irradiation with the USH-500 is controlled within
± 1°C at any desired temperature between 35° and 80°C other-
wise stated.

The monomer is held between two glass plates which absorb UV radiations below 300 nm. The intensities of UV at 365 nm are 4.1 x 10^{-2} and 9 x 10^{-2} cal/g sec for USH-500 and H-1000 arcs, respectively.

The degree of curing is followed by a ratio of O.D. at 1410 cm^{-1} to that at 1710 cm^{-1} which indicates the relative abundance of terminal double bonds in the specimen. The curing process is further investigated using a differential scanning calorimeter (DSC).

In Fig. 1, the ratios of $O.D._{1410}/O.D._{1710}$ are plotted against dose for EB (A) and UV (B) irradiations, both of
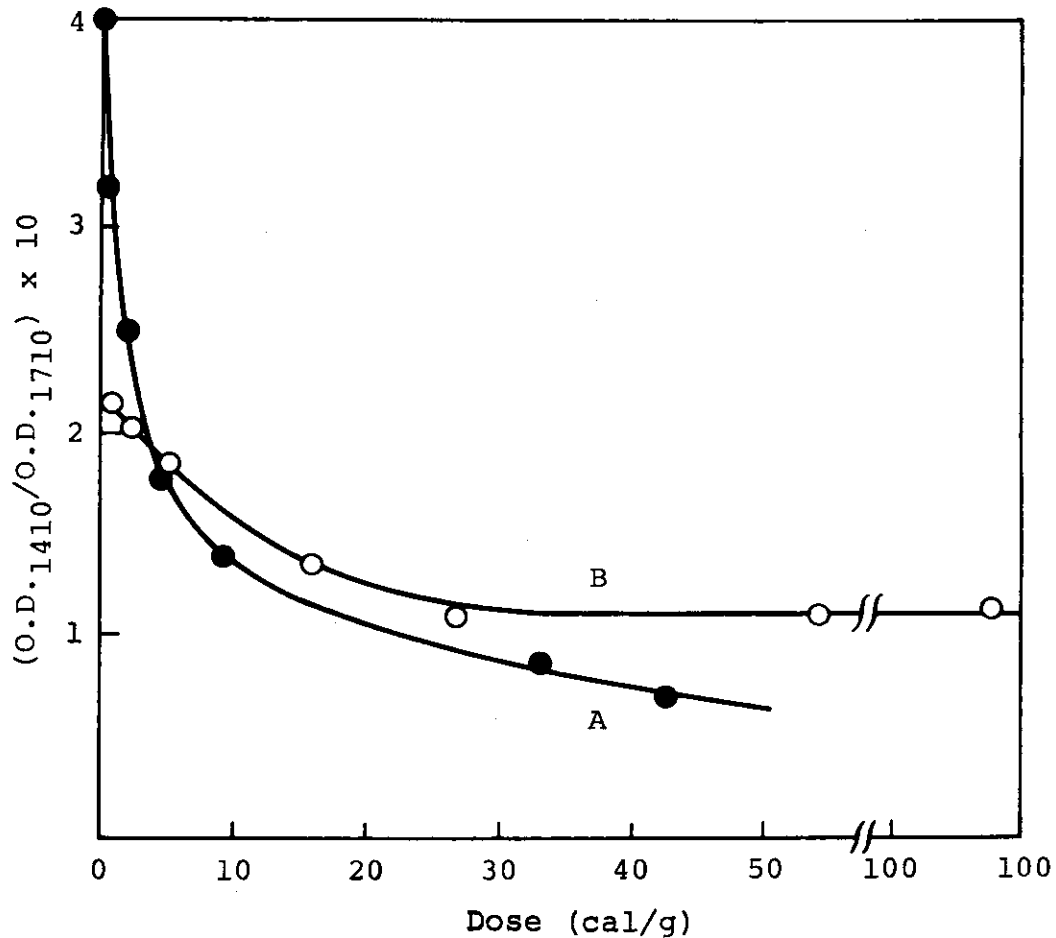

Fig. 1. Decrease of double bond with irradiation time:
●, EB;   o, UV curing.

which are carried out without temperature control. The number of terminal double bonds decreases rapidly at the early stage of irradiations, and then gradually in the case of EB irradiation as the dose increases, while in the case of UV irradiation the number of double bonds does not decrease by further irradiation above 30 cal/g. The temperature of the specimen during the UV irradiation is found to increase from 20°C to 40°C.

The difference found here for EB and UV irradiations may be due to the difference in temperatures. In order to confirm this, conversion curves are obtained at 35°C and 60°C. The fact that the conversion at 60°C is higher and closer to that obtained by EB irradiation suggests that the temperature of the specimen during EB irradiation is about 60°C.

The DSC curves of the EB and UV cured specimens at different doses are shown in Fig. 2. The DSC curves for EB cured specimens show an endothermic peak at glass transition temperature and the base line shifts toward endothermic side. On the other hand, in the DSC curves for UV cured specimens, an endothermic peak appears at lower temperature and then an exothermic one follows. The exothermic peak appeared in the DSC curves for UV cured specimens decreases with decreasing amount of the sensitizer in the specimen and with increasing irradiation temperature. The exothermic peak also disappears on rescanning.
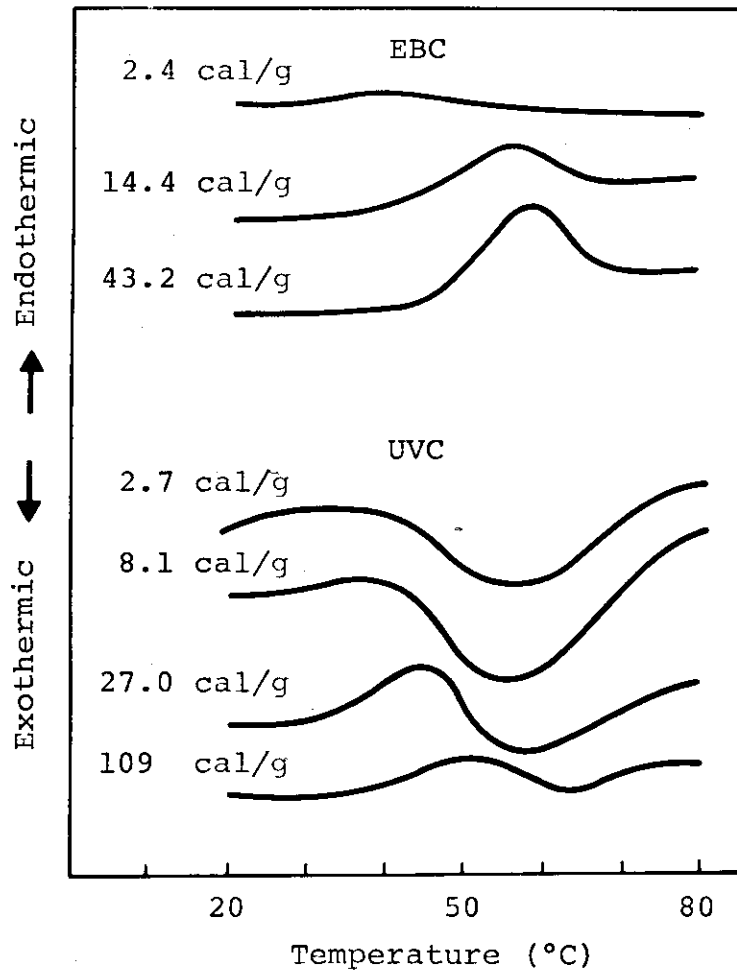
Fig. 2. DSC curves for EB and UV cured specimens.

The difference of specific heat before and after the transition, (ΔC_p), is calculated from the difference of the base lines before and after the transition, and the resulting ΔC_p's are plotted against dose in Fig. 3. Since the ΔC_p is related to the amount of the cross-links, the curves in Fig. 3 indicate that the number of cross-links increases with dose and then levels off, and that the number of cross-links is larger for EB cured specimens. Since the cross-linking behavior on dose is similar to that found for vinyl bond disappearance vs. dose curves in Fig. 1, the difference may
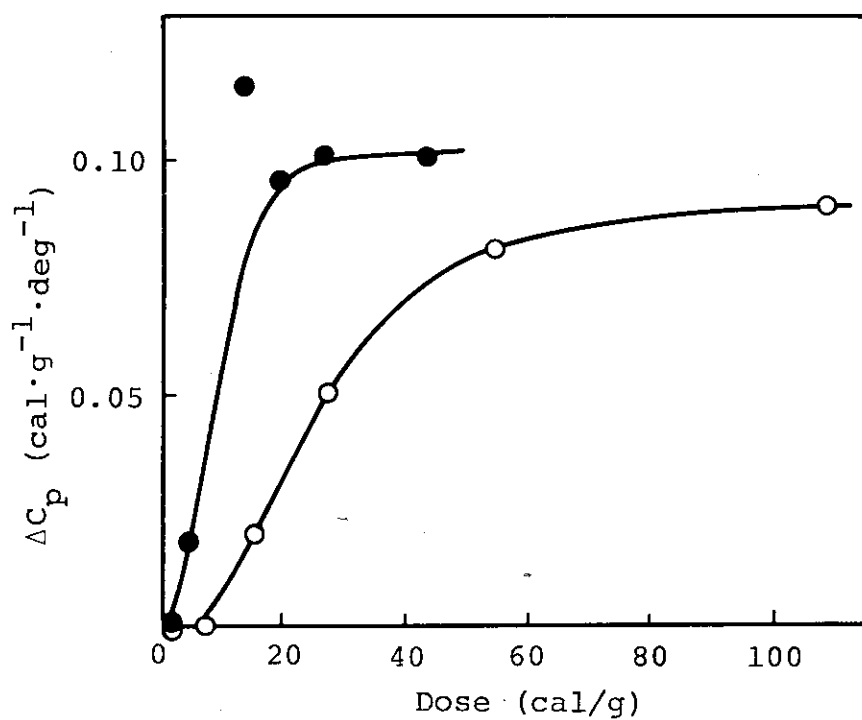
Fig. 3. Plots of ΔC_p vs. dose: ● , EB ; o , UV curing.
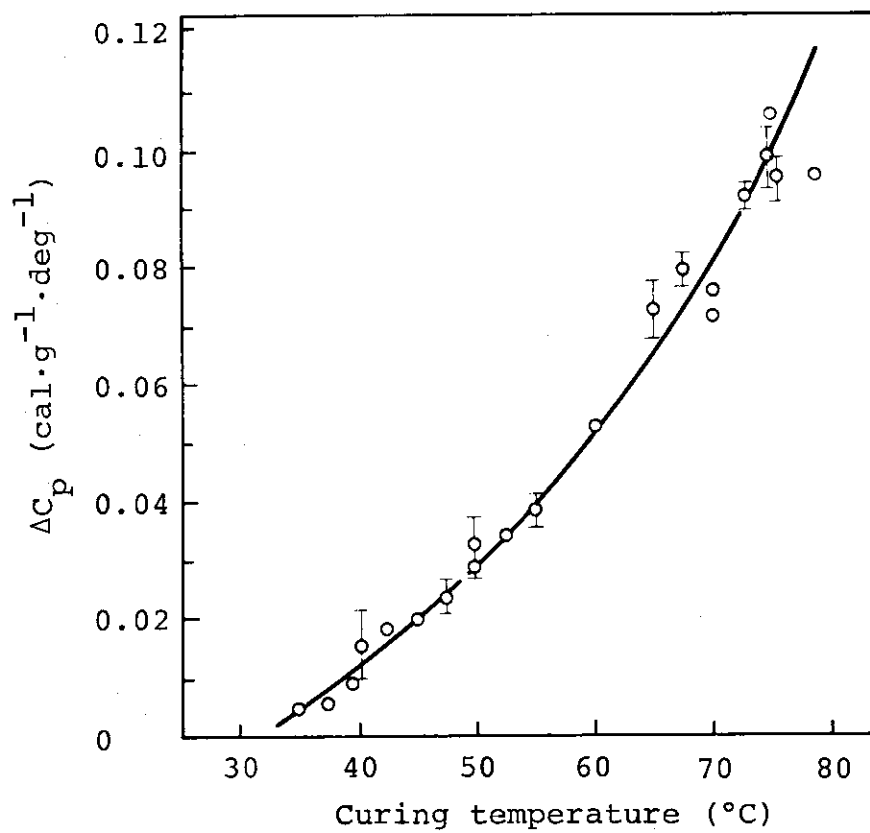
Fig. 4. Plots of ΔC_p vs. curing temperature.

again be ascribed to the difference in temperature during irradiations. This is supported by the results shown in Fig. 4, where it is clear that ΔC_p obtained for UV cured specimen increases with curing temperature.

The above results suggest that the difference found for UV and EB cured samples arises only from the difference in the temperature of the specimens during the irradiations.

1) M. Gotoda, K. Yanagi, T. Hanyuda, and K. Mori, JAERI, 5030, 105 (1975).

[Appendix]   High Dose Rate Electron Accelerator

A rectified transformer type electron accelerator manufactured by Nisshin-High Voltage Co., Ltd., and its appurtenant equipments had been installed in Osaka Laboratory and were completed at the end of this fiscal year as a second electron irradiation facility. It became operational on May 31, 1975.

The general performance ratings of the accelerator are the accelerating voltage between 300 and 800 kV, the beam current between 10 μA and 25 mA and the maximum scanning width of 45 cm. The facility is so constructed that the accelerator unit is movable in a definite area of the irradiation room. Main appurtenant equipments are a system to remove ozone and nitrogen oxide formed by the operation of the accelerator, and a conveyor system to send samples from outside of the irradiation room. A new building, 383 m^2 in area was constructed to house the accelerator and the equipment to move it.

The accelerator consists of the following components as shown in Fig. 1; they are (1) transformer power supply with a high voltage bushing, (2) electron accelerator unit consisted of high voltage cable, bushing, pressure tank, terminal, acceleration tube, vacuum pumping system, focusing system, scanning system and beam exit window, and (3) control consoles, a cabinet for the power supply and a desk for the accelerator control.
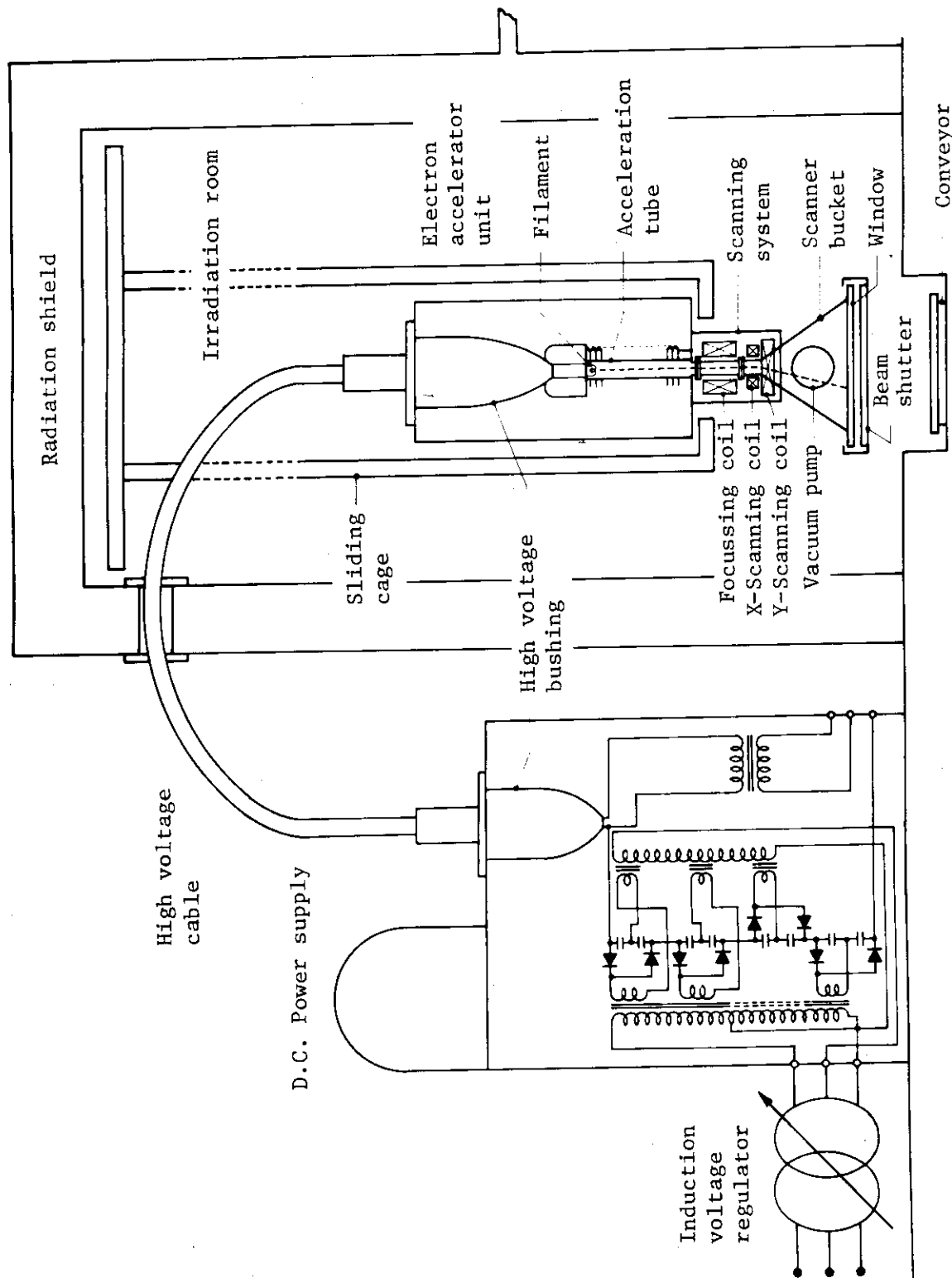
The apparatus to move the accelerator unit consists of

Fig. 1. Layout of main components of the high dose rate accelerator.

an overhead travelling crane and sliding cage hung from the crane, in which cage the accelerator unit is mounted. The beam exit window along with the accelerator unit is free to move within the area of 4 x 6 m and 0 to 2 m in height from the floor level.

The main part of the apparatus to remove ozone and nitrogen oxides is tandem absorbers filled with active carbon, and the air of the irradiation room is sent through flexible or fixed duct into the absorbers by turbo blower.

The conveyor system carries samples to be irradiated from the mock-up room through a pit, past the irradiation field and back again to the mock-up room for unloading. The pit for the conveyor system is situated under the floor level and when the conveyor is not used, it is covered with concrete plates to provide a flat floor. For irradiation with the conveyor system, accelerator unit can be inserted into the pit by removing one of the pit covers. The conveyor speed can be changed continuously between 1 and 120 m/min. and the speed is displayed on a digital tachometer. The position of sample tray can be monitored at the console by means of a series of microswitches. The conveyor is fitted with a reversing operation system, which permits a back and forth movement for extremely high dose irradiation.

After the installation of all the equipments, functional tests are made with special attention to the interlock systems among each units. Along with the test operation, safety checks for the radiation shield of walls of the irradiation room and for the treatment of ozone and nitrogen oxides are

carried out. The results are quite satisfactory as might be expected.

Generally, the dosimetry of electron beams of such energy region as is obtained from the present accelerator is much more difficult than that of higher energy exceeding 1 MeV because of the greater influence of scattered electrons and other experimental difficulties. In the energy region between 100 and 1,000 keV, no systematic results are available as to the electron absorption and scattering at titanium window, in air, and in other materials of basic interest. Therefore, we have two major problems concerning the dosimetry of such electron beams; first, to obtain the basic knowledge of electron absorption and scattering in various materials and second, development of convenient secondary dosimeter for practical use.

As an approximate means of the dosimetry, a CTA dosimeter,
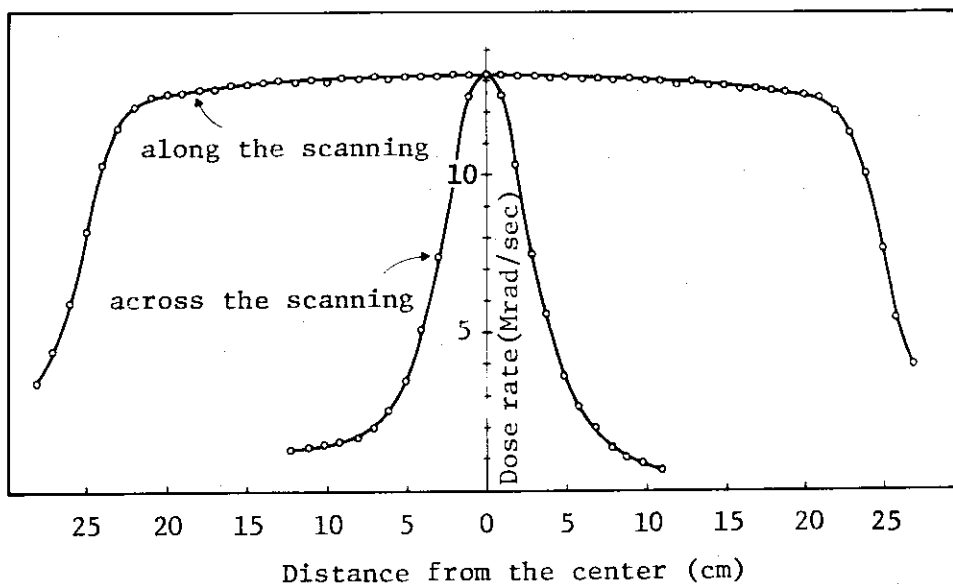
Fig. 2. Dose rate distribution of the high dose rate
accelerator. Accelerating voltage, 800 keV;
beam current 25 mA; scanning width, 45 cm;
distance from the window, 12 cm.

which was developed at CAPRI, Saclay, CEA, France and Takasaki

Establishment, JAERI in collaboration, is employed without

further critical evaluation. In many cases, it is quite

available for a relative evaluation of dose rate. A dose rate

distribution obtained by CTA method is shown in Fig. 2. From

the figure, the maximum dose rate attained is found to be ca.

1.3×10^7 rad/sec. The dose received per one path of the

conveyor is approximately 7.5 Mrad at the speed of 10 m/min,

using the same irradiation condition as that in Fig. 2.

Further studies on dosimetry by other means are now in

progress.

III. LIST OF PUBLICATIONS

[1] Published Papers

1. M. Kumakura, A. Ito, and T. Sugiura, "Ion-Molecule
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