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ANNUAL REPORT OF THE
OSAKA LABORATORY FOR RADIATION CHEMISTRY
JAPAN ATOMIC ENERGY RESEARCH INSTITUTE

(No. 10)
April 1, 1976 - March 31, 1977

October 1977

Osaka Laboratory for Radiation Chemistry

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

Osaka Laboratory for Radiation Chemistry
Japan Atomic Energy Research Institute
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This report describes research activities of Osaka Laboratory for Radiation Chemistry, JAERI during one year period from April 1, 1976 through March 31, 1977. The latest report, for 1976, is JAERI-M 6702.

Detailed descriptions of the activities are presented in the following subjects: studies on reactions of carbon monoxide and hydrogen; polymerization under the irradiation of high dose rate electron beams; modification of polymers, degradation, cross-linking, and grafting.

Previous reports in this series are:

Annual Report, JARRP, Vol. 1	1958/1959*
Annual Report, JARRP, Vol. 2	1960
Annual Report, JARRP, Vol. 3	1961
Annual Report, JARRP, Vol. 4	1962
Annual Report, JARRP, Vol. 5	1963
Annual Report, JARRP, Vol. 6	1964
Annual Report, JARRP, Vol. 7	1965
Annual Report, JARRP, Vol. 8	1966
Annual Report, No. 1, JAERI 5018	1967
Annual Report, No. 2, JAERI 5022	1968
Annual Report, No. 3, JAERI 5026	1969
Annual Report, No. 4, JAERI 5027	1970
Annual Report, No. 5, JAERI 5028	1971
Annual Report, No. 6, JAERI 5029	1972
Annual Report, No. 7, JAERI 5030	1973
Annual Report, No. 8, JAERI-M 6260	1974
Annual Report, No. 9, JAERI-M 6702	1975

*Year of the activities

Keywords: Electron Beam Irradiation, γ-irradiation, Carbon Monoxide-Hydrogen Reaction, Radiation-Induced Reaction, Polymerization, Grafting, Curing, Polymer Modification, Cross-Linking, Vinyl Monomer, Octadecyl Acrylate, Polystyrene, Polyvinyl Chloride Fiber, Polyester Fiber, Wholly Aromatic Polyamide, Vinyl Phosphonate, Cellulose Triacetate Film Dosimeter, Radiation Chemistry

JAERI－M 7355

昭和51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

（1977年9月30日受理）

本報告は、大阪研究所において昭和51年度に行な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、架橋ならびにクラフト重合に関する基礎的研究などである。

日本放射線高分子研究会年報	Vol. 1			1958/1959
日本放射線高分子研究会年報	Vol. 2			1960
日本放射線高分子研究会年報	Vol. 3			1961
日本放射線高分子研究会年報	Vol. 4			1962
日本放射線高分子研究会年報	Vol. 5			1963
日本放射線高分子研究会年報	Vol. 6			1964
日本放射線高分子研究会年報	Vol. 7			1965
日本放射線高分子研究会年報	Vol. 8			1966
日本原子力研究所大阪研における放射線化学の基礎研究	No.1	JAERI	5018	1967
日本原子力研究所大阪研における放射線化学の基礎研究	No.2	JAERI	5022	1968
日本原子力研究所大阪研における放射線化学の基礎研究	No.3	JAERI	5026	1969
日本原子力研究所大阪研における放射線化学の基礎研究	No.4	JAERI	5027	1970
日本原子力研究所大阪研における放射線化学の基礎研究	No.5	JAERI	5028	1971
日本原子力研究所大阪研における放射線化学の基礎研究	No.6	JAERI	5029	1972
日本原子力研究所大阪研における放射線化学の基礎研究	No.7	JAERI	5030	1973
Annual Report, Osaka Lab., JAERI,	No.8	JAERI−M	6260	1974
Annual Report, Osaka Lab., JAERI,	No.9	JAERI−M	6702	1975

CONTENTS

[4] Modification of Polymers

[5] Electron Beam Curing

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 merged with 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 research on radiation chemistry.

The results of the research activities of the Laboratory were published from 1958 until 1966 in the Annual Reports of JARRP which consisted essentially of original papers. During the period between 1967 and 1973, the publication had been continued as JAERI Report which also consisted mainly of original papers. From 1974, the Annual Report has been published as JAERI-M Report which contains no original papers, but presents outlines of the current research activities in some detail. Readers who wish to have more information are advised to contact with individuals whose names appear under subjects.

The present annual report covers the research activities of the Laboratory between April 1, 1976 and March 31, 1977.

Most of the studies carried out in the Laboratory are continuation from the previous year, emphasis being laid on two projects; one is "Effect of radiation on the reaction of carbon monoxide and hydrogen" and the other, "Radiation-induced polymerization by high dose rate electron beams".

Our new high dose rate electron accelerator (HDRA) has been operated since May 31, 1975, and many results were obtained using the HDRA.

The apparatus to irradiate gaseous mixture of hydrogen and carbon monoxide under forced circulation was completed. The studies using this apparatus revealed that the yields of some condensable products were increased by removal of the products from the gas flow system with cold traps to prevent further radiolysis of the products.

A series of radiolysis studies on non-circulating flow of the reactant with or without solid catalysts give information on the role of the catalysts in the radiation chemical reactions of the gaseous mixture, suggesting the possibilities that the catalysts convert some unstable intermediate compounds to more stable products. The studies are expected to provide more informations on the catalytic reactions of intermediates formed by irradiation during next fiscal year using a fluidized bed catalytic reactor which was installed at the end of this fiscal year.

Studies on polymerization of vinyl monomers by electron beams at high dose rate are continued. The studies carried out on styrene this year together with the results obtained in the previous year enable us to give a clear insight on radiation-induced polymerization of styrene of different water concentration in the wide range of dose rates explaining the relation between chain length and number of polymer chains. Studies are also carried out on isobutyl vinyl ether and α-methyl styrene and a number of data are accumulated on the effects of dose rate and water content in the monomer on the rate of polymerization and the molecular weight distribution from oligomer to very high molecular weight polymer region.

Studies on grafting to obtain flame-retardant fabrics and fibers are carried out in two ways: one is to give flame-retardancy to polyester fabrics and the other to improve the properties of flame retardant poly vinyl chloride (PVC) fiber. The flame-retardant polyester fabrics are obtained by 10% graft of oligomeric vinyl phosphonate. The PVC fibers are found to hold their self-extinguishing property when acrylic acid, or acrylamide is grafted up to graft percents of 112, and 51%, respectively.

Radiation effects on two wholly aromatic polyamides are studied by tenacity, viscometric and thermogravimetric measurements. The results indicate that the wholly aromatic polyamides are very stable to radiations. Free radials produced by mechanical rupture of these polymers are investigated by ESR technique.

From results of experiment to determine whether or not electron beam irradiation can be replaced with γ-ray irradiation to accelerate deterioration test of insulating materials for electric cables, it is concluded that the electron beam irradiation can be used for deterioration test for some properties.

Radiation curing of mixtures of chlorinated polymer and vinyl monomers was continued using acrylic oligoester acrylate as a crosslinking agent. Composites containing some stabilizers were found to be successful in that no coloration occurred during accelerating weathering test.

A method of calibrating film dosimeter by beam current measurement has been developed to establish more accurate and simpler method of calibration than that of total ionization method which was developed in the previous year. Excellent agreement with the results of the previous study was obtained.

Administrative changes were made in the Laboratory. Masao Gotoda moved to Takasaki Radiation Chemistry Research Establishment as the establishment director and Tomomichi Kasamatsu was appointed Head on October 1, 1976.

August 31, 1977

Tomomichi Kasamatsu, Head
Osaka Laboratory for Radiation Chemistry
Japan Atomic Energy Research Institute

II. RECENT RESEARCH ACTIVITIES

[1] Radiation Effects on the Reaction of Mixtures of Carbon Monoxide and Hydrogen

During the past two years, it was revealed that the electron beam irradiation on gaseous mixture of hydrogen and carbon monoxide at ordinary temperature and pressure yielded several compounds such as methane, methanol, acetaldehyde, acetic acid, formaldehyde and its cyclic oligomers which are not formed at these conditions without irradiation. It is noteworthy that the G value of trioxane increases with increasing pressure, and with decreasing temperature, dose rate, and incident electron energy, while the G values of other products are less sensitive to these parameters.

The presence of Fischer-Tropsch catalyst in this system yields hydrocarbons at about 200°C indicating that the catalytic reactions predominate over the radiation effects.

The studies are continued this year in an attempt to discuss comparatively the results of the studies on two lines stated above, with use of several techniques; 1. irradiation of gaseous mixtures under forced circulation; 2. irradiation of the gaseous mixtures containing additives at static condition; 3. irradiation of the gaseous mixtures under flow in which the irradiated gas is not recycled; 4. reaction of pre-irradiated gaseous mixtures on solid catalysts; 5. irradiation of gaseous mixtures in the presence of catalysts; 6. detection of intermediates by spin trapping technique.

1. Irradiation of Gaseous Mixtures under Forced Circulation

A new apparatus for the irradiation of gaseous mixture under circulation of the reactant gas is designed and constructed in order to analyze the concentration of the products during irradiation periodically and to remove the products continuously from the gaseous mixture to avoid radiation chemical decomposition of the products by the repeated irradiation.

An irradiation vessel (the same specifications as those reported in the previous report; 7 liter in volume) is connected with a gas circular system which is composed of a circulation pump (Metal Bellows Co., type MB301XP), three cold traps in series, a flow meter, and a by-pass to recycle the reacted gas through a gas sampling system of a gaschromatograph (Hitachi Model 163). The sampling interval is 7 min. Experimental conditions are listed in Table 1 together with the irradiation conditions employed.

Table 1 Experimental conditions

Conditions	C-9	C-10
Use of cold traps	No	Yes
Pressure (Torr) (20°C)	995	1000
CO % in the reactant	15.1	15.0
Electron accelerating voltage	0.4	0.4
Beam current	0.5	0.5
Dose rate (ev. mole^{-1}. sec^{-1})	9.4x10^{-5}	9.4x10^{-5}
Irradiation time (sec)	10,104	10,034
Temperature of gas (°C)	-13.4	-19.5
Flow rate (l/min)	45	45

Two runs of experiments are performed in order to see the effect of repeated irradiation of the products. In run C-10, the condensable products are condensed in three traps in series, two of which are cooled by dry ice-ethanol bath and the other by liquid nitrogen.

In Fig. 1, the concentrations of methane and ethane are plotted against irradiation time for the two cases. The fact that the formation curve of methane for C-9 lies above that for C-10 seems to indicate that a part of methane in C-9 run comes from radiolysis of products such as methanol,

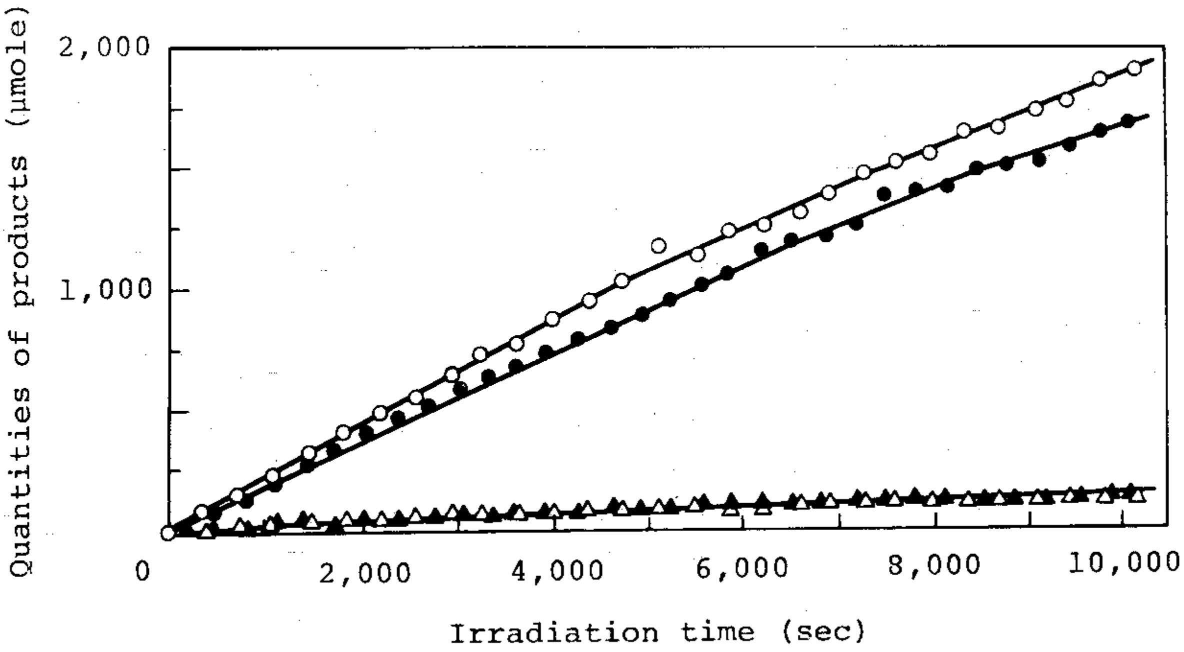


Fig. 1 Formation curves of methane (o), (●) and ethane (Δ), (▲); $H_2/CO = 6$; electron beams of 0.4 MeV and 0.5 mA; open symboles denote results without traps and filled symbols denote those with traps.

acetaldehyde, trioxane or tetraoxane. Since the temperature of the gaseous mixture during irradiation is not exactly the same for the two cases, the difference in methane formation may be also due to temperature effect. There is no difference in ethane formation curves obtained for the two cases.

After irradiation, the gaseous mixture was pumped out through two traps in series to collect the condensable products which are analyzed by use of a mass spectrometer and a gas chromatograph. The quantities of the products trapped in the two traps during irradiation are also determined by the same methods.

The trap efficiencies defined as quantity (g) of a product recovered from the trap divided by the total yield (g) of the product are 0.0 for methane, 0.91 for formaldehyde, 0.83 for methanol, and 0.93 for trioxane.

G values of the products are listed in Table 2 for C-9 and C-10. Larger G(HCHO), G(TOX) and G(TEOX) for C-10 where

Table 2 G Values of Products with (C-10) or without (C-9) use of Cold Traps

	C-9	C-10
CH_4	0.62	0.49
C_2H_6	0.035	0.035
C_3H_8	0.007	
C_4H_{10}	0.001	
HCHO	0.29	0.45
CH_3OH	0.06	0.06
CH_3CHO	0.07	0.03
$HCOOCH_3$	0.11	0.03
CH_3COOH	0.11	0.04
Trioxane	0.09	0.34
Tetraoxane	0.008	0.04

the products are effectively removed from the reactant indicate that these products are further decomposed by repeated irradiation if the traps are not used in the system.

On the other hand, G(CH_3CHO), G($HCOOCH_3$) and G(CH_3COOH) are higher in C-9 where traps are not used. This is probably resulted from the secondary reaction of the products in the irradiation zone.

The circulating system for the irradiation used in the present study has an advantage in that the formation of the lower hydrocarbons which could not be determined in the previous study are quantitatively determined as a function of irradiation time, and most of the condensable products are removed from the reactant to keep the products away from further radiolysis by succeeding irradiation thus to exclude unambiguity arising from secondary reactions. (S. Sugimoto, M. Nishii, T. Sugiura)

1) S. Sugimoto, M. Nishii, and T. Sugiura, JAERI-M, 6702, 4(1976).

2. Effects of Additives

Since some additives are known to enhance or inhibit certain reactions in the radiation chemical reactions of gases, we examined the effects of additives to see whether or not an additive enhances the formation of a particular product. Among the additives we used, effects of ammonia are studied in some detail, because ammonia is known to be a scavenger of cationic intermediates which have, we assume, an important role in the radiation chemical reaction of the present system.

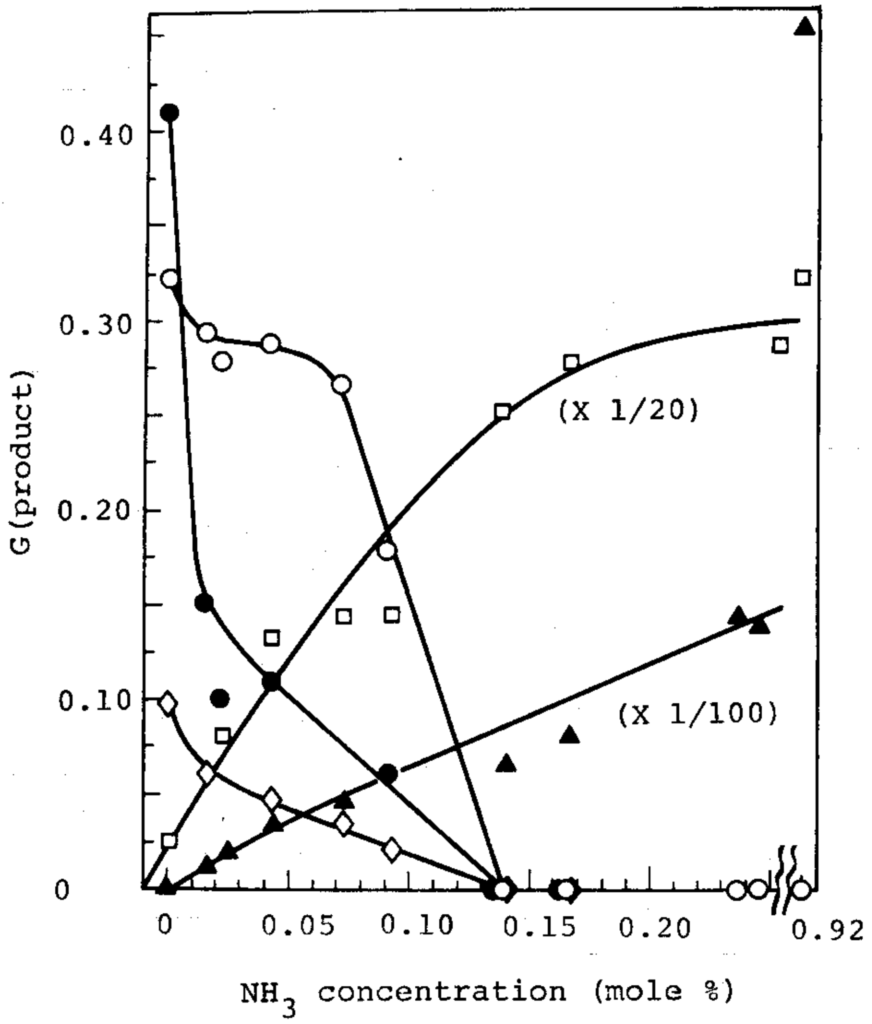


Fig. 1 G values of the products as a function of concentration of ammonia, 0.4 MeV, 0.5 mA; irradiation time, 200 sec; (o) trioxane; (◇) tetraoxane; (●) formaldehyde; (□) water; (▲) consumption of ammonia.

Apparatus used for the scavenger studies is the batch type and is the one reported in the last year1). A part of the experiment is carried out using the circulation irradiation apparatus reported in the previous section to know the behavior of lower hydrocarbons.

The techniques of irradiation and analyses of the products are the same as those reported in the previous sections.

G values of the products are plotted against the concentration of ammonia in Fig. 1, where it is apparent that the G values of HCHO, TOX and TEOX decreased sharply with increasing ammonia concentration. This result suggests that ionic species are involved in the formations of these products. G values of water formation and ammonia consumption increase with increasing concentration of ammonia.

Table 1 Deuterium Contents of Water Molecule Produced in the Radiolysis of CO and X_2 by NX_3 Addition (X denotes H or D atom)

Run No.	B-25	B-40	B-33	B-41	B-42	B-43
Reactants (torr)						
CO	152	153	148	147	150	150
H_2	840	-	848	-	-	846
D_2	-	839	-	848	722	-
NX_3	-	-	2.46	3.87	2.44	2.43
D content of NX_3 before irradiation (%)	-	-	0	93.7	0	96.2
D content of NX_3 after irradiation (%)	-	-	0	77.8	26.1	68.2
$G(-NH_3)$	-	-	8.20	9.88	5.40	6.18
$G(H_2O)$	0.334	1.11	5.86	6.13	5.10	4.73
D content of X_2O produced (%)						
D_2O	0	5.43	0	50.1	11.0	43.0
HDO	0	27.8	0	34.8	37.6	43.5
H_2O	100	67.7	100	11.4	51.4	13.4
D contents (%)	0	18.4	0	69.4	29.7	64.8

It is evident from Fig. 1 that G value of H_2O formation increases markedly with increasing NH_3 concentration.

Since hydrogen atoms from both hydrogen molecules in the reactant and ammonia may contribute to the formation of water, it is interesting to know the origin of hydrogen atoms in water. In order to study this, tracer study using deuterium is performed, and the results are summarized in Table 1. Memory effect and exchange reactions of deuterium atoms exist, but we may conclude that hydrogen atoms in water come mainly from ammonia.

G values of the products obtained by use of the circulating irradiation apparatus in the presence of ammonia are

Table 2 G values of the Products with or without Ammonia

Run No.	C-11*) 5	C-10 5
Initial concentration of ammonia (mol %)	0.15	0
Irradiation time (sec)	200.	10035.
$-NH_3$	3.85	-
CH_4	0.46	0.49
C_2H_6	0.04	0.04
CH_3OH	0.03	0.06
CH_3CHO	0.05	0.03
$HCOOCH_3$	0.005	0.03
CH_3COOH	0.01	0.04
HCHO	0.14	0.45
TOX	0.05	0.34
TEOX	0.00	0.04

*) Since G values of some compounds depend on irradiation time, there may be some ambiguity arising from the large difference in irradiation time for the two runs. But short irradiation time for C-11 is inevitable because of quick consumption of ammonia.

Table 3 Effects of Additives on G values of Products

Additive (mole %)	no (0)	CO_2 (0.81)	CH_4 (0.73)	N_2O (0.10)	NH_3 (0.92)
HCHO	0.41	0.52	0.29	0.30	0.11
CH_3OH	0.48	0.23	0.20	0.20	0.08
$HCOOCH_3$ + CH_3COOH	0.10	0.06	0.05	0.05	0.01
Trioxane	0.32	0.44	0.43	0.33	0.00
Tetraoxane	0.10	0.11	0.12	0.05	0.00
H_2O	0.32	0.90	0.42	0.60	6.50

CO/H_2 = 1/6 0.4 MeV 0.5 mA 200 sec. 1000 torr.

listed in Table 2 together with those obtained without ammonia. It is noticed that the addition of ammonia decreases G(-oxygenates), while it has little effect on G(CH_4) and G(C_2H_6). This result indicates that hydrocarbons are formed from precursors which are not quenched by ammonia.

Table 3 shows the G values of the main products with or without additives. The presence of methane and carbon dioxide seems to enhance the formation of trioxane and water, but the G(HCHO) increases by the presence of carbon dioxide and decreases by the presence of methane. (S. Sugimoto, M. Nishii, T. Sugiura)

1) S. Sugimoto, M. Nishii and T. Sugiura, JAERI-M, 6702, 4(1976).

3. Irradiation of the Gaseous Mixture under Flow without Circulation

In the last annual report$^{1)}$, it was described that radiolysis of mixture of carbon dioxide and hydrogen in the presence of Fischer-Tropsch catalyst produces hydrocarbons and carbon dioxide, but produces no oxygenates. The result was quite different from that obtained in the radiolysis study conducted in a non-flow system in the absence of the catalyst2) where oxygenates such as alcohols and aldehydes were found to be the main products. The present study is undertaken with the principal purpose to see if the oxygenates are produced by irradiation of the flow of the gaseous mixture in the absence of catalyst.

We made a new fixed bed catalytic reactor (FIXCAT-II) of stainless steel in order to cool the reactant flow effectively during irradiation. The dimensions of the vessel are 500, 20, and 2 mm, the longest being the direction of the reactant gas flow and that of electron beam scanning, and the shortest being along that of the electron beams which penetrate into the vessel through a titanium window (30 μ thick) equipped at the top. The bottom of the vessel is cooled with running water. In this system, the reactant gas is not recycled and always fresh reactant is supplied to the reaction vessel.

Irradiations are carried out using electron beams from the HDRA (0.6 MeV, 0.5 - 15 mA) and the irradiated gaseous mixture emerged out from the reaction vessel is analyzed by a gaschromatograph (Yanagimoto G 80 equipped with 3 m Porapak Q columns).

Absorbed electron energy in the reactant gas flow is measured using N_2O dosimeter in which the decrease of N_2O is determined by gaschromatography. Typical dose absorbed by gaseous mixture ($H_2/CO = 3$) at the flow rate of 84 ml/min and beam current of 5 mA is 1.2×10^8 rad, assuming $G(-N_2O) = 18$.

G values of the products determined in the present study (Run No. 51777-1) are compared in Table 1 with those (Run No. C-9) reported in the previous section3).

Table 1 G values of the Products

Run No.	CO_2	H_2O	HCHO	CH_4	C_2H_6	CH_3OH	CH_3CHO	$HCOOCH_3$	TOX
51777-1	0.32	0.88	0.27	0.18	0.02	0.06	0.03	0.01	-
C-93)	0.18	0.49	0.29	0.62	0.04	0.06	0.07	0.11	0.09

Oxygenates such as methanol, formaldehyde, acetaldehyde and methyl formate are found to be produced in addition to hydrocarbons already found. The G values of these compounds agree well with those obtained for the systems without catalyst previously described³⁾.

In Fig. 1 a and b, the yields of the products are plotted as a function of the residence time in the irradiation zone.

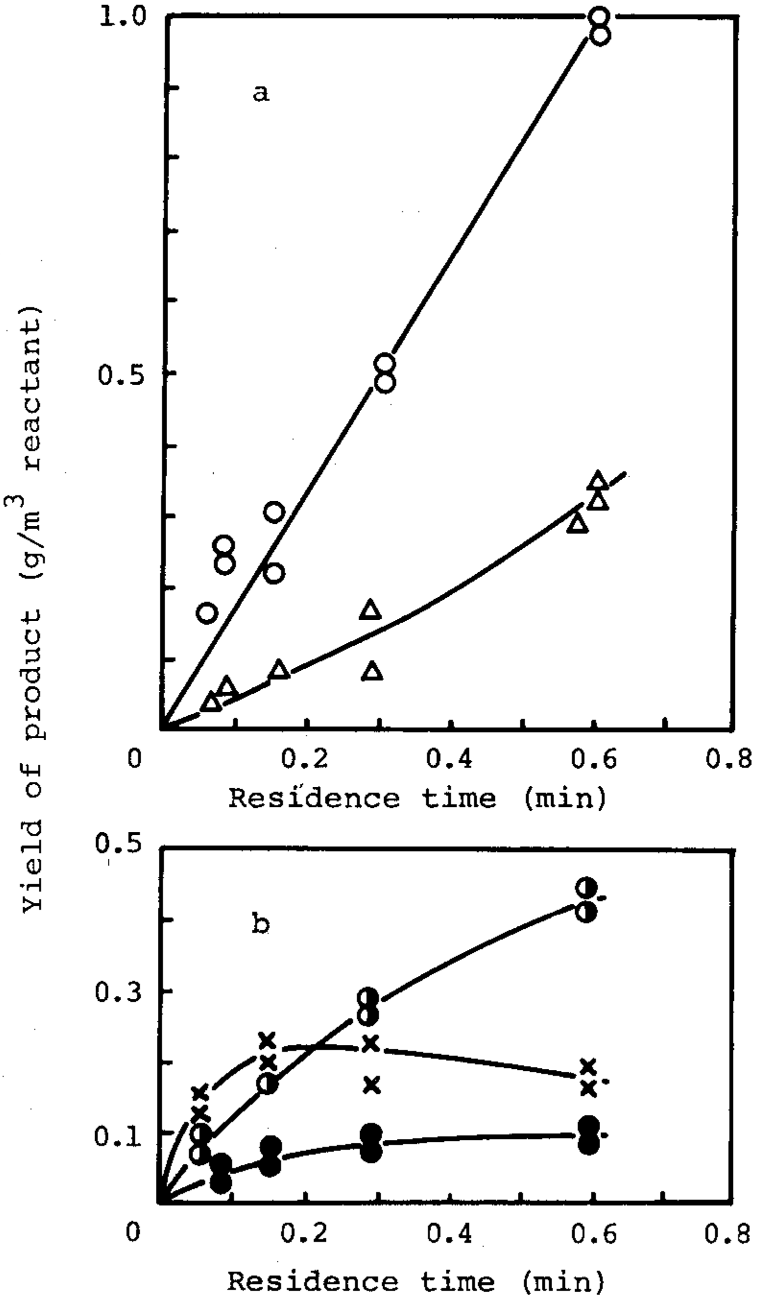


Fig. 1 The yields of the products vs. residence time; (o) carbon dioxide; (Δ) methane; (◐) methanol; (●) acetaldehyde; (x) formaldehyde.

As shown in Fig. 1 a, the yields of methane, methanol and carbon dioxide increase with increasing residence time. The yield of methane, however, increases sharply at longer residence time. On the other hand, the yields of formaldehyde and acetaldehyde increase with increasing residence time at earlier period of the reaction and then level off after 0.15 min (Fig. 1 b). These results seem to indicate that methane is produced not only primarily from hydrogen and carbon monoxide but also partly from other products secondarily by longer period of irradiation, and that aldehydes produced primarily are converted to other compounds by further irradiation.

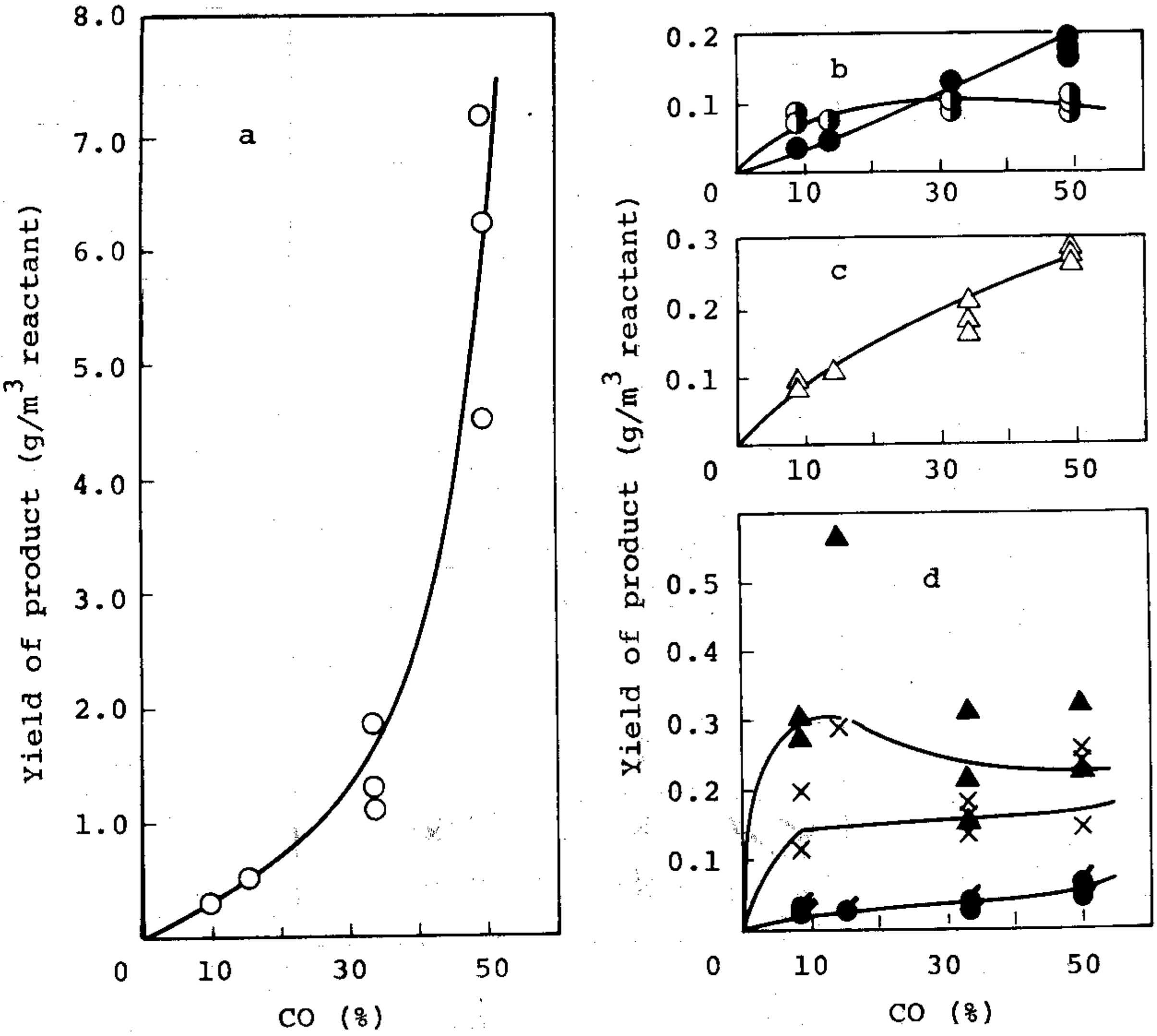


Fig. 2 The yields of the products vs. carbon monoxide content in the reactant gas flow (84 ml/min); (o) carbon dioxide; (Δ) methane; (◑) methanol; (●) acetaldehyde; (x) formaldehyde; (●) ethylene; (▲) water; beam current, 5mA.

The yields of products are shown in Fig. 2 a through d as a function of carbon monoxide content in the reactant flow. The yield of carbon dioxide increases sharply with carbon monoxide content. The yields of methane, ethane and acetaldehyde also increase with carbon monoxide content but not so steeply as in the case of carbon dioxide. On the other hand, yields of methanol, water, and formaldehyde level off or decrease after reaching maximum.

In Table 2, G values of the products are listed for

TABLE 2 Effects of Electron Beam Current on G values

Date, Time	51877-3	51777-6	51777-3	51877-4
Beam curr. (mA)	5	5	5	15
Temperature (°C)	58	60	60	104
Products				
CO_2	0.89	0.54	0.64	0.48
H_2O	0.20	0.37	0.26	0.35
HCHO	0.13	0.13	0.11	0.08
CH_4	0.28	0.24	0.25	0.28
C_2H_4	0.00	0.00	0.00	0.00
C_2H_6	0.03	0.02	0.02	0.03
C_3H_6	0.00	0.00	0.00	0.00
C_3H_8	0.00	0.01	0.01	0.01
CH_3OH	0.07	0.06	0.07	0.04
CH_3CHO	0.06	0.05	0.05	0.02
$HCOOCH_3$	0.01	0.01	0.00	0.01
C_4H_{10} + EtOH	0.01	0.01	0.01	0.01
X_1	0.00	0.00	0.01	0.00
X_2	0.00	0.00	0.00	0.00
X_3	0.00	0.00	0.00	0.00
X_4	0.00	0.00	0.00	0.00
Dose (ev/m^3)	$0.28\text{x}10^{25}$	$0.28\text{x}10^{25}$	$0.28\text{x}10^{25}$	$0.84\text{x}10^{25}$
Dose (rad)	$0.12\text{x}10^{9}$	$0.12\text{x}10^{9}$	$0.12\text{x}10^{9}$	$0.35\text{x}10^{9}$

Flow rates; H_2, 63.0 mℓ/min; CO, 21.0 mℓ/min.

different beam currents. The G values of carbon dioxide, formaldehyde, acetaldehyde, methanol seem to decrease with increasing beam current, whereas those of the other compounds remain practically constant. (K. Matsuda, S. Nagai, H. Arai, M. Hatada)

1) M. Hatada and K. Matsuda, JAERI-M, 6702, 11(1976), Int. J. Rad. Phys. Chem., 1977 in press.
2) S. Sugimoto, M. Nishii, and T. Sugiura, JAERI-M, 6702, 4(1976).
3) S. Sugimoto, M. Nishii, and T. Sugiura, This annual report.

4. Catalytic reaction of irradiated gaseous mixtures

Since oxygenates are found in the flow system using FIXCAT-II without catalyst, and their G values agree well with those reported for the gas circulation system described in section 1, we examined the reaction in the system where irradiation and catalytic reaction occur at different places in order to evaluate the contributions of the two effects separately. In this system intermediate or active species that are produced in the irradiation vessel may react on the surface of catalyst upon which the irradiated gas subsequently contacts, thus being converted to a certain compound selectively.

The FIXCAT-II is used as an irradiation vessel. The gaseous mixture irradiated in the FIXCAT-II is further reacted on Fischer-Tropsch catalyst through 13 m stainless steel tubing (2 mm inner diameter). Estimated time after the irradiation until contact with the catalyst is about 1 min.

The catalyst is prepared from Fe, Cu, and diatomaceous earths by the method previously described[1]. The method of irradiation is the same as that reported in the annual report of the previous year.

The results are summarized in Table 1. The yields of the products are close to those reported for the FIXCAT-II

Table 1 The Amounts of Products (g/m^3 reactant)

	70877-10	20877-7	30377-5	42177-8	42177-7	31877-1	42177-
H_2 (mℓ/min)	120	120	120	120	120	180	120
CO (mℓ/min)	20	20	20	20	20	30	20
(mA)	5	5	3	3	0	1.5	3
Temp. 1R. Zone (°C)	82	96	35	50	20	300	50
Temp. Cat Zone (°C)	-	23	108	245	245	300	70
TYP. of catalyst	NO	Fe-Cu-KG	Fe-Cu-KG	Fe-Cu-KG	Fe-Cu-KG	Fe	Fe-Cu-KG
The amounts of products							
CO_2	0.474	0.150	0.182	3.874	3.612	1.236	0.128
CH_4	0.094	0.323	0.091	6.556	6.205	0.367	0.205
C_2H_4	0.000	0.000	0.000	0.148	0.136	0.000	0.000
C_2H_6	0.002	0.006	0.002	0.679	0.646	0.028	0.008
C_3H_6	0.000	0.003	0.000	0.487	0.461	0.000	0.000
C_3H_8	0.010	0.003	0.000	0.312	0.309	0.036	0.004
CH_3OH	0.081	0.034	0.381	0.150	0.041	0.014	0.402
CH_3CHO	0.048	0.001	0.000	0.043	0.036	0.006	0.027
$HCOOCH_3$	0.012	0.068	0.000	0.012	0.017	0.025	0.014
C_4H_{10}+EtOH	0.021	0.001	0.025	0.865	0.841	0.021	0.034
X_1	0.005	0.001	0.000	0.012	0.011	0.000	0.002
X_2	0.000	0.000	0.000	0.010	0.017	0.000	0.003
X_3	0.000	0.001	0.000	0.140	0.099	0.000	0.114
X_4	0.000	0.000	0.000	0.339	0.358	0.000	0.004
Conversion (%)	0.53	0.17	0.26	5.35	5.02	0.68	0.37

system without catalyst when the temperature of the catalyst is below 30°C. When the temperature of the catalyst is increased to 50 - 70°C where no catalytic reaction of carbon monoxide and hydrogen takes place if unirradiated gaseous mixture is introduced, the yields of methanol and ethanol increase markedly. This may possibly be resulted from the catalytic hydrogenation of formaldehyde and acetaldehyde which are formed radiation chemically from the mixture of hydrogen and carbon monoxide.

Increase of flow rate results in increase of methanol yield. The result indicates the possibility that unstable intermediates such as formaldehyde are converted to a more stable compound; competing with polymerization of the intermediate, thus preventing the formation of unwanted polymeric products. Unfortunately, the results shown in this study are obtained with an analysis system which does not detect formaldehyde, and therefore we can not discuss the relation between methanol formation and formaldehyde consumption.

When the temperature of the catalyst is increased further above 200°C, where the catalytic reaction proceeds rapidly, the distribution of the products becomes closer to those reported previously for the catalytic reaction during irradiation[1)], i.e., the yields of hydrocarbons increase while those of oxygenates decrease.

These results support the previous conclusion that the catalytic reaction predominates over radiation chemical reaction when the catalyst is irradiated during the reaction.
(S. Nagai, K. Matsuda, M. Hatada)

1) M. Hatada and K. Matsuda, JAERI-M, 6702, 11(1976);
Int. J. Rad. Phys. Chem. (1977) in press.

5. Irradiation of Gaseous Mixtures in the Presence of Catalysts of Various Types

In the previous annual report[1)], the experimental results of radiolysis of gaseous mixtures of carbon monoxide and hydrogen in the presence of Fe-Cu-diatomaceous catalyst were described. This section concerns with the experimental results obtained with different solid catalysts other than the catalyst used in the previous study.

The methods of experiment are the same as those reported in the last annual report. The same reaction vessel (FIXCAT-I) which was used in the previous year is used. The catalysts used are diatomaceous earths (KG), iron supported diatomaceous earths (Fe-KG, 1 : 1 by weight), cobalt supported diatomaceous earths (Co-KG, 1 : 1), ruthenium supported alumina ($Ru\text{-}A\ell_2O_3$, 0.005 : 1), and Manganese oxide supported diatomaceous earths (MnO_2-KG, 1.5 : 1). The methods of analyses and irradiation are also described in the earlier publications except for some runs where the same method of analysis as in the previous section is employed.

The results are summarized in Table 1. As seen from the table, the yields of the products catalytically formed are quite low except for the case of MnO_2 where carbon dioxide is selectively formed in rather high yield. Irradiation causes the increase in the yields of the products, the degree of which is dependent on the types of the catalysts used.

Little products are found when KG is used. The yields of the products formed when Fe-KG is present are comparable to those found in the previous experiment using Fe-Cu-KG, which may indicate that copper in the catalyst has little effect on the product yields. Irradiation in the presence of Co-KG gives yields of the products higher than those with Fe-KG, but the distribution of the products is similar to that with Fe-KG. $Ru\text{-}A\ell_2O_3$ enhances the yield of methane selectively on irradiation, but this may arise from rise of the catalyst temperature by 40 degrees since $Ru\text{-}A\ell_2O_3$ is highly active to produce methane at the temperature.

MnO_2 selectively produces carbon dioxide. The activity to produce hydrocarbons is low, but it is noted that olefins are produced to appreciable amounts while yields of parafins are quite low. On irradiation the yield of carbon dioxide increases and the yields of most hydrocarbons especially olefins

Table 1 The Radiolysis Products from Gaseous Mixtures in the Presence or Absence of Various Types of Solid Catalysts

Run No.	71976-2	71976-3	92476-15	92476-17	92276-11	92276-17	92776-12	92276-17	71476-2	71476-3
Reactant										
Flow rate (mℓ/min)	55		93		100		99		60	
H_2/CO (by vol)	1		2.2		2.2		2.2		2.2	
Type of catalyst	KG		Fe-KG		CO-KG		Ru-$A\ell_2O_3$		MnO_2-KG	
Beam current (mA)	0	0.08	0	0.08	0	0.08	0	0.08	0	0.08
Temp. of catalyst (°C)	220	295	200	220	203	233	195	235	235	275
The amounts of products in g from 1 m^3 reactant.										
CO_2	0.6	3.0	6.9	116.4	0.7	123.1	0^*	314.6	143.4	361.4
CH_4	0.2	0.04	0.1	4.2	0.2	24.9	0.5	190.7	0.2	0.1
Gasol										
$C_2H_4+C_2H_6$	0.04	0.01	0.3	7.7	0.2	12.9	0.3	21.8	0.2	0.1
C_3H_8	0.02	0.02	0.1	2.5	0	5.2	0.2	3.2	0	0.3
C_3H_6	0.2	0.0	0.5	6.7	0.6	14.2	1.3	0.1	0.3	0.0
C_4H_{10}	0.03	0.02	0.1	1.6	0	4.6	0.5	0.7	0.0	0.0
ΣC_4H_8	0.12	0.0	0.6	5.7	0.9	14.0	2.0	0.2	0.3	0.1
(Total Gasol)	(0.4)	(0.05)	(1.5)	(24.2)	(1.7)	(51.0)	(4.2)	(25.9)	(0.8)	(0.5)
Benzin										
C_5H_{12}	0.0	0.0	0.1	0.6	0.0	4.8	1.6	0.1	0.0	0.0
ΣC_5H_{10}	0.0	0.0	0.4	2.9	0.0	7.6	3.2	0.0	2.2	0.0
C_6H_{14}	0.0	0.0	0.0	1.0	0.0	4.8	1.1	0.0	0.0	0.0
(Total Benzin)	(0.0)	(0.0)	(0.5)	(4.5)	(0.0)	(17.2)	(5.9)	(0.1)	(2.2)	(0.0)
Conv. (%)	0.1	0.5	2.2	36.3	0.5	48.8	2.4	100.	33.3	82.2
(%)	50	2.9	23.3	22.0	41.7	43.0	100.	40.8	2.2	0.2

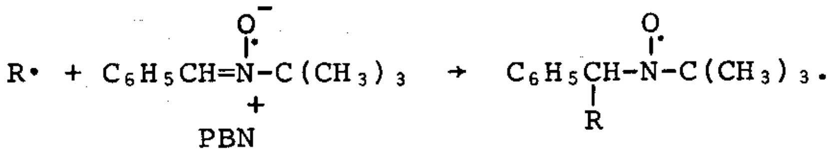
decrease. The products that may be formed as a counter part of carbon dioxide are not found by the analysis system employed in the present study. (S. Nagai, K. Matsuda, M. Hatada)

1) M. Hatada and K. Matsuda, JAERI-M, 6702, 11(1976); Radiat. Phys. Chem. (1977) in press.

6. Application of the Spin Trapping Technique to the Radiation Chemistry of Mixtures of CO and H_2

Selectivity of radiation chemical reaction of mixtures of CO and H_2 could be found if active species such as radicals or ions formed by radiation would react on solid catalysts. For the purpose to study such a reaction, it is important to know the structure and lifetime of the active species. The present study is undertaken with the principal purpose to detect radicals in the active species formed in gas phase by electron irradiation of CO and H_2.

Phenyl-t-butylnitron (PBN) is used as a spin trap. Unstable radical R• reacts with PBN to produce a relatively stable nitroxide (spin adduct) as follows;

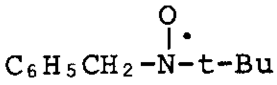


$$R\cdot + \underset{\text{PBN}}{C_6H_5CH{=}\overset{O^-}{\underset{+}{N}}{-}C(CH_3)_3} \rightarrow C_6H_5\underset{R}{CH}{-}\overset{O\cdot}{N}{-}C(CH_3)_3 .$$

The analysis of the ESR spectrum due to the nitroxide permits the determination of the structure R•.

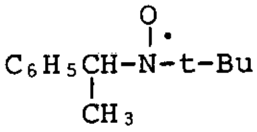
PBN powder dispersed on glass wool is placed near the outlet of the reaction vessel, Fixcat-II. Care is taken to shield PBN from incident electron beams by placing a Pb block over PBN. A mixture of CO and H_2 gases with the ratio H_2/CO of 6 is introduced at the flow rate of 140, 175 or 350 mℓ/min to Fixcat-II where the gaseous mixture is subjected to irradiation with electron beams of 600 kev and 3 mA or 5mA. The irradiated gas passes the glass wool dispersed with PBN and a nitrogen trap attached to the outlet of FIXCAT-II. After irradiation for 30 min, the PBN powder and products collected in the nitrogen trap are dissolved in benzene, outgassed under vacuum, and the ESR spectra were recorded at room temperature.

Five types of nitroxides I ∿ V are detected, including H atom adduct(I) and CH_3 radical adduct(II). The nitroxides



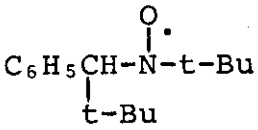
$\mathrm{C_6H_5CH_2-\overset{O\cdot}{\overset{|}{N}}-t-Bu}$

(I)



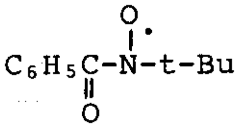
$\mathrm{C_6H_5\underset{CH_3}{\underset{|}{CH}}-\overset{O\cdot}{\overset{|}{N}}-t-Bu}$

(II)



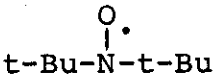
$\mathrm{C_6H_5\underset{t-Bu}{\underset{|}{CH}}-\overset{O\cdot}{\overset{|}{N}}-t-Bu}$

(III)



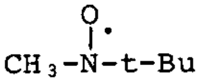
$\mathrm{C_6H_5\underset{O}{\underset{\|}{C}}-\overset{O\cdot}{\overset{|}{N}}-t-Bu}$

(IV)



$\mathrm{t-Bu-\overset{O\cdot}{\overset{|}{N}}-t-Bu}$

(V)



$\mathrm{CH_3-\overset{O\cdot}{\overset{|}{N}}-t-Bu}$

(VI)

III ∿ V are produced by decomposition of PBN. The H atom adduct(I) and nitroxides III ∿ V are also detected in an experiment conducted on H_2 gas flow instead of the $CO\text{-}H_2$ flow.

Although H atoms and CH_3 radicals are successfully detected in our experiment, the formation of nitroxides III ∿ V indicates appreciable decomposition of PBN, most likely due to scattered electron beams and secondary X-rays. Thus there is some doubt if the detected H atoms and CH_3 radicals would be produced not from $CO\text{-}H_2$ but from PBN. It is in fact found that γ-irradiation of PBN powder to a dose as high as 10 Mrad gives the H atom adduct(I).

In order to solve the problem, the experiment is carried out on the spin trapping of PBN irradiated in the $CO\text{-}H_2$ flow. PBN powder is placed at the central part of FIXCAT-II. The results are compared with those obtained in a similar experiment where PBN is irradiated in a He gas flow.

The irradiation of PBN is found to yield the nitroxides I, III ∿ VI irrespective of the atmosphere. The relative concentration of the nitroxides, however, is quite dependent on the atmosphere of irradiation. The ESR spectrum of the irradiated PBN powder showed the formation of the H atom adduct(I) and the nitroxide III, where the latter clearly arises from decomposition of PBN. The concentration of the H atom adduct(I) relative to the nitroxide III, produced in the CO-H_2 flow, is three times higher than that in the He flow. The ESR spectra of the products collected in the nitrogen trap, on the other hand, showed the presence of the CH_3 radical adduct(VI) and nitroxide V. The concentration of the CH_3 radical adduct(VI) relative to the nitroxide V in the CO-H_2 flow is above 30 times higher than that in the He flow.

These findings indicate that the H atoms and CH_3 radicals detected in the present study are formed from the mixture of CO and H_2 although some of them may be produced by radiation decomposition of PBN. (S. Nagai, K. Matsuda, M. Hatada)

[2] Radiation-Induced Polymerization of Mixed Multilayers of Octadecyl Acrylate and Octadecane-Nitrile

As a continuation from the previous study in an attempt to prepare skeletonized polymer multilayer$^{1)}$, we examined the possibility to prepare skeletonized polymer multilayer from octadecyl acrylate (ODA) and octadecane-nitrile (ODN) this year.

The methods of preparing multilayers and of irradiation were described in the last annual report. The type of deposition is that of Y type, and the number of layers of the mixed multilayer is 170 and 230.

Surface pressure-area (ΠA) curves of mixed monolayer from which the mixed multilayer is prepared give information on the state of aggregates or patches of molecules in the monolayer. Thus, the difference between a ΠA curve of a two component monolayer delivered from a mixed solution of ODA and ODN and one prepared by spreading one component followed by spreading the other indicates the difference in miscibility of the two components in the monolayers.

Fig. 1 shows ΠA curves of the monolayers. Curve (a) is the ΠA curve of the monolayer spread from the mixed solution of ODA and ODN. Curves (B) and (C) are the ΠA curves of monolayers of ODA and ODN, respectively. Curve (D) is obtained for the monolayer spread by successive depositions of ODA and of ODN. Curve (E) is the one predicted as a superposition of curves (B) and (C). Larger deviation of curve (A) of the mixed multilayer from the calculated curve (E) than that between (D) and (E) indicates that the patches of one component are small enough to exhibit the interaction of one to the other.

Since the deviation found here is larger than that observed in ODA-EA system, the patches in the ODA-ODN system are smaller than those in the ODA-EA system.

X-ray reflection curve of the ODA-ODN multilayer (Fig. 2) shows the presence of reflection due to ODA alone and the

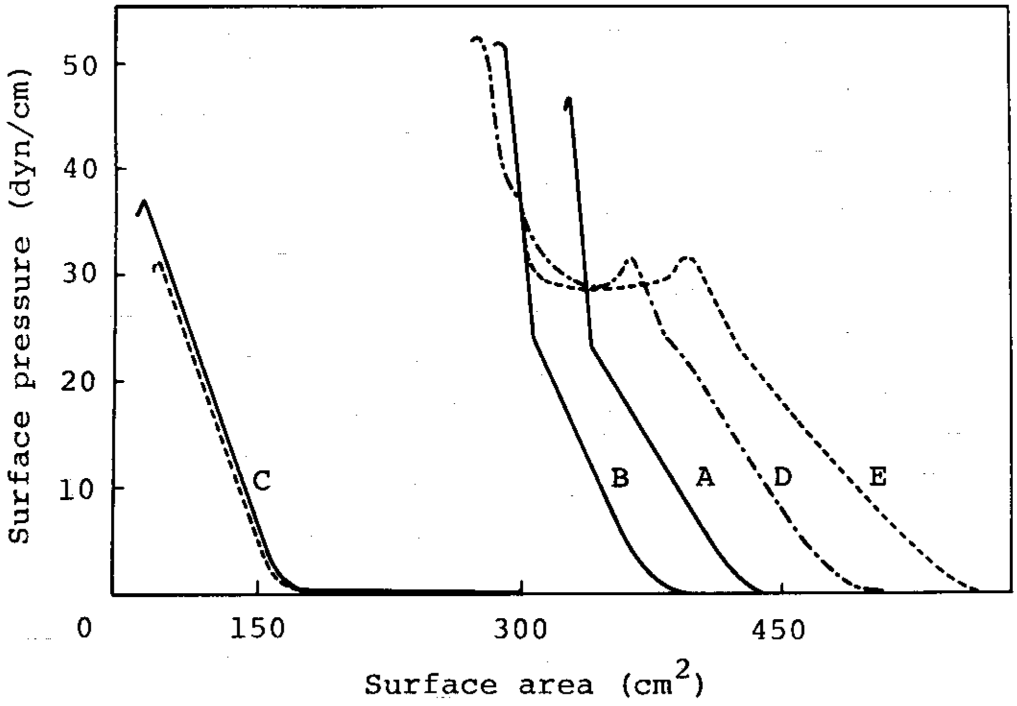


Fig. 1 Surface pressure-area curves. A, mixed monolayer of ODA and ODN delivered from a mixed solution (ODA : ODN = 9 : 2 by weight) (0.11 mg); B, ODA monolayer (0.09 mg); C, ODN monolayer (0.02 mg); D, monolayer of ODA (0.09 mg) and ODN (0.02 mg) delivered successively; and E, superposition of B and C.

spacing of ODA in the multilayer seems to be close to but a little bit smaller than that of pure ODA multilayer, supporting the above idea that the patches are still too small to be detected by X-ray diffractometry.

Infrared spectrum of the mixed multilayer seems to appear as a superposition of those of the two components, but the contribution of the ODN is not very clearly seen because of weak key bands. The absorptions due to vinyl group of ODA disappear on irradiation, confirming that the polymerization of ODA takes place.

The intensities of reflections due to ODA decrease on irradiation in nitrogen atmosphere, and new reflections due to poly (ODA) appear when the irradiation is continued further as was found in the polymerization of pure ODA multilayer$^{2)}$,

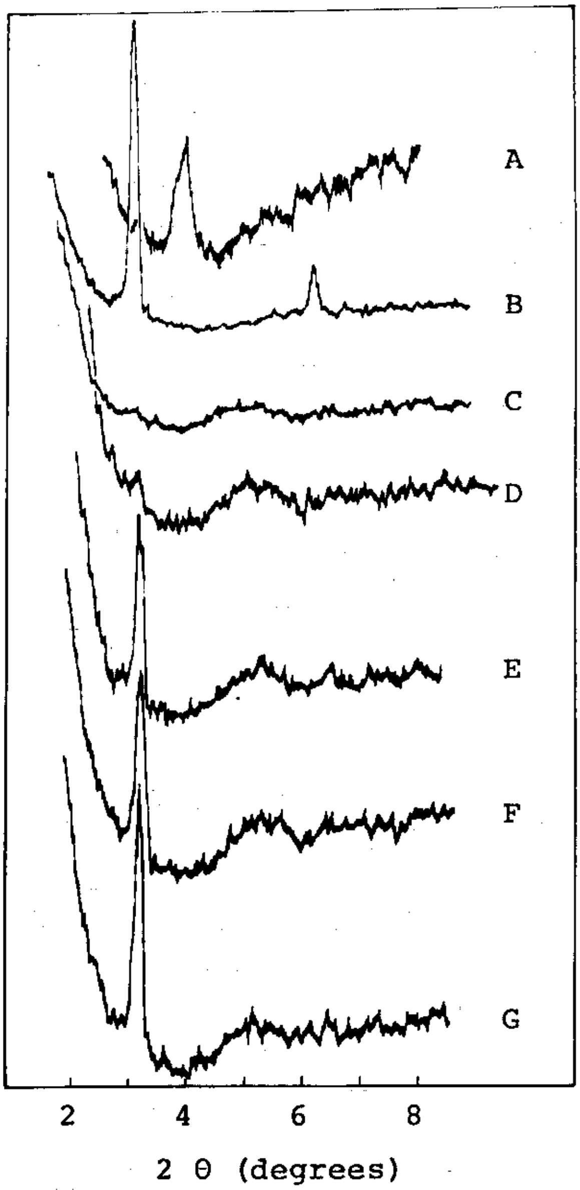


Fig. 2 Change in X-ray diffraction curves of mixed multilayer of ODA and EA upon irradiation: A, ODN multilayers; B, before irradiation; C, 0.75; D, 1.5; and E, 2.3; F, 5; G, 15 Mrad.

and ODMA multilayer[3)] (Fig. 2C - G).

The $^{\nu}C{\equiv}N$ absorption band due to ODN disappears but the bands due to ODA do not change when the irradiated mixed multilayer (dose, 35 Mrads) is immersed in n-Hexane for 5 min, suggesting that ODN molecules are dissolved out and porous skeletonized polymer multilayer is formed. Both visible inspection and X-ray diffractometry of the immersed multilayer show that a part of the poly (ODA) is missing. This may indicate that the ODN molecules distributed among ODA molecules affect the polymerization of ODA in a way that the ODN decreases the degree of polymerization. (M. Hatada, M. Nishii)

1) M. Hatada and M. Nishii, JAERI-M, 6702, 27(1976).

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

3) M. Hatada and M. Nishii, J. Polym. Sci., (1977) in press.

[3] Polymerization of Vinyl Monomers by High Dose Rate Electron Beams

1. Radiation-Induced Polymerization of Styrene in a Wide Range of Dose Rate

Radiation-induced polymerization of the moderately dried (water content 3.2×10^{-3} mole/l) and water saturated (water content 3.5×10^{-2} mole/l) styrenes was carried out up to a very high dose rate as 1.8×10^{7} rad/sec. Molecular weight distribution curves by GPC of the polymerization products of the former showed that they consisted of three parts, namely oligomers, radical and ionic polymers. In the case of the water saturated styrene the fourth peak was observed in the curves for the formation of polymer of very high molecular weight, which was designated as super polymer. Contributions of the four (or three) constitutents for the polymerization and their number average degrees of polymerization (DP) were evaluated by the graphical analysis of the GPC curves, and the individual rates of the four types of polymerization were calculated.

The rate of radical polymerization and DP of radical polymers are quite independent of the water content of styrene. The dose rate dependences of the polymerization and DP agree with the well known square root and inverse square root law, respectively, of radical polymerization of styrene. It is noteworthy that the same stationary state condition as found in the catalytic polymerization for styrene is applicable to radiation-induced polymerization at very high dose, which is comparable in its activity to a catalyst employed at a concentration six orders of magnitude higher than the conventional one. G-value, i.e. the radiation chemical yield of the initiating radical formation is calculated to be 0.66.

Fig. 1 shows G-value of the initiating radical formation based on our experimental results in a dose rate range between 10^{3} rad/sec and 10^{7} rad/sec; the figure contains also values picked up from Chapiro's book for a dose rate range between 10^{-2} rad/sec and 10 rad/sec, where ionic polymerization can be neglected. It is noteworthy that there is no difference of the G-values for the very low and very high dose rate ranges. It seems that initiating radicals are formed in a ten orders of magnitude different range by a same mechanism without intrusion of other effects.

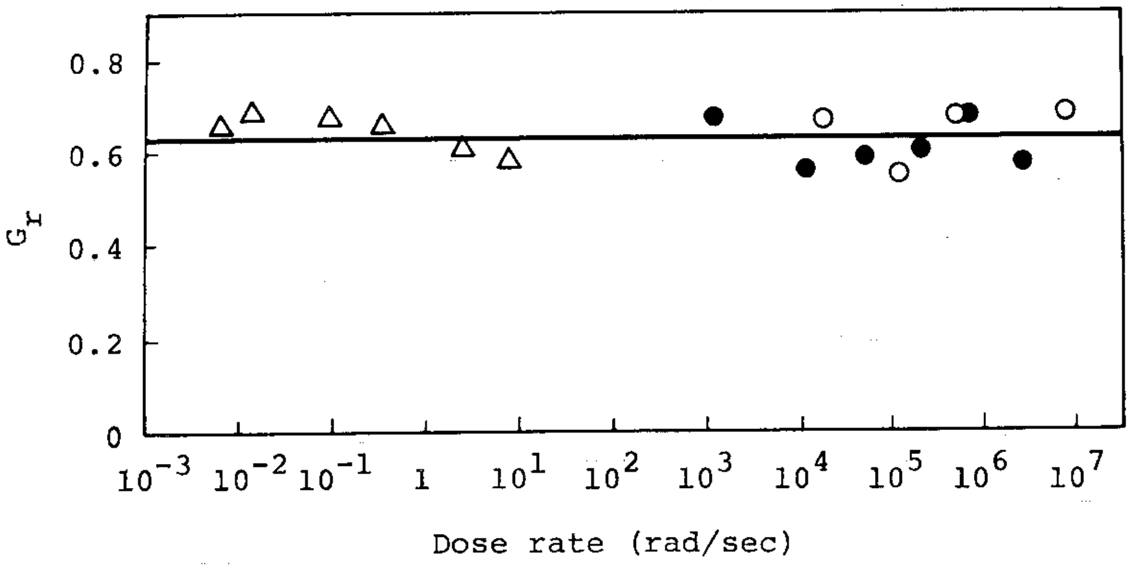


Fig. 1 G_r-value of initiation for the polymerization of styrene over the wide range of dose rates. (o) Moderately dried styrene; (●) Water saturated styrene; (Δ) Chapiro (Calculated from total polymerization).

So long as the water content is kept constant the rate of ionic polymerization is directly proportional to the dose rate, but it decreases with increasing water content, because water is a terminator for the cationic polymerization.

Fig. 2 shows plots of ionic polymerization rates of moderately dried and water saturated styrenes. We see clearly that the rate of the wet styrene is about one tenth of the value for the moderately dried styrene. This is that what was expected in the previous report i.e., the ionic polymerization rate was inversely proportional to the water content. The ratio of the water content of the two styrenes is calculated to be 10.9.

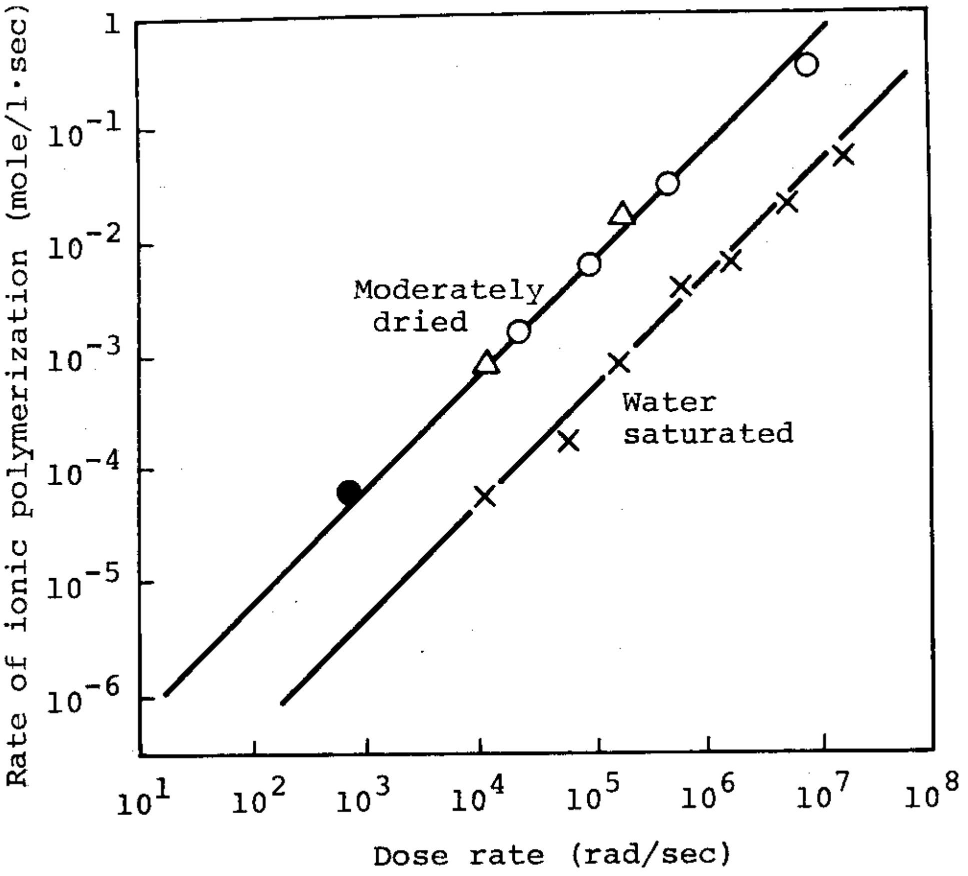


Fig. 2 Ionic polymerization of moderately dried and water saturated styrene; (o), (x) HDRA; (Δ) VdG; (●) 60 Co.

DP of the radical polymers decreases rapidly with increasing dose rate whereas DP of the ionic polymer is independent of the dose rate. On the other hand, DP of the radical polymer is independent of the water content, but DP of ionic polymer decreases with increasing water content due to the same reason as in the case of polymerization rate. Fig. 3 shows schematically the dependences of DP and number of molecules for the radical and ionic polymers on the dose rate of radiation and water content of styrene. The number of radical polymers is dependent neither on the dose rate nor on the water content; in the case of the ionic polymers, the number is independent of the dose rate, but it decreases with increasing water content. In styrene of lower water content, growing ions have more chance of chain transfer to monomer to start another growing ion before undergoing chain termination by water molecule.

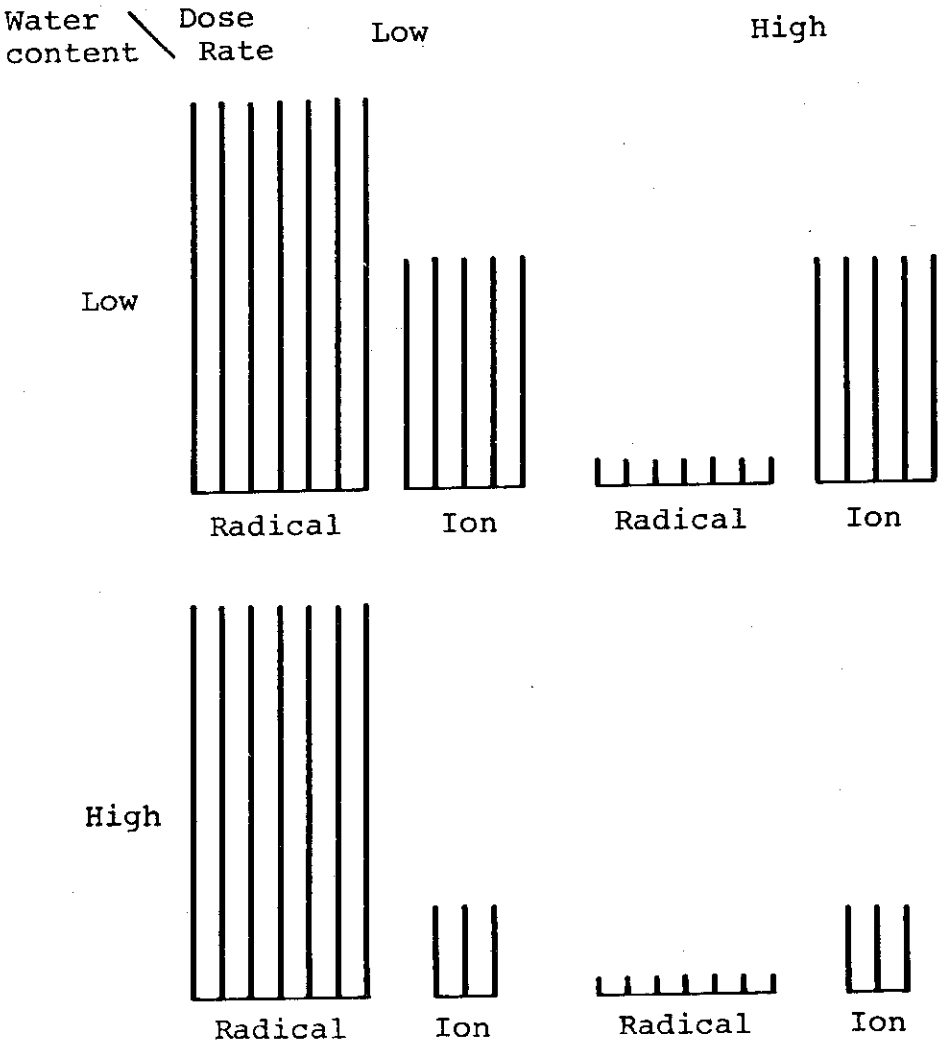


Fig. 3 Schematic representation of number and length of polymer chain from styrene of different water contents at high or low dose rate.

It is calculated that the G-value of the initiating ion formation is 0.027 independent of the dose rate and water content. Numbers of ionic polymers produced (mole/l/rad) for the moderately dried and water saturated styrenes are 1.28×10^{-10} and 0.28×10^{-10}, respectively.

It is interesting to carry out similar experiment with styrene of still higher content of water. However, it is unable because the experiments have been carried out with water saturated styrene. Consequently the use is made of methanol instead of water as an additive, and it is found that an addition of methanol, in an amount similar to the water content of the water saturated styrene, reduces the rate of the total polymerization to the same level as water.

Experiments of radiation induced polymerization have been limited only to the initial stage of conversion. Studies are now extended up to a higher conversion.
(I. Sakurada, T. Okada, Ka. Hayashi, J. Takezaki)

2. Polymerization of Isobutyl Vinyl Ether

In the previous report$^{1)}$, it was found that isobutyl vinyl ether (IBVE) polymerized with radical mechanism at low dose rate with γ-rays but with electron beams which gave dose rates higher than 10^4 rad/sec, it polymerized with radical and cationic mechanisms concurrently. However, molecular weight distribution of the reaction products obtained at high dose rate was always single-peaked and its number-average molecular weight was ca. 1,000 though the cationic product was supposed to have higher molecular weight than radical one formed at high dose rate.

The water present as an impurity in the monomer is the most probable inhibitor for the cationic polymerization. Further addition of water to saturate the monomer gives no significant change in R_p as shown in Fig. 1. Also no change is observed in molecular weight distribution. It is difficult to determine the content of water in IBVE by chemical titration probably due to the hydrolysis of the monomer. A rough estimate of the water content is made using its absorption in near IR region. The concentration of water in water-saturated sample is found to be higher than ordinary IBVE dried with calcium hydride by 0.12 - 0.24 mole/l.

Further experiment is carried out on well dried monomer. IBVE is dried with sodium mirror and sealed in metal cells. These procedures are carefully made in a vacuum system. The

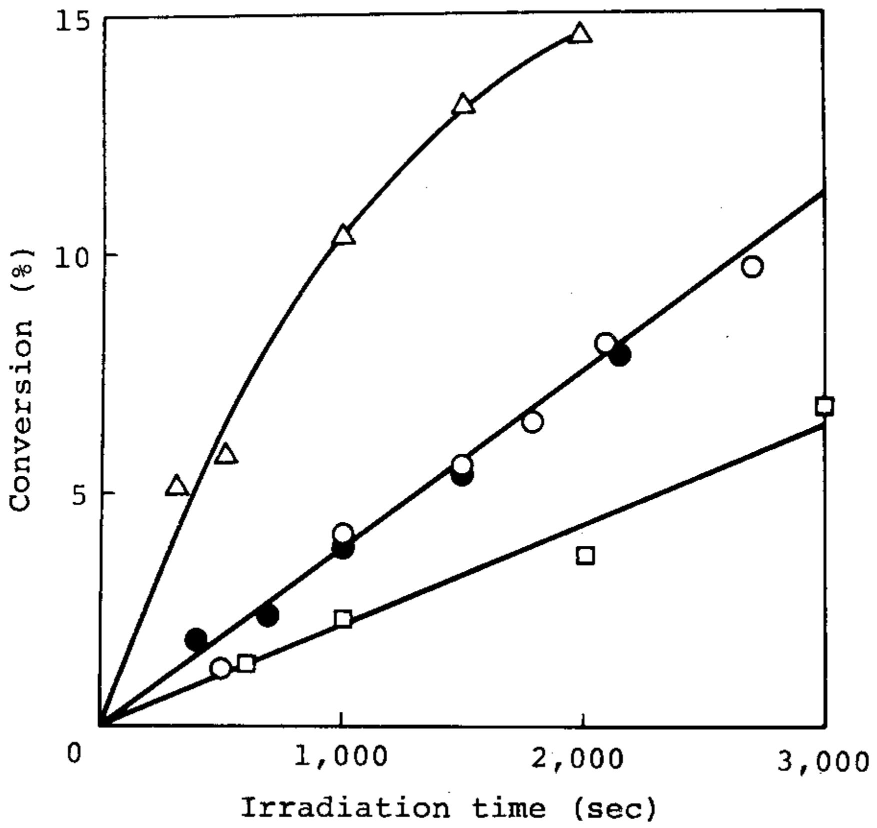


Fig. 1 Polymerization of IBVE at 25°C. Dose rate, 8.8×10^4 rad/sec. (o) ordinary monomer; (●) saturated with water; (□) 0.059 mole/l IPA; (Δ) dried with sodium mirror.

R_p's for these samples are found to be 2 - 4 times greater than those of ordinary ones as shown in Fig. 1. Typical molecular weight distribution of the polymer is shown in Fig. 2. Apparently it is composed of two fractions. A large peak appeared at the elution count of 23.0 is obviously attributed to the promotion of the cationic polymerization with drying the monomer.

We presume that the reaction by cationic species are completely inhibited by the addition of 0.059 mole/l isopropylamine (IPA). The R_p when IPA was added is 55 % of that of ordinary monomer; the conversion is also given in Fig. 1. A substraction of molecular weight distribution of the reaction product obtained in the presence of IPA from the

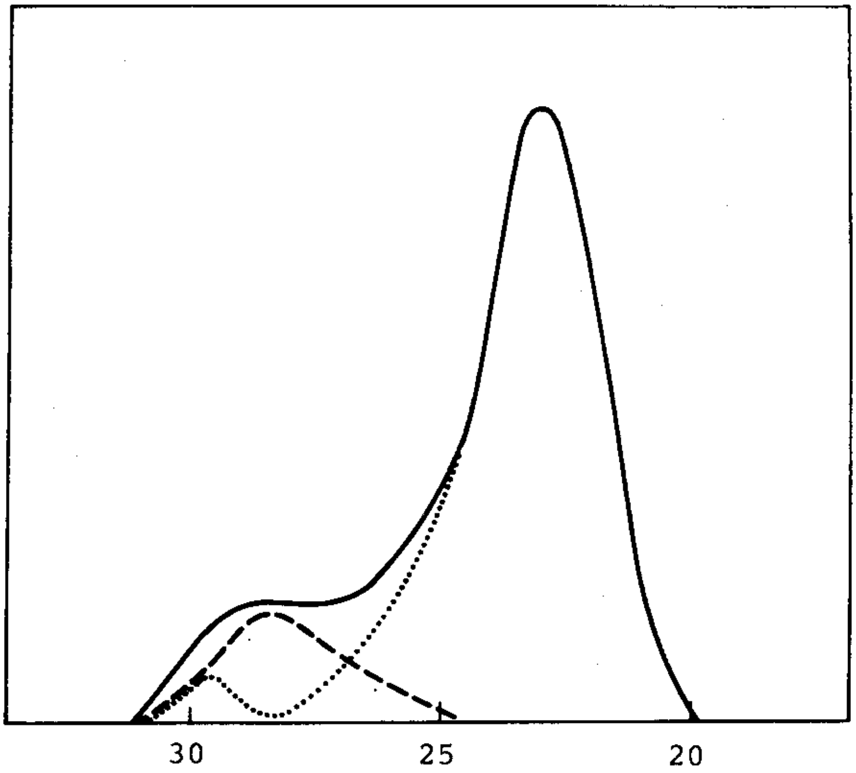


Fig. 2 Molecular weight distributions of the polymer from the monomer dried with sodium mirror (solid line) and of the polymer when IPA was added (broken line). The dotted line denotes the difference between the two.

distribution of the product from well dried system shows the presence of two distinct peaks, which is shown in Fig. 2. Apart from the high molecular weight fraction due to the cationic mechanism, a small fraction of oligomer is also supposed to be due to ionic mechanism since it is also inhibited with IPA. Molecular weights for oligomer, radical polymer, and cationic polymer are approximately 500, 800 and 5,000, respectively. The G_i values are 0.12 for oligomer, 0.64 for radical polymer assuming termination of radical recombination. The G_i for cationic polymer is evaluated to be 0.24 assuming its molecular weight is solely governed by a termination reaction with water. The latter two G_i values are in fair agreement with reference values for other vinyl compounds or IBVE itself at low dose rate. (T. Okada, Ka. Hayashi, J. Takezaki)

1) JAERI-M, 6702, 42 (1976).

3. Polymerization of α-Methylstyrene

Polymerization of α-methylstyrene is studied to investigate the mechanism of cationic polymerization at high dose rate since it is expected that practically no radical polymerization takes place with this monomer. Details of the experimental technique are described in the last issue of this report$^{1)}$.

Results of the polymerization with electron beams from a Van de Graaff accelerator are given in Fig. 1. Monomer employed is purified in a conventional way. It is washed with distilled water and distilled at reduced pressure after drying with calcium hydride. A sample saturated with water [(H_2O) = 0.017 mole/l] is denoted as run 1. Differences among run 2 - 8 are due to storage time before use in the presence or absence of calcium hydride and further distillation over alkali metal; the higher the run No., the more dried the sample. With run 8 for which exceedingly high R_p is achieved, sampling of monomer is made immediately after the redistillation over sodium. These results indicate that R_p is greatly enhanced with drying. With an addition of 0.60 mole/l triethylamine (TEA), the R_p is reduced to ca. 70 % of run 1.

Molecular weight distributions of reaction products of several runs in Fig. 1 are shown in Fig. 2. Product from water-saturated monomer, run 1, is oligomer of $\overline{DP}$ = ca. 5. Comparing the distributions of run 3, 6 and 8 with that of run 1, a new peak of higher molecular weight appears with the increase of R_p. Here we call the high molecular weight fraction which appeared on drying "polymer fraction" and the remaining part, "oligomer fraction". On estimate of the area

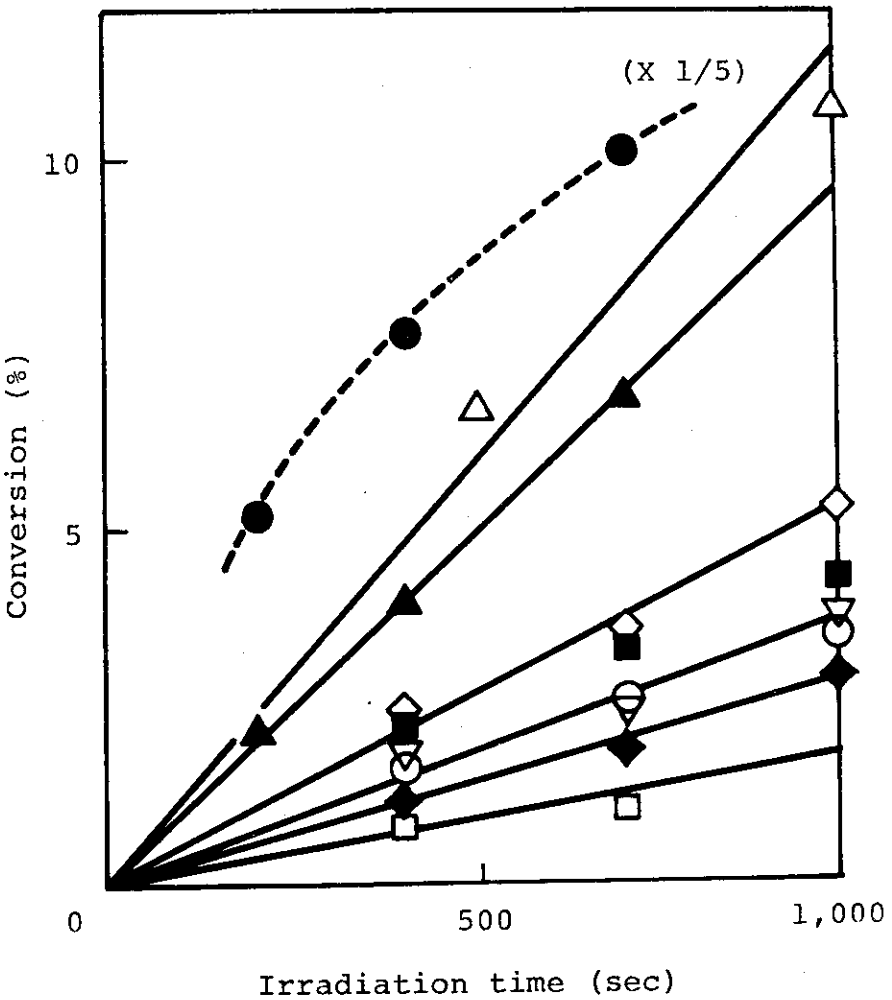


Fig. 1 Polymerization of α-methylstyrene of different drying at 8.5 X 10^4 rad/sec (25°C); (◆) run 1; (o) run 2; (∇) run 3; (■) run 4; (◇) run 5; (▲) run 6; (Δ) run 7; (●) run 8; (□) in the presence of TEA (0.6 mole/l).

of the polymer fraction on GPC curves, it is found that the increases of R_p is attributed to the formation of the polymer fraction. In other words, the rate of oligomer formation does not change with R_p at all. Distributions of products from run 6 and 8 indicate that the molecular weight of the polymer fraction keeps almost a constant value in spite of a large increase in R_p. On addition of TEA, the polymer fraction disappears entirely and higher molecular weight part of the oligomer fraction is also cut out. The number-average

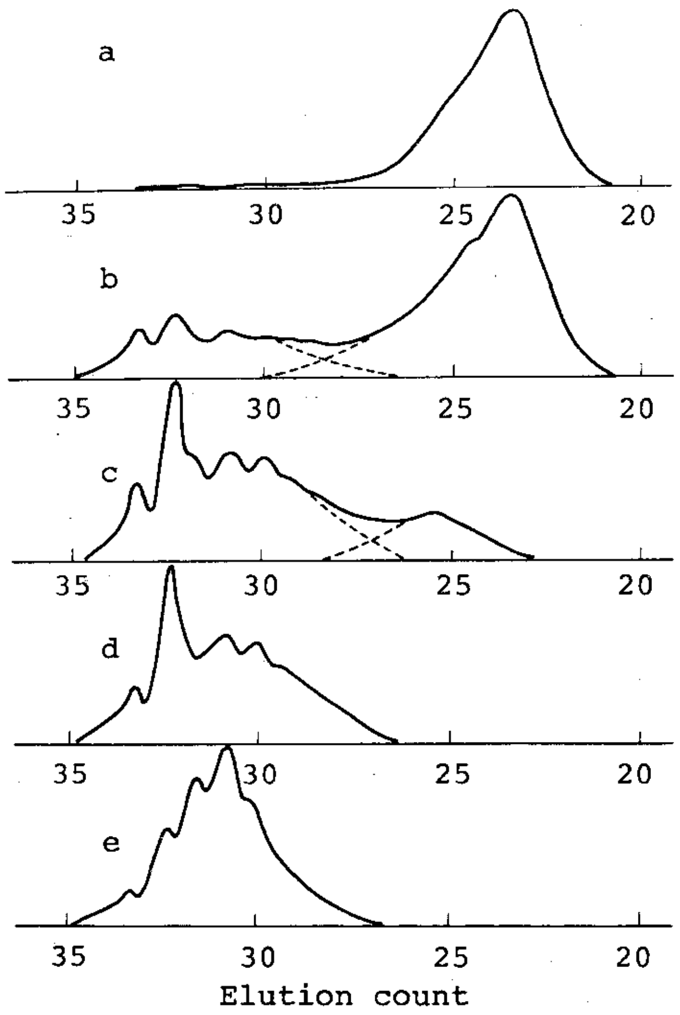


Fig. 2 Molecular weight distributions of poly-α-methyl-styrenes polymerized at 8.5×10^4 rad/sec; a, run 8; b, run 6; c, run 3; d, run 1; e, in the presence of TEA (0.6 mole/l).

molecular weight determined by vapor pressure osmometry is 450 for the product when TEA is added, 500 - 550 for the product from run 1 and ca. 5,000 for the polymer fraction.

Dose rate dependence of R_p for several runs is studied between 8.5×10^3 and 2.1×10^5 rad/sec, as shown in Fig. 3. Appearance of molecular weight distributions of the products obtained for runs at these dose rates is quite similar to one another. Peak position of the polymer fraction does not change with dose rate. For all runs except run 8, R_p is

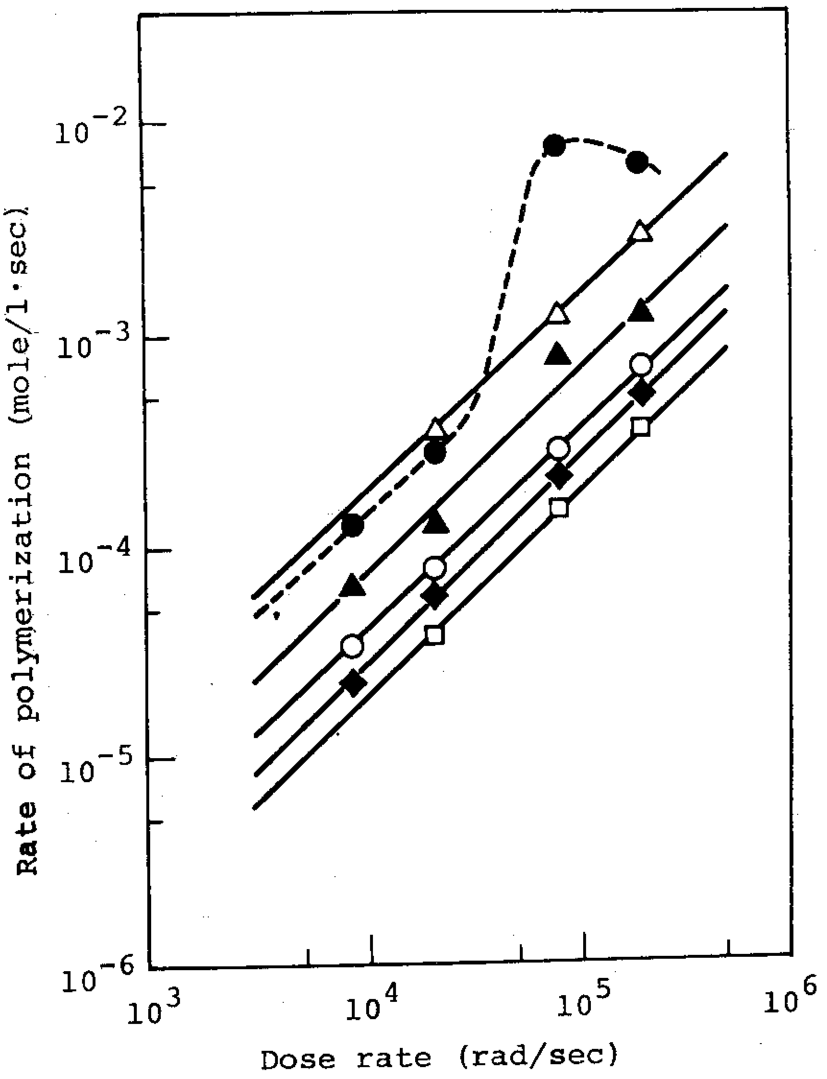


Fig. 3 Effect of dose rate on the polymerization of α-methylstyrene; symbols are the same as those in Fig. 1.

proportional to the dose rate. An exceedingly high R_p at 8.5 X 10^4 rad/sec of run 8 reflects an immediate sampling after redistillation over sodium, while samples at the other dose rates are sealed 1 - 2 hours after the drying. When TEA is added, the molecular weight distributions of the reaction products do not change greatly with dose rate and with TEA concentration. These results indicate that oligomer fraction is derived from different origin from that of the polymer fraction.

It is no doubt that the polymer fraction which appears on drying is due to cationic mechanism. γ-Ray polymerization of superdry monomer gives polymer of the similar molecular weight distribution of $\overline{M}_n = 5,000$, which is governed by chain transfer to the monomer. The formation of oligomer is considered to be due to ionic mechanism at present since it is retarded with large amount of amine and its rate of formation is directly proportional to dose rate. (T. Okada, Ka. Hayashi, J. Takezaki)

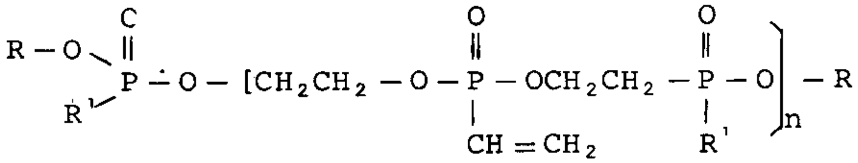
1) JAERI-M, 6702, 87 (1976).

[4] Modification of Polymers

1. Preparation of Flame-Retardant Polyethylene Terephthalate Fabrics by Electron Beam-Induced Grafting of Vinyl Phosphonate

In the previous report we have shown that radiation-induced chlorination imparts flame-retardancy to polyethylene-terephthalate (polyester) fiber. The heat stability of the fiber estimated by thermogravimetry is, however, more or less damaged, particularly in the fiber of chlorine content above 20 %.

The purpose of the present report is to make polyester fiber flame-retardant by grafting phosphorous containing compound to the fiber. Grafting was carried out onto polyester fabric with electron beams from an accelerator and the properties of the graft fabric were measured. The compound used was oligomeric vinyl phosphonate having molecular weight of about 700 and the structure shown below.



R: $HO-CH_2-CH_2-$, R': alkyl

The fabric was immersed in methanol solution of the oligomer at different concentrations, impregnated with the solution and excess methanol was evaporated in open air at room temperature. Fiber with desired oligomer picked up was obtained either by varying the concentration of the oligomer solution or by squeezing out excess solution. The fabric impregnated with oligomer was irradiated with electron beams from a transformer type accelerator (HDRA) at a dose rate of 3.3 Mrad/sec, for the graft polymerization. The irradiated fabrics were washed to remove residual oligomer and soluble

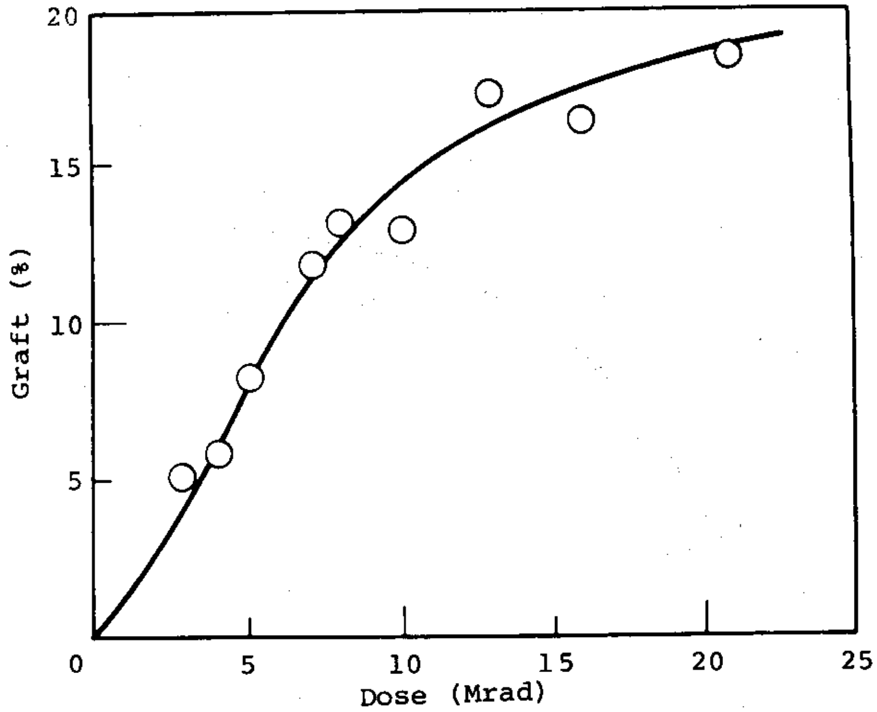


Fig. 1 Effect of dose on the grafting of oligomeric vinyl phosphonate onto polyester fabrics; impregnated with 40% methanol solution of oligomer; transformer type accelerator (HDRA), 800 KeV, 3.3 mA; dose rate, 3.3 Mrad/sec.

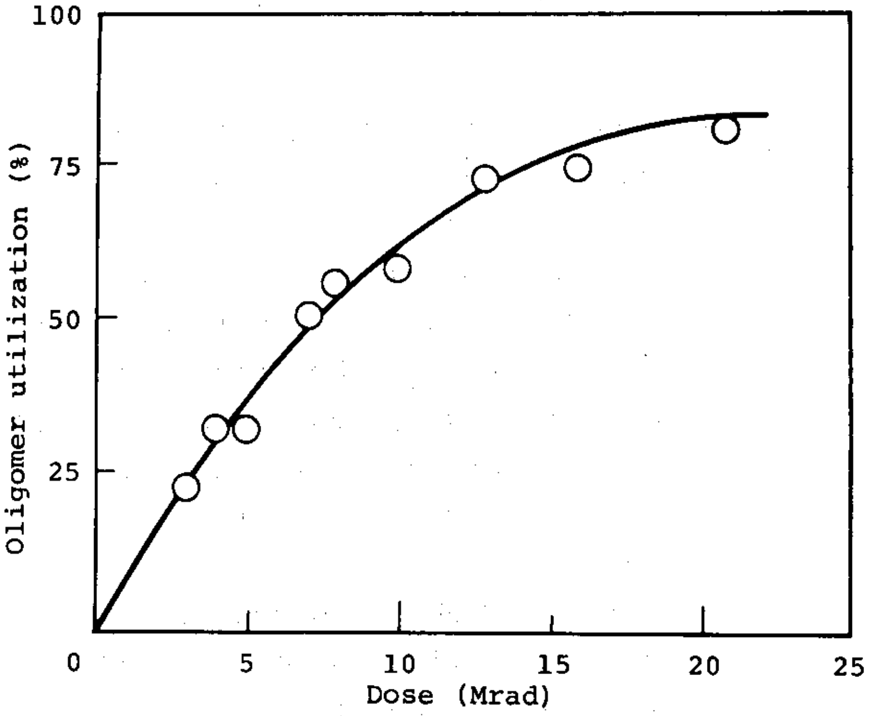


Fig. 2 Grafting of oligomeric vinyl phosphonate onto polyester fabric with electron beams; effect of dose on oligomer utilization.

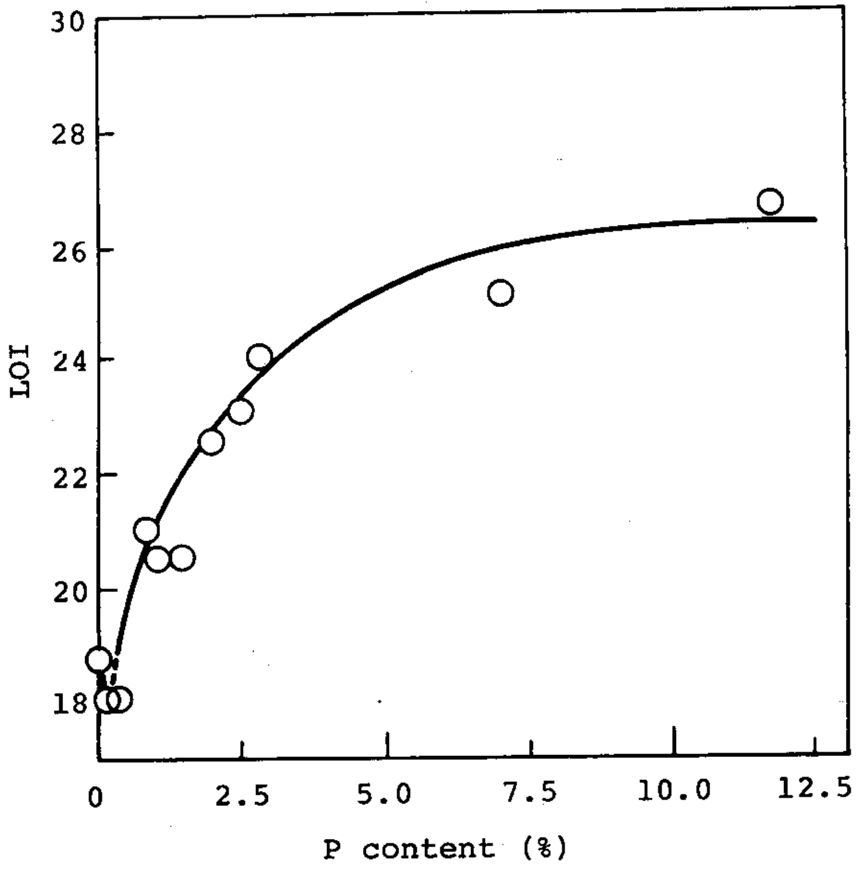


Fig. 3 Effect of phosphorous content on the limiting oxygen index of polyester fabrics.

polymer. In the present report "graft" means only an apparent one and it is very probable that most of the oligomer is deposited on the surface of the fibers as insoluble polymer due to cross-linking. When 25 % methanol solution of the oligomer was used average amount of the oligomer picked up was about 22 %. Fig. 1 and Fig. 2 show the percent graft and oligomer utilization, respectively, as a function of dose. As seen in the figures the percent graft increases gradually to attain 18 % at 21 Mrad, whereas the utilization of the oligomer is about 80 %.

Flame retardance of the fabric is much improved by the grafting. As shown in Fig. 3 limiting oxygen index (LOI) increases from 18.5 of the original fabric to 26 of the fabric containing 12 % phosphorous. The fabric of 10 % graft (phosphorous content, 3 %) was exposed to open flame for 2 seconds.

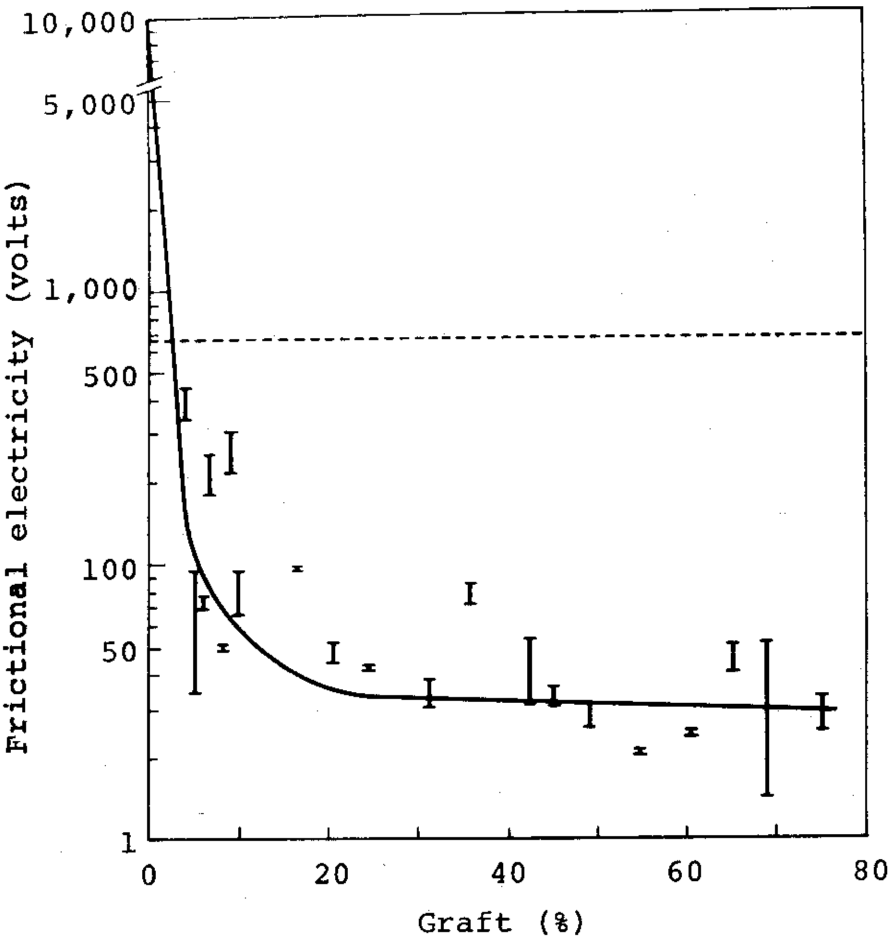


Fig. 4 Frictional electricity of polyester fabric grafted with vinyl phosphonate at 22°C, 55 % RH.

Although the fabric was ignited, the fire was extinguished immediately after the flame was removed. It shows that flame-retardance is obtained at LOI of 23.

The fabric was also found to be improved in its hydrophilicity by the grafting. The results of frictional electricity measurements are shown in Fig. 4.

At above 3 % graft the electric static charge dropped to the same level as that of cotton fabric. This effect is caused by the presence of hydrophilic $-CH_2CH_2OH$ groups in the oligomer. Thermal stability of the graft fabric tested by thermogravimetric analysis shows that it is far better than the chlorinated fabrics. (T. Okada, K. Kaji)

2. Flame Retardance of Poly(vinyl chloride) Fibers Grafted with Various Monomers

Flame retardance of poly(vinyl chloride) (PVC) fibers is excellent among many common synthetic fibers, but it has a serious disadvantage that the softening temperature is low and begins to show a remarkable shrinkage at about 70°C.

We have carried out grafting of various monomers such as acrylonitrile, acrylic acid, calcium acrylate and acrylamide for the purpose of modifying properties without loss of the flame-retardance of the original fibers. Method of preparation of the graft fibers and some of their properties have also been reported.

In the present studies evaluation of their flammability is carried out by determining the limiting oxygen index [LOI] of the graft PVC fibers. LOI means the minimum fraction of oxygen in the test atmosphere which will just support a flame

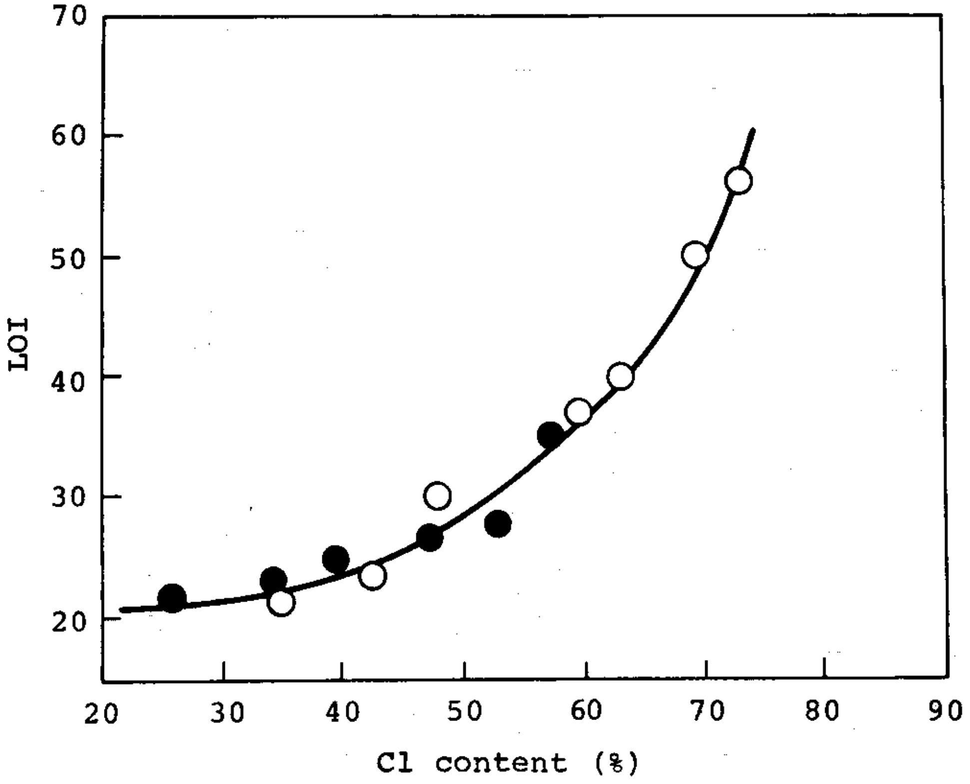


Fig. 1 Relationship between limiting oxygen index and chlorine content of graft fibers; (o) AN graft PVDC; (●) AN graft PVC.

of the material tested.

At first flammability of acrylonitrile(AN) graft PVC fiber is examined. For comparison flammability tests are carried out also on AN graft polyvinylidene chloride(PVDC) fiber. Polyacrylonitrile is an easily combustible polymer whose LOI is 16.5. Fig. 1 shows LOI as a function of chlorine content of AN graft-PVC and PVDC fibers. All points lie on a single curve, showing that these AN graft fibers from both PVC and PVDC loose their self-extinguishing property at about 42 % chlorine content which corresponds to LOI of 23. Fig. 2 shows the plots of the reciprocals of LOI against chlorine content of AN graft-PVC fibers. As may be seen from Fig. 2 all experimental points lie on a straight line. LOI extrapolated to zero chlorine content is 15 which is close to the observed LOI of PAN.

According to P.R.Johnson$^{1)}$, various synthetic and natural polymers, covering a wide range of flammability and chemical compositions, fall sufficiently close to a straight line,

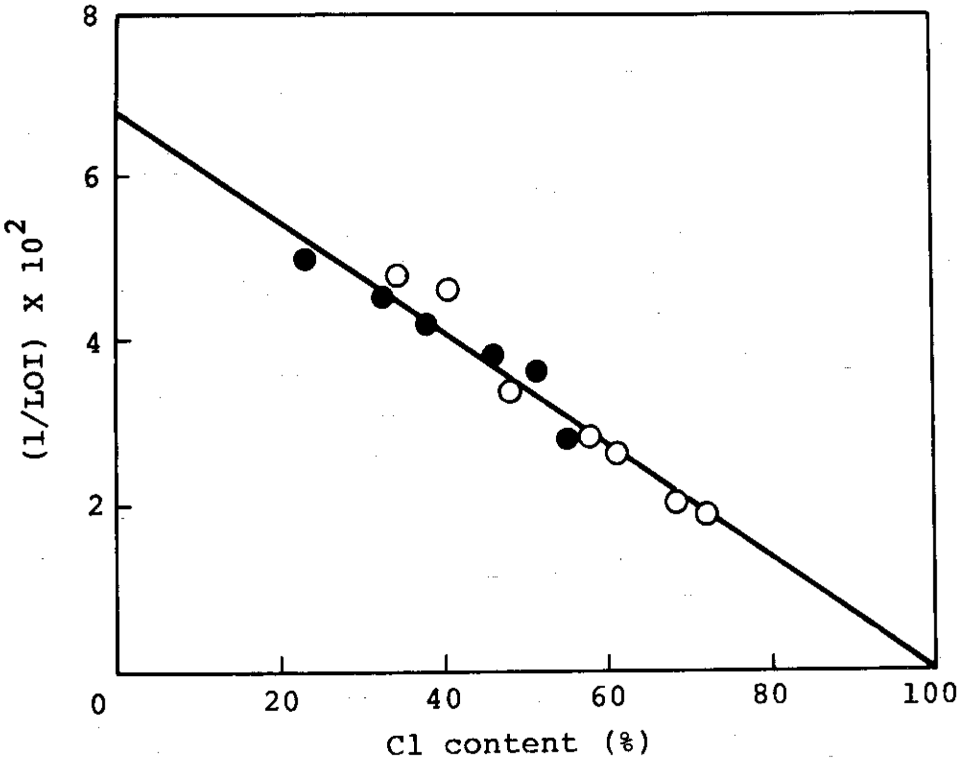


Fig. 2 Correlation of reciprocal of limiting oxygen index with chlorine content for graft fibers; (o) AN graft PVDC; (•) AN graft PV

which shows that the specific heat of combustion of solid materials and their LOI are fundamentally related.

Calculation of the specific heat of combustion for graft fiber having different degrees of grafting is done assuming that there is a proportional relationship between the content of AN and the specific heat of combustion of the graft fiber. The specific heat of combustions are plotted against the reciprocal of LOI for AN graft-PVC and PVDC fibers as shown in Fig. 3.

The figure shows clearly that in this case also the flammability is closely related to the heat of combustion of the graft polymers.

Flammability of acrylic acid, calcium acrylate and sodium acrylate graft fibers are shown in Table 1. All the graft fibers examined are self-extinguishing. LOI of PVC fiber changes only a little by the grafting; between 34 - 35 % graft, LOI 38 of the original fiber drops to 36. It is noteworthy that polyacrylic acid is self-extinguishing, its LOI being 24,

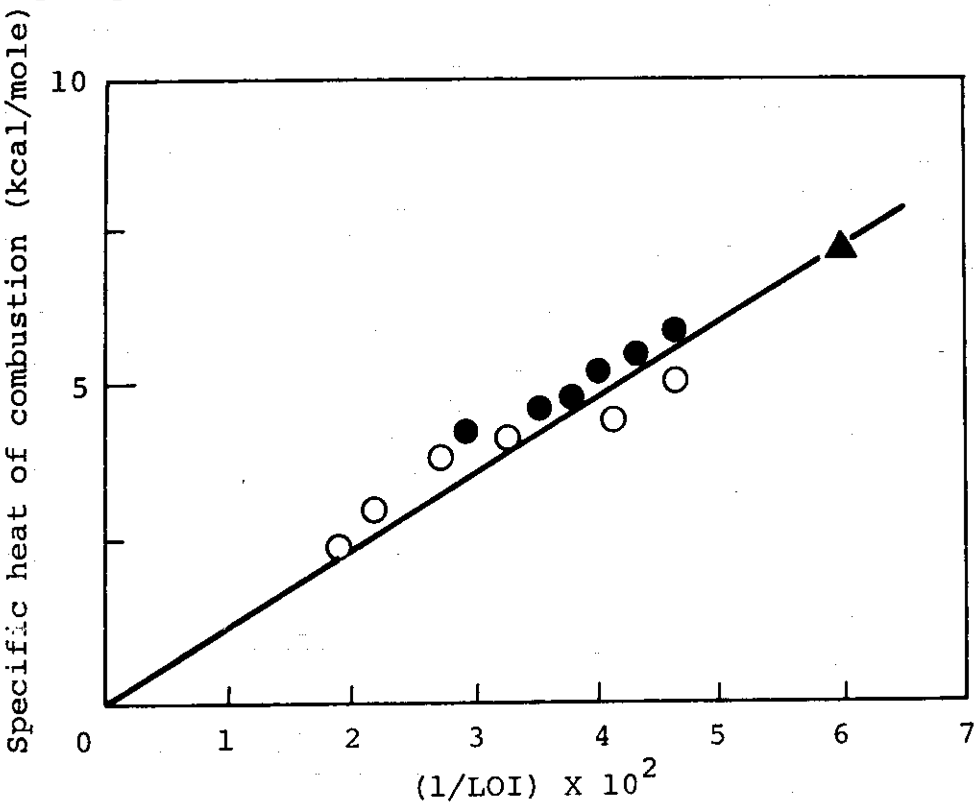


Fig. 3 Correlation of specific heat of combustion with reciprocal of LOI for graft fibers; (o) AN graft PVDC; (●) AN graft PVC; (▲) PAN.

Table 1. Flame Retardance of AA, AA-Ca, and AA-Na Graft PVC Fibers

Sample	Graft, %	Cl Content, %	Flame Retardance	LOI
Original PVC	0	56.8	S.E.*	38
PVC-AA	11.7	50.9	S.E.	—
	34.2	42.3	S.E.	36
	53.8	36.9	S.E.	—
	70.2	33.4	S.E.	—
	112.4	26.7	S.E.	—
PVC-Ca	34.7	42.1	S.E.	37
PVC-Na	35.1	42.0	S.E.	37
PAA	—	0	S.E.	24

* Self-extinguishing

hence even PVC fiber with about 110 % graft of acrylic acid is self-extinguishing.

Results of flammability tests of acrylamide graft fibers are shown in Table 2. Since polyacrylamide is self-extinguishing the graft fibers up to 51.0 % graft is also self-extinguishing. It is interesting that though LOI of polyacrylamide is higher than PVC fiber, LOI of

Table 2. Flame Retardance of AAm Graft PVC Fiber

Sample	Graft, %	Flame Retardance	LOI
Original PVC	0	S.E.*	38.5
PVC-AAm	6.2	S.E.	—
	14.0	S.E.	35.0
	36.8	S.E.	33.5
	51.0	S.E.	31.5
PAAm	—	S.E.	39.5

* Self-extinguishing

graft fiber decreases with increasing degree of grafting of acrylamide. (I. Sakurada, T. Okada, K. Kaji)

1) P. R. Johnson, Appl. Polym. Sci., 18, 491 (1974).

3. Radiation Effect on Wholly Aromatic Polyamides

Radiation effects on polyamide were the object of some investigations, but most studies were limited to aliphatic polyamides and little systematic studies reported on wholly aromatic polyamides.

We have studied radiation effects on poly-p-phenylene terephthalamide (p-PTA) and poly-m-phenylene isophthalamide (m-PIA) by use of γ-rays and electron beams. These polyamides, which attract much attention as fibers of high performance, are expected to be stable against radiation, since the polymers contain phenyl rings in the main chain. However, wholly aromatic polyamides are known to be rather unstable to ultraviolet radiations.

Fibers employed for the experiments were Kevlar (filaments, 1.5d) of Du Pont Co. as p-PTA and Conex (staple fiber, 2d) of Teijin Co. as m-PIA. The fibers were irradiated up to 1000 Mrad either with γ-rays from a ^{60}Co source (2.8 X 10^5 rad/hr) or with electron beams from a VdG accelerator (3.5 X 10^5 rad/sec) at room temperature.

Tables 1 and 2 show the effect of radiation dose on the mechanical properties of p-PTA and m-PIA, respectively. Only very small decrease in the mechanical properties was observed for both types of fibers even in the case of irradiation in air. Since irradiation of only 10 Mrad was required for nylon 6 to decrease its tenacity to 80 % of the original value, it is clear that the wholly aromatic polyamides are far more stable to radiation than aliphatic polyamides. The results indicate also that the presence of air favors the degradation of wholly aromatic polyamides as in the case of aliphatic polyamides, although a much larger irradiation dose is needed in the case of the former than the latter to show the same

Table 1. Effect of Radiation Dose on Mechanical Properties of Poly-p-Phenylene Terephthalamide

	Dose (Mrad)	Tenacity (g/d)	Retention of Tenacity (%)	Elongation (%)	Retention of Elongation (%)
^{60}Co γ-Rays (in Vacuo)	0	26.9	100	6.3	100
	15	27.4	102	7.1	113
	500	27.3	101	6.6	105
	1000	28.4	106	7.0	111
^{60}Co γ-Rays (in Air)	15	28.6	106	6.8	108
	500	24.7	92	6.5	103
	1000	21.5	80	5.5	87
VdG Electrons (in Air)	15	29.2	109	6.9	110
	500	27.3	101	6.5	103
	1000	25.3	94	5.6	89

Table 2. Effect of Radiation Dose on Mechanical Properties of Poly-m-Phenylene Isophthalamide

	Dose (Mrad)	Tenacity (g/d)	Retention of Tenacity (%)	Elongation (%)	Retention of Elongation (%)
^{60}Co γ-Rays (in Vacuo)	0	4.9	100	31	100
	8	5.5	111	35	113
	487	4.9	100	29	94
	1000	5.7	116	29	94
^{60}Co γ-Rays (in Air)	8	4.9	100	30	98
	487	4.8	97	24	77
	1000	4.4	90	22	71
VdG Electrons (in Air)	15	5.1	104	30	97
	500	4.4	90	18	58
	1000	4.0	82	16	52

drop of mechanical properties by the irradiation.

When the two types of fibers were irradiated up to 1000 Mrad with electron beams in air, the tenacities of p-PTA and m-PIA were 94 % and 82 %, respectively, of the original fibers showing that p-PTA was more stable to irradiation than m-PIA.

Viscometric studies were carried out on the irradiated fibers in 95 % sulfuric acid. Only a small change in viscosities of p-PTA was found even after irradiation both in the presence and absence of air up to a large dose, whereas gel was formed in m-PIA, particularly after γ-ray irradiation of about 200 Mrad in vacuum.

No or a very small change in TGA curves for p-PTA and m-PIA was observed even after the irradiation of 1000 Mrad, showing that the irradiation at room temperature had no appreciable effect on the thermal degradation properties of these polymers. (K. Kaji, T. Okada, I. Sakurada)

4. ESR Studies of Radicals Produced in Wholly Aromatic Polyamides

As described in a preceding report, evidence has been obtained for crosslinking and degradation of wholly aromatic polyamides, poly-p-phenylene terephthalamide (p-PTA) and poly-m-phenylene isophthalamide (m-PIA), to occur when the polyamides subjected to large doses of ionizing radiation. The present study is carried out in an attempt to investigate the mechanism for the crosslinking and degradation by studying radicals produced by γ-irradiation or mechanical rupture.

γ-Irradiation of p-PTA fibers in vacuo at room temperature predominantly yields a singlet ESR spectrum at $g = 2.003$ with the linewidth (ΔH_{msl}) of ca. 17 G. p-PTA irradiated at low temperature and warmed to room temperature shows the identical spectrum. The similar spectrum is obtained from p-PTA sliver after cutting with scissors in liquid nitrogen or in air at room temperature. m-PIA after γ-irradiation in vacuo at room temperature, on the other hand, shows a singlet spectrum having shoulders on both wings. On warming the irradiated m-PIA to 108 °C, the spectrum changes to another singlet spectrum with $\Delta H_{msl} = 8$ G. Cutting of m-PIA fibers either at 77 °K or at room temperature gives the similar spectrum.

Attempts are made to identify the singlet spectra for irradiated p-PTA and m-PIA by studying ESR spectra of four model compounds of the aromatic polyamides after γ-irradiation and by the spin trapping technique.

Benzoic acid, isophthalic acid, and benzamide irradiated at room-temperature give ESR spectra due to cyclohexadienyl-type radicals formed by H atom addition to the benzene ring. The same type of radicals is found to form in the irradiated polyamides, but it cannot explain the observed singlet spectra. γ-Irradiated benzanilide shows a singlet with $\Delta H_{msl} = 8$ G, identical with the spectrum from m-PIA.

Phenyl-t-butylnitron(PBN) is used as a spin trap for our spin trapping experiment. The aromatic polyamides irradiated or mechanically ruptured are immersed into a benzene solution of PBN followed by degassing, and subjected to ESR measurement. For comparison, ESR spectrum is obtained for irradiated benzanilide after dissolving in a benzene solution of PBN.

The spectrum for benzanilide is a sextet with the hyperfine splitting values of $a_N = 14.5$ G and $a_N = 2.3$ G. These values lead us to assign the radical formed in benzanilide to the phenyl-type of radical produced either by C-C(=0) or C-N bond scission or by removal of H atom from the benzene ring.

The spectra for the aromatic polyamides immersed in a benzene solution of PBN are found to change with time elapsed after immersion. The singlet spectra of the irradiated polyamides disappear gradually and the sextet spectrum same as observed from benzanilide grows in intensity. This fact indicates that the singlet spectra of irradiated p-PTA and m-PIA are due to the phenyl-type radicals.

Finally, G values for the radicals responsible for the singlet spectra are estimated from the radical accumulation curves. The results are 0.5 for p-PTA and 0.4 for m-PIA, which are fairly lower than those for polyamides such as nylon 6, showing high stability to high energy radiation. (S. Nagai, K. Kaji, T. Takagaki, T. Okada, I. Sakurada)

5. Polymer Electret by Electron Irradiation

When polymer materials are irradiated with electron beams from an accelerator the electrons are trapped in a plane perpendicular to the incident beams, hence a negative space charge builds-up in the polymer, resulting in forming an electret. We studied the build-up and decay of electric charges in polymer films. Various types of polymers, polytetrafluoroethylene-co-hexafluoropropylene(FEP), polypropylene (PP), polyethylene terephthalate(PET), polyvinyl chloride

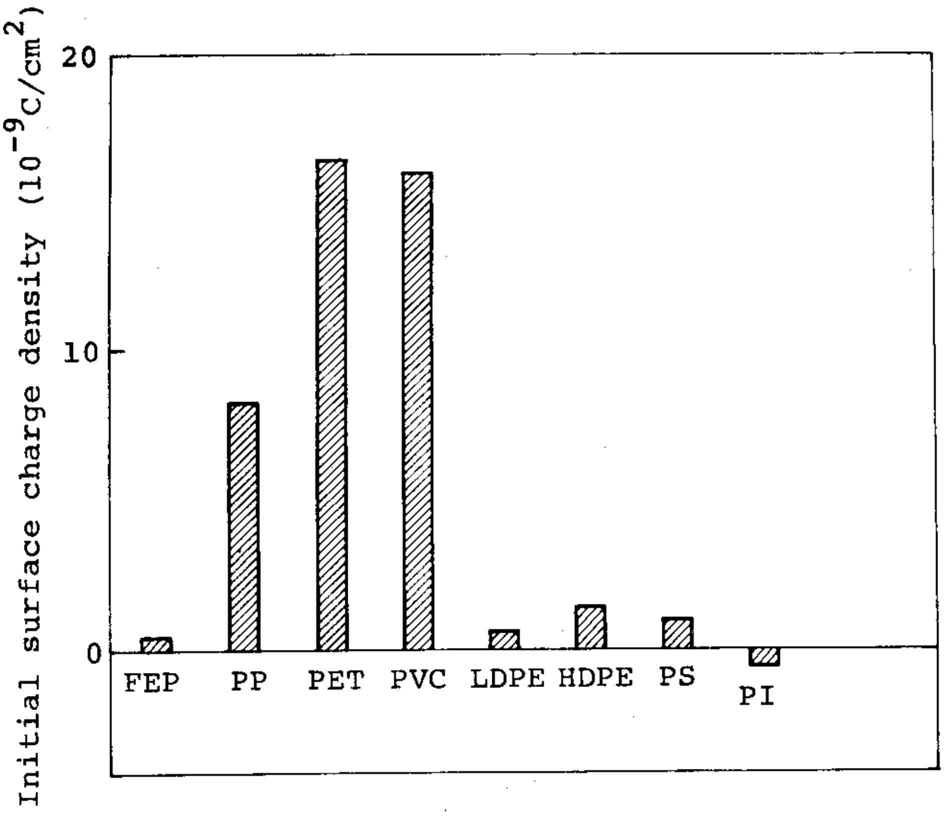


Fig. 1 Initial surface charge density of various polymer film induced by electron beam bomberdment; accelerating voltage, 1.5 MeV; current density, 0.48 μA/cm^2; dose rate, 1.8 X 10^4 rad/sec; dose, 0.05 Mrad.

(PVC), low density polyethylene(LDPE), high density polyethylene(HDPE), polystyrene(PS), and polyimide(PI) were examined in a film of 20 to 50 μ in thickness. Each film was placed on a polymethylmethacrylate(PMMA) plate of 10 mm thickness and irradiated with electron beams from an accelerator. Retained charges in the film were measured by an induction type electrometer.

Fig. 1 shows retained charge in various polymer films as an initial surface charge density. The irradiation was performed to a dose of 0.05 Mrad at an accelerating voltage of 1.5 MeV, a current density of 0.48 μA/cm^2, and a dose rate of 1.8 X 10^4 rad/sec. As is seen from the figure the polymer films are divided into two groups, the high charge density group consisting of PP, PET, and PVC, and low charge density group consisting of FEP, LDPE, HDPE and PI.

Influence of the accelerating voltage, dose rate and

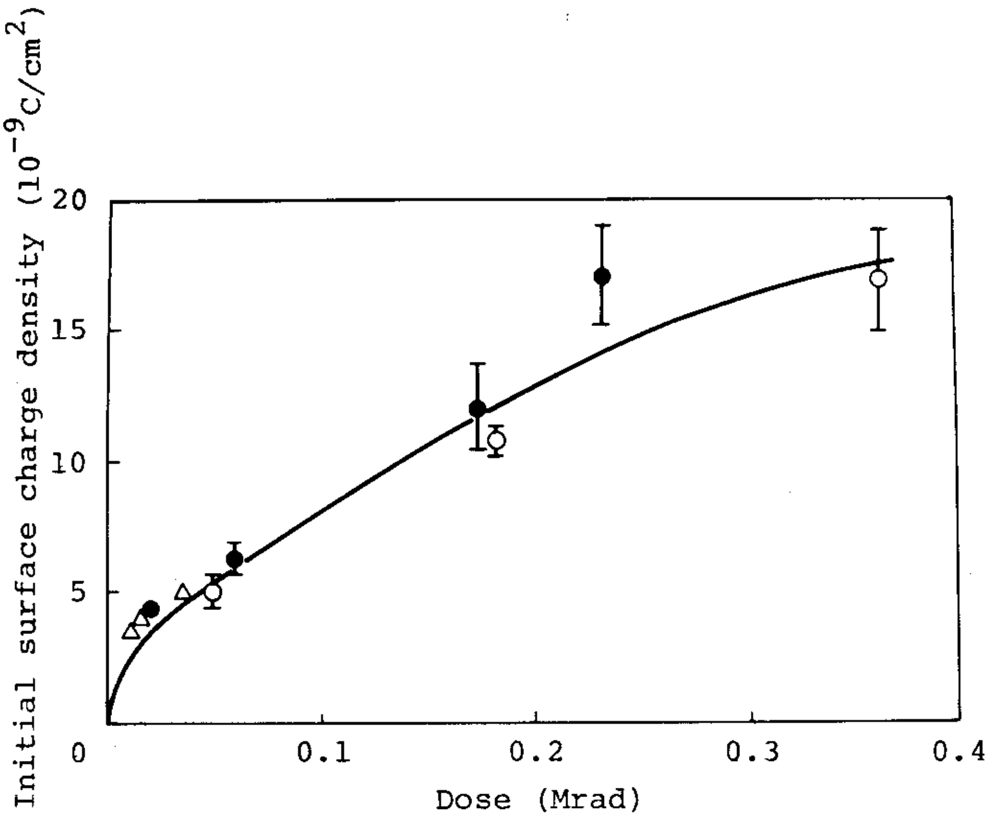


Fig. 2 Effect of irradiation dose on initial surface charge density of polypropylene; (o) accelerating voltage, 1.5 MeV; dose rate 1.8 X 10^4 rad/sec; (Δ) 1.5 MeV, 0.36 X 10^4 rad/sec; (●) 0.8 MeV, 0.58 X 10^4 rad/sec.

irradiation dose on the charge formation of PP film (30 μ thick) was studied. Fig. 2 shows the initial surface charge density against the irradiation dose for different accelerating voltages and dose rates. Although the points are somewhat scattered the relationship between the initial surface charge density and irradiation dose can be represented by a single curve. It is of interest that the retained charge is dependent neither on the accelerating voltage nor on the dose rate, but on irradiation dose of high-energy electron beams.

The retained charge on polypropylene electret is very stable for a long period of time. Typical decay curves of the retained charge of both sides of the film are shown in Fig. 3.

In the preparation of polymer electret electron beam impinges on the polymer film which is in contact with a relatively thick PMMA plate. Without PMMA plate, retained charge of the film is smaller than that with the PMMA plate. To know the role of the PMMA in producing polymer electret, electron irradiation was performed and the measurements of the surface charge were made. The results revealed the

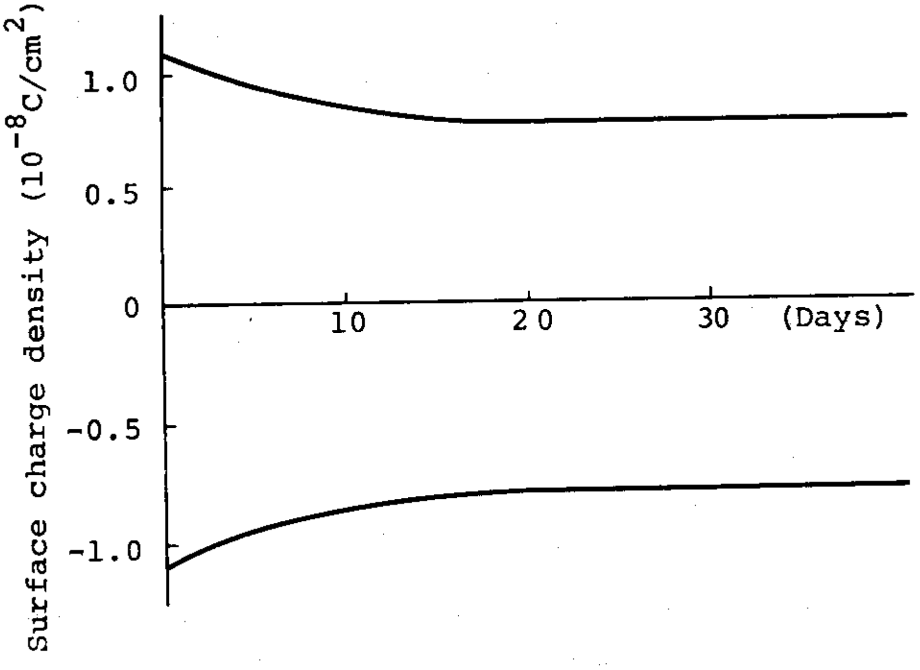


Fig. 3 Decay curve of surface charge density for polypropylene film electret at room temperature.

production of negative charge on the upper side of the plate.

When uncharged PP film is placed on the irradiated PMMA plate the film becomes electrically charged and an electret is formed. These results suggest that an electric charge is injected from PMMA plate to the lower side of the polymer film during and after the electron irradiation.

From the above results it seems that the polymer electret is formed by two different processes. One part of the charge is directly formed by trapping of incident electrons without any recombination of trapped electrons and induced positive charge. Additional charge is transferred from the adjacent PMMA plate in which electrons are trapped, and the charge increases with increasing potential difference between the film and the PMMA plate.

The above electret formation processes are also supported by thermally stimulated discharge(TSD) experiments.

TSD spectra are shown in Fig. 4. Curve A is TSD spectrum of the PP film electret which has been produced by the direct irradiation on the PMMA plate. Curve B is that of PP film electret which has been produced not by direct-irradiation

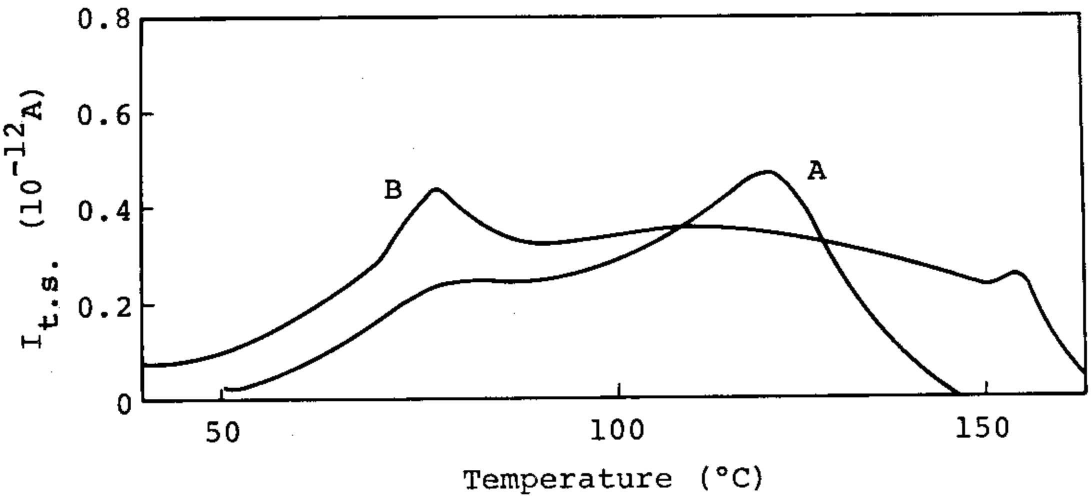


Fig. 4 Thermally stimulated current ($I_{t.s.}$) of polypropylene electret at the heating rate 2°C/min; A, polypropylene film irradiated on PMMA plate; B, PMMA plate is irradiated and then brought into contact with PP film; accelerating voltage, 1.5 MeV; current density 0.48 μA/cm^2; dose rate, 1.8 X 10^4 rad/sec.

by placing the unirradiated PP film on the irradiated PMMA plate. Charges were injected from the irradiated PMMA plate to unirradiated PP film to form an electret. As seen in Fig. 4 each TSD curve has two peaks which appear at different temperatures. In curve A the main peak appears at about 120 °C and a small peak at about 75 °C. On the other hand, in curve B the main peak appears at about 75 °C and a very small peak at about 160 °C. We may tentatively assign the first peak at about 70 °C to the release of the charge which is stored on the surface region of the film and the second peak at higher temperature to the release of the charge which is stored inside of the film. The TSD features are strongly affected by the preparation method of the electret.
(M. Kajimaki, T. Okada)

6. Radiation Deterioration of Insulating Polymer Materials for Electric Power Cables

There is a rather plenty of experimental results available on the radiation deterioration of polymer materials by γ-rays, and we are able to roughly estimate the deterioration of various polymer materials. However, there is a draw back that γ-ray test of material requires a very long time for the irradiation.

Experiments are now carried out to know whether the irradiation of γ-rays and electron beams have their own special effects on the deterioration or not; to know the possibility whether or not the electron beams can be replaced with γ-rays for the irradiation and shorten the time of testing.

Specimens for irradiation are conventional PVC (DP = 1300), PVC for high temperature use (DP = 2500), PVC of low HCℓ*), conventional PE (ρ = 0.925 g/cm^3), cross-linked PE, flame retardant and crosslinked PE, and EP rubber. They are all in the form of sheets having thickness of 1.0 - 1.5 mm.

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*) PVC of low HCℓ evolution on heating

The specimens are irradiated with γ-rays from a ^{60}Co source at the dose rate of 1 X 10^6 rad/hr. The electron beam irradiations are performed using the HDRA (0.8 MeV, 20 mA, scanning width 45 cm, 10.6 Mrad/sec on a conveyer which travels under the irradiation window back and forth at the dose rate of 10 Mrad/pass, and the irradiations are repeated until the required dose is accumulated. After the irradiation, mechanical and electric properties of the samples are measured.

As shown in Fig. 1, the tensile strength of PVC specimens decreases markedly with increasing dose in the case of γ-irradiation, but in the case of electron beam irradiation the change with dose is rather small. The brittle point increased markedly at high dose in the case of γ-irradiation (Fig. 2a), but not so in the case of electron beam irradiation (Fig. 2b). However, the effects of dose on the elongation, volume electric resistance and dielectric constant are the same for the two types of radiations.

Similar tests are made for PE and EP rubber specimens, and a part of the results are given in Fig. 3a and b. The

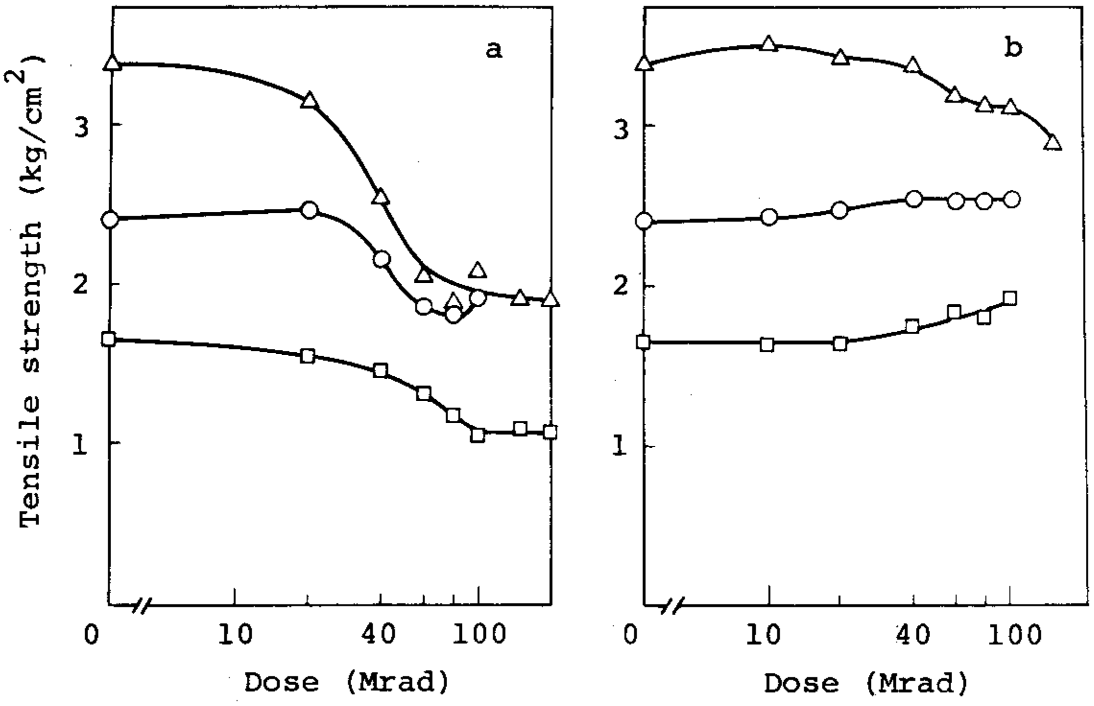


Fig. 1 Tensile strength of PVC specimens as a function of dose; a, γ-ray irradiation and b, electron beam irradiation; (o), PVC; (Δ) PVC for high temperature use; (□) PVC of low HCℓ.

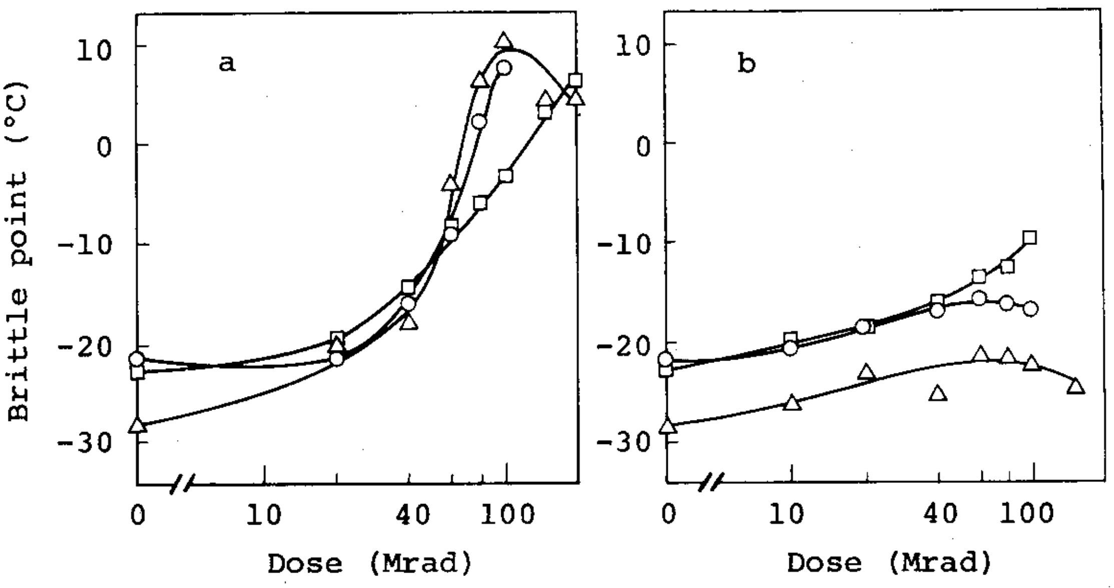


Fig. 2 Brittle point of PVC specimens as a function of dose; a, γ-ray irradiation and b, electron beam irradiation: (o), PVC; (Δ), PVC for high temperature use; (□), PVC of low HCℓ.

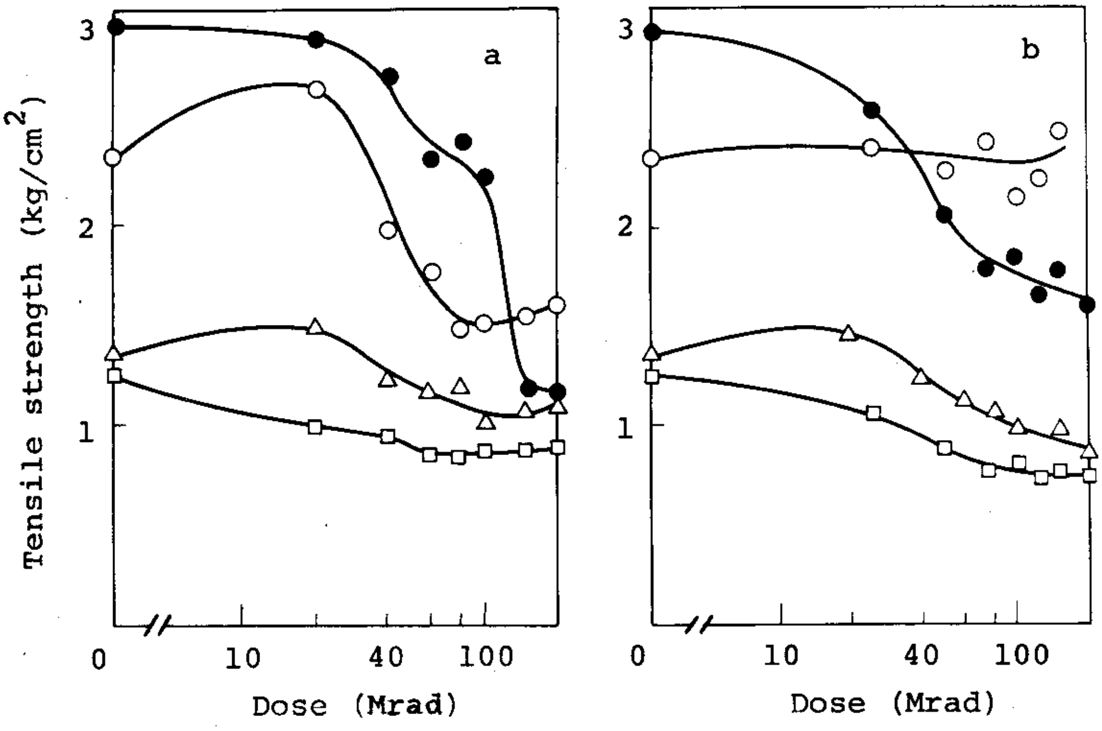


Fig. 3 Tensile strength of PE and EP rubber specimens as a function of dose; a, γ-ray irradiation and b, electron beam irradiation; (o), PE; (●) cross-linked PE; (Δ), flame retardant PE; and (□), EP rubber.

results on PE specimens indicate that a little more deterioration of the properties takes place in the case of γ-ray irradiation than in the case of electron beam irradiation.

The difference between the effects of the two types of radiations on the properties of insulating materials may be regarded to be due to the competition of radiation chemical reaction and diffusion of atmospheric oxygen into polymers. In order to prove this, the infrared spectra of the surface are successively measured using ATR technique, the thin surface layer (10 μ) of the irradiated specimen being successively scraped off for the new measurements. The spectra are shown in Fig. 4a and b, comparatively, for specimens irradiated with γ-rays and with electron beams. For the spectra of the latter the band due to carbonyl group disappears at 10 μ below the original surface, but the band can

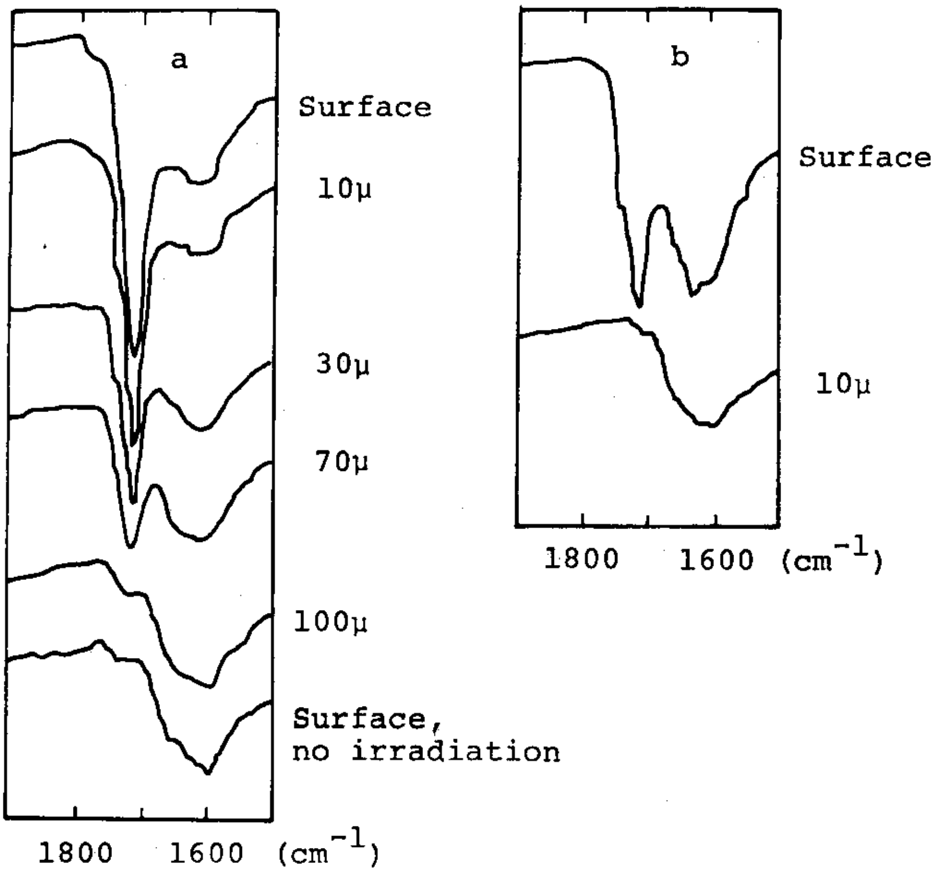


Fig. 4 Infrared spectra of irradiated PE as a function of depth from the surface; a, γ-ray irradiation and b, electron beam irradiation; the distances from the surface are given in the figure.

be still observed even at 100 μ below the original surface for the spectra of the former. This clearly indicates that the diffusion rate of oxygen can not compete with the high rate of oxygen consumption in the case of electron beam irradiation where little oxidative reaction takes place leading to little deterioration of the specimens.

Deteriorations of the properties are examined when the specimens are exposed to heat and radiation simultaneously. There is little difference between the degrees of deterioration caused by the radiations of the two types and heat, but the degrees of deterioration derived by combined effects of radiation and heat are larger when compared with those observed by radiation effect alone.

The conclusion derived from the results obtained in the present examination is that for the deterioration test of some properties which show similar deterioration behaviors by the radiations of the two types, it is possible to replace γ-ray with electron beam to save time required for the irradiation of high dose. (M. Gotoda, T. Yagi, H. Todoroki, Y. Honda)

7. Wettability of Hydrogels

Hydrogels have been reported to be promising as biomedical material because of their good biocompatibility. Since the surface characteristics would have a decisive effect on the biocompatibility, we have measured contact angles of various hydrogels against water to evaluate their water wettability. The polymers selected for the hydrogels are polyvinyl alcohol(PVA), polyacrylamide(PAAm), polyvinyl pyrrolidone(PVP), polyethylene oxide(PEO) and dextran. The hydrogels were prepared by electron-beam irradiation of concentrated aqueous solutions of the polymers placed between two glass plates. The soluble part was removed from the crosslinked hydrogels by extraction with water. Irradiation with different doses allowed us to obtain the hydrogels with a wide range of water content. Details of the hydrogel preparation were described elsewhere.

The contact angle was determined for the hydrogel films with equilibrium water content at room temperature by the sessile droplet method. The diameter of water droplet is about 2 mm and the angle was read 1 min after deposition of the droplet on the gel surface. To prevent the gel films from drying, a cotton whool absorbed with water was placed near the film in a cuvette.

The contact angles are plotted as a function of the water content of the hydrogels in Fig. 1. The result for a polyhydroxyethyl methacrylate(PHEMA) gel is also given for comparison. It is clearly seen that water does not spread on the hydrogels spontaneously and that for all the hydrogels the contact angles are independent of the water content in the range investigated. We could not determine the contact angle for the hydrogels having water content higher than 0.96, because their mechanical strength was very low and it was difficult to blot the excess water from their gel surface. Another interesting feature seen in Fig. 1 is that the contact angle varies considerably with the nature of the

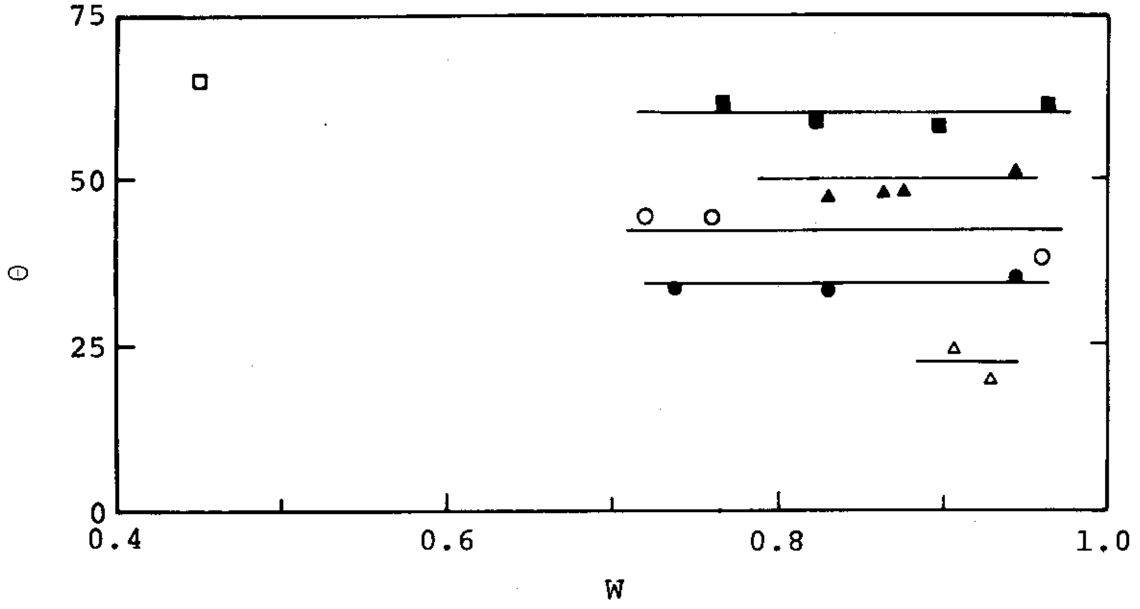


Fig. 1 Contact angles (θ) of radiation-crosslinked hydrogel membranes as a function of water content; (o) PVA; (●) PAAm; (■) PVP; (▲) PEO; (Δ) dextran; (□) PHMA.

polymers forming the matrix of the hydrogels, though the polymers are all water-soluble when not crosslinked; PVP exhibits the highest contact angle and dextran the lowest. The reason for this large difference is not clear, but we can point out a trend that the polymers which are soluble in water as well as organic solvents like chloroform(PVP and PEO) have higher contact angles, in other words, are more hydrophobic than those which are soluble only in water (dextran and PAAm).

Fig. 2 shows the contact angles of the hydrogels containing no chemical crosslinkage but crystalline parts which act as crosslinkage. The contact angle of water-swollen PVA films is the same as that of the chemically crosslinked gels. Cellulose gels have the contact angle as low as the crosslinked dextran. This suggests that the contact angle of carbohydrate polymers is generally low compared with that of water-soluble vinyl polymers. The rigid pyranose ring might be responsible for the low contact angle. It is likely that the main-chain of vinyl polymers $\left(CH_2-\underset{|}{C}H \right)_n$ is relatively mobile in the hydrogel phase with high water content and

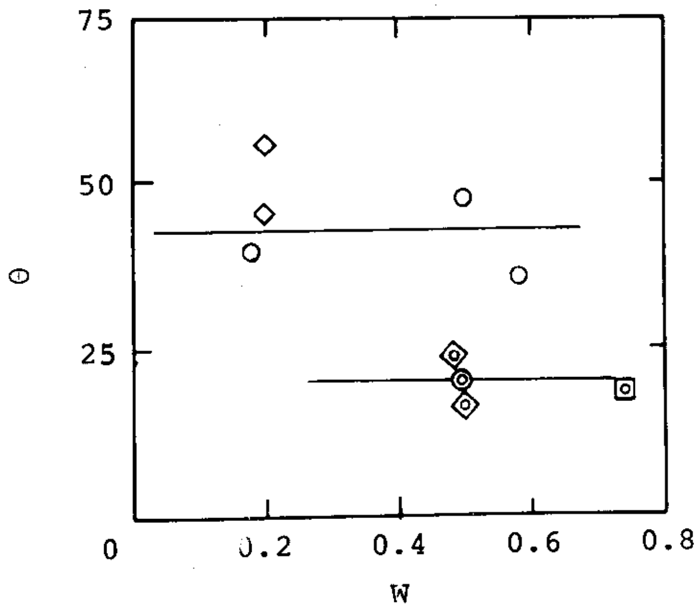


Fig. 2 Contact angles (θ) of water-swollen PVA and cellulosic films as a function of water content; (o) PVA; (◎) cuprophan; (◈) cellophane for dialysis; (⊡) gel cellophane; (◇) DAS.

hence would be able to locate at the interface between the hydrogel and the air phase, leading to decrease in interfacial free energy, i.e., to increase in the contact angle against water. On the contrary it is impossible for all the hydroxyl groups in the carbohydrate molecule to orient towards the inside of the hydrogel, since the hydroxyl groups are bonded to the rigid ring. This would result in the low contact angle. (Y. Ikada and T. Mita)

[5] Electron Beam Curing

1. Radiation Curing of Chlorinated Polymer/Vinyl Monomer Mixtures by High Dose Rate Electron Beams

This is a continuation of the study of the previous year on the radiation curing of chlorinated polymer(Cl-polymer)/ vinyl monomer mixtures. In the previous experiments, the irradiation was carried out at a fixed dose rate, say, 1 Mrad/sec and a fixed conveyer speed; the irradiation was repeated up to a required total dose. Such a technique is unpractical. Therefore in the present study the dose to be delivered to the specimens is given by just an one way travel under irradiation window on a conveyer, the dose to be given to the specimen being varied by changing the travelling speed of the conveyer which carries the specimen.

The Cl-polymers used are chlorinated polypropylene (Adekaplene CP-100, abbreviated as Cl-PP) and chlorinated rubber (CR-5) both supplied by Asahi Denka Co. Butyl acrylate (BA) is used as a vinyl monomer, and tetraethyleneglycol diacrylate (TEGDA) or oligoester acrylate having functional groups (Alonix M-8030) is used as a crosslinking agent.

The Cl-polymer/BA mixture (50/50 by weight) contained in a rectangular aluminum vessel with a polyester film (0.1 mm thick) is irradiated with electron beams from an HDRA or a VdG accelerator on a conveyer which travels under the irradiation window at different travelling speed. Examples of the irradiation conditions and corresponding doses absorbed by the specimens are given in Table 1. The method of determining the extent of curing is the same as that in the previous1).

The results of the electron beam curing for the CR/BA and Cl-PP/BA mixtures are shown in Fig. 1a and b, respectively. Unlike the results obtained in the previous year, little gel fraction is formed by the present method of irradiation at any dose rate investigated.

Table 1. Irradiation Conditions and Dose Rates

Accelerator	Acc.Volt.	Beam Curr.	Dose Rate	Conveyer speed	Dose received by specimen per pass
	(MeV)	(mA)	(Mrad/sec)	(m/sec)	(Mrad/Pass)
VdG	1.5	0.1	0.7	0.12	8
				0.48	2
HDRA	0.8	9.4	5.0	2.8	14
				14.0	2
		25.0	13.3	7.5	10
				37.0	2

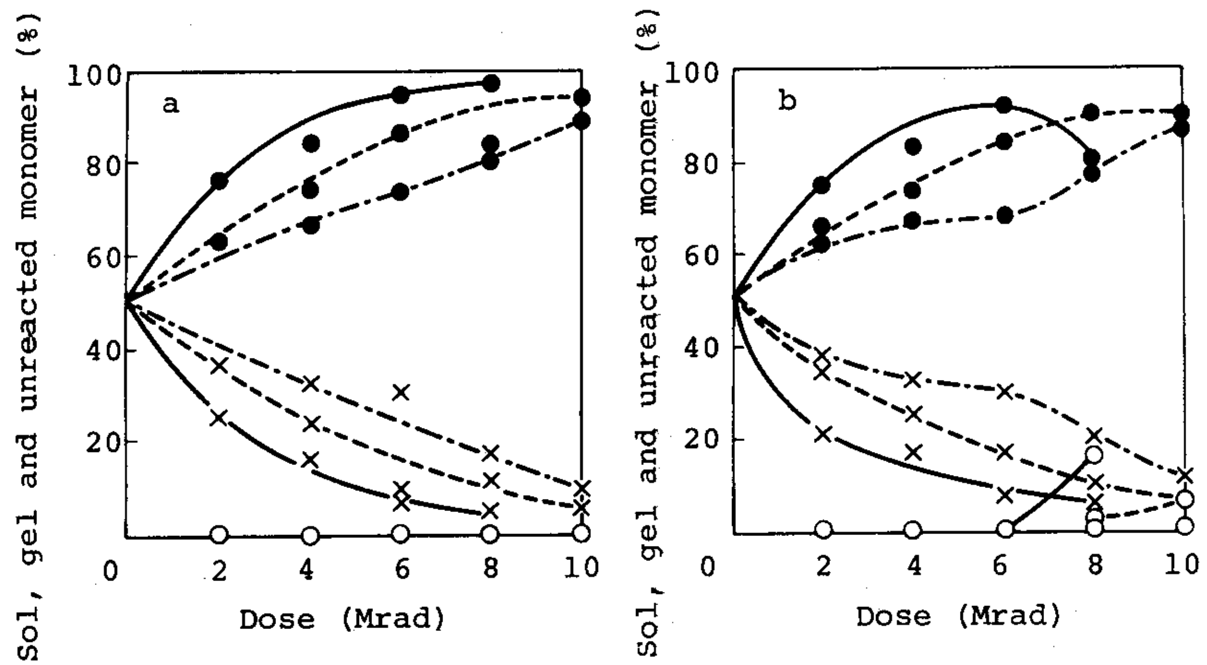


Fig. 1 Electron beam curing of Cl-polymer/vinyl monomer mixtures; a, CR/BA (50/50) and b, Cl-PP/BA (50/50); dose rates in Mrad/sec; (——) 0.7; (---) 50; (-·-) 13.3; (•) sol fraction; (o) gel fraction; (x) fraction of unreacted monomer.

Fig. 2a and b show the results obtained for the Cl-PP/BA mixtures containing Alonix M-8030 and TEGDA, respectively. As obvious from the figures, gel formation is found to pro-

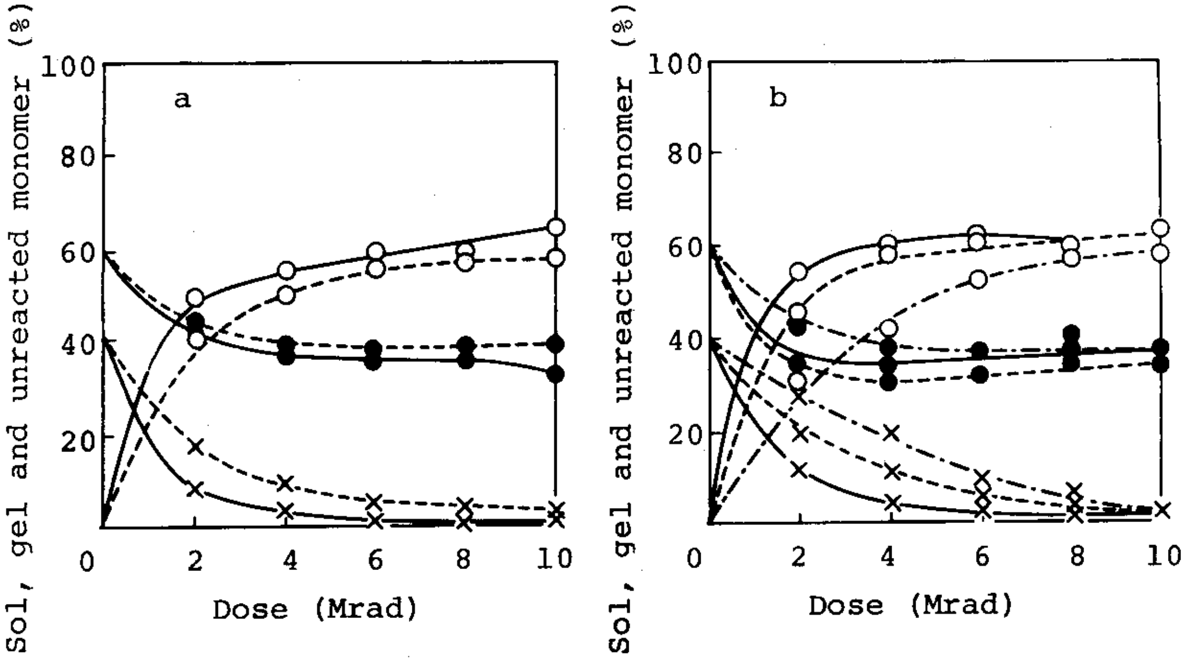


Fig. 2 Electron beam curing of Cl-polymer/vinyl monomer mixtures; a, Cl-PP/BA/Alonix (50/40/10) and b, Cl-PP/BA/TEGDA (50/40/10); dose rate in Mrad; (——) 0.7; (---) 5.0; (-·-) 13.3; (●) sol fraction; (o) gel fraction; (x) fraction of unreacted monomer.

ceed by the presence of the cross-linking agents, and over 60 % gel is formed by 10 Mrad irradiation. The product is colored by the curing.

As reported in the previous report[1]) an addition of phenyl glycidyl ether successfully prevents coloration. We further investigate the effect of other stabilizers such as (A) epoxides, (B) carboxylic acids (citric acid), and (C) polyesters, which are conventionally used as a stabilizer of chlorinated rubber. The Cl-polymer/BA/TEGDA (50/40/10) mixture containing one of these stabilizers (3 %) is painted on a mild steel panel and cured with electron beam irradiation (13.3 Mrad/sec, 8 Mrad). No coloration of the cured resin is observed after 24 hrs either at room temperature or at 50 °C. The CR-5/BA/Alonix M-8030 (50/40/10) mixture containing 3 % epoxy stabilizer is painted on a wood panel precoated with oil stain and cured by electron beam irradiation (13.3

Mrad/sec, 8 Mrad). The accelerated weathering test indicates its successful availability for the interior in that no change of color is seen up to a testing time of 200 hr. (M. Gotoda, T. Yagi)

1) M. Gotoda and T. Yagi, JAERI-M, 6702, 69 (1976).

2. Curing of Epoxy Compounds by Ionic Polymerization

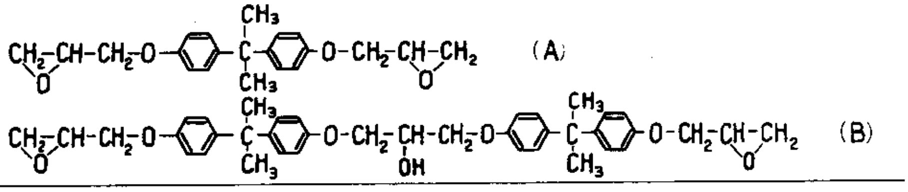
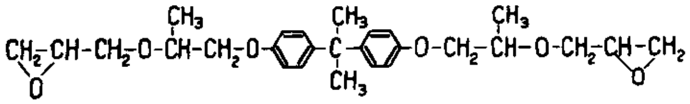
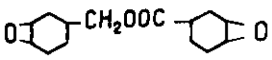
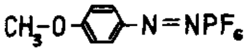
The curing of epoxide resins with Lewis acid catalysts generated photochemically from diazonium salts has been developed recently, but the application of this method of ionic polymerization is limited to thin films below 1 mil thickness, because nitrogen bubbles are formed by the decomposition of the diazonium salts. This is the reason why the practical application of this type of ionic polymerization is limited only as a printing technique. Investigation on this problem reveals that these bubbles remain in the resins because the surface layers are so rapidly cured by UV radiation that N_2 gas can not escape from the resin. Since electron beams penetrate deeper in the medium than UV, use of electron beam curing on this system is expected to solve this problem.

Another advantage of the application of electron beam curing on this system containing diazonium salts is that ionic polymerization does not require inert gas atmosphere which is necessary for the curing of acrylate which proceeds with radical mechanism.

Diepoxides and catalysts used in the present examination are supplied from Asahi Denka Co., and are listed in Table 1.

An aluminum frame (10 X 50 mm, 1 mm thick) is filled with resin containing catalyst, and the specimens are irradiated with electron beams from the VdG electron accelerator (1.5 MeV, 50 - 100 μA, 0.18 - 0.70 Mrad/sec) and from the HDRA (0.8 MeV, 9.4 - 25 mA, 5 - 13.3 Mrad/sec). Irradiation at low dose rate are carried out using ^{60}Co γ-ray source (3.6 X 10^{-5} rad/sec).

Table 1. Diepoxides and Catalyst

Epoxide notation	Chemical structure
EP-4100	Mixture of A and B (A / B = 9) 
EP-4000	
CY-179	
Catalyst	

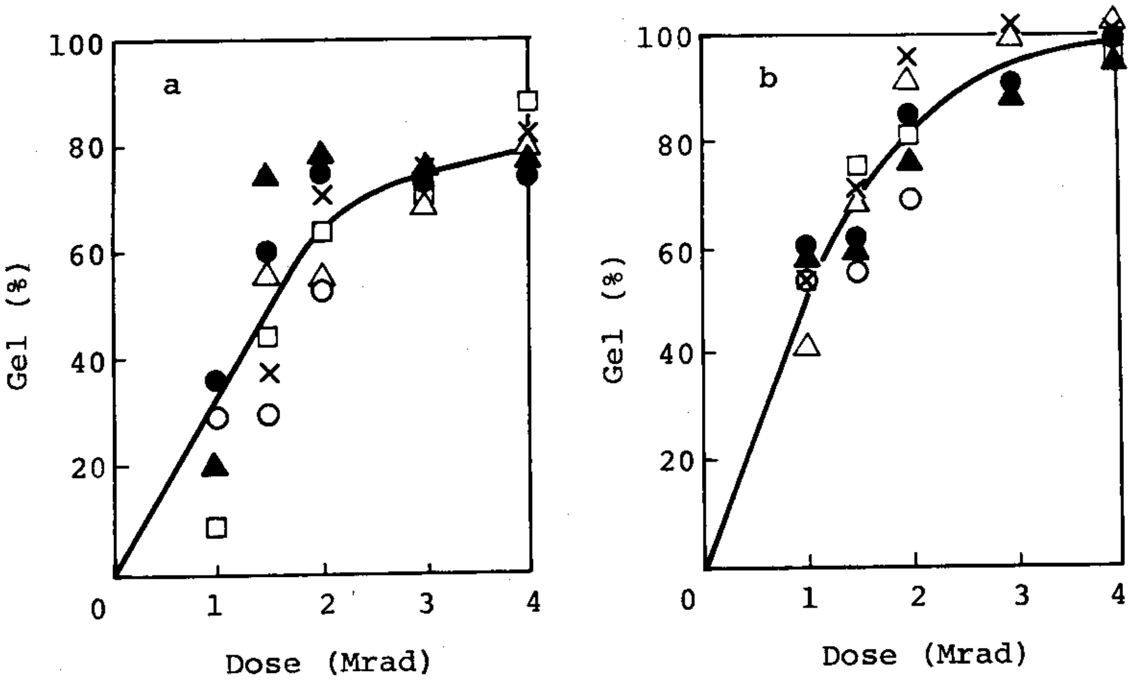


Fig. 1 Electron beam curing of diepoxides at different dose rates; a, CY-179; b, EP-4100; dose rates in rad/sec; (□) 3.6 X 10^{-5}; (△) 0.70; (o) 0.18; (●) 5.0; (x) 0.35; and (▲) 0.33.

The gel percent of the irradiated sample is determined by weight decrease of the sample before and after Soxhlet extraction with acetone.

The results thus obtained by the irradiation of CY-179 and EP 4100, each containing 3% catalyst at different dose rates are shown in Fig. 1a and b, respectively. Little dose rate dependence on gel formation is found for both epoxide resins. The appearance of the cured resins, however, depends on the dose rate employed; more cracks and bubbles are formed when the irradiations are carried out at high dose rates.

The irradiations are carried out at low temperatures such as 25 °C and 0 °C. The results are given in Fig. 2a and b for EP 4100 and CY-179, respectively. It is obvious from the figures that the cured resins are obtained more effectively when the irradiations are carried out at lower temperature; for CY-179, gel percent (80 %) which is obtained by 4 Mrad irradiation at 26 ° C increases to 100 % at 0 °C, and EP-4000 which gives 50 % gel percent at the same dose at 26 °C gives 90 % gel percent when the irradiation is carried out at 0 °C.

The effects of additives on the curability are examined.

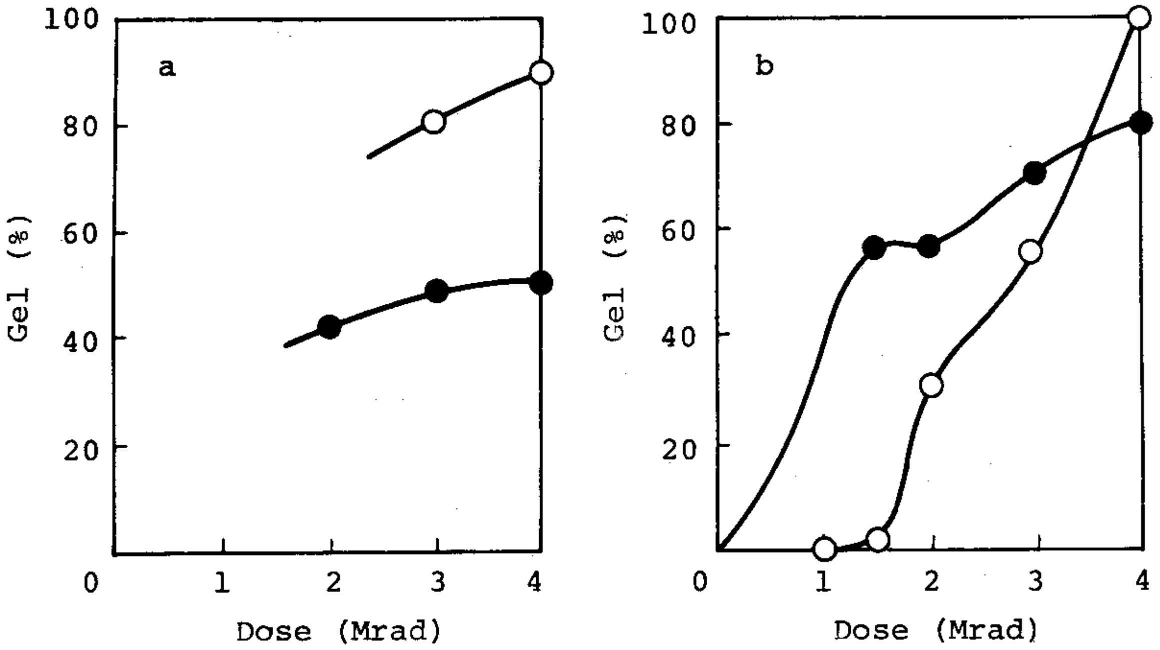


Fig. 2 Effect of temperature on electron beam curing of diepoxides; a, EP-4000; b, CY-179; dose rate, 0.7 Mrad/sec; temperature, (o) 0 °C; (•) 26 °C.

The addition of Fe_2O_2 up to 100 Phr favors slightly the curing, but by the addition beyond this amount, reduces the curability. The addition of TiO_2 decreases the curability with increasing amount of the additive. The effects of addition of the pigments found here may come from some impurities contained in the pigments and will be the problem of the future study. (M. Gotoda, T. Yagi)

3. Temperature Effect on Radiation Curing of Epoxyacrylate

It is known that the rate of UV curing of epoxyacrylate of bisphenol type (RE-1, Showa Kobunshi K.K.) increases with the rise of temperature. For comparison to UV, curing by electron beam is carried out, and the effect of the rise of temperature during the curing on the curing reaction is studied.

Irradiation by electron beams from a VdG is carried out in an aluminium cell of 2 mm depth and 25 mm diameter. The initial temperature is varied between room temperature and 80 °C, and the dose rate and the time of the irradiation are 0.05 Mrad/sec and 40 sec, respectively. The rise of temperature during the irradiation is measured by a combined apparatus of a thermocouple and a memoriscope.

As Fig. 1 shows the rise of temperature is affected only a little by change of the starting temperature, and the dose required to attain the highest temperature is in all cases ca. 0.5 Mrad. Fig. 2 shows the effect of the starting temperature on the rate of gel formation.

It may be seen that the initial rate is high at the starting temperature of 40 °C, but the necessary dose to attain the perfect gelation is, in fact, not affected by the difference of the starting temperature. It is noteworthy that the epoxyacrylate which does not show complete curing at room temperature can easily be cured at 40, 60 and 80 °C.

The curing reaction which proceeds after formation of 100 % gel is followed by studying the change of glass tran-

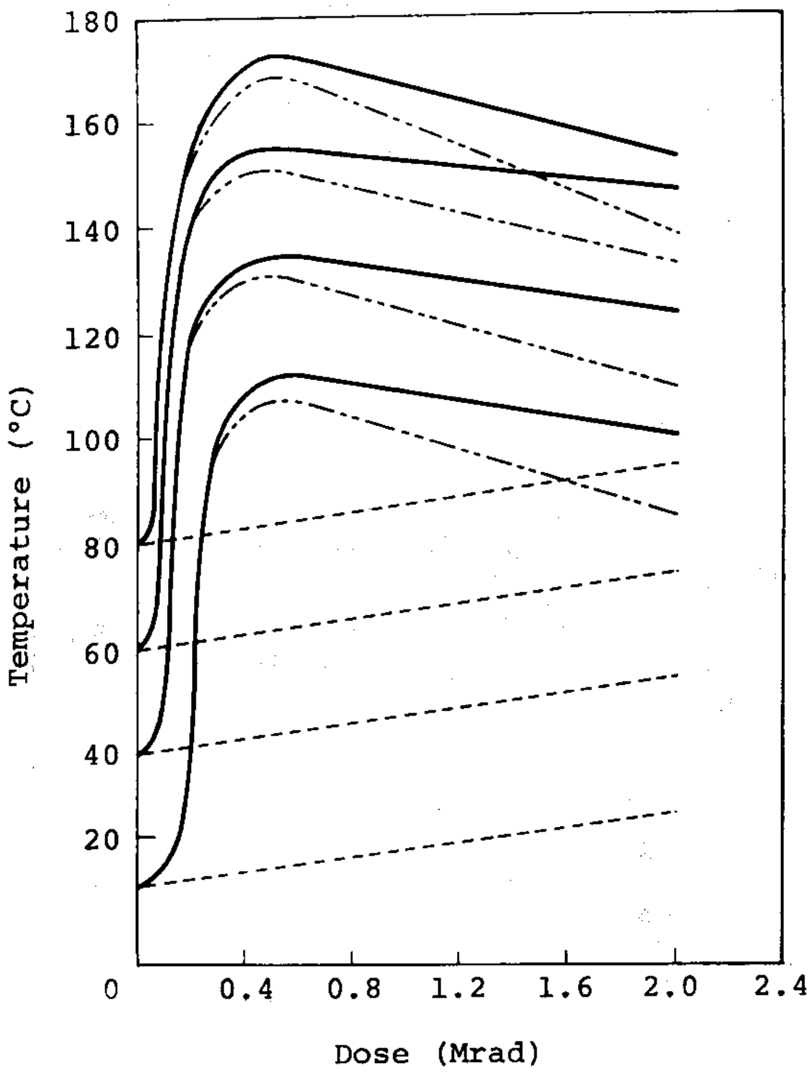


Fig. 1 Temperature rise of epoxyacrylate during E.B irradiation electron energy, 0.8 MeV; dose rate, 0.05 Mrad/sec; weight of sample, 1645 mg; (——) samples; (---) sample and container; (- -) container (A-B).

sition temperature T_g. Curing is carried out in two series of experiments: one is the curing at different starting temperatures under constant dose rate, and the other is the curing at constant starting temperature under different dose rates. Fig. 3 shows the relation between T_g and the highest temperature attained in each run.

It is clear that T_g rises with the rise of the starting temperature, showing clearly that the curing reaction proceeds after 100 % gelation. The increase of the dose rate also results in the rise of T_g. However, the increase of the dose rate also contributes to the rise of the temperature and it

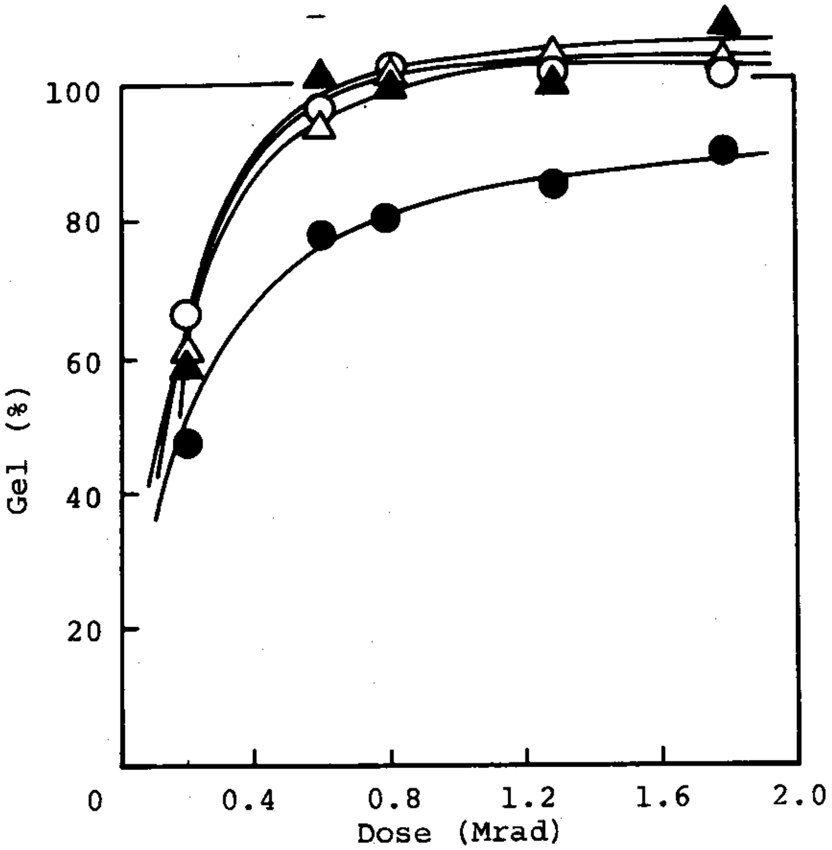


Fig. 2 Effect of starting temperature on electron beam curing of epoxyacrylate; electron energy, 0.8 MeV; dose rate, 0.05 Mrad/sec; initial temperature; (●) room temperature; (▲) 40 °C; (o) 60 °C; (Δ) 80 °C; weight of sample, 1645 mg.

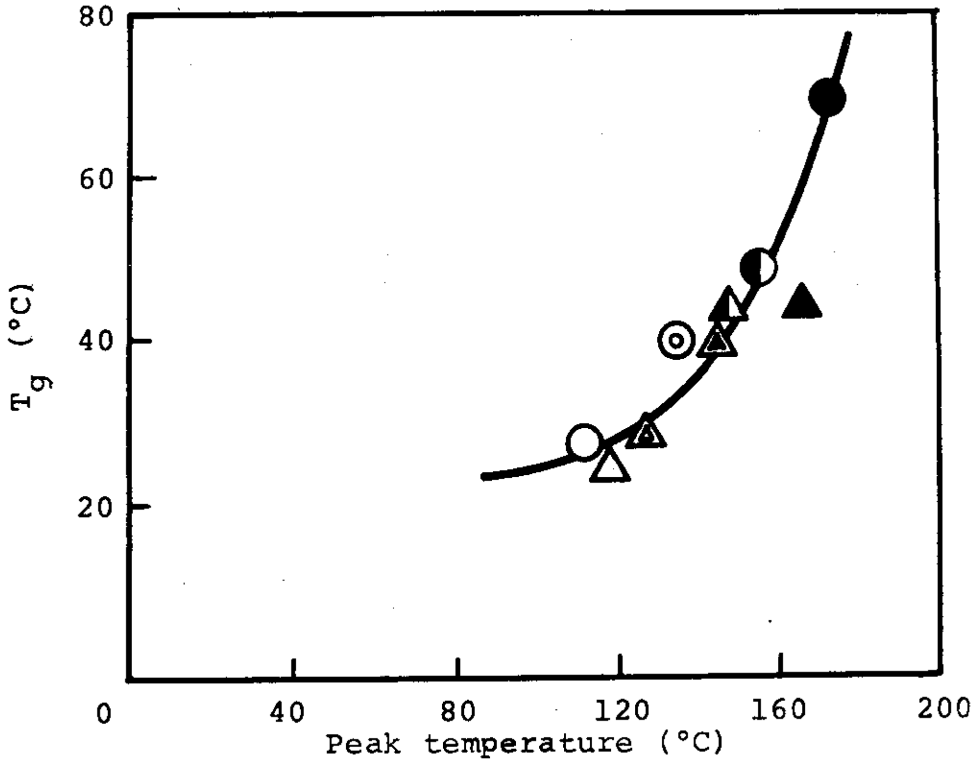


Fig. 3 Effect of temperature on electron beam curing of RE-1 epoxyacrylate; dose rates and initial temperatures; (o) 0.05 Mrad/sec, 15 °C; (◎) 0.05 Mrad/sec, 40 °C; (◐) 0.05 Mrad/sec, 60 °C; (●) 0.05 Mrad/sec, 80 °C; (△) 0.09 Mrad/sec, 15 °C; (◬) 0.18 Mrad/sec, 15 °C; (◭) 0.35 Mrad/sec, 15 °C; (◮) 0.70 Mrad/sec, 15 °C; (▲) 1.00 Mrad/sec, 15 °C.

seems that the effect of the starting temperature is more important than the dose rate for the curing of the epoxyacrylate. (J. Kumanotani, M. Gotoda, T. Yagi)

[6] Measurement of W-Values for Carbon Dioxide-Hydrogen Mixtures

In the previous report, we described ionization measurement to determine the W-values for gaseous mixtures of H_2 and CO of various components.

The ionization measurement is essential to determine the total absorbed energy in the gaseous mixture. This year the study is extended to binary mixture of CO_2 and H_2 in the expectation that CO_2 might be of interest in the future study. The energy absorbed in a gas, E is given by,

$$E = W \cdot I \tag{1}$$

where I denotes the total number of ion pairs and W the average energy spent by a charged particle to give an ion pair in the gas. In the binary system, the W value at partial pressure of $P(CO_2)$ or $1-P(H_2)$, $W[P(CO_2)]$ is given by the following formula when the ionization yields of the gas and pure hydrogen, $I[P(CO_2)]$ and $I[H_2]$ are determined experimentally.

$$W[P(CO_2)] = W[H_2] \cdot \frac{P(CO_2) \cdot S(CO_2) + P(H_2) \cdot S(H_2)}{I[P(CO_2)]} \cdot \frac{I[H_2]}{S[H_2]} \tag{2}$$

$S(CO_2)$ and $S(H_2)$ denote the stopping power of the gas, CO_2 and H_2, respectively, which were calculated by Berger et al$^{2)}$. $W[H_2]$ was determined to be 36.3 eV by Jesse$^{3)}$.

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

$$Z = \frac{S(CO_2) \cdot P(CO_2)}{S(CO_2) \cdot P(CO_2) + S(H_2) \cdot P(H_2)} \tag{3}$$

The solid, straight line means the expected relationship when there is no interaction between CO_2 and H_2 gases under

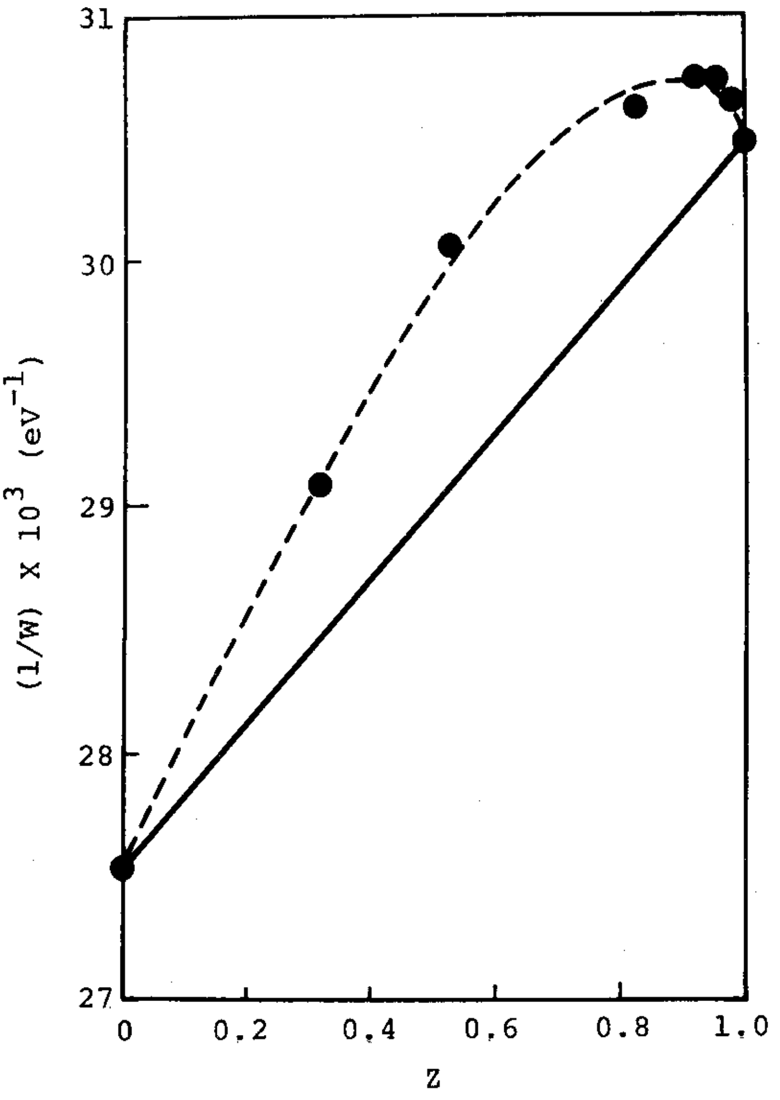


Fig. 1 Reciprocal of W-value as a function of Z for CO_2-H_2 mixture; incident electron energy, 0.8 MeV; total pressure, 760 Torr.

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 dioxide through energy transfer between two molecules. The possibility of the second effect means that it is not correct to use the stopping power of the incident electron energy if the ionization by secondary electrons is significant.

(K. Matsuda, T. Takagaki, Y. Nakai)

1) Y. Nakai, K. Matsuda, and T. Takagaki, JAERI-M, 6260, 9(1975).
2) M.J. Berger and S.M. Seltzer, NASA Report, SP-3012 (1964).
3) W.P. Jesse and J. Sadaukis, Phys. Rev., 107, 766 (1957).

[7] Calibration of Cellulose Triacetate Film Dosimeter by Beam Current Measurement

As a continuation from a previous study in which the aim was to study the simple and accurate calibration method of film dosimeter, the present study is carried out to test the possibility of using the beam current density method.

The cellulose triacetate (CTA) film used in this work is obtained from Numelec Co., France, in a form of rolled film; 8 mm in width and 125 μ in thickness. The film is cut to a piece of 6 cm length and piled on a casette made of acryl glass in order to establish electron equilibrium between the CTA film stack and the casette. The film stack is irradiated with electron beams from the HDRA on a conveyer travelling under irradiation window back and forth toward the direction perpendicular to that of beam scanning. The electrons fallen on the film stack is estimated by measuring beam current collected by a beam current collector which is irradiated on the conveyor at the same conditions.

The beam collector made of aluminium (30 mm diameter and 3 mm in thickness) is placed in a grounded aluminium block 0.5 mm appart from its wall and the upper surface of the beam collector is covered with mylar film of 20 μ thickness for insulation purpose to avoid ions formed in a space above the collector, which may disturb the current measurement.

The curves A and B of Fig. 1 are obtained using the VdG and the HDRA, respectively by plotting relative dose estimated from optical density change of the film as a function of film thickness, x; the ordinate being normalized so that the integrated areas of the curve A or B is equal to energy fluence E passing through the surface of the CTA film stack. Thus,

$$\frac{1}{a_1}\int_{R_0}^{R_{max}} \dot{J}\,(x)\cdot d\,x = E = \int_{R_0}^{R_{max}} J\,(x)\cdot d\,x \qquad (1)$$

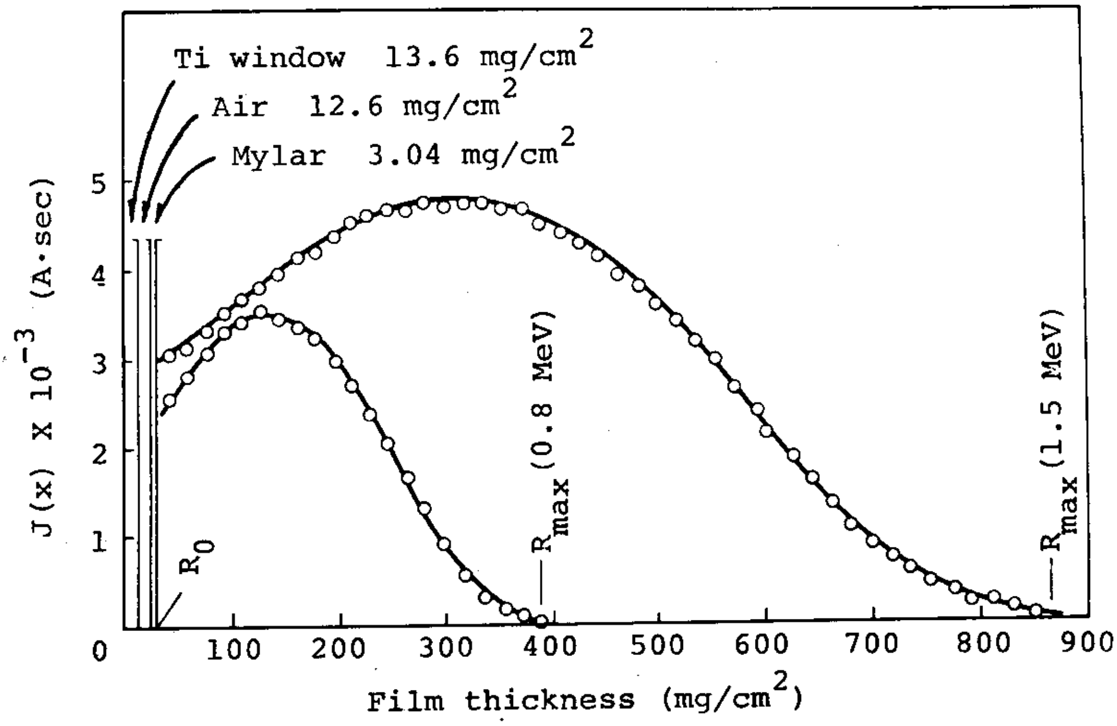


Fig. 1 Energy dissipation curves in the CTA film; A, 1.5 MeV; B, 0.8 MeV; beam current, 50 μA; scanning width, 15 cm; distance from the window, 10 cm; conveyer speed, 60 cm/min; number of passes, 10.

where R_0 is the sum of thicknesses of the irradiation window, mylar film, and air in-between, R_{max}, maximum range of electrons, a_1, normalization factor, and $\mathring{J}(x)$ and $J(x)$ are relative and absolute value of electron energy dissipated in the film thickness dx. The E is calculated from the following equation;

$$E = C.V. \frac{(1 - \eta_{CTA})}{(1 - \eta_{A\ell})} \cdot \frac{1}{S} \cdot 10^7 \quad [\text{erg.cm}^2] \qquad (2)$$

where C is the total electric charge deposited on the aluminum beam collector in Coulomb, V is incident electron energy in volt, η_{CTA} and $\eta_{A\ell}$ are back scattering coefficients of the CTA film and the collector. The η's are theoretically calculated values from atomic number of target materials and incident electron energy and are given in Table 1. The

Table 1. Back Scattering Coefficient of Aluminium and CTA.

E_0	$\eta_{A\ell}$	η_{CTA}
0.8	0.03	0.006
1.5	0.02	0.004

normalization factors a_1 of equation (1) are determined to be 630 for 0.8 MeV electrons and 642 for 1.5 MeV electrons, respectively.

The dose X in Mrad is determined from the depth dose curve shown in Fig. 1 and a_1 thus determined. The dose is related to optical density change Y by the following equation:

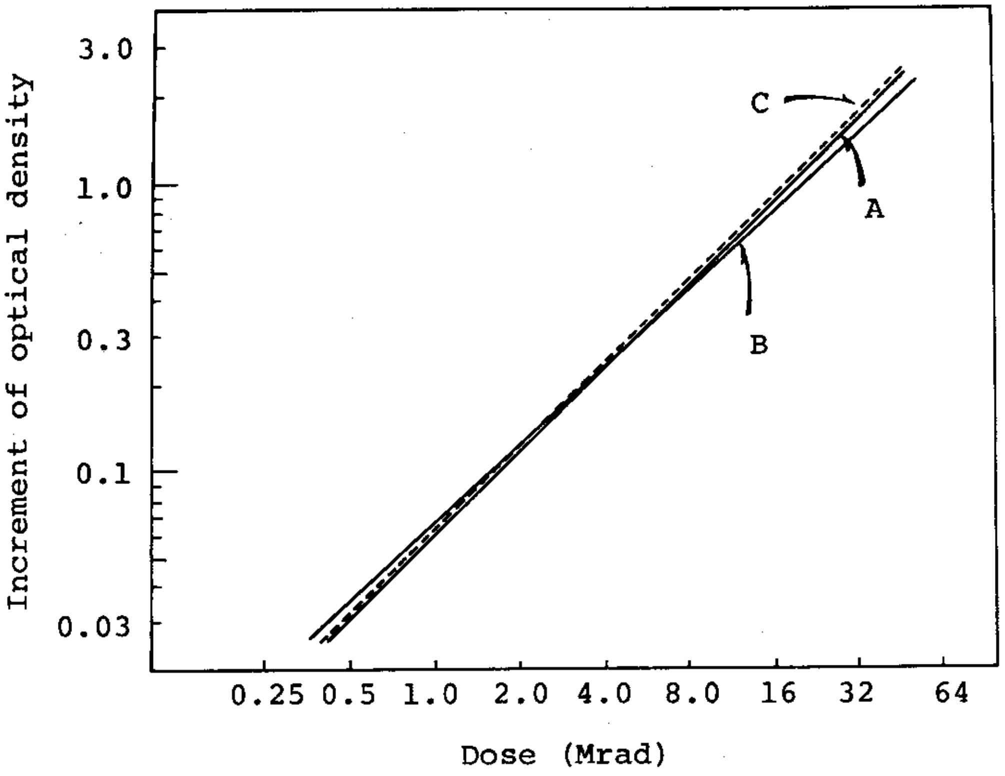


Fig. 2 Change in optical density at 280 nm as a function of absorbed dose in the CTA film; A, 1.5 MeV (present work); B, 0.8 MeV (present work); C, 1.5 MeV (ionization chamber method).

$$Y = a x^{b} \qquad (3)$$

where a and b are parameters which are determined to be 0.0650 and 0.882 for 0.8 MeV electrons and 0.0593 and 0.952 for 1.5 MeV electrons, respectively from the plots of equation (3) shown in Fig. 2, along with the plot previously obtained by the ionization chamber method1) for 1.5 MeV electrons where a and b are 0.0604 and 0.952, respectively.

The agreements between the values a and b obtained for 1.5 MeV electrons by the present method and by the ionization chamber method carried out previously are excellent. The slope of the plot for 0.8 MeV electrons is a little bit smaller than that obtained for 1.5 MeV, but the agreements between the two are still well within 10 % in the dose range from 0.5 to 30 Mrad.

The present study reveals that the calibration of film dosimeters can be simply carried out with enough accuracy using the electron beam current density method. (K. Matsuda, T. Takagaki, T. Kasamatsu).

1) N. Nakai, K. Matsuda, and T. Takagaki, JAERI-M, 6260, 80(1975).

III. LIST OF PUBLICATIONS

[1] Published Papers

1. K. Kaji, T. Okada, and I. Sakurada, "Radiation Induced Grafting of Acrylonitrile onto Poly (Vinylidene Chloride) Fiber", Sen-i Gakkai-shi (J. of the Society of Fiber Science and Technology, Japan), 32, T-340 (1976).

2. K. Kaji, T. Okada, and I. Sakurada, "Modification of Poly (Vinyl Chloride) Fiber by Radiation Grafting of Acrylic Acid", Sen-i Gakkai-shi (J. of the Society of Fiber Science and Technology, Japan), 33, T-12 (1977).

3. Y. Ikada, T. Mita, F. Horii, I. Sakurada, and M. Hatada, "Preparation of Hydrogels by Radiation Technique", Radiat. Phys. Chem., 9, 633(1977).

4. M. Gotoda, and T. Yagi, "Radiation Curing of Chlorinated Polymer/Vinyl Monomer Mixtures by High Dose Rate Electron Beams", Radiat. Phys. Chem., 9, 653(1977).

5 J. Kumanotani, T. Koshio, T. Yagi, and M. Gotoda, "A Comparative Study of Electron Beam and Ultra Violet Curing of Epoxy Acrylate", Radiat. Phys. Chem., 9, (1977).

6. Y. Ikada, Y. Nishizaki, Y. Uyama, T. Kawahara, and I. Sakurada, "Reaction of Poly (Vinyl Alcohol) with Pentavalent Vanadium Ion", J. Polymer Sci: Polymer Chem. Ed., 14, 2251(1976).

7. Y. Ikada, Y. Nishizaki, H. Iwata, and I. Sakurada, "Reaction of Poly (Vinyl Alcohol) with Tetravalent Ceric Ion", J. Polymer Sci: Polymer Chem. Ed., 15, 451 (1977).

8. H. Iwata, S. Nagaoka, and Y. Ikada, "End-Group Determination of Polymers Obtained by Chain-Transfer Radical Polymerizations", Nippon Kagakusen-i Kenkyusho Koenshu, 33, 29(1976).

9. T. Okada, "Radiation-Induced Emulsion Polymerization" J. of the Adhesion Society of Japan, 12, 128(1976).

[2] Oral Presentations

1. S. Sugimoto, M. Nishii, and T. Sugiura, "Homogeneous Gas Reaction in the Binary Mixtures of CO and H_2 by Electron Irradiation (III) ... Effect of Dose Rate and Temperature", The 34th Annual Meeting of the Chemical Society of Japan, Apr. 1, 1976.

2. M. Hatada and K. Matsuda, "Reaction of Gaseous Mixtures of CO and H_2 Induced by Electron Beam Irradiation in the Presence of Solid Catalyst", The 39th Discussion Meetings on Catalysis, Aug. 31, 1976.

3. S. Sugimoto, M. Nishii, and T. Sugiura, "Homogeneous Gas Reaction in the Binary Mixtures of CO and H_2 by Electron Irradiation (IV) ... Effect of Addition of Ammonia and Reaction Mechanism", The 19th Discussion Meeting on Radiation Chemistry, Oct. 10, 1976.

4. K. Kaji, C.K. Lee, T. Okada, and I. Sakurada, "Radiation-Induced Grafting of Acrylic Acid onto Poly (Vinyl Chloride) Fiber", The 25th Annual Meeting of the Society of Polymer Science, Japan, May 31, 1976.

5. T. Okada, "Radiation and Adhesion", The 14th Annual Meeting of Adhesion Society of Japan, Jun. 9, 1976.

6. Y. Mori and T. Okada, "Application of Electron-Beam Irradiation to Adhesion Processing", The 14th Annual Meeting of Adhesion Society of Japan, Jun. 10, 1976.

7. K. Kaji, T. Okada, and I. Sakurada, "Radiation-Induced Grafting of Acrylamide onto Poly (Vinyl Chloride) Fiber", Annual Meeting of the Society of Fiber Science and Technology, Jun. 18, 1976.

8. I. Sakurada, T. Okada, and A. Tsuchiya, "Radiation Effects on Polyacrylamide", The 22nd Regional Meeting of the Society of Polymer Science (Kobe), Jul. 13, 1976.

9. T. Okada, "Modification of Poly (Vinyl Chloride) Fiber by Radiation Grafting", International Meeting on Chemical Science, (Katada, Shiga), Nov. 20, 1976.

10. Ka. Hayashi, "Polymerization of Isobutylvinylether by Electron-Beam Irradiation", The 19th Discussion Meeting on Radiation Chemistry, Oct. 11, 1976.

11. H. Kamiyama, "Molecular Struction of Water Contained in Cellulose Acetate Membrane. [2] Studies on Isothermal Adsorption Curves of Water Vapor", The 25th Annual Meeting of the Society of Polymer Science, Japan, May 31, 1976.

12. M. Hatada and M. Nishii, "Radiation-Induced Polymerization of Mixed Multilayers of Octadecyl Acrylate and Elaidic Acid", The 22nd Regional Meeting of the Society of Polymer Science (Kobe), Jul. 13, 1976.

13. S. Nagai and T. Gilbro, "ESR Studies of Radicals Produced by γ-Irradiation of Thiophene and Its Related Compounds", The 15th Discussion Meeting on ESR, Oct. 15, 1976.

14. S. Takami, F. Horii, R. Kitamaru, and Y. Ikada, "Behaviors of Water in Various Hydrogels", The 25th Annual Meeting of the Society of Polymer Science, Japan, May 30, 1976.

15. H. Iwata and Y. Ikada, "Sol. Gel Transition of Acetal-Crosslinked Polymers, The 25th Annual Meeting of the Society of Polymer Science, Japan, May 31, 1976.

16. Y. Ikada, T. Mita, and M. Hatada, "Preparation of Hydrogels by Electron-Beam Irradiation and their Water Permeability", The 25th Annual Meeting of the Society of Polymer Science, Japan, May 31, 1976.

17. S. Nagaoka, H. Iwata, and Y. Ikada, "Synthesis of PVA Carrying One Terminal CHO Group by Polymerization of Vinyl Acetate in the Presence of $CC\ell_4$", The 25th Annual Meeting of the Society of Polymer Science, Japan, May 31, 1976.

18. S. Nagaoka, H. Iwata, and Y. Ikada, "Radiation Polymerization of Vinyl Acetate in the Presence of Carbon Tetrachloride", The 19th Discussion Meeting on Radiation Chemistry, Oct. 11, 1976.

19. H. Iwata and Y. Ikada, "Kinetics of Acetalization of PVA with Terminal Aldehyde Groups", The 25th Discussion Meeting of the Society of Polymer Science, Japan, Oct. 18, 1976.

20. Y. Ikada and F. Horii, "Some Properties of Hydrogels", The 34th Annual Meeting of the Research Institute for Chemical Fibers, Japan, Oct. 7, 1976.

21. Y. Ikada and T. Mita, "Contact Angles of Hydrogels", The 14th Discussion Meeting on "Polymers and Water" of the Society of Polymer Science, Japan, Nov. 30, 1976.

22. J. Kumanotani, S. Uesugi, and M. Gotoda, "Curing of Unsaturated Polyester by Electron Beam and UV irradiations", The 26th Congress on Thermosetting Resins, Oct. 26, 1976.

23. J. Kumanotani, S. Uesugi, and M. Gotoda, "Crosslinking Reaction in Electron Beam- and UV-Induced Curing", The 26th Congress on Thermosetting Resins, Oct. 26, 1976.

24. Y. Ikada, T. Mita, F. Horii, I. Sakurada, and M. Hatada, "Preparation of Hydrogels by Radiation Technique", The 1st International Meeting of Radiation Processing, May 11, 1976.

25. M. Gotoda and T. Yagi, "Radiation Curing of Chlorinated Polymer/Vinyl Monomer Mixtures by High Dose Rate Electron Beams", The 1st International Meeting of Radiation Processing, May 11, 1976.

26. J. Kumanotani, T. Koshio, T. Yagi, and M. Gotoda, "A Comparative Study of Electron Beam and Ultraviolet Curing of Epoxy Acrylate", The 1st International Meeting of Radiation Processing, May 12, 1976.

IV. LIST OF SCIENTISTS

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Masao KAJIMAKI, Physicist, Duskin Co., Ltd. (May 1975 -)

Shuichi TANIGUCHI, Electrical engineer, Nissin-High Voltage Co., Ltd. (May 1976 - Mar. 1977)