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Osaka Laboratory for Radiation Chemistry
Takasaki Radiation Chemistry Research Establishment
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Research activities of Osaka Laboratory for Radiation Chemistry, JAERI during three year period from April 1, 1989 through March 31, 1992 are described. The latest report. for 1988, is JAERI-M 91-054.

Detailed descriptions of the activities are presented in the following subjects : laser-induced organic synthesis, modification of polymer surface by laser irradiation, polymerization and modification of polymers by electron beam, and electron beam dosimetry.

Previous reports in this series are :

Annual report of the Japanese Association for Radiation Research on Polymers (JARRP), Vol. 1 (1958/1959) through Vol. 8 (1966).

Fundamental Studies in the Osaka Laboratory for Radiation Chemistry (Annual Report) No. 1, JAERI 5018 (1967); No. 2, JAERI 5022 (1968); No. 3, JAERI 5026 (1969); No. 4, JAERI 5027 (1970), No. 5, JAERI 5028 (1971); No. 6, JAERI 5029 (1972); No. 7, JAERI 5029; No. 7, JAERI 5030 (1973).

Annual Report of the Osaka Laboratory for Radiation Chemistry, No. 8, JAERI-M 6260 (1974); No. 9, JAERI-M 6702 (1975); No. 10, JAERI-M 7355 (1976); No. 11, JAERI-M 7949 (1977); No. 12, JAERI-M 8569 (1978); No. 13, JAERI-M 9214 (1979); No. 14, JAERI-M 9856 (1980); No. 15, JAERI-M 82-192 (1981); No. 16, JAERI-M 83-199 (1982); No. 17, JAERI-M 84-239 (1983);

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日本原子力研究所大阪支所年報 (No.23,24,25)

1989年4月1日 - 1992年3月31日

日本原子力研究所高崎研究所
大阪支所

(1992年8月10日受理)

本報告書は、大阪支所において平成元年度から平成3年度の間に行われた研究活動を述べたものである。主な研究題目は、レーザー光による有機合成、レーザー光による高分子表面改質、電子線照射による重合反応の研究、ポリマーの改質に関する研究および線量測定
の基礎研究等である。

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

日本原子力研究所大阪支所における放射線化学の基礎研究, No.1,JAERI5018 (1967); No.2,JAERI5022 (1968); No.3,JAERI5026 (1969); No.4,JAERI5027 (1970); No.5,JAERI5028 (1971); No.6,JAERI5029 (1972); No.7,JAERI5029; No.7,JAERI5030 (1973).

Annual Report of the Osaka Laboratory for Radiation Chemistry, No.8, JAERI - M 6260 (1974); No.9, JAERI - M 6702 (1975); No.10, JAERI - M 7355 (1976); No.11, JAERI - M 7949 (1977); No.12, JAERI - M 8569 (1978); No.13, JAERI - M 9214 (1979); No.14, JAERI - M 9856 (1980); No.15, JAERI - M 82 - 192 (1981); No.16, JAERI - M 83 - 199 (1982); No.17, JAERI - M 84 - 239 (1983); No.20, JAERI - M 88 - 272 (1986); No.21, JAERI - M 90 - 054 (1987); No.22, JAERI - M 91 - 054 (1991).

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I. INTRODUCTION

Osaka laboratory was founded in 1958 as a laboratory of 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 on June 1, 1967, and the laboratory has been operated as Osaka Laboratory for Radiation Chemistry, Takasaki Radiation Chemistry Research Establishment. The research activities of the laboratory have been oriented towards fundamental research on applied radiation chemistry.

In 1990, investigation on activities of all JAERI laboratories was carried out by the government inspection bureau which recommended several improvements and reforms to the Science and Technology Agency for more active research in the Osaka laboratory: (i) the research should be focussed to the ones in the most advanced fields which most industrial companies do not consider for direct development purposes, and promising results should be transferred to industry for development as soon as possible and (ii) irradiation facilities should be opened to industrial companies or universities for their own research. In order to meet these recommendations and encouragements, some alterations and revisions on our research subjects were made.

STUDY ON LASER-INDUCED ORGANIC CHEMICAL REACTIONS, which was initiated in 1988, has continued extensively as an advanced frontier subject. Monochromatic laser beam of very high intensity can possibly cause selective reactions or particular reactions when the beam is applied to organic chemical syntheses. Fundamental studies are in progress using the powerful excimer laser beam in an attempt to synthesize chemicals of high value, to prepare excellent functional surface, and to search for new selective chemical processes. Currently, laser beam irradiation is carried out on methane, carbon dioxide, or alcohols in order to obtain valuable fine chemicals from natural resources which are not used at present. Creative studies are also carried out on simultaneous irradiations of laser beam and electron beam on polymer, and the chemical change or chemical

activities of surface after the irradiation are investigated in order to prepare excellent functions.

STUDY ON BASIC RADIATION TECHNOLOGY FOR FUNCTIONAL MATERIALS was initiated in 1989 as a new technological frontier research subject, when STUDY ON RADIATION CHEMISTRY OF POLYMERS was terminated after a successful result was transferred to an industrial company. On the basis of the result of our study, Sanwa Kako Co. established a semi-commercial plant in Fukui where developing research is in progress to establish technique to produce the non-flammable polyethylene foam by thin layer grafting of phosphor containing oligomer under financial support of Research Development Corporation of Japan (JRDC) since 1989.

Under the new research subject initiated in 1989, studies have been carried out on radiolysis of aqueous solution of metal ion or gas mixture containing metal complex vapor in an attempt to prepare ultra-fine metallic particles in a hope that these particles are useful for functional materials such as highly active catalysis. Studies to prepare organized polymer substances such as hydrophilic gel, LB film, or emulsion, which support these particles, are also in progress in collaboration with universities and industries.

Irradiation service is extended to industrial companies and universities for radiation research and developments since April 1991.

Joint research programs with industrial companies were carried out: 3 companies joined in 1989, 2 in 1990, and 1 in 1991. Cooperate research programs with universities were also carried out: with 8 groups in 1989, 7 in 1990, and 8 in 1991.

A training program which is offered for scientists and engineers from industries has been carried out once a year since 1968. This one week program includes lectures and laboratory experiences concerned with the radiation chemistry of polymers. We accepted 16 trainees each year.

A seminar was offered to local citizens (most of them are housewives and senior citizens) since it helps them understand what the nuclear power and radiation are and how it is essential for our living. This one day seminar welcomed 20 citizens and was held four times a year in fall since 1989. Similar program was held for a group of middle school students (science club)

and they enjoyed the program.

Two scientists from China joined our laboratory in 1990 and 1991 under STA Nuclear Science Exchange Research program. They spent busiest 6 months for research.

In our deepest grief we have to announce that Mr. Koji Matsuda passed away on June 23rd, 1991. He worked as the chief radiation physicist since 1958 when the laboratory was founded, and his contribution to research activities in our laboratory was enormous through his careful management and devotion to studies on radiation dosimetry. The deepest grief is shared by all those who knew him.

In order to keep the annual report in time since the last time we published our annual report No. 22 (JAERI-M 91-054) in 1991 two years behind, we publish three issues of successive three years in one volume, where abstracts prepared for annual discussion meetings of our laboratory in March in 1990, 1991 and 1992 are included.

July 31st, 1992

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

II. RESEARCH ACTIVITIES (APR. 1989 -MAR. 1990)

1. Extinguishing Properties of Foam Materials Obtained by Radiation-Induced Grafting of Vinyl Phosphonate Oligomer onto Bromine Containing Polyethylene Foam

Preparation of non-flammable polyethylene foam by radiation-induced grafting of vinyl phosphonate oligomer of polyethylene foam containing anti-flammable bromine compounds has been carried out to reduce degree of grafting of the oligomer which is required for giving enough non-flammability to pass the FAR (Federal Aviation Regulation) 25.853 (b). In a conventional method to prepare non-flammable foam, non-flammable compound has to be kneaded in polymeric substance to be foamed in advance to the foaming process. However, the amount of non-flammable compound to be added to the polymeric substance cannot be increased exceeding a limiting value without sacrificing quality of the foam. Our grafting method was successful to solve this problem by grafting non-flammable oligomer on the inner surface of foam cells, but the degree of grafting required for this purpose was high as 80%. By the addition of perbromotoluene in the polyethylene before the foaming process, the degree of grafting to give the non-flammability necessary to pass the FAR 25.853 (b) test decreased to 30%. (K. Kaji, I. Yoshizawa *, C. Kohara *, K. Komai *, and M. Hatada)

*Sanwa Kako Co.

2. Radiation-Grafting of Acrylic Acid onto Ultra-High Molecular, High Strength Polyethylene Fibers

Radiation-induced grafting of acrylic acid onto ultra-high molecular weight (UHMW) high strength polyethylene fibers to impart heat resistance and dyeability. A pre-irradiation method was employed for grafting in an aqueous solution of acrylic acid containing a small amount of Mohr's salt as inhibitor. The grafting rate for UHMW high strength polyethylene fibers is one tenth of that for high density PE fibers currently in use, and one hundredth for high density polyethylene film. It has become clear that pre-irradiation dose should be as low as 1 Mrad to keep the high strength of the starting fibers. The starting UHMW high strength polyethylene fiber begins to shrink remarkably around 145°C showing maximum shrinkage of 90% and then breaks at 154°C. When a 24% acrylic acid graft is converted to calcium salt, the grafted fiber retains

the fiber form even at 300 °C and gives only a maximum shrinkage of 11%. The less than 1% acrylic acid graft UHMW high strength polyethylene fibers and their calcium salt can be dyed to deep shade with cationic dyes, whereas the starting fibers cannot be dyed with usual dyes including cationic dye. (K. Kaji, Y. Abe*, M. Murai*, N. Nishioka* , and K. Kosai*)

* Osaka Electrocommunication University

3. Polymerization and Curing of Vinyl Phosphonate Oligomer Induced by Electron Beam Irradiation

Studies on polymerization and curing of vinyl phosphonate oligomer induced by electron beam irradiation have been carried out in order to know the conversion to the polymer or gel under various experimental and irradiation conditions in the cell of polyethylene foam which is important for the radiation-induced inflammability process of polyethylene foam. The irradiation was carried out using electron beam from a Van de Graaff accelerator (1.5 MeV) and polymer conversion and gel fraction were determined as the insoluble fractions in acetone and water, respectively.

It was found that (i) 80 to 90% conversion to polymer with high gel percent was obtained by 150 to 200 kGy irradiation, (ii) presence of oxygen below 1% did not affect the conversion, (iii) higher conversion was obtained as the number of repeated irradiation increased if the dose was the same, but the presence of water or methanol decreased the conversion to the polymer. (K. Kaji, I. Yoshizawa, C. Kohara, K. Komai, and M. Hatada)

4. Formation of Fine Particles by γ -Ray Irradiation of Aqueous Solutions of Silver Nitrate and Palladium Chloride

Many studies to prepare extremely fine metal particles are being in progress to prepare new highly functional materials. Formation of sub-colloidal metal particles by irradiation of aqueous solutions of metal ions were reported by Beloni, et al. and Henglein, et al. The radiation method has advantage in that the particles can be prepared at lower temperature, thus in non-annealed active states. However, information on particle size distribution and chemical composition are not yet reported. A preliminary study to obtain these data which will be important when one considers use of the particles for

chemical catalysis.

An aqueous solution of silver nitrate (0.1 mol/l) was irradiated with γ -rays at room temperature under nitrogen or air saturated condition, and it was found that broad absorption at 400 nm appeared by the irradiation, which was assigned as the plasmon oscillation in the metal particle. The absorption intensity decreased with time, indicating that the sub-colloidal particles coagulate to precipitate from aqueous phase. The initial intensity of the absorption was stronger for nitrogen saturated solution than for air saturated solution.

An acidic aqueous solution of palladium chloride (0.001 mol/l, 0.001N HCl) was irradiated by γ -rays and it was found that the absorption at 371 nm decreased with increasing dose. The absorption at 431 nm increased with dose but then decreased with dose and disappeared at 5 Mrad irradiation. (J. Takezaki, Y. Nakase, K. Kaji, and M. Hatada)

5. Morphology of Radiolysis Products of Iron Pentacarbonyl

Vapor phase radiolysis of iron pentacarbonyl has been carried out to obtain metal containing particle, since the iron pentacarbonyl has high vapor pressure (40 Torr at 20 °C) which is suitable for vapor phase radiolysis study.

Brown particles were formed by the radiolysis of iron pentacarbonyl under argon atmosphere with electron beam or γ -rays either in flow system or batch system. Scanning electron micrographic observation revealed the formation of 0.5 - 2 μ m particles which were further identified as ensembles of finer particles of 10 - 30 nm. The ensembles were dispersed in water using an ultrasonic agitator, and subjected to particle diameter distribution measurement which gave a distribution curve having a maximum at 0.3 - 0.5 μ m.

Elemental analysis of the ensembles detected extremely high content of oxygen, and thermogravimetric analysis combined with mass spectrometry indicated that formation of materials giving peaks at $m/e = 18$ and 44 at 100 and 400 °C, respectively. An XPS measurement of solid product (Fig. 1) indicated that it consists of iron oxides and a small amount of carbon containing compounds. Measurements of magnetic properties and X-ray diffraction indicated that the product was amorphous and its magnetization was 700 - 900 Oe (55.7 - 71.6 kA/m) with magnetic susceptibility of 0.5 emu/g. (Y. Nakase)

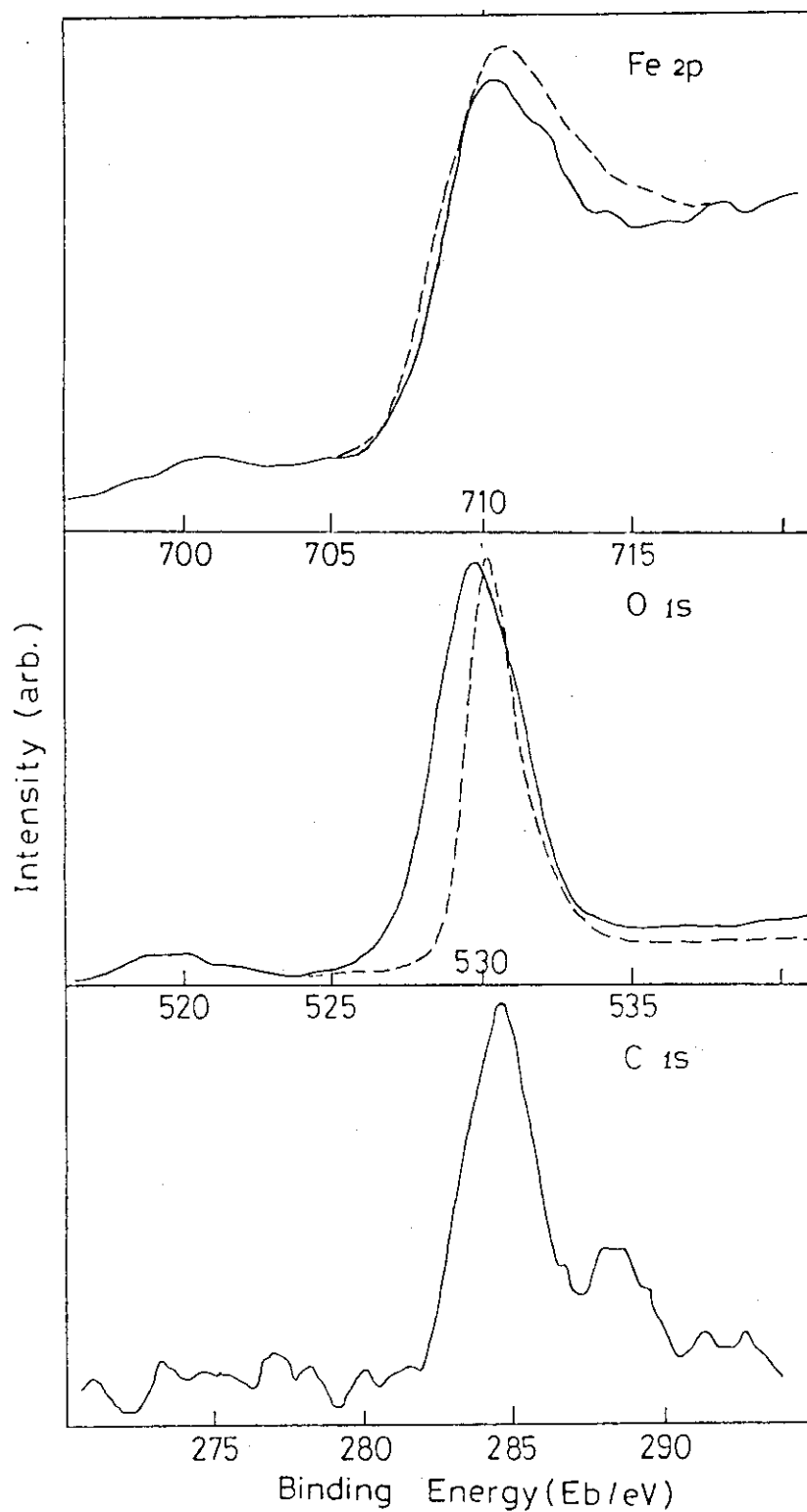


Fig.1. X-ray photoelectron spectra of solid particles obtained from iron pentacarbonyl by electron beam irradiation: Al anode was used (130W, 13 kV).
: as-obtained, ---- : after Ar⁺ ion sputtering (8kV) for 30 min.

6. A New Electron Beam Dosimeter Using Photo-Stimulated Luminescence

Photo-stimulated luminescence (PSL) is widely used to obtain X-ray image in place of conventional photographic technique in the field of X-ray diagnosis. Study has been initiated in an attempt to develop an electron beam dosimeter of wide range of dose response and two-dimensional dose distribution of extremely high resolution using this technique. PSL phosphor was obtained by heating mixture of BaF_2 and $BaBr_2$ containing a small amount of Europium metal in an electric oven under argon stream and then the calcined solid was crushed to fine powder. Irradiation was carried out with electron beam (0.6 MeV, $10\mu A$) at a dose rate of 50 Gy/sec. PSL at 390 nm was observed when the irradiated phosphor was stimulated with He-Ne laser beam at 633 nm and PSL intensity at 390 nm increased linearly with increasing dose up to 1.7 kGy. The study is in progress to elucidate the effect of PSL response on the amount of europium in the phosphor. (K. Matsuda, H. Atsumi *, A. Kuwano*, and Y. Tsuji *)

* Kinki University

7. Bacillus Pumilus as a Sterilization Indicator

Survival-dose curve of *Bacillus pumilus* supported on different materials were measured using electron beam from a Van de Graaff in order to confirm whether *Bacillus pumilus* can be used as a biological standard to determine a minimum sterilization dose for electron beam sterilization.

Aqueous suspension of *Bacillus pumilus* was applied on materials for medical use or metal foils, and then radiochromic film dosimeter was placed on this surface. The sample was placed and sealed in a Hoky sterilization bag and irradiated with electron beam (1.5 MeV, $20\mu A$). Survival-dose curve was almost independent of supporting materials and was similar to that obtained in γ -ray irradiation. Thus, *Bacillus pumilus* used in this study seems to be used as a biological standard. (M. Furuta *, K. Matsuda, and A. Takeda*)

*Osaka Prefectural Center of Radiation Research

8. Polymerization of Unsaturated Lipid Monolayer Chemically Adsorbed on Silicone

Studies on polymerization of chemically adsorbed 18-nonadecenyl

trichlorosilane (V-NTS) on silicone wafer initiated by electron beam irradiation have been carried out in an attempt to establish technique to build-up long conjugate double bond which serves as a conductor in a future molecular element. A monolayer of V-NTS was formed on silicone wafer by dipping the wafer in organic solution of V-NTS. The wafer covered with V-NTS was irradiated with electron beam in nitrogen atmosphere to convert terminal double bond to imino or amino group which reacts with V-NTS to form the second layer of V-NTS when the irradiated wafer is dipped in the solution. By alternate repeating cycles of the chemical absorption and electron irradiation, build-up film of V-NTS was successfully formed on the silicone wafer. One cycle of this process using 19-trimethylsilyl-18-nonadecynylsilane (SA-NTS) instead of V-NTS resulted to form a monolayer of SA-NTS, the terminal acetylenic bond of which was reacted with neighbouring SA-NTS molecules to form conjugated double bond which was tentatively identified from spectra of UV-visible and infrared regions. However, the length of the conjugation is not long enough to give measurable conductivity at present. (K. Ogawa * , H. Tamura* , N. Mino* , and M. Hatada)

*Matsushita Electric Industries, Co.

9. Actinometry of Laser Beam Using Ferric Oxalate Chemical Actinometer

Conventional actinometry of excimer laser is carried out using physical method, but this method has disadvantages in that it cannot directly determine the absorbed quanta in a system of photo-chemical interest and sensitivity of the sensor may change with time. In order to dissolve these problems, investigations have been carried out to demonstrate whether the ferric oxalate actinometer which is widely used as an actinometer for experiments using conventional ultra-violet lamps can be used as an actinometer for excimer laser beam.

Aqueous solution (70 ml) of potassium ferric oxalate was irradiated in a Pyrex glass vessel equipped with synthetic quartz window with laser beams of 193 nm, 248 nm and 350 nm. A small amount of the solution was taken out intermittently during irradiation, and the amount of ferrous ion formed by the irradiation was determined by the absorption at 510 nm of the solution which was colored by the addition of 1, 10-phenanthroline. Quantum yield of ferrous ion formation was measured as a function of incident beam intensity,

concentration of initial ferrous ion, and oxygen. It was concluded that the ferric oxalate actinometer can also be successfully used as actinometer for excimer laser beams. (Y. Izumi, K. Ema *, T. Yamamoto *, S. Kawanishi, Y. Shimizu, S. Sugimoto, and N. Suzuki)

*Osaka University

10. Photochemical Reaction of Alcohols Containing Hydrogen Peroxide--A Selective Synthesis of Diols

Studies has been initiated on laser-induced photochemical reactions of methanol and ethanol, both containing hydrogen peroxide in order to synthesize valuable compounds from raw chemical materials.

Methanol or ethanol (56 - 64 ml) was irradiated at room temperature in a Pyrex glass vessel equipped with synthetic quartz windows, during irradiation, 30% aqueous solution of hydrogen peroxide being added at 5.3 to 14.4 ml/h under constant agitation (500 r.p.m.) in nitrogen atmosphere. KrF laser beam (400 mJ/pulse; frequency, 16 Hz) was used for the irradiation. Products were subjected to gas chromatography and ion chromatography.

It was found that ethylene glycol was selectively formed from methanol, the yield of the ethylene glycol increased with increasing feeding rate of hydrogen peroxide, and the selectivity of ethylene glycol was high as 95 - 97%, whereas formation of ethylenglycol was prohibited by the presence of oxygen. 2,3-Butanediol and 1,3-butanediol were the main products from mixture of ethanol and hydrogen peroxide and the yields of the diols were found to depend on the feeding rate of hydrogen peroxide. (Y. Shimizu, S. Kawanishi, S. Sugimoto, and N. Suzuki)

11. Chemical Reactions Induced by Simultaneous Irradiation of Electron Beam and Laser Beam on Gas Mixture of Methane and Oxygen Containing Compounds

Studies have been initiated on chemical reactions induced by simultaneous irradiation of electron beam (0.4 MeV, 0.05-0.5 mA) and laser beam (ArF, 250 mJ/pulse, 50 Hz) on gas mixture of methane and carbon monoxide and that of methane and carbon dioxide. Gas mixture was irradiated in a batch type stainless vessel equipped with a titanium window at the top, through which electron beam penetrates and a quartz window at the side for laser beam

irradiation. Gas pressure was 700 Torr. Products were analyzed by a gas chromatograph.

Ethane was found as the main product when gas mixture containing 20% carbon monoxide or 20% carbon dioxide was irradiated with electron beam and laser beam simultaneously. The yield of ethane obtained by the simultaneous irradiation was higher by 1.5 than sum of the yields obtained separately by electron beam irradiation and laser beam irradiation on the mixture of methane and carbon monoxide. This factor was 1.2 for the mixture of methane and carbon monoxide. The yields of hydrocarbons of C2 to C4 increased, and those of C5 and higher decreased by the simultaneous irradiation. The yield enhancement by the simultaneous irradiation was observed for mixture and not for pure methane. (S. Sugimoto, Y. Shimizu, S. Kawanishi, and N. Suzuki)

12. Irradiation of Ethylene-Tetrafluoroethylene Copolymer by Laser Beam

As a series of studies on modification of polymer surfaces, studies have been carried out on laser beam irradiation of ethylene-tetrafluoroethylene copolymer (ETFE) using x-ray photoelectron spectroscopy. Studies have also been carried out on electron beam irradiation for reference purpose. ETFE was selected since this polymer has excellent thermal stability and strong chemical resistivity.

Examination of change of photoelectron spectrum after laser beam irradiation revealed that selective removal of F atom occurred and that double bond and carbonyl group were formed significantly by ArF laser beam, while carbonization occurred by KrF laser beam irradiation. Electron beam irradiation resulted smaller change compared to that caused by laser beam of the same dose.

The results are explained by that in the laser beam irradiation, formation of optical absorption bands at initial stage of irradiation enhances absorption of laser beam, resulting chemical reactions significantly. (S. Kawanishi, S. Sugimoto, Y. Shimizu, and N. Suzuki)

III. RESEARCH ACTIVITIES (APR. 1990 - MAR. 1991)

1. Formation of Fine Solid Particles from Palladium Chloride or Silver Nitrate Aqueous Solution by Gamma Ray Irradiation

Solid precipitates were formed when aqueous solution of palladium chloride (pH=2) or silver nitrate (both, 0.001 mol/l) were irradiated with gamma rays. Suspension of these solid particle was found to form when sodium dodecyl sulphate or vinyl pyrrolidone were added in the solution. Number of particles in the suspension and average particle size were determined from scattered light intensity and analysis of fluctuation of the scattered light intensity using dynamic light scattering technique. Number of particles increased with dose. Average diameter of the particles was 20 nm upto 6 Mrad and above this dose it increased to 50 nm. (J. Takezaki, M. Hatada, and Y. Nakase)

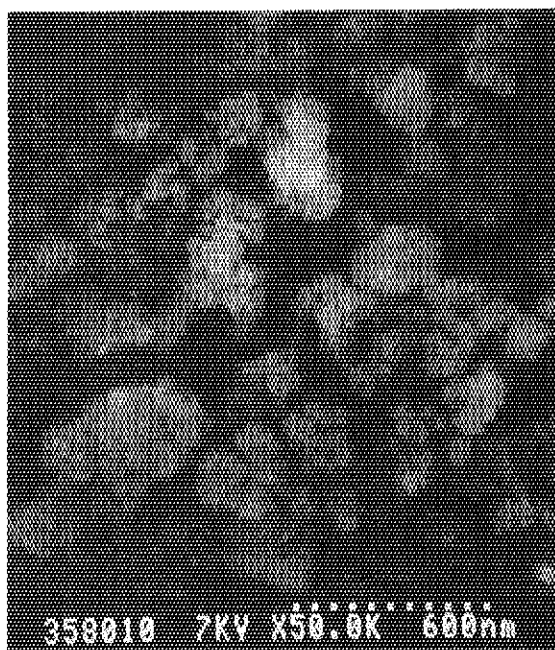
2. Formation of Fine Solid Particles from Metal Carbonyl Vapor by Irradiation of High Energy Radiation

Study has been carried out in an attempt to prepare fine particles from metal carbonyl by irradiation of high energy radiations. Two metal carbonyls, $\text{Cr}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8$ were used for the present study. The chromium carbonyl was heated to vaporize in a vessel, and the vapor was irradiated with electron beam (1MeV). Brown-gray fine particles were obtained by the irradiation, which were recognized as aggregates (100-500 nm in diameter) of finer particles of 10-30 nm diameter by scanning electron micrographic observation (Fig. 2). Further observation by atomic force micrograph confirmed the presence of fine particles of 10-30 nm diameter.

Particles suspended in water by forced super sonic agitation was subjected to particle diameter analysis which indicated the presence of two peaks in a particle size distribution curve, one at 20 nm and the other at 250 nm for chromium, and 15 nm and 300 nm for cobalt.

Thermogravimetric analysis and XPS measurement of these particles revealed that these particles were composed of metal oxide and carbonaceous compounds.

(Y. Nakase)



A:e-beam

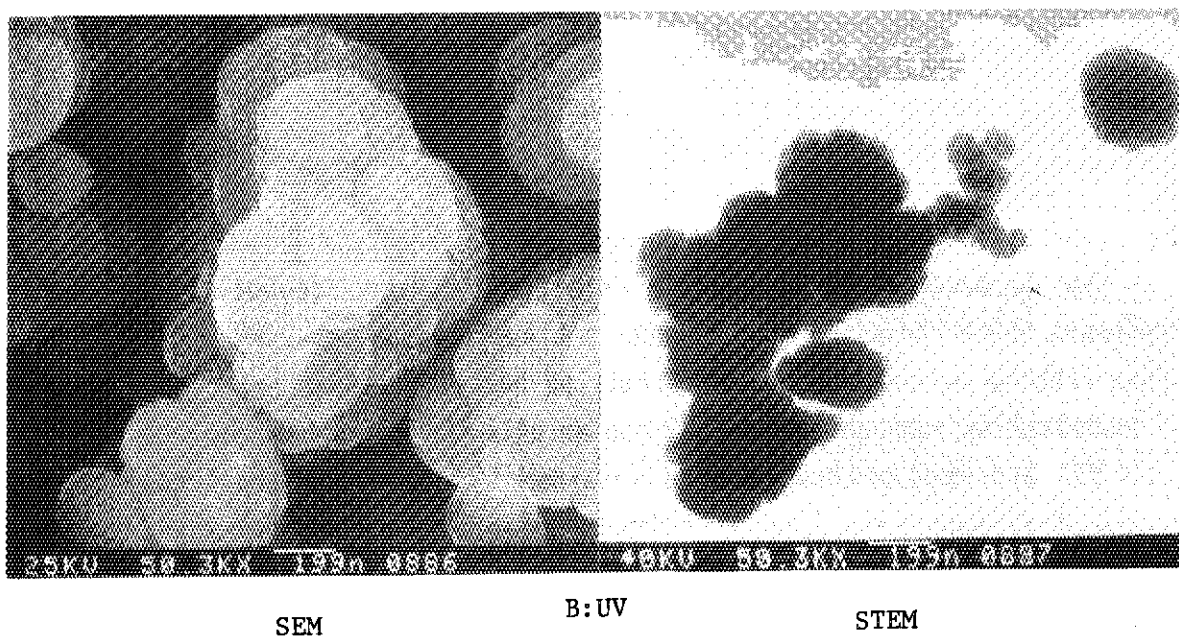


Fig.2 SEM and STEM photographs of solid particles obtained from chromium carbonyl by electron beam (A) and UV irradiation(B);

Magnification:50,000;

Irradiation condition:(A) 1.0 MeV, 50 μ A,

(B) 400 W mercury lamp(320nm~400nm)

Atmosphere:Ar/ O₂ =25/75 vol%

3. Physical Properties of Monomolecular Film prepared by Chemical Absorption Technique

It is known that the monomolecular film prepared by chemical absorption method has more stable structure than that prepared by conventional Langmuir-Blodgett technique, because strong covalent bond (siloxane bond) was formed between molecules and substrate and between molecules.

18-Nonadecenyltrichlorosilane (V-NTS) was reacted with hydroxyl groups on silicon wafer in an organic solvent in nitrogen atmosphere to form monolayer of V-NTS and then the wafer was irradiated with electron beam in nitrogen atmosphere to convert terminal double bond to a polar group to which another V-NTS was reacted to form the second V-NTS layer when the irradiated wafer was immersed in the organic solvent. By repeating cycle of the procedures, V-NTS multilayer was successfully built on the wafer. Measurements were carried out on break voltage, leak current, critical surface energy and dynamic friction coefficient of the multilayer as a function of the number of layers. It was found that the break-off voltage increased, leak current decreased, dynamic friction coefficient decreased, and anti-abrasion property became poor as the number of layers increased. Critical surface energy did not depend on the number of layers. (N. Mino*, K. Ogawa*, and M. Hatada)

* Matsushita Electric Industries Co.

4. Preparation of PVA Hydrogel Membranes by Electron Beam Irradiation

The purpose of the work is to obtain poly(vinyl alcohol)(PVA) hydrogel membranes using radiation to construct a bioartificial pancreas. The radiation cross linking method seems to be promising because it does not require the use of crosslinking compounds which may contaminate the bioproduct.

PVA hydrogel membranes were obtained by electron beam irradiation of deaerated aqueous solutions of polymer having viscosity-average degrees of polymerization (DP_v) of 1,750 and 7,000. The diffusive properties of the PVA hydrogel membranes were investigated on the basis of permeability measurements of insulin, immunoglobulin, and glucose. The diffusion coefficients of the solutes across the membranes of different densities of crosslinking and thus different water contents have been calculated. The linear dependence of the diffusion coefficients on the water contents is an evidence for that diffusion

occurs primarily through the hydrating liquid in the polymer network. (Krystyna Burczak **, T. Fujisato* , Y. Ikada *, M. Hatada)

*Research Center for Biomedical Engineering, Kyoto University

**Institute of Applied Radiation Chemistry, Technical University of Lodz, Lodz, Poland

5. Radiation Effects on Polyethylene Foam of Open Cell Type

A study has been carried out on radiation effects on open cell type polyethylene foam. The foam was irradiated with electron beam from a Van de Graaff accelerator either in nitrogen or in air and changes of strength, elongation, and gel fraction were measured. The gel percent of the original foam (50%) increased by 30% after irradiation in nitrogen, while strength measured at room temperature, 70 and 100 °C did not change by the irradiation. However, elongation measured at 70 and 100 °C decreased considerably and dimension stability above 70°C was also improved. (Tang Beilin, K. Kaji, I. Yoshizawa, C. Kohara, and M. Hatada)

6. Alternate Graft-polymerization of Acrylic Acid and Vinylpyrrolidone onto Polyethylene Film by γ -ray Irradiation

In order to establish method of grafting to introduce different functional groups to polyethylene film, kinetic study has been carried out on successive or simultaneous grafting of acrylic acid (AA) and vinylpyrrolidone (VP) using simultaneous grafting technique initiated by γ -rays. In the grafting of VP on the film previously grafted with AA, the rate of grafting was found to increase with increasing degree of grafting of the first grafting, reach maximum value at 20%, and then decreased when the degree of the first grafting increased further. In the case where the order of the grafting was reversed, the degree of AA increased monotonously with the degree of the first grafting. In the simultaneous grafting using monomer solution containing both AA and VP, grafted film of higher ratio of AA to VP than that in the monomer solution was obtained. (Qin Gen-Min, K. Kaji, M. Hatada)

7. Non-flammability of Polyethylene Sheet Containing Three-Component Anti-flammable Additives---Inorganic Filler, Bromine Containing and Phosphor

Containing Compounds---

Addition of inorganic filler to polymer is frequently effective to reduce the amount of smoke during burning, but at the same time it enhances burning due to "candle stick" effect. In order to clarify the effect of added inorganic filler to non-flammability, flammability tests by oxygen index (LOI) method and UL94 (Underwriter's Laboratory, NO. 94) method have been carried out on polyethylene sheet to be foamed, which was kneaded with Fyrol or PBT, either separately or combined, and was further added with an inorganic filler. The inorganic fillers used in the present investigation were $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{CO}_3)$, and ultra carbon.

For the sheet added with Fyrol, PBT or $\text{Al}(\text{OH})_3$ separately, LOI of the sheet increased monotonously with increasing amount of the additive. For the sheet added with PBT- $\text{Al}(\text{OH})_3$ or Fyrol- $\text{Al}(\text{OH})_3$ of different compositions, LOI becomes smaller than the sum of those observed for each component but not smaller than the corresponding values of the three additives when these additives were added separately. Test by UL94 revealed that both flaming time and charred distance became longer with decreasing amount of PBT, but in the presence of large amount of Fyrol (40 phr), the flaming time and charred distance did not increase when the amount of added PBT was reduced. (I. Yoshizawa, T. Shibata, K. Kaji, and M. Hatada)

8. Photo-Emission from Excited CF_2 Radical by High Energy Electron Irradiation of Chlorofluorocarbons

Chlorofluorocarbons CCl_2F_2 (CFC-12) and CHClF_2 (HCHC-22) in the gas phase were irradiated with high energy electron beam from a Van de Graaff accelerator and emission intensity of the excited CF_2 radical was measured as a function of sample gas. The results show that a formation path via a precursor exists besides of the direct formation by electron impact. Experiments were also made for mixtures of chlorofluorocarbons and helium or argon. (I. Fujita *, K. Matsuda, T. Kijima **, M. Sakamoto*, and M. Hatada)

*Osaka Electrocommunication University

** Osaka Institute of Technology

9. Electron Beam Dosimeter Using Photo-Stimulated Luminescence

Study has been carried out to seek possibility whether recently developed X-ray imaging process technique using photo-stimulated luminescence (PSL) can be used for electron beam dosimetry which has advantages of (i) wide range of linear response to dose and (ii) high positional resolution.

PSL phosphor was prepared by the following procedure; a known amount of europium (0.1 to 3.0 mol%) was added to equimolar mixture of BaF₂ and BaBr₂, the mixture was heated at 1000 °C, and then the calcined block was crushed to fine powder. The PSL phosphor was irradiated with electron beam (0.6 MeV, 0.01 mA), and then the intensity and spectrum of the luminescence were measured by scanning He-Ne laser beam on the irradiated surface. Observed luminescence spectrum showed peak at 390 nm, the intensity of which increased with increasing amount of europium doped upto 1.25 mol%, and then decreased when europium was added further. The results indicate that Eu³⁺ and F center, which were formed by the irradiation contributed to PSL as proposed by Miyahara, et. al., and that addition of europium increased the amount of Eu²⁺ which is a precursor of Eu³⁺, but simultaneously consumed F⁺ which is a precursor of F. (K. Matsuda, H. Atsumi*, and Y. Tsuji *)

*Kinki University

10. Photochemical Reaction of Alcohols Containing Hydrogen Peroxide--A Direct Synthesis of Diols

Studies have continued on laser-induced photochemical reactions of methanol and ethanol, both containing hydrogen peroxide in order to synthesize valuable compounds from raw chemical materials.

Mixture of methanol and ethanol (56 - 64 ml) was irradiated at room temperature in a Pyrex glass vessel equipped with synthetic quartz windows, and during irradiation, 30% aqueous solution of hydrogen peroxide being added at 3.0 to 16.0 ml/h under constant agitation (500 r.p.m.) in nitrogen atmosphere. KrF laser beam (248 nm, 400 mJ/pulse; frequency, 16 Hz) was used for the irradiation. Products were subjected to gas chromatography and ion chromatography.

It was found that diols containing 1,2-propanediol (main product), ethyleneglycol and 2,3-butanediol were selectively formed from the mixture. The yield of 1,2-propanediol depended on methanol content and became maximum at 67%

methanol content, giving maximum quantum yield of 0.25. The quantum yield and selectivity of total diol were 0.58 and 83.2%, respectively. The mechanism of the diol formation was discussed. (Y. Shimizu, S. Kawanishi, S. Sugimoto, and N. Suzuki)

11. Chemical Reactions Induced by Simultaneous Irradiation of Electron Beam and Laser Beam on Gas Mixture of Methane and Carbon Dioxide

A comparative study has been carried out on chemical reactions induced by irradiation of electron beam (0.4 MeV, 0.03 mA) and laser beam (ArF, 193 nm, 250 mJ/pulse, 50 Hz), separately, and those induced by simultaneous irradiation of the electron beam and the laser beam, on gas mixture of methane and carbon dioxide (80 mol%).

Gas mixture was irradiated in a batch type stainless vessel equipped with a titanium window at the top, through which electron beam penetrates and a quartz window at the side for laser beam irradiation. Gas pressure was 700 Torr. Products were analyzed by a gas chromatograph.

By laser beam irradiation, carbon monoxide was found to be formed as the main product with a small amount of ethane and water, but no oxygen containing compounds were formed. By electron beam irradiation, carbon monoxide and ethane were the main products. Small amounts of higher hydrocarbons (C3-C6), and oxygen containing compounds such as methanol, formic acid and acetone were also formed. By the simultaneous irradiation, sum of the yields of carbon monoxide and ethane is higher by 1.3 than that obtained for the irradiation by either beam separately, and acetaldehyde was the only product among the oxygen containing compounds. No enhancement of the sum of the yields of carbon monoxide and ethane was observed when KrF (248 nm) was used instead of ArF in the simultaneous irradiation, and also ArF and electron beam were irradiated successively. (S. Sugimoto, Y. Shimizu, S. Kawanishi, and N. Suzuki)

12. Change of Surface Chemical State of Polyethersulphone by Excimer Laser Irradiation

In order to elucidate effects of laser beam irradiation on polyethersulphone (PES), study has been carried out on change of surface chemical change of PES using photoelectron spectroscopy (XPS). PES was selected since this polymer has excellent anti-heat property and strong

chemical resistivity.

Contamination of PES film (Idemitsu Kousan Co., 100 μm) was removed by super sonic cleaning in ethanol. The film was irradiated with ArF (193 nm) laser beam in vacuum (10^{-7}a) and the change of surface chemical state was measured by XPS without exposing to air.

Examination of change of photoelectron spectrum after laser beam irradiation revealed that the component assigned as $-\text{SO}_2-$ group in the O_{1s} peak and the component assigned as $-\text{SO}_2-$ group in the S_{2p} peak decreased markedly, and a new component of assigned as $-\text{S}-$ group appeared in the S_{2p} peak, indicating that $-\text{SO}_2$ group was selectively decomposed releasing oxygen atom. When KrF laser beam was used instead of ArF laser beam, similar change of photoelectron spectrum was observed, but the effect of irradiation was smaller than that observed for ArF laser beam irradiation, due to the fact that PES has strong absorption bands at 200 nm which absorbs more energy of ArF laser beam than that of KrF. It was also found that nitrogen can be introduced in the surface by exposing the irradiated surface to ammonia gas. (S. Sugimoto, S. Kawanishi, Y. Shimizu, N. Suzuki, K. Ohnishi*, and S. Arai *)

* Kyoto Institute of Technology

13. Irradiation Effects of Fluorine Containing Polymer and Aromatic Polymers by Excimer Laser Radiation

As a series of studies on modification of polymer surface, studies have been carried out on laser irradiation of ethylene-tetrafluoroethylene copolymer (ETFE) and polyetheretherketone (PEEK) using x-ray photoelectron spectroscopy. ETFE and PEEK were selected since these polymers have excellent thermal stability and strong chemical resistivity.

Examination of change of photoelectron spectrum of ETFE after laser beam irradiation as a function of dose revealed that selective removal of F atom occurred and that large change of surface atom ratio was observed at certain dose, possibly due to "impulsive" carbonization reaction resulted by effective absorption of laser radiation in carbonyl group which were formed during earlier period of irradiation. The irradiation of ArF laser radiation on PEEK resulted destruction of one phenyl ring out of three phenyl rings in a monomer unit, increase of $-\text{COO}-$ group in sacrifice of $-\text{C-O-C}-$ and $-\text{C=O}$ groups. The irradiation effect observed for KrF laser irradiation is smaller than that for ArF laser beam irradiation. (S. Kawanishi, S. Sugimoto, Y. Shimizu, and N. Suzuki)

IV. RESEARCH ACTIVITIES (APR. 1991 - MAR. 1992)

1. Optical Emission from Excited Carbon Dioxide Produced by Electron Beam Irradiation

Gas mixture of helium and carbon dioxide was irradiated with electron beam (0.6 MeV, 0.03 mA) from a Van de Graaff accelerator and emission from excited carbon dioxide ion was measured as a function of pressure, concentration of carbon dioxide in wide ranges in order to get information of energy transfer from one component to the other when the binary gas mixture was irradiated with electron beam. The information seems to be important to determine accurate energy absorption in one component in electron beam irradiation of the gas mixture.

Partial pressure of each component was varied from 0.001 to 760 Torr while the total pressure was kept at 760 Torr. Two series of emission, one from A and the other from B state, were observed. The inverse of the emission intensity of the former increased linearly with increasing inverse of the partial pressure of carbon dioxide, and a quenching coefficient determined from this relation is valid to fit to experimental data obtained under whole range of experimental conditions studied. Behavior of the emission intensity from the latter state was too complex to make simple fit of the experimental data. (K. Nakato, K. Matsuda, M. Tsuda *, and I. Fujita *)

*Osaka Electrocommunication University

2. Particle Size Sistribution of Fine Solid Particles Formed from Silver Nitrate Aqueous Solution by γ -Ray Irradiation

It is known that metal small particles were formed when aqueous solutions of metal ions were irradiated with high energy radiation, but no information was yet obtained on particle size distribution which may be important when one considers application of these fine particle as chemical functional materials such as catalysts. This study has been carried out in order to obtain particle size distribution of fine metal particles produced by the irradiation of silver nitrate aqueous solution.

When aqueous solution of silver nitrate (0.001 mol/l) was irradiated with γ -rays, solid precipitate was formed and no stable suspension was obtained. Stable suspension was formed by the irradiation of silver nitrate aqueous solution (0.001- 0.01 mol/l) containing vinyl pyrrolidone (0.01 mol/l) and ethyl

alcohol (0.03 mol/l). Dose rate and dose of the irradiation were 2.23 kGy/h and 1.2 - 18 kGy, respectively. Number of particles increased with increasing dose. Average diameter was about 10 nm upto 80 kGy and increased to about 50 nm above this dose. Number of particles increased with increasing concentration of silver ion. Average diameter of particles also increased with increasing concentration of silver ion, but seemed to reach constant value above 5 mmol/l. Absorption at 240 nm which is assigned to vinyl group of vinyl pyrrolindone decreased, and absorption at 400 nm which is assigned to aggregate of silver increased with dose. (M. Hatada, J. Takezaki, and Y. Nakase)

3. Structure of Fine Solid Particles from Metal Carbonyl Vapor by Irradiation of High Energy Radiation

Study has been carried out in an attempt to prepare fine particle from metal carbonyl by irradiation of high energy radiations, and of UV radiation for comparison. Three metal carbonyls $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8$ were used for the present study.

Metal particles obtained were subjected to particle shape observation, particle size analysis, XPS measurement (Fig. 3), thermogravimetric analysis, gas analysis during heating at constant rate (Fig. 4), and elemental analysis, and the results were comparatively examined.

It was found that the particles were of 100 nm of diameter, which were further recognized as aggregate of smaller particles of 20 - 30 nm diameter, the particles were metal oxides, and they released carbon dioxide and water on heating. These results indicate that the following chemical formulae may be assigned for these particles:

Carbonyls	Products	
	Electron beam irradiation	UV irradiation
$\text{Fe}(\text{CO})_5$	$\text{Fe}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$	$2\text{Fe}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$
$\text{Cr}(\text{CO})_6$	$\text{Cr}_2\text{O}_3 \cdot \text{CO}_2 \cdot 2\text{H}_2\text{O}$	$\text{Cr}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$
$\text{Co}_2(\text{CO})_8$	$\text{Co}_3\text{O}_4 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$	

Products obtained from $\text{Fe}(\text{CO})_5$ or $\text{Co}_2(\text{CO})_8$ can be reduced by heating in inactive gases. (Y. Nakase)

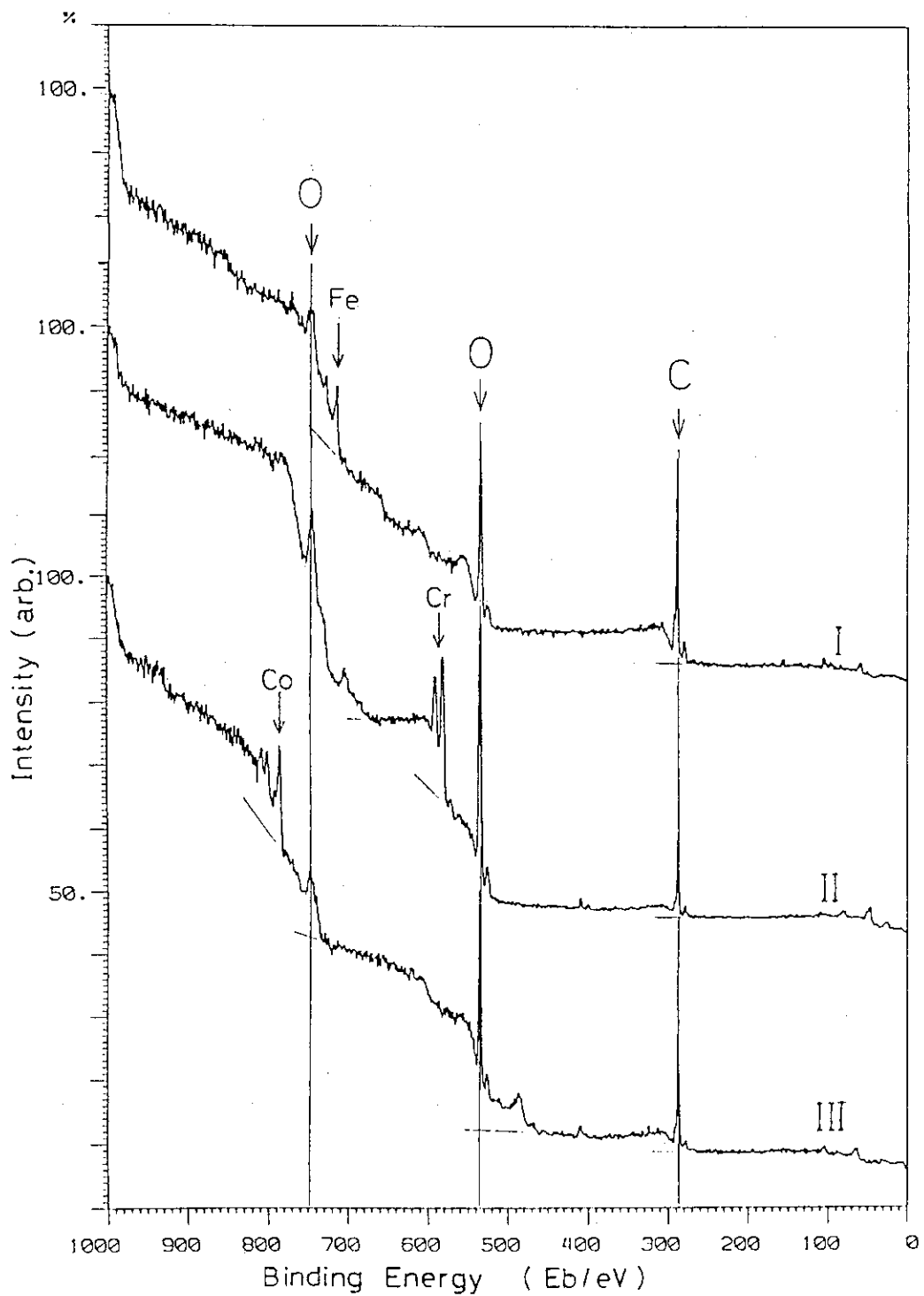


Fig. 3. X-ray photoelectron spectra of solid particles obtained from metal carbonyls by electron beam irradiation; Mg anode was used (360W, 12 kV).
I: Iron pentacarbonyl, II: Chromium hexacarbonyl, III: Cobalt octacarbonyl.

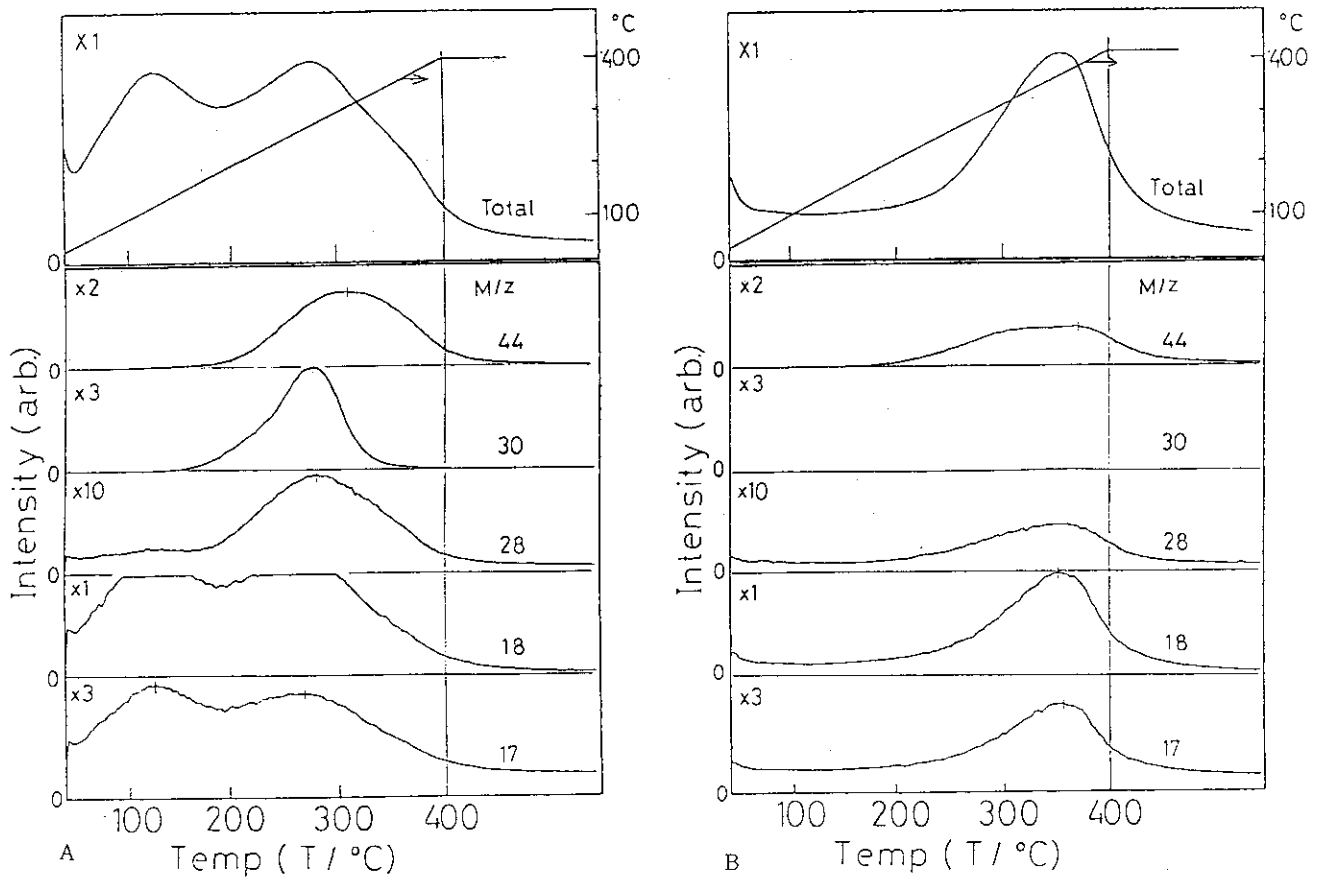


Fig.4. Mass spectral peak intensities from solid particles obtained from chromium hexacarbonyl as a function of temperature; Heating rate: 20 °C/min.
 A: Particles obtained by electron irradiation.
 B: Obtained by UV irradiation.

4. Polymerization of Spin-Casted Epoxy Films Induced by Electron Beam or UV Irradiations

Polymerization of spin-casted epoxy oligomer resin films was initiated by electron beam (EB) or UV irradiations and conversion to polymer was studied as a function of thickness of the film. Film thickness was varied from 1 to 25 μm .

In the EB irradiation, number of oligomer molecules reacted by 100 eV absorption (G-value) increased with increasing thickness up to 10 μm but did not depend on thickness above this value. In the UV irradiation, the G-value increased linearly with increasing film thickness. The result was explained by the difference of the penetrating power of the two radiations by detailed analysis of the data. The G-value and quantum yield of the polymerization were compared on the basis of the same unit of energy absorbed in the system, and it was found that EB is more sensitive than UV. Some anomalous polymerization behavior was observed for thin spin-casted films. (J. Takezaki, K. Matsuda, Y. Tanaka *, and I. Fujita *)

*Osaka Electrocommunication University

5. Electrical Properties of Multilayer Films Prepared by Chemical Absorption Technique

It is known that the monomolecular film prepared by chemical absorption method has more stable structure than that prepared by conventional Langmuir-Blodgett technique, because strong covalent bond (siloxane bond) was formed between molecules and substrate and between molecules.

Films of different number of 18-Nonadecenyltrichlorosilane (V-NTS) layers were built-up on a silicon wafer using the method previously reported. Thickness of the multilayer as measured by an ellipsometry and infrared absorption method increased with increasing cycle of the building-up cycles, but reached to an asymptote value at the later stage of the building-up process. This change of the layer thickness can be explained by two effects added up together: one, increase of layer thickness in the build-up cycle and the other, decrease of layer thickness due to decomposition of a part of the film substance during the irradiation processes.

For the multilayers from 1 through 5 layers, the current did not obey Ohmic rule, but obeyed the space limiting current law in the electric field between 5

$\times 10^6$ and 5×10^7 volt/m. For the multilayers from 10 through 40 layers, the current obeyed the ohmic law below 10^7 volt/m and above this value, obeyed the space limiting current law. The break off field was independent of number of layers. (N. Mino* , K. Ogawa* , and M. Hatada)

*Matsushita Electric Industries Co.

6. Radiation Crosslinking of Biopolymers

Crosslinking is an effective means for controlling the biodegradation rate of biomaterials, preventing rapid elution of the materials into wound fluids and increasing the tensile properties of the materials to the level where they can be handled or sutured conveniently. The purpose of the work is to learn the applicability of the radiation method for crosslinking of collagen- and gelatin-based biomaterials which may be used in surgery to prevent postoperative adhesion of damaged tissues. It should be mentioned that irradiation of these materials may simultaneously bring about their sterilization besides crosslinking.

Natural human amniotic and artificial membrane, prepared from physically gelled gelatin, were subjected to an electron beam from a Van de Graaff accelerator and γ -radiation from a ^{60}Co source. Their tensile strength and elongation at break, as well as swelling ratio, have been measured and compared with those of the chemically crosslinked materials.

The results of experiments demonstrated that the native human collagen membrane did not undergo significant deterioration in the range of dose to about 30 kGy, if access of oxygen during irradiation was avoided. No distinct difference in the mechanical properties has been found between the types of ionizing radiation for the amniotic membrane. Gelatin membranes could not acquire enough mechanical strength to be used as biomaterials by radiation crosslinking, although they became water-insoluble at 37°C . (K. Burczak * , ** , K. Tomihata * , Y. Ikada* , and M. Hatada)

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**Technical University of Lodz, Institute of Applied Radiation Chemistry, Poland

7. Photochemical Reaction of Maleic Acid Containing Hydrogen Peroxide--A

Direct Synthesis of Hydroxy Acids

Studies have been carried out on laser-induced photochemical reactions of maleic acid aqueous solution containing hydrogen peroxide in order to synthesize valuable compounds from raw chemical materials.

Aqueous solution of maleic acid (20 mmol, 54- 64 ml) was irradiated at room temperature in a Pyrex glass vessel equipped with a synthetic quartz window, during irradiation, 30% aqueous solution of hydrogen peroxide being added at 3.2 to 24.6 ml/h under constant agitation (500 r.p.m.) in nitrogen atmosphere. XeF laser beam (351 nm, 220 mJ/pulse; frequency, 16 Hz) was used for the irradiation. Products were subjected to gas chromatography and ion chromatography.

Glycolic acid, tartaric acid, and malic acid were found as main products. The yield of glycolic acid increased with increasing rate of hydrogen peroxide addition. The maximum yields of tartaric acid and malic acid were found at rate of hydrogen peroxide addition at 13 ml/h. At the rate of hydrogen peroxide addition of 13 ml/h and number of absorbed photons of 1×10^{20} , the amounts of glycolic acid, tartaric acid and malic acid formations were 13.5, 0.7, and 0.5 mmol and selectivity to total hydroxy acids formation was 77%. (Y. Shimizu, S. Sugimoto, M. Nishii, and N. Suzuki)

8. Surface Modification of Polytetrafluoroethylene by Excimer Laser Irradiation

(1) Photo-Sensitization of Aromatic polyester

Fluorine containing polymers have excellent thermal stability, strong chemical resistivity, and excellent electric properties, but adhesion to other material is difficult due to its inactive chemical nature, and therefore, development of a new chemical modification technique has been a target of many studies.

Study has been carried out on effect of laser beam irradiation on the surface chemical change and surface morphological change of polytetrafluoroethylene (PTFE) containing aromatic polyester which has strong thermal stability and absorption in UV region using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), in an attempt to develop a technique to modify inactive surface of PTFE by laser beam irradiation.

Examination of change of photoelectron spectrum of PTFE after laser beam

irradiation (fluence, 153 mJ/cm²/pulse; room temperature; in air) that little change was observed. However, the irradiation of the laser beam at the same condition on PTFE containing a small amount of aromatic polyester resulted removal of F atom, formation of carbonyl group, and carbonization, and at higher fluence, abrasion was observed. The marked change of surface chemical change observed can be explained by photo-sensitization; the photon energy absorbed by aromatic polymer was transferred to PTFE. (M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, T. Nagase * , M. Endo * , and Y. Hirajima *)

*Kurabo Industries, Ltd.

9. Surface Modification of Polytetrafluoroethylene by Excimer Laser Irradiation (2) Improvement of Adhesive Property by the Addition of Aromatic Polyester

Study has been carried out on whether the adhesive property of polytetrafluoroethylene (PTFE) film can be improved by laser irradiation of PTFE film containing total aromatic polymer. Adhesive property was evaluated by 180° peel strength between the irradiated film and stainless steel plate which had been adhered together using epoxy resin adhesive.

Peel strength did not change when the PTFE film was irradiated at room temperature by KrF laser beam (153 mJ/cm²/pulse, 53 mJ/cm²) in air. However, peel strength was markedly improved by the laser beam irradiation of the PTFE film containing 1-20% aromatic polymer, and simultaneously, wettability of the film was also improved. Peel strength was increased from 0.03 kg/25 mm to 9 kg/25 mm by 5% addition of total aromatic polymer. Peel strength also increased by increasing fluence above 50 mJ/cm²/pulse and reached 9 kg/25 mm at 130 mJ/cm². (M. Nishii, S. Sugimoto, N. Suzuki, T. Nagase * , M. Endo * , and Y. Hirajima *)

*Kurabo Industries, Ltd.

10. Change in Surface Chemical State of Polyethersulphone by Excimer Laser Irradiation (2)

Following the study carried out in the previous year on effect of oxygen on surface state change induced by laser beam irradiation on polyethersulphone

(PES), study has been carried out on effect of fluence of laser beam on the surface chemical change of PES using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

Contamination of PES film (Idemitsu Kousan Co., 100 μm) was removed by super sonic cleaning in ethanol. The film was irradiated with ArF (193 nm) and KrF (248 nm) laser beam in vacuum (10^{-7}Pa) and the change of surface chemical state was measured by XPS without exposing to air. Similar experiment was carried out in air.

Examination of change of XPS after laser beam irradiation revealed that the surface atomic ratio of O/C decreased with increasing fluence when the irradiation was carried out in vacuum. On the other hand, the ratio O/C increased with increasing fluence, reached maximum (0.30) at 5 $\text{mJ}/\text{cm}^2/\text{pulse}$, and then sharply decreased down to 0.08 at 20 $\text{mJ}/\text{cm}^2/\text{pulse}$ when the irradiation was carried out in air. Similar fluence effect was observed for KrF laser beam irradiation. The increase of O/C ratio observed at low fluence region in the ArF laser beam irradiation in air may be caused by the formation of oxide (C=O) by the reaction of oxygen in air. The sharp decrease of O/C at high fluence region is explained by loss of oxygen atoms by surface ablation which was further confirmed by SEM observation. (K. Ohnishi, S. Arai *, S. Sugimoto, M. Nishii, Y. Shimizu, and N. Suzuki)

*Kyoto Institute of Technology

11. Change in Surface Chemical State of Polyphenylenesulfide by Excimer Laser Irradiation

Studies have been carried out surface state change induced by laser irradiation on polyphenylenesulfide (PPS), which has a similar chemical structure to that of polyethersulphone using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

Examination of change of XPS spectrum after KrF laser beam irradiation revealed that the surface atomic ratio of O/C increased with increasing fluence, reached maximum (0.14) at 6 $\text{mJ}/\text{cm}^2/\text{pulse}$, and then decreased down to a constant value above 50 $\text{mJ}/\text{cm}^2/\text{pulse}$ when the irradiation was carried out in air. The surface atomic ratio of S/C decreased with increasing fluence, and reached a constant value above 50 $\text{mJ}/\text{cm}^2/\text{pulse}$. The ablation was observed at 30

mJ/cm²/pulse.

In the laser irradiation in vacuum, smaller change of O/C and S/C was observed compared to that observed in the irradiation in air. Ablation, which was observed above 40 mJ/cm²/pulse for PES, was not observed to occur by the irradiation even at 76 mJ/cm²/pulse, indicating that oxygen atoms in the polymer molecule has strong effect on laser ablation. (S. Sugimoto, M. Nishii, Y. Shimizu, N. Suzuki, K. Ohnishi, and S. Arai *)

*Kyoto Institute of Technology

V. LIST OF PUBLICATIONS

1. PUBLISHED PAPERS

(Apr. 1989 - Mar. 1990)

Y. Nakase, "Low Energy Ion Generator--Performance Results and Test Irradiation", JAERI-M 89-151 (1989).

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Y. Shimizu and S. Nagai, "Effects of Water Vapor on the Radiolysis of Methane over Molecular Sieve 5A", Radiat. Phys. Chem., 33, 567(1989).

Y. Shimizu, "Effects of Irradiation Temperature on the Radiolysis of Methane over Molecular Sieve 5A", Radiat. Phys. Chem., 34, 743(1989).

Y. Shimizu, S. Sugimoto, S. Kawanishi, and N. Suzuki, "Photo-induced Direct Synthesis of Formic Acid and Methyl Formate from Methanol in the Presence of Hydrogen Peroxide", Chem. Lett., 1539 (1989).

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Y. Shimizu, S. Sugimoto, S. Kawanishi, and N. Suzuki, "Photo-induced Organic Transformation. Selective Synthesis of Ethylene Glycol or Formic Acid and

Methyl Formate from Methanol in the Presence of Hydrogen Peroxide", Bull. Chem. Soc. Japan, 63, 97 (1990).

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3. PATENT APPLICATIONS

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VI. LIST OF SCIENTISTS
(Apr. 1, 1989 - Mar. 31, 1992)

[1] Staff Members

Motoyoshi HATADA	Dr., physical chemist, Director
Seizo OKAMURA	Professor emeritus, Kyoto University, Advisor Dr., polymer chemist
Nobutake SUZUKI	Dr., physical chemist
Kiyori NAKATO	Physicist (Nov. 1, 1991 -)
Yoshiaki NAKASE	Dr., polymer chemist
Kanako KAJI	Dr., polymer chemist (- Aug. 31, 1991)
Koji MATSUDA	Physicist (- Jun. 23, 1991)
Shunichi KAWANISHI	Dr., physicist (- Mar. 31, 1991)
Shun'ichi SUGIMOTO	Physical chemist
Jun'ichi TAKEZAKI	Physical chemist
Masanobu NISHII	Dr., polymer chemist (Apr. 1, 1991 -)
Yuichi SHIMIZU	Organic chemist

[2] Visiting Researchers

Choji KOHARA	Organic Chemist, Sanwa Kako Co., Ltd (Apr. 1, 1989 - Jul. 31, 1990)
Tang Beilin	Polymer Chemist, Institute of Atomic Energy, China (Mar. 27, 1990 - Sep. 31, 1990)
Katsuhiko OIKAWA	Organic Chemist, Gunze Corp. (Apr. 1, 1989 - Mar. 31, 1990)
Tomoyoshi SHIBATA	Organic Chemist, Sanwa Kako Co., Ltd (Aug. 1, 1990 -)
Qin Genmin	Physicist, South-west Center for Nuclear Engineering Research and Design, China (Nov. 26, 1990 - May. 25, 1991)

[3] Graduate Students

Yoshinobu IZUMI	Osaka University (Apr. 1, 1989 - Mar. 31, 1990)
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