VIII-II-1. Project Research

Project 5

PR5 Project Research on Material Science Using Short-Lived Nuclei and Radiations

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Objective and Participating Research Subjects

The main objectives of this project research are the investigation of the local properties of materials using short-lived radioactive nuclei and its related subjects, and the synthesis of new functional materials employing radiation from ^{60}Co.

Although in this first year the number of researches participating in the project was not many, we expect that it will much increase in the next two years, during which the research reactor will have come back.

The participating research subjects (PRS) in this period are as follows:

PRS-1 Observation of Local Field in Indium-Doped ZnO (Y. Ohkubo *et al.*).

PRS-2 Measurement of the Hyperfine Field in Four-Coordinate Complexes by the PAC Method Using ^{111}Cd Probe (A. Yokoyama *et al.*).

PRS-3 ^{57}Fe Mössbauer Studies on Lanthanum Iron Oxypnictide Superconductors (M. Seto *et al.*).

PRS-4 Micell Monolayers of Radiation-Prepared Graft Polysilanes (N. Sato *et al.*).

PRS-5 Gamma-Irradiation Effect on the Oxidative Thermal Degradation of Several Polymers (M. Minagawa *et al.*).

Main Results and Contents of This Report

Zinc oxide, a semiconductor with a relatively large band gap, has several favorable properties in materials science. W. Sato *et al.* (PRS-1) measured, using TDPAC technique with commercially-available radioactive ^{111}In, electric field gradients at ^{111}Cd arising from ^{111}In introduced in 0.05 and 0.5 at.% In-doped ZnO and undoped ZnO at various temperatures. Drastic differences between the latter two sets of the TDPAC spectra indicate that conduction electrons much produced with In doping avoid the ^{111}Cd probes. This hindrance is considered due to the formation of a local structure with In doping. Since each TDPAC spectrum for 0.05 at.% In-doped ZnO is a superposition of the other two at the corresponding temperature, this local structure must be unique.

I. Yamazaki *et al.* (PRS-2) measured the electric field gradient (EFG) at ^{111}Cd arising from ^{111}Ag incorporated in various four-coordinate complexes, the metal site of each being considered similar to that of mavicyanin, a protein molecule with a single metal site. Radioactive ^{111}Ag sources were produced at JRR-3 of Japan Atomic Energy Agency. They compared the EFG values with those obtained with different parent nuclei, ^{111}In, ^{111m}Cd, both decaying to the same ^{111}Cd as ^{111}Ag does, and also with the EFG data using ^{117}In probe arising from ^{117}Cd. For the same ligand, some EFG values agree among different parent nuclei. However, large disagreement is also seen in several cases.

Recently, iron-based oxypnictides LaFePO were found to exhibit superconductivity, although these compounds include a magnetic element Fe which had been considered to destroy superconductivity. The superconducting transition temperature has reached 55 K. The most concern issue is the superconducting mechanism. In order to examine whether ferromagnetism coexists with superconductivity on the microscopic scale, Y. Kobayashi *et al.* (PRS-3) measured ^{57}Fe-Mössbauer spectra for $La_{0.87}Ca_{0.13}FePO$ at 4.2 K under no magnetic field, 7 T, and 14 T. They found that the observed magnetic field at ^{57}Fe is essentially the same as the external field, and concluded that $La_{0.87}Ca_{0.13}FePO$ is paramagnetic.

Polysilanes, linear Si-catenated polymers, exhibit useful electronic and optical properties originating from the delocalization of Si-Si σ-electrons along the polymer main chain. It is difficult to synthesize polysilanes with reactive side chains using conventional preparation methods. N. Sato et al. (PRS-4) synthesized poly(methyl-*n*-propylsilane) grafted with poly (methyl acrylate) through ^{60}Co-γ-ray-induced grafting of methyl acrylate onto preformed poly(methyl-*n*-propylsilane), and then prepared micelle monolayers using this graft polysilane. With an atomic force microscope, they observed that polysilane micelle monolayers were formed at the air/water interface and were successfully transferred onto the quartz substrate.

From a practical point of view, it is important to study oxidative thermal degradation of polymers. First, M. Minagawa *et al.* (PRS-5) defined the degradation temperature (T_d) as the intersection between the base line and tangential line in the thermogravimetry curve for a polymer. Then, they compared the T_d's of two types of polymers, vinyl and condensation, obtained under the atmospheres of N_2, air, and O_2, and found that especially in the O_2 atmosphere, vinyl polymers are not stable while condensation polymers are relatively so. They also studied γ-ray-irradiation effects on T_d, and obtained an unexpected result that irradiated polycarbonate is resistant to oxidative degradation.

採択課題番号 20P5 短寿命核および放射線を用いた物質科学研究 プロジェクト
（京大・原子炉）大久保嘉高

PR5-1 Observation of Local Fields in Indium-Doped ZnO

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INTRODUCTION: Zinc oxide (ZnO) is an intrinsic *n*-type semiconductor having optoelectronic properties. For its wider industrial application as conduction-controlling devices, it is of great importance to study the relation between the conductivity and concentration of impurities doped. In the present work, we have synthesized indium-doped ZnO and observed conduction-electron behavior at the impurity sites by means of the time-differential perturbed angular correlation (TDPAC) method with the probe ^{111}Cd formed in the disintegration of ^{111}In. We here report the temperature dependence and dopant-concentration dependence of the density of conduction electrons at the probe nuclei.

EXPERIMENTS: For the synthesis of 0.5 and 0.05 at.% In-doped ZnO, stoichiometric amounts of $In(NO_3)_3 \cdot 3H_2O$ and ZnO powder were mixed in ethanol. The suspension was heated to dryness while being stirred. The In-doped and undoped ZnO powder samples were then separately pressed into each disc, and they were sintered in air. Commercially available ^{111}In HCl solution was added in droplets onto each of the discs. They again underwent heat treatment in air. TDPAC measurements were performed for the annealed samples at various temperatures for the probe ^{111}Cd($\leftarrow$^{111}In) on the 171-245 keV cascade γ rays with the intermediate state of I = 5/2 having a half-life of 85 ns.

RESULTS: Fig. 1 shows the TDPAC spectra of ^{111}Cd embedded in the ZnO samples, where dopant concentrations and measurement temperatures are indicated. The directional anisotropy on the ordinate, $A_{22}G_{22}(t)$, was deduced with the following simple operation:

$$A_{22}G_{22}(t)=\frac{2[N(\pi,t)-N(\pi/2,t)]}{N(\pi,t)+2N(\pi/2,t)}. \qquad (1)$$

Here, A_{22} denotes the angular correlation coefficient, $G_{22}(t)$ the time-differential perturbation factor as a function of the time interval, t, between the relevant cascade γ-ray emissions, and $N(\theta, t)$ the number of the coincidence events observed at an angle, θ. The oscillating patterns reflect typical electrostatic interactions between the probe nucleus and the surrounding charge distribution for I = 5/2. As has already been reported[1], there is obvious distinction in the frequencies of the spectra for the samples of different dopant concentrations. What is to be noted is that the spectra for the 0.05 at.% In-doped ZnO consist of a mixture of the components observed in those for the undoped and 0.5 at.% In-doped samples. This suggests that the local field at the ^{111}Cd nuclei does not gradually change along with the In concentration. Because it is considered that the ^{111}Cd atoms reside in substitutional Zn sites[1], the occurrence of another component may arise from some local structural change brought by In doping. Another remarkable observation is the temperature dependence of the amplitude of the TDPAC spectra for the In-doped samples. Spectral damping, which may be caused by the so-called aftereffect[1], is seen only for the component of high frequency at low temperature. That is, the access to the probe by conduction electrons is more difficult for the relevant site. For the understanding of this mechanism, the residence site of the probe for this component needs to be determined.

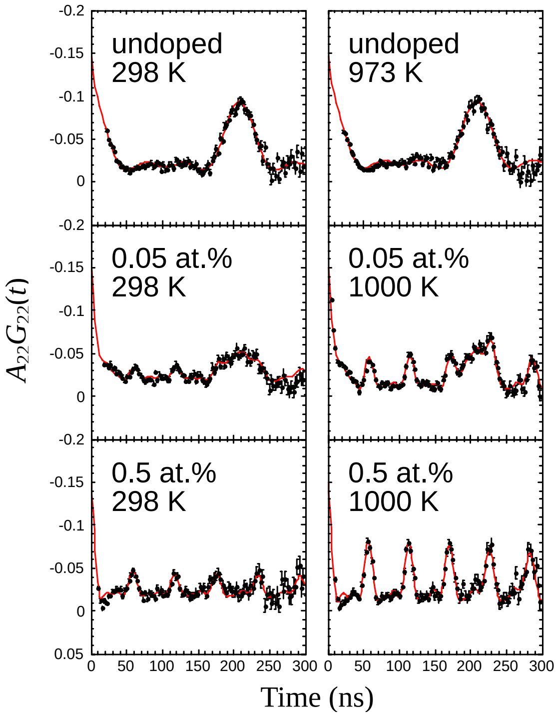

Fig. 1. TDPAC spectra of ^{111}Cd($\leftarrow$^{111}In) in ZnO doped with indium at different concentrations. Measurements were performed at the temperatures indicated.

REFERENCE:

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採択課題番号 20P5-1　　PACを用いた金属酸化物中の超微細場の測定　　プロジェクト
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PR5-2

Measurement of the Hyperfine Field in Four-Coordinate Complexes by the PAC Method Using ^{111}Cd Probe

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INTRODUCTION: The structure around the metal site of mavicyanin, a protein molecule with a single copper site, and those for four-coordinate chelate complexes having similar structures around their metal sites to that of the protein have been investigated by using time-differential perturbed angular correlation (PAC) of γ-rays from parent nuclei ^{117}Cd, ^{111m}Cd *etc.* [1-6]. In the present study, ^{111}Ag parent nuclei ($T_{1/2}$ = 7.47d) were introduced for similar measurements in order to compare with the previous results obtained with other PAC parent nuclei including ^{111m}Cd and ^{111}In decaying to the same PAC probe, namely ^{111}Cd as ^{111}Ag does. Therefore, it allows one to check the effects of the introduction processes of the probes into samples such as metal complexes containing the tracers.

EXPERIMENTS: The parent nuclei ^{111}Ag were obtained by irradiating metal foil of Pd of natural abundance with thermal neutrons at JRR-3 of Japan Atomic Energy Agency. The nuclei were produced via the ^{110}Pd(n, γ)^{111}Pd reaction followed by β^{-} decay of ^{111}Pd ($T_{1/2}$ = 23.4 min). The irradiated metal was let stand for 5 days for growth of the products of interest and disintegration of the by-products. Then, it was transported to Research Reactor Institute, Kyoto University and dissolved with Ag carrier to prepare for complexes with the ligands listed in Table 1, after chemical processes for isolation and purification of Ag. For the preparation of oxine and o-phenanthroline complexes, the tracer was added as it was in the Ag^{+} state or was oxidized to the Ag^{2+} state to some extent prior to the preparation.

The sample solutions obtained in the procedure above were analyzed by the PAC technique at room temperature.

RESULTS: Table 1 lists the electric field gradient values determined from the spectra, along with those for other parent probes of ^{111m}Cd, ^{111}In, and ^{117}Cd reported previously. The present field gradient values agree well among ^{111}Ag^{2+}, ^{111}In, and ^{111m}Cd data for oxine, but this is not always the case for the other data. Now we consider it necessary to check the chemical processes of introduction of the probe and analyze the prepared samples in detail.

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[3] A. Yokoyama *et al.*, KURRI Prog. Rep. **2004**, (2005) 60.
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[5] A. Yokoyama *et al.*, KURRI Prog. Rep. **2006**, (2007) 85.
[6] A. Yokoyama *et al.*, KURRI Prog. Rep. **2007**, (2008) 115.

Table 1. Electric field gradient values with uncertainties for four-coordinate complexes.

probe ligand	**$^{111}\mathrm{Ag}^{+}\rightarrow{}^{111}\mathrm{Cd}$**	**$^{111}\mathrm{Ag}^{2+}\rightarrow{}^{111}\mathrm{Cd}$**	$^{111}\mathrm{In}^{3+}\rightarrow{}^{111}\mathrm{Cd}$	$^{111m}\mathrm{Cd}^{2+}\rightarrow{}^{111}\mathrm{Cd}$	$^{117}\mathrm{Cd}^{2+}\rightarrow{}^{117}\mathrm{In}$
oxine	**1.37 (0.15)**	**0.85 (0.28)**	0.83 (0.05)*	0.84 (0.09)*	0.92 (0.04)*
DDC	**1.00 (0.33)**	—	0.72 (0.26)*	0.94 (0.15)*	0.85 (0.06)*
BPHA	**1.11 (0.40)**	—	—	0.33 (0.40)*	0.33 (0.25)*
quinaldic acid	**1.40 (0.13)**	—	—	—	0.78 (0.03)*
o-phenanthroline	2.15 (0.25)*	**1.45 (0.15)**	—	—	—

*from the references

採択課題番号 20P5-2　　ガンマ線摂動角相関法による銅タンパク活性位　　　　プロジェクト
の動的挙動の研究
（金沢大院･自然科学）横山明彦、山﨑逸郎、鈴木大介、荒木幹生、南里朋洋、浅野敦史
（金沢大・理）西尾正樹（阪大院・理）佐藤　渉（京大・原子炉）高宮幸一、大久保嘉高

PR5-3 ^{57}Fe Mössbauer Studies on Lanthanum Iron Oxypnictide Superconductors

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Introduction : It was recently discovered by Y. Kamihara *et al* that iron-based oxypnictides LaFePO exhibit superconductivity [1]. Ca-doping and F-doping have been performed and adequately-doped samples show increases in superconducting transition temperature (T_c). In addition, replacing La with other rare earth elements raises T_c, and the highest T_c reaches 55 K in $SmFeAsO_{1-x}F_x$ [2]. This new series of superconductors is very interesting, because they contain a magnetic element, Fe, which is thought to destroy the superconductivity. To elucidate the superconducting mechanism, we studied their magnetic properties using Mössbauer spectroscopy under an external magnetic field up to 14 T [3].

Experimental Procedure : A $La_{0.87}Ca_{0.13}FePO$ sample was prepared at Frontier Research Center, Tokyo Institute of Technology [4]. LaFePO was synthesized by heating a mixture of LaP, FeP, Fe_2P and dehydrated La_2O_3. Ca-doping was performed by adding a mixture of CaO and LaP to the starting material. The T_c value was determined to be 5.4 K from an electrical resistivity measurement. For the Mössbauer measurement, we used a superconducting solenoid (Spectromag SM2000M-16 by Oxford Instruments) to cool the sample and to apply an external magnetic field. The solenoid and the samples were cooled by liquid He. The direction of the external magnetic field was parallel to that of the Mössbauer γ-ray. The velocity scale of each spectrum was calibrated using an α-Fe foil and referenced to it.

Results and Discussion : Fig. 1 shows the ^{57}Fe Mössbauer spectra of $La_{0.87}Ca_{0.13}FePO$ at 4.2 K. Without external magnetic field (fig. 1(a)), extremely small quadrupole splitting doublet pattern was observed. This result shows the electronic structures of Fe atoms in this superconductor are almost isotropic. The spectrum shape did not change between above and below T_c (not shown in the figure).

The Mössbauer spectra measured with external magnetic fields show 4-line spectra (Figs. 1(b) and 1(c)). These 4-lines spectra are due to the suppression of the 2nd and 5th peaks of magnetically split sextet. This result shows that the observed magnetic fields at Fe nuclei are parallel to the γ-ray direction, which is parallel to the direction of the external magnetic field. The observed values of the magnetic fields at the Fe nuclei coincide with the corresponding external magnetic fields within the experimental error. Therefore, the observed magnetic fields are due to the external magnetic fields, and no contribution of magnetic fields from local magnetic moments on the Fe atoms. These results show that the magnetic feature of the $La_{0.87}Ca_{0.13}FePO$ is most likely to be paramagnetism.

Conclusion : We have performed ^{57}Fe Mössbauer spectroscopic study on iron-based layered superconductor $La_{0.87}Ca_{0.13}FePO$ under external magnetic fields and found that the observed magnetic fields agree with the external magnetic field. Our results revealed that the hyperfine fields induced by the local magnetic moments are extremely small. Moreover, it was revealed that the conduction Fe atoms are most likely to exhibit paramagnetism with itinerant electrons. The magnetic order does not coexist with the superconductivity.

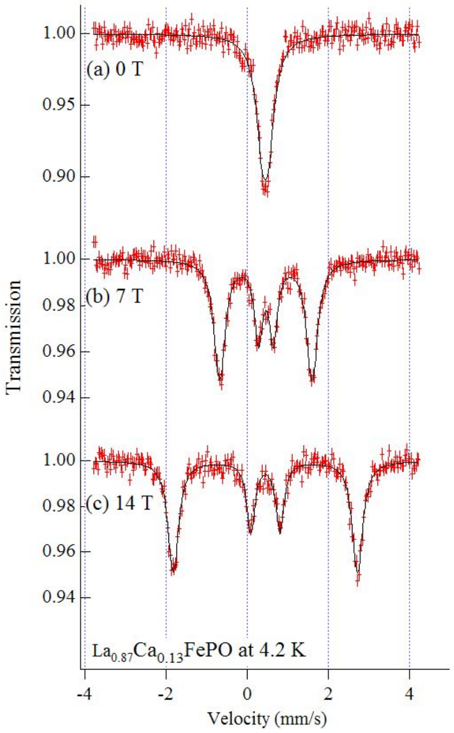

Fig. 1. ^{57}Fe Mössbauer spectra of $La_{0.87}Ca_{0.13}FePO$ at 4.2 K (a) without and under magnetic fields of (b) 7 T and (c) 14 T.

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採択課題番号 20P5-3 メスバウアー分光法によるナノ物質化学研究 プロジェクト
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PR5-4 Micelle Monolayers of Raditation-Prepared Graft Polysilanes

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INTRODUCTION: Polysilanes have unique optical and electronic properties due to the σ-conjugated structure of their main chain. We have been studying polysilanes aiming at fabricating novel functional materials. Radiation-induced functionalization is a key concept of our study for developing such functional polymers. γ-Rays can generate reactive species in materials even without any additives or catalysts. Therefore the synthesis of polysilanes with reactive side chains, which is difficult to prepare via severe Wurtz-type coupling reaction using sodium metal, becomes possible through radiation-induced chemical modification of preformed polysilanes. While our former studies have focused on primary structure of functional polysilanes, supramolecular structure of polysilanes is another attracting theme for developing functional polysilanes. Amphiphilic polysilanes prepared by radiation-induced grafting was revealed to form monolayers at the air/water interface. This class of polymer also forms micelles in selective solvents. From the above facts, it is reasonable to consider that monolayers of polysilane micelles can be formed at the air/water interface by use of this type of radiation-prepared polysilanes. In this view, we investigated monolayer formation of micelles of poly(methyl-*n*-propylsilane) (PMPrS) grafted with poly(methyl acrylate) (PMA). Here, we report interfacial behavior of PMA-grafted PMPrS micelle monolayers and the atomic force microscopy (AFM) observation of this monolayer.

EXPERIMENTS: PMPrS was synthesized by the conventional Wurtz-type coupling reaction of dichlorosilane. PMA-grafted PMPrS was prepared through γ-ray-induced grafting of methyl acrylate onto PMPrS. PMA-grafted PMPrS (grafting yield 0.33) was first dissolved in benzene and then acetone was added to the benzene solution to give polysilane micelles. This micelle solution was dropped onto the surface of pure water to form monolayers. The monolayers were transferred onto a quartz substrate by the vertical dipping method. Surface morphology of the transferred monolayers was observed by AFM.

RESULTS: Surface pressure (π) – Area (A) isotherms measured with two different content solutions indicate the structural difference of formed monolayers. When the solution with a ratio of benzene/acetone 50/50 is spread onto water, the π-A isotherms shows a more condensed profile compared with the case of the pure benzene solution. It was found from another experiment that this graft polymer forms micelles in the 50/50 benzene/acetone solution while it is molecularly dispersed in the pure benzene solution. Therefore the π-A isotherm result indicates that the PMA-grafted PMPrS is spread at the interface keeping micelle structure and thus occupies smaller area than the isolated polymer.

AFM images of the transferred monolayer prepared from the 50/50 benzene/acetone solution are shown in Fig. 1. When the micelle monolayer is transferred at the surface pressure of 5 mN/m, small granules are observed (top) which is absent for the molecular monolayer. This clearly shows the micelles are successfully transferred onto the quartz substrate. At the higher surface pressure (10 mN/m), the transferred monolayer shows larger granular morphology (bottom). In this case, the monolayer structure is partly collapsed and the large three-dimensional aggregation structure is formed. Thus it is required to apply moderate surface pressure in order to obtain micelle monolayers. The relatively low surface pressure to maintain micelle monolayer structure indicates instability of micelle assembly. Radiation-crosslinking of outer shells of the micelles is planned to improve the monolayer stability.

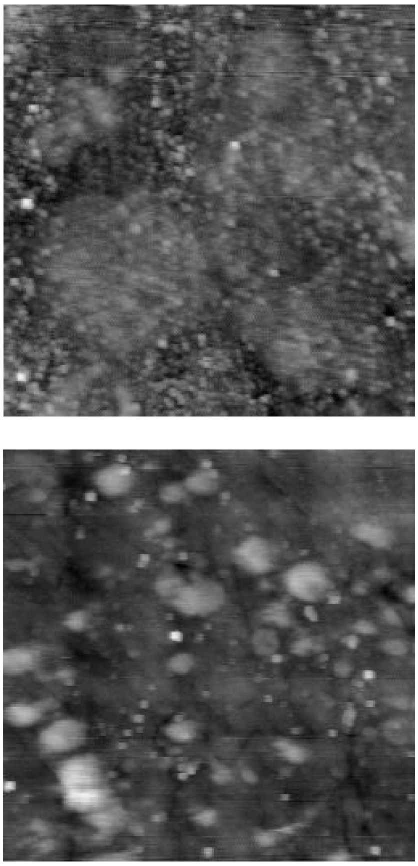

Fig. 1. AFM images of PMA-grafted PMPrS micelle monolayers. Surface pressure at the monolayer transfer is 5 mN/m (top) and 10 mN/m (bottom). The size of the images is 10 μm × 10 μm.

採択課題番号 20P5-4　　γ線誘起プロセスによる機能性高分子の開発　　プロジェクト
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PR5-5

Gamma-Irradiation Effect on the Oxidative Thermal Degradation of Several Polymers

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INTRODUCTION: Oxidative thermal degradation of polymers is quite important from a practical point of view. No new characterization method has ever been presented. We have developed quite a new type of characterization method. Here the effect of gamma-irradiation on the thermal properties was studied.

EXPERIMENTS: A Rigaku Thermoflex TG/DTA (Thermogravimetry/Differential Thermal Analysis) instrument (micro-type), which enables simultaneous measurements of weight loss and thermo-balance, was used. Typical heating conditions were as follows: sample weight, 5 mg; heating rate, 5–40°C/min; atmosphere, under N_2, in air, and under O_2 stream (20ml/min).

RESULTS: Degradation temperature (T_d) is strongly affected by such factors as the amount of sample, heating rate, and the kind of atmosphere. Under strictly controlled conditions, however, we can obtain significant information on the degradation.

Zone-representation was employed. The T_d is defined as the cross-over-point between the base line and the tangential line in the TG curve. Degradation zone is drawn by the temperature interval between a start and a finish of the degradation.

Fig. 1 shows the comparison of T_d between vinyl and condensation type of polymers. Under an inert atmosphere, both showed good thermal properties. Under an oxidative condition, however, they had quite different results. Condensation polymers were relatively stable, whereas vinyl polymers were not. The latter was easily decomposed under strongly oxidized conditions.

Fig. 2 shows the effect of gamma-irradiation on PC. After the irradiation, the sample became stable toward the oxidative reaction. The degradation was rather restrained in this polymer. This result is quite interesting. This is because under ordinary conditions, gamma-irradiation generally causes chain scission reaction, and the degradation of the irradiated sample is highly accelerated. But the result was quite opposite. The degradation was rather prohibited. This interesting reaction mechanism is now under investigation. It is expected that some kind of cross-linking reaction and the like may have prevailed in this case.

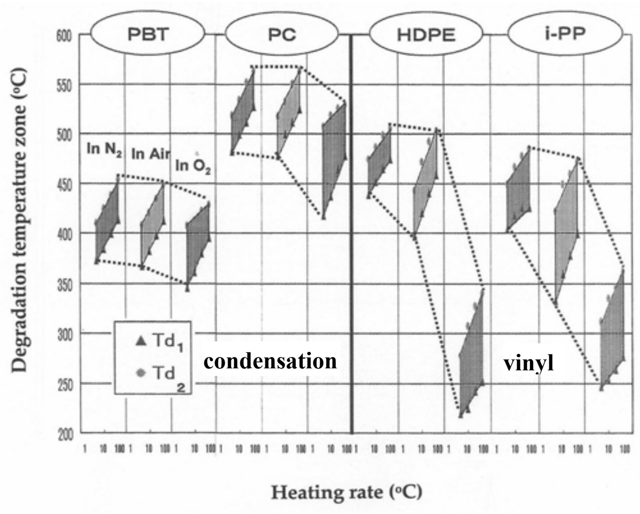

Fig. 1. Comparison of T_d between vinyl and condensation type of polymers.
PBT: polybutylene terephtalate; PC: polycarbonate
HDPE: high density polyethylene; i-PP: isotactic polypropylene

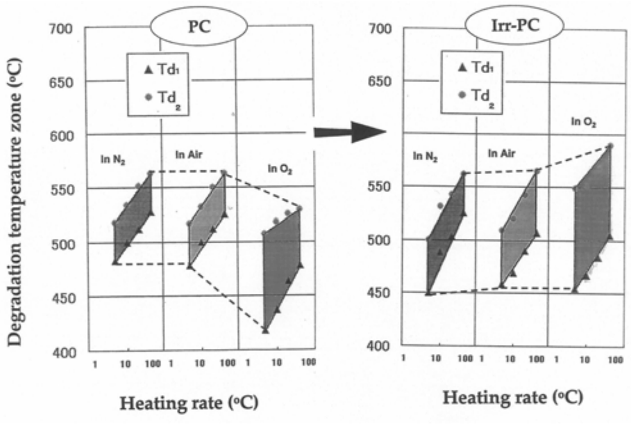

Fig. 2. Effect of gamma–irradiation on T_d.

採択課題番号 20P5-5　ガンマ線照射による縮合ポリアミド・ポリエステル類の　　　プロジェクト
強酸化雰囲気下における耐熱性の向上
（山形大工）皆川雅朗、佐藤昴史（京大・原子炉）佐藤信浩