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INTRODUCTION: We have previously reported that the property of structure change in a cyclic monoamide resin consisting of poly-*N*-vinyl- ϵ -caprolactam (VEC) with a 7-membered ring by γ -ray irradiation in HNO_3 is different from that in polyvinylpyrrolidone (PVPP), another cyclic monoamide resin with a 5-membered ring[1]. Namely, while relatively stable plural neighboring C=O groups (structure (a) in Fig. 1) were introduced for PVPP[2], such neighboring C=O groups were not observed for VEC. In this study, to clarify the more detailed degradation property of VEC, other irradiated samples were prepared and analyzed. Water-soluble *N*-methyl- ϵ -caprolactam (MEC) was also irradiated in HNO_3 to evaluate the stability of VEC quantitatively.

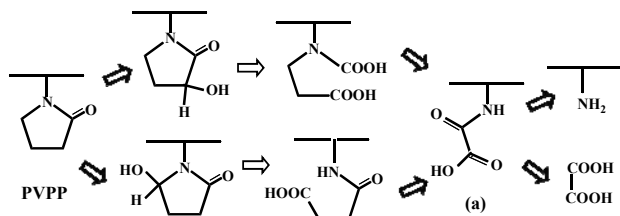


Fig. 1. Expected major route of change in chemical structure of PVPP by γ -ray irradiation in HNO_3 [2].

EXPERIMENTS: γ -Ray irradiation to VEC was carried out similarly to the earlier study (max. 1.5 MGy)[1]. For the sample of MEC, a solution containing 1 mol/dm³ (= M) MEC and 6 M HNO_3 was prepared. The sample solution was put in a Pyrex tube and irradiated by the ⁶⁰Co source at max. 8.8 kGy/h up to 2.1 MGy at room temperature under ambient atmosphere. Irradiated samples were analyzed by ¹H and ¹³C NMR. DMSO-d₆ containing a known weight of TMS which is a standard material was used as the NMR solvent. The residual ratio of MEC was calculated by the area ratio of each signal with that of TMS.

RESULTS: A crystal was observed from the supernatant obtained from the irradiated VEC. The crystal was identified as succinic acid by ¹³C NMR analysis. The structure change in VEC is expected from the result as shown in Fig. 2, which suggests that the major route of change in chemical structure of VEC is basically identical to that of PVPP and that the resulting dicarboxylic acids differ corresponding to the number of carbon in the cyclic monoamides. The scheme is consistent with the above-mentioned fact that plural neighboring C=O groups were not observed for VEC. These facts also imply that a

5-membered ring would be necessary to obtain plural neighboring C=O groups under the present irradiation condition.

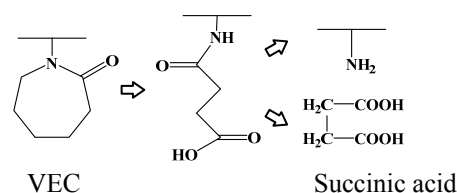


Fig. 2. Expected major route of change in chemical structure of VEC by γ -ray irradiation in HNO_3

In a ¹H NMR spectrum, neat MEC showed four signals; (A)3.4, (B)2.9, (C)2.4, (D)1.6 ppm, respectively. The calculated residual ratios are shown in Fig. 3 together with the relationship between the position of hydrogen in the structure of MEC and that of the signal. The residual ratios calculated from (A), (B) and (D) show a nearly identical trend, where the residual ratios decrease linearly with an increase in dose, and ca. 50 % and 75 % are decomposed at 1 and 2 MGy, respectively. On the other hand, the residual ratio calculated from (C) is found higher than the three other systems, which would be because the signal (C) overlaps with that of degraded compounds. The dependence of residual ratio of *N*-butylpyrrolidone (NBP), one of the water-soluble 5-membered rings, under the irradiation in 6 M HNO_3 on dose is difference from that of MEC. Namely, the decrease in the residual ratio of NBP decreased steeply and then gently[3]. As the result, comparing the stability of MEC with that of NBP, the residual ratio of MEC is higher than that of NBP at less than ca. 0.6 MGy, and vice versa at more than 0.6 MGy.

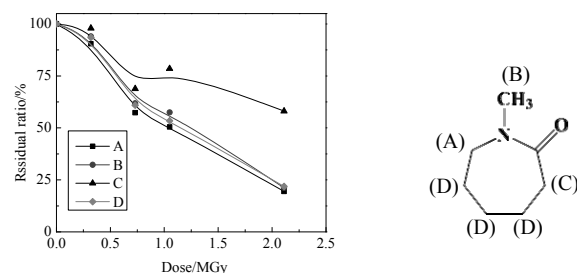


Fig.3. Dependence of residual ratio of MEC on dose.

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INTRODUCTION: The first excited state of ^{229}Th lies in extremely low energy level. The excitation energy was reported to be 7.8 ± 0.5 eV [1]. This energy corresponds to vacuum ultraviolet light, and it is expected that the decay rate of $^{229\text{m}}\text{Th}$ varies drastically depending on their chemical forms [2]. Furthermore, chemical conditions can affect the decay mode of $^{229\text{m}}\text{Th}$ (internal conversion and/or gamma ray transition). It is also expected that $^{229\text{m}}\text{Th}$ can be applied to a nuclear clock which has about two orders higher precision than the most precise optical clock [3]. Hence, many studies have been performed to observe the decay of $^{229\text{m}}\text{Th}$, especially on photon detection. However, there are not clear results directly observing the decay. It is important to observe the photons emitted from the $^{229\text{m}}\text{Th}$ on various chemical conditions to understand the decay property of the state.

This report describes the results of photon detection for the several samples containing $^{229\text{m}}\text{Th}$ with different chemical forms: hydroxide and fluoride.

EXPERIMENTS: Thorium-229m was separated from the mother nuclide ^{233}U by using anion-exchange method. About 200 mg of ^{233}U , containing less than 1 ppm of ^{232}U , was adsorbed on the anion-exchange resin (Dowex 1×8, 200-400 mesh, 2.5 mL). Five-milliliters of 9 M HCl solution was poured into the column several times to remove $^{229\text{m}}\text{Th}$ and the daughter nuclides. After $^{229\text{m}}\text{Th}$ was grown in the column for a certain time: about 2 or 13 h, 5 mL of 9 M HCl solution was passed through the column to elute $^{229\text{m}}\text{Th}$. To prepare the hydroxide samples, 20 μL aliquot of samarium standard solution was added and then aqueous NH_3 was added to the eluent until the solution became basic. When the fluoride samples were prepared, 30 μL aliquot of samarium standard solution and 2 mL of HF solution were added to the eluent and the solution was stirred for 2 min. Thorium-229m was coprecipitated with samarium as hydroxide or fluoride form. Each precipitate was collected on a polypropylene-exchange and heated to dryness.

Setup for photon detection is schematically illustrated in Fig. 1. To measure vacuum ultraviolet ray from $^{229\text{m}}\text{Th}$ samples, we used a photomultiplier tube (PMT) for photon counting, Hamamatsu R6837, which detects 4-10 eV photons with higher than 10 percent quantum efficiency. Signals from PMT were amplified with the pre-AMP and PM-AMP. Noise was cut with the discriminator, and the signal data were accumulated in the multichannel analyzer.

RESULTS: In the case of the hydroxide and fluoride samples of $^{229\text{m}}\text{Th}$ grown for about 2 h, the count rates of photons were almost the same with those of the background. In contrast, for the $^{229\text{m}}\text{Th}$ samples grown for about 13 h, the photon emissions decaying for time were detected and the half-lives were about 1 h for hydroxide and 3 h for fluoride. For example, the result for the $^{229\text{m}}\text{ThF}_4$ sample grown for about 13 h is shown in Fig. 2. These decaying photon emissions, however, did not seem to be the simple decay curve. In addition, if the half-lives of $^{229\text{m}}\text{Th}$ were several hours, the photon emissions are expected to be observed for the samples grown for 2 h. Therefore, these photons might derive from the Cherenkov radiation induced by the decay of daughter nuclides such as Bi or Pb. To clarify the origin of these photons, we plan to purify $^{229\text{m}}\text{Th}$ before measurement.

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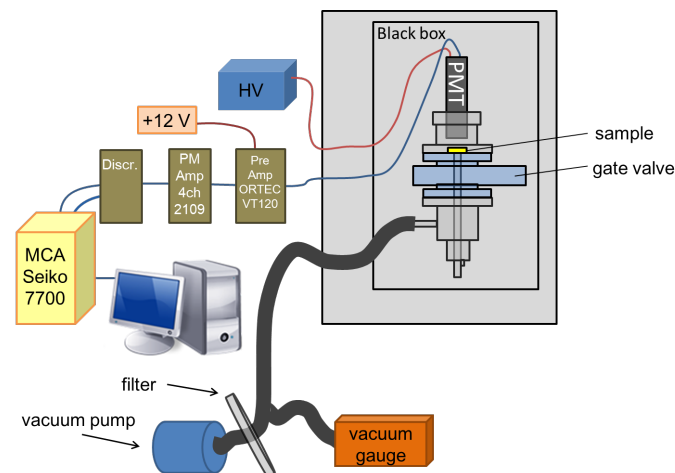


Fig. 1. Schematics of the experimental setup for photon detection.

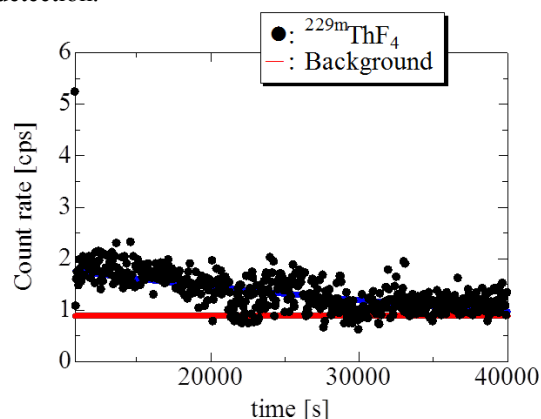


Fig. 2. Count rate of photons for the $^{229\text{m}}\text{ThF}_4$ sample grown for about 13 h.