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Notes

Investigation of the Reactions of the OH Radical with Poly(acrylic acid) and Poly(methacrylic acid) in Aqueous Solution Using the Tb^{3+} Fluorescence Probe

H. Nishide,[†] M. D. Cho, T. Kaku, and Y. Okamoto*

Department of Chemistry and Polymer Research Institute,
Polytechnic University,
6 Metrotech, Brooklyn, New York 11201

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Introduction

Fluorescence properties of lanthanide ions are extremely sensitive to their coordinate environment.[1] These metal ions, particularly Eu^{3+} and Tb^{3+}, have been used as fluorescence probes to study ionomer structures[2–4] and ion bonding properties of synthetic polyelectrolytes.[5–11] Although the fluorescence intensities of the ions are quite weak in aqueous solution due to efficient fluorescence quenching by coordinated water molecules, the intensity is enhanced by replacement of the coordinated water with polycarboxylate ligands. The enhanced fluorescence spectrum is also strongly affected by the chemical structure of the polymers to which the ions are bound, because a chromophore residue in the polymer contributes to the intracomplex transfer of absorbed energy to the ion and results in the enhancement of the specific fluorescence peak intensities.

There are numerous investigations of effects of ^{60}Co γ irradiation on polymers in the solid state.[12] However, there has been little investigation of the γ irradiation effect of water soluble polymers which leads to chain degradation or scission of the polymers.[13] Behzadi and Schnabel reported that the reactivity of OH radicals generated in water by γ-ray irradiation with water soluble polymers depended on the molecular weight and conformation. However, the reaction mechanism, such as the formation of terminal groups produced in the chain scission, has received little attention. Therefore, we initiated an investigation of the reaction of OH radicals generated by γ-ray irradiation of an aqueous solution of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) using Tb^{3+} as a fluorescence probe.

Experimental Section

PAA was prepared by radical polymerization (MW = 2.5×10^5). PMA (MW = 3.2×10^5) and terbium chloride ($TbCl_3 \cdot 6H_2O$) were purchased from Polyscience Inc. and Research Chemicals, respectively.

The PAA–Tb^{3+} and PMA–Tb^{3+} aqueous solutions were prepared by slowly adding the $TbCl_3$ solution to the PAA and PMA solutions ([Tb] = 2 mM, [carboxylate]/[Tb] = 10). The pH of the solution was adjusted by adding aqueous NaOH. It is important to maintain the low ionic strength (μ) of our solutions, because a high μ leads to counterion condensation.

Emission and excitation spectra were measured on a fluorescence spectrometer (Perkin-Elmer MPF-4). The UV absorption spectrum was taken with a Carry 2300 spectrometer. The viscosity of the solution was measured at 30 °C using an Ubelohde viscometer.

OH radicals were generated by radiolysis of water. The aqueous solution was saturated with N_2O gas and was irradiated in a glass syringe using a ^{60}Co γ-ray source at Brookhaven National Laboratory, Upton, NY. The dose rate employed was 7.4×10^2 rad min^{-1}, as determined by the ferrous sulfate dosimeter. The irradiation was performed at room temperature.

Results and Discussion

OH radicals are produced by γ-ray radiolysis of water. In radiolysis of a solution the energy is absorbed mainly by water, and so the initial products, i.e, radical species, are characteristic of the medium and not the solutes, i.e, polyelectrolytes and lanthanide ions. It has been established that water saturated with N_2O preferentially forms OH radicals (90% of the radical species) during radiolysis.[14]

Figure 1 shows the fluorescence of the PAA–Tb^{3+} solution: An excitation peak appears at 310 nm and the emission peak at 545 nm after the complexation of Tb^{3+} with PAA. We found that the fluorescence spectra of the PAA–Tb^{3+} solutuion were greatly enhanced through γ-ray irradiation of the solution, as shown in Figure 1b,c. Figure 2 shows the plot of the enhanced fluorescence intensity of the PAA–Tb^{3+} solution against the γ-ray irradiation time proportional to the concentration of OH radicals generated in the solution. An approximately linear relationship was observed for the PAA–Tb^{3+} solutions in the Tb concentration range of 0.01–2 mM, and this tendency was also observed for the solution prepared by adding the Tb^{3+} ion to the irradiated PAA solution. When the irradiated solution was allowed to stand at room temperature, the enhanced fluorescence decreased very slowly (half-reduction time ca. 11 days). However, it was reduced to the intensity at preirradiation after heating the solution for 1 h at 80 °C. This may be due to the oxidation of the residual β-ketone carboxylic acid.

A logarithmic plot of the enhanced fluorescence intensity and the Tb concentration for the PAA–Tb solution ([PAA] = 0.1 mM) is linear (Figure 3). This shows that the fluorescence spectra of Tb^{3+} in this system can be detected at a Tb^{3+} concentration as low as 10^{-6} M. The Tb^{3+} ion forms a very stable complex with PAA.

The different conformation behaviors of PAA and PMA solutions upon their ionization are well documented.[15,16] However, a fluorescence enhancement by irradiation for a PMA solution at a pH from 7 to 11 was not observed, while we confirmed a highly extended conformation of PMA at pH 7.5 by viscometry. It is well-known that γ-ray radiolysis causes chain degradation of polymers. Figure 4 shows the decrease in solution viscosity or molecular weight of PAA and PMA on γ-ray irradiation. The progress of the chain scission was similar for both polymers. The number of chain scissions for PAA and PMA could be porportional to the number of OH radicals formed by the radiolysis. For example, the molecular weight of PAA was reduced ca. by a factor of 5 after 10 min of irradiation. Substituting this value with [PAA] = 20 mM yields $\sim 10^{-5}$

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* To whom correspondence should be addressed.

[†] Visiting professor from Waseda University Tokyo 169, Japan, Spring, 1992.

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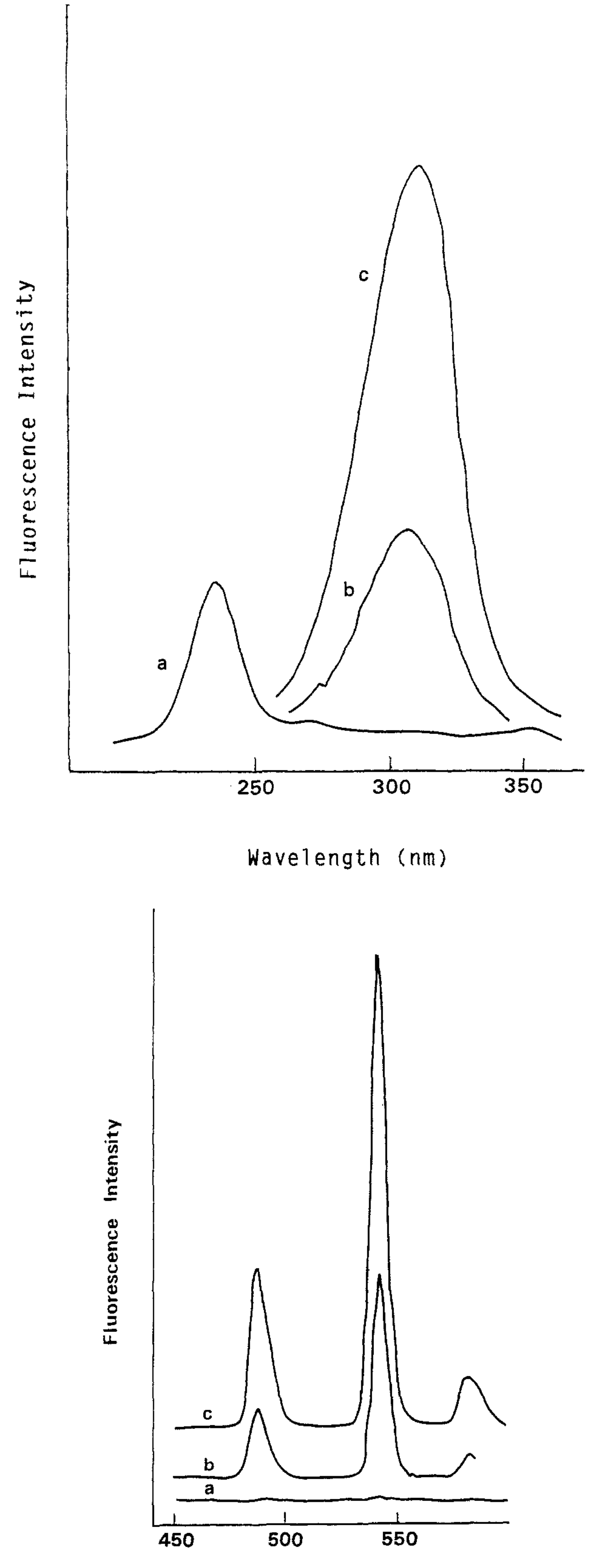


Figure 1. Excitation (A, top) and emission (B, bottom) spectra of PAA–Tb^{3+} in aqueous solutions before and after γ irradiation. $[Tb^{3+}]$ = 2 mM, [PAA] = 20 mM, pH = 10.5, λ_{em} = 545 nm, and λ_{ex} = 310 nm for Tb^{3+}. Irradiation time: (a) 0 min; (b) 2 min; (c) 8 min. The intensity scale is arbitrary.

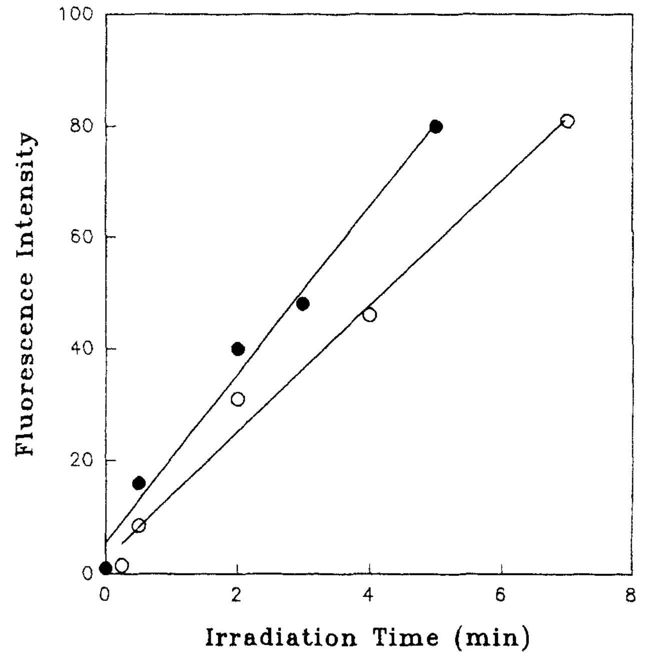


Figure 2. Fluorescence intensity of the PAA–Tb^{3+} solution after γ irradiation. Emission intensity at 545 nm by the excitation at 310 nm. Key: (○) PAA–Tb solution ([Tb] = 2 mM, [PAA]/[Tb] = 10, pH = 10.5); (●) irradiated PAA solution and added Tb^{3+} ion.

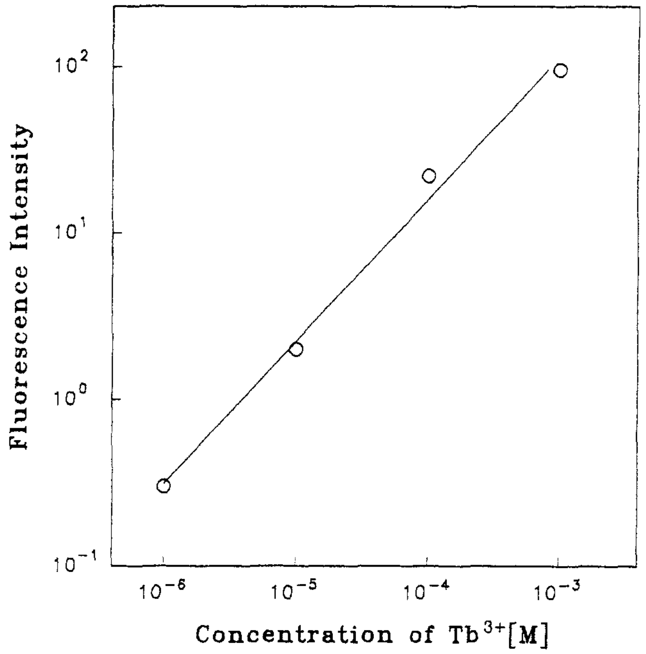


Figure 3. Effect of Tb^{3+} concentration on the fluorescence intensity. Tb^{3+} was added into the irradiated (8 min) PAA solution, pH = 10.5 and [PAA] = 10 mM.

M as the concentration of the terminal groups produced by the irradiation.

UV spectra of the PAA solution before and after the irradiation are shown in Figure 5. After the irradiation, a broad band appeared at 280 nm, which is attributed to the carbonyl group. Its intensity increases with the irradiation time (Figure 5). No UV peaks corresponding to this region were observed for the irradiated PMA solutions. PAA and PMA structures differ in the presence of a tertiary hydrogen at the α-position of the carboxylic groups in the PAA chain. The OH radical is known to attack predominantly tertiary hydrogen atoms.[17] Therefore, we assume that the OH radical generated by the γ irradiation of aqueous PAA solution abstracts the α-hydrogen atom from the PAA chain and produces a carbonyl group at the end of the cleaved polymer chain (Scheme I).

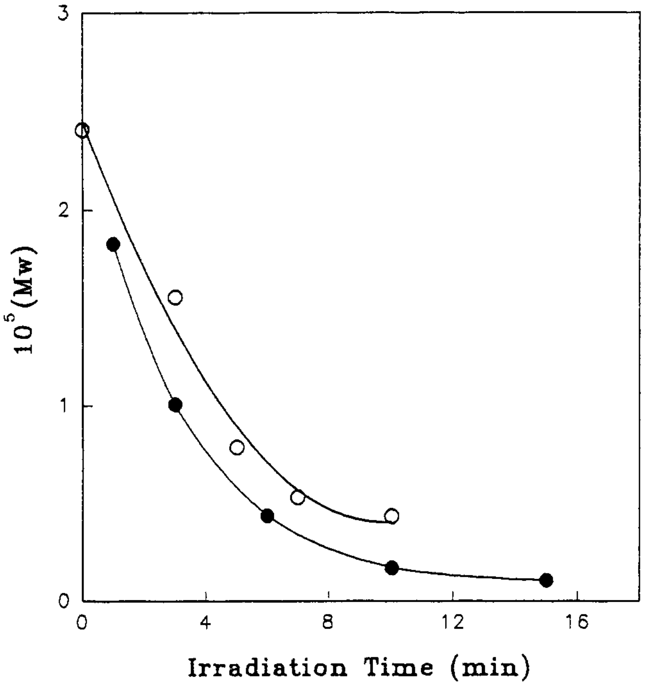


Figure 4. Molecular weights (MW) of PAA and PMA after γ irradiation in aqueous solutions: (○) PAA; (●) PMA.

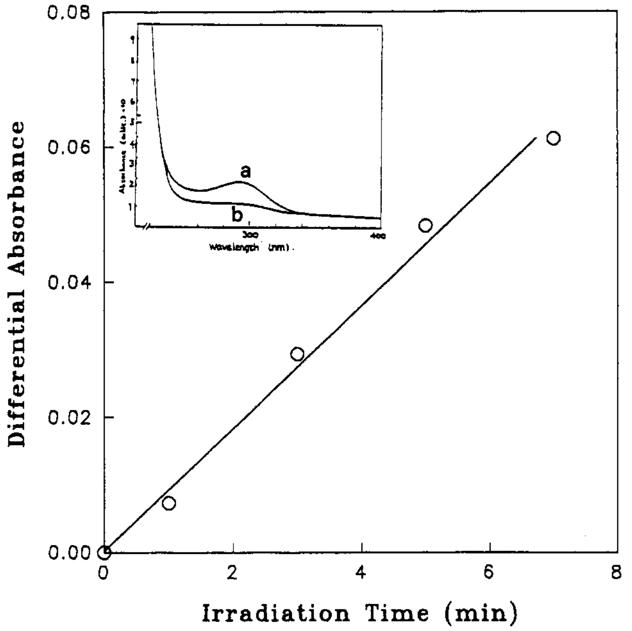
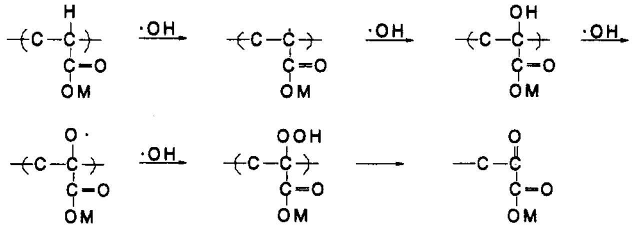


Figure 5. UV absorption spectra of the PAA solution before (a) and after (b) the γ irradiation (top left) and the absorption change with the irradiation time. [PAA] = 20 mM.

We have reported previously that the fluorescence of the Tb^{3+} ion is sensitized by the complexation with carboxylic acid compounds attached to a ketone or aldehyde moiety such as acetone dicarboxylic acid and succinic semialdehyde, and we observed a nonradiative energy transfer to the Tb^{3+} ion.[18] Thus, it is presumed that the energy absorbed by the chromophore moiety produced in the PAA solution by the reaction with OH radicals is transferred to Tb^{3+} ions, resulting in an increase of their fluorescence intensities. Such a chromophore was not produced by the irradiation of PMA. The structure of the terminal group for the cleaved PMA chain could not be identified using conventional IR and NMR spectra measurements, because the concentration of the terminal groups produced by the irradiation ($\sim 10^{-5}$ M) was too small to identify. The Tb-fluorescence sensitizing technique is effective in detecting such dilute defect species in a polymer chain. It is suggested that the PAA–Tb^{+3} system may be used as a convenient and fast OH radical detector in an aqueous solution.

Scheme I
Proposed Mechanism for the OH Radical Reaction with PAA Salt (M = Na or Tb Ion)



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