Matrix Effects on the Proton-beam Induced Reaction of Spirophenanthrooxazine

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Photochromism has been the subject of great interest due to their potential applications in various fields, such as display systems, optical switching and optical memory storage.[1-4] Although photochromic dyes were discovered more than 100 years ago, researches on the compounds and their applications were not widely spread until 1956, when Hirshberg demonstrated photochromic dyes could be applied as an optical memory medium.[5]

Recently, Irie *et al*. observed that photochromic diarylethene exhibits color change under the γ-irradiation.[6] Because its radiation-induced reaction proceeded in a quite similar manner to its photochromic reaction, they proposed its use as the radiation dosimeter. And they predicted photochromic spirocompounds cannot be used for the radiation dosimeter because its colored form is thermodynamically unstable.

However, Moscovitch *et al*. showed that ionizing radiation such as heavy charged-particles (HCP) is capable of changing the information originally stored within the spiropyran (SP) doped in polymethyl methacrylate (PMMA), a three-dimensional optical random access memory materials.[7-11] Exposure of SP in PMMA (SP/PMMA) to ionizing radiation resulted in the permanent color change. Depth profiles obtained using a confocal laser scanning microscope prove that the use of SP/PMMA for real-time dosimeter of neutron or HCPs is possible.

Very recently, we reported the effects of proton-beam on spirophenanthrooxazine (1,3-dihydro-1,3,3-trimethyl-spiro[2*H*-indol-2,3'-[3*H*]-phenanthr[9,10-b][1,4]oxazine], SPO) dissolved in chloroform (SPO/CHCl$_3$).[12] Under the proton-beam irradiation, SPO permanently decomposes into two main products, 1,3,3-trimethyl-2-oxyindol and phenanthro[9,10-d]-oxazole. The reaction is first-order with a rate constant of 0.275 min^{-1} and proceeds in a different way from its photochromic reaction.

In this study, we report the matrix effects on the proton-beam induced reaction of SPO and propose a new type of color dosimeter based on the reaction. Because the reaction rates drastically vary from matrix to matrix, the results were discussed using stopping power instead of solvent polarity scale.

Experimental Section

SPO, PMMA, polystyrene (PS) and spectroscopic grade solvents (chloroform and ethanol) were purchased from Aldrich and used as received. 4.0×10^{-4} M SPO solutions were prepared by dissolving appropriate amount of SPO in various solvents. SPO doped thin films were prepared on the silicon wafer from the chloroform solutions containing polymer and SPO (3 wt.%) by spin coating method. The films were air-dried for 3 days at room temperature and the average film thickness was about 100 μm.

The liquid samples were irradiated by 25 MeV proton-beam from a MC-50 cyclotron at Korea Institute of Radiological and Medical Sciences (KIRAMS). The proton-beam, which exited the cyclotron through the exit window, was directed to the sample located in the atmosphere. The beam current was 10 nA ~ 1 μA and the fluence was adjusted to the range of $1.0 \times 10^{10} \sim 1.0 \times 10^{14}$ ions/cm^2 by changing the irradiation time.

The polymer films were irradiated either by 25 MeV proton beam from the cyclotron or by 3.4 MeV proton beam from a Tandem accelerator. In the Tandem accelerator at Korea Institute of Geoscience and Mineral Resources (KIGAM), the irradiations were performed by beam scanning under vacuum at 100 nA or 1 μA and the fluence was $1.0 \times 10^{12} \sim 4.0 \times 10^{14}$ ions/cm^2.
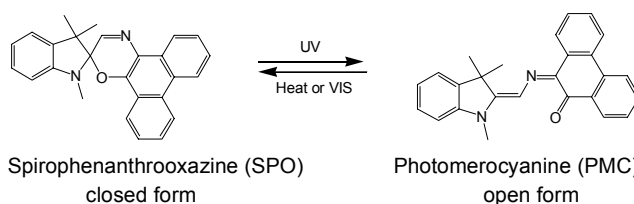
The UV-Vis spectra were measured using a Cary 4000 spectrophotometer (Varian). For liquid samples, a cell with appropriate path lengths (2, 5 and 10 mm) was selected by considering absorbance in the visible region and then the difference in the path lengths was corrected to give overlaid spectra.

SRIM 2003[13] was utilized to calculate stopping power and range of ions in matter. In the calculations, energy loss by the sample vial was taken into account for liquid samples.

Results and Discussion

SPO is a photochromic and thermochromic compound.[2,3,14] Under UV radiation, SPO experiences a photochemical transformation to its colored photomerocyanine form (PMC), which reverts back to SPO in the dark (Scheme 1).

Figure 1 is a plot depicting the effects of proton fluence on the absorption spectra of SPO/CHCl$_3$ solution. Before the irradiation, the solution shows an absorption band at 350 nm

Spirophenanthrooxazine (SPO)
closed form

Photomerocyanine (PMC)
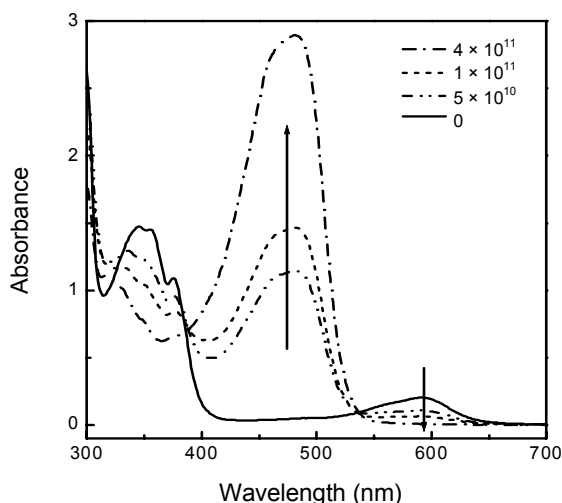open form

Scheme 1. Photochromism of SPO

Figure 1. Effects of proton fluence on the spectra of SPO/CHCl$_3$. The ion energy was 25 MeV and the numbers in the figure indicate ion fluence in the unit of ions/cm^2.
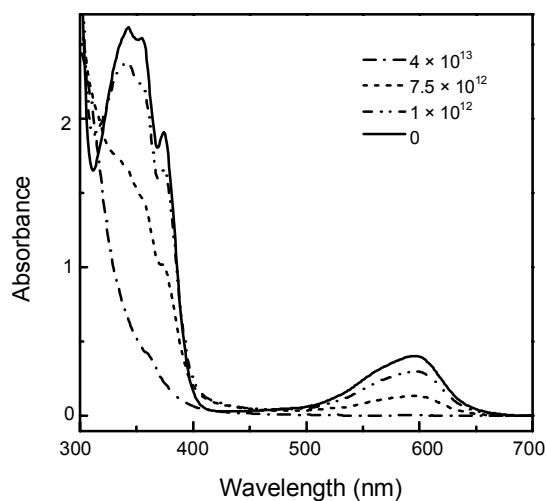

Figure 3. Effects of proton fluence on the spectra of SPO/ethanol. The ion energy was 25 MeV and the numbers in the figure indicate ion fluence in the unit of ions/cm^2.
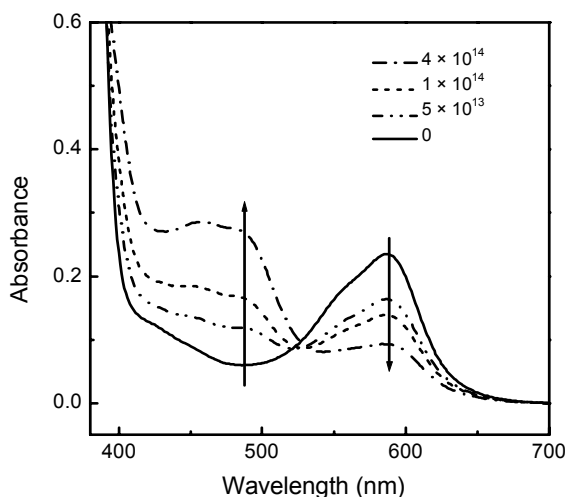

Figure 2. Effects of proton fluence on the spectra of SPO/PS. The ion energy was 25 MeV and he numbers in the figure indicate ion fluence in the unit of ions/cm^2.
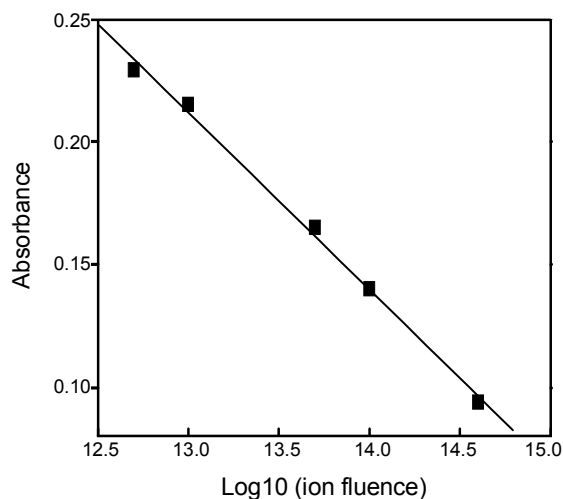

Figure 4. Proton fluence response curve of absorbance at 590 nm for SPO/PS. The proton energy was 25 MeV.

and a smaller one at 590 nm, which corresponds to PMC produced by thermochromic reaction. Upon the proton irradiation (25 MeV), a new band grows at 480 nm, while the bands at 350 nm and at 590 nm concomitantly decrease. The band at 480 nm rapidly grows with the further irradiation and maximized at the fluence of 4×10^{11} ions/cm^2. In the previous paper,[12] we interpreted this results as a proton-beam induced decomposition reaction, which is different from photochromic reaction. Because PMC is in equilibrium with SPO, decomposition of SPO accompanies with reduction in PMC concentration and, therefore, results in simultaneous decrease in both bands. The species absorbing at 480 nm, we referred it as "B", was attributed to a minor product possessing extended conjugated double bonds.

Figure 2 represents the change in the absorption spectra of SPO in PS (SPO/PS) under 25 MeV proton beams. Trends in

the spectral changes are very similar to those of SPO/CHCl$_3$ except fluence at which 470 nm-band starts growing. The fluence is about 5×10^{12} ions/cm^2, while it is as low as 1.0×10^{10} ions/cm^2 in SPO/CHCl$_3$.

Under 3.4 MeV proton beams, SPO/PS and SPO/PMMA behave similarly to Figure 1 and 2 except onset fluence of 470 nm-band. The fluence is 5×10^{11} ions/cm^2 and 2.5×10^{11} ions/cm^2, respectively. These results show that in PS matrix, the reaction under 3.4 MeV beams is about 10 times faster than under 25 MeV beams and that the rate is slightly faster in PMMA than in PS if the ion energy is same. The results seem to indicate that proton-beam induced reaction proceeds in the same mechanism but at different rate in chloroform, PS and PMMA environments.

In ethanol (Figure 3), there is only a slight decrease in the absorbance throughout the whole spectral range even at the

fluence of about 4×10^{11} ions/cm^2, at which SPO completely decomposed in chloroform.[12] It was not until the fluence reaches 4×10^{13} ions/cm^2, which is about 100 times higher than in chloroform solution, that SPO completely decomposes. However, there is no indication of B production. Because in chloroform the molar absorption coefficient of B at 480 nm seems to be greater than that of SPO at 350 nm, it is expected that B will be easily observed if there is any. However, B is not traced even 1 month after terminating the irradiation. This fact seems to support that B cannot be formed in ethanol, not that its formation rate is too slow.

Solvent effects on organic reactions are usually explained using solvent polarity.[15] Shin *et al.* reported that π^*-scale well explains the solvent effects on the thermal decay reaction of PMC form of spironaphthooxazine (SNO) produced by laser flash photolysis method.[16] SNO has one phenyl ring less on oxazine moiety than SPO and experiences photochromic and thermochromic reaction in a similar manner to SPO. They showed that the thermal bleaching reaction of PMC is operative in a single mechanism in various solvents although the kinetic behavior of the reactions is classified into three classes, polychlorinated aliphatic solvents, alcoholic solvents and non-chlorinated solvents. Chloroform (0.58) and ethanol (0.54) are pretty much the same in π^* value[17] and the reaction in chloroform was about two times faster than in ethanol.[16] The ratio of the highest- to lowest-rate constant among twelve solvents is about 10 at the most.

However, things are quite different in the ion-beam induced reaction. The ion-beam induced reaction in chloroform is about 40 times faster than in ethanol and about 1000 times faster than in PS. Such a big difference in the reaction rate between two solvents cannot be properly explained using solvent polarity. Furthermore, the fact that the reaction rate of SPO in PS depends on the ion energy cannot be explained by the solvent polarity. Instead, it seems to be closely connected with stopping power, that is, the interaction of the ionizing radiation and the matter. When ion beams traveling through materials, charged particles ionize atoms or molecules which they collide and, therefore, gradually lose their energy in many steps. Stopping power means the average energy loss of each particle per unit path length and is expressed: $S(E) = -\dfrac{dE}{dx}$ where E is energy and x is the path length. In particular, the polymer within the penetration depth will experience chain scission or cross linking and transform to other molecular structure when collide with energetic ions. In the present paper, their contribution to the spectral change in visible region is assumed to be negligible because under the given condition the absorbance change of SPO is drastic.

We observed that no matter whether proton energy is 3.4 MeV or 25 MeV, PMMA and SPO/PMMA films melt if ion current is 1.0 μA and if ion fluence is higher than 5×10^{14} ions/cm^2. However, those films do not melt under the same condition but the ion current of 100 nA or less. Meanwhile, PS and SPO/PS do not melt under any of above conditions. Because the melting points of PS and PMMA are 240 and 130 - 140 °C, respectively, it is deduced that the temperature of PMMA films during irradiation is higher than at least 130 °C at the ion

current of 1.0 μA and at the ion fluence of 5×10^{14} ions/cm^2. The facts that both doped and undoped PMMA films melt at same condition and SPO content is only 3 wt.% in the film imply that the melting is mainly caused by energy absorbed by PMMA matrix itself. Moscovitch *et al.* calculated that the temperature along each HCP track far exceeds 300 °C in PMMA.[7] These results may imply that the decomposition reaction of SPO proceed either thermally or radiationally.

According to SRIM calculation, the Bragg peak of PS is located at 174 μm and 6.0 mm for 3.4 and 25 MeV protons, respectively, and stopping power is 1.4 and 0.23 eV/Å, respectively. Because the film thickness is about 100 μm, it is easily seen that both 3.4 MeV and 25 MeV ions pass through the matrix. The fact that stopping power for 3.4 MeV proton is about 6 times higher than that for 25 MeV proton implies that the energy absorbed from 3.4 MeV proton is about 6 times more than that from 25 MeV proton. This agrees well with the experimental result that the reaction under 3.4 MeV beams is about 10 times faster than that under 25 MeV.

For 3.4 MeV protons, the stopping power of PMMA and PS are calculated to be 1.58 and 1.4 eV/Å, respectively. Because PMMA has higher stopping power than PS, more energy will be deposited to PMMA than to PS for same charged particle. This result predicts that the proton-beam induced reaction is slightly faster in PMMA than in PS and the prediction agrees with the experimental result mentioned earlier.

For color dosimeter application, it is needed to show a linear relationship between the ion fluence and the radiation induced absorbance change. Figure 4 shows that the absorbance of SPO/PS at 590 nm linearly decreases with the proton fluence. The linear relationship indicates that the SPO/PS can be applied to a color dosimeter. Because the radiation induced reaction of SPO is permanent, the film is not reusable.

In summary, the rate of the proton-beam induced reaction of SPO depends on the ion energy and greatly influenced by matrix. The results are qualitatively explained in terms of stopping power and showed that SPO has the potential application in a new type of color dosimeter based on the reaction.

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