Coloration of Pentacosadiynoic Acid Polycrystalline Powder Dispersed in Polymer Layer by Gamma-ray Irradiation and UV Illumination

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Coloration of pentacosadiynoic acid (PDA) dispersed in polyalkylacrylate layer (color indicator layer) by gamma and UV irradiations has been studied comparatively in an attempt to obtain basic data for development of radiation color indicator of high sensitivity useful at low dose region (below 50 Gy) where the irradiation is carried out to suppress immunity in blood transfusion. Dispersion of PDA at high concentration in polyalkylacrylate layer gives a color indicator sensitive enough for this purpose. A small positive dose rate dependence and large temperature effect were observed on the reaction rate.

Keywords: Pentacosadiynoic acid, Coloration, Color indicator, Gamma ray irradiation, UV illumination

1. Introduction

Recent extension of radiation application toward medical uses such as immunity suppression at blood transfusion increases the necessity of simple indication of irradiation of low dose below 50 Gy. Many organic dye systems are proposed as radiation color indicators [1], but most of them are good for dose range above 100 Gy. Recent studies revealed that some pH indicator dyes exhibit sensitivity high enough to cover the low dose range [2]. It is known that when Pentacosadiynoic acid (PDA) and related diynoic compounds in a form of LB multilayers or solid state were irradiated by UV light or gamma rays, they were topo-chemically polymerized to form polymers having backbone chains that consist of double-triple bond with strong optical absorption band in visible range [3, 4, 5]. The diynoic acids deposited on filter paper were also proposed for radiation color indicators [6], among them, 4BCMU being the most sensitive to gamma radiations high enough to be used at these low dose ranges. PDA in the form of LB layers was considered for dosimetry [7], but the sensitivity is not high enough to cover the low dose range due to the number of chromophores involved was small. Dispersion of the diynoic acids at high concentration in a polymer medium is expected to offer promising technique to develop a mechanically stable and highly sensitive color indicator used for the above-mentioned purpose.

The present studies have been carried out in an attempt to obtain basic data, which are necessary for the development of the color indicator. PET film supported polyalkylacrylate layer dispersed with PDA fine powder at different concentrations (color indicator layer) were prepared and the color
indicators thus obtained were used in the present study. Absorbance of the color indicator resulted by gamma ray irradiation and UV illumination was measured using a visible absorption spectrophotometer and the data obtained by the both types of radiations was examined on the scale of the same unit of radiation absorption. Reflectivity was measured on a reflection meter as an index of more directly related to visual inspection. Effects of temperature and dose rate on coloration by the UV illumination were also studied.

2. Experimental

2.1. Materials

PDA was obtained from GFS Chemicals Inc. and used after re-crystallization from dioxane solution. Forty percent ethyl acetate solution of polyacrylates (Aron, S-403H; melting point, 100°C) was obtained from Toa Gousei Chemicals and used as obtained. Dioxane was of Chemical reagent grade purchased from Wako Chemicals Inc.

2.2. Preparation of the radiation-sensitive color indicators

Stock solution of PDA (6.36g PDA dissolved in 40 ml dioxane at 60 °C) was added to 15 g polyalkylacrylate solution (40 wt %) and stirred vigorously for 40 minutes using a shaker. The clear colorless viscous liquid thus obtained was applied on PET film (0.1 mm thickness) using a 0.3 mm applicator. The liquid coated film was kept at 25 °C for a night to evaporate off the solvents leaving the PDA containing color indicator layer on the PET film. The thickness of the film was measured using a digital micrometer. The PET-film supported color indicator was cut to pieces of 10 x 35 mm that were subjected to gamma ray irradiation and UV illumination. The content of PDA in the color indicator was adjusted from 2.6 to 22 wt percents by dilution of the PDA stock solution. The whole process was carried out in a dark room 2 m below a 10-watt tungsten lamp.

2.3. Gamma ray irradiations

Gamma ray irradiations were carried out using a Co-60 gamma ray source at 20 °C. Dose rate was 0.5-5 Gy/sec and dose was varied from 5 to 500 Gy. In the experiment to determine the conversion to polymer, PDA of polycrystalline powder form was irradiated in a glass bottle with a plastic screw cap sealed in a light protected plastic bag. The polycrystalline sample after irradiation was added to chloroform. Undissolved red polymer was collected on a Millex Millipore filter (polyethylene, pore size: 0.45 μm) and dried in vacuum for 24 hrs, and the amount of the polyPDA was determined on a weighing balance. The color indicator was irradiated by gamma rays in a light protected bag.

2.4. UV illuminations and the energy absorbed

Illumination was carried out using a 4 w low-pressure mercury arc (UV lamp) at 23 °C. The intensity on the surface of the sample, I0, was monitored using a Topcon UV radiometer with a UVR254 head at 254 nm and was 0.16 J/m²/sec at 33 cm below the UV lamp. In the experiment to study dose rate dependence of the reaction rate, the intensity of the UV light was changed by gauze of different meshes, which was placed between the UV lamp and the color indicator to be illuminated, and illumination time was adjusted so that the dose absorbed by the color indicator was 9.7 Gy. In the illuminations at different temperatures, the color indicator was illuminated on a hot plate through a quartz glass window. Five minutes were allowed before illumination to equilibrate the color indicator thermally to the hot plate.

2.5. Optical absorbance measurement

Optical absorption spectra were recorded on a Parkin-Elmer UV/Visible spectrophotometer Lambda 11 at 20 °C.

2.6. Reflectance measurement

Reflectance reading was taken on a Minolta color meter CR-200 at 20 °C.

2.7. Calculations

The G-value of the polymer formation defined as the number of monomer units of the polyPDA produced by 100 ev energy absorption is calculated using the following equation:

\[ G = \frac{M}{mw \times \text{mass of polyPDA}} \times 6.02 \times 10^{23} \times 100 \times \left( \frac{Q}{6.242 \times 10^{18}} \right) \]  

where M is the mass of polyPDA formed from 1 g PDA in g, mw is the molecular weight of the monomer unit (=374.6), and Q is the amount of energy absorbed in the color indicator in Gy.

The molar extinction coefficient of polyPDA at 680nm, \( \epsilon \) (polyPDA, 680) was calculated by the following equation:
\( \varepsilon (\text{polyPDA,680}) = \frac{A}{c(\text{PDA})} \times 1 \)  
(2)

where \( A \) is the absorbance of the color indicator at 680 nm and \( c(\text{PDA}) \) is the concentration of PDA in the color indicator layer in mole/l.

The reflectance of the color indicator, \( R \) was related with \( \lambda \)-averaged optical absorbance by the following equation:

\[
R = (R_{bc} - R_{bk}) 10^{-2B} + R_{bk}  
(3)
\]

where \( R_{bc} \) and \( R_{bk} \) are the reflectance from an unirradiated color indicator and a black standard surface, respectively, and \( B \) is the \( \lambda \)-averaged optical absorbance over wavelength region from 550 through 750 nm that is covered by the present reflectance measurements.

The energy of the UV absorbed in the sample, \( \Delta I \), was calculated using the following equation:

\[
\Delta I = I_0 - I = I_0 (1 - 10^{-E(254)})  
(4)
\]

where \( I \) is the intensity of the UV after passing through the color indicator in J/m²/sec. \( E(254) \) is the absorption coefficient of the color indicator at 254 nm in 1 mole⁻¹ cm⁻¹, and calculated by the following equation:

\[
E(254) = (\varepsilon(254,\text{PDA})c(\text{PDA}) + \varepsilon(254,\text{PA})c(\text{PA})) 
(5)
\]

where \( \varepsilon(254,\text{PDA}) \) and \( \varepsilon(254,\text{PA}) \) are the molecular extinction coefficients of PDA and polyalkylacrylate, respectively, and \( c(\text{PDA}) \) and \( c(\text{PA}) \) are the concentrations of the respective components in mole/l, and \( l \), optical length through the color indicator layer in cm.

The UV energy absorbed by PDA in the color indicator (in J/m²/sec) was calculated using the following equation:

\[
\Delta I(\text{PDA}) = \Delta I (\text{polyPDA})c(\text{PDA})/ 
(\varepsilon(254,\text{PDA})c(\text{PDA}) + \varepsilon(254,\text{PA})c(\text{PA}))  
(6)
\]

To convert this value to Gy/sec (=J/kg/sec), the value was divided by mass of PDA in the color indicator layer (kg/m²).

3. Results and Discussion

The conversion to polymer is plotted as a function of dose up to 500 Gy in Fig. 1, where it is noted that the polymer conversion increased almost linearly with dose. The G value of the polyPDA formation on the basis of the monomer unit was calculated to be 4200 using equation (1).

In Fig. 2, absorption spectra of the color indicators irradiated at different doses are shown. Two absorption peaks appeared by 15 Gy irradiation at 680 and 620 nm, and the intensities of these peaks increased with increasing dose. The shape of the absorption spectrum became broad and the peaks shifted toward shorter wavelength gradually with increasing dose to 670 and 615 nm.

![Fig. 1. Conversion to polymer as a function of dose.](image)

![Fig. 2. Visible absorption spectra of color indicator after gamma irradiation; a: 0 Gy, b: 15, c: 100, d: 200, e: 500. Back ground levels are arbitrary shifted to avoid over rapping of the spectra.](image)
form the Beer's law. The change of the spectrum and the deviation from the Beer's law probably indicate that the formation of polyPDA having conjugated backbone main chains of different degrees of "worm-like" distortion resulting various shorter effective lengths of the conjugated system at the later stage of irradiation [5].

The molar extinction coefficient at 680 nm of the color indicator (PDA concentration: 14.7%) was calculated on the basis of the yield of the polyPDA and the absorbance observed at 25 Gy where the absorbance is approximately regarded to increase linearly with dose. The value calculated by equation (2) was $2.7 \times 10^4$ mole cm$^{-1}$ which is 1.7 times higher than that reported for LB films of 8-28 layers ($1.6 \times 10^4$, [3]).

The absorbance increased with dose, and the increment was larger for higher content of PDA. The effect of PDA concentration on absorbance was more clearly shown in Fig. 4, where the absorbance was plotted as a function of PDA concentration, the dose being as a parameter. The absorbance change of 0.2 was observed even by a small dose as 5 Gy for the color indicator that contains 22.1 % PDA. The plots indicate that higher sensitivity to radiation is expected when the concentration of PDA in the color indicator layer increased further.

In Fig. 5, the reflectance of the color indicator was plotted as a function of dose for the color indicators of different concentrations of PDA. The reflectance from the color indicator decreased with increasing dose and
the dose sensitivity was higher for the color indicator containing higher concentration of PDA. Since the decrease of reflectivity of 5% was easily recognized by visual inspection, dose of 5 Gy or less can be detected by this method with the presence of 20% or higher PDA in the color indicator layer.

The $\lambda$-averaged absorbance (▲) and reflectance (●) of the color indicator were plotted as a function of dose in Fig. 6. The reflectance calculated from the $\lambda$-averaged absorbance using equation (3) (□) is also plotted in the figure, where the calculated and observed reflectance agreed satisfactory.

In Fig. 7, the absorbance of the color indicator illuminated by UV light was plotted as a function of dose in Gy unit that is converted from UV intensity, molar extinction coefficients and concentrations of the respective components of the color indicator layer using equations (4), (5) and (6). For comparison purpose, the absorbance-dose plots observed for the gamma irradiation were also shown in this figure. The absorption-dose plots

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Fig. 5. Reflectance from the color indicator as a function of dose; Gamma irradiation. Concentrations of PDA in the color indicator are listed in the figure.

Fig. 6. $\lambda$-averaged absorbance ▲, reflectance observed ●, and calculated □ from absorbance as a function of dose; Gamma ray irradiation.

Fig. 7. Absorbance as a function of dose; UV (open symbols) and Gamma (filled symbols) irradiation.

Fig. 8. Absorption as a function of dose rate; UV illumination.
observed for UV illuminations (PDA concentrations of 18.4 and 5.54 %) came close to those observed for the gamma irradiations, except for the plots obtained for the color indicator containing 5.54% PDA where the UV plots come above the gamma plots. Since most of UV energy was absorbed in the color indicator layer due to its large absorption coefficient, the distribution of the UV energy absorption on the depth direction was not uniform in the color indicator. Therefore, the UV-absorbed energy in Gy is considered only as a rough average indication for UV illumination. However, observed close correlation between absorbance-dose plots obtained for UV illumination and gamma ray irradiation may allow us to use the data obtained for the UV illumination to simulate the response of the color indicator for gamma radiations.

The plot of absorption against dose rate is shown in Fig. 8, where a small positive dose rate dependence on reaction rate was observed. The shape of the spectrum did not change for the dose rate region studied.

The absorption spectra observed for the color indicators at a dose of 4.8 Gy at different temperatures are shown in Fig. 9, where it is shown that the peaks at 680 and 620 nm (spectra a through d) shifted toward shorter wavelengths (660 and 600 nm, respectively; spectra e and d) as the temperature increased. The spectrum was not observed when the color indicator was illuminated at 66°C (g). The maximum absorbance of the spectrum was plotted as a function of illumination temperature is shown in Fig. 10. The absorbance increased with increasing temperature, reached at a maximum at about 40°C, and then decreased when the temperature increased further; and above the melting point, it was zero. The result indicates that the polymerization proceeds favorably when movements of PDA molecules are allowed within certain extent, but more rigorous movements disturb the topo-chemical polymerization of PDA, and the polymerization is prohibited completely in the liquid phase. The radiation response was quite low when the irradiation was carried out below 10 °C, indicating that the color indicator is stable without coloration when it was stored at low temperatures.

The spectrum observed for the color indicator that was once melted, cooled down to 51, and then illuminated at this temperature is shown in this figure (spectrum h) where the peaks appeared at 660 and 600nm which are blue shifted by 20 nm from those observed for the film indicator illuminated at the same temperature (51 °C, spectrum d) without the thermal re-crystallization. This observation may indicate that a small difference in modification of the monomer crystal that may affect the rate of polymerization exists between the crystals crystallized from the solution by evaporation and that obtained from the molten state by cooling, and that the
polyPDA formed on the annealed color indicator has the conjugated backbone chains of a similar structure to that of polyPDA obtained at higher temperatures (57 and 62 °C, spectra e and f, respectively).

The absorbance observed for the thermal annealed color indicator (h) was higher by 25% than that without thermal annealing (d). This result suggests that a precaution is necessary to avoid storage at higher temperature above the melting point.

4. Conclusions

The polycrystalline PDA dispersed in polymer medium supported on PET film can be used as radiation-sensitive color indicator that is sensitive enough at low dose as less than 10 Gy. Increasing PDA content in the color indicator can increase the sensitivity.

A small positive dose rate dependence of the polymerization was observed. The large temperature effect on the reaction rate indicates that a proper correction must be considered when the radiation sensitive color indicator is used in different environment temperatures.

It is desirable that the color changes discretely at a desired threshold dose for easy visual inspection to distinguish “irradiated” or “unirradiated”, but gradual coloration with increasing dose was observed in the present research. Therefore, the use of a simple reflection meter on this color indicator is recommended to develop a simple technique to evaluate radiation dose of low level.

5. References