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Effect of γ-radiation on the physical properties of poly(vinyl alcohol) dyed with tetrabromophenolphthalein ethyl ester

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Abstract

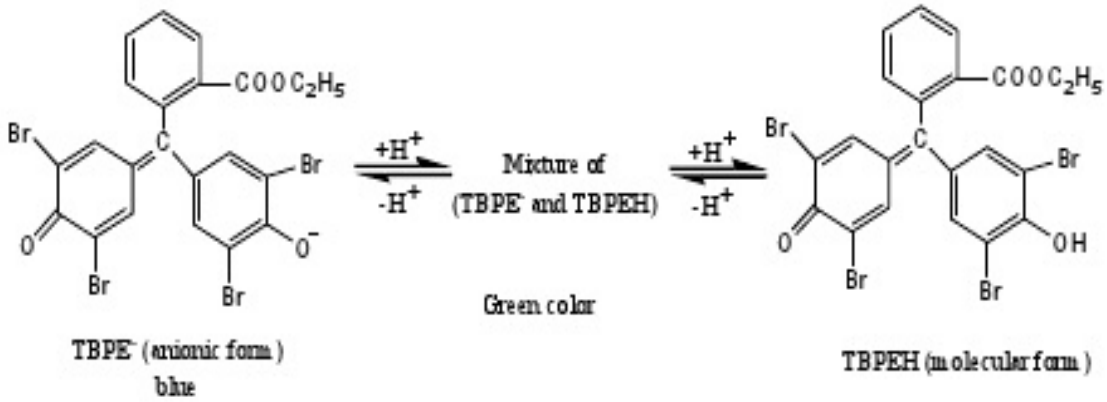
In the present investigation the radiation sensitive indicators based on dyed poly(vinyl alcohol) (PVA) containing acid sensitive dye tetrabromophenolphthalein ethyl ester (TBPE) and tri-chloro acetamid (TCA) have been developed. These plastic film dosimeters undergo color change from blue to green to pale green, indicating acid formation. These films can be used as dosimeters for food irradiation applications where the maximum of the useful dose ranges are between 1-5 kGy depending on (TCA) concentration in the film. The films have the advantage of negligible humidity effects on response in the intermediate range of relative humidity from 10 to 50 % and good stability before and after irradiation under different storage conditions.

Key words: (tetrabromophenolphthalein ethyl ester), poly(vinyl alcohol), gamma ray dosimeter.

Introduction

Many radiation sensitive indicators for qualitative indication of radiation exposure have been manufactured, to distinguish processed irradiation units from unprocessed irradiation units **[Abdel-Rehim et al., 1996; Abdel-Rehim and Abdel-Fattah, 1993]**. These indicators may be labels, papers, inks which undergo a visual color change when exposed to ionizing radiation **[Abdel-Rehim et al., 1985]**. These indicators based mainly on radiochromic dye **[McLaughlin et al., 1977; Chen Wenxiu et al., 1985; Kovacs et al., 2000; Akhava et al., 2002; Butson et al., 2001, 2003]**, pH-indicator dye **[Sidney et al., 1990; Abdel-Fattah et al., 1996, 2002; Abdel-Fattah and El-Kelany, 1998]** and radiation sensitive diacetylenes **[Patel, 1979, 1981; Ogawa, 1995]**. They are not used for quantitative dose measurements while label dosimeters may be used for quantitative dose measurements during radiation processing. A new plastic film dosimeter has prepared from (PVA) incorporating an acid-sensitive dye (bromophenol red, BPR) and water soluble chlorine containing substance [CCl_3COONa or chloral hydrate ($CCl_3CH(OH)_2$, 2,2,2-trichloroethan-1,1-diol)]. This film is easy to prepare in laboratory and can be used as a dosimeter in the relatively low dose range up to 5 kGy **[Abdel-Fattah et al., 1996]**. A new thin transparent cellophane film was developed for high-dose dosimetry by **[McLaughlin, 2003]**. This film containing disazo"Direct" dyes, e.g. blue Cellophane, have long been used as monitors of large absorbed doses of ionizing radiation (10-300 kGy) and especially for mapping electron-beam dose profiles. The radiation response is markedly dependent on temperature and relative humidity during irradiation. Radiation bleachable organic dyes were widely investigated **[Ebraheem et al., 2005]**. For dose monitoring in radiation processing, the polymeric dyed flexible films are considered to be most commonly used as dosimeters, indicators **[Abdel-Rehim and Abdel-Fattah, 1993]** and for monitoring the absorbed dose delivered by electron beams and gamma rays **[Kovaces et al., 2002]**. **[Ueno, 1988]** developed a radiation dosimeter from acid indicators by coating a high molecular weight polymer support (e.g. polyester film) with a composition

containing a halogen-containing polymer (e.g. PVC), a pigment which changes color with the changes of pH and basic material (e.g. KOH in EtOH). A chlorine-containing polymer is not necessary for this reaction to occur. The current work deals with the investigation of a new dyed poly(vinyl alcohol) film to enable their use in food irradiation processing applications.



Experimental procedures

Preparation of stock solution of TBPE ($C_{22}H_{14}Br_4O_4$ – M.W. = 661.96)

The stock solution of the indicator was prepared by dissolving 0.025 g of (TBPE) (Sigma-Aldrich, Inc., USA) in 25 ml ethanol.

Preparation of TBPE/PVA films

Films were prepared by dissolving 10 g of PVA powder (average M.W. 25,000 fully hydrolyzed 99-100% product of J.T. Baker Chemical Co. USA) in 250 ml double distilled water at about 60°C. The solution was kept well stirred at the temperature for about 48 h; then left to cool. To each 30 ml of PVA solution 2, 4, and 8 ml of dye stock solution were added and kept stirred for about 3h at room temperature in order to obtain a uniformly dyed solution. (TCA) was added in certain concentration ranged from 0.2 to 0.8 phr to solution containing 0.66 phr of TBPE. The dyed PVA solutions were stirred, casted on a 10 × 10 cm horizontal glass plate and dried at room temperature for about 48 h. The film thickness was found to be 0.055 ±0.02 μm, 1σ.

Instrumental Analysis

The absorption spectra of unirradiated and irradiated films were measured throughout the wavelength range 200-800 nm using a UV4–visible spectrophotometer. The film thickness was measured using Digitrix-Mark II thickness gauge (precision ± 1μm). Gamma irradiation was carried out in the ^{60}Co gamma chamber 4000Å (product of India). The absorbed dose rate in the irradiation facility was measured to be 5 kGy/h and the electronic equilibrium conditions were maintained during irradiation.

Results and discussion

Absorption Spectra

The absorption spectra of the unirradiated and irradiated films were measured throughout the wavelength range 300-800 nm. The absorption spectra of the TBPE/PVA films (0.66 phr TBPE) without tri chloro acitamide recorded before and after irradiation to different doses are shown in fig. (1). The absorption spectrum of unirradiated film shows a main absorption band in the visible region characteristic of a blue color peaking at 606 nm (Fig. 1). The amplitude of this band decreases gradually with the increase of absorbed dose of gamma ray photons. It is clear from the spectra of irradiated film that the TBPE dye degraded by applying of gamma rays on the film.

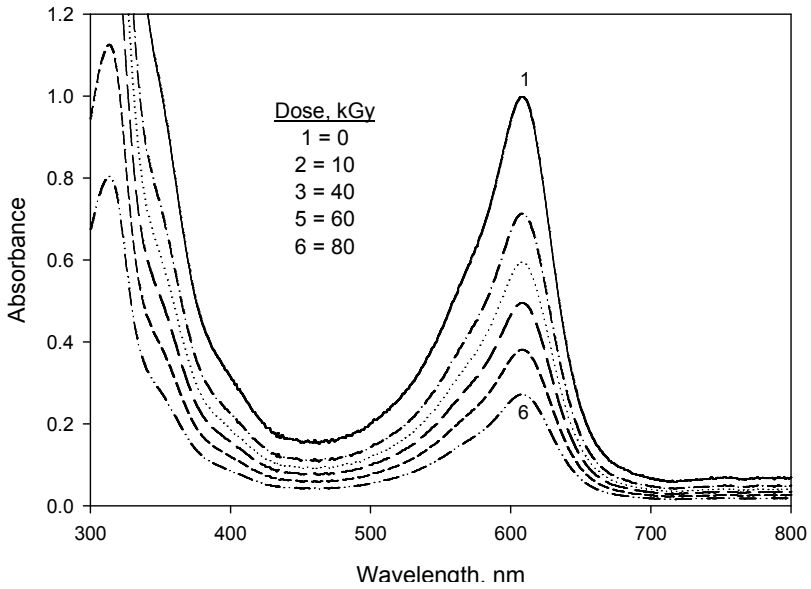


Fig. (1) The absorption spectra of TBPE/PVA films (without TCA) unirradiated and irradiated to different doses (absorbed dose = 0-80 kGy).

Fig. (2) shows the absorption spectra of TBPE/PVA films unirradiated and irradiated to different doses. These films contain 0.4 phr tri chloro acitamide and 0.66 phr TBPE. The spectrum shows a main absorption band peaking at 606 nm. The amplitude of this band decreases gradually with the increase of gamma ray. Upon irradiation, these films change their color from blue to green and finally to pale green indicating acid formation. The green color is observed due to the visual sensation of mixed ratios of unchanged part of indicator and changed part.

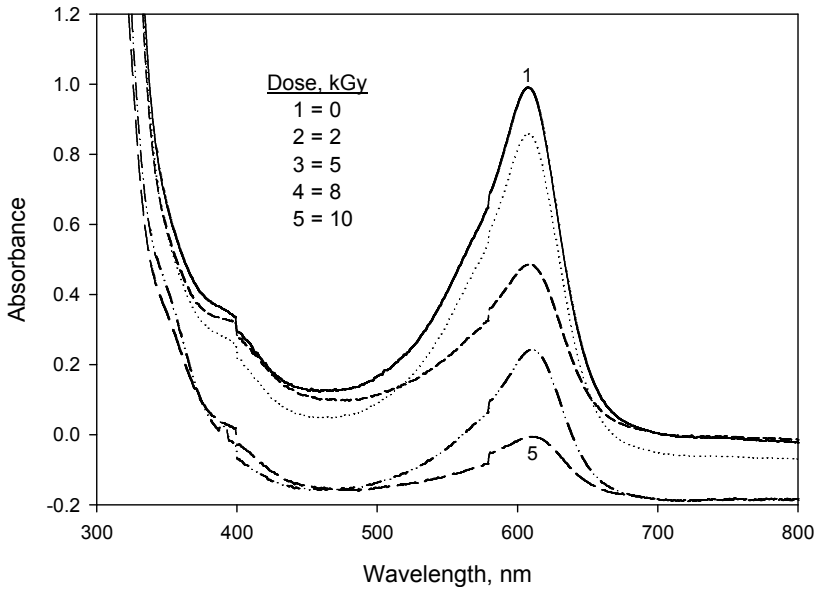


Fig. (2) The absorption spectra of TBPE/PVA films unirradiated and irradiated to different doses [TCA] = 0.4 phr

Four different tri chloro acitamide concentrations; 0.2, 0.4, 0.6, 0.8 phr with 0.66 phr TBPE were examined. It was found that the useful dose range of these films 1-5 kGy. It was noticed that the bleaching reaction takes place faster within films containing TCA than that without TCA (i.e. TCA act as sensitizer).

Response Curves

Fig. (3) shows the response curves of TBPE/PVA films containing different dye concentrations (0.16, 0.33,0. 66 and 1 phr). It can be noticed that the four curves have S-shape, characteristic of pH indicator in an acid base titration. Each curve reach saturation at different dose depending on the concentration of TBPE.

Its show the response curves in terms of change optical density per unit thickness in terms of change optical density per unit thickness $\Delta A = A_o - A_i$ and A_o and A_i are values of optical density for the unirradiated and irradiated films respectively. The curves show that the useful dose range extends up to 40 kGy.

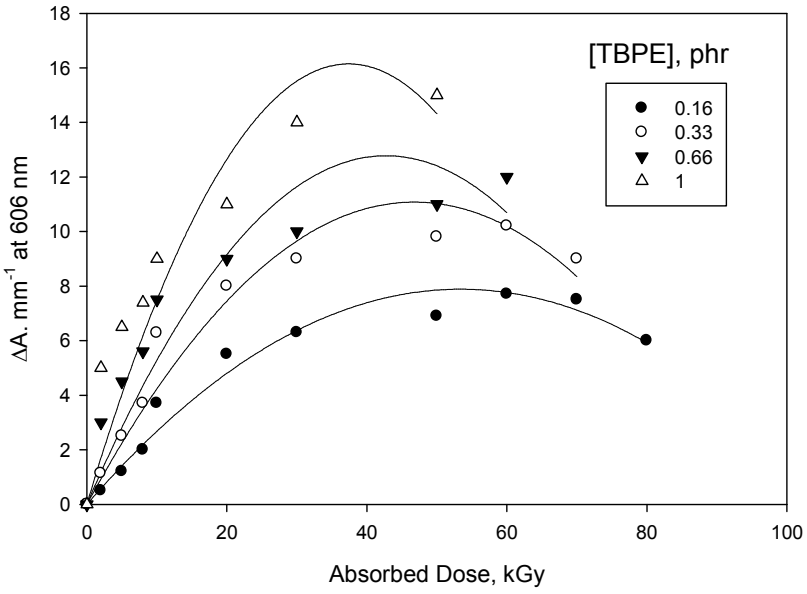


Fig. (3) Change of $\Delta A.mm^{-1}$ as a function of absorbed dose of TBPE/PVA films with different concentrations of TBPE

By applying gamma ray to the films containing tri chloro acitamide (TCA), the response completely changed. Fig. (4) show that the response of the films containing different (TCA) concentrations (0.2, 0.4, 0.6 and 0.8 phr) was decreased to be ranged from 1-5 kGy, meaning the presence of TCA inside the matrixes of the polymer led to accelerate the degradation of TBPE dye ten folds than that one than that one dose not containing TCA. This means that the resulting species produced from the irradiation of TCA act as a major factor of the dye degradation in the case of TBPE/PVA film.

Fig. (5) shows the slope of the linear parts in response curves given in fig. (3) as a function of TBPE concentration at absorption band, 606 nm. It can be seen that the radiation sensitivity of TBPE/PVA film increases with increasing the TBPE concentrations.

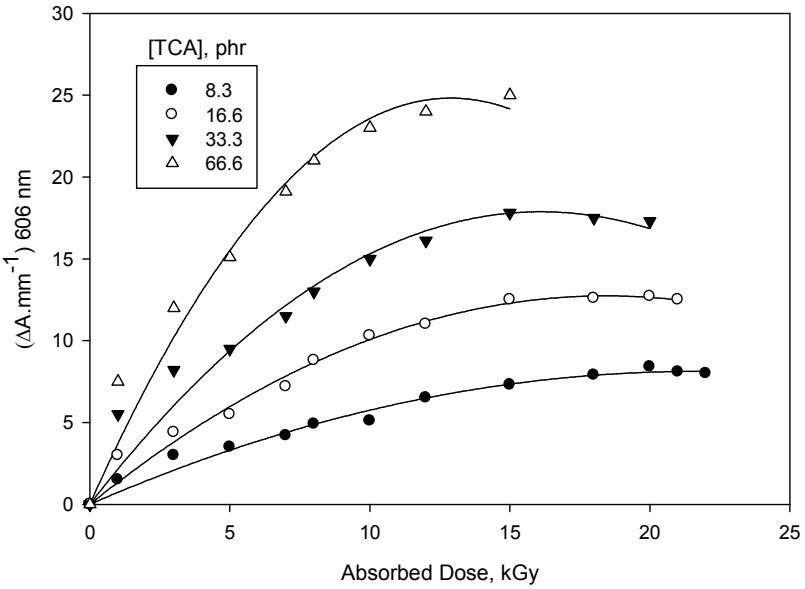


Fig. (4) Change of $\Delta A.mm^{-1}$ as a function of absorbed dose of TBPE/PVA films with different concentration of tri chloro acitamide, [TBPE] = 0.66 phr.

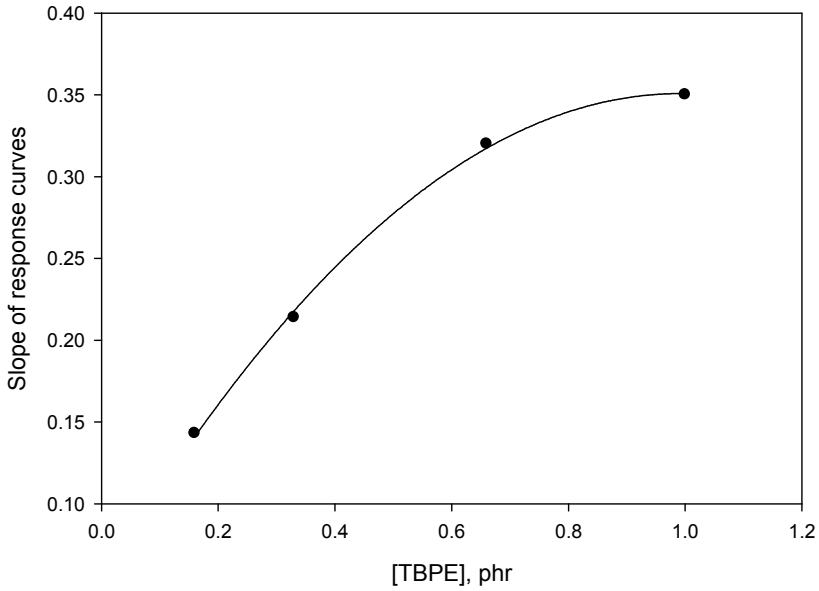


Fig (5) Radiation sensitivity of TBPE/PVA films against the concentration of TBPE.

It can be seen that response curves at different concentrations of TCA are non-linear and tend to saturate at high doses of γ-ray. The response curves(Fig. 4) were fitted with third-order polynomial functions

$$Y = ax + bx^2 + cx^3$$

Where, ***Y*** is absorbed dose, kGy for TBPE/PVA films, ***x*** is the change of absorbance as indicated by ($\Delta A\ mm^{-1}$) at 606 nm of these films, ***a, b*** and ***c*** are constants. The calculated value of the constants ***a, b*** and ***c*** is tabulated in Table (1).

Table (1) The constants ***a, b*** and ***c*** for TBPE/PVA films containing different conc. of TCA.

[TCA] phr	a	b	c
0.2	0.137	0.012	4.10×10¯3
0.4	0.031	0.023	6.81×10¯5
0.6	0.043	0.03	3.1×10¯4
0.8	0.047	0.04	-1.1×10¯4

Radiation-Chemical yield

The radiation-chemical yield (G-value) is defined as the number of moles of dye degraded by the absorption of 1 J of energy. The G-value is calculated from the general relation (McLaughlin, et al., 1989).

$$G(-Dye) = \Delta A / D.\varepsilon.\rho.b \qquad (mol/J)$$

Where ΔA is the change in absorbance at λ_{max}, b is the optical path length (cm), ε is the molar extinction coefficient at λ_{max} ($L\ mol^{-1}\ cm^{-1}$), ρ is the density of dosimeter ($g.cm^{-3}$) and D is the absorbed dose (Gy).

Using the dye concentration in mol/L and the average value $L\ mol^{-1}\ cm^{-1}$ of A_o/b. The molar extinction coefficient is calculated as 1030.05 $L\ mol^{-1}\ cm^{-1}$ and the density of PVA 1.25 gm cm^{-3}. The G(-TBPE) for the different dye concentration 0.16, 0.26, 0.33 and 0.48 μmol/J. It can be seen that the G(-TBPE) values increase with the increase of TBPE concentration. In presence of TCA the G(-TBPE) values was calculated to be 0.54, 0.72, 1.2 and 2.6 μmol/J for 0.2, 0.4, 0.6 and 0.8 phr TCA concentrations respectively. It is clear that the presence of TCA accelerates the degradation of TBPE about 5 folds, which is very important to control the dose response range according to the kind of application needed.

Humidity during irradiation

The effect of relative humidity (RH) during irradiation on the response was investigated by irradiating TBPE/PVA films (10 kGy) at different relative humidities (0, 12, 33, 54, 76 and 92 %). Irradiation was carried out while the films were suspended over various saturated-salt solutions in an enclosed jar, except for the 0 % RH which was suspended over dried silica gel. Fig. (6) shows the variation in response ($\Delta A.\ mm^{-1}$) as a function of percentage RH during irradiation relative to that at 33%. It was found that, for these films there is no appreciable effect in the range of relative humidity RH (10-50%), although the response shows somewhat different sensitivities at both higher and lower humidities.

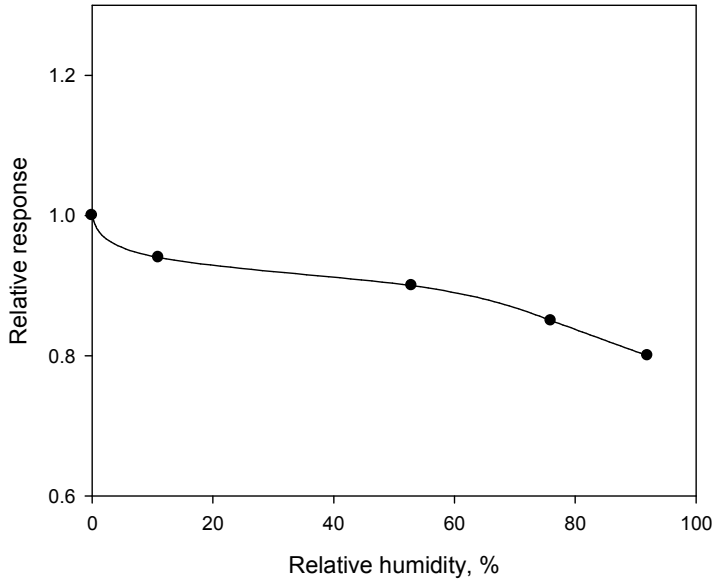


Fig. (6) Variation of response of TBPE/PVA films as a function of relative humidity during irradiation where response in $\Delta A.mm^{-1}$ at 5 kGy. [TBPE] = 0.66 phr.

Post-irradiation stability

The post-irradiation stability of TBPE/PVA films ([TCA = 0.4 phr]) irradiated to 5 kGy is investigated by storing them in the dark at room temperature. The absorbance of these films was measured at 606 nm at different intervals of time during the post-irradiation storage period of 60 days, as shown in fig. (7). The films show good stability, but we have to left films 7 days for stability requirements. The response of irradiated films decreases gradually for about one week, where the absorbance changes within ±10% overall the storage period. On the other hand, the film stored shows excellent stability overall the storage period.

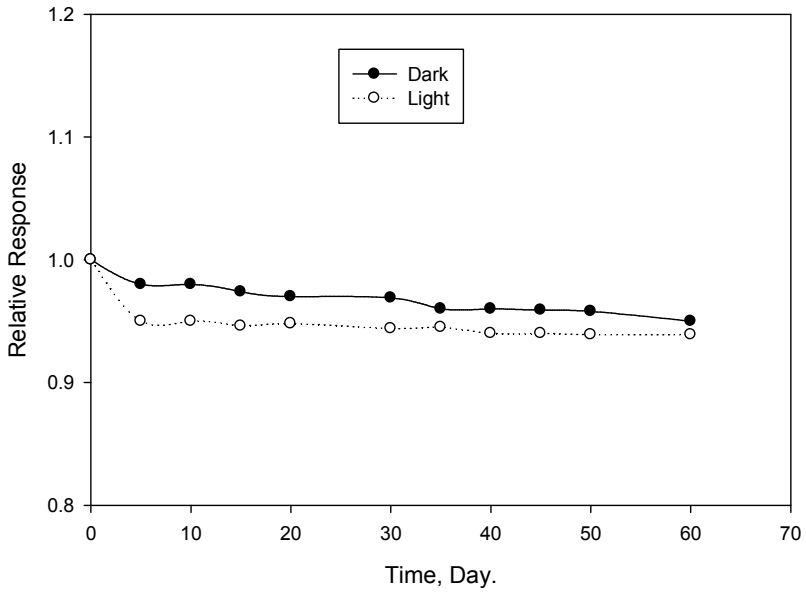


Fig.(7) Post–irradiation stability of TBPE/PVA films stored in dark and light at room temperature.

Conclusion

On irradiating TBPE/PVA films containing tri chloro acitamide, the color of the films change from blue to green and finally to pale green indicating acid formation. The amount of acid formed due to irradiation depends on the absorbed dose and the concentration of tri chloro acitamide. These films have clear visual change in color in the dose 1-5 kGy reflecting their suitability for use as radiation indicators in some food irradiation applications. The response of this film was investigated spectrophotometrically at wavelength 606 nm. The response of these films has negligible humidity effects in the intermediate range of relative humidity from 10- 50 % as well as good post-irradiation stability when stored in dark and light at room temperature.

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