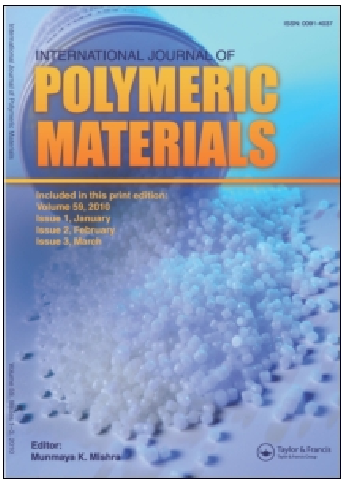

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RADIATION-CHEMICAL FORMATION OF HCL IN POLY(VINYL BUTYRAL) FILMS CONTAINING CHLORAL HYDRATE FOR USE IN RADIATION DOSIMETRY

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A new method for calculation of concentration of radiation-formed HCl in poly(vinyl butyral) (PVB) films containing chloral hydrate [$CCl_3CH(OH)_2$, 2,2,2-trichloroethane-1,1-diol] and acid-sensitive dye (thymol blue, TB), was developed. These plastic films undergo color change from yellow (the alkaline form of TB) to red (the acidic form of TB), indicating acid formation. The concentration of radiation-formed HCl in the films containing various concentrations of chloral hydrate was calculated at different doses. The kinetics of the acid-formation reaction is discussed, indicating a 0.35-order reaction with respect to chloral hydrate concentration. These films can be used as labels and dosimeters for some applications of food irradiation and wastewater treatment where the maxima of the useful dose ranges are between 2 and 4 kGy depending on chloral hydrate concentration in the film. Although, the response of these films depends on temperature during irradiation, it has negligible humidity effects in the range of relative humidity from 0 to 60% as well as good post-irradiation stability when stored in the dark at room temperature.

Keywords: thymol blue, poly(vinyl butyral), chloral hydrate, radiation dosimetry, thin polymeric films

INTRODUCTION

Radiation-sensitive materials consisting of chlorine-containing polymers and an acid-sensitive dye are widely known [1–5]. The chlorine-containing polymer is dehydrochlorinated when the material is irradiated, thereby decreasing the pH and causing the acid-sensitive dye to change color. Such materials are reported, however, to be relatively insensitive and poorly quantitative at relatively low radiation doses. A chlorine-containing polymer is not necessary for this reaction to occur. A similar color change

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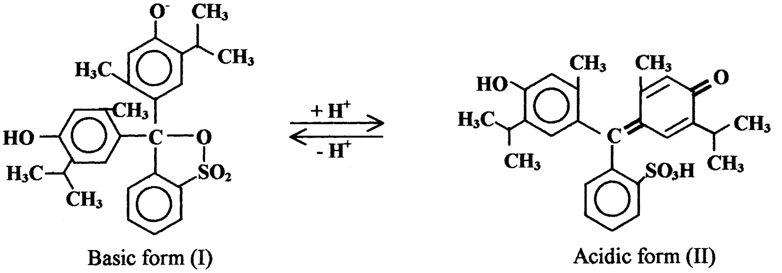
can be produced if halogen-containing compounds are present in the dye-containing matrix [6–8]. Chloral hydrate has previously been used as an acid-releasing agent in indicator dosimetry systems [7–11]. Radiation-sensitive indicator may be used to show that products have been exposed appreciably to a radiation source. These indicators may be labels, papers, inks that undergo a visual color change when exposed to ionizing radiation [12]. Therefore, they can be used to distinguish irradiation-processed units from unprocessed irradiation units.

It is known that acid-base indicators can exist in equilibrium between two tautomeric forms having different colors and the ratio of the two forms depends on the concentration of hydrogen ion in the medium. In our case, thymol blue (TB) is yellow at $2.8 < pH < 8$ (form I) and red at $pH < 1.2$ (form II) as represented by the schematic diagram (Scheme 1):

The quantitative estimation of radiation-formed acid in polymeric films containing an acid releasing agent is very important, particularly, for the application of these systems in radiation dosimetry. The knowledge of the amount of acid formed in a polymeric system at a specific dose (*i.e.*, the pH in the film after irradiation) helps in choosing a suitable pH-indicator to give a clear visual change in color at this dose. The first attempt to develop a method for calculating the concentration of radiation-formed acid in PVB films containing chloral hydrate was carried out by Abdel-Fattah and El-Kelany, 1998 [8]. This method of calculation based on the presence of bromophenol blue (BPB) indicator in the film and using its equilibrium constant and the ratio between its two tautomeric forms.

In the current work, a new method for calculation of concentration of radiation-formed acid in PVB films containing chloral hydrate is developed and compared with the method given by Abdel-Fattah and El-Kelany, 1998 [8]. The radiation-chemical yield and the kinetics of acid-formation in the films are discussed. For the application in dosimetry, the effects of temperature and relative humidity during irradiation as well as pre- and post-irradiation stability on the response of films are described.



SCHEME 1

EXPERIMENTAL PROCEDURES

Preparation of Stock Solution of Indicator

A stock solution of the sodium salt of the indicator was prepared by dissolving 0.08 g of thymol blue indicator (TB) (product of CHEMAPOL, Czech Republic) in 1.7 mL of an aqueous solution of NaOH ([NaOH] = 0.1 mol/L) and then the volume was completed by ethanol in a 50 mL volumetric flask. It should be noted that the TB stock solution is almost neutral (the pH was found to be 6.8) when the NaOH in its preparation is used in equimolar concentration.

Preparation of the Film

Poly(vinyl butyral) has previously been used successfully to make free-standing dyed films cast on a flat glass surface, from which they can be stripped as flexible foils [8, 13]. 12.5 grams of polyvinyl butyral (PVB) (Pioloform BM18, product of Wacker Co., USA) were well dissolved in 250 mL of *n*-butanol at about 50°C. The solution was kept well stirred at the same temperature for about 24-h, left to cool and then divided into ten parts each one of 25 mL volume. To six parts of the polymer solution, TB stock solution was added as 3 mL to each 25 mL part. 0.5, 1.0, 1.5, 2.0 or 3.0 g of chloral hydrate (product of Merck, Germany) were added to five parts and the sixth one was left without chloral hydrate. To each solution of the rest four parts 1 g of chloral hydrate and 1, 2, 4 or 5 mL of TB stock solution were added, respectively. The ten solutions were kept well stirred at room temperature for about 3 hours in order to obtain a uniformly mixed solution. Each solution was poured onto a 15 × 15 cm horizontal glass plate and dried at room temperature for about 48 hours. Ten films were obtained, six of them contain the same concentration of TB (0.33 phr[1]) and different concentrations of chloral hydrate (0, 34, 68, 103, 137 and 205 phr). The other four films contain the same concentration of chloral hydrate (68 phr) and different concentrations of TB (0.11, 0.22, 0.44 and 0.55 phr). After drying, the films were stripped from the glass plate, then cut into 1 × 1 cm pieces and stored for different investigations. The thickness of the obtained films was found to be 0.075 ± 0.005 mm ($1\,\sigma$).

Apparatus

Irradiations were carried out with gamma radiation in the ^{60}Co gamma chamber 4000A (product of India). The absorbed dose rate in the irradiation facility was measured to be 3.0 kGy/h, using Fricke dosimetry

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[1] phr = part per hundred parts by weight of resin.

[$G(Fe^{3+}) = 1.62\,\mu mol/J$] [14]. Five films at each dose are grouped together, sandwiched between two PMMA plates of 3 mm thickness (to maintain electronic equilibrium conditions) and irradiated at the central spatial position of the sample chamber using a specially designed holder made from polystyrene. The temperature during irradiations was ca. 30°C.

Unicam UV4 spectrophotometer (product of Unicam Co. Ltd., England) was used to measure the absorption spectra of the unirradiated and irradiated films. The film thickness was measured using a Digitrix-Mark II thickness gauge (precision $\pm$ 1 μm, 1 σ).

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of different TB/PVB films were recorded before and after irradiation to different doses. The results with films containing 0.33 phr of TB indicator and 68 phr of chloral hydrate are shown in Figure 1. The absorption spectrum of unirradiated film shows a main absorption band in the visible region characteristic of a yellow color peaking at 435 nm (curve 1, Fig. 1). The amplitude of this absorption band decreases gradually and shifts to lower wavelengths with the increase of absorbed dose of γ-ray photons.

A new absorption band peaking at 551 nm, characteristic of a red color, is formed and its amplitude increases gradually with the increase of absorbed dose. Upon irradiation, these films change their color from yellow (the alkaline form of TB with $\lambda_{max} = 435$ nm) to red (the acidic form of TB with $\lambda_{max} = 551$ nm) indicating acid formation. The dose at which the color appears depends on the concentration of both TB and chloral hydrate in the film. The sequence of approximate change of color of different films containing various concentrations of TB and chloral hydrate at different doses are presented in Table 1. From this table, one can choose the suitable concentrations of TB and chloral hydrate in a film for a specific application.

Figure 2 shows the absorption spectra of TB/PVB films without chloral hydrate unirradiated and irradiated to 5, 15 and 60 kGy absorbed doses. The absorption band at 435 nm decreases slowly with the increase of absorbed dose, however, no apparent bleaching occurs at dose of 5 kGy. Also, this figure indicates the absence of any absorption band at 551 nm, *i.e.*, there is no appreciable radiation-formed acid to change the color.

Response Curves

Figure 3 shows the response curves of TB/PVB films containing 0.33 phr of TB and different concentrations of chloral hydrate in terms of change in optical density per unit thickness, $(\Delta A \cdot mm^{-1})_{551}$, at 551 nm wavelength

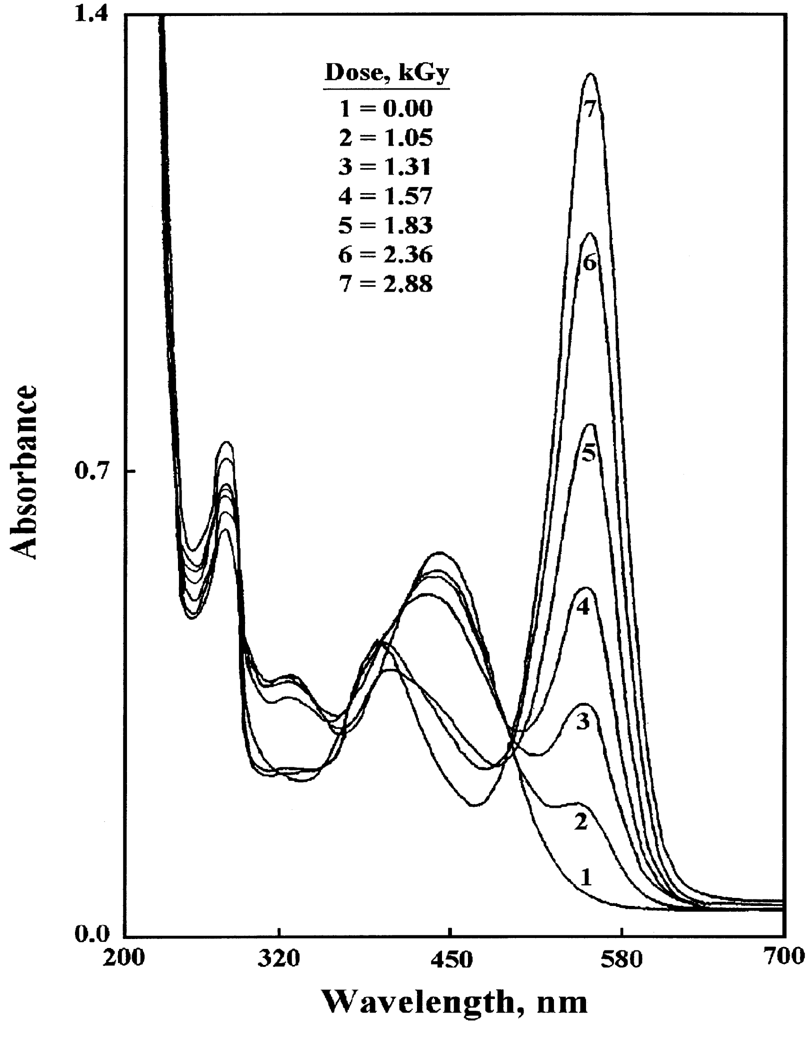

FIGURE 1 The absorption spectra of TB/PVB films unirradiated and irradiated to different absorbed doses. [TB] = 0.33 phr; [chloral hydrate] = 68 phr.

versus the absorbed dose ($\Delta A = A_i - A_o$, where A_o and A_i are optical densities of the unirradiated and irradiated films, respectively). It can be noticed that all curves have the same S-shape, characteristic of the irradiation response of a pH indicator in an acid–base titration with different sensitivities. It may be observed from the data illustrated in Figure 3 that the initial part of the curves depends on the concentration of chloral hydrate. As a matter of fact, the flattening of this portion of the curves

TABLE 1 Sequence of color change of different PVB films containing various concentrations of chloral hydrate and TB at different absorbed doses

Film composition		*Color of the film*								
		Dose, kGy								
[*TB*], *phr**	[*chl. hyd.*], *phr*	0	0.79	1.05	1.31	1.57	1.83	2.36	2.88	3.51
0.11	68	Y	O	R–O	R	R	R	R	R	R
0.22	68	Y	Y–O	O	R–O	R	R	R	R	R
0.33	34	Y	Y	Y	Y	Y–O	O	R–O	R	R
0.33	68	Y	Y	Y	Y–O	O	R–O	R	R	R
0.33	103	Y	Y	Y–O	O	R–O	R	R	R	R
0.33	137	Y	Y–O	O	R–O	R	R	R	R	R
0.33	205	Y	Y–O	O	R–O	R	R	R	R	R
0.44	68	Y	Y	Y	Y–O	O	R–O	R	R	R
0.55	68	Y	Y	Y	Y–O	Y–O	O	R–O	R	R

Y = Yellow, O = Orange, YO = Yellowish orange, R = Red, RO = Reddish orange.
* phr = parts per hundred parts by weight of resin.

decreases with increasing the concentration of chloral hydrate. Accordingly, this behavior may be attributed to the $[H^+]$ formed on irradiation as its concentration would be expected to increase with increasing the chloral hydrate concentration. A certain $[H^+]$ ought, therefore, to be present, corresponding to certain pH value, for the indicator TB to start changing its color. After reaching this pH value the indicator starts to change color linearly within its specific range giving the linear sections in the curves. The occurrence of end levelling-off section of the curves, may be ascribed to the complete transformation of the indicator from its basic form to the acidic one. The relation between the slope of the straight sections of the curves and the concentration of chloral hydrate is shown in Figure 4. It can be seen that the slope increases exponentially with the increase of chloral hydrate concentration.

Figure 5 shows the response curves of TB/PVB films containing 68 phr chloral hydrate and different concentrations of TB indicator. It can be seen that all curves have the same S-shape, which reaches saturation at doses proportional to the concentration of TB. The dose at saturation was found to increase linearly with the increase of TB concentration from 0.11 up to 0.55 phr as shown in Figure 6.

Calculation of Acid Concentration

The results indicate that in the dose range up to 5 kGy, radiation-induced bleaching of TB indicator (*i.e.*, the decrease in absorbance of TB/PVB films

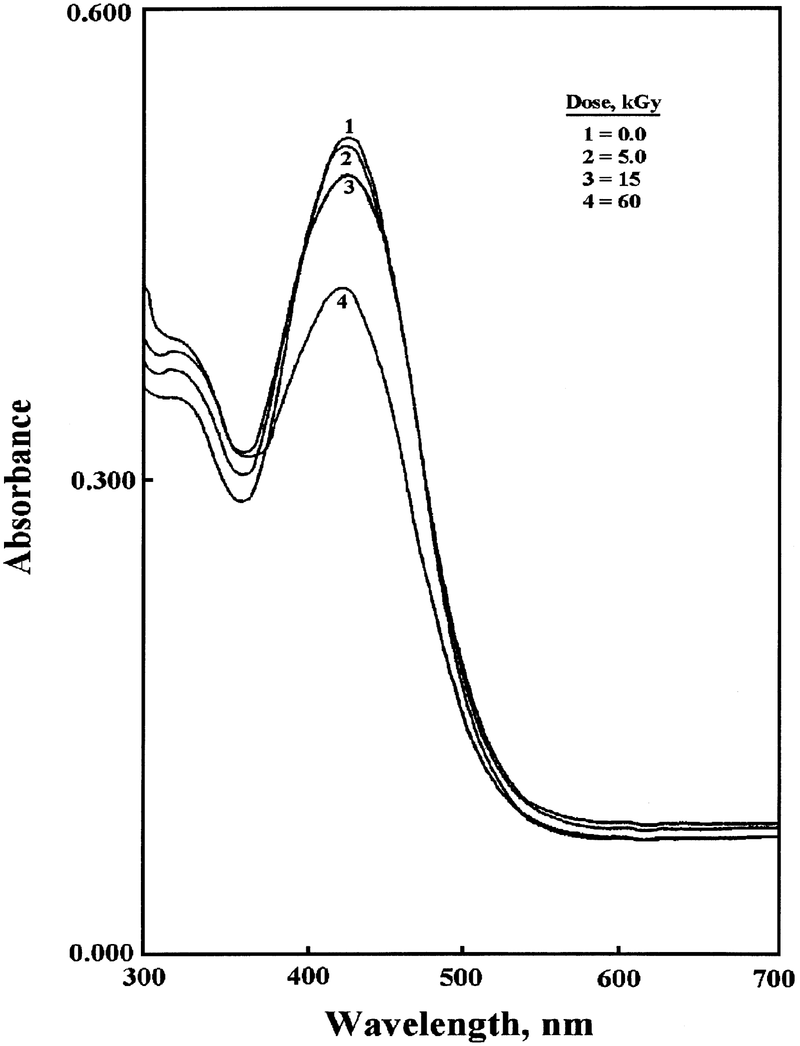

FIGURE 2 The absorption spectra of TB/PVB films (without chloral hydrate) unirradiated and irradiated to different absorbed doses. [TB] = 0.33 phr.

without chloral hydrate at 435 nm) is very small, calculated to be less than 2% of the initial absorbance (see Fig. 2). Therefore, it can be concluded that radiation-induced change in color of TB/PVB films containing chloral hydrate is only due to the formation of acid. It is known that acid–base indicators exist in equilibrium between two tautomeric forms and the ratio of the two forms depends on the concentration of hydrogen ion in the

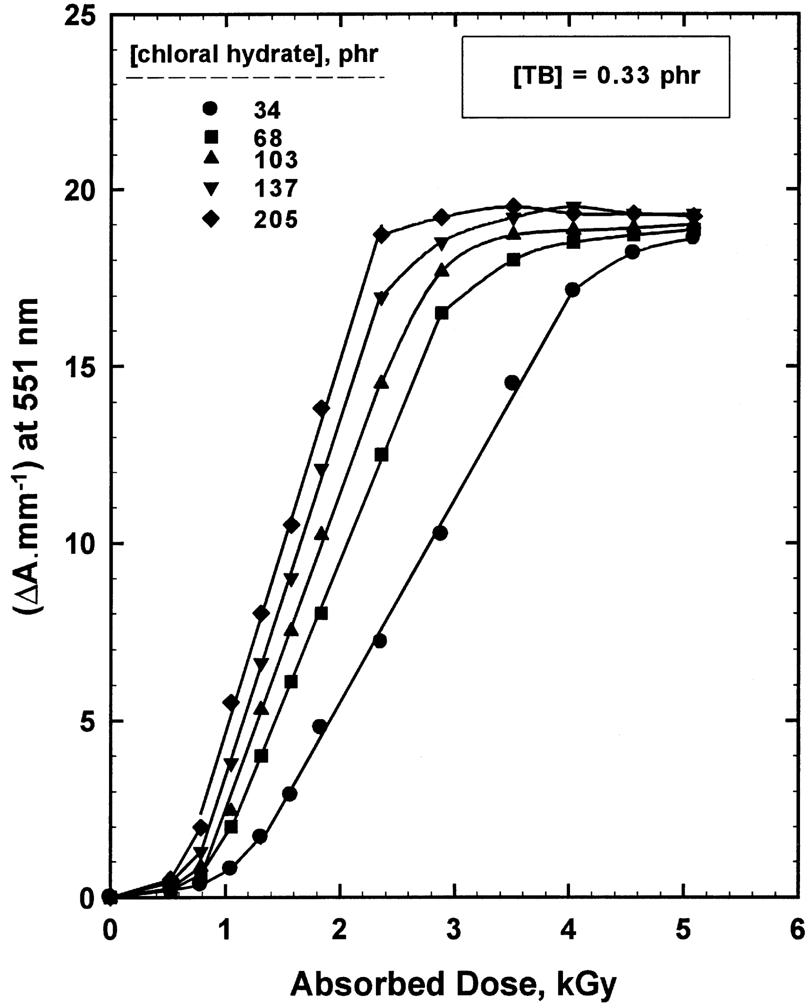

FIGURE 3 Change of $\Delta A \cdot mm^{-1}$ as a function of absorbed dose of TB/PVB films with different concentrations of chloral hydrate. [TB] = 0.33 phr; $\lambda_{max} = 551$ nm.

medium. Let us consider the equilibrium between the two forms of TB indicator represented as follows:

$$H^{+} + TB^{-} \rightleftharpoons HTB \tag{1}$$

In a previous work [8], the concentration of radiation-formed H^{+} in PVB films containing chloral hydrate and bromophenol blue (BPB) indicator was calculated on the basis of equilibrium between the two forms of the

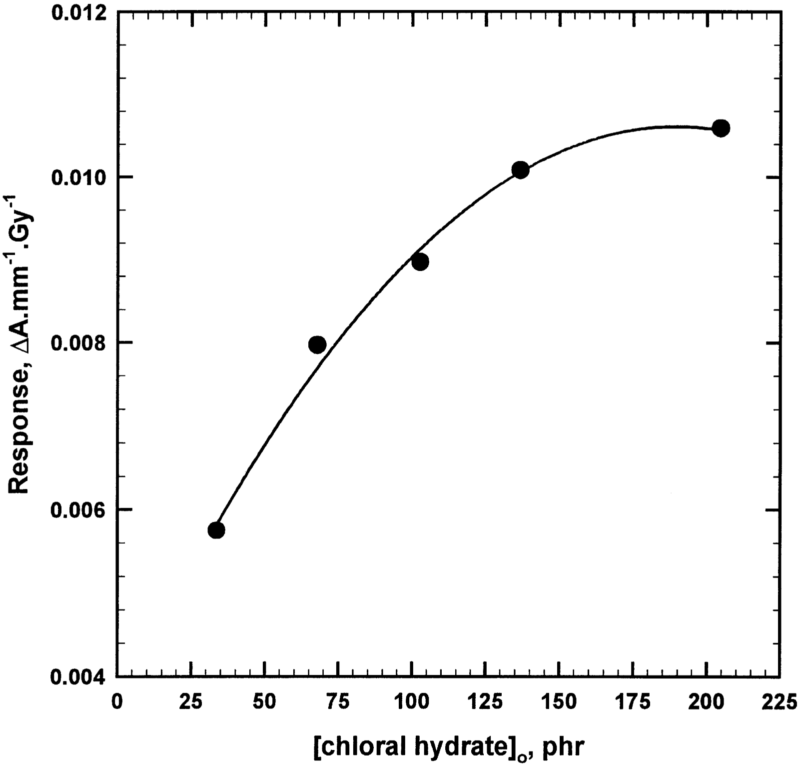

FIGURE 4 Change of response, slope of straight sections of curves given in Figure 3, as a function of the concentration of chloral hydrate in the films.

indicator using its equilibrium constant. The amount of hydrogen ion formed due to the irradiation to a dose D was calculated by the following equation:

$$[\text{total}\,\mathrm{H}^+]_D = [\mathrm{HIn}]_D + K_{\mathrm{In}}\frac{[\mathrm{HIn}]_D}{[\mathrm{In}^-]_D} \qquad (2)$$

where, $[\mathrm{HIn}]_D$ and $[\mathrm{In}^-]_D$ are the concentration of changed and unchanged indicator after irradiation to a dose D, respectively. K_{In} is the indicator equilibrium constant.

This method of calculation is examined by calculating the amount of radiation-formed H^+ in TB/PVB films and comparing the results with those given in the previous work for BPB/PVB films. Figure 7 shows a comparison between the results obtained with BPB/PVB and TB/PVB films containing almost the same concentration of chloral hydrate (33.7 ± 0.4 phr) where calculations were carried out using the method given by Abdel-Fattah

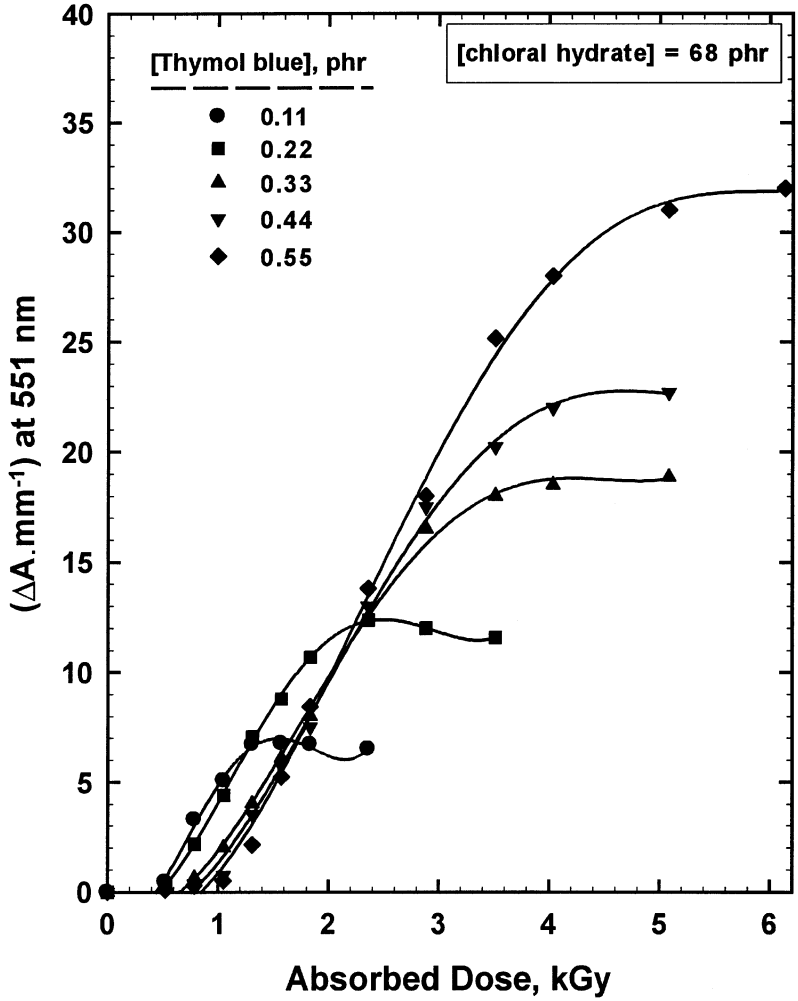

FIGURE 5 Change of $\Delta A \cdot mm^{-1}$ as a function of absorbed dose of TB/PVB films with different concentrations of TB. [chloral hydrate] = 68 phr; $\lambda_{max} = 551$ nm.

and El-Kelany, 1998 [8]. It can be seen that the concentrations of H^+ in TB/PVB are much higher than those obtained with BPB/PVB and the difference increases dramatically at high doses. For example, at dose of 3.5 kGy $[H^+]$ in TB/PVB is about 25 times that in BPB/PVB. These results indicate the invalidity of that method of calculation. Unfortunately, the authors in the previous work assumed that the indicator behavior in the polymeric matrix (PVB polymer) is the same as in liquid solution, while it was known that the mobility of H^+ ions in a solid state matrix would be difficult.

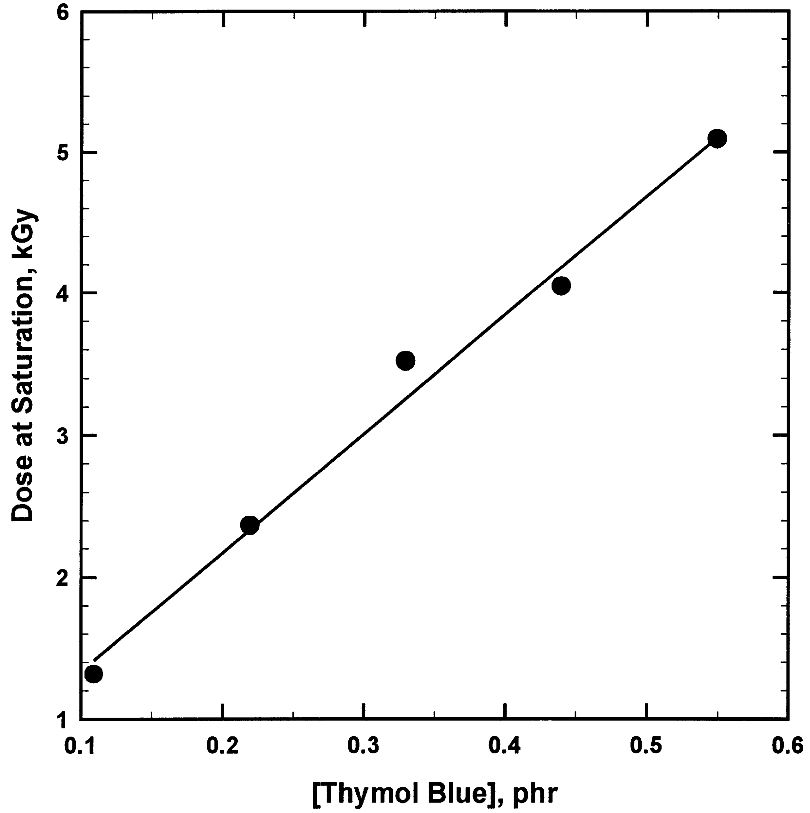

FIGURE 6 Variation of dose at saturation of TB/PVB films as a function of concentration of TB. [chloral hydrate] = 68 phr.

As we are dealing with a solid-state polymeric medium, the equilibrium given by Eq. (1) could shifts strongly to the direction of formation of HTB. Accordingly, the equilibrium between the two forms of TB indicator may be represented as follows:

$$H^+ + TB^- \rightleftarrows HTB \tag{3}$$

As was mentioned before, a certain concentration of H^+ is required for the indicator to start changing color as seen from the first sections in the curves given in Figure 3. Accordingly, it can be assumed that, after reaching a certain pH, most radiation-formed hydrogen ions should react directly with TB^- forming HTB according to the equilibrium given by Eq. (3).

On the basis of this assumption, the concentration of H^+ formed due to the irradiation of TB/PVB films to a dose *D* is given by the sum of the

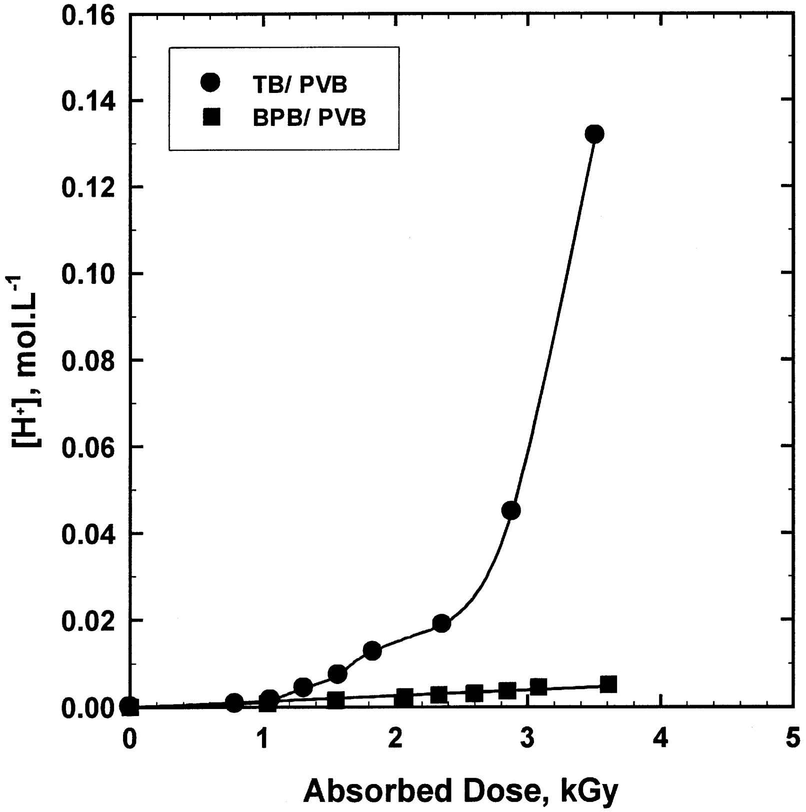

FIGURE 7 Comparison between calculated [H^+] in TB/PVB and BPB/PVB films containing the same concentration of chloral hydrate (33.7 ± 0.4 phr). Calculations of H^+ were carried out using the method given by Abdel-Fattah and El-Kelany, 1998.

concentration of H^+ necessary for TB to start changing color, $[H^+]_I$, and the concentration of hydrogen reacting with TB^-, $[TBH]_D$, *i.e.*,

$$[H^+]_D = [H^+]_I + [TBH]_D \tag{4}$$

where, $[TBH]_D$ is the concentration of changed thymol blue due to irradiation to a dose D. The small amount of free H^+ maintaining the equilibrium given by Eq. (3) is neglected.

Using the reported density of PVB (1.1 g · cm^{-3}), the concentration of TB before irradiation in the films containing 0.33 phr of sodium salt of TB is calculated as 7.43×10^{-3} mol/L. Assuming that Beer's law is valid in the used range of concentration of TB indicator, $[TBH]_D$ may be calculated by using the increase in response at 551 nm due to irradiation to a dose D as follows:

$$[\mathrm{TBH}]_D = 7.43 \times 10^{-3} \frac{(\Delta\mathrm{A} \cdot \mathrm{mm}^{-1})_D}{(\Delta\mathrm{A} \cdot \mathrm{mm}^{-1})_s} \tag{5}$$

where $(\Delta\mathrm{A} \cdot \mathrm{mm}^{-1})_D$ is the increase in response at 551 nm due to irradiation to a dose D and $(\Delta\mathrm{A} \cdot \mathrm{mm}^{-1})_s$, is the response at 551 nm at saturation, *i.e.*, when all TB^- is changed to TBH. From Figure 3, it can be seen that $(\Delta\mathrm{A} \cdot \mathrm{mm}^{-1})_s$ is equal to 19 ± 0.3. Substituting the value of $(\Delta\mathrm{A} \cdot \mathrm{mm}^{-1})_s$ in (4), gives,

$$[\mathrm{TBH}]_D = 3.91 \times 10^{-4} (\Delta\mathrm{A} \cdot \mathrm{mm}^{-1})_D \tag{6}$$

$[\mathrm{H}^+]_I$ which is the concentration of H^+ necessary for thymol blue to start changing its color may be calculated by extending the straight sections of the response curves given in Figure 3, to the zero dose point. It was found that all curves meet the negative Y-axis at very close points, with an average of -6.4 ± 0.3 $(1\,\sigma)$ which is equivalent to a concentration of TB of 2.5×10^{-3} mol/L (calculated by using Eq. (6)).

By substitution in Eq. (4), $[\mathrm{H}^+]_D$ is calculated as follows:

$$[\mathrm{H}^+]_D = 2.5 \times 10^{-3} + 3.91 \times 10^{-4} (\Delta\mathrm{A} \cdot \mathrm{mm}^{-1})_D \tag{7}$$

The validity of this new method of calculation of $[\mathrm{H}^+]_D$ in PVB films containing chloral hydrate was examined by calculating $[\mathrm{H}^+]$ formed in TB/PVB and BPB/PVB films containing almost the same concentrations of chloral hydrate (33.3 ± 0.4 phr). The results are shown in Figure 8 as a function of absorbed dose. It can be seen that in both films the concentration of H^+ increases linearly with the dose and the difference between them is about 35%. These results suggest the validity of this method of calculation of concentration of radiation-formed acids in PVB containing chloral hydrate by using acid-sensitive indicators. The 35% difference between TB/PVB and BPB/PVB films may be attributed to the neglected amount of H^+ maintaining the equilibrium in Eq. (3) as well as the differing conditions between the two experiments.

The concentration of H^+ formed in PVB films containing different concentrations of chloral hydrate at different doses was calculated by using Eq. (7) and the results are shown in Figure 9. It can be seen that the amount of acid formed increases linearly with the increase of absorbed dose.

Kinetics of Acid Formation

In these films (TB/PVB containing chloral hydrate) the acid is formed due to the irradiation of chloral hydrate. The radiolysis products of chloral hydrate

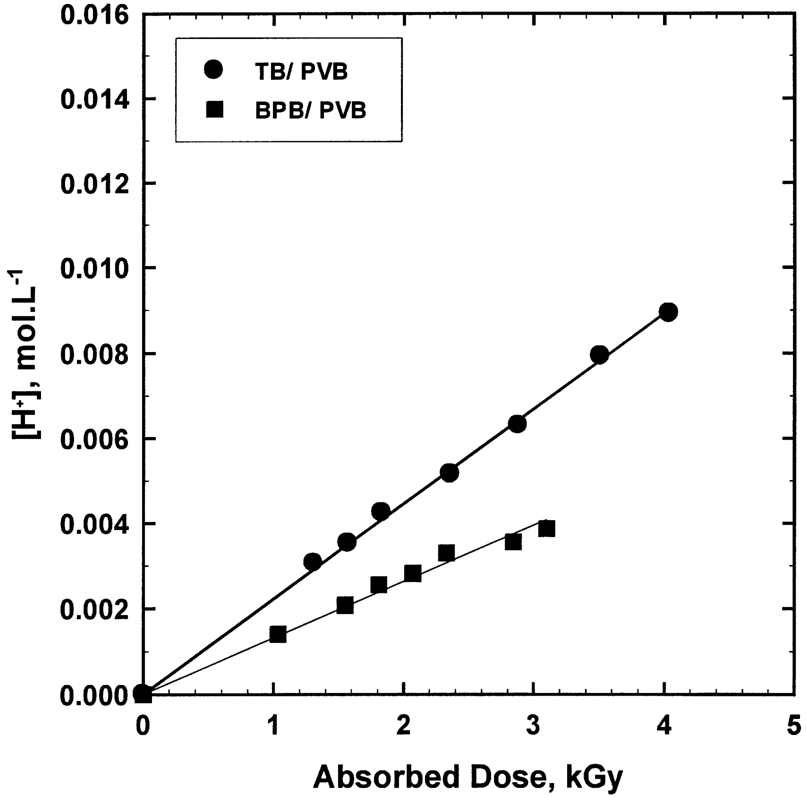

FIGURE 8 Comparison between calculated $[H^+]$ in TB/PVB and BPB/PVB films containing the same concentration of chloral hydrate (33.7 ± 0.4 phr). Calculations of H^+ were carried out using the new method of calculation.

may involve the following:

$$CCl_3CH(OH)_2 \rightsquigarrow {}^{\cdot}Cl + {}^{\cdot}CCl_2CH(OH)_2 \qquad (8)$$

$$CCl_3CH(OH)_2 \rightsquigarrow {}^{\cdot}OH + CCl_3\,{}^{\cdot}CHOH \qquad (9)$$

$$CCl_3\,{}^{\cdot}CHOH \rightsquigarrow {}^{\cdot}H + CCl_3CHO \qquad (10)$$

The produced radicals are expected to react rapidly together to form variety of products, among them:

$$H^{\cdot} + {}^{\cdot}Cl \longrightarrow HCl_{(g)} \qquad (11)$$

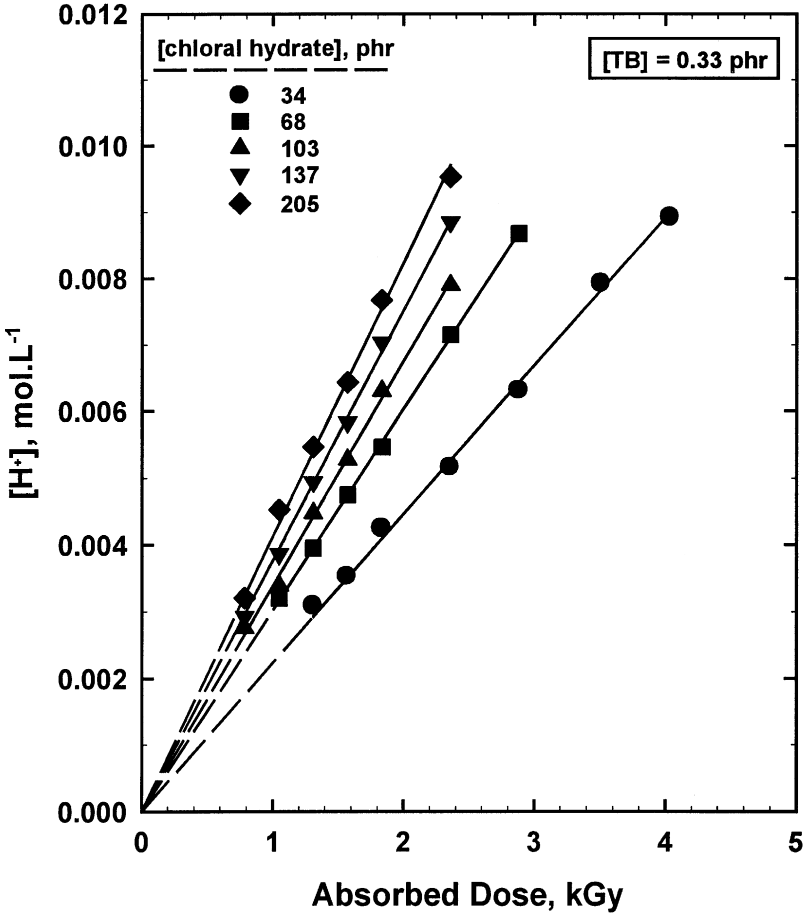

FIGURE 9 Concentration of radiation-formed HCl in TB/PVB films containing different concentrations of chloral hydrate as a function of absorbed dose. [TB] = 0.33 phr.

$$H^{\cdot} + {}^{\cdot}OH \longrightarrow H_2O \tag{12}$$

$$H^{\cdot} + {}^{\cdot}H \longrightarrow H_{2(g)} \tag{13}$$

From these radiolysis products, it can be seen that there is only one acid product, which is (HCl). The rate law of HCl formation (Eq. (11)) is presumed to have the form:

$$-d[CCl_3CH(OH)_2]/dt = d[HCl]/dt = k[CCl_3CH(OH)_2]^a \tag{14}$$

where a is the order of the reaction and k is the kinetic rate constant $[(\mathrm{mol} \cdot \mathrm{L}^{-1})^{1-a}\,\mathrm{s}^{-1}]$. The order a can be determined by using the initial slopes method [15]. At the start of the reaction, when the concentration of chloral hydrate is $[\mathrm{CCl_3CH(OH)_2}]_o$, the rate equation is:

$$(d[\mathrm{HCl}]/dt)_{\mathrm{initial}} = k[\mathrm{CCl_3CH(OH)_2}]_o^a \tag{15}$$

$(d[\mathrm{HCl}]/dt)_{\mathrm{initial}}$ can be calculated from the slopes of the straight lines given in Figure 9, through multiplying the slope by the dose rate (3.144 kGy/h). Plotting the initial rate against various initial concentrations of chloral hydrate (on log–log scale) gives the order a from the slope and the rate constant k from the intercept. Figure 10 shows the logarithmic relationship between the initial rate, $d[\mathrm{HCl}]/dt)_{\mathrm{initial}}$, and chloral hydrate concentration $[\mathrm{CCl_3CH(OH)_2}]_o$. A straight line is obtained: its slope is 0.35 and its

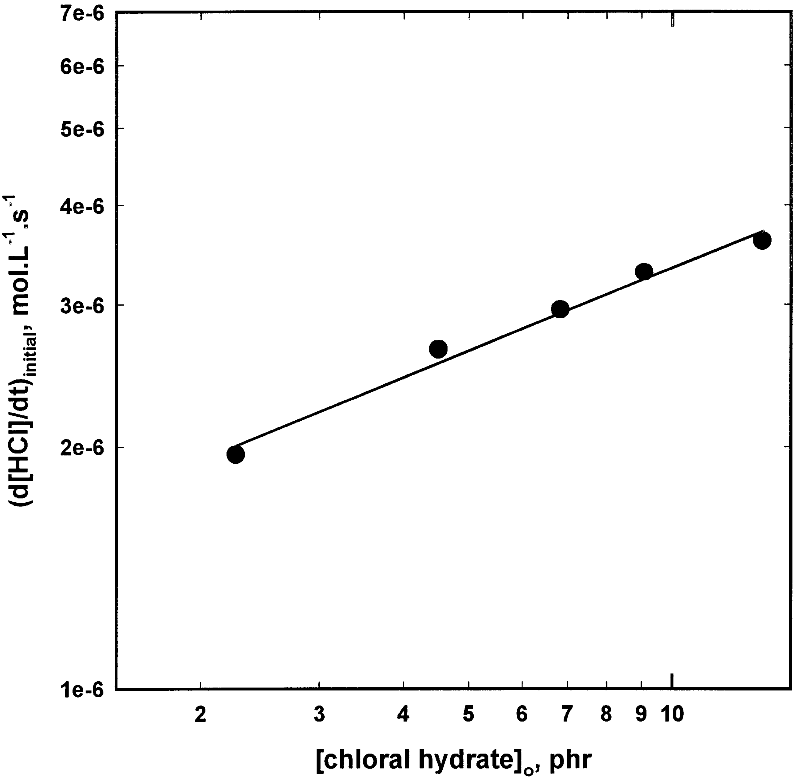

FIGURE 10 The logarithmic relationship between the initial rate, $(d[\mathrm{HCl}]/dt)_{\mathrm{initial}}$, and the initial concentration of chloral hydrate in TB/PVB films. [TB] = 0.33 phr.

intercept is (-5.82). Accordingly the order of the reaction is 0.35 and the kinetic rate constant is $1.51 \times 10^{-6}(\mathrm{mol} \cdot \mathrm{L}^{-1})^{0.65} \cdot \mathrm{s}^{-1}$.

Let's consider $[\mathrm{CCl_3CH(OH)_2}]$ is [C]. Equation (14) may be expressed as follows:

$$-d\mathrm{C}/dt = k\mathrm{C}^{0.35} \tag{16}$$

$$-\mathrm{C}^{-0.35} \cdot d\mathrm{C} = k \cdot dt \tag{17}$$

$$-\int_{\mathrm{C}_o}^{\mathrm{C}_t} \mathrm{C}^{-0.35} \cdot d\mathrm{C} = k \int_0^t dt \tag{18}$$

or,

$$\frac{\mathrm{C}_o^{0.65}}{0.65} - \frac{\mathrm{C}_t^{0.65}}{0.65} = kt \tag{19}$$

i.e.,

$$\mathrm{C}_o^{0.65} - \mathrm{C}_t^{0.65} = 0.65kt \tag{20}$$

where C_o is the initial concentration of chloral hydrate and C_t is the concentration of chloral hydrate at time t that may given by the following equation:

$$\mathrm{C}_t = \mathrm{C}_o - [\mathrm{H}^+]_t \tag{21}$$

Plotting $(\mathrm{C}_o^{0.65} - \mathrm{C}_t^{0.65})$ as a function of irradiation time gives a straight line its slope is $0.65k$ (see Fig. 11). The kinetic constant, k, was found to be 1.49×10^{-6} $(\mathrm{mol} \cdot \mathrm{L}^{-1})^{0.65} \cdot \mathrm{s}^{-1}$ which is in a good agreement with the value obtained before by using the initial slope method. This also confirms the proposed and calculated order of reaction (0.35). From Figure 11, it can be seen that all results for different initial concentrations of chloral hydrate are very close. This may be a good evidence for that the rate of consuming chloral hydrate is almost constant with irradiation time for different initial concentrations of chloral hydrate. This result may be understood in light of the high concentrations of chloral hydrate used in this study and the small reaction order.

Humidity during Irradiation

The effect of relative humidity during irradiation on the response of three TB/PVB films containing different concentrations of TB and chloral

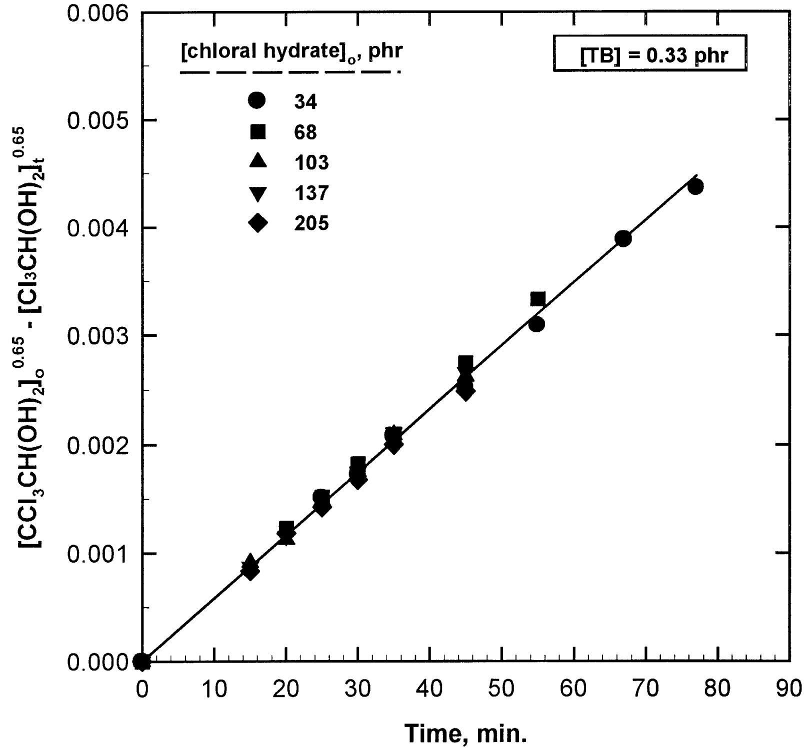

FIGURE 11 The radiation-induced decrease of chloral hydrate concentration as a function of irradiation time.

hydrate was investigated by irradiating the films to a suitable dose at different relative humidities. The first film ([TB] = 0.11 phr and [chloral hydrate] = 68 phr) was irradiated to a dose of 1 kGy. The second film ([TB] = 0.33 phr and [chloral hydrate] = 68 phr) was irradiated to a dose of 1.8 kGy while the third ([TB] = 0.33 phr and [chloral hydrate] = 205 phr) was irradiated to a dose of 1.5 kGy. The different relative humidity values were maintained by using different saturated salt solutions [16]. The films were stored before irradiation for a 3-day period under the same relative humidity conditions as when irradiated, so that equilibrium moisture content in the dosimeter has been established during irradiation. Figure 12 shows the variation in response ($\Delta A \cdot mm^{-1}$) at 551 nm, as a function of percentage relative humidity during irradiation relative to the response value at 33% relative humidity. It is shown that the response is relatively flat within ± 5% for relative humidities in the range of 0–60%, with reduced sensitivity at higher humidities. The increase of the water content in the film would facilitate the mobility of ionic species in the film leading to shift the equilibrium given in Eq. (2) towards the direction of dissociation of TBH,

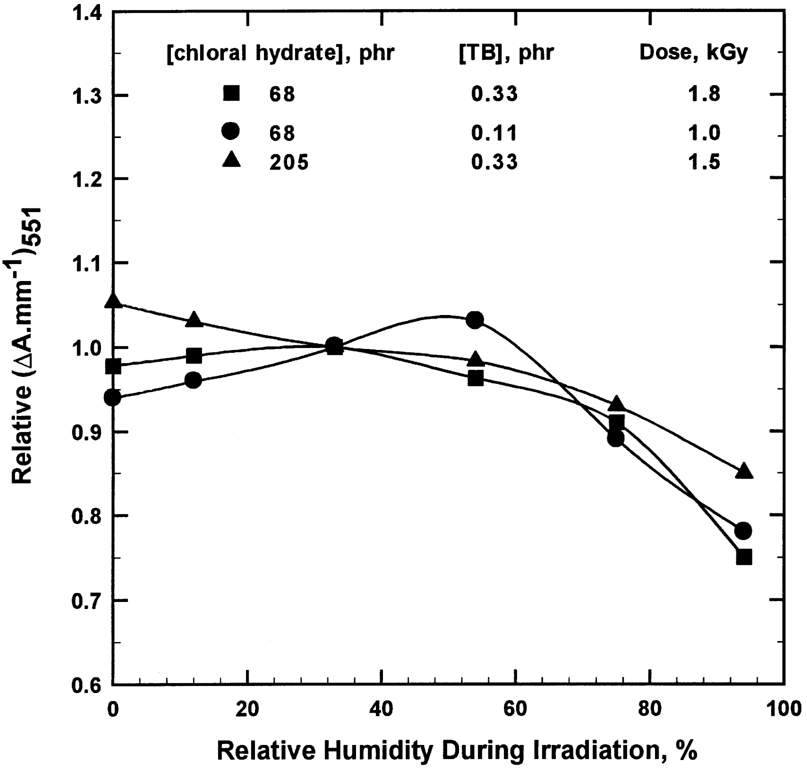

FIGURE 12 Variation of response of TB/PVB films ($\Delta A \cdot mm^{-1}$, at 551 nm) containing different concentrations of TB and chloral hydrate as a function of relative humidity during irradiation to different doses. Concentrations of TB and chloral hydrate as well as irradiation dose were indicated.

i.e., the back reaction. This may explain the reduced sensitivity of the film at high relative humidities.

It can be concluded that TB/PVB films have negligible humidity effects in the intermediate range of humidity from 0 to 60%. To avoid the effects of other humidity levels, the films should be packaged and sealed under intermediate humidity condition (0–60%) or, if that is impractical, one should maintain conditions of calibration as close as possible to the conditions of use.

Temperature during Irradiation

The effect of irradiation temperature was investigated by irradiating TB/PVB films ([TB] = 0.33 phr and [chloral hydrate] = 68 phr) to a dose of 1.6 kGy at different temperatures (0, 30, 45, 60, 70°C) by using liquid thermal baths [17]. The variation in response, $\Delta A \cdot mm^{-1}$, as a function of temperature during irradiation is shown in Figure 13. It is found that, the response of this film depends on the irradiation temperature, where the response ($\Delta A \cdot mm^{-1}$) decreases linearly with the increase of irradiation temperature in the range (0–70°C). Accordingly, a correction should be applied if these films are irradiated at any temperature different from that used during establishment of the calibration curve.

Considering that the dose response curve is established at irradiation temperature, t_1, a correction should be applied to the response values obtained at any other irradiation temperature, t_2, according to the following equation:

$$(\Delta A \cdot mm^{-1})_c = (\Delta A \cdot mm^{-1})_m + 0.0614(t_2 - t_1) \qquad (22)$$

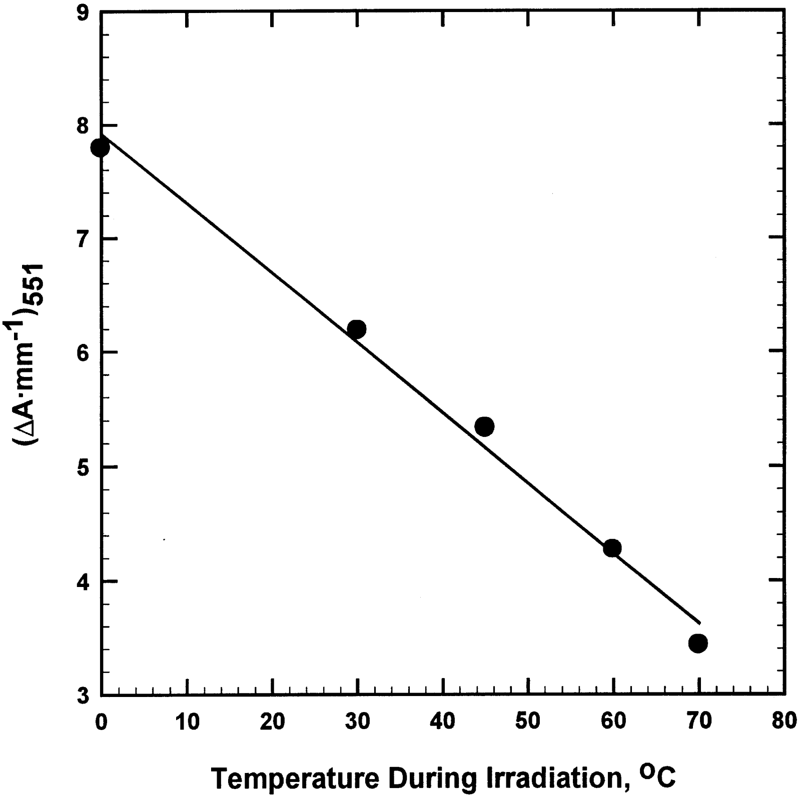

FIGURE 13 Variation of response of TB/PVB films ($\Delta A \cdot mm^{-1}$ at 551 nm) as a function of temperature during irradiation to a dose of 1.6 kGy. [TB] = 0.33 phr; [chloral hydrate] = 68 phr.

where, $(\Delta A \cdot mm^{-1})_c$ is the corrected response value that should be used to obtain the dose from a response curve established at irradiation temperature t_1. $(\Delta A \cdot mm^{-1})_m$ is the measured response value at irradiation temperature t_2.

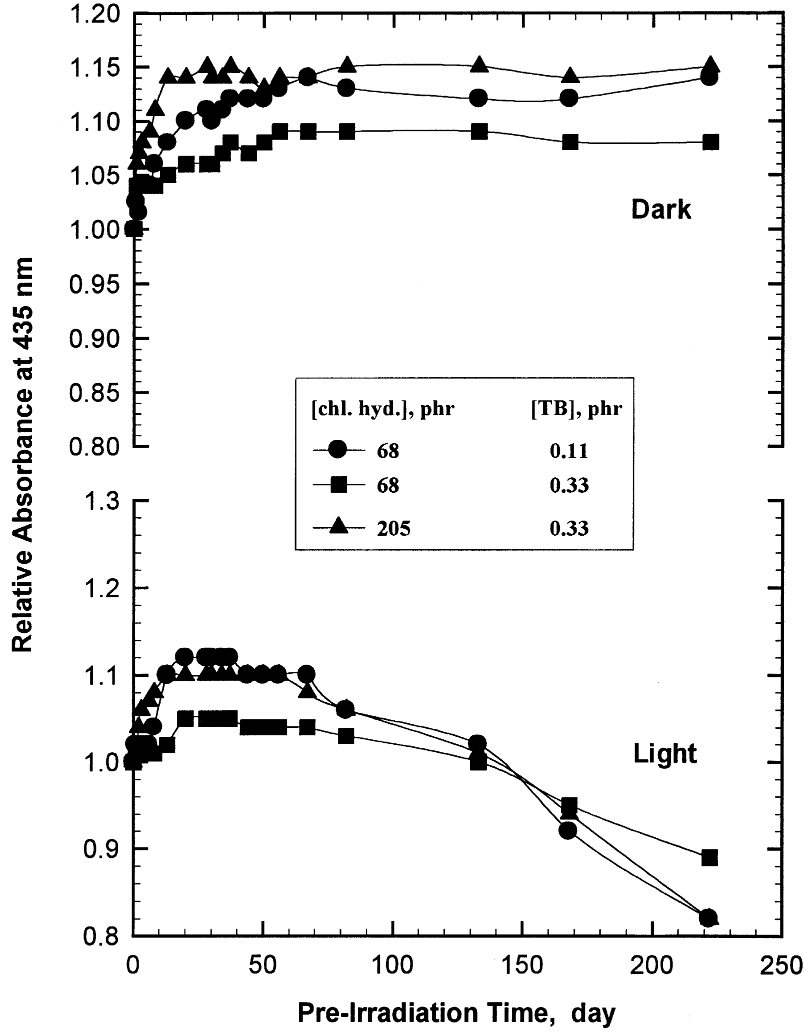

FIGURE 14 Pre-irradiation stability of TB/PVB films stored in dark and light at room temperature. Concentrations of TB and chloral hydrate were indicated. Wavelength of analysis is 435 nm.

Pre-Irradiation Stability

The color stability of three TB/PVB films containing different concentration of TB and chloral hydrate before irradiation were tested by storing the films

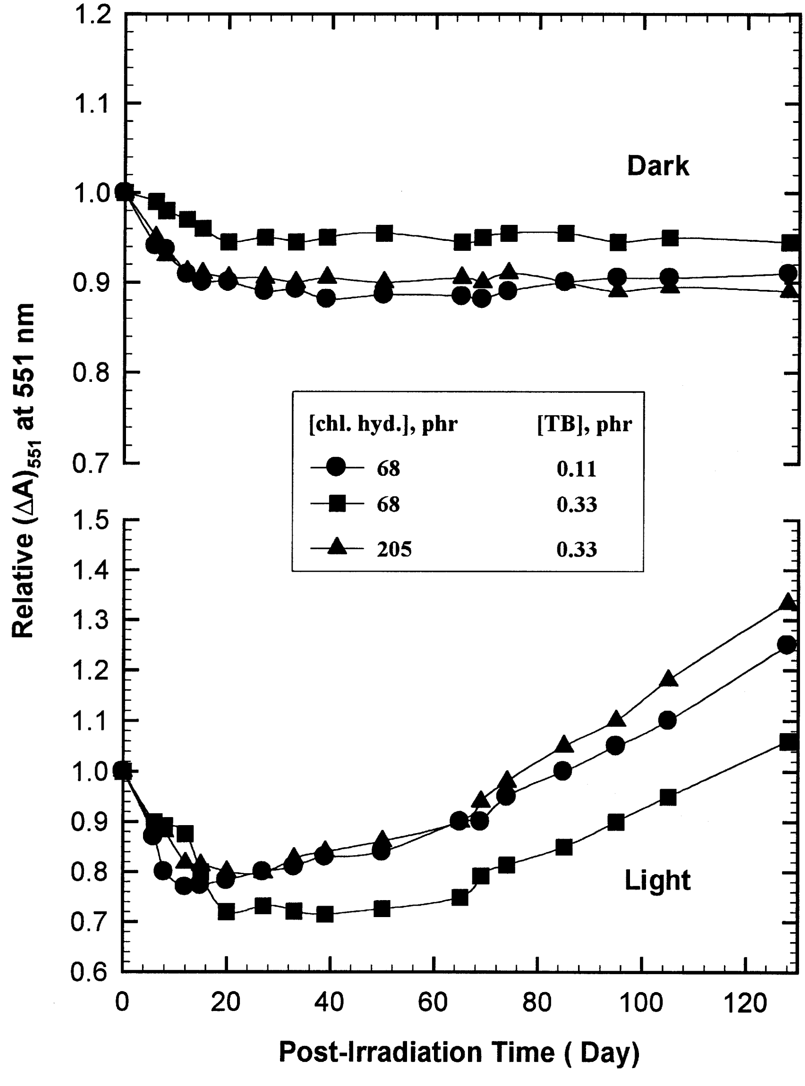

FIGURE 15 Post-irradiation stability of TB/PVB films stored in dark and light at room temperature. Concentrations of TB and chloral hydrate were indicated. Wavelength of analysis is 551 nm.

at 35% RH and at room temperature (25 ± 3°C) in the dark and under laboratory fluorescent lights. The absorbance of the films was measured at 435 nm wavelength at different time intervals during the pre-irradiation storage period of 225 days. The change in absorbance at 435 nm as a function of storage time relative to that before storage (immediately after stripping) is shown in Figure 14. It can be seen that the films stored in the dark show about 5 – 15% increase in absorbance during the first two weeks of storage depending on the concentration of TB and chloral hydrate in the film. Thereafter, the films tend to be stable to the end of the storage period. On the other hand the films stored in ambient light show about 5 – 12% increase in absorbance during the first two weeks of storage and then tend to be stable for about 3 months, after that, the absorbance decreases gradually.

Post-Irradiation Stability

The color stability of three TB/PVB films containing different concentration of TB and chloral hydrate after irradiation were tested by storing the films at 35% RH and at room temperature (25 ± 3°C) in the dark and under laboratory fluorescent lights. The absorbance of the films was measured at 551 nm wavelength at different intervals of time during the post-irradiation storage period of 128 days. The changes in response, ΔA_{551}, at 551 nm wavelength of TB/PVB films as a function of storage time relative to that before storage (zero time) are shown in Figure 15. It can be seen that the response of the films stored in the dark decreases gradually with about 5% during the first two weeks after irradiation, thereafter, it tends to be stable to the end of the 128-day storage period. On the other hand, the response of TB/PVB films stored in fluorescent day light shows a gradual decrease for about three weeks after irradiation and after that it tends to be stable for about 40 days, then begins to increase gradually to the end of the 128-day storage period.

CONCLUSION

TB/PVB films containing chloral hydrate change their color from yellow to red upon irradiation, indicating acid formation. The amount of acid formed due to irradiation depends on the absorbed dose and the concentration of chloral hydrate in the film. A new method for calculation of the amount of the radiation-formed HCl in the films was developed. The generation of HCl in TB/PVB films was found to follow 1/3-order kinetics with respect to chloral hydrate concentration. TB/PVB films have a clear visual change in color (yellow – red) in the dose range 2 – 4 kGy reflecting their suitability for use as radiation indicators in some food-irradiation applications. Although, the response of these films depends on temperature during irradiation, it has negligible humidity effects in the range of relative humidity from 0 to 60% as well as good post-irradiation stability when stored in the dark at room temperature.

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