9.5 *Effects of Additives on PVG Dosifilm

CHEN Wenxiu LIU Aiguo
Department of Chemistry
Beijing Normal University
Beijing 100875 CHINA

ABSTRACT

Dosifilm PVG is a new radiochromic film dosimeter composed of matrix material polyvinyl butyral(PVB), leuco malachite green (LMG) and additive halogenated organic compound (RX), etc. The control of the dose range on PVG dosifilm was examined. The addition of halogenated compounds played an important role in the radiation reaction of LMG beyond the concentration of LMG. Bromide is more effective than chloride in this system, the oxidative species are $X\cdot$ and $X_2\cdot^-$. PVB with N-bromosuccinimide (NBS) can induce the oxidation of LMG before irradiation. The reaction mechanism of PVG was discussed.

Different linear ranges of radiation response on PVG dosifilm could be controlled by alternating the relative concentrations of halogenated compounds and LMG.

KEYWORDS

polyvinyl butyral; leuco malachite green; halogenated compounds; radiation oxidation; dosimeter.

INTRODUCTION

Leuco malachite green (LMG) in various systems has been utilized for radiation processing dosimetry purpose (Liu Aiguo et al.,1994;Wang Yanqiao et al., 1985; Stoltz et al., 1965). The discolor mechanism of LMG in polystyrene (PS) was also studied (Stoltz et al., 1965). The radiation chemistry in LMG organic solution has been reported (Vereshchinskiis et al., 1957; Bakh et al., 1960; Dejehet et al., 1972,1973; Grodkowski et al., 1990). Other leuco triarylmethane compounds have been studied, too (Armstrong et al., 1958; Bobrowski et al., 1985).

Polyvinyl butyral (PVB) film containing LMG and halogenated organic compounds as a dosimeter PVG has been developed and characterized (Liu Aiguo et al., 1994). Oxidation of LMG into its cation malachite green MG^+ with green color can be induced by gamma ray; its accumulation was proportional to the radiation dose.

Detailed study of LMG-PVB system in the presence of different halogenated organic compounds (RX) was carried out in this paper. By alternating the matrix and the concentration of LMG or RX, the linear relations of $\Delta A/L$ [i.e, $(A-A_0)/L$, mm^{-1} , see EXPERIMENTALS] vs dose (kGy) were obtained. The optimum composition and control of PVG dosifilm was deduced. The mechanism of radiation discoloration in the systems was discussed.

EXPERIMENTALS

Leuco malachite green (LMG, SIGMA, USA), polyvinyl butyral (PVB, Tianjing Organic Chemistry Industrial Experimental Factory, CHINA). $CCl_3CHO\cdot H_2O$ (A.R), C_2Cl_6 (A.R), CBr_4 (C. P), N-bromosuccinimide (NBS, A.R), PVC powder (Industrial Grade) and tetrahydrofuran (THF, A.R) were all manufactured in the Beijing Chemical Factory. The manufacture procedure of PVG dosifilm has been reported (Liu Aiguo et al., 1994). Irradiations were carried out using a 5.55×10^{14} Bq ^{60}Co-γ irradiation facility at Beijing Normal University with a dose rate of 16.2kGy/h. All the samples were kept in eletronic equilibrium during irradiation. Dose was calibrated by Fricke dosimeter. The dose values are expressed in terms of dose in water.

After irradiation the films were stored in a brown desiccator at room temperature(i.e, in air about 25-30℃). Absorbance of the films before (A_0) and after (A) irradiation was read out at a given wavelength using a HITACHI 200-20 double-beam UV spectrophotometer. The absorbance of each film was measured immediately after irradiation. The thicknesses (L) of the film pieces were measured using an Elecont micrometer made by Mitutoyo (JAPAN) with a reproducibility of $\pm0.2\,\mu$m.

RESULTS AND DISCUSSIONS

1. Formation of MG^+ in Irradiated PVB-LMG Film Containing Additive Halogenated Compounds (RX)

Exposed to ^{60}Co-γ, the PVB-LMG film with RX turned green owing to the formation of MG^+ (shows two absorption bands in the visible range with maximum absorption at 425 and 627nm). The PVB-LMG film without RX didn't change color after irradiation. Plots of ΔA/L vs dose were shown in Fig. 1 and Fig.2.

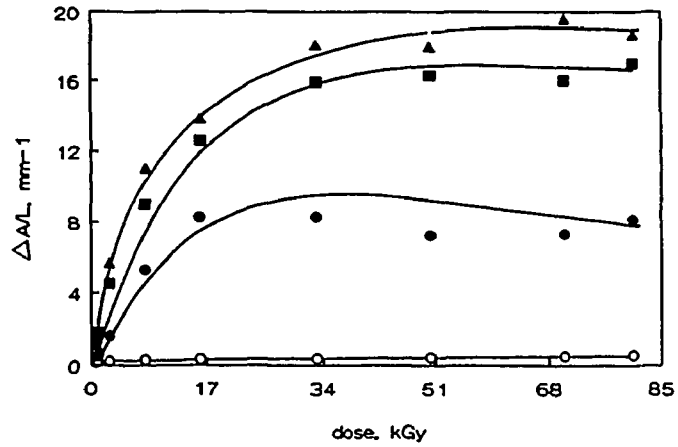


Fig.1 Response functions (ΔA/L,mm-1 vs dose, kGy) for PVB-LMG film with LMG concentration as 2×10^{-5} mole per gram PVB and varied halogenated compound (RX), in which RX:LMG > 50:1 (mole:mole), as CBr_4 (▲), C_2Cl_6 (■), $CCl_3CHO \cdot H_2O$ (●) and no additive (○).

As illustrated by Fig. 1, even the absorbed dose was up to 80 kGy, the ΔA/L in irradiated PVB-LMG system without RX increased far less than others. ΔA/L increased obviously with the increasing of dose in PVB-LMG systems with additives CBr_4, C_2Cl_6 or $CCl_3CHO \cdot H_2O$. The effect of these additives were in the order as bromide > chloride and C_2Cl_6 > $CCl_3CHO \cdot H_2O$ in the case of RX : LMG > 50:1 (mole : mole). The maximum doses related with ΔA/L in linearity in the three systems were no more than 20 kGy.

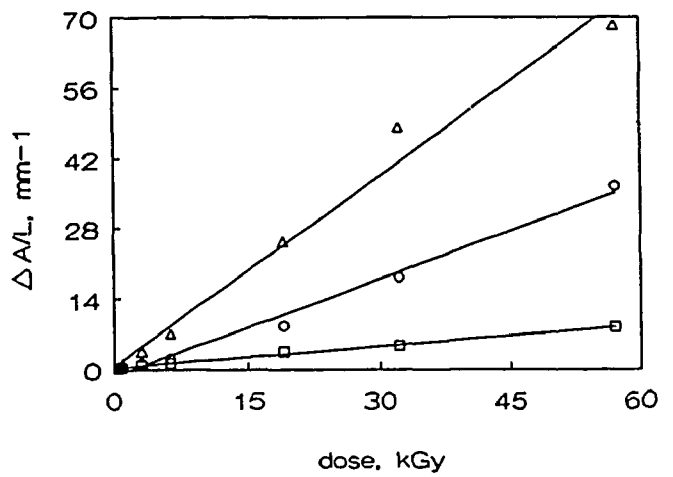
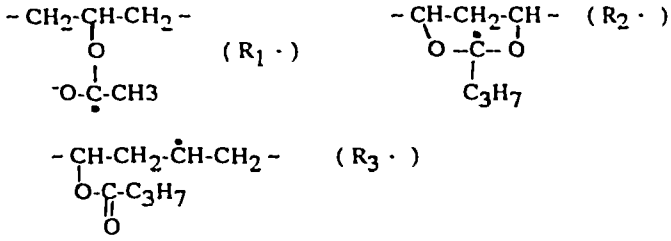


Fig.2 Response functions for PVB-LMG film with additives (RX:LMG=2:1, mole:mole) CBr_4 (△), C_2Cl_6 (□) and $CCl_3CHO \cdot H_2O$ (○) dye concentrations 1×10^{-4} mole LMG per gram PVB.

As shown in Fig.2, the maximum doses in the linear ranges expanded to about 60 kGy in the systems with higher concentration of LMG and lower concentration of RX (i.e, RX:LMG=2:1, mole : mole).

Irradiation of PVB without any additives radicals $R_1 \cdot$, $R_2 \cdot$ and $R_3 \cdot$ were as follows (Mikhallik et al., 1981):



$R_1 \cdot$, $R_2 \cdot$ and $R_3 \cdot$ were reductive intermediate species, LMG can not be oxidized by them. So that MG^+ can not be produced in the film without RX, as shown in Fig. 1. Addition of CBr_4, C_2Cl_6 or $CCl_3CHO \cdot H_2O$ to PVB-LMG system induced the radiation oxidation of LMG to MG^+ by the reactions:

$$RX + e^- \rightarrow R \cdot + X^-$$
$$\rightarrow R \cdot + X \cdot + e^-$$
$$X^- + P^+ \rightarrow X \cdot + P \cdot$$
$$X \cdot + X^- \rightarrow X_2 \cdot^-$$
$$X_2 \cdot^- + LMG \rightarrow MG^+ + 2X^-$$

Here, RX represented one of the halogenated compounds, $X \cdot$ and $X_2 \cdot^-$ were the oxidizing species.

Because the bond energy of C-Br is lower than that of C-Cl, so that the oxidative effect was in the order as $CBr_4 > C_2Cl_6$ and $CCl_3CHO \cdot H_2O$. In $CCl_3CHO \cdot H_2O$, atom Cl located on the α-carbon of ` =C=O ', the C-Cl bond was weakened so that the yield of MG^+ was higher in the composition with $CCl_3CHO \cdot H_2O$. The RX was much excessive in the system with RX : LMG > 50 : 1 (mole : mole), the reductive group -CHO in $CCl_3CHO \cdot H_2O$ may diminish the oxidation of LMG. Thus the linearity relation of radiation response (seen in Fig. 2) were limited at dose about 25kGy. If the system contained RX : LMG = 2:1 (mole : mole), the maximum dose of linearity went up to 60 kGy due to less amount of reductive group -CHO.

2. Formation of MG^+ in Irradiated Polyvinyl Chloride (PVC) - LMG Film

In view of what mentioned above, the $X \cdot$ and $X_2 \cdot^-$ derived from additive RX played an important role in the discoloration of irradiated PVB-LMG system. If PVC was used as the matrix, whether the chlorine induced by irradiation from PVC-LMG system will also play a similar role as above?

The PVC-LMG system was composed of as follows:

2.5 g PVC
0.0826 g LMG (1×10^{-4}mol LMG / g PVC)
35 ml THF

After irradiation, the colorless film turned green with the similar spectrum as in PVB-LMG system. The relation of $\Delta A/L$ vs dose can be seen in Fig. 3.

The linearity was good up to about 60 kGy. This meant that MG^+ was formed by reaction of LMG with chlorine from irradiated PVC.

$$PVC \rightarrow [P^+, e^-]$$
$$\rightarrow P^*$$
$$P^* \rightarrow P \cdot + Cl \cdot$$
$$P + e^- \rightarrow P \cdot + Cl^-$$
$$Cl \cdot + e^- \rightarrow Cl^-$$
$$Cl^- + P^+ \rightarrow Cl \cdot + P$$
$$Cl \cdot + Cl^- \rightarrow Cl_2 \cdot^-$$

i.e, PVC provided oxidative species Cl · and $Cl_2 \cdot^-$ during irradiation, and then LMG was oxidized:

$$Cl \cdot + LMG \rightarrow MG^+ + Cl^-$$
$$Cl_2 \cdot^- + LMG \rightarrow 2Cl^- + MG^+$$

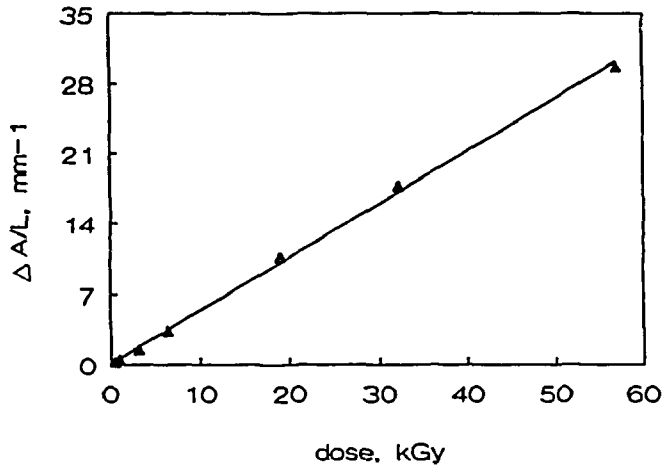


Fig.3 Response function for PVC-LMG film with LMG concentration as 1×10^{-4} mole per gram PVC. Its absorbance was measured at 627 nm.

3. Formation of MG^+ in PVB-LMG with Additive N-bromosuccinimide (NBS)

To confirm the oxidization mechanism furthermore, NBS was used as an oxidative species source. PVB-LMG film with NBS was composed as follow:

1×10^{-4} mol LMG per g PVB
LMG : NBS = 1 : 2 (mole : mole)

The PVB-LMG-NBS film turned green immediately without irradiation and and showed two absorbed bands (λ_{max}=629 nm and 427 nm, respectively) similar to that in section. 1 irradiated systems. It meant that LMG can be oxidized by NBS directly, because NBS was a Br · donor initiated by light or heat.

4. Effect of LMG Concentration in PVB-LMG Film with RX

Dye LMG concentrations were adopted as 8×10^{-5}, 4×10^{-5} and 2×10^{-5} mol per g PVB with RX : LMG > 50:1 (mole : mole). As shown in Fig. 4, the maximum doses in the linear relations of Δ A/L vs dose in three systems were about 20 kGy due to excessive concentration of RX which limited oxidation of LMG. The slopes of the linear part of the response functions 1.63, 1.10 and 0.51 corresponded to the LMG concentrations of 8×10^{-5}, 4×10^{-5} and 2×10^{-5} mole per g PVB, i.e, the higher the concentration of LMG was, the higher sensitivity of response was.

5. Effect of RX Concentration in PVB-LMG Film with RX

As derscribed above, the concentration of RX also affected the dose range of linear relation in PVB-LMG film.If the dye LMG concentration was kept as 1×10^{-4} mol per gram PVB in three systems, the RX concentrations varied as RX : LMG=10:1, 5:1 and 2:1 (mole : mole). After irradiation, the results were illustrated by Fig. 5 and table. 1. The sensitivity of reponse functions (i.e, 'b' values in Table. 1) increased with the increasing of RX concentrations (RX:LMG) and the maximum dose of linear relation (second column in Table. 1) decreased from 70 to 40 kGy though the concentrations of LMG were same.

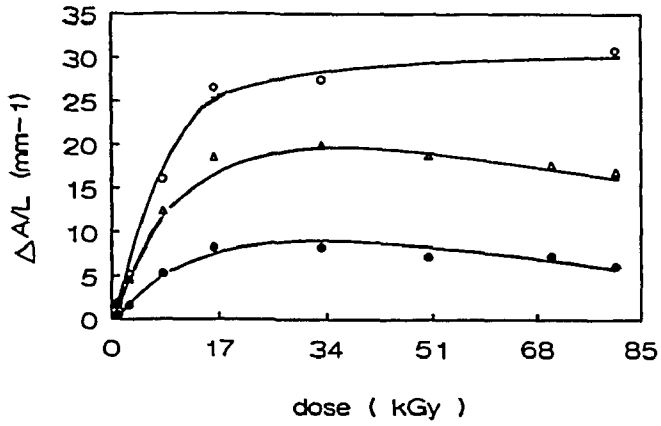


Fig.4 Response functions for PVB-LMG film with LMG concentrations $.8 \times 10^{-5}$ (○), 4×10^{-5} (△) and 2×10^{-5} (●) mol per gram PVB with additive RX : LMG > 50:1 (mole : mole).

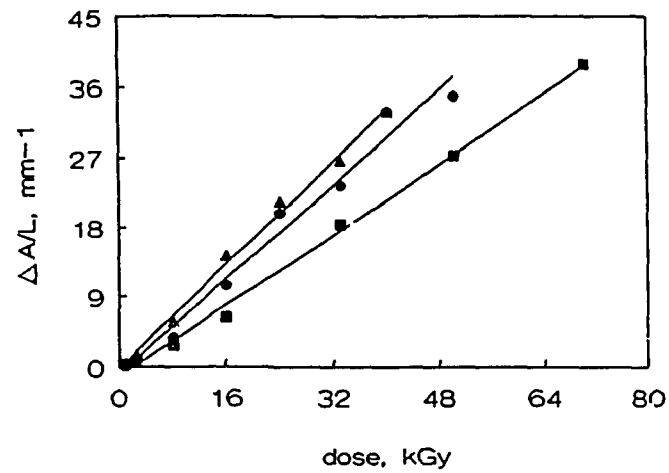


Fig.5 Response functions for PVB-LMG film containing LMG 1×10^{-4} mole per gram PVB with RX concentrations as RX:LMG=10:1 (▲), 5:1 (●) and 2:1 (■).

Table.1 Effect of RX concentration on the dose range of linear relation in PVB-LMG system ($\Delta A/L = a + bD$, a and b were constant)

RX : LMG (mole:mole)	Dose range (kGy) in linear relation	Linear correlation coefficient	a (Intcp)	b (Slope)
10:1	1 ~ 40	0.9987	-0.3751	0.8238
5:1	2.5 ~ 50	0.9966	-1.0757	0.7063
2:1	5 ~ 70	0.9991	-1.8250	0.5803

CONCLUSION

Addition of halogenated organic compounds was extremely necessary for the radiation oxidation of LMG to MG^+ in PVB-LMG system. By alternating the halogenated compounds RX, the relative concentrations of RX and LMG in PVB-LMG system, different sensitivities and dose ranges of linear relation of $\Delta A/L$ vs dose were obtained. These were important factors to select the optimum composition of PVG dosifilm. Oxidation of LMG occured in PVB-LMG-NBS system without irradiation was an evident to illustrate that MG^+ generated from reactions of LMG with oxidizing species in irradiated PVG dosifilm or PVC film.

REFERENCE

Armstrong, W. A. and G. A. Grant. (1958). Radiation Chemistry of Solutions. 1. Use of Leuco Triarylmethane Compounds for Chemical Dosimetry. *Radiat. Res.*, 8, 375-387.

Bakh, N. A., G. G. Babicheva and V. A. Larin. (1960). Radiation Oxidation of Leuco Bases in Ketones in the Absence of Oxygen. *Doklady Akad. Nank S.S.S.R.* 134,1079-82.

Bobrowski, K., G. Dzierzakowska, J. Grodkowski, Z. Stuglik, Z. P. Zagorski and W. L. McLaughling. (1985). A Pulse Radiolysis Study of the Leucocyanide of Malachite Green Dye in Organic Solvents.*J. Phys. Chem.*, 89, 4358-66.

Dejehet, F. G., F. G. Coget, D. J. Apers and P. C. Carpron. (1972). Radiolytic Oxidation of MG Leuco Base in Acetone solution. *Radiochem. Radioanal. Lett.*, 9(2), 93-103.

Dejehet, F. G., A. G. De Kimpe and D. J. Apers. (1973). Radiation-induced Oxidation of the Malachite Green Leucobase in Acetone Solution in the Presence of Calcium Chloride.*Radiochem. Radioanal. Lett.*, 15(3), 177-86.

Grodkowski, J., Z. Stuglik and W. Czajkowski. (1990). Oxidizing Properties of CCl3O2 · Radicals Studied by Pulse Radiolysis. *Radiat. Phys. Chem.*, 36(2), 177-9.

Liu Aiguo, Chen Wenxiu and Jia Haishun. (1994). A New Leuco Dye Dosifilm PVG (in press).

Mikhailik, O. M., Ye. N. Seropegina, M. Ya. Melnikov and N. V. Fock. (1981). The Kinetics amd Mechanism of Photoageing of Polyvinylbutyral. *Eur. Polym. J.*, 17, 1011-9.

Stolz, W. and K. Prokert. (1965). Chemishe Dosimetric Ionisieren der Strahlungen mit den Leukoverbindungen eniger Triphenylmethanfarbstoffe in Polystyrol. *Kernenergie*, 8(7), 425.

Vereshchinskii, I. V., L. T. Karpushkin and V. N. Shcheglov. (1959). Synthesis and Reaction of Leuco compounds of Dye under the Effect of Co-60 gamma Irradiation. *Proc. All-Union Conf. Radiat. Chem.*, 1st, Moscow, Pt. 5, 237-41 (English translation).

Wang Yanqiao, Zhou Xiaomin, Tang Zhangxiong and Zhang Gongming. (1986). CN 85,104,437