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# Radiation physical chemistry effects on organic detectors

C.H. Mesquita<sup>a,b</sup>, C.L. Duarte<sup>a</sup>, M.M. Hamada<sup>a,\*</sup><sup>a</sup>*Instituto de Pesquisas Energéticas e Nucleares—IPEN/CNEN-SP, Travessa R, n. 400, Cidade Universitaria, Sao Paulo 05508-900, Brazil*<sup>b</sup>*Faculdade de Ciências Farmacêuticas—USP, Av. Lineu Prestes, Sao Paulo 05508-900, Brazil*

## Abstract

The radiation damage effect on a liquid scintillating system was evaluated in the PPO and POPOP solutes. Samples containing PPO (1%w/v) and POPOP (0.2%w/v) diluted in toluene were irradiated at different doses, using a <sup>60</sup>Co irradiator at 1.8 Gy/s. The transmittance and the chemical degradation of those solutes were evaluated as a function of dose. The PPO transmittance at 360 nm decayed exponentially with the dose, while the POPOP transmittance at 420 nm decayed linearly. The chemical degradation on the PPO and POPOP was fitted to a bi-exponential mathematical model as a function of dose. The first exponential (fast slope) was interpreted as damage produced by toluene radiolitics whereas the second exponential (slow slope) was interpreted as the damage caused by primary interaction of the  $\gamma$ -radiation with targets, i.e.,  $\gamma$  photons that hit PPO and POPOP directly. The  $w$  (eV/damage molecule) and  $G$  (damaged molecules/100 eV) parameters were estimated in this paper.

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## 1. Introduction

There is a continuous effort for developing new detectors capable of resisting high level of radiation to be used in high-energy accelerators, nuclear reactors and industrial irradiation plants [1]. The researchers have been stimulated to develop innovative detectors based on polystyrene scintillators due to their high light yield, fast luminescence decay constant and low cost [1–3]. These detectors are often composed of several chemical elements; however, the radiation damage was

studied emphasizing their overall aspects [1,4–6]. These studies are suitable when the radiation hardness is used to compare the quality among different types of detectors or to evaluate the suitability of their use in inhospitable environments. Otherwise, this approach is not suitable to infer the causes of the quality loss of the detector. For instance, damages in the organic detectors are caused due to: (i) the disarrangement in the polymeric chain matrix (e.g. polystyrene) [3] or (ii) the break or degradation of the scintillator component (e.g. PPO, POPOP). Furthermore, the organic detector degradation is a complex matter, which needs studies including the kernel of the detecting system, i.e., the scintillators.

\*Corresponding author. Fax: +55-11-816-9186.

E-mail address: [mmhamada@net.ipen.br](mailto:mmhamada@net.ipen.br) (M.M. Hamada).

Although the comprehension of the damage mechanism in the chemical constituents can be valuable to develop optimized detectors, capable of resisting high level of radiation, few studies in this field have been described [8].

The energy necessary to produce the damage can be an important parameter to select the scintillators and the solvents. It is known that damages on the scintillators may be increased when solvents are present during the irradiation. Damages can occur by direct and indirect actions of radiation [7]. The direct action of the  $\gamma$  photon hit directly the target (scintillator), while the indirect damage is induced by free radicals primarily produced in the solvent. Consequently, scintillators with low cross-section for  $\gamma$ -radiation associated to solvents with low yield free radicals are important parameters to be considered to develop organic detectors capable of resisting high-level radiation.

In this paper, the damage produced on the PPO and POPOP under  $^{60}\text{Co}$  gamma irradiation was evaluated by (a) the optical transmission measurements and (b) the energy involved in the chemical degradations.

## 2. Material and methods

Although plastic scintillators have been often chosen for high-energy physics studies [1] the liquid scintillator was chosen in this study because it allows to isolate the scintillator solutes from the liquid solvent by evaporation procedure. On the other hand, the toluene was used as solvent because it is not polymerized under gamma irradiation.

Twenty samples, in duplicate, containing toluene and PPO and other 20 samples containing toluene and POPOP were irradiated in a Gamma-cell irradiator containing  $^{60}\text{Co}$  source of 334 TBq (9021 Ci), at a dose rate of 1.8 Gy/s. The doses were extended up to 1000 kGy, to emphasize the production of damages. After irradiation, 1 ml was used to measure the transmittance (Shimadzu spectrophotometer mod. UV-1601 PC). A small aliquot of the irradiated solution was evaporated in an oven at 40°C and diluted with pentane. An

aliquot of 1  $\mu\text{l}$  from each sample was taken for GCMS analysis (Shimadzu mod. GCMS-QP5000).

Experimental data points from PPO and POPOP degradation were fitted to a bi-exponential function using the non-linear least-squares method obtaining the half doses  $D_{1/2}$ .

The necessary energy “ $w$ ” to produce  $6.02 \times 10^{23}$  molecules damaged in the target (a mole of PPO or POPOP), was estimated by the equation:

$$w \text{ (J/mol)} = \text{MM (g/mol)} \times \frac{D_{1/2}}{\log_e(2)} \quad (1)$$

where MM (g/mol) is the molecular mass of the target. On the other hand, the energy “ $w$ ” required to produce one damaged molecule was estimated by the equation:

$$w \text{ (eV/damage)} = w \text{ (J/mol)} \times 1.036 \times 10^{-5}. \quad (2)$$

The conversion factor,  $1.036 \times 10^{-5}$ , is the ratio of

$$\frac{\text{joule} \rightarrow \text{eV convorsor Factor}}{\text{Avogadro number}} = \frac{6.2415 \times 10^{18} \text{ (eV/J)}}{6.0225 \times 10^{23} \text{ (Target/mol)}} \quad (3)$$

The radiation chemical yield, the  $G$  value, was calculated as

$$G \text{ (mol/J)} = \frac{1}{w \text{ (J/mol)}} \quad (4)$$

The  $G$  value is the number of target molecules that is damaged per joule of the  $\gamma$ -radiation dissipated in the medium. In the literature, the  $G$  value is often described in terms of damaged molecules per 100 eV, i.e.,

$$G \left( \frac{\text{damaged molecules}}{100 \text{ eV}} \right) = \frac{1}{w \text{ (eV/damage)}} \quad (5)$$

## 3. Results and discussion

The PPO transmittance curves ranging from 320 to 800 nm are exhibited in Fig. 1, while Fig. 2 shows the POPOP transmittance

The transmittance decreased as a function of dose for both PPO and POPOP (Figs. 1 and 2). Similar results were described by Hamada et al. [4] and Chong et al. [3]. Considering that the PPO

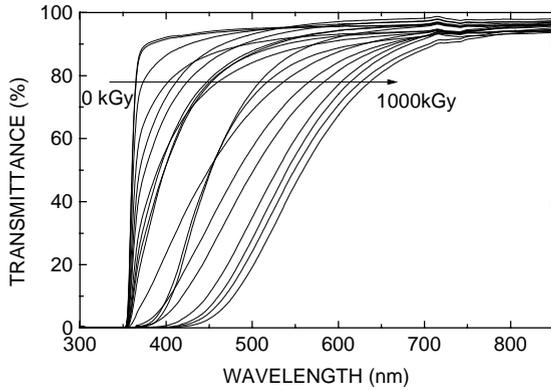


Fig. 1. Transmittance of the PPO samples irradiated with different doses.

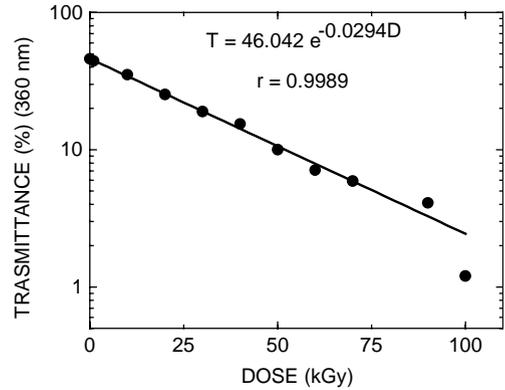


Fig. 3. Transmittance of PPO at 360 nm for irradiated samples and reconstituted with no irradiated toluene.

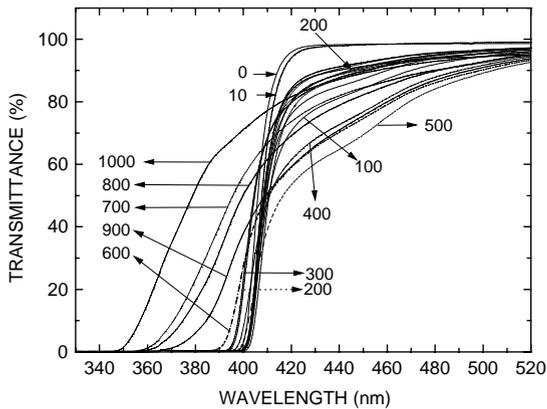


Fig. 2. Transmittance of the POPOP samples irradiated with different doses. The numbers inside the graph indicate the irradiation dose in kGy.

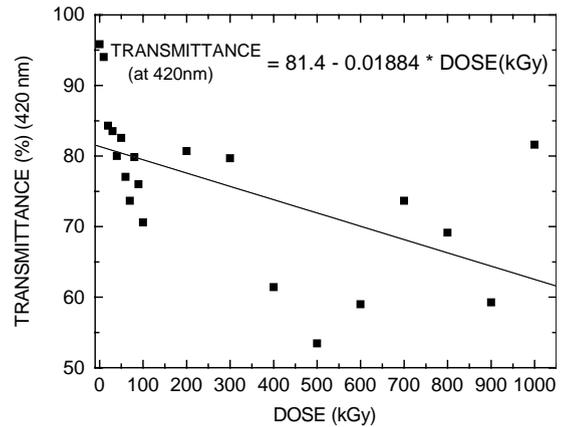


Fig. 4. Transmittance of POPOP at 420 nm for irradiated samples and reconstituted with no irradiated toluene.

fluorescence peak occurs at 360 nm and the POPOP at 420 nm, the transmittance was evaluated using those values, respectively (Figs. 3 and 4). For PPO the transmittance decreased exponentially as the dose increased, showing a strong correlation ( $r = 0.9989$ ) as shown in Fig. 3. The same behavior was not well observed for POPOP.

Fig. 5 shows the behavior of the PPO and POPOP as a function of dose. The curves showed that both PPO and POPOP fit to a bi-exponential function (Fig. 5). The fast slope can be explained as indirect damage. Firstly, the  $\gamma$  photons interact with the molecules of toluene, which generate radiolytic products. Photoelectric and compton

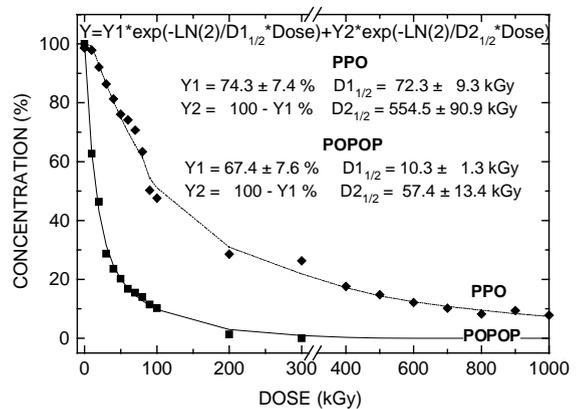


Fig. 5. Concentration of PPO (2,5-dipheniloxazole) and POPOP 1,4-bis(5-phenyl-2-oxazolyl)benzene as a function of dose (kGy).

Table 1  
Degradation parameters for PPO (2,5-dipheniloxazole) and POPOP (1,4-bis(5-phenyl-2-oxazolyl)benzene)

Compound	Concentration		Half dose (kGy)	$w$		$G$ (damages/100 eV)
	(%)	(g)		(J/mol) $\times 10^3$	(eV/damage)	
PPO (C <sub>15</sub> H <sub>11</sub> NO)	74.3 $\pm$ 4.6	0.0743	72.3 $\pm$ 9.3	23 $\pm$ 3	0.239 $\pm$ 0.031	418 $\pm$ 54
Molecular Mass: 221.26 g/mol	25.7 $\pm$ 4.1	0.0257	554.5 $\pm$ 90.9	177 $\pm$ 29	1.83 $\pm$ 0.30	55 $\pm$ 9
POPOP (C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	67.4 $\pm$ 7.6	0.0135	10.3 $\pm$ 1.3	5 $\pm$ 1	0.0561 $\pm$ 0.0071	1782 $\pm$ 225
Molecular Mass: 364.40 g/mol	32.6 $\pm$ 7.6	0.0065	57.4 $\pm$ 13.4	30 $\pm$ 7	0.313 $\pm$ 0.073	320 $\pm$ 75

Both PPO and POPOP degraded bi-exponentially as a function of dose (kGy). The first exponential represents the degradation of the molecules by the pathway of free radical (produced primarily in toluene) reactions. The second exponential represents the degradation due to direct radiation interactions on the PPO and POPOP molecules.

interactions are capable of generating primary electron  $e^-$  that loses its energy by excitation and ionization (secondary electrons). Subsequently, these electrons are energetically thermalized and they combine electrostatically with ions and polarized molecules, producing solvated electrons  $e_s^-$ . This sequence of events acts as a major role in the radiolytic products as it can be inferred from the literature [7].

On the other hand, the slow slope component can be interpreted as the damage caused by primary interaction of the  $\gamma$ -radiation with targets, i.e.,  $\gamma$  photons hit the scintillator molecules directly. As the dose increases, the amount of radiolytic products tends to saturation or reaches the equilibrium by the neutralizing action of scavengers. Thus, a high-absorbed dose increases the probability of the  $\gamma$  photon to hit directly the scintillator molecules. The direct hit of  $\gamma$  photon in the scintillator molecule gives us information about the process of the detector damage.

Table 1 shows the main parameters related to the degradation of the scintillators. The PPO is more resistant to the radiation than POPOP, in other words, the  $\gamma$  photon cross-section for POPOP is higher than for PPO. Probably, this is due to the larger complexity and size of the POPOP molecule compared to the PPO.

For indirect interaction, PPO requires 0.239  $\pm$  0.03 eV per molecule damaged against 0.0561  $\pm$  0.0071 eV for POPOP. For direct interaction, PPO requires 1.83  $\pm$  0.30 eV per damage, meanwhile POPOP needs only 0.313  $\pm$  0.073 eV. Similar inferences were observed for  $G$  values (Table 1).

PPO and POPOP chemical degradations decayed bi-exponentially as a function of dose; 74.3  $\pm$  4.6% of the PPO degraded with half dose of 72.3  $\pm$  9.3 kGy. This pathway of degradation can be associated to damages induced by free radicals produced in toluene. Free radicals enhance the damage in the PPO and as a consequence only 0.239  $\pm$  0.031 eV is capable of destroying the PPO molecule. A second pathway is responsible for 25.7  $\pm$  4.1% of PPO degradation. Energy of 1.83  $\pm$  0.30 kGy is necessary to produce the damage in the PPO molecule by direct interaction of the radiation.

For POPOP, energy of 0.0561  $\pm$  0.0071 eV is sufficient to produce damage by the free radicals pathway (67.4  $\pm$  7.6 of the molecules). The energy of 0.313  $\pm$  0.073 eV is necessary to produce the damage in the POPOP by the direct action of the radiation.

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