

# Polyimide-Based Scintillating Thin Films

A. Quaranta, S. Carturan, G. Maggioni, P. M. Milazzo, U. Abbondanno, G. Della Mea, F. Gramegna, and U. Pieri

**Abstract**—The production procedure and the scintillation characteristics of thin polyimide films containing rhodamine B are reported. Fluorinated polyimide has been chosen as host matrix for its well known radiation hardness, in order to improve the lifetime of detector systems based on plastic thin film scintillators. 6FDA (4, 4'-hexafluoroisopropylidene diphthalic anhydride) and DAB (diaminobenzophenone) have been used as polyimide precursor monomers. The samples have been cured in air at temperatures ranging from 80 °C up to 250 °C. The scintillation spectra have been collected by irradiating the samples with a 5.478 MeV alpha particle source and their shape and intensity have been investigated as a function of dopant concentration and curing temperature. The total number of photons emitted from the films has been compared with a bulk NE102 plastic scintillator. On the basis of literature data on the bulk NE102, the intrinsic scintillation efficiency of the hybrid polyimide films has been calculated. Scintillation efficiencies of about 14% relative to NE102 have been obtained. The scintillation intensity as a function of curing temperatures and dye concentrations has been correlated to the absorption and photoluminescence features in order to study the energy transfer process into the matrix during the polymer condensation.

**Index Terms**—Energy transfer, plastic scintillator, polyimide, rhodamine B, scintillation efficiency.

## I. INTRODUCTION

IN EXPERIMENTS of fundamental nuclear physics on intermediate ( $10 \leq E \leq 100$  MeV/nucleon) energy heavy-ion processes, complex  $\Delta E$ - $E$  telescopes are commonly used [1], [2]. But, whereas the residual energy  $E$  measurements have reached a satisfactory standard by using scintillation counters, some problems are still open with regard to energy loss  $\Delta E$  determination. Gas detectors have been successfully used for the measurement of the large energy loss of the heaviest ions ( $Z \geq 20$ ) [3], but the well known problems related to their feasibility and use encouraged the search for alternative methods. Among them a promising one is the use of thin scintillating films, coupled to traditional bulk crystals giving the so-called phosphor sandwich (PHOSWICH) detectors. At present, plastic scintillators thin films are commonly used as  $\Delta E$  detectors and inorganic scintillators, such as CsI(Tl), are used as  $E$  detectors. This kind of coupling fulfills the need for scintillators with very different emission lifetimes, that is a few ns for plastics and

some hundred of ns for inorganic ones. On the other hand, organic thin films undergo an appreciable radiation damage, with loss of sensitivity and energy resolution during the analysis.

The reduction of light yield in organic scintillators under prolonged irradiation is mainly ascribed to the polymer chemical structure degradation rather than decomposition of the dye molecule [4]. For this reason, most of the approaches to limit these losses involve the addition of stabilizers to the polymer network [5], the use of fluorescent compounds whose emission does not overlap with the absorption bands typically found in deteriorated polymers [4] and the thermal annealing of the detector to recover the pristine performance [6]. New materials have also been investigated in order to achieve higher radiation resistance. At present, good results have been obtained with plastic scintillators based on polysiloxanes, whose radiation resistance is higher than polyvinyltoluene or polystyrene, the two polymers commonly used as basis for the manufacture of plastic scintillators [7].

The class of polyimides presents interesting physical properties, such as high thermal stability and radiation hardness [8], but until now no attempt to process thin film scintillators based on a polyimide matrix has been performed. In this work, preliminary results on the light response and scintillation light yield of thin films of fluorinated polyimide (FPI) doped with rhodamine B (RB) as fluorescent compound are presented. Fluorinated polyimide has been chosen for its high optical transparency in the visible range, which avoids the self-absorption of the scintillation light. Since polyimides are not intrinsically efficient as scintillating materials, their yield must be improved by dispersing a suitable light emitter in the matrix. In this case, rhodamine B was chosen since its absorption maximum overlaps with the fluorescence emission band of the polyimide, so that the transfer of the energy released from the ionizing particle from the host to the dye molecule is allowed.

The scintillation yield of the produced films at different curing temperatures and RB concentrations has been studied by exposing the samples to an  $\alpha$  source. The emitted light has been detected as a function of the emission wavelength with a dispersing system and a comparison with photoluminescence and absorption spectra was made in order to study the energy transfer process during the polymer condensation.

In order to estimate the scintillation efficiency of the FPI system with dispersed RB, the light yield under alpha irradiation has been compared with the yield of bulk NE102 measured in the same experimental conditions.

## II. SAMPLE PREPARATION

Thin films of polyimide pure and RB doped were obtained by first dissolution of the diamine (DAB) in N-methylpyrrolidinone (NMP), followed by addition of an equimolar amount

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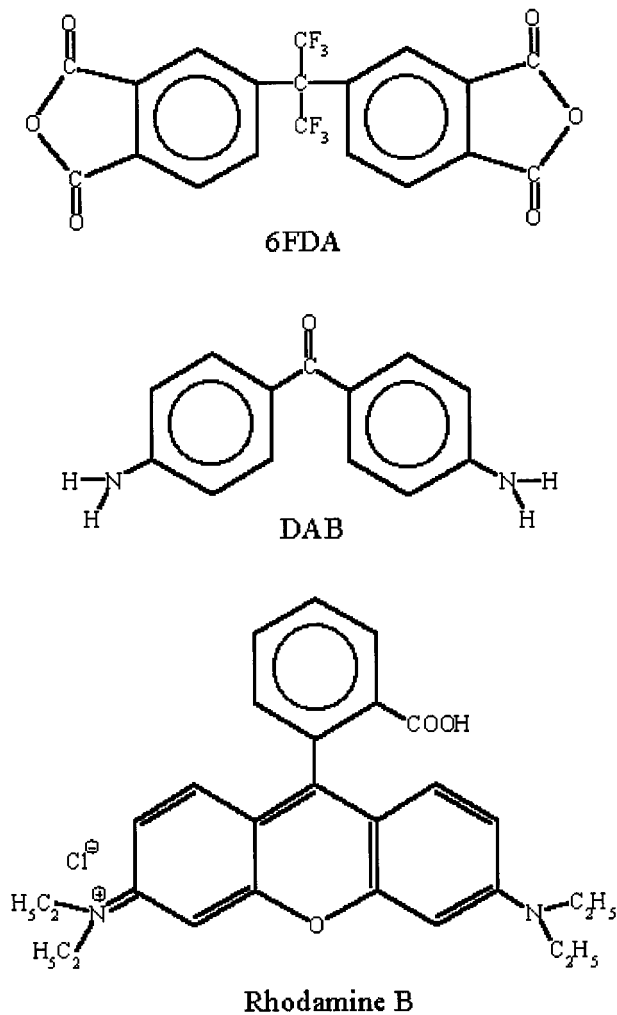


Fig. 1. Chemical structure of monomers and dye used for the film synthesis.

of dianhydride (6FDA). The chemical structures of both monomers and dye are reported in Fig. 1. The amount of solids has been fixed at 30% wt. (grams of monomers per 100 g of total solution). The mixture was then stirred under nitrogen flux for six hours, thus obtaining a viscous and dark brown solution of polyamic acid. The specific amount of RB was then added and the hybrid resin was stirred for two hours, prior to filtering with teflon membranes of 0.45  $\mu\text{m}$  pore size. In order to allow the complete outgassing of air bubbles, the resin was stored for one night in a dry nitrogen atmosphere.

A spin-coating process has been performed using a two step procedure. By means of the static method, a drop of resin was poured on the center of the substrate and then spun at 2000 rpm for 40 s. Pure silica glass plates, previously cleaned by ultrasonic washing in Alconox solution and rinsed with bidistilled water, were used as substrates. Final thermal treatments, needed to complete the imidization process, were performed in air for one hour at different temperatures (80, 150, 200, and 250  $^{\circ}\text{C}$ ). The film thickness was measured by means of a stylus profilometer after every curing stage and its value decreased from about 6  $\mu\text{m}$  at 80  $^{\circ}\text{C}$  to about 5  $\mu\text{m}$  at 250  $^{\circ}\text{C}$ .

Three dye concentrations were chosen: 0.5, 1.0, and 1.5 wt.% (grams of RB per 100 g of monomers) in order to allow a

dipole-dipole resonance energy transfer between the polyimide and the RB.

### III. OPTICAL ANALYSIS SET-UP

The optical properties of the films were analyzed by means of absorption and fluorescence spectroscopy. Absorption spectra were recorded with a Milton-Roy Spectronic 1201 spectrophotometer and photoluminescence spectra, corrected for the spectral response of the acquisition system, were collected with a Fluoromax spectrofluorimeter. The films were excited at a front surface geometry and the emission yield was not corrected for the self absorption of the sample.

In order to investigate the films response to charged particles, the scintillation emission spectra as a function of the light wavelength have been obtained by exciting the samples with a  $^{241}\text{Am}$   $\alpha$  source ( $E_{\alpha} = 5.478$  MeV). The emitted light was collected from the rear side of the sample through a 1-mm wide silica fiber bundle and dispersed by an Acton spectrometer equipped with a 150 g/mm grating. The light spectrum was detected by a cooled ( $-100^{\circ}\text{C}$ ) charge coupled device (CCD), consisting of a matrix of  $1340 \times 100$  pixels, each of  $20 \mu\text{m} \times 20 \mu\text{m}$ .

### IV. THE ENERGY TRANSFER PROCESS IN PLASTIC SCINTILLATOR

As known, the scintillation process in plastic detectors is based on the energy transfer from the polymer matrix, named donor, to dispersed dye molecules, named acceptors, with high emission quantum efficiency. Two energy transfer processes can occur, depending on the dye concentration: the radiative energy transfer, through the emission and reabsorption of photons, and the nonradiative transfer, associated with the dipole-dipole resonance between donor and acceptor [9]. The radiative process occurs mainly at low acceptor concentrations, of the order of 0.01 wt.%, and its rate constant  $k_R$  depends on the overlap between the emission and absorption spectra respectively of the donor and acceptor [9]

$$k_R = k_{Df} \frac{\int I_D(\nu) (1 - e^{-\epsilon_A(\nu)d[A]}) d\nu}{\int I_D(\nu) d\nu} \quad (1)$$

where

- $k_{Df}$  fluorescence rate constant of the donor;
- $[A]$  acceptor concentration;
- $I_D(\nu)$  donor emission spectrum as a function of the light frequency;
- $\epsilon_A(\nu)$  acceptor extinction coefficient as a function of the light frequency;
- $d$  sample thickness.

In this process, the complete energy transfer occurs at a mean distance of about 100  $\mu\text{m}$ , depending on the value of the acceptor extinction coefficient.

The nonradiative energy transfer from the polymer chain to the fluorescent molecule is induced by Coulomb force interactions and occurs mainly at higher acceptor concentrations, from about 0.1 wt.%. The rate constant  $k_{NR}$  of this process depends

not only on the overlapping between the emission and absorption spectra, but also on the mean donor-acceptor distance  $R$  [10]

$$k_{NR} = \frac{9000 \ln 10 \kappa^2 q_D}{118 \pi^6 n^4 N_A \tau_{0D} R^6} \int_0^\infty I_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4}$$

$$= \frac{1}{\tau_{0D}} \left( \frac{R_0}{R} \right)^6 \quad (2)$$

where

- $\kappa$  orientation factor (equal to 2/3 for a random distribution of molecules);
- $q_D$  intrinsic quantum efficiency of the donor;
- $n$  polymer refractive index;
- $N_A$  Avogadro's number;
- $R_0$  critical transfer distance;
- $\tau_{0D}$  donor radiative lifetime.

Even if the value of  $R_0$  is a few nanometers, the effective mean distance of the nonradiative energy transfer ranges from 3 to 10  $\mu\text{m}$  due to the mean free path of the excitation energy carried by the excitons in the polymer [11].

In most bulk plastic scintillators, both processes are present. For example, in NE102 the dye molecules p-terphenyl (TP) and 1,4-bis-[2-(5-phenyloxazolyl)] benzene (POPOP) are dispersed in polyvinyltoluene at concentrations of 10 g/l and 0.01–0.1 g/l respectively. The incident ionizing particle deposits in the matrix its energy, which is transferred to TP by means of a nonradiative process and then to POPOP by means of a radiative one. The resulting light emitted from the rear face of bulk scintillators is the POPOP emission spectrum.

In order to produce a scintillator detector based on polyimide, an activating molecule whose absorption spectrum overlaps with the polymer emission band must be chosen. Photoluminescence analysis on pure polyimide thin films, excited at 460 nm, shows a broad emission band at about 550 nm, which overlaps with the RB absorption band centered at about 560 nm. In Fig. 2, the normalized emission spectrum of a pure 6FDA-DAB film cured at 200°C is compared with the absorption spectrum of a 1 wt.% doped film cured at 150°C. The overlap needed for an efficient energy transfer can be clearly observed.

In the choice of the dye concentration, it must be taken into account that the radiative energy transfer occurs at a mean distance of 100  $\mu\text{m}$ , so that this process is ineffective in film scintillators of a few micrometers thickness. For this reason, we chose to insert RB in polyimide films at concentrations ranging from 0.5 to 1.5 wt.%, in order to promote the dipole–dipole resonance energy transfer.

## V. RESULTS AND DISCUSSION

### A. Photoluminescence and Absorption Analyses

The photoluminescence spectra of RB doped films show the dye emission band centered at about 600 nm, whose excitation maximum is at about 560 nm and whose intensity is two orders of magnitude greater than the pure polyimide. In Fig. 3(a), the emission spectra of samples with 1.0 wt.% RB concentration and heated at 80, 150, 200, and 250 °C are shown. The exciting

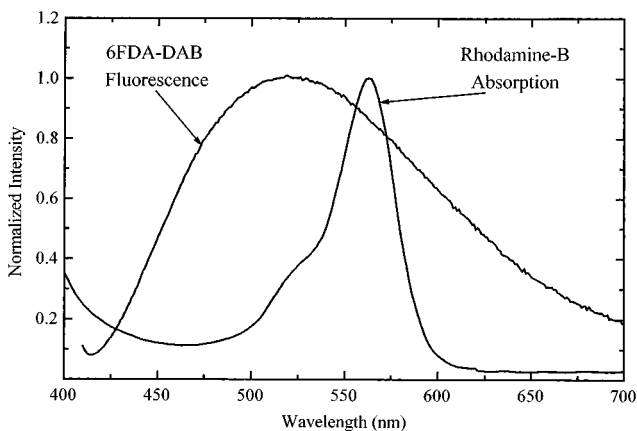


Fig. 2. Comparison between the normalized emission spectrum of pure polyimide cured at 200°C and absorption spectrum of 1.0 wt.% RB doped film cured at 150°C.

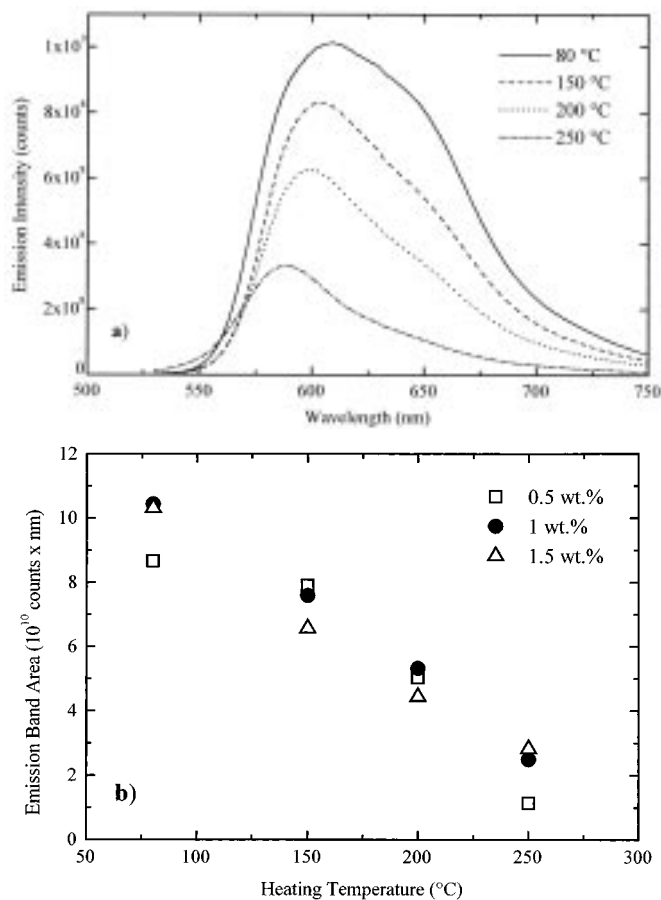


Fig. 3. (a) Emission spectra of 1.0 wt.% doped films as a function of the curing temperature. (b) Band areas as a function of dye concentration and curing temperature.

wavelength was 520 nm. The yield of the emission feature of doped films does not show a clear dependence on the dye concentration and decreases monotonically with increasing heating temperature, as can be seen in Fig. 3(b), where the band areas at different concentrations and temperatures are reported.

Absorption spectra of the undoped films show an absorbance edge at 400 nm and no absorption features at greater wavelengths. Doped films exhibit the typical RB absorption band at

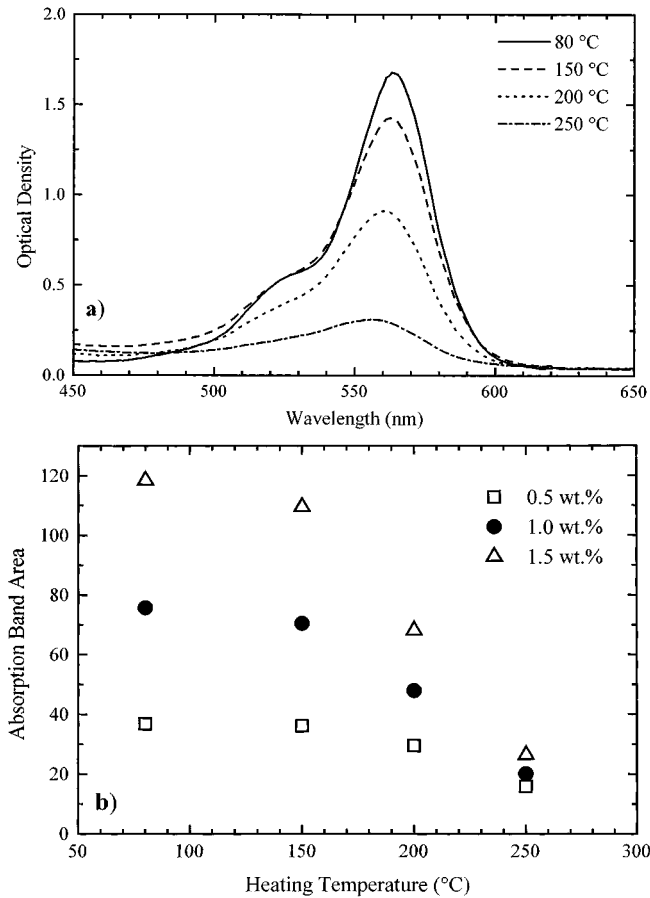


Fig. 4. (a) Absorption spectra of 1.0 wt.% doped films as a function of the curing temperature. (b) Band areas as a function of dye concentration and curing temperature.

about 560 nm, whose intensity increases with the dye concentration and decreases at increasing temperatures. In Fig. 4(a) and (b), the absorption spectra as a function of the temperature of the 1.0 wt.% RB-doped films and the band areas as a function of concentration and temperature are shown.

As can be seen, the relative band intensities as a function of the concentration are different for absorption and emission spectra. This can be explained by the presence of the RB non-fluorescent dimer, which contributes only to the absorption yield [12], [13].

The decrease of the spectroscopic features by increasing the heating temperature can be ascribed to the progressive thermal degradation of RB molecules, which decompose at 210 °C, as reported in the technical data sheet of the manufacturer.

### B. Scintillation and Efficiency Analyses

The scintillation efficiency of pure polyimide films is too low to be detected by an optical collection system. In fact, no emission features are displayed for these samples under  $\alpha$  source excitation. On the other hand, scintillation spectra collected from doped films exhibit the RB emission band centered at about 600 nm. In Fig. 5, the scintillation bands of films doped with 1.5 wt.% of RB and cured at 80, 150, and 200 °C are shown. The samples cured at 250 °C do not show any scintillation band.

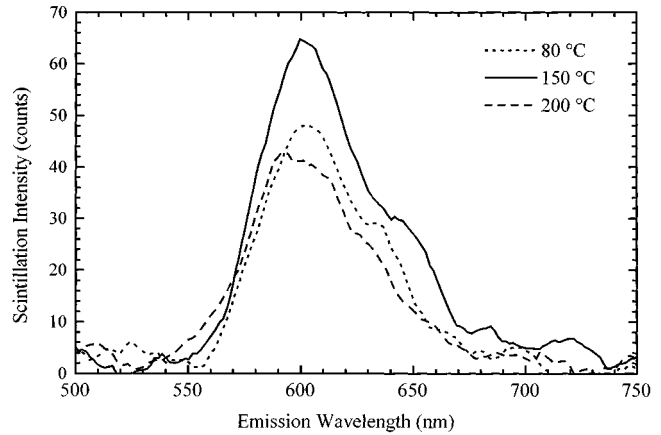


Fig. 5. Scintillation spectra of 1.5 wt.% doped films cured at 80, 150, and 200 °C.

In order to investigate the scintillation efficiency of the doped FPI samples, the areas under the emission bands have been compared with that of a bulk NE102 spectrum obtained in the same experimental conditions. The area  $A$  of any experimental spectrum is proportional to the effective scintillation yield  $Y$  (in photons per  $\alpha$  particle) according to the equation

$$A = \eta(\lambda) \times G \times N_{\alpha} \times Y \quad (3)$$

where

$\eta(\lambda)$  mean efficiency of the optical system, due to the grating reflectivity and to the detector quantum efficiency, calculated in the wavelength range of the sample emission band;

$N_{\alpha}$  total number of impinging particles;

$G$  wavelength independent geometrical factor of the collection system.

The efficiency  $R$  relative to NE102 must be calculated taking into account that the RB and POPOP emission bands are centered at different wavelengths, 600 and 410 nm, respectively

$$R = \frac{Y_{RB}}{Y_{NE}} = \frac{\eta(\lambda_{NE})}{\eta(\lambda_{RB})} \times \frac{A_{RB}}{A_{NE}} \quad (4)$$

where  $\eta(\lambda_{NE})$  and  $\eta(\lambda_{RB})$  are the mean spectral efficiencies in the wavelength range of the two emission bands,  $A_{RB}$  and  $A_{NE}$  are the measured band areas. In Fig. 6, the films relative yields as a function of the RB concentration and of the curing temperature are shown.

In order to give a first evaluation of the intrinsic efficiency of the doped polyimide, the number of photons emitted from the films per MeV of energy released by the  $\alpha$  particle,  $N_{phot/MeV}$ , was calculated as follows:

$$N_{phot/MeV} = \frac{Y_{RB}}{\Delta E_{RB}} = R \times \frac{Y_{NE102}}{\Delta E_{RB}} \quad (5)$$

In this expression,  $\Delta E_{RB}$  is the energy deposited by the  $\alpha$  particle in the doped film. The NE102 yield was obtained from literature [14], while  $\Delta E_{RB}$  was calculated by means of the Monte Carlo program TRIM95 [15].

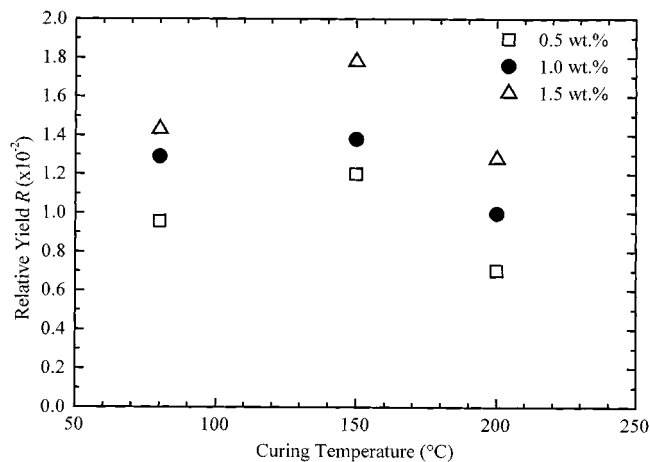


Fig. 6. Relative scintillation yields of doped films as a function of RB concentration and curing temperature.

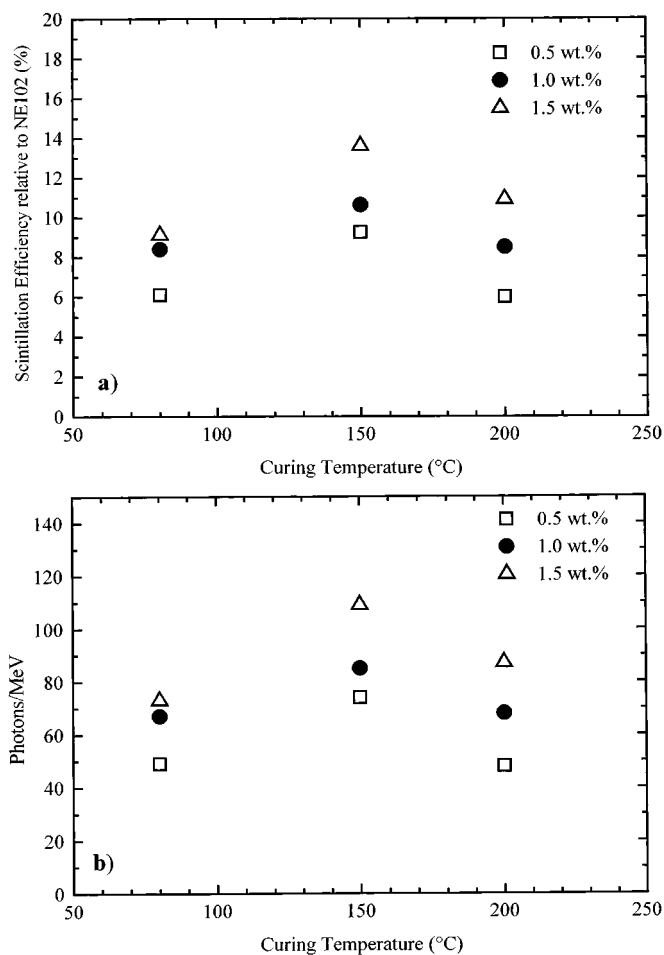


Fig. 7. Doped polyimide scintillation efficiency as a function of dye concentration and curing temperature. (a) Relative to NE102. (b) As emitted photons per  $\alpha$  particle.

The obtained values of  $N_{phot}/MeV$  range from about 40 to 110 photons per MeV, which correspond to a relative efficiency, with respect to NE102, ranging from 6% to 14%. These values, although affected by some uncertainty due to the different parameters involved, give an indication of the material intrinsic efficiency. In Fig. 7(a) and (b), both values are reported as a

function of concentration and temperature. As can be seen the film efficiency increases with the dye concentration, at a fixed temperature and, by varying the curing temperature, increases from 80°C to 150°C, and at 200°C, decreases at a value slightly lower than 80°C.

This behavior is in contrast with the trend of the absorption and fluorescence yields, which monotonically decrease at increasing temperatures. In order to explain this phenomenon, it must be taken into account that the emission rate of plastic scintillators depends not only on the activating dye concentration but also on the energy transfer efficiency from the polymer host to the acceptor. The enhancement of the scintillation yield at 150°C is due to the polymer condensation and to the release of NMP solvent, which nonradiatively dissipates the energy absorbed from the matrix. At this step the matrix poly-condensation is advanced enough to allow an efficient energy transfer to RB, such as to exceed the dye loss. On the other hand, at 200°C the amount of decomposed RB molecules becomes too high and a lowering of the scintillation efficiency can be observed.

The efficiency values obtained in this work are interesting premises for the application of plastic scintillators based on polyimide matrix in radiation detection systems.

## VI. CONCLUSION

The performance of 6FDA-DAB thin films containing rhodamine B has been tested for the application in new scintillating detector systems. The scintillation efficiency and the fluorescence properties have been studied as a function of the dye concentration and of the curing temperature in order to enhance the light emission. The best emission efficiency has been obtained for samples cured at 150°C with 1.5% of RB content. In this case, the scintillation efficiency has been estimated to be about 14% with respect to a bulk NE102 scintillator. Further work is needed in order to improve the efficiency of this kind of material, by enhancing both the intrinsic emission efficiency of the polyimide host and the energy coupling between the polymer and the dispersed dye molecules, and in order to test its efficiency stability after prolonged irradiation.

## REFERENCES

- [1] P. E. Hodgson, *Nuclear Heavy Ion Reactions*. London, U.K.: Oxford Univ. Press, 1978.
- [2] L. G. Moretto and G. J. Wozniak, "Multifragmentation in heavy-ion processes," *Ann. Rev. Nucl. Part. Sci.*, vol. 43, pp. 379–456, 1993.
- [3] I. Iori, L. Manduci, A. Moroni, R. Scardaoni, S. ChongWen, Z. Yuzhao, Z. Guangming, F. Giglio, E. Mora, and G. Di Pietro *et al.*, "A multi-element detector array for heavy fragments emitted in intermediate energy nuclear reactions," *Nucl. Inst. Methods Phys. Res. A*, vol. A325, pp. 458–464, 1993.
- [4] A. D. Bross and A. Pla-Dalmau, "Radiation damage of plastic scintillators," *IEEE Trans. Nucl. Sci.*, vol. 39, pp. 1199–1204, Oct. 1992.
- [5] V. G. Senchishin, F. Markley, V. N. Lebedev, V. E. Kovtun, V. S. Koba, A. V. Kuznichenko, V. D. Tizkaja, J. A. Budagov, G. Bellettini, V. T. Seminozhenko, I. I. Zalubovsky, and I. E. Chirikov-Zorin, "A new radiation stable plastic scintillator," *Nucl. Inst. Methods Phys. Res. A*, vol. A364, pp. 253–257, 1995.
- [6] B. Bicken, A. Dannemann, U. Holm, T. Neumann, and K. Wick, "Influence of temperature treatment on radiation stability of plastic scintillator and wave-length shifter," *IEEE Trans. Nucl. Sci.*, vol. 39, pp. 1212–1216, Oct. 1992.
- [7] M. Bowen, S. Majewski, D. Pettey, J. Walker, R. Wojcik, and C. Zorn, "A new radiation-resistant plastic scintillator," *IEEE Trans. Nucl. Sci.*, vol. 36, pp. 562–566, Feb. 1989.

- [8] H. Inoue, H. Okamoto, and Y. Hiraoka, "Effect of the chemical structure of acid dianhydride in the skeleton on the thermal property and radiation resistance of polyimide," *Radiat. Phys. Chem.*, vol. 29, no. 4, pp. 283–288, 1987.
- [9] J. B. Birks, *The Theory and Practice of Scintillation Counting*. London, U.K.: Pergamon, 1964, p. 60.
- [10] —, *The Theory and Practice of Scintillation Counting*. London, U.K.: Pergamon, 1964, p. 310.
- [11] —, *The Theory and Practice of Scintillation Counting*. London, U.K.: Pergamon, 1964, pp. 201–204.
- [12] J. E. Selwyn and J. I. Steinfeld, "Aggregation equilibria of xanthenes dyes," *J. Phys. Chem.*, vol. 76, no. 5, pp. 762–774, 1972.
- [13] A. Quaranta, S. Carturan, G. Maggioni, G. Della Mea, M. Ischia, and R. Camprostrini, Optical study of dye containing fluorinated polyimide thin films.
- [14] W. W. Wilcke, J. R. Birkelund, J. P. Kosky, H. J. Wollersheim, A. D. Hoover, J. R. Huizenga, W. U. Schroeder, and L. E. Tubbs, "A two-dimensional position sensitive  $\Delta E-E$  counter for energetic light charged particles," *Nucl. Instr. Methods Phys. Res.*, vol. 188, pp. 293–303, 1981.
- [15] J. P. Biersack and L. G. Haggmark, "A Monte-Carlo computer program for the transport of energetic ions in amorphous targets," *Nucl. Instr. Methods Phys. Res.*, pp. 257–269, 1980.