Optical and Scintillation Properties of Polydimethyl-Diphenylsiloxane Based Organic Scintillators

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Abstract—**Polysiloxane based scintillators with high light yield have been synthesized. The polymer consists in cross-linked polydimethyl-co-diphenylsiloxane with different molar percentages of phenyl units. 2,5-diphenyl oxazole (PPO) and 2,5-bis(5-ter-butyl-2-benzoxazolyl)thiophene (BBOT) have been dispersed in the polymer as dopants. The energy transfer and scintillation capabilities have been investigated, for two different amounts of phenyl groups in the polymer network and for different concentrations of dye molecules, by means of fluorescence spectroscopy, ion beam induced luminescence (IBIL) and scintillation yield measurements with α particles from an ^{241}Am source. The luminescence features and the scintillation yields have been correlated to the composition of the scintillators.**

Index Terms—**Energy transfer, ion beam induced luminescence, polysiloxane, scintillation detectors.**

I. INTRODUCTION

POLYMER-BASED scintillators are widely used in many fields, from nuclear physics experiments to medical applications, due to their low cost, ease of fabrication and fast response times. The main drawback of these materials is their poor radiation hardness. The radiation energy released to the polymer matrix not only excites the luminescence centers but also breaks chemical bonds, thus drastically modifying the polymer properties at high incident doses [1]. Scission of the C-H bond produces free radicals and hydrogen release from the polymer and the residual material becomes rich in unsaturated carbon bonds [2]. The carbonaceous species act as color centers in the polymers, giving rise to a reduction of the light yield. The damage

of polymers occurs at lower doses with respect to inorganic materials, due to the lower binding energy of organic compounds. Polystyrene (PS) and polyvinyltoluene (PVT), which are usually employed for the fabrication of commercial plastic scintillators, are affected by a significant yellowing after 1 MRad of exposure [3].

This problem may be bypassed by dispersing dye molecules, like 3-hydroxyflavone, with a large Stokes shift and with an emission band lying beyond the absorption edge of the damaged matrix [4]. Another approach is to synthesize polymers with higher radiation hardness with respect to PS or PVT. Until now, two kinds of radiation resistant polymers have been exploited: polyimides and polysiloxanes. Polyimide thin film scintillators exhibited a fairly good resistance under ion beam irradiation [5], but the procedure for preparing bulk samples is costly and time consuming, thereby limiting their applications to beam monitoring systems, where high ion fluxes are involved. In this case the radiation hardness of the system is given by the intrinsic radiation hardness of the dispersed dyes [6].

Polysiloxane based scintillators were studied in the late 1980s [7] and early 1990s [8]–[10] since they proved promising for use in harsh environments. In fact, silicone rubbers preserve their transparency even after 10 Mrad dose exposure, compared with exposure limits (1–3 Mrad) of PS and PVT.

Besides the radiation hardness, polysiloxanes exhibit further advantages over standard organic scintillator matrices, such as PVT and PS. One further drawback when using plastic scintillators is that they undergo ageing, which diminishes the light yield. Exposure to solvent vapors, high temperatures, mechanical flexing, irradiation, or rough handling will aggravate the process [11]. A particularly fragile region is the surface which can "craze", that is develop microcracks rapidly destroying the capability of plastic scintillators to efficiently transmit light, owing to enhanced light loss through scattering. Crazing is particularly likely where oils, solvents, or fingerprints have touched the surface. In this respect, polysiloxanes are intrinsically different from PS and PVT, owing to their belonging to the class of elastomers instead of plastics. In fact, at room temperature they are in the rubbery state and their physical properties are constant over a wide range of temperature from -100 up to $250°C$, while PS and PVT are plastic materials with a glass transition temperature of about $90°C$ [12], [13]. Physical properties of siloxanes arise from the flexibility of the siloxane backbone induced by the long Si-O bond (1.64 Å versus 1.54 Å for C-C or 1.43 Å for C-O), the low Si-O torsional barrier, and the wide bond an-

gles at the Si and O atoms that alternate between 110° and 142° [14], [15]. In rigid polymers, solvent casting or extrusion techniques force the polymer chains in non equilibrium conformations, thus inducing residual stresses, which are released *a posteriori* through the formation of crazes. Silicone rubbers, owing to their elastomeric nature, intrinsically relax to non equilibrium conformations avoiding the formation of microcracks.

On the other hand, the flexibility of the Si-O-Si bridge does not entail bond weakness. The thermal stability and chemical inertness of these polymers is explained by the Si-O bond dissociation energy of 4.61 eV relative to 3.59 eV for C-C and 3.71 eV for C-O bonds, which arises from the partial ionic nature of the Si-O bond [16].

Polysiloxane rubbers can be synthesized through Pt catalyzed addition polymerization. Commercial base resins for addition polymerization are available with different pendant groups, such as phenyl, thereby enabling the possibility to modify some basic properties of the finally cross-linked silicone rubber. Among these, the most crucial is that the insertion of phenyl moieties enables intrinsic fluorescence of the polysiloxane matrix, with emission lying at about 270–300 nm [17]. The fluorescence capability of the base matrix in organic scintillators is a key requirement and it accounts for the widespread use of polystyrene and polyvinyltoluene as suitable polymers, owing to the presence of phenyl substituents in their repeating unit. As a matter of fact, polymethylmetacrylate (PMMA), which could be regarded as an optimal base for organic scintillator production for its outstanding transparency, radiation resistance and ease of processing, cannot be used unless a suitable amount of naphthalene is added to the acrylic formulation, so as to produce strong luminescence in the UV region [18].

Previous work on polysiloxanes as organic scintillators was performed at the University of Florida. The authors synthesized a crosslinked structure by using a two component resin system constituted of 10 parts of vinyl-terminated polydiphenyl-co-dimethylsiloxane and one part of a cross linker consisting of polymethylhydro-co-methylphenylsiloxane [7]–[9]. The samples exhibited a stable transparency in the visible range upon exposure to 18 Mrad of gamma irradiation in argon atmosphere [7]. The dyes were chosen in order to reach a good solubility in the aromatic polymer. By dispersing dyes like PMP (commercially unavailable) or OLIGO 347A and tetraphenylbutadiene (TPB) as primary and secondary fluorophore, they obtained a yield up to 90 or 55% with respect to BC-408 [7]. In a later work [10], the same research group produced a silicone polymer with linear chains, more suitable for the production of fibers, by alternating diphenyl, dimethyl and phenylmethyl units. In order to avoid the partial crystallization of phenyl rich structures, giving rise to a loss of transparency, random sequence structures composed by diphenyl and methylphenyl (1:1) siloxane were synthesized, thus giving transparent samples.

More recently, Bell and co-workers renewed the interest on polysiloxanes scintillators by producing and testing silicone rubber scintillators for the detection of neutrons. They synthesized a cross-linked polymer consisting of 23% diphenylsiloxane and 77% dimethylsiloxane, obtained from a two-part system containing vinyl terminated polydiphenyl-co-dimethyl-

TABLE I
PRECURSORS FOR THE SYNTHESIS OF POLYDIMETHYL-DIPHENYL SILOXANES

Trade name	Chemical name	% mol diphenyl groups
PDV-0525	Vinyl Terminated Diphenylsiloxane-Dimethylsiloxane Copolymers	4-6
PDV-1625	Vinyl Terminated Diphenylsiloxane-Dimethylsiloxane Copolymers	15-17
PDV-2331	Vinyl Terminated Diphenylsiloxane-Dimethylsiloxane Copolymers	22-25
HPM-502	MethylHydrosiloxane - PhenylMethylsiloxane copolymer, hydride terminated	50 (phenyl)

siloxane (23% in moles of diphenyl units) and methyl-terminated poly(dimethyl-co-methylhydro)siloxane (8:1) [19], [20]. Suitable fluors for dissolution in the polysiloxane network were chosen, such as 2,5-diphenyloxazole (PPO) and triphenyl pyrazoline (TPY). The resulting samples were polymerized in glass or polycarbonate vials, previously coated at the inner walls with a silicone grease as release agent and easily freed from the molds, giving soft but firm and non sticky samples. Organic compounds containing boron (m-carborane) and gadolinium (gadolinium nitrate tributylphosphate) were then dispersed in the polymer in order to sensitize the scintillator to thermal neutrons.

In this work, cross-linked polydimethyl-co-diphenylsiloxane scintillators (PMPS) with different molar percentages of phenyl units have been synthesized following a procedure similar to that of Bell and co-workers, in order to obtain a rigid, self-supporting rubber structure with a high concentration of phenyl groups. In particular, the aim of this work is to relate the optical and scintillation properties to the concentration of phenyl groups and dyes. 2,5-diphenyl oxazole (PPO) and 2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene (BBOT) were employed as primary and secondary fluors, respectively. The comparison between fluorescence, Ion Beam Induced Luminescence (IBIL) and scintillation yield measurements on samples with different concentrations of phenyl pendant groups and dye molecules allowed the study of energy transfer mechanism between the chromophores, thus finding the best set of synthesis parameters to obtain a PMPS with a light yield comparable with NE102 (EJ-212).

II. EXPERIMENTAL

A. Synthesis Procedure

All the precursors for the synthesis of polysiloxanes, as detailed in Table I, were purchased from ABCR GmbH (Karlsruhe, Germany) and used as received.

PMPS were synthesized by mixing vinyl terminated poly-dimethyl-co-diphenyl siloxane (component A in Fig. 1) with hydride terminated poly methylphenyl-co-methylhydrosiloxane (component B in Fig. 1). Hydrosilylation, the addition of an Si-H bond across a π-bond—which in silicone chemistry is generally an alkene $(C = C)$—occurs in the presence of Pt(0) catalyst (Karstedt's catalyst). The part B resin (cross-linker) also contains phenyl groups (about 50% mol of phenylmethyl moieties), thus a greater solubility—and a better homogeneity-
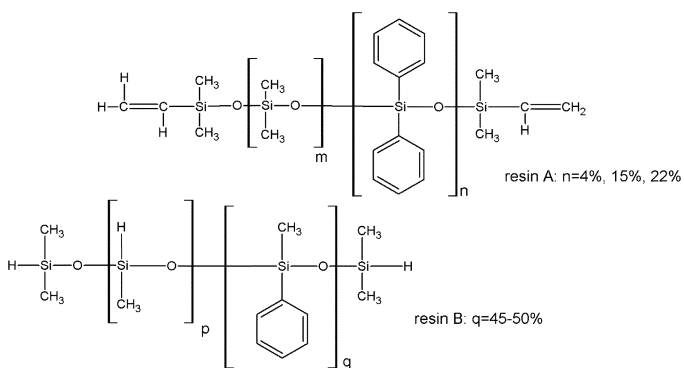
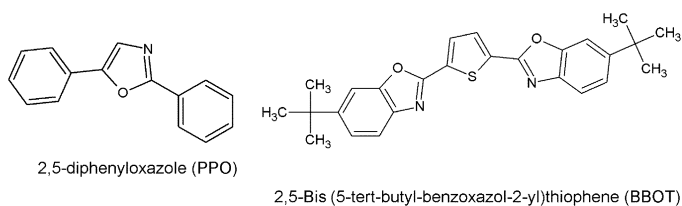Fig. 1. Component A and component B used for the synthesis of PMPS samples.

2,5-diphenyloxazole (PPO)

2,5-Bis (5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT)

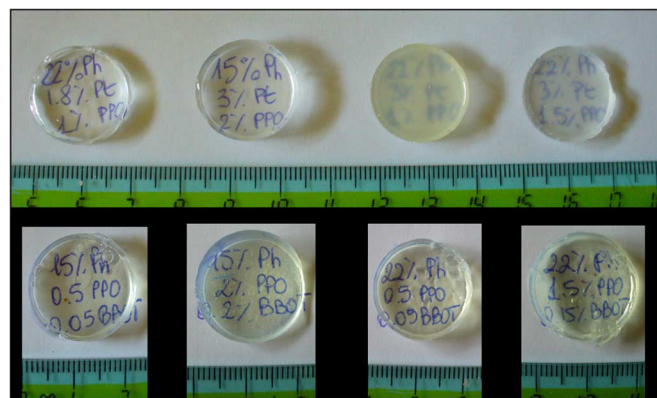Fig. 2. Structure of the dye molecules dissolved into the polysiloxane network: PPO and BBOT.

Fig. 3. Photographs of some prepared samples: in the upper figure the PPO containing samples, in the lower one some samples with both PPO and BBOT. The composition is readable through each sample.

of part B in part A resin can be expected, as a result of stronger chemical affinity. Different Karstedt's catalysts were used for the cross-linking reaction, namely platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt content 3–3.5% or 2.1–2.4%, trade names SIP6830.30 and SIP6831.2, respectively) henceforth named Pt(3%) and Pt(2.1%), and platinum carbonyl cyclovinylmethylsiloxane (Pt content 1.85–2.1%, trade name SIP6829.2) henceforth named Pt(1.8%). The amount of Pt(0) used for each silicone formulation was kept constant at 20 ppm.

The fluorophores were dispersed in the desired amounts in component A and, after complete dissolution, Pt catalyst and component B were added. The mixed resin was poured in polyethylene vials and kept in vacuo $(1 \times 10^{-1} \text{ mbar})$ in order to remove all the trapped air bubbles. Afterwards, the resin was heated in vacuo at $60°C$ overnight. The resulting samples were easily extracted from the vials in the form of pellets 2 cm in diameter and a few mm in thickness.

The phenyl concentration (molar % of diphenyl siloxane groups) was determined by the composition of component A. In particular, two concentrations were chosen for the synthesis: 15% and 22%. The mass ratio between A and B components was 100:5.2 for 15% samples and 100:8 for the 22% samples. A sample with 4% of diphenyl groups was also synthesized in order to inspect the polysiloxane optical properties as a function of the diphenyl concentration. This kind of rubber was quite sticky and opaque, and for this reason it was deemed unfit for the production of PMPS.

PMPS were produced with 0.5%, 1.0%, 1.5% and 2.0% of PPO (weight of dye per 100 g of resin A), while the concentration of BBOT was kept constant at 10% wt of PPO. The structures of the two dyes are shown in Fig. 2, and the images of some selected samples are reported in Fig. 3.

B. Characterization Techniques

Fluorescence measurements were performed in front face geometry with a Jasco FP-770 spectrofluorimeter, equipped with a 150 W Xe lamp. Emission and excitation spectra were collected with 5 nm of spectral bandwidth and corrected for the spectral responsivity of the detection equipment. Optical transmittance spectra were recorded with a dual beam Jasco V-570 spectrophotometer.

IBIL spectra were obtained by irradiating the samples with a 4.6 MeV He^+ beam at the CN accelerator of the INFN Laboratori Nazionali di Legnaro. A quartz fiber bundle, connected to a spectrometer with a nitrogen cooled CCD detector, collected the spectrum in front of the sample. The spectrometer was an Acton 308i, (focal length 300 mm) equipped with a 150 g/mm grating. The CCD (Princeton) is made by 1340×100 pixels, $20 \times 20 \ \mu m^2$ each. The use of a CCD for the detection of IBIL spectra allows collecting the full spectrum (from 300 to 780 nm) at once. The wavelength calibration was performed with an Avantes HgAr discharge lamp and the correction factor accounting for the spectral response of the overall detection system (fiber, spectrometer and CCD) was calculated by comparison with the spectrum of one deuterium and one halogen calibrated lamp (Avantes Cal-HD2000).

Scintillation measurements were made by exciting the samples with a 241Am α source (3 kBq, 5.484 MeV). Pulse height spectra were obtained by coupling the scintillator samples to an H6524 Hamamatsu PMT. Optimal coupling of the samples to the PMT windows was obtained without the use of optical grease, as the silicone rubber (bottom surface) perfectly adhered to the PMT glass, whereas the source was set only few mm apart from the PMPS sample top surface. Afterwards, the whole system, PMT-PMPS-source, was wrapped with Teflon tape in order to maximize the light collection by the PMT cathode. The apparatus was closed in a small scattering chamber in order to insulate the PMT from the background light. The PMT was fed with a bias of -1450 V supplied by a C3830 Hamamatsu HV supplier. The scintillation pulses produced by the PMT were amplified by a CANBERRA 2024 spectroscopy amplifier, giving Gaussian pulses whose amplitude is the integral of the incoming pulses. Since pulses from organic scintillators are

very fast (few ns), a shaping time of 0.25 μs was chosen for the amplifier. Moreover, a gain of 150 was chosen for all the measurements. The yields were compared with that obtained from a slab of EJ-212 plastic scintillator (NE102A equivalent from Eljen Technology Products) in the same experimental conditions.

The time width of the pulse was measured with a Tektronix DPO4054 oscilloscope (2.5 Gs/s).

III. RESULTS AND DISCUSSION

A. Undoped Siloxanes

In organic scintillators the energy released by the ionizing radiation is collected by the network in part as electronic excitation states. Part of the excitation energy is transferred to a fluorescent dye (usually dissolved in about 1% by weight), through a resonant dipole-dipole interaction, first described by Förster, or by exciton diffusion mechanisms, converting excitation energy into light [21]. The energy transfer rate is proportional to the overlap between the fluorescence band of the base polymer and the absorption band of the dye. Since transparent aromatic polymers usually emit in the UV range between 250 and 300 nm, the major requirement for the fluorophore is to possess a strong absorption in this region. Unfortunately, a fluor which fulfills this requirement is usually not completely adequate with respect to the emission wavelength, which usually lies in the range 350–400 nm, where non negligible "self-absorption" can occur, leading to shortened attenuation length. Self-absorption could be avoided by using primary fluors with very large Stokes shift, where the overlap between absorption and emission spectra is very low. This one-component system has attracted a great deal of attention in the past and it is still under development [22] However, to overcome the problem of self-absorption it is very common to add yet another waveshifter (the secondary fluor), at fractional percent levels. The role of the second dye is to shift the light of the first dye at higher wavelengths, where absorption by the polymer matrix or the primary fluor is negligible. The most common examples are p-terphenyl and POPOP, which are respectively the primary and secondary dye dispersed in commercial PS/PVT based plastic scintillators. This set of fluorophores represents the best choice for the design of a high yield plastic scintillator, owing to the optimal overlap between secondary dye absorption and first dye emission, superior quantum yield (defined as the ratio of photons emitted to photons absorbed) of both the fluors. However, the set presents some relevant shortcomings: p-terphenyl displays good solubility in highly aromatic polymers, such as polyvinyltoluene and polystyrene, but very low solubility in alternative polymers with better radiation resistance, such as polyimides and polysiloxanes. Moreover, whereas p-terphenyl possesses a fairly good radiation resistance itself, being a highly conjugated aromatic system, the heteroatom containing secondary dye, 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP), undergoes remarkable radiation damage, with a G value (defined as the number of damaged molecules under γ irradiation per 100 eV of dissipated energy) of 320 damages/100 eV versus a much lower G value for PPO (55 damages/100 eV) [23] and the even lower G value of 0.065 damages/100 eV for p-terphenyl [24].

The investigation of the spectroscopic properties of the undoped polysiloxane as a function of the diphenyl siloxane groups concentration brought about the selection of the primary dye whose spectroscopic properties best fulfill the conditions for the energy transfer.

Fig. 4 shows the excitation and emission spectra of undoped polysiloxane with 4%, 15% and 22% mol of diphenyl siloxane groups (see Fig. 1). The emission spectra, obtained by exciting the samples at 260 nm, show a band with two features peaked at about 290 and 320 nm. The excitation spectra, collected by recording the light emitted at these two wavelengths, either 290 nm or 320 nm, are quite different, showing a major component at 270 nm in the first case and two components at 245 and 278 nm in the second case.

By increasing the phenyl group content, the emission peak at 320 nm increases in relative intensity as compared to the component at 290 nm, which is visible as a shoulder in both spectra (b) and (c), where the content of diphenyl siloxane groups is 15% and 22%, respectively. The intensity ratio between the component at 290 nm and that one at 320 nm (I_{290}/I_{320}) decreases from 1.4 in spectrum (a) down to 0.4 in spectra (b) and (c). According to the literature on the optical features of polydimethyl-co-diphenylsiloxanes [17], this behavior permits to the assignment of the peak at 290 nm to the phenyl chromophores of the polymer and the peak at 320 to the excimers formed between an electronically excited chromophore and a second, identical, chromophore in its ground state. The formation of excimers in aromatic polymers is a well known mechanism [25], [26]. The excitation energy migrates along the polymer network between the phenyl rings, until it is trapped at an excimer site. Depending on the phenyl concentration, the excimer emission feature can be observed together with the single phenyl band or can dominate the fluorescence spectrum, as it occurs for PS [25]. At the moment it is not clear if the energy transfer between the polymer and the primary dopant occurs due to excimers or to the single phenyl excitation migration. In any case, the usual approach is to insert a dye into the matrix whose absorption spectrum overlaps the main fluorescence band of the matrix.

B. PPO Doped Polysiloxanes

PPO was chosen as the dye for collecting the excitation energy of the network, since in cyclohexane it displays a wide absorption band in the range 300–340 nm and an emission band between 340 and 420 nm with a quantum yield of 1.0 [27], [28]. These optical features match the requirements for the energy transfer from the matrix to the primary dye. Moreover, as highlighted above, PPO was proved to display a fair radiation resistance, with a fivefold lower G value (radiation chemical yield) with respect to POPOP.

PPO was dispersed only in samples with 15% and 22% diphenyl siloxane units, since in 4% of the samples PPO exhibited poor solubility, thus producing opaque samples.

The fluorescence spectra of all the PPO doped samples exhibit an emission peak at 360–365 nm with an excitation band centered at about 340 nm.

In general, the samples exhibit a good transparency, dependent on the preparation conditions. Samples with 15% diphenyl

Fig. 5. Excitation and emission spectra at different wavelengths of a PPO doped sample (PMPS with 15% of diphenyl siloxane groups, 1.0% PPO and Pt(1.8%) as catalyst).
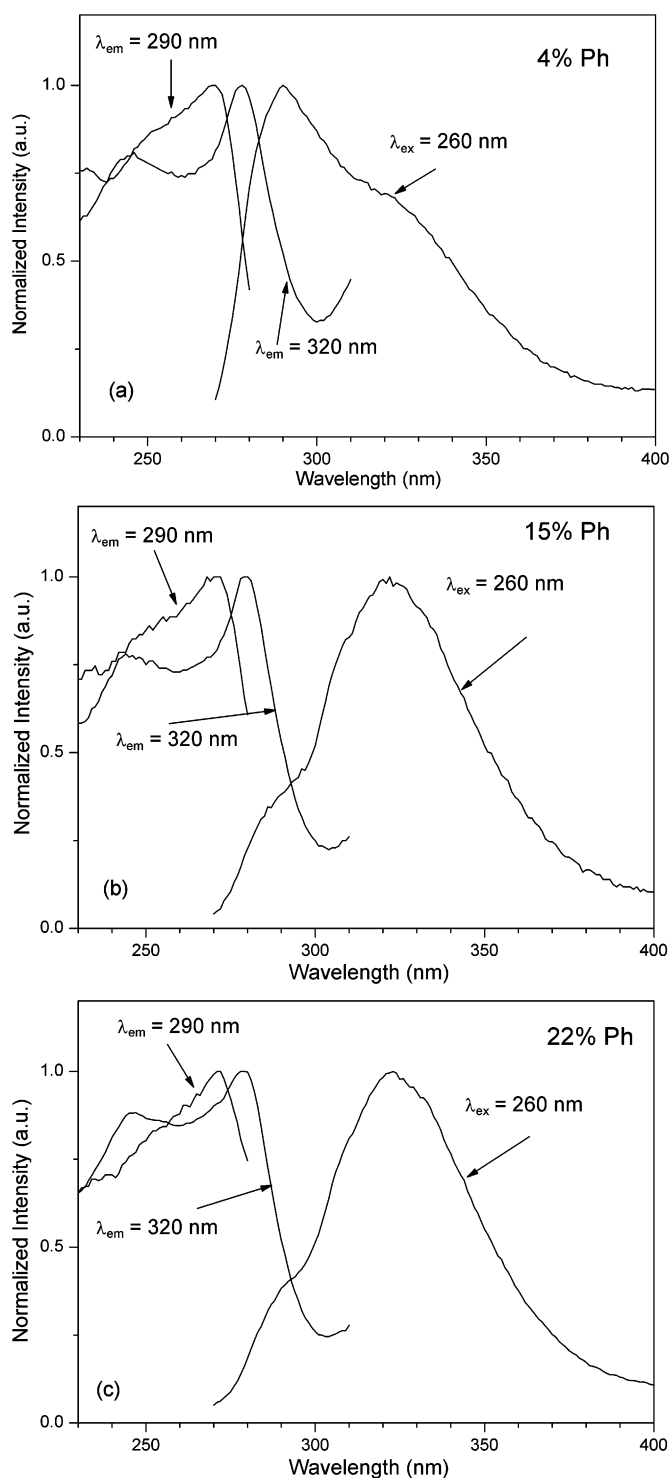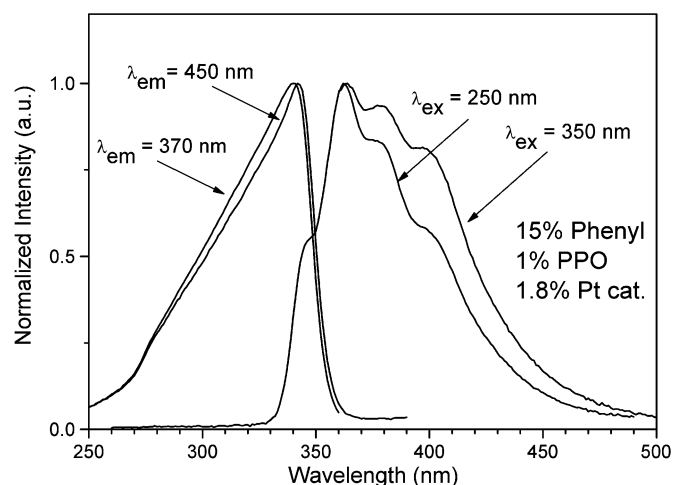
Fig. 4. Excitation ($\lambda_{em} = 290$ and 320 nm) and emission ($\lambda_{ex} = 260$ nm) spectra of polysiloxane samples with 4% (a), 15% (b) and 22% (c) of diphenyl siloxane units, Pt(2.1%) was used as catalyst.

siloxane units and Pt(1.8%) as catalyst reach a transmittance value of about 85% in the visible range, with an absorption edge at about 390 nm, while samples synthesized with 22% of diphenyl siloxane groups and Pt(3.0%) as catalyst are opaque, with transmittance values of 30–50%, as can be clearly noticed from the photographs of Fig. 3. The lower optical quality of these samples can be related to the enhancement of the reaction rate induced by the different catalyst used, giving rise to a more

inhomogeneous network, where phenyl rich phases precipitate. Opacity of siloxane polymers with high content of diphenyl siloxane moieties had already been observed in literature [29].

The PPO fluorescence intensity is nearly the same for all the samples, since concentration quenching effects counteract the increase of dye molecules.

Irrespective of the high transparency, in some cases an inhomogeneous distribution of PPO into the network is evidenced by the different shape of the emission spectra observed by increasing the excitation wavelength, as shown in Fig. 5.

Beside the inspection of the PPO fluorescence spectra, the behavior as a function of the PPO concentration of the UV optical features of the polymer was analyzed by exciting the samples at 250 nm. As shown in Fig. 6(a), (b), the single phenyl emission feature can be observed at about 285 nm and its intensity decreases as the amount of PPO increases, becoming barely visible in samples with 2% of PPO. This trend can be ascribed to the energy transfer process from the single phenyl excited state of the polymer network to the PPO molecules, whose efficiency is proportional to the amount of dispersed dye. Moreover, by increasing the concentration of phenyl groups in the network, under the same PPO concentration, the intensity of the single phenyl emission feature was almost cut by half, as can be observed by comparing Fig. 6(a) and 6(b), owing to the formation into the polymer of a higher amount of excimers.

C. PPO-BBOT Doped Polysiloxanes

BBOT was chosen as secondary fluor and dispersed with PPO in PMPS samples. According to literature data [30], this molecule is characterized by an absorption band from 320 to 410 nm and by an emission spectrum from 410 nm to 520 nm in cyclohexane, thus meeting the requirements for energy transfer from PPO.

PMPS with both PPO and BBOT were synthesized with Pt(2%) as catalyst, in order to obtain transparent samples, which are characterized by a flat transmittance spectrum with values ranging from 70% to 80% in the visible range and with an absorption edge at about 410 nm. For BBOT concentration
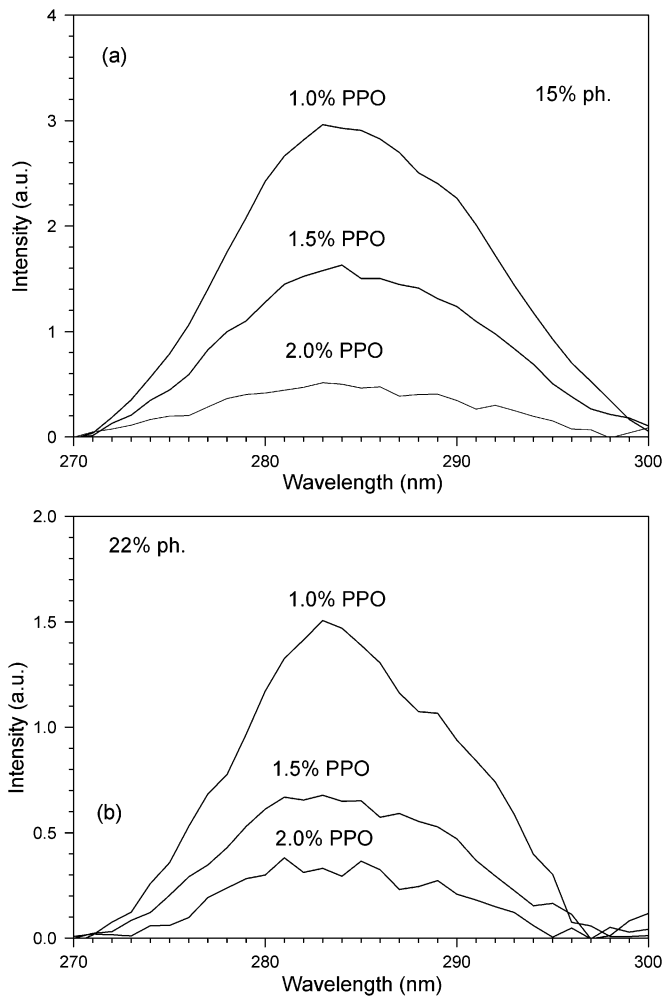
Fig. 6. Emission spectra in the UV range of PPO doped samples (excitation wavelength $\lambda ex = 250$ nm) with 15% (a) and 22% (b) of diphenyl siloxane groups and with different PPO concentrations.

Fig. 7. Emission spectra of samples doped with different concentrations of PPO and BBOT (excitation wavelength $\lambda ex = 270$ nm) and with 15% (a) and 22% (b) diphenyl siloxane units. Normalization was done on the PPO component.

higher than 0.1%, a slight yellowing, with a corresponding shift of the transmittance edge, was observed.

In Fig. 7(a), (b) the fluorescence spectra of PPO/BBOT doped PMPS containing 15% (a) and 22% (b) of diphenyl siloxane units (excitation wavelength $\lambda_{ex} = 270$ nm) are shown. The emission bands of both PPO, peaked at 360 nm, and BBOT, with a maximum at 430 nm, can be observed. In particular, even though at this excitation wavelength (270 nm) the BBOT absorbance is expected to be much lower than PPO, its intensity in emission is higher than PPO itself. This evidence points out that efficient energy transfer occurs from PPO to BBOT. More-over, the absence of distortions in the PPO emission features indicates that the energy transfer is more likely encompassed through a non-radiative resonant mechanism than through a ra-diative process. In fact, in the radiative energy transfer processes the emission band of the donor is distorted by the absorption band of the acceptor. Even if the former works of Birks [31] supposed a radiative transfer between the first and the second dye, the presence of non-radiative mechanisms has been con-firmed by recent works [32]. However, the energy transfer ef-ficiency does not seem to be affected by the dopants concen-tration in the series 15%, as the BBOT intensity keeps almost
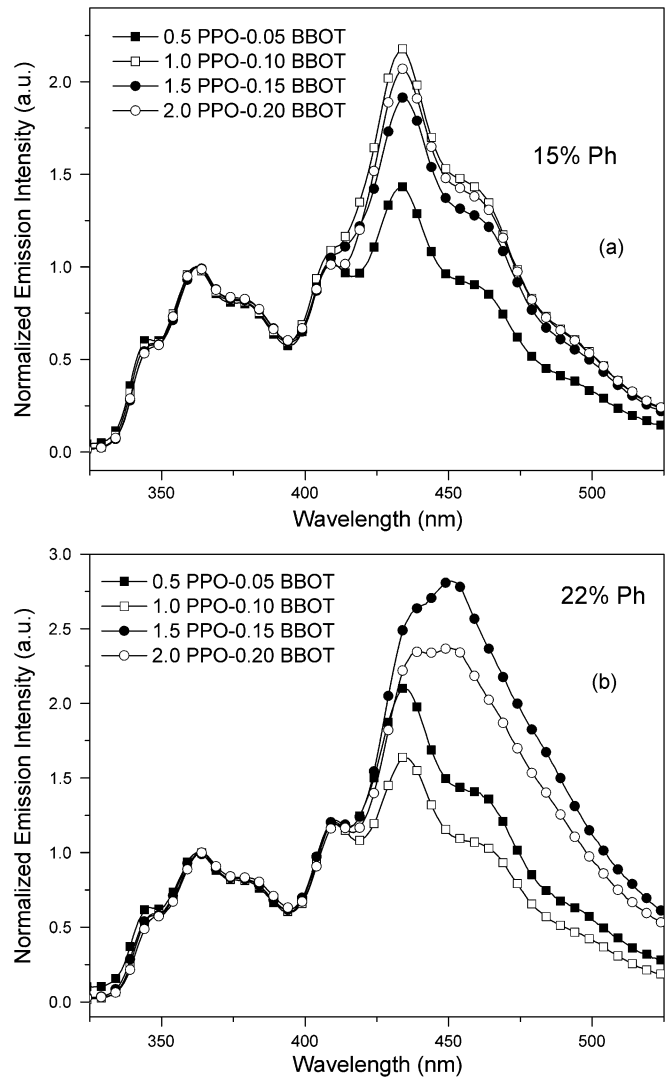
constant for PPO concentrations higher than 0.5% (Fig. 7(a)). In the samples with 22% diphenyl groups the trend is much less comprehensible (Fig. 7(b)). In passing from 0.5% PPO to 1.0% PPO, a decrease in BBOT emission is observed. Moreover, for higher dyes amounts the emission spectra in this series appear as distorted and the main BBOT peak shifts to longer wavelength varying from 435 nm (BBOT 0.10%) to 450 nm (BBOT 0.20%). This behavior had been previously observed for BBOT doped sol-gel derived glasses and it had been ascribed to aggregation phenomena of the dye at high concentrations in a low polarity environment [33]. This explanation is further confirmed by the spectra of Fig. 8, collected from the same sample by changing the excitation wavelength.

The evident change in the emission spectrum shape indicates that different excited states of the dye molecule co-exist in the siloxane network, as a result of aggregation and microcrystal precipitation.

This result, together with the slight yellowing of some of the scintillators, indicates that BBOT can present solubility prob-lems in a phenyl rich structure.
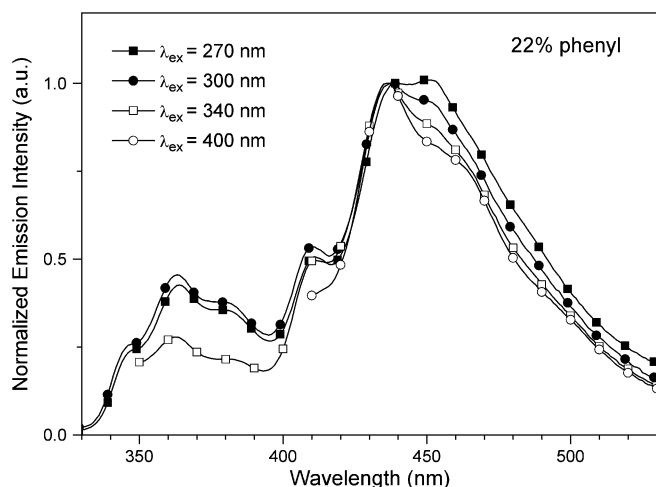
Fig. 8. Emission spectra of sample with 22% diphenyl siloxane units and doped with 2.0% PPO and 0.2% BBOT at different excitation wavelengths.
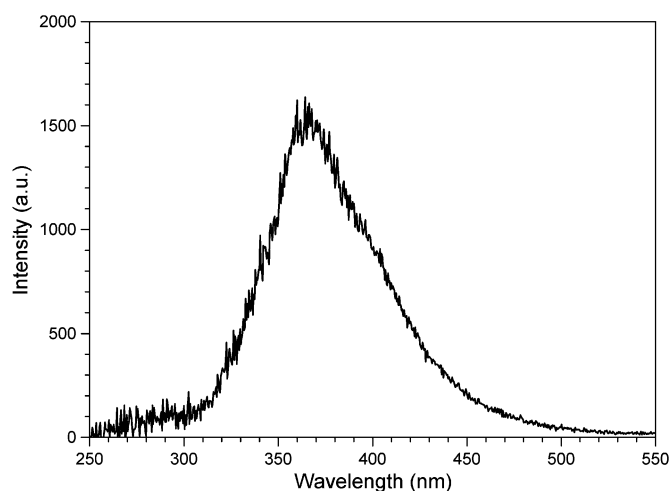

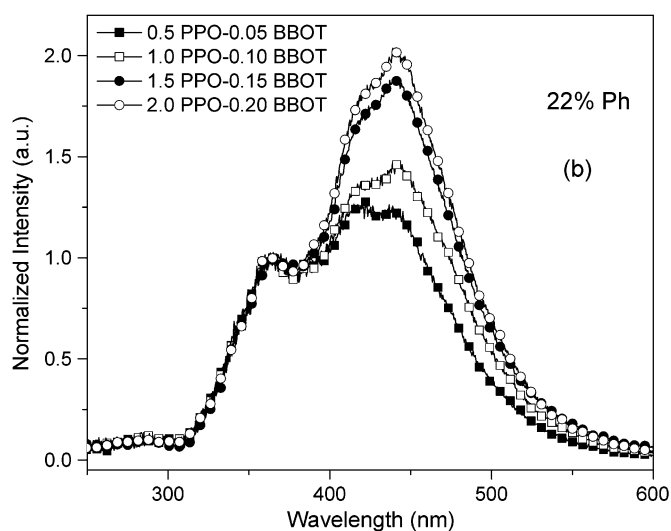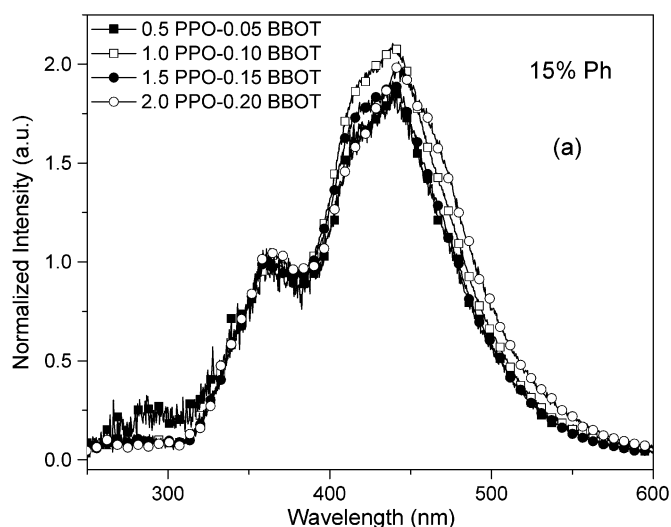Fig. 9. IBIL spectrum of a sample with 2.0% PPO doped polysiloxane.

Fig. 10. Normalized IBIL spectra of samples with 15% diphenyl siloxane units (a) and 22% diphenyl siloxane units (b) and with different concentrations of PPO-BBOT. Normalization was done on the PPO component.

D. IBIL Measurements

IBIL spectra of samples containing only PPO show the dye peak at about 365 nm, as shown in Fig. 9.

A more interesting behavior can be observed in spectra of Fig. 10, collected from PPO-BBOT containing samples.

In all of them, the contribution of both the dyes can be observed. Moreover, a faint band due to the polysiloxane at about 290 nm can be observed, whose contribution decreases by increasing the dye concentration. As stated for the luminescence spectra, the observed decrease can be attributed to the enhancement of the energy transfer from the polymer network to the dye. As shown in Fig. 10(a), (b), in samples with 15% diphenyl siloxane groups the ratio between the two dye bands is almost the same for all the concentrations $(I_{BBOT}/I_{PPO} \approx 2.0)$, while for samples with 22% diphenyl siloxane groups the BBOT relative intensity increases by increasing the amount of dyes, with the intensity ratio I_{BBOT}/I_{PPO} rising from 1.3 at the lower concentration up to 2.0 at the higher concentration. The comparison between IBIL spectra and fluorescence spectra of Fig. 7 is not straightforward.

It had to be noticed that, in the case of emission spectra, the incident UV light at 270 nm was directly exciting the PPO molecule, whereas excitation of the phenyl siloxane matrix and of the secondary dye BBOT was absent or negligible. In contrast, when exciting the scintillating material with charged particles at high energy, as in the case of IBIL spectra collection, most part of the excitation energy is transferred to the polymer matrix through ionization, hence the excitation of the fluorophores occurs through indirect processes of energy transfer from the base polymer to the dissolved dyes. As for the 15% phenyl series, the trend in intensity observed in IBIL spectra of Fig. 10(a) is not fully compliant with the previously reported results on the emission features of PPO/BBOT containing samples, as shown in Fig. 7(a), where the intensity ratio I_{BBOT}/I_{PPO} varied negligibly in the series 15% for dyes concentration higher than 0.5% PPO. In the present case, an enhancement in BBOT intensity, though weak, is clearly visible at increasing concentrations. For the 22% series, the enhancement is much more appreciable. The observed different behavior in IBIL spectra of both the series can be related to the improved energy transfer from the base siloxane matrix and the PPO primary dye. As a matter of fact,
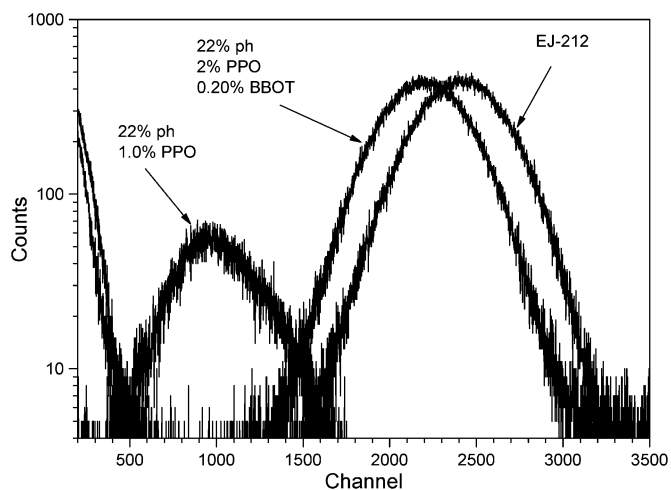
Fig. 11. Scintillation pulse height spectra of samples with 22% diphenyl groups-1.0% PPO and 2.0% PPO plus 0.2% BBOT. The spectrum of NE102 is also shown for comparison.

it was already proved in the spectra of Fig. 6 that the higher the phenyl content, the higher the energy transfer between the siloxane network and PPO, owing to the higher amount of excimers formed.

Nonetheless, the correlation between the fluorescence features of the scintillating materials and the light yield emitted as a result of impinging ions cannot be fully established in this context, and a more thorough study through photoluminescence (excitation and emission spectra) and IBIL spectroscopy is required. In particular, in order to investigate the complex energy transfer mechanisms involved in the whole scintillation process, the primary fluor amount should be kept constant, whereas the amount of the secondary dye should be changed. Since the exhibited results point out that the BBOT fluor presents severe solubility problems, this type of study is in progress on a system where such a complication can be ruled out.

E. Scintillation Yield Measurements

The light yield of the examined scintillators is proportional to the position, in the pulse height spectra, of the peaks related to the α particles from the ^{241}Am source. Fig. 11 shows the peaks of two samples (22% of diphenylsiloxane units and 1.0% of PPO, 22% of diphenyl siloxane units, 2.0% of PPO and 0.20% of BBOT) and of the NE102 plastic scintillator. In the following, the efficiency of all the samples will be indicated as NE102%, for which a yield in terms of ph/MeV can be calculated from the table reported by Wilcke et al. [34]. In particular, for α particles of about 5.5 MeV, a yield of 3700 ph/MeV can be assumed.

As can be observed in Fig. 12, for samples derived from Pt(1.8%), which display optimal transparency (Fig. 3), the light yield increases with the concentration of phenyl groups and with PPO concentration. Furthermore, transparent samples containing 15% of diphenyl groups and derived from Pt (3.0%) show improved light yield with respect to the samples that were cross-linked through Pt(1.8%). This trend can be ascribed to a stronger interaction between the network and the embedded dyes, related to the higher cross-linking promoted by the catalyst. The main drawback of this procedure is that it can be detrimental to the optical properties of samples with 22%
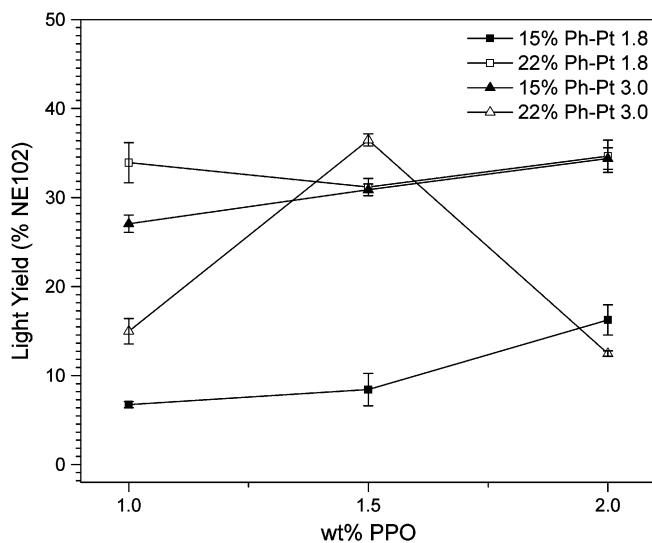

Fig. 12. Light yield (expressed as % of NE102) of samples with different concentrations of PPO, diphenyl siloxane groups and catalyst. Samples with 22% diphenyl siloxane units, Pt(3.0%) and PPO 1.0% and 2.0% are characterized by the lower transmittance. Each datum represents the average value of three measurements, performed on three samples, formally identical from the compositional point of view. The error bars are the standard deviation of the mean value.
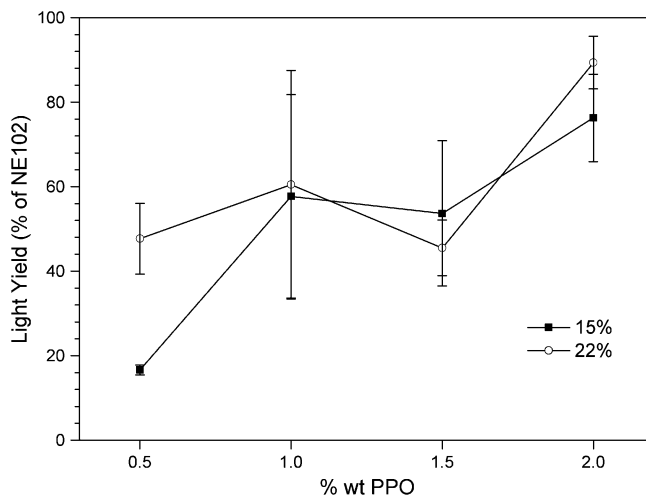

Fig. 13. Scintillation yield of PPO-BBOT samples in function of the PPO concentration. For each sample, BBOT concentration is ten times lower than PPO. The same considerations on the error bars reported in the caption of Fig. 12 applied to this graph.

diphenyl groups, where the enhanced cross-linking reaction rate can lead to the separation of phenyl groups rich phases with high cristallinity, thereby hindering the transparency, as discussed previously.

As a matter of fact, samples of the 22% series display a poor correlation between the light yield and the composition, owing to severe lacking in transparency, as shown in Fig. 3.

The addition of BBOT increases the yield of PMPS, as shown in Fig. 13. In particular, 96% of NE102 yield is reached by samples with 2.0% PPO and 0.2% BBOT.

As can be observed from the data of Fig. 13, both the samples with 15% and 22% diphenyl siloxane units display an almost linear trend of light output versus dopants concentration and no striking differences can be pointed out between the two series.
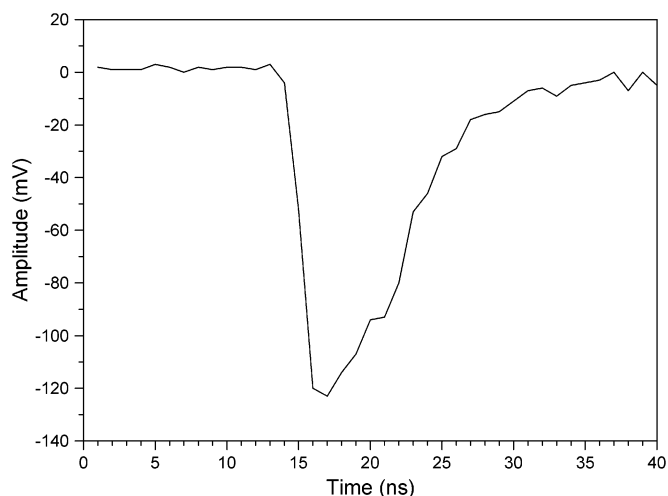
Fig. 14.   Pulse shape of a PPO doped PMPS.

In both cases, remarkably higher errors are evidenced for PPO-BBOT concentrations higher than 0.5/0.05, thus evidencing that BBOT cannot be dissolved homogeneously inside the siloxane network. This fact was also evident in the photographs of Fig. 3 taken from samples with 0.2% BBOT. Irrespectively of the matrix phenyl groups content, small acicular crystals of BBOT are visible by inspecting the samples through the thickness.

This result indicates that the addition of a secondary fluorophore as wavelength shifter favorably affects the light yield of the siloxane based scintillators, though more careful synthetic procedures or the choice of a more soluble secondary fluor should be envisaged to afford a homogeneous distribution of dyes in the network and a more transparent polymer.

Preliminary pulse shape measurements evidenced a pulse width of about 8 ns and a rise time of about 3 ns, as shown in Fig. 14, outlining that PMPS are quite fast scintillators.

IV. CONCLUSIONS

Polysiloxane scintillators with a light yield comparable with commercial plastic scintillators have been synthesized from precursors promoting a 3-D cross linking of the network and by dispersing PPO and BBOT into the polymer. This kind of scintillators present several intriguing properties owing to their high radiation hardness and mechanical stability. Moreover, large samples suitable for particle analysis experiments can be cheaply realized without the need of extrusion techniques. In the samples studied in this work, the energy transfer between the siloxane matrix and the primary fluor (PPO) was enhanced by the increase of diphenyl siloxane groups, as demonstrated by fluorescence spectroscopy, and the scintillation efficiency was shown to increase accordingly. On the other hand, binary system, containing BBOT as secondary fluor did not give straightforward results, owing to the limited solubility of the chosen fluorophore in the siloxane polymer. However, the addition of a second fluor considerably improved the scintillation yield, allowing to reach about 90% of NE102 in the detection of α particles. The pulse shape of these scintillators exhibits a width of about 8 ns and a rise time of about 3 ns. Further improvements can be obtained by choosing dyes with higher solubility in polysiloxanes. In fact,

the poor solubility of BBOT in the matrix can account both for the absence of a clear trend with the concentration and for the scarce reproducibility of the scintillation yield, as evidenced by the large error bars. Moreover, the long term stability of these systems has still to be examined.

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