ORGANIC SCINTILLATORS WITH LARGE STOKES SHIFTS
DISSOLVED IN POLYSTYRENE

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Abstract

Since several years, PMP and 3-HF have been known as scintillators with large Stokes shifts. We have synthesized four new aromatic pyrazoline compounds with similar properties. Their absorption and emission spectra, scintillation yields, extinction coefficients, and self-absorptions were measured and compared with the corresponding data for PMP and 3-HF. All scintillators are dissolved in polystyrene samples, in order to select the most promising candidates for future production of scintillating fibres.

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1. INTRODUCTION

Most scintillating fibres used for tracking ionizing particles consist of polystyrene (PS) as their basic matrix doped with a scintillator. They convert part of the absorbed ionization energy into visible light. Low density (1.03 g cm$^{-3}$) and average atomic number ($Z_{PS} = 3.5$) of PS induce only small fractions of unwanted particle interactions and gamma conversions. Moreover, its monomer can readily be doped with aromatic compounds whose fluorescence lifetimes are shorter than 5 ns, and which allow high counting rates.

The energy lost by an ionizing particle first excites the electronic and vibrational levels of PS. Since the PS-quantum yield is rather poor, it must be enhanced by adding an aromatic scintillator. The necessary energy transfer between the respective quantum levels requires that the PS-emission band overlaps the scintillator absorption band. A sufficiently high concentration (above 0.5 weight %) of the scintillator provides mainly non-radiative energy transfer (Förster transitions) [1] between the PS and the scintillator quantum levels.

If the scintillator emits in the opaque region of PS, e.g. p-terphenyl, a wavelength shifter is needed to cause light emission in the transparent region of PS. With two dopants of comparable low concentrations, their molecules are too distant from each other to enable non-radiative transitions between their respective quantum levels. Therefore, normal radiative exchange takes place which requires optical absorption lengths longer than 100 μm and, consequently, causes cross-talk between fibres of small diameters. This can be avoided by doping the PS matrix with a scintillator having a large Stokes shift between its absorption and emission bands, e.g. PMP(*) (1-phenyl-3-mesityl-2-pyrazoline) [2] or 3-HF (3-hydroxyflavone).

In an earlier paper [3] we have published the spectroscopic properties of four newly synthesised aromatic pyrazoline compounds, PMP 430, PMP 440, PMP 450 and PMP 460, which were dissolved in toluene. This paper reports on measurements with the same new scintillators, but this time dissolved in PS bulks. Their properties are therefore even more relevant to their application in scintillating fibres and the most promising compound can be selected for further fibre production.

2. EXPERIMENTAL
2.1 Substances

All PMP compounds listed in table 1 were prepared by standard procedures [4], i.e. either by condensation of the appropriately substituted Mannich bases with appropriately

(*) In the following text this compound will be called PMP 420.
substituted phenylhydrazines or by condensation of mesityl vinyl ketone with the appropriately substituted phenylhydrazines. The PMP derivatives are purified by several steps of recrystallisation from ethanol. All new compounds furnished correct data for elemental analysis and were further characterised by their fluorescence spectra, NMR spectra as well as by their mass spectroscopic fragmentation [5]: 1-p-tolyl-3-mesityl-2-pyrazoline, mp 105–106°C (PMP 430); 1-p-tolyl-3-(2', 6'-dimethoxyphenyl)-2-pyrazoline, mp 182–183°C (PMP 440); 1-p-anisyl-3-mesityl-2-pyrazoline, mp 88–89°C (PMP 450); 1-p-anisyl-3-(2', 6'-dimethoxyphenyl)-2-pyrazoline, mp 187–188°C (PMP 460). The photophysical properties of these organic scintillators in solution are listed in ref. [3].

Table 1 Spectroscopic properties of the investigated scintillators added to polystyrene at 0.025 molar concentration. The scintillation yields are normalised to PMP 420

<table>
<thead>
<tr>
<th>Scintillator 0.025 mole/l in PS</th>
<th>Absorption maximum [nm]</th>
<th>Emission maximum [nm]</th>
<th>Stokes shift [cm⁻¹]</th>
<th>[eV]</th>
<th>Maximum Extinction coefficient l/mole.cm</th>
<th>Scintillation yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMP 420</td>
<td>302</td>
<td>414</td>
<td>8960</td>
<td>1.11</td>
<td>10100</td>
<td>100</td>
</tr>
<tr>
<td>PMP 430</td>
<td>302</td>
<td>420</td>
<td>9300</td>
<td>1.15</td>
<td>9630</td>
<td>102</td>
</tr>
<tr>
<td>PMP 440</td>
<td>307</td>
<td>428</td>
<td>9210</td>
<td>1.14</td>
<td>10200</td>
<td>95.8</td>
</tr>
<tr>
<td>PMP 450</td>
<td>304</td>
<td>436</td>
<td>9960</td>
<td>1.24</td>
<td>10150</td>
<td>83.5</td>
</tr>
<tr>
<td>PMP 460</td>
<td>311</td>
<td>440</td>
<td>9430</td>
<td>1.17</td>
<td>10140</td>
<td>78.7</td>
</tr>
<tr>
<td>3 HF</td>
<td>343</td>
<td>528</td>
<td>10215</td>
<td>1.27</td>
<td>13200</td>
<td>27.2</td>
</tr>
</tbody>
</table>

2.2 Preparation of the scintillating plastics

For all measurements listed in table 1 and displayed in figs 3 to 6 scintillator concentrations of 0.025 mole l⁻¹ in polystyrene bulk samples were used which we prepared in the following way. Measurements on PS scintillators had shown that the scintillation efficiency is highly dependent upon the purity of the initial monomer. To eliminate, as far as possible, contaminants present during polymerization, styrene was distilled twice in vacuum. A special apparatus allowed all the products to be handled without contact with the atmosphere. Before each use, the apparatus was cleaned with sulfochromic acid, rinsed with distilled water and then carefully dried in vacuum. The glass polymerization tube (of 40 cm length and 3 cm diameter) was cleaned with sulfochromic acid, rinsed with distilled water, treated for about ten minutes in a 3% solution of dimethylidichlorosilane in chloroform, and finally rinsed consecutively with chloroform, methanol and de-ionized water. By this treatment a hydrophobic Langmuir
layer was built up on the walls of the tube which makes easier to remove the sample after polymerization.

The specified amounts of scintillator and antioxydants were placed into the tube located in the purification apparatus. The monomer was injected in vacuum and then the mixture was degassed in several freezing-thawing cycles (usually 6 cycles) until no more bubbles developed in the liquid. Finally, the tube was sealed off in vacuum.

The monomer thus prepared was immersed into an oil bath and stirred. This allowed the desired sample temperature to be maintained within ±0.1°C. The temperature was set at 130°C for a period of time (110 hours) which was long enough to complete polymerization. Finally, the tube was cooled to room temperature, sawed across in its upper part, and the polymer was easily extracted (it did not stick to the glass). The final sample was a cylinder, 30 cm long and 28 mm in diameter.

Several PS samples were prepared in this way, with different scintillators used. Each sample was subsequently cut and polished so that samples with thicknesses ranging between 0.1 and 100 mm were obtained.

2.3 Instrumentation

The spectral light absorption of the PS samples was measured with a double beam spectrophotometer (Lambda 6, Perkin Elmer, Norwalk, USA). The reference beam I₀ was transmitted through an undoped PS sample prepared by the same procedure as the doped ones placed in the measuring beam of intensity I. The recorded fractions I/I₀ (λ) of the transmitted light intensities were then transformed into decadic molar extinction coefficients and absorption lengths. The limiting sensitivity for the molar extinction coefficients was 2 × 10⁻² ℓ mole⁻¹ cm⁻¹. Due to uncontrolled chemical degradation of the end faces of the polished sample, induced by exposure to air, this sensitivity is worse than that obtained with toluene solutions in quartz cuvettes [3] but still fully adequate to our purpose.

The fluorescence emissions from the bulk samples were excited and analyzed with a self-correcting spectrofluorimeter (Mod. 8000, SLM Instruments Inc., Urbana IL, USA), described in more detail in ref. [3]. To measure the emission spectra of our samples we arranged them in the sample compartment of the spectrofluorimeter (as shown in fig. 1) in such a way that the exciting light hit their surfaces at 45 degrees. The excitation penetrated only about 5 μm into the bulk before it was fully absorbed by the polystyrene. This arrangement is called "surface excitation". The self-absorption of these samples was measured by inserting bulks of identical compositions into their emission paths.

The scintillation yields were determined with the arrangement depicted in fig. 2. The sample in question was placed without any optical coupling on the entrance face of a
phototube (EMI 9813 B) and irradiated from above with a β-emitting Sr$^{90}$ – Y$^{90}$ source. The dc-anode current of the tube was recorded with a 1 s sampling nano amperometer (Mod. 485, Keithley Instruments, Inc., Cleveland, Ohio, USA). The phototube voltage was varied over a range of values between 1000 V and 1800 V, corresponding to typical anode currents between 10 nA and 4 µA. In this way, a single response figure for each sample was determined with ± 2% accuracy.

3. RESULTS AND DISCUSSION

The measured absorption and emission bands of undoped PS samples, of 3-HF and PMP 420 doped PS samples and of PS bulks doped with the new scintillators PMP 430, PMP 440, PMP 450 and PMP 460 are shown in fig. 3. The absorptions are due to the scintillators only, since we inserted an undoped PS sample into the reference beam of the spectrophotometer to measure them.

Figure 4 displays for all scintillators investigated the decadic molar extinction coefficients (see ref.[3]) within the important wavelength region of their emission bands. The extinction coefficients in this region should be affected as little as possible by tails of the scintillator absorption bands, in order to minimise reabsorption of the emitted light during its transmission through the scintillating fibres. A comparison with the molar extinction coefficients obtained for the same pyrazoline compounds dissolved in toluene [3] shows a general increase for the same scintillators in polystyrene. Figure 5 is a presentation which is more directly connected to the problem of light transmission, namely the absorption lengths of the scintillators defined as the distances at which the original light intensities are reduced to 1/e. From fig. 5 we learn that, besides 3-HF with 10 m absorption length, the pyrazoline compound PMP 450 exhibits the greatest absorption length of 0.9 m. At the same time, its 83.5% scintillation yield, which is listed in table 1, is at the same level as for the other PMP compounds, in contrast to that of 3-HF of only 27.2%.

The favourable absorption properties of PMP 450 are underlined by fig. 6 in which the self-absorptions for its emission spectra are compared with those of PMP 420 for different absorber lengths. The samples were arranged according to fig. 1 and their emission were stimulated by "surface excitation" with a 270 nm light beam. The effect of self-absorption on the spectral shapes was provoked by inserting into the emission path samples of different lengths but of the same composition as the stimulated one. The spectra obtained in this way at the exit of the spectrofluorimeter show directly the impact of self-absorption. Again, PMP 450 looks more promising for future applications in scintillating fibres than PMP 420 used so far.
All relevant spectroscopic properties measured with PS samples doped with the scintillators indicated are listed in table 1. The absorption and emission maxima are affected by error margins of $\pm 3$ and $\pm 1$ nm, resp., due to repeatedly determined band peaks. These errors reflect to the Stokes shifts accordingly with $\pm 2.5\%$ maximum deviations. The molar extinction coefficients of the absorption maxima are associated with about $\pm 10\%$ errors, since the scintillator absorption bands in these regions overlap with the strongly absorbing PS matrix. A comparison with table 2 of ref. [3] shows that for the pyrazoline compounds the absorption maxima in table 1 are shifted to longer and the emission maxima to shorter wavelengths. This accordingly results in smaller Stokes shifts for the scintillators dissolved in polystyrene as compared to toluene.

The scintillator yields listed in the last column of table 1 are normalized to that of PMP 420. In general, the scintillation yields increase compared to those listed in table 2 of ref. [3] which were also normalized to PMP 420. These yields are not corrected for the spectral response of the bialkali-phocathode employed (fig. 2). This affects slightly the yields of PMP 450 and PMP 460, and even more strongly that of 3-HF, since the photocathode quantum yield drops with increasing wavelength. An estimated correction of the 3-HF yield would increase it from 27% to about 45%. But such a correction would be of academic relevance only, since in all applications we have to put up with the spectral responses of photocathodes which are all considerably lower at 528 nm (3-HF emission peak) than at around 420 nm.

Taking into account the measured molar extinction coefficient $\varepsilon(\nu)$ and the "surface emission" spectra $I_0(\nu)$, we calculated the transmitted light yield $Y(\ell)$ of the listed scintillator compounds as a function of the absorption path $\ell$:

$$Y(\ell) = \int_{\text{scint}} I_0(\nu) e^{-\varepsilon c \ell} d\nu \left( \int_{\text{PMP 420}} I_0(\nu) d\nu \right)^{-1}$$

(1)

where $\nu$ is the wavenumber (cm$^{-1}$) and $c$ is the scintillator concentration (0.025 mole $\ell^{-1}$). The scintillator integrals span the entire emission bands in question and normalization to PMP 420 is achieved by division by its emission integral. The measured light transmissions within the critical first 40 mm of self-absorption agree satisfactorily well with the values calculated from relation (1) (fig. 7). Extension of these calculations to cover much longer absorption lengths should therefore allow reasonable comparisons to be made between the scintillators investigated.

The transmitted light intensities calculated from relation (1) on the basis of measured extinction coefficients and spectral shapes of emission bands are plotted in fig. 8 for the scintillators investigated. The slopes of these curves indicate, in agreement with figs 4 and 5, that self-absorption is lowest for PMP 450 and 3-HF, as has been the case for their
toluene solutions [3]. In conclusion, our measurements indicate that: for applications where the transmitted light intensity is important, i.e. digital readout of scintillating fibres, doping PS with PMP 430 or PMP 450 would be advantageous. For all cases where transmitted light nearly independent of path length is the main issue, i.e. analogue readout of scintillating fibres, doping with 3-HF is recommended.

Acknowledgements

We wish to thank Professor A. Zichichi for his continuous interest and support for our work.

REFERENCES

FIGURE CAPTIONS

Fig. 1  The excitation bulk is arranged at 45 degrees with respect to the exciting light and the emitted light in order to achieve "surface excitation" without noticeable self-absorption. Different absorption paths are obtained with absorption bulks ranging from zero length to 40 mm.

Fig. 2  Set-up to compare scintillation yields for different scintillator compounds.

Fig. 3  Absorption (left) and emission (right) bands of undoped polystyrene and polystyrene doped with 0.025 molar concentrations of the indicated compounds. The absorption bands of the scintillators do not include the contribution by PS.

Fig. 4  Extinction coefficients of the investigated scintillators within the overlap regions of their absorption and emission bands (the maxima of the emission wavelengths (see table 1) are indicated for each scintillator by horizontal lines. 1 nm spacing between measuring points). The indicated error bars are mainly due to uncontrolled surface degradations of the bulk samples.

Fig. 5  Absorption lengths $\Lambda$ of 0.025 molar scintillator concentrations in polystyrene. $\Lambda$ means the optical path length at the end of which the initial light intensity is reduced to 1/e due to absorption of the emitted light. The absorption lengths at the emission maximum are indicated for each scintillator.

Fig. 6  Impact of self-absorption on the spectral shapes of two pyrazoline scintillators of 0.025 molar concentration in polystyrene. The samples were arranged as shown in fig. 1 and the shape distortions correspond to different absorber lengths of the same compositions as those stimulated by "surface excitation".

Fig. 7  Measured transmitted light intensities (points) compared to the values obtained from relation (1).

Fig. 8  Estimation of transmitted light intensities for the scintillators indicated. The curves are calculated from relation (1) by taking into account the measured molar extinction coefficients and shapes of the emission bands. The initial scintillation yields at zero path length are normalized to PMP 420 (table 1).
SAMPLE COMPARTMENT OF SPECTROFLUORIMETER

Fig. 1
Fig. 2
Fig. 8