

## CHAPTER 1

# PMP, a Novel Scintillation Solute with a Large Stokes' Shift

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### ABSTRACT

The excellent fluorescence properties of PMP (1-phenyl-*e*-mesityl-2-pyrazoline) such as a long wavelength emission of 425 nm, a high fluorescence quantum yield, and a short fluorescence decay time make this compound a promising solute for scintillation counting. Due to a very large Stokes' shift, which is more than twice as large as that of commonly used organic scintillators, PMP is suited as a primary solute requiring no secondary solute as wavelength shifter. The exceptionally large Stokes' shift results in a small overlap between the absorption and emission spectra of the solute, even at high concentrations; hence a much longer light attenuation path length compared to common scintillators. The structural features of the new solute also give rise to a unique self-quenching behavior of PMP. Unlike other scintillators, a shallow maximum of light output vs solute concentration curve is exhibited between 0.01 and 1 *M* in common solvents or solvent mixtures used in large-volume scintillation chambers. As to other scintillation characteristics such as the scintillation efficiency for  $^{14}\text{C}$  and  $^3\text{H}$ , the performance of PMP is similar to that of good commercial liquid or plastic scintillators. PMP is now used successfully in an 80,000 L large-volume scintillation detector applied in neutrino physics. The unique spectroscopic scintillation properties of PMP also suggest its use in plastic scintillating fibers.

### INTRODUCTION

We have shown recently that the class of 1,3-diphenyl-2-pyrazolines (DPs) exhibit exceptionally large Stokes' shifts when properly substituted by bulky substituents in the ortho' positions of the phenyl rings.<sup>1</sup> These sterically hindered DPs have promising potential as novel primary solutes for liquid scintillation counting.<sup>2,3</sup> Among the sterically hindered DPs tested for liquid scintillation counting, 1-phenyl-3-mesityl-2-pyrazoline, henceforth called PMP,<sup>4</sup> is the best compromise in terms of good photophysical and scintillation properties and ease of synthesis. In this chapter the results obtained on the application of PMP in scintillation counting are summarized.

**Table 1. Photophysical Properties of PPO, DP, PMP, and POPOP in Benzene at Room Temperature**

Scintillator	S <sup>a</sup> (g/l)	Q <sup>b</sup> <sub>F</sub>	$\tau$ ( $\mu$ s)	$\lambda_A$ (nm)	$\lambda_F$ (nm)	$\Delta St$ (cm <sup>-1</sup> )
PPO	414	0.79	1.3	308	365	5,240
DP	49	0.92	3.2	362	444	4,980
PMP	335	0.88	3.0	295	425	10,370
POPOP	≈ 1	0.85	1.5	362	418	3,540

<sup>a</sup>In toluene at 20°C.

<sup>b</sup>In degassed solution.

## EXPERIMENTAL

A detailed description has been given<sup>5,6</sup> of the techniques used to measure the photophysical data such as the absolute fluorescence spectra, the fluorescence quantum yields, and fluorescence decay times, as well as the scintillation characteristic.<sup>4</sup> The method used to evaluate and optimize the attenuation length of various scintillators consists in measuring the intensity of light collected by a photomultiplier placed at one end of a 2 m long quartz rod when this is orthogonally crossed by the ionizing radiation of a <sup>60</sup>Co or <sup>137</sup>Cs source at various distances from the photomultiplier. The light output of the different scintillators has been measured relative to NE 235 H using the techniques described by Kowalski et al.<sup>7</sup> With <sup>60</sup>Co, the 70% value of the Compton maximum was used.

## RESULTS AND DISCUSSION

The main photophysical properties of PMP, DP, the parent compound of PMP, and the two widely used organic scintillators, PPO and POPOP, are compiled in Table 1. PMP combines very good photophysical properties such as a high fluorescence quantum yield Q<sub>F</sub>, a short decay time ( $\tau$ ), and the long wavelength emission of the fluorescence maximum ( $\lambda_F$ ), with a high solubility (S). The most striking difference of PMP in comparison to DP and the common scintillators PPO and POPOP is the exceptionally large Stokes' shift ( $\Delta St$ ) of more than 10,000 cm<sup>-1</sup>. Since there is no fine structure in the absorption and fluorescence spectra of these large organic molecules at room temperature, the 0-0 transition is difficult to determine, and the energy difference of the absorption and emission maxima is therefore taken as a measure of the Stokes' shift. A comparison of the parent compound DP with PMP, where three methyl groups are substituted in the 2,4,6-position of the phenyl ring, reveals that the large Stokes' shift is introduced only by the sterical hindrance of the bulky methyl groups in 2- and 6-positions of the phenyl ring. The result of this sterical hindrance is that in a large hypochromic shift the absorption is shifted from 362 to 295 nm, while the fluorescence spectrum of PMP in comparison to DP remains nearly unaffected energetically.<sup>1,2</sup> Thus, the Stokes' shift of PMP is more than twice as large as that of commonly used organic

scintillators. A comparison of the absorption and fluorescence spectra of PMP and POPOP is shown in Figure 1.

The advantage of the large Stokes' shift and the broad absorption spectrum of PMP is that PMP can be used as a single wavelength shifter in scintillation counting. Thus, contrary to the classical combinations of primary and secondary solutes used in scintillation counting for more than 35 years, with the use of PMP, secondary solutes are no longer necessary. In several standard tests in  $^{14}\text{C}$  and  $^3\text{H}$  scintillation counting, the results obtained with PMP and with common organic scintillators were intercompared.<sup>4</sup> The results will not be repeated here. In general, PMP resembles good commercial liquid or plastic scintillators in its scintillation characteristics. Better results are obtained in samples exploiting the large Stokes' shift of PMP, as in the case of samples where color quenching reduces the counting efficiency.<sup>4</sup>

### Large-Volume Scintillation

Since all common organic scintillators show some overlap of their absorption and emission spectra (see Figure 1), self-transfer can occur at high concentrations by reabsorption of light emitted from the scintillator molecule. The importance of reducing the reabsorption effects in scintillators by employing solutes with large Stokes' shifts was stressed recently by Renschler and Harrah.<sup>8</sup> Due to the large Stokes' shift of PMP, the self-absorption of its own scintillation light is lower than in conventional scintillators. This is of great importance in large-volume applications such as whole-body counters, neutrino detectors, as well as scintillating fibers of tracking detectors for the new generation of particle accelerators. Since the intensity of the transmitted photons is related to the solute concentration and the length the emitted photons have to travel to reach the photomultiplier, the light attenuation length should be greater with solutes having a larger Stokes' shift. Otherwise, each time reabsorption occurs some quanta of energy are lost due to the deactivation processes inherently associated with the fate of the electronically excited singlet state of the solute molecule. A comparative study of five commercially available large-volume scintillators revealed that the attenuation length of scintillators with PMP is greater by 23–48% while the light output is in the range of 57–62% of an anthracene crystal (= 100%). These light output values are obtained with all scintillators tested. A solvent combination called PPP 2-25 with PMP as the only solute proved to be the best choice for large-volume application. This scintillator had an attenuation length of 320 cm with 57% light output. This scintillator is now operating successfully in the 80,000 L KARMEN detector (Karlsruhe–Rutherford Medium Energy Neutrino experiment) at the Rutherford–Appleton Laboratory.<sup>9</sup> An even greater attenuation length of nearly 4 m has been obtained with PMP in a new solvent combination called PMP ND 380.

There is another benefit when PMP is used as a large-volume scintillator. Unlike the common organic scintillators, PMP shows little tendency to self-

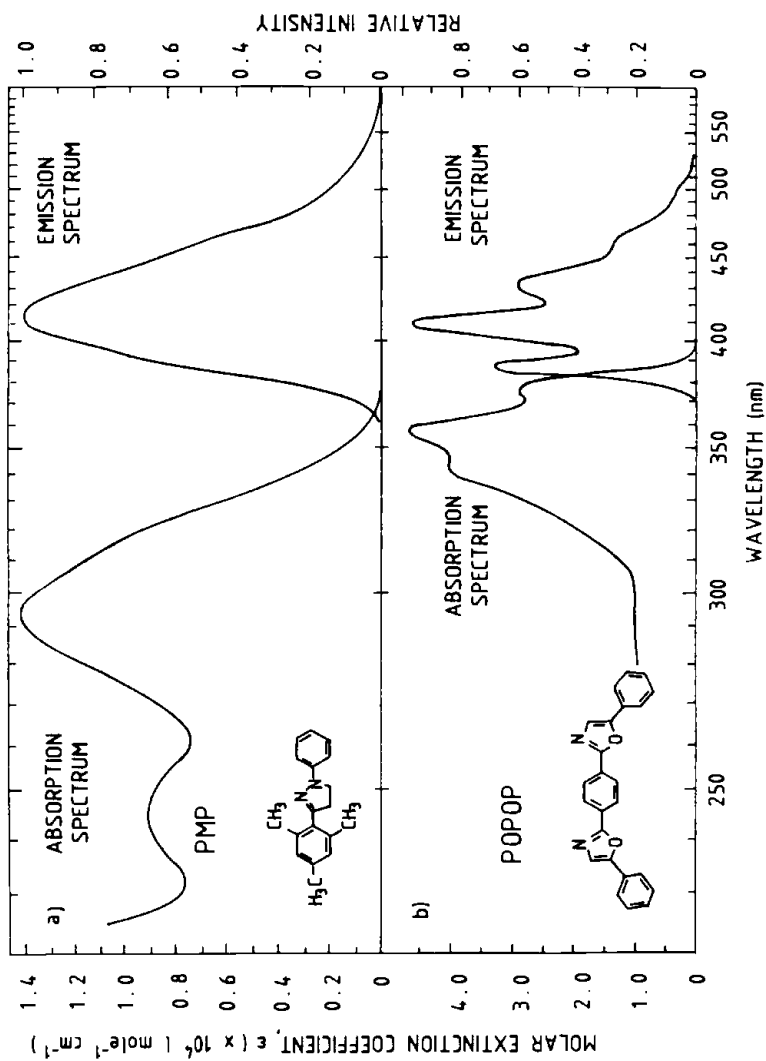


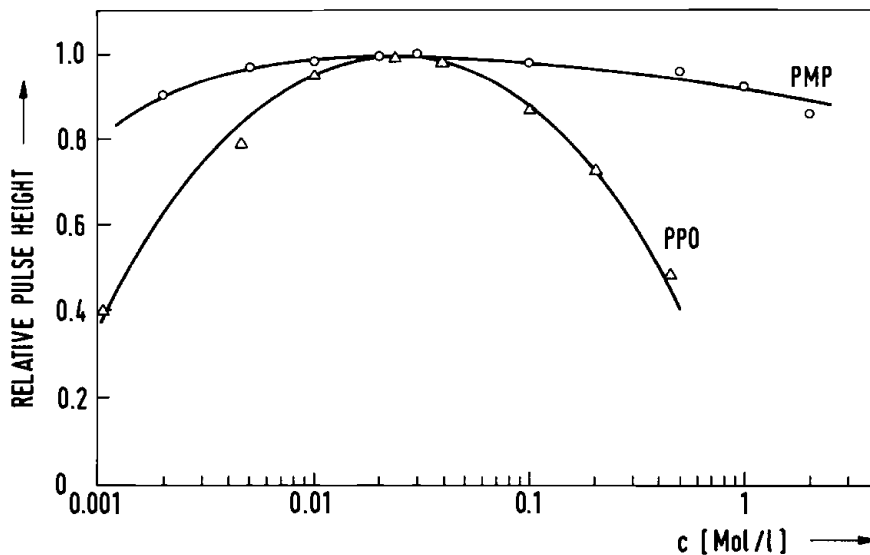
Figure 1. Absorption and fluorescence spectra of PMP and POPOP in cyclohexane at room temperature.

quenching. Most scintillators exhibit a narrow maximum in their light output vs. solute concentration curves. This phenomenon is partly due to the reabsorption processes described, partly to concentration quenching of the fluorescent state of the fluorophore by its own molecule in the ground state.

In Figure 2 the relative pulse heights of PMP and PPO, in a  $^{14}\text{C}$  standard toluene solution at  $10^\circ\text{C}$ , is plotted vs the solute concentration. While PPO shows a fairly narrow maximum at  $0.025\text{ M}$ , PMP displays a shallow maximum between  $0.01$  and  $0.1\text{ M}$ . Even at a concentration of  $1\text{ M}$  PMP ( $264\text{ g/l}$ ) the relative pulse height has dropped only by about  $10\%$ . Consequently, by use of PMP the doping concentration can be raised to values at which only non-radiative energy transfer is effective. We explain this low tendency to self-quenching of PMP by the different geometries of PMP in the ground and in the electronically excited singlet state.

### Scintillating Fibers

The new generation of tracking detectors use parallel bundles of scintillating optical fibers of extremely small diameters.<sup>10</sup> Theoretical reasoning about plastic-based scintillating fibers has pointed to the need for improving the attenuation length of common scintillators.<sup>11</sup> It was shown recently that PMP in polyvinyl toluene (PVT) or polystyrene reach nearly the scintillation efficiency of NE 110 while the transparency of PMP is better by at least one order of magnitude in the concentration range of  $0.025$  to  $0.050\text{ M}$  over the entire wavelength range of its emission spectrum from  $400$ – $450\text{ nm}$ .<sup>10,12</sup> Since the



**Figure 2.** Dependence on concentration of the relative pulse height of PMP and PPO in a  $^{14}\text{C}$  standard toluene solution at  $10^\circ$ .

PVT emission is effectively absorbed at a distance of  $< 10 \mu\text{m}$ , plastic scintillators that contain PMP can now be used for the production of efficient small diameter plastic scintillating fibers.<sup>10,12</sup> Furthermore, PMP in polysiloxane showed good radiation resistance in an argon atmosphere.<sup>13</sup> This is another important feature because a radiation hardness of  $10^6$  rads is required to ensure a reasonable operational lifetime of the scintillating fiber.

## ACKNOWLEDGEMENTS

We thank Drs. K. F. Schmidt and R. Maschuw of the Institute of Nuclear Physics of the Kernforschungszentrum Karlsruhe for the measurements of the attenuation lengths.

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