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Optical characteristics of pure poly (vinyltoluene) for scintillation applications

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ABSTRACT

Advanced refining techniques have enabled the application of high-purity aromatic ring polymers with favourable scintillation characteristics for radiation detection, without requiring doped fluorescent guest molecules. Here, we show the optical characteristics of pure poly (vinyltoluene) (PVT). It has a 285-nm excitation maximum and a 315-nm emission maximum. The effective refractive index is 1.66, which was derived from its emission spectrum. Light yields were determined by irradiation with ^{137}Cs and ^{207}Bi radioactive sources. The light attenuation length is an unexpectedly high 40.5 ± 0.3 mm. These results indicate that thick samples of undoped PVT can be used as effective scintillation materials, and will stimulate future applications.

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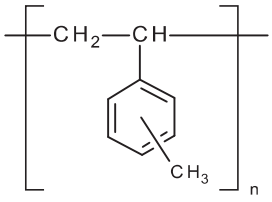
1. Introduction

When excited by radiation, organic scintillation materials with doped fluorescent guest molecules generate light at detectable wavelengths *via* base substrates composed of aromatic ring polymers [1,2]. Critical optical characteristics for radiation detection include the excitation and emission wavelengths, refractive indices, and light attenuation lengths [3–5]. State-of-the-art refining methods produce aromatic ring polymers with high purity [6]. These substrates have favourable characteristics for radiation detection that do not require fluorescent guest molecules, and thus they are becoming attractive scintillation materials [7–18]. Examples include common polymers such as poly (ethylene terephthalate) and polycarbonate [19–23].

Poly (vinyltoluene) (PVT) has been used for many years as a base substrate for doped scintillation materials. The structural repeat unit of PVT is:



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The attenuation length for short-wavelength light emitted from PVT has been reported to be several millimetres [24]. This limits the quantities and types of fluorescent guest molecules that can be used. Here, we characterise the optical characteristics of undoped, high-purity PVT and demonstrate that it is a suitable scintillation material for radiation detection.

2. Materials and methods

A 60–40% mixture of *meta* and *para* vinyltoluene monomer (98% purity, Wako Pure Chemical Industries, Ltd.) was distilled to reduce the level of p-tert-butylcatechol inhibitor to <1 ppm. The monomer was then poured into a glass vessel through a 0.2-μm membrane filter and vacuum-encapsulated. Polymerisation was performed without initiators in an oil bath. In this way, coloration and impurities, caused by thermal degradation or oxygen contamination, were reduced in the PVT. Polymerisation was 98.0%, with an average molecular weight of 550,000 and a density of 1.02 g/cm^3.

A single PVT sample was cut into 62×62 mm^2 blocks with thicknesses of 5, 15, 25, and 35 mm. All surfaces for each block were polished. Fluorescence from the PVT was characterised with a fluorescence spectrophotometer (F-2700; Hitachi High-Technologies Co.). To characterise the refractive index of a scintillation material in detail, it is important to take into account its emission spectrum. Thus, the wavelength dependence for the PVT

refractive index was acquired with a refractometer (PR-2; Carl Zeiss Jena) at the g line of a mercury lamp (436 nm), the F and C lines of a hydrogen lamp (486 and 656 nm), and the D line of a sodium lamp (589 nm).

Figure 1 is a schematic of the experimental arrangement for determining the PVT light yields. The samples are excited by ^{137}Cs (CS21; Japan Radioisotope Association) or ^{207}Bi (BIRB4391; High Technology Source Ltd.) radioactive sources that emit monoenergetic internal conversion electrons. The light was detected with a short-wavelength-sensitive photomultiplier tube (PMT; R878-SBA, Hamamatsu Photonics Co., Ltd.) [4]. The PMT window was interfaced to a 62×62 mm^2 block faces *via* a thin layer of optical grease (EJ-550; Eljen Technology), while the radioactive sources were positioned at the centre of the opposite face. A 12 bit charge-sensitive ADC (RPC022; REPIC Co.) was used to digitise output pulses from the PMT.

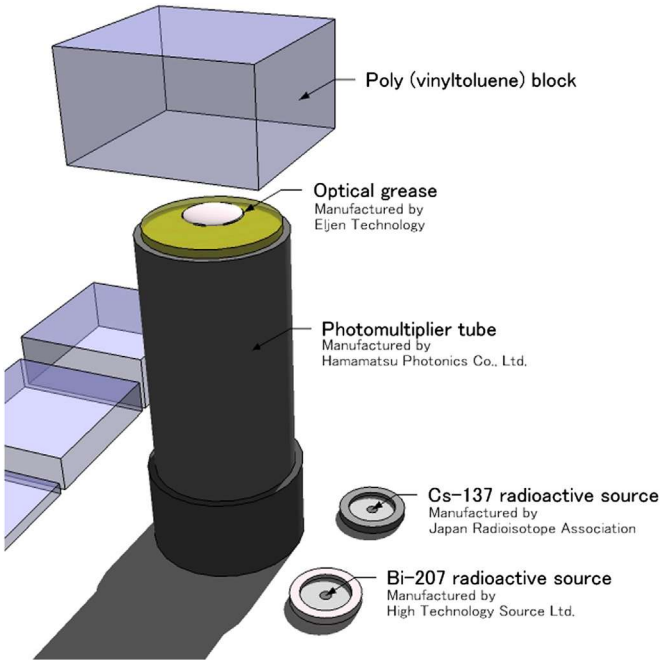

Fig. 1. Apparatus for acquiring light yields from PVT excited by a radioactive source. High-purity 62×62-mm^2 PVT blocks with thicknesses of 5, 15, 25, and 35 mm were used. ^{137}Cs- and ^{207}Bi-radioactive sources were positioned at the centre of the 62×62 mm^2 face.

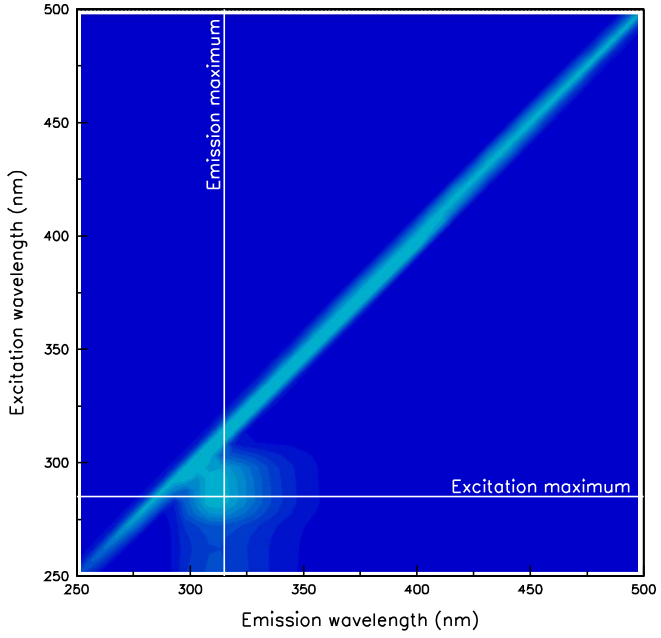

Fig. 2. Correlation between excitation and emission wavelengths for PVT fluorescence. The white lines are the 285-nm excitation and the 315-nm emission maxima. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

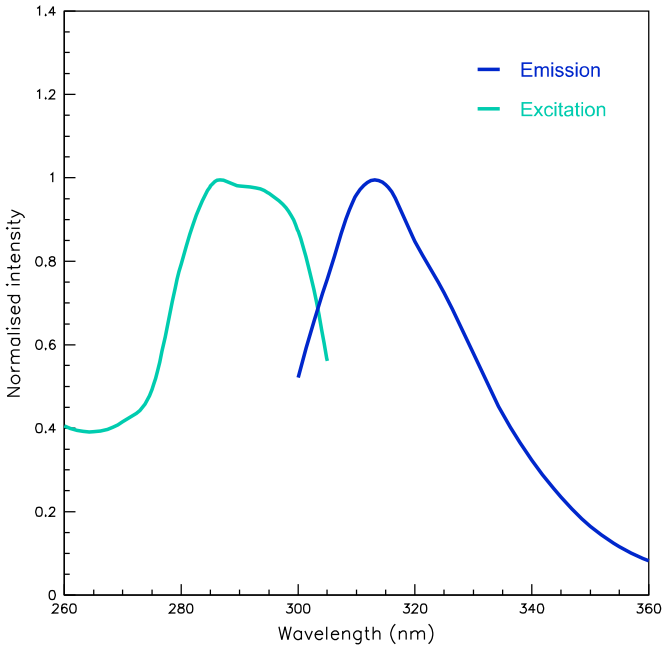

Fig. 3. PVT excitation and emission spectra. The excitation spectrum (green) was monitored at the 315-nm emission maximum, while the emission spectrum (blue) was acquired at the 285-nm excitation maximum. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

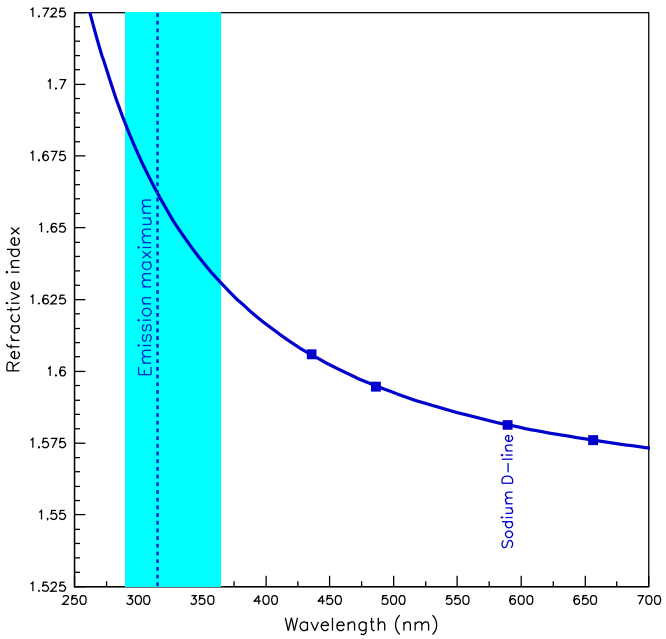

Fig. 4. PVT refractive indices at specific wavelengths. The dominant emission is highlighted in light blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

Figure 2 plots the correlation between excitation and emission wavelengths for PVT fluorescence. The blue contrast represents the light intensity, while the two white lines indicate the 285-nm excitation and the 315-nm emission maxima. The excitation and emission spectra are plotted in Fig. 3.

As previously reported, the refractive index (N_D) of PVT at the 589-nm sodium D line is 1.58 [24]. However, because PVT does not emit yellow light, this refractive index is not appropriate for scintillation applications. Instead, a refractive index effective over the actual emission spectrum must be determined. Thus, in Fig. 4, we plot the PVT refractive indices at the wavelengths of the four atomic lines. The refractive index n *vs* wavelength λ was fit with the Sellmeier dispersion function [6,25] $\sqrt{1+C_1/(1+C_2/\lambda^2)}$, where C_1 and C_2 are constants. From this fit and from the light intensity I at wavelength λ in the PVT emission spectrum, an effective refractive index $N_{eff} = \int n(\lambda)I(\lambda)d\lambda / \int I(\lambda)d\lambda = 1.66$ was determined.

For the 5-mm-thick PVT block, the light yield distribution excited by the ^{137}Cs radioactive source is plotted in Fig. 5. The sharp peak corresponds to 624 keV internal conversion electrons. The counts in the low light-yield region were created by beta particles with an endpoint-energy of 514 keV and Compton recoil electrons generated by 662 keV gamma-rays. Similarly, for the same block, Fig. 6 plots the light-yield distribution excited by the ^{207}Bi radioactive source, where the sharp peak corresponds to 976 keV internal conversion electrons. The shoulder in the low light-yield region was generated in part by 482 keV internal conversion electrons.

The peak values in the light-yield distributions generated by the 624 and 976 keV internal conversion electrons are plotted in Fig. 7

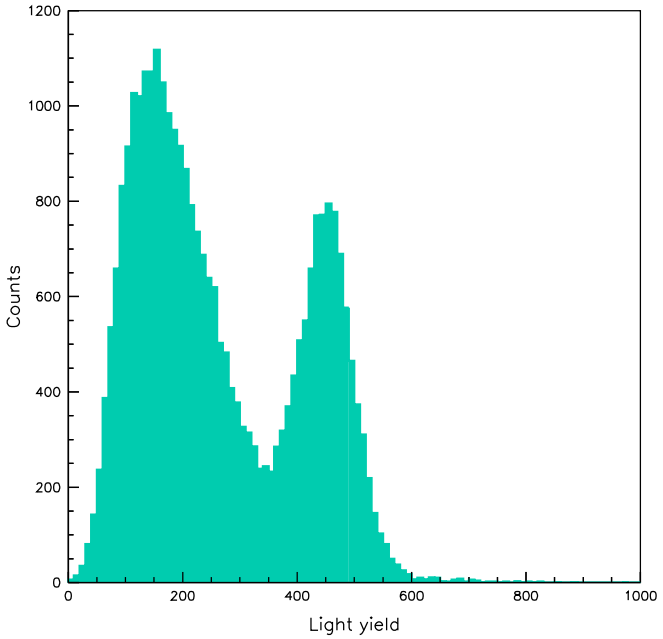

Fig. 5. Light yield distribution for a 5-mm-thick PVT block excited by a ^{137}Cs radioactive source. 624 keV internal conversion electrons appear as the sharp peak in the distribution. Additionally, beta particles with 514-keV endpoint energies and Compton recoil electrons generated by 662-keV gamma-rays create counts in the low light-yield region.

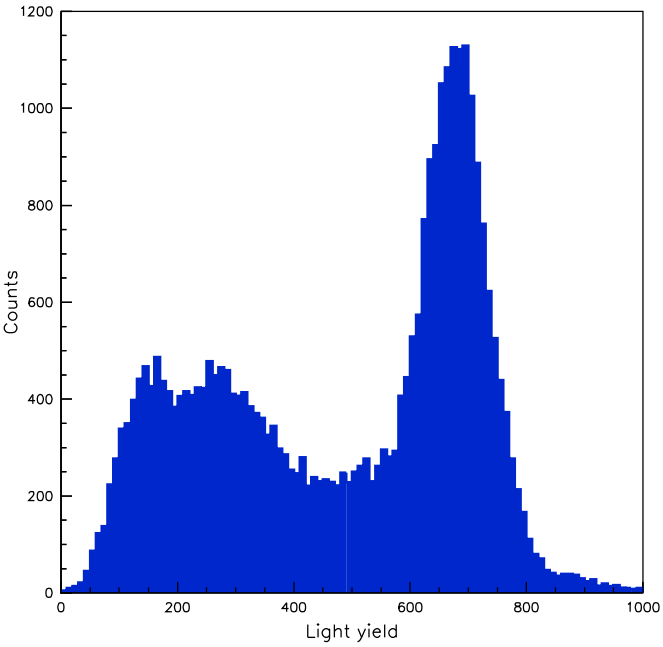

Fig. 6. Light yield distribution for a 5-mm-thick PVT block excited by a ^{207}Bi radioactive source. The sharp peak in the distribution is produced by 976 keV internal conversion electrons, while 482 keV internal conversion electrons contribute to the small shoulder.

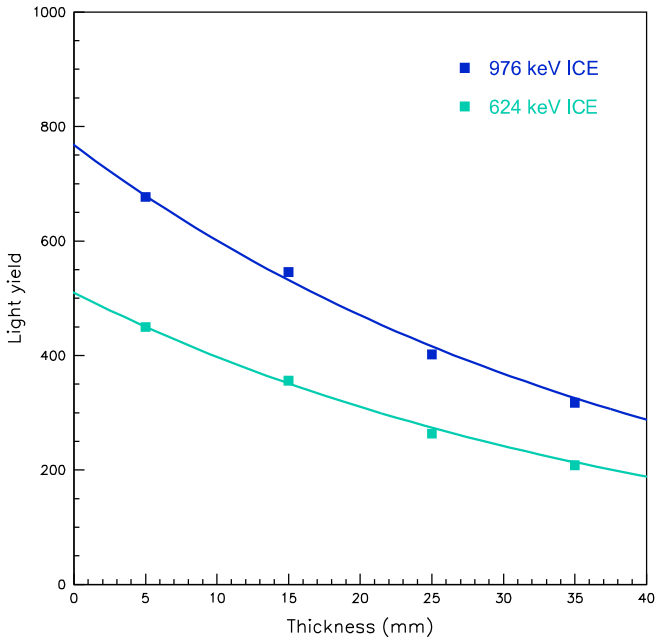

Fig. 7. Light attenuation in PVT. Each peak in the light-yield distributions (due to monoenergetic internal conversion electrons (ICEs) from the ^{137}Cs- and ^{207}Bi sources) is plotted as a function of block thickness. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Optical characteristics of pure poly (vinyltoluene).

Substrate	Formula	Density	Emission maximum	Refractive index		Attenuation length
				[a]N_D	[b]N_{eff}	
PVT	C_9H_{10}	1.02 g/cm^3	315 nm	1.58	1.66	40.5 ± 0.3 mm

[a] N_D indicates the refractive index at the sodium D line.
[b] N_{eff} indicates the effective refractive index by taking into account its emission spectrum.

as a function of block thickness. The data is fit by $C\exp(-x/L_{att})$, where C is a constant. The light attenuation length L_{att} is 40.2 ± 0.5 mm and 40.8 ± 0.2 mm for light emission excited by the 624 and 976 keV internal conversion electrons, respectively. The average value of 40.5 ± 0.3 mm exceeds previous reports by a factor of ten. These results demonstrate that thick substrates of undoped PVT are effective scintillation materials. All of the results are summarised in Table 1.

4. Conclusions

We have demonstrated that purified PVT has suitable optical characteristics to be an effective scintillation material. PVT has a 285-nm excitation maximum, a 315-nm emission maximum, and an effective refractive index of 1.66 over its emission spectrum. The light attenuation length is 40.5 ± 0.3 mm. Thus, thick PVT can be used for radiation detection without doping. This work should stimulate potential applications as scintillation materials.

Acknowledgements

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References

[1] G. Knoll, Radiation Detection and Measurement, fourth ed., Wiley, New York, 2010.
[2] W.R. Leo, Techniques for Nuclear and Particle Physics Experiments: A How-to Approach, second ed., Springer-Verlag, Berlin, Heidelberg, 1992.
[3] H. Nakamura, Y. Shirakawa, H. Kitamura, N. Sato, O. Shinji, K. Saito, S. Takahashi, Sci. Rep. 3 (2013) 2502. http://dx.doi.org/10.1038/srep02502.
[4] H. Nakamura, H. Kitamura, O. Shinji, K. Saito, Y. Shirakawa, S. Takahashi, Appl. Phys. Lett. 101 (2012) 261110. http://dx.doi.org/10.1063/1.4773298.
[5] Y. Shirakawa, H. Nakamura, T. Kamata, K. Watai, M. Mitsunaga, Z. Shidara, F. Murakawa, Radioisotopes 62 (2013) 879. http://dx.doi.org/10.3769/radioisotopes.62.879.
[6] H. Nakamura, Y. Shirakawa, H. Kitamura, N. Sato, O. Shinji, K. Saito, S. Takahashi, Appl. Phys. Lett. 103 (2013) 161111. http://dx.doi.org/10.1063/1.4824467.
[7] H. Nakamura, Y. Shirakawa, H. Kitamura, N. Sato, S. Takahashi, Nucl. Instrum. Methods Phys. Res. A 739 (2014) 6. http://dx.doi.org/10.1016/j.nima.2013.12.021.
[8] S. Nagata, H. Katsui, K. Hoshi, B. Tsuchiya, K. Toh, M. Zhao, T. Shikama, E. R. Hodgson, J. Nucl. Mater. 442 (Suppl. 1) (2013) S501. http://dx.doi.org/10.1016/j.jnucmat.2013.05.039.
[9] H. Nakamura, Y. Shirakawa, S. Takahashi, H. Shimizu, Europhys. Lett. 95 (2) (2011) 22001. http://dx.doi.org/10.1209/0295-5075/95/22001.
[10] H. Nakamura, T. Yamada, Y. Shirakawa, H. Kitamura, Z. Shidara, T. Yokozuka, P. Nguyen, M. Kanayama, S. Takahashi, Appl. Radiat. Isot. 80 (2013) 84. http://dx.doi.org/10.1016/j.apradiso.2013.06.011.
[11] I. Sen, M. Urffer, D. Penumadu, S.A. Young, L.F. Miller, A.N. Mabe, IEEE Trans. Nucl. Sci. NS59 (4) (2012) 1781. http://dx.doi.org/10.1109/TNS.2012.2201503.
[12] H. Nakamura, Y. Shirakawa, T. Yamada, P. Nguyen, S. Takahashi, Phys. Educ. 48 (2013) 556. http://dx.doi.org/10.1088/0031-9120/48/5/F02.
[13] H. Nakamura, Y. Shirakawa, N. Sato, S. Takahashi, Phys. Educ. 49 (2014) 135. http://dx.doi.org/10.1088/0031-9120/49/2/135.
[14] S. Nagata, M. Mitsuzuka, S. Onodera, T. Yaegashi, K. Hoshi, M. Zhao, T. Shikama, Nucl. Instrum. Methods Phys. Res. B 315 (2013) 157. http://dx.doi.org/10.1016/j.nimb.2013.03.027.
[15] H. Nakamura, Y. Shirakawa, H. Kitamura, N. Sato, S. Takahashi, Appl. Radiat. Isot. 86 (2014) 36. http://dx.doi.org/10.1016/j.apradiso.2013.12.028.
[16] H. Nakamura, Y. Shirakawa, N. Sato, T. Yamada, H. Kitamura, S. Takahashi, Appl. Radiat. Isot. 91 (2014) 131. http://dx.doi.org/10.1016/j.apradiso.2014.05.013.
[17] H. Nakamura, Y. Shirakawa, N. Sato, H. Kitamura, S. Takahashi, Nucl. Instrum. Methods Phys. Res. A 759 (2014) 1. http://dx.doi.org/10.1016/j.nima.2014.05.053.
[18] R. Uppal, I. Sen, D. Penumadu, S. Young, M.J. Urffer, L.F. Miller, Adv. Eng. Mater. 16 (2013) 196. http://dx.doi.org/10.1002/adem.201300237.
[19] H. Nakamura, H. Kitamura, R. Hazama, Proc. R. Soc. A 466 (2010) 2847. http://dx.doi.org/10.1098/rspa.2010.0118.
[20] V. Kumar, Y. Ali, R.G. Sonkawade, A.S. Dhaliwal, Nucl. Instrum. Methods Phys. Res. B 287 (2012) 10. http://dx.doi.org/10.1016/j.nimb.2012.07.007.
[21] H. Nakamura, Y. Shirakawa, H. Kitamura, T. Yamada, Z. Shidara, T. Yokozuka, P. Nguyen, T. Takahashi, S. Takahashi, Radiat. Meas. 59 (2013) 172. http://dx.doi.org/10.1016/j.radmeas.2013.06.006.
[22] Y. Shirakawa, H. Nakamura, T. Kamata, K. Watai, Radiat. Meas. 49 (2013) 155. http://dx.doi.org/10.1016/j.radmeas.2012.12.001.
[23] H. Nakamura, Y. Shirakawa, N. Sato, H. Kitamura, S. Takahashi, Jpn. J. Health Phys. 49 (2) (2014) 98. http://dx.doi.org/10.5453/jhps.49.98.
[24] J. Beringer, et al., Particle Data Group, Phys. Rev. D 86 (2012) 010001. http://dx.doi.org/10.1103/PhysRevD.86.010001.
[25] W. Sellmeier, Ann. Phys. 219 (1871) 272. http://dx.doi.org/10.1002/andp.18712190612.