VUV-VIS optical characterization of Tetraphenyl-butadiene films on glass and specular reflector substrates from room to liquid Argon temperature

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Evaporated TPB Films

Layer density (µg/cm²)

<table>
<thead>
<tr>
<th>Glass substrate</th>
<th>165</th>
<th>200</th>
<th>350</th>
<th>725</th>
<th>900</th>
<th>1175</th>
<th>1450</th>
<th>1875</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric reflector substrate VM2000 - VIKUITI</td>
<td>50</td>
<td>75</td>
<td>175</td>
<td>370</td>
<td>475</td>
<td>550</td>
<td>600</td>
<td>770</td>
</tr>
<tr>
<td></td>
<td>810</td>
<td>1045</td>
<td>1375</td>
<td>1500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Samples obtained by dip-coating of glass substrates in polystyrene containing TPB

<table>
<thead>
<tr>
<th>Fraction of TPB in polystyrene (Weight fraction %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>40</td>
</tr>
</tbody>
</table>

Samples obtained by evaporation of TPB on different substrates

Investigated TPB samples were grown at the Gran Sasso National Laboratory LNGS, INFN L’Aquila, Italy
Configurational coordinates diagram

PhotoLuminescence (PL) Spectra

Absorption Spectra
Photo Excitation (PE) Spectra
TPB evaporated on glass

A fraction of the emitted radiation can undergo several absorption and re-emission processes before escaping from the sample surface. This results in a red shift of the emission band peak.
TPB evaporated on VIKUITI: the Temperature Effect

unresolved vibronic structures at 300 K, spaced by ~170 meV, become clearly visible at Lar T and below.
Emission Spectra
Excited at 128 nm

Absorption Spectra

re-absorption mechanisms at about 350. It corresponds to the HOMO-LUMO transition of TPB (Highest Occupied Molecular Orbital)-to-((Lowest Unoccupied Molecular Orbital)
TPB in polystyrene

TPB in PMMA


5/30/13
TPB in polystyrene on glass
Temperature effects

Emission Spectra Excited at 128 nm

Emission Spectra of TPB on VIKUITI and in polystyrene
Excited at 128 nm
Temperature 87 K (LAr)

vibronic structures not observed neither at room temperature nor at lower temperatures. This behavior closely resembles that of TPB in liquid solutions, where the randomness of the environment geometry around the TPB molecule induces the observed inhomogenous broadening of the vibronic structures, which merge in a single, unresolved band.
Photoluminescence (PL) and Photoexcitation (PE) in the UV-VIS range

TPB in polystyrene on glass – $T = 300$ K

TPB evaporated on VM2000 – 600 $\mu$g/cm$^2$ – $T = 300$ K
Detail of the PhotoExcitation Spectra around 128 nm for two representative samples of TPB on VIKUITI and TPB in polystyrene on glass. The Spectra are normalized to a Sodium Salicylate reference.
Hemispheric optical reflectance $R$ and transmittance $T$ (and absorbance $A$)

\[ R + T + A = 1 \]
In a typical spectrophotometer, while the impinging probe beam is filtered in wavelength, the reflected (transmitted) beam is detected with no spectral filtering.

**PROBLEM!**

Measurements of R and T (and A) of an optically-active sample are heavily affected by unwanted Stokes-shifted PL which is excited by the probe beam.

Is there a way to “clean” measured photometric spectra of TPB from PL?
Let us insert a suitable low-pass filter...

Photoluminescence affects the measurement of $R$

... no more *detected* photoluminescence!

Of course, some *data elaboration* is needed...
A suitable low-pass filter is needed...

For TPB, range \( \text{range} \) spans from well below \( \lambda = 250 \text{ nm} \) (lower measurement limit) up to \( \lambda \sim 380 \text{ nm} \). Range \( \text{range} \) is roughly \( 380 \text{ nm} < \lambda < 420 \text{ nm} \).
Measurement correction (reflectance):

\[ T_F(\lambda) \approx \varepsilon (\text{= small constant}) \text{ for } \lambda \in \Lambda_{PL} \quad T_F(\lambda) > \varepsilon \text{ for } \lambda \notin \Lambda_{PL} \quad \text{low-pass filter requirements} \]

\[ R(\lambda) = R_S(\lambda) + \frac{\Omega_R}{4\pi} N_R \sigma_{PE}(\lambda) \int_{\Lambda_{PL}} \Gamma_R(\lambda') \sigma_{PL}(\lambda') d\lambda' \]

as measured spectrum (without filter)

\[ \tilde{R}(\lambda) = R_F(\lambda) + T_F^2(\lambda) R_S(\lambda) + \varepsilon \frac{\Omega_R}{4\pi} T_F(\lambda) N_R \sigma_{PE}(\lambda) \int_{\Lambda_{PL}} \Gamma_R(\lambda') \sigma_{PL}(\lambda') d\lambda' \]

spectrum with filter placed between sample and detector

\[ R_S(\lambda) \approx \frac{\tilde{R}(\lambda) - R_F(\lambda) - \varepsilon T_F(\lambda) R(\lambda)}{T_F(\lambda) \left[ T_F(\lambda) - \varepsilon \right]} \quad (\lambda < \lambda_0) \]

evaluation of true sample reflectance

\[ \text{LEGEND} \]
\[ T_F(\lambda) \text{ and } R_F(\lambda) : \text{spectral transmittance and reflectance of the optical filter} \]
\[ \Lambda_{PL} : \text{spectral range where PL is present} \quad \Omega_R : \text{detection solid angle} \quad \lambda_0 : \text{cutoff wavelength} \]
\[ R(\lambda), \tilde{R}(\lambda), \text{ and } R_S(\lambda) : \text{as measured (without filter), measured with filter, and true sample reflectance} \]
\[ N_R : \text{number of optically active centres} \quad \sigma_{PL} \text{ and } \sigma_{PE} : \text{PL and PE cross sections} \]
Spectrophotometer and integrating sphere

Perkin-Elmer Lambda 19
(dual-beam UV-Vis spectrophotometer)

Perkin-Elmer mod. B013-8277
(15 cm diameter integrating sphere)

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TPB layer over Reflector: null transmittance over all the examined range.
High R at $\lambda > 420$ nm due to TPB and/or Reflector.
Low R at $\lambda < 380$ nm, lower than R of Reflector, ascribed to low R and high absorbance A of TPB itself.
The plots demonstrate that TPB has an absorption band at about 350 nm (3.54 eV). The further absorption cutoff at $\lambda < 300$ nm for the polystyrene-diluted TPB is ascribed to the glass substrate.
Comparison of spectral properties of TPB layers as a function of surface density

Hemispheric T and R, and direct T for various TPB surface densities of TPB layer on glass.
Conclusions

The main spectral features and optical characteristics of TPB films on different substrates, commonly employed elements of DM detector optical systems, have been investigated and presented here to provide means for more accurate simulations and designs of current and future LAr experiments.

TPB emission spectra by VUV excitation at 128 nm with lineshape and relative intensity variation down to LAr temperature were measured.

For TPB films evaporated on specular reflector substrates, the unresolved vibronic structures at room temperature become clearly visible as the temperature is decreased. At 87 K one can observe at least four distinct structures and the PL intensity increases of about 10% with respect to the luminescence at room temperature.
Vacuum Monochromator
McPherson model 234/302
Focal length 0.2 m equipped
with a 30 Watts Deuterium lamp model 632
with MgF₂ window,
Spectral range 115 – 380 nm.

Closed-cycle Helium Cryostat
Temperature range
12 – 300 K
Spectrophotometer Lambda 950 PERKIN ELMER UV/VIS/NIR, compatible with optical cryostat cooled at LNT

Spectrofluorometer Fluorolog 3 ISA JOBIN YVON-SPEX Mod.FL3-11 compatible with optical cryostat cooled at LNT

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