Temperature-dependent fluorescence emission spectra of acrylic (PMMA) and tetraphenyl butadiene (TPB) excited with UV light

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ABSTRACT: Acrylic (poly(methyl methacrylate) or PMMA) is commonly used as a material for vessels to hold scintillating liquids in rare-event searches. Certain types of PMMA can fluoresce with a low efficiency at room temperature. We have investigated the fluorescence spectra under 280 nm ultraviolet (UV) excitation of the PMMA used in the DEAP-3600 dark matter search at various low temperatures. Fluorescence of this PMMA is observed, with an increasing intensity as the sample is cooled from a temperature of 300 K down to 4 K. The common wavelength-shifter tetraphenyl butadiene (TPB) is also measured for use as a reference.

KEYWORDS: Scintillators, scintillation and light emission processes (solid, gas and liquid scintillators); Noble liquid detectors (scintillation, ionization, double-phase); Dark Matter detectors (WIMPs, axions, etc.); Large detector systems for particle and astroparticle physics

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1 Introduction

Several rare-event search experiments use a scintillating target contained in support structures made from plastics. The DEAP-3600 experiment, for instance, uses an acrylic vessel to contain the liquid argon (LAr) target [1]. Acrylic, or poly(methyl methacrylate) (PMMA), has been reported to fluoresce at a low intensity when excited by ultraviolet (UV) light ([2] and references therein). The unexpected fluorescence of construction and support materials, even at a very low efficiency, could be a concern for experiments that look for rare events at low energies. For this reason, we have previously investigated the fluorescence response of acrylic and polytetrafluoroethylene (PTFE) to vacuum UV photons from 130 nm to 250 nm at room temperature [2]. These wavelengths span the range of LAr and LXe scintillation light, as well as the far UV and part of the mid-UV spectral range of Cherenkov light created within the acrylic. However, the samples were not measured at the corresponding cryogenic temperatures of 87 K (LAr) or 165 K (LXe), even though the luminescence of a material can depend on its temperature [3]. No fluorescence was observed, so [2] gives limits on the level of fluorescence of the measured samples at room temperature.

In view of a future comparison of the fluorescence of PMMA to a well-known reference, we have also measured the low-temperature spectra of the wavelength shifter 1,1,4,4-tetraphenyl-1,3-butadiene (TPB). TPB is commonly used to shift liquid noble gas scintillation light to the blue spectral range, so that it is easier to detect. In many experiments, including DEAP-3600 [1], MiniCLEAN [4], and MicroBooNE [5], it is used in combination with acrylic. Therefore, it is a good reference for wavelength shifting efficiencies. In a first step toward characterizing the potential fluorescence of acrylic and PTFE at cryogenic temperatures, we have measured the response of acrylic to 280 nm excitation photons at temperatures from 300 K down to 4 K.

2 Samples, procedures and set-up

The principle of these measurements was to excite the samples with continuous 280 nm light and measure their fluorescence emission spectra at temperatures from 300 K to 4 K. Since the UV photons do not penetrate far into the material, the treatment of the surface can have a large effect on the fluorescence response. Furthermore, the response can be modified by impurities, additives, and
by the conditions under which the material was machined or otherwise treated. Therefore, we use a sample of acrylic from the same batch the DEAP-3600 acrylic vessel was made from. The sample is the same as that described in [2] as ‘RPT acrylic,’ supplied to the DEAP-3600 Collaboration by Reynold’s Polymer Technology. The TPB sample was vacuum evaporated onto a piece of generic acrylic of the same size as the RPT acrylic sample. The thickness of the deposited TPB layer was measured with a profilometer to be $(0.35 \pm 0.03) \mu m$.

The samples were installed into a custom copper sample holder which rotated the sample approximately $8^\circ$, relative to the incoming light beam, around the vertical axis. The holder was then attached onto the cold finger of the cryostat, as shown in figure 1.

![Figure 1](image_url)

_Figure 1. Left: TPB coated sample installed into the copper sample holder, which is then attached to the cold finger of the cryostat. All of this is shown enclosed in the inner-most cryostat chamber. Right: Top-down cross-sectional view of the schematic used for this experiment. The light shines from the LED through the bandpass filter, three cryostat windows (only one window is illustrated) and reaches the sample. If the sample fluoresces at visible wavelengths, the fluorescence light goes through the adjacent windows, longpass filter, and then into the optical fibre. In the case of the TPB sample, the TPB coating is on the side facing the LED._

The cryostat is closed-cycle, with a compact optical geometry to optimize light-collection efficiency [6]. The cold finger is enclosed within a vacuum shroud and two radiation shields. The sample can be viewed from the outermost shroud through a corresponding series of Spectrosil 2000 fused silica windows, which have more than 90% transmission at the wavelengths of interest [6].

A schematic of the experiment is shown in figure 1. A commercial 280 nm UVTOP LED was attached to the side of the outer cryostat chamber. When the TPB-coated sample was installed, the LED was shining onto the coated surface; when the RPT acrylic sample was installed, the LED was shining onto the smoother finished surface. The LED was powered in direct-current (DC) mode, and used with an Edmund Optics Hard Coated 280 nm bandpass filter to ensure that only monochromatic $(280 \pm 5) \text{ nm}$ light reached the samples. We used the Horiba Scientific Symphony II CCD Detector and MicroHR Automated Imaging Spectrometer for spectral imaging. The optical fibre of the spectrometer was attached to the opposite window of the outer chamber, facing the opposite surface than the LED was shining onto. A longpass filter made of transparent, UV-absorbing (UVA) acrylic was installed in front of the optical fibre, to eliminate any UV light that may have reached the fibre’s position through or around the sample. The shape of the transmittance curve is relatively flat above approximately 400 nm, as is evidenced by the curve of another sample from the same batch measured in [2] and shown in figure 3.
The optical cryostat was put under vacuum for all measurements. An external CryoCon 24 temperature controller system was used to set and monitor the cold finger’s temperature. All external components were at room temperature. Spectra were taken in descending order through temperatures \((300.0 \pm 1.0)\) K, \((163.0 \pm 1.5)\) K (LXe), \((87.0 \pm 1.5)\) K (LAr), and \((4.0 \pm 0.1)\) K.

3 Analysis and results

Spectra from the sample were corrected for the spectrum from a dark exposure of equal duration. The scanning range of one window of the spectrometer is approximately 285 nm, so multiple windows were recorded at each temperature to scan from the approximately 350 nm to the near infrared.

Figure 2. Top: spectra of the TPB sample over all measured temperatures. Bottom: spectra of the TPB sample measured in this work (not corrected for any spectrometer wavelength dependence) and TPB spectra from literature at 300 K and 87 K [7], all normalized to a unit area. In both panels, an arbitrary vertical offset was applied between temperatures to better show each spectral shape.
The top panel of figure 2 shows the spectra of TPB over all measured temperatures. The intensity shows a mildly increasing trend from 300 K to 4 K over the main emission peak from 375 nm to 450 nm. An additional peak not seen at room temperature, at approximately 400 nm, also increases as temperature decreases. This feature has been seen in previous measurements of TPB films down to LAr temperature, and has been attributed to vibrational structures in the molecules [7]. The bottom panel of figure 2 shows an overlay of our measured spectra with spectra measured from [7] at 87 K and 300 K. All spectral curves in the bottom panel are normalized to their own total integrated intensity, such that the area under each curve sums to one.

Figure 3. Top: emission spectra of the RPT acrylic sample over all measured temperatures. An arbitrary vertical offset was applied to better show each spectral shape. Bottom: emission spectrum of the RPT acrylic sample (not corrected for any spectrometer wavelength dependence), emission spectrum measured by [9] in response to excilamp UV light, and the transmittance of the material measured in [2] of same type used as the longpass PMMA filter of this work.
The emission spectra of RPT acrylic are shown in the top panel of figure 3. We detect visible fluorescence light from the sample well above the noise level of the spectrometer between approximately 370 nm and 450 nm, and at a lower level over 450 nm to 600 nm. On the shorter-wavelength side, the structure may be cut off by the longpass filter. The intensity of the emission feature increases as the temperature decreases, particularly in the main emission peak around 400 nm. A dedicated room-temperature measurement was carried out with and without the acrylic sample which confirmed that the fluorescence originates from the sample, as opposed to other components of the setup.

Fluorescence in response to 222 nm UV light from a KrCl excilamp has been reported in acrylic samples previously [9]. The spectrum measured by [9] is shown in the bottom panel of figure 3, and its main feature around 490 nm does not appear in the spectra from RPT measured in this work. The shape of the transmittance of our longpass filter is also shown in the bottom panel of figure 3. As it is relatively flat above 400 nm, it can not explain the discrepancy between our curve and that in [9].

4 Conclusion

We measured the temperature-dependent emission spectra of TPB and RPT acrylic excited with 280 nm light. As seen in figure 2, the TPB spectra are consistent with previous results at higher temperatures [7], showing more clearly the vibrational structures at decreasing temperatures. The fluorescence emission spectrum of this batch of acrylic at low temperatures was measured for the first time, and its intensity increased as temperature decreased. This effect could be due to the decrease of non-radiative transitions at low temperatures, or decrease of quenching of fluorescence [8, section 3.2.3].

On the usage of acrylic in a detector for rare-events, this fluorescence can shift UV Cherenkov light produced in acrylic to the visible range. Since the UV part of the Cherenkov spectrum is not otherwise transmitted through the acrylic to be detected by the light sensors, this wavelength-shifting response must be included in detector Monte-Carlo simulations to accurately model the detector and expected backgrounds.

Comparing the fluorescence spectra we measure to previously measured PMMA under UV excitation [9], we see some consistency, but the dominant emission peak occurs at different wavelength ranges. This is an indication that the fluorescence is dependent on the batch of acrylic.

In future work, we will quantify the fluorescence of acrylic relative to TPB and study its time structure, by using a photomultiplier tube in place of a spectrometer. The systematics of our setup will be investigated thoroughly, in order to allow us to quantify both the change in intensity of TPB for decreasing temperatures, and the wavelength shifting efficiency (WLSE) of acrylic relative to TPB. We also plan to measure the fluorescence response of PTFE, as well as the response of both acrylic and PTFE at cryogenic temperatures and under excitation with photons down to 130 nm.

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