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Ultraviolet-induced fluorescence of poly(methyl methacrylate) compared to 1,1,4,4-tetraphenyl-1,3-butadiene down to 4 K

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Abstract

Several particle-physics experiments use poly(methyl methacrylate) (a.k.a. PMMA or acrylic) vessels to contain liquid scintillators. Superluminal charged particles emitted from radioactive impurities in or near the acrylic can emit Cherenkov radiation in the ultraviolet (UV) spectra range. If acrylic fluoresces in the visible range due to this UV light, it could be a source of background in experiments where the main signal is visible scintillation light, or UV scintillation light that is absorbed and re-emitted at visible wavelengths by a wavelength shifter. Some of these experiments operate at low temperature. The fluorescence of these materials could change with temperature so we have studied the fluorescence of the acrylic used in the DEAP-3600 experiment down to a temperature of 4 K, and compared it to the common wavelength shifter 1,1,4,4-tetraphenyl-1,3-butadiene (TPB). The light yield and wavelength spectra of these materials were characterized by exciting the sample with 285 nm UV light which acted as a proxy for Cherenkov light in the detector. Spectral measurements indicate at least part of the fluorescence of the acrylic is due to additives. Time-resolved measurements show the light yields of our acrylic sample, TPB sample, and the relative light between both samples, all increase when cooling down. At room temperature, the light yield of our acrylic sample relative to the TPB sample is 0.3 %, while it reaches 0.5 % at 4 K. The main fluorescence time constant of the acrylic is less than a few nanoseconds.

Keywords: fluorescence, wavelength shifter, light yield, poly(methyl methacrylate), acrylic, 1,1,4,4-tetraphenyl-1,3-butadiene

1. Introduction

Liquid scintillators are used as the detection medium by current and planned particle physics detectors for rare event searches like neutrino and dark matter experiments, such as MicroBooNE [1], Daya Bay [2], DarkSide [3], and SNO+ [4]. Acrylic, which is composed of poly(methyl methacrylate) (PMMA) possibly with trace amounts of additives, is a popular structural material because it is optically transparent and radio-pure. The DEAP-3600 [5] dark matter experiment uses liquid argon (LAr) as the scintillator in a vessel made of acrylic. The inside of the vessel is coated with 1,1,4,4-tetraphenyl-1,3-butadiene (TPB), a wavelength shifter, which converts 128 nm ultraviolet (UV) LAr scintillation to visible light that better matches the quantum efficiency of the standard photomultiplier tubes (PMTs) used. However, UV scintillation light may reach the acrylic in uncoated areas. In addition, fast charged particles can produce Cherenkov UV light within, or entering, the acrylic. For both these mechanisms, the AVA absorbs UV light and prevents it from reaching the PMTs. However, UV-induced fluorescence has been observed in certain types of acrylic [6]; this could contribute to the background in very sensitive rare-event searches.

The wavelength shifting properties of TPB have been investigated previously. Upon UV irradiation, a sample of TPB will emit visible (~ 420 nm) fluorescence corresponding to the \sim nanosecond de-excitation of occupied singlet states [7]. It is possible to evaporate TPB onto glass substrates [8], reflectors [9], and the inside of large acrylic vessels [5]. Features of the re-emission peaks and quantum yield can be manipulated by changing various parameters of the sample such as the thickness [10], incident wavelength [10] and sample age [11]. At ~ 10 K, the light yield of TPB is 1.3 ± 0.1 times higher than at room temperature [12]. While studies of TPB at vacuum ultraviolet (VUV) wavelengths like 128 nm are rare, longer-wavelength UV irradiation experiments can provide a basis for extrapolation to the VUV spectrum [13].

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37 Investigations of acrylic luminescent properties have been previously carried out [14, 15]. These are not
38 necessarily representative of all types of acrylic, since impurities, additives, defects, and the surface finish of
39 the material potentially contribute to the luminescence signal. Fluorescence and optical properties of acrylic
40 were measured under visible laser light excitation [14]. Additionally, the luminescence of laser-etched acrylic
41 chips was found to increase compared to a bulk sample of acrylic [15]. Both samples exhibited re-emission at
42 a wavelength of approximately 625 nm. Luminescence of nominally pure PMMA was studied in the context
43 of embedded metallic clusters [16], showing a broad spectrum around 440 nm when excited at 355 nm. In
44 addition, the luminescence of acrylic was studied under excitation with an electron beam and ~ 222 nm UV
45 light [6]. Samples that are 6 and 10 mm thick show a broad band at ~ 490 nm. The 3 mm thick sample showed
46 an additional band at 400 nm and the absorption spectrum was shifted from 300 nm to 350 nm, which can be
47 explained by the presence of impurities [6].

48 Moreover, investigations were done with acrylic from the same batch that was used for the DEAP-3600
49 vessel, referred to as AVA for this study. At room temperature, the AVA time-resolved response was measured
50 under UV excitations ranging from 130 nm to 250 nm [17], which showed that the fluorescence of the AVA
51 sample was at most 0.2% relative to TPB. In addition, our group has previously measured the AVA and TPB
52 fluorescence spectra under 280 nm excitation in the 300 K to 4 K temperature range [18] with samples which will
53 be referred to as AVA3 and TPB3. Fluorescence was clearly visible around 400 nm, and there was a qualitative
54 increase in the light yield during cooling of the sample. In this work, we investigate fluorescence of a newer set
55 of AVA and TPB samples that are referred to as AVA1 and TPB1. The samples used in the spectrometer, AVA2
56 and TPB2, are identical samples to AVA1 and TPB1 used for the time-resolved measurements. We quantify the
57 time-resolved light yield of the AVA1 and TPB1 samples over a range of temperatures, including 87 K and 4 K,
58 the boiling points of argon and helium. Compared to earlier work [18], we have reduced systematic uncertainties
59 related to the stability of the excitation, which should improve the precision of our light yield measurements.

60 2. Sample and Equipment Details

61 The purpose of this experiment was to measure how the relative light yield of the AVA compared to TPB
62 changes with temperature under 285 nm UV excitation. The measurements were done in a closed-cycle optical
63 cryostat at the following temperatures: 300, 292, 273, 250, 210, 163, 120, 100, 87, 77, 50, 27, 15, 10, 8, 6, 5 and
64 4 K. The cryostat has a compact geometry that optimizes the light collection efficiency [19]. The general setup
65 of the experiment is illustrated in Figure 1.

66 The samples used for our main study were designed to be attached directly to the cryostat coldfinger and
67 fit within the cryostat. They are rectangular parallelepipeds, with a thickness in the optical direction of 5 mm,
68 and width and height of 24×30 mm², and with tabs for fixing to the coldfinger (see Fig. 2 of Ref. [20]). Both of
69 the samples used were made from acrylic specifically using the same batch manufactured by Reynolds Polymer
70 Technologies that was used in building the acrylic sphere for DEAP-3600. The faces of the samples were finished
71 to rough sanded quality. One of the samples was coated on one face with 1 μ m of TPB, the WLS coating that
72 is on the inner surface of DEAP-3600, using thermal vacuum evaporation.

73 The setup consists of a ~ 10 ns FWHM pulse of 285 nm UV light from an LED which passes through
74 a shutter and the windows of each of the three layers of the cryostat into the main chamber. A function
75 generator is used to trigger the Kapustinsky [21] circuit producing the short pulse fed to the LED, and the
76 same generator pulse acts as the trigger for the data acquisition (DAQ). The light interacts with the sample
77 producing fluorescent light at longer wavelengths than the initial 285 nm UV LED light. This light then passes
78 through a broad bandpass filter with a lower limit of 375 nm which is intended to eliminate any stray UV light
79 from the LED. For the time-resolved measurements, this light is then detected by a Hamamatsu R6095-100
80 PMT with a super bialkali photocathode to look at the fluorescence pulses and determine the light yield. For
81 the spectrometer measurements, the Horiba spectrometer replaces the PMT in the setup, the broad bandpass
82 filter is removed and the LED is run in DC mode so it is on continuously. This setup is intended to show
83 wavelength dependent features of the samples' fluorescence spectra. Spectra were taken before instabilities in
84 the LED were resolved, meaning that though the shapes of the spectra can be compared, it is more difficult for
85 their intensities. Instabilities were resolved for the time-resolved measurements, as described in a more complete
86 explanation of the system [20].

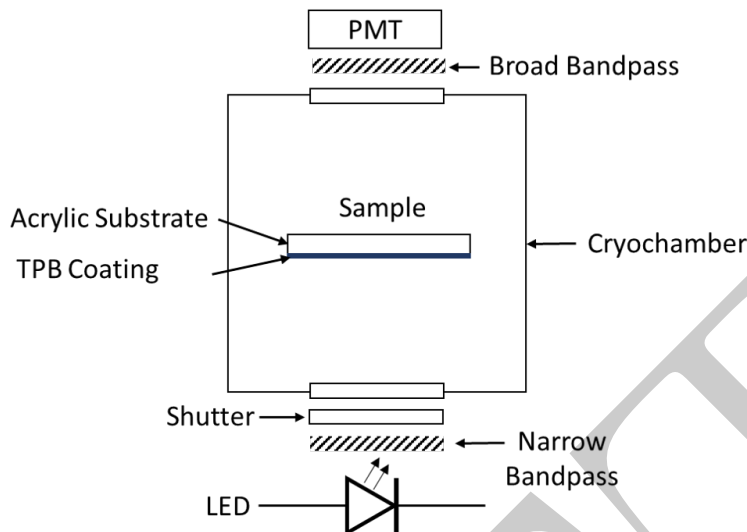


Figure 1: Optical cryostat sample setup for time-resolved measurements of the sample fluorescence light.

87 For the time-resolved measurements, the PMT output is fed into one of the digitizer channels of the DAQ
 88 system and it is triggered by the function generator pulse which also controls the LED pulsing. The DAQ setup
 89 consists of a digitizer controlled by a program where all of the relevant parameters can be set. A single event
 90 consists of 12 μs long waveform made up of 30000 digitizer samples with 0.4 ns between each sample. The first
 91 10% of the waveform is the pretrigger. A full data set at a single temperature is 45000 of these events. The
 92 time-resolved measurements for the AVA1 acrylic were taken with a ± 0.1 V vertical range on the digitizer since
 93 the majority of the waveforms show single photoelectron response with small amplitudes. Meanwhile, the more
 94 fluorescent TPB1 sample waveforms were measured with a ± 2.5 V vertical range to capture the entire waveform
 95 without saturation. Lastly, for the spectrometer measurements, the signal is read out in the computer by a
 96 program specific to the spectrometer for a 10 s exposure.

97 In addition to the main samples described above, for comparison, the spectra of three other samples were
 98 measured at room temperature only in a Photon Technology International (PTI) QuantaMaster fluorescence
 99 spectrometer. These samples were taken from the acrylic used in the light-guides found in DEAP (DEAP-LG),
 100 the DEAP acrylic vessel (AVA4), and the SNO acrylic vessel (SNO-AV). The samples can be differentiated by
 101 their manufacturer and the additives used to change the optical properties of the respective acrylic samples. The
 102 ultraviolet absorbing (UVA) acrylic used in the light guides of the DEAP experiment was supplied by Sparteck,
 103 and the ultraviolet transmitting (UVT) acrylic was used in SNO-AV. Though the setups and geometries differ,
 104 it should be possible to compare the shapes of the spectra with our main measurements.

105 3. Analysis

106 3.1. Analyzing Time-Resolved Fluorescent Light Pulses

107 At each temperature, the 45000 recorded waveforms are analyzed separately in order to determine the
 108 mean light yield from the sample. There are two initial steps to processing the individual pulse data: baseline
 109 subtraction and noise subtraction. First, the baseline is taken from the average of the first 6% of the individual
 110 waveform so subtracting the data from this baseline produces waveforms with a new baseline around zero. The
 111 next step is to address the noise in the waveforms. Oscillations around the baseline are observed in the PMT
 112 readout from the LED pulses in addition to regular electronic noise. These fluctuations begin in the pretrigger
 113 area and overlay on the light pulse in the integration window. To understand this noise, dedicated noise runs
 114 are taken at select temperatures by following the same data taking procedure as the pulsed LED data runs
 115 except that the shutter between LED and the cryochamber is closed so that no LED light reaches the sample
 116 or PMT. Fig. 2 shows the average noise-only event. The noise has the same time structure in all events, and
 117 can be subtracted from the individual pulses.

118 Fig. 3 shows example of individual waveforms from AVA1 and TPB1 after baseline and noise were subtracted.
 119 The next step in the analysis is to integrate the pulses over a 50 ns window as illustrated. This window is set
 120 to limit the amount of remaining noise while still containing almost all of the fluorescent light from the sample
 121 (also see average pulse shapes in Fig. 7). The distribution of these integrals is then used to determine the light
 122 yield, as discussed in the next section. The integral values of the noise fluctuations are centered on zero, and
 123 are negligible compared to those of a single photoelectron (Fig. 4).

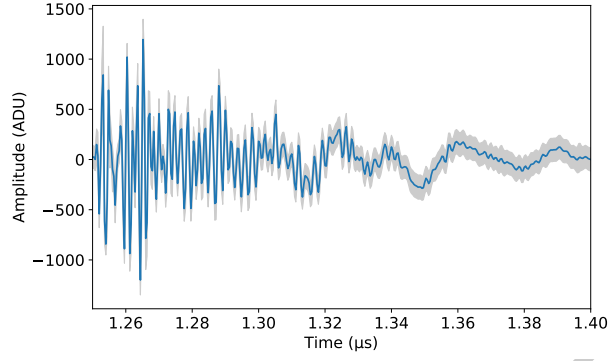


Figure 2: Average signal from all events in a noise run. The grey region is the standard deviation of the distribution of amplitudes at each sample for the 45000 events in the run.

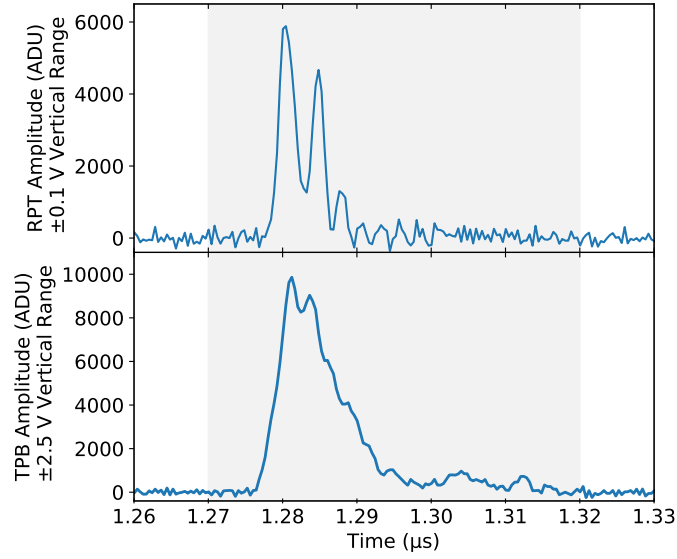


Figure 3: Examples of individual pulses from the AVA1 and TPB1 samples which are both baseline and noise subtracted. The AVA1 pulse (top) was taken with a ± 0.1 V DAQ vertical range to see more detail on a small pulse while the TPB1 data was taken with a ± 2.5 V vertical range. Shaded area is the integration region.

124 3.2. Calculating Light Yield

125 The distribution of pulse integrals obtained in the previous section are used to determine the light yield.
 126 Acrylic is expected to have little to no fluorescence. Despite having increased the LED intensity for AVA1
 127 compared to TPB1, the PMT records at most a few photoelectrons per trigger. The integral distribution from
 128 these single-photoelectron (SPE) pulses can be fit with a model of the PMT response [22], as seen in Fig. 4.
 129 The model accounts for the distribution of the number of photoelectrons and provides the average number of
 130 photoelectrons and the average single-photoelectron integral.

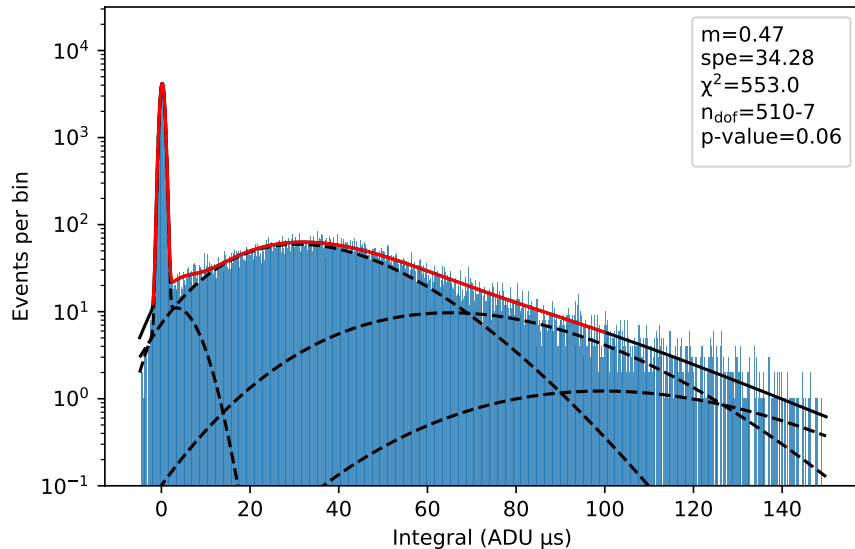


Figure 4: Integral distribution of AVA1 luminescence at 300 K. Red curve is overall fit to model in fit range, solid black is overall model outside of fit range, dashed black curves are individual model components. Parameter m is the average number of photoelectrons per pulse; spe is the average integral of a single photoelectron. The p-value is the probability of obtaining a larger χ^2 by statistical fluctuations if the model is correct. In addition to providing the light yield for the acrylic samples (m), analyses of this type applied to acrylic or TPB provide the conversion factor from integrals to photoelectrons for the TPB samples (spe).

131 In general, TPB is expected to produce much more fluorescent light than acrylic so it is impractical to use
 132 the previous model to obtain the light yield. Instead, the integral distribution is fit with a skew normal; the
 133 mean of that fit is then divided by the average SPE integral determined on the appropriate vertical range to
 134 compute the light yield. To avoid saturation while maximizing light output, all of the TPB1 data were taken
 135 with the same LED voltage of 13.4 V at all temperatures. The AVA1 data were taken at a higher LED voltage
 136 of 13.7 V to ensure that enough light was produced to observe at least a single-photoelectron response. To
 137 compare the light yields of both materials, the data must be taken with the same excitation intensity (i.e. LED
 138 voltage) at a given temperature. Alternatively, when working with different excitations for each material as in
 139 our case, a correction factor, which is the ratio of light yields of one of the materials under both excitations,
 140 must be determined. [Appendix A](#) details the correction process.

141 4. Results

142 4.1. Emission Spectra

143 The spectra of two samples, AVA2 and TPB2, were taken using the optical cryostat setup and the spec-
 144 trometer described in [20] with a 10 s exposure and 285 nm excitation. The samples used for the spectrometer
 145 measurements, AVA2, and TPB2, are made with the same materials, geometry, and have identical properties
 146 to AVA1 and TPB1 respectively, which were used in the time-resolved measurements. The spectra observed for
 147 the TPB2 and AVA2 samples depend on the properties of the physical sample like the thickness of the acrylic
 148 sample, the surface finish, and the thickness of the TPB coating.

149 Figure 5 shows the spectra of the TPB2 sample at 300 K, 87 K and 4 K. It is apparent from the spectra
 150 that as the temperature decreases, the overall integral under these spectral curves, and therefore the light yield,
 151 increase. In addition, at 300 K there is a single major peak in the spectrum at 425 nm. Heat in the sample
 152 allows for the TPB molecules to vibrate, which causes the re-emitted photon to be observed with a Doppler shift
 153 related to the temperature of the sample. This Doppler shift causes the luminescent spectral lines to expand,
 154 a process known as thermal broadening [23]. As the temperature diminishes, so does the effect of thermal
 155 broadening, and the most prominent peak appears to shift closer to 427 nm. A second peak corresponding to
 156 an energy sublevel becomes more prominent at 403 nm, while a third appears around 455 nm.

157 The AVA2 spectrum exhibits a broad main peak around 395 nm, which shifts to slightly longer wavelengths
 158 with increasing temperature, possibly cut at lower wavelengths by the broad bandpass filter or self-absorption.
 159 At 4 K, small peaks are observed near 475, 505 and 545 nm. A similar triple peak structure coming from low-
 160 temperature phosphorescence is typical for hydroxyphenyl benzotriazoles [24, 25], some of which are compounds
 161 commonly added to polymers to mitigate their degradation by absorbing UVs [26, 27, 28].

162 In addition, Fig. 5 shows the quantum efficiency of the PMT and the transmission of the broad bandpass
 163 filters used in the time-resolved measurements of TPB1 and AVA1 (Sec. 4.3 and 4.4). Neither of those com-
 164 ponents is present in the spectrometer measurements. The inclusion of these curves illustrates how the light

165 yield of the time-resolved measurements could be affected by different efficiencies and transmissions depending
 166 on how the spectrum changed with temperature.

167 Figure 6 consists of subplots to compare the spectra from this study to previous measurements and literature.
 168 Fig. 6(a) and (b) show that our TPB2 re-emission spectra are consistent with previous work under UV excitation
 169 which was done by our group with the TPB3 sample [18], and by other groups at various temperatures with
 170 samples of a different origin [12]. At room temperature (Fig. 6(c)), our AVA2 spectra are consistent with
 171 our previous measurements of material from the same batch (AVA3) [18]. They are also consistent with the
 172 spectrum of another sample of the same AVA acrylic from the DEAP-3600 vessel (AVA4), the acrylic used for
 173 the light guides in DEAP-3600 (DEAP LG), and with the spectrum of the acrylic used for the SNO/SNO+
 174 vessel (SNO AV), both excited at 280 nm (Fig. 6(d)). Elsewhere, nominally pure PMMA excited at 355 nm
 175 shows a broad spectrum shifted up to 440 nm [16]. Similar spectra, with some dependence on the excitation
 176 wavelength, have been reported for pure copolymers of methyl methacrylate and acrylic acid [29]. Our spectra
 177 (Fig. 6(c)) differ from those reported by [6] for acrylic samples excited using an electron beam and a KrCl
 178 excilamp. This could be due to differences in the excitation source, or the creation of colour centers [30,
 179 31], or properties of the material itself such as the nature of additives and impurities. To the best of our
 180 knowledge, the impurities mainly investigated in DEAP-type acrylic are radioactive ones from the uranium
 181 and thorium chains [32]. In our data (Fig. 6(e)), at lower temperatures, when the longer-wavelength peaks are
 182 most visible for the AVA2 sample, the wavelengths of those peaks are similar to the position of the spectral
 183 peaks of several compounds from the hydroxyphenyl benzotriazol (HBzT) class [24], including 2-(2-hydroxy-
 184 5-methylphenyl)benzotriazole (Tinuvin P), which can serve as a representative example [25]. This suggests
 185 that if a similar compound is an additive in the AV acrylic, it could account for part of the luminescence
 186 observed in the sample. However, the room-temperature similarity with the DEAP-LG and SNO-AV samples
 187 implies there is some intrinsic photoluminescent mechanism as well, or a common photoluminescent additive.
 188 Indeed, low-temperature fluorescence has been observed for certain HBzT compounds at ~ 395 nm [24, 26].
 189 The overall spectral behavior can be explained as follows: at room temperature, the PMMA dominates, with a
 190 broad, asymmetric peak around 410 nm. As the sample is cooled, the additives come into play, augmenting the
 191 short-wavelength structure and pushing it to slightly shorter wavelengths, and contributing the long wavelength
 192 features.

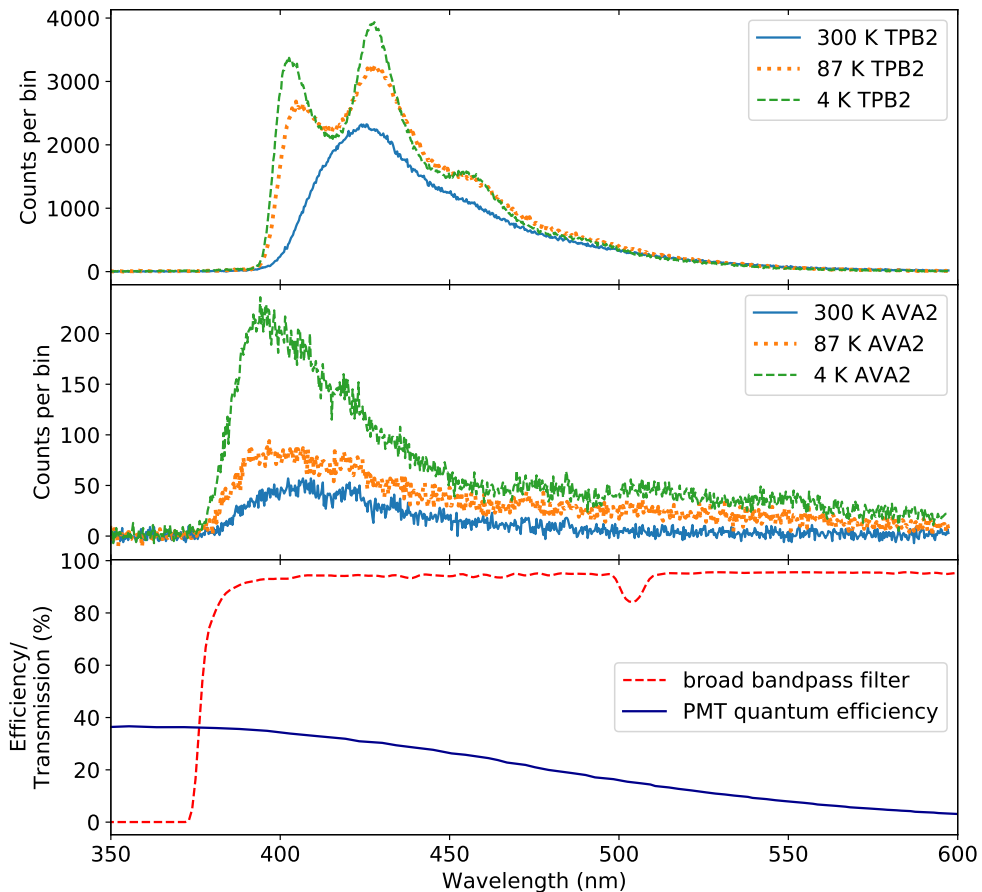


Figure 5: Wavelength spectra of TPB2 (top) and AVA2 acrylic (middle) luminescence at different temperatures. See text for details. The bottom plot shows the quantum efficiency of the PMT used in the time-resolved measurements and the broad bandpass filter that was present only for the time-resolved measurements.

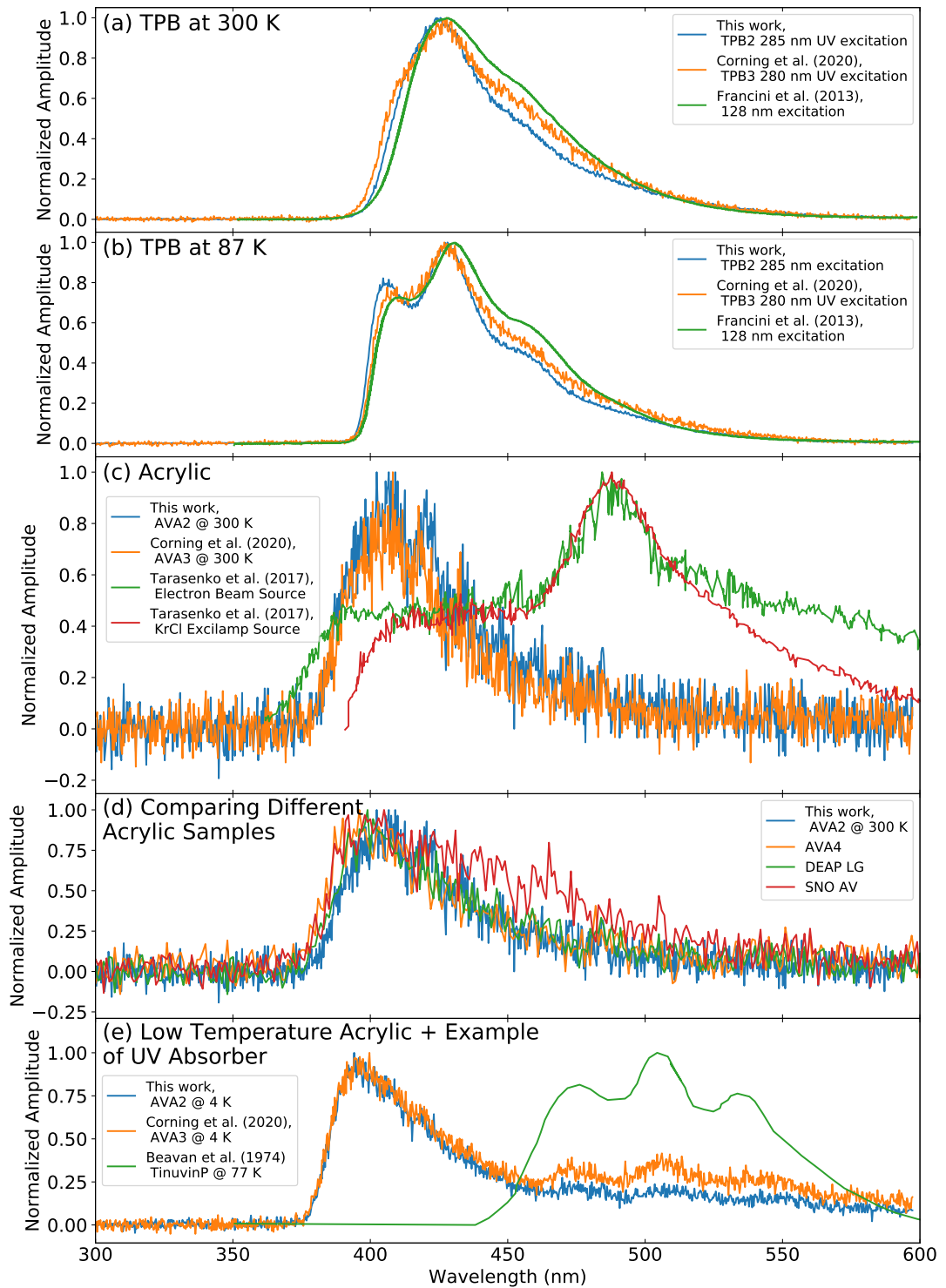


Figure 6: Comparing wavelength spectra from this work to spectra from literature or previous measurements. (a) spectra of TPB taken at 300 K. (b) spectra of TPB at 87 K. (c) spectra of acrylic at around 300 K. (d) comparing spectrometer measurements of different acrylic samples; the blue and orange curves are data from the spectrometer for this study. (e) sample of Tinuvin P with EP glass excited at 380 nm, as an example of a compound from the hydroxyphenyl benzotriazole class, which shares similar spectral features.

193 *4.2. Normalized Pulse Shapes*

194 To investigate the time structure of the TPB1 and AVA1 fluorescence pulses, in addition to the response
 195 with the samples in place, it is important to know the instrument response. For this, we took data using the
 196 same setup but with neither sample nor broad bandpass filter. The filter was removed because the LED emits
 197 light at 285 nm, and the broad bandpass has a lower wavelength limit of 375 nm, so it should block most of
 198 the light from the LED. The LED, AVA1 and TPB1 all produce different amounts of light in the detector so
 199 average pulses were normalized to unit area.

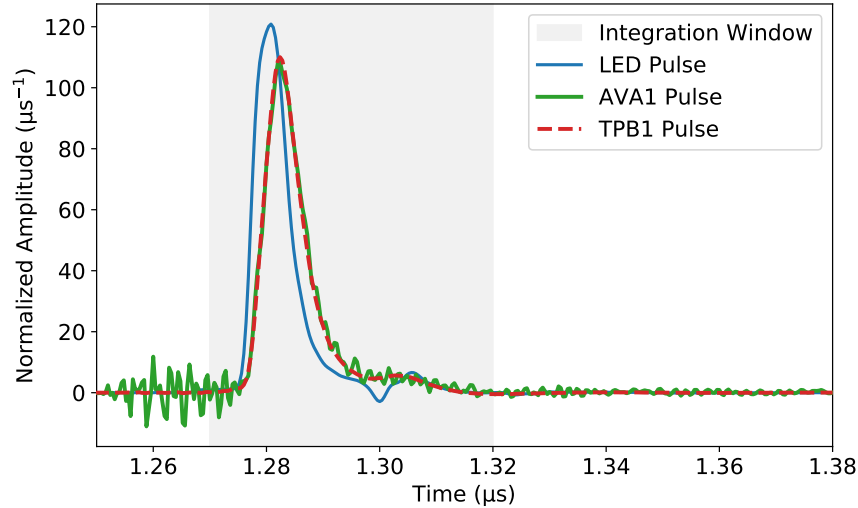


Figure 7: Average pulses from the LED directly shining light onto the PMT and from the AVA1 and TPB1 fluorescent light at 300 K. The shaded region indicates the 50 ns integration region used to calculate the light yield for AVA1 and TPB1. The response of the AVA1 and TPB1 are similar to within the noise.

200 Fig. 7 shows the comparison of the average pulses for the LED, AVA1, and TPB1 at 300 K, normalized to
 201 unit area. The shaded region indicates the 50 ns integration region that is used for the light yield analysis to
 202 help visualize where the integration window is relative to the fluorescence pulses. The TPB1 and AVA1 pulse
 203 shapes look identical to within the noise, and are similar to that of the LED. This suggests that the pulse shape
 204 observed for both samples is dominated by the instrument response, which is a combination of the LED pulse
 205 shape, the time response of the PMT and readout electronics. It also suggests that the main time constants of
 206 TPB1 and AVA1 are shorter than a few nanoseconds. This is consistent with observation of a \sim ns response
 207 of acrylic under excitation by a subnanosecond electron beam [33]. Spectral information (Sec. 4.1) suggests the
 208 presence of UV-absorber, possibly from the HBzT class, in the AVA. For such compounds, fluorescence and
 209 phosphorescence has been reported at low temperatures, the latter with a time constant of \sim 1 s [24, 26]. Our
 210 spectrum implies the amount of phosphorescence light is less than or equal to the amount of fluorescence light.
 211 The latter is less than a photoelectron per event on average in our time-resolved measurements (Sec. 4.4). As
 212 the phosphorescence photoelectrons are spread out over nearly a second, they would be masked by the few
 213 hundred Hertz of dark counts in our PMT, making phosphorescence unobservable in our pulse shape.

214 *4.3. TPB Light Yield*

215 As explained in Sec. 3.1, to determine the light yield, individual waveforms are integrated. The integral
 216 distribution was fit with a skew normal function and the mean and error on the mean are used in the calculation
 217 of the light yield. Fig. 8 shows the integral distribution of TPB1 events at multiple temperatures in the number
 218 of photoelectrons. The systematic uncertainty for the TPB light yield was found to be 0.56 photoelectrons
 219 stemming from the choice of integration window.

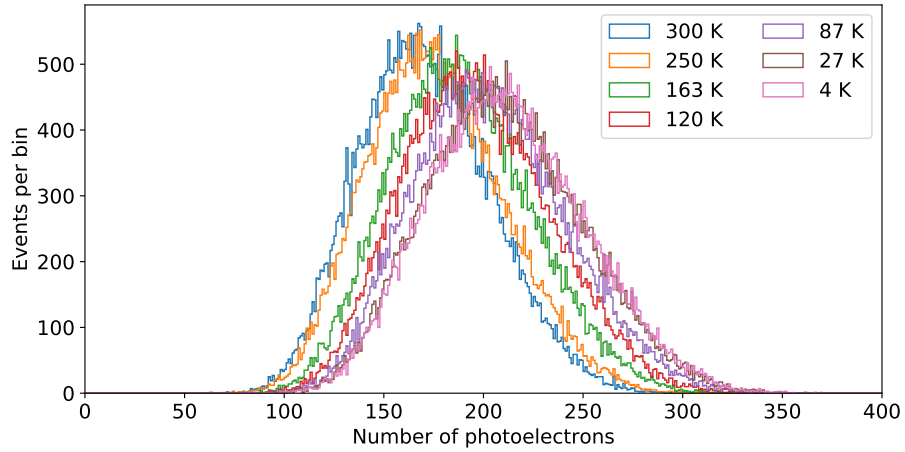


Figure 8: Integral distributions of TPB1 luminescence in terms of the number of photoelectrons at different temperatures

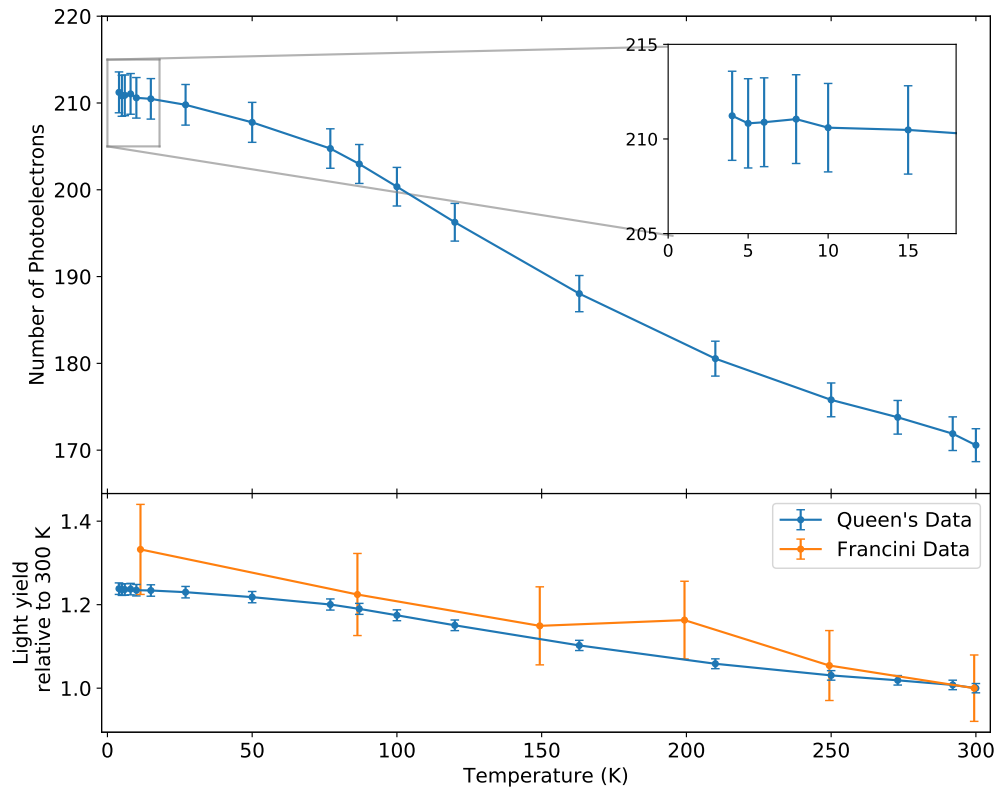


Figure 9: Top: TPB1 detected light yield as a function of temperature given in terms of the number of photoelectrons. Bottom: TPB1 detected light yield normalized to 300 K compared to results from Francini [12] also normalized to 300 K. Evolution is consistent within errors.

220 Fig. 9 shows that as the temperature decreases the light yield of the TPB1 sample increases. At 87 K there
 221 is a 19.0% increase in light yield compared to 300 K, while at 4 K, the light yield has increased by 23.8%
 222 relative to 300 K. These numbers are consistent within errors with previous characterizations of TPB down to
 223 low temperatures [12], and specifically at 87 K [9].

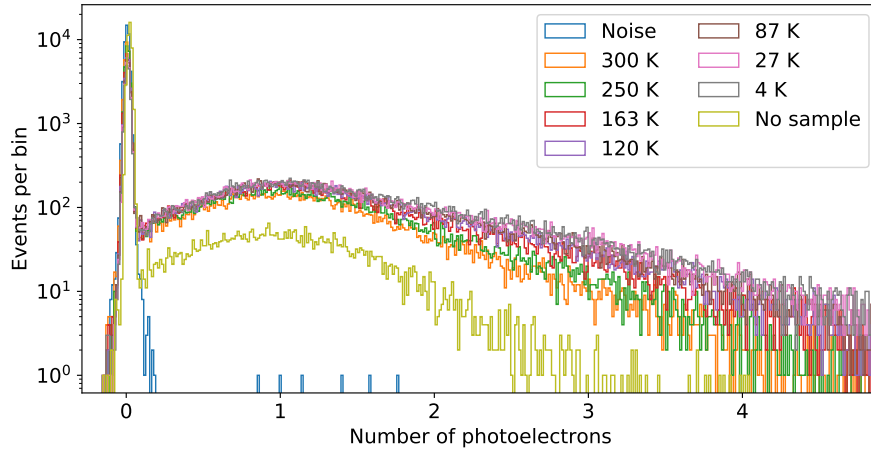


Figure 10: Integral distributions of AVA1 luminescence at different temperatures. The integral distribution for a noise run and a run when there was no sample in the detector are also shown. The no-sample run averages less than a quarter of the photoelectrons per event than the runs with a sample (see text for details).

225 Fig. 10 shows the distribution of event integrals from the AVA1 sample at various temperatures. The
 226 numbers of photoelectrons are quite low, so it is important to confirm that they come from fluorescence of the
 227 sample and are not some form of background. Fig. 10 also includes data taken with no sample. Photoelectrons
 228 are observed, but at a significantly lower level (0.120 ± 0.004 SPE/evt) than the lowest level when the sample
 229 is present (0.465 ± 0.007 SPE/evt). This low background may come from residual LED light making it through
 230 the various filters, or possibly from fluorescence of cryostat material such as low-level fluorescence of glasses and
 231 filters. Regardless of the origin of the light, this no-sample measurement probably overestimates the amount of
 232 background light when the sample is in place, since in the no-sample measurement the LED has a direct line of
 233 sight to the PMT, whereas the sample may act as a baffle. For this reason, we consider the measured light the
 234 actual fluorescence of the sample, as opposed to an upper limit on it. Note that if we integrate all noise events
 235 in the same 50 ns window as the LED pulse data, we get a zero-centred distribution, known as the pedestal,
 236 also shown on Fig. 10, and much narrower than the SPE integrals.

237 From the distributions of photoelectrons at each temperature in Fig. 10, we obtain the evolution of the light
 238 yield as a function of temperature in Fig. 11. The trend is similar to TPB1 as the light yield increases with
 239 decreasing temperature. The overall fluorescence light yield of AVA1 is quite low; at most temperatures less
 240 than 1 photoelectron was observed on average per event. Relative to the light yield at 300 K, at 87 K the light
 241 yield increased by $\sim 85\%$ while at 4 K it had increased by $\sim 120\%$. The systematic error on the light yield was
 242 calculated by the same method used in the analysis of the TPB1 sample, i.e. looking at different integration
 243 windows, and was set to 0.04 SPE for these measurements.

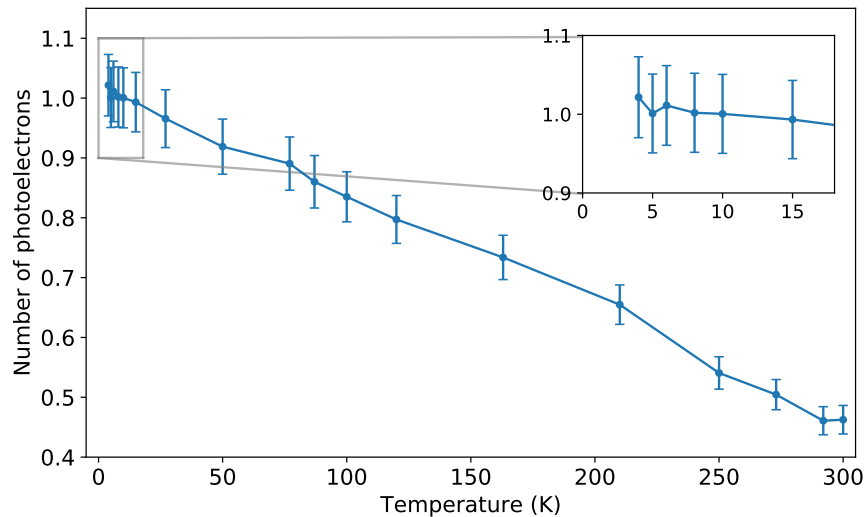


Figure 11: AVA1 detected light yield vs temperature

244 It is possible to calculate a relative light yield between AVA1 and TPB1 by applying corrections for the LED
 245 voltage (Sec. 3.2 and Appendix A), and accounting for the differing vertical ranges used on the digitizer. Fig. 12
 246 shows this relative light yield at different temperatures. The relative light yield varies from approximately 0.3%
 247 at 300 K to 0.5% at 4 K. A previously published work, with similar samples, but different excitation wavelengths
 248 and methods, sets an upper limit of 0.2% at 300 K [17]. It also shows the response depends on various factors,
 249 including the excitation wavelength in particular.

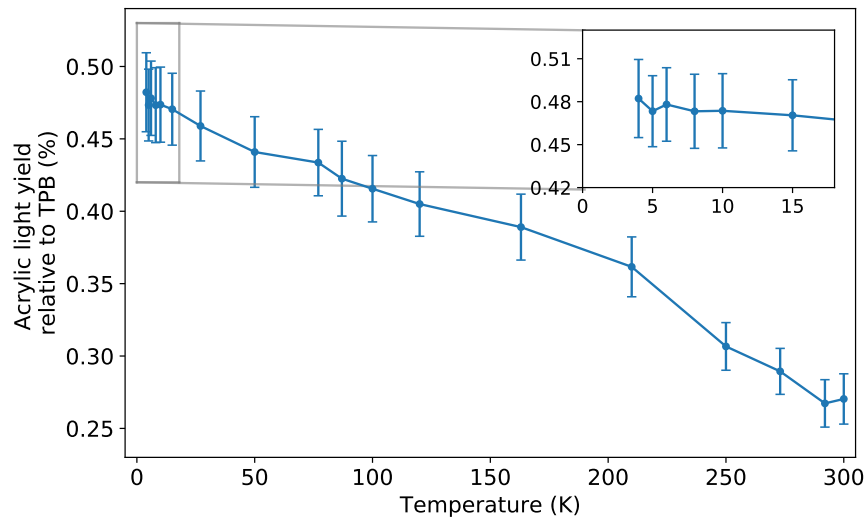


Figure 12: AVA1 light yield relative to TPB1 vs. temperature

250 5. Conclusion

251 We studied the fluorescence of acrylic and TPB-coated acrylic samples in a cryostat using an excitation
 252 wavelength of 285 nm. The fluorescence spectra and pulseshapes were obtained in a range of temperatures
 253 from 300 K down to 4 K. The TPB spectra are consistent with previous work [12, 18] and well-resolved at
 254 low temperatures, where an increased light yield and reduced thermal broadening reveal substructure including
 255 peaks at ~ 400 nm and ~ 425 nm. The acrylic spectra show one main peak with a maximum at ~ 395 nm
 256 and additional longer-wavelength features at low temperatures. The long-wavelength features are attributed
 257 to phosphorescence of UV-absorber in the acrylic. Short-wavelength similarities between spectra of different
 258 acrylic samples suggest that in addition to the contribution from additives, part of the fluorescence is related
 259 to the acrylic itself, though we can't exclude that an additive common to all the samples plays a role.

260 The light yields of both acrylic and TPB increase as the temperature falls. The TPB light yield shows a
 261 similar evolution with temperature as reported in [12]. The light yield of acrylic relative to TPB also increases

262 with decreasing sample temperature up to a maximum of 0.5%. At 300 K the acrylic relative light yield reaches
263 0.3%. This is close to the 0.2% reported in earlier work [17] despite that work using a shorter excitation
264 wavelength and different samples in a completely different experimental setup. The dominant time constants
265 of acrylic and TPB are shorter than the ~ 10 ns instrument response.

266 Understanding the fluorescence of acrylic is important for rare-event searches using that material as a detector
267 component because it can contribute to the background, for instance when superluminal charged particles emit
268 Cherenkov light in the acrylic. As impurities and additives may contribute to the fluorescence, a good knowledge
269 of the fluorescence properties of the specific acrylic used in a given experiment is therefore needed to account
270 for these background events.

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279 References

- 280 [1] MicroBooNE Collaboration, [Design and Construction of the MicroBooNE Detector](#), J. Instrum. 12 (02)
281 (2017) P02017–P02017, arXiv: 1612.05824. doi:10.1088/1748-0221/12/02/P02017.
282 URL <http://arxiv.org/abs/1612.05824>
- 283 [2] M. Krohn, B. R. Littlejohn, K. M. Heeger, [Long-Term Testing and Properties of Acrylic for the Daya
284 Bay Antineutrino Detectors](#), J. Instrum. 7 (08) (2012) T08001–T08001, arXiv: 1206.1944. doi:10.1088/
285 1748-0221/7/08/T08001.
286 URL <http://arxiv.org/abs/1206.1944>
- 287 [3] DarkSide-20k Collaboration, [DarkSide-20k: A 20 Tonne Two-Phase LAr TPC for Direct Dark Matter
288 Detection at LNGS](#), Eur. Phys. J. ArXiv: 1707.08145 (Jul. 2017). doi:10.1140/epjp/i2018-11973-4.
289 URL <http://arxiv.org/abs/1707.08145>
- 290 [4] SNO+ Collaboration, [Current Status and Future Prospects of the SNO+ Experiment](#), Adv. High Energy
291 Phys. 2016 (2016) 6194250, publisher: Hindawi Publishing Corporation. doi:10.1155/2016/6194250.
292 URL <https://doi.org/10.1155/2016/6194250>
- 293 [5] DEAP Collaboration, [Design and construction of the DEAP-3600 dark matter detector](#), Astropart. Phys.
294 108 (2019) 1 – 4.
- 295 [6] V. Tarasenko, et al., [Luminescence of polymethyl methacrylate excited by runaway electron beam and by
296 a KrCl excilamp](#), IEEE Trans. Plasma Sci. 45 (1) (2017) 76 – 84.
- 297 [7] J. M. Flournoy, et al., [Substituted tetraphenylbutadienes as fast scintillator solutes](#), Nucl. Instr. Meth. A
298 351 (2) (1994) 349–358. doi:10.1016/0168-9002(94)91363-3.
299 URL <https://www.sciencedirect.com/science/article/pii/0168900294913633>
- 300 [8] W. M. Burton, B. A. Powell, [Fluorescence of Tetraphenyl-Butadiene in the Vacuum Ultraviolet](#), Appl. Opt.
301 12 (1) (1973) 87–89. doi:10.1364/AO.12.000087.
302 URL <https://www-osapublishing-org.proxy.queensu.ca/ao/abstract.cfm?uri=ao-12-1-87>
- 303 [9] G. R. Araujo, et al., [R&D of Wavelength-Shifting Reflectors and Characterization of the Quantum Effi-
304 ciency of Tetraphenyl Butadiene and Polyethylene Naphthalate in Liquid Argon](#), Eur. Phys. J. C ArXiv:
305 2112.06675 (Dec. 2021).
306 URL <http://arxiv.org/abs/2112.06675>
- 307 [10] V. M. Gehman, et al., [Fluorescence efficiency and visible re-emission spectrum of tetraphenyl butadiene
308 films at extreme ultraviolet wavelengths](#), Nucl. Instr. Meth. A 654 (1) (2011) 116–121. doi:10.1016/j.
309 nima.2011.06.088.
310 URL <https://www.sciencedirect.com/science/article/pii/S0168900211013271>

- 311 [11] J. R. Graybill, et al., [Extreme ultraviolet photon conversion efficiency of tetraphenyl butadiene](#), *Appl. Opt.*
312 59 (4) (2020) 1217–1224. doi:10.1364/AO.380185.
313 URL <https://www-osapublishing-org.proxy.queensu.ca/ao/abstract.cfm?uri=ao-59-4-1217>
- 314 [12] R. Francini, VUV-Vis optical characterization of Tetraphenyl-butadiene films on glass and specular reflector
315 substrates from room to liquid Argon temperature, *J. Instrum* 8 (2013) 09006. doi:[https://doi.org/](https://doi.org/10.1088/1748-0221/8/09/P09006)
316 [10.1088/1748-0221/8/09/P09006](https://doi.org/10.1088/1748-0221/8/09/P09006).
- 317 [13] E. Segreto, et al., Evidence of delayed light emission of tetraphenyl-butadiene excited by liquid argon
318 scintillation light, *Phys. Rev. C* (91) (2015) 035503.
- 319 [14] A. Piruska, et al., The autofluorescence of plastic materials and chips measured under laser irradiation,
320 *Lab Chip* 5 (2005) 1348 – 1354.
- 321 [15] H. Miyashita, [Autofluorescence of Electrophoresis Chip Grooved by Excimer Laser](#), *J. Laser Mi-*
322 *cro/Nanoeng.* 3 (2) (2008) 88–94. doi:10.2961/jlmm.2008.02.0006.
323 URL http://www.jlps.gr.jp/jlmm/archive/03/03_02/
- 324 [16] Y. Molard, et al., [Red-nir luminescent hybrid poly\(methyl methacrylate\) containing covalently linked](#)
325 [octahedral rhenium metallic clusters](#), *Chem. Eur. J.* 16 (19) (2010) 5613–5619. arXiv:[https://](https://chemistry-europe.onlinelibrary.wiley.com/doi/pdf/10.1002/chem.200902131)
326 chemistry-europe.onlinelibrary.wiley.com/doi/pdf/10.1002/chem.200902131, doi:[https://doi.](https://doi.org/10.1002/chem.200902131)
327 [org/10.1002/chem.200902131](https://doi.org/10.1002/chem.200902131).
328 URL <https://chemistry-europe.onlinelibrary.wiley.com/doi/abs/10.1002/chem.200902131>
- 329 [17] G. R. Araujo, et al., Photoluminescence response of acrylic (PMMA) and polytetrafluoroethylene
330 (PTFE) to ultraviolet light, *Eur. Phys. J. C* (79) (2019) 653. doi:[https://doi.org/10.1140/epjc/](https://doi.org/10.1140/epjc/s10052-019-7152-2)
331 [s10052-019-7152-2](https://doi.org/10.1140/epjc/s10052-019-7152-2).
- 332 [18] J. M. Corning, et al., Temperature-dependent fluorescence emission spectra of acrylic (PMMA) and
333 tetraphenyl butadiene (TPB) excited with UV light, *J. Instrum.* 15 (3) (2020) C03046. arXiv:1912.02073,
334 doi:10.1088/1748-0221/15/03/C03046.
- 335 [19] M. A. Verdier, A 2.8 K cryogen-free cryostat with compact optical geometry for multiple photon counting,
336 *Rev. Sci. Instrum.* 80 (4) (2009) 046105. doi:DOI:10.1063/1.3116443.
- 337 [20] H. Benmansour, et al., [Fluorescence of pyrene-doped polystyrene films from room temperature down to 4](#)
338 [K for wavelength-shifting applications](#), *J. Instrum.* (Oct. 2021).
339 URL <http://arxiv-export-lb.library.cornell.edu/abs/2110.08103v1>
- 340 [21] J. S. Kapustinsky, A fast timing light pulser for scintillation detectors, *Nucl. Instr. Meth. A* A241 (2-3)
341 (1985) 612–613. doi:DOI:10.1016/0168-9002(85)90622-9.
- 342 [22] I. Chirikov-Zorin, et al., [Method for precise analysis of the metal package photomultiplier single pho-](#)
343 [toelectron spectra](#), *Nucl. Instr. Meth. A* 456 (3) (2001) 310–324. doi:[https://doi.org/10.1016/](https://doi.org/10.1016/S0168-9002(00)00593-3)
344 [S0168-9002\(00\)00593-3](https://doi.org/10.1016/S0168-9002(00)00593-3).
345 URL <https://www.sciencedirect.com/science/article/pii/S0168900200005933>
- 346 [23] J. Tatum, *Stellar Atmospheres*, University of Victoria, 2020, Ch. Thermal Broadening, [Online; accessed
347 2021-12-16].
- 348 [24] A. P. Fluegge, et al., [Probing the Intramolecular Hydrogen Bond of 2-\(2-Hydroxyphenyl\)benzotriazoles in](#)
349 [Polar Environment: A Photophysical Study of UV Absorber Efficiency](#), *J Phys. Chem. A* 111 (39) (2007)
350 9733–9744, publisher: American Chemical Society. doi:10.1021/jp0721189.
351 URL <https://doi.org/10.1021/jp0721189>
- 352 [25] S. Beavan, P. Hackett, D. Phillips, [Phosphorescence of carbonyl compounds produced by thermal and](#)
353 [photo-oxidation of polybutadiene](#), *European Polymer Journal* 10 (10) (1974) 925–932. doi:[https://doi.](https://doi.org/10.1016/0014-3057(74)90030-5)
354 [org/10.1016/0014-3057\(74\)90030-5](https://doi.org/10.1016/0014-3057(74)90030-5).
355 URL <https://www.sciencedirect.com/science/article/pii/0014305774900305>
- 356 [26] G. Kirkbright, R. Narayanaswamy, T. West, [The fluorescence and phosphorescence characteristics of some](#)
357 [antioxidants and ultraviolet absorbers](#), *Anal. Chim. Acta* 52 (2) (1970) 237–246. doi:[https://doi.org/](https://doi.org/10.1016/S0003-2670(01)80954-5)
358 [10.1016/S0003-2670\(01\)80954-5](https://doi.org/10.1016/S0003-2670(01)80954-5).
359 URL <https://www.sciencedirect.com/science/article/pii/S0003267001809545>

- 360 [27] H. H. Neidlinger, P. Schissel, *Polymer glazings for silver mirrors*, Sol. Energy Mater. 14 (3-5) (1986) 327–
361 339. doi:10.1016/0165-1633(86)90056-0.
362 URL <https://linkinghub.elsevier.com/retrieve/pii/0165163386900560>
- 363 [28] V. Shlyapintokh, V. Gol'Denberg, *Effect of photostabilizers on the rate of photodegradation of polymethyl-*
364 *methacrylate*, Eur. Polym. 10 (8) (1974) 679–684. doi:10.1016/0014-3057(74)90179-7.
365 URL <https://linkinghub.elsevier.com/retrieve/pii/0014305774901797>
- 366 [29] R. Sosa Fonseca, et al., *Evidence of energy transfer in er3+-doped pmma-paac copolymer samples*, J.
367 Lumin 93 (4) (2001) 327–332. doi:[https://doi.org/10.1016/S0022-2313\(01\)00167-3](https://doi.org/10.1016/S0022-2313(01)00167-3).
368 URL <https://www.sciencedirect.com/science/article/pii/S0022231301001673>
- 369 [30] R. L. Clough, et al., *Color formation in irradiated polymers*, Rad. Phys. Chem. 48 (5) (1996) 583–594.
370 doi:10.1016/0969-806X(96)00075-8.
371 URL <https://www.sciencedirect.com/science/article/pii/0969806X96000758>
- 372 [31] R. Elgul Samad, et al., *Production of color centers in PMMA by ultrashort laser pulses*, Rad. Phys. Chem.
373 79 (3) (2010) 355–357, publisher: Pergamon. doi:10.1016/j.radphyschem.2009.08.017.
374 URL [https://www-sciencedirect-com.proxy.queensu.ca/science/article/pii/](https://www-sciencedirect-com.proxy.queensu.ca/science/article/pii/S0969806X0900423X)
375 [S0969806X0900423X](https://www-sciencedirect-com.proxy.queensu.ca/science/article/pii/S0969806X0900423X)
- 376 [32] C. Nantais, *Radiopurity measurement of acrylic for the DEAP-3600 dark matter experiment*, MSc thesis,
377 Queen's University, Kingston, Canada (Jan. 2014).
- 378 [33] B. M. Bolotovskii, *Vavilov – cherenkov radiation: its discovery and application*, Phys-Usp+ 52 (11) (2009)
379 1099–1110. doi:10.3367/ufne.0179.200911c.1161.
380 URL <https://doi.org/10.3367/ufne.0179.200911c.1161>

381 **Appendix A. Correction factor**

382 At each temperature T , we measure a number of photoelectrons from AVA1 at a 13.7 V LED voltage
 383 ($n_{AVA1}(T; 13.7)$), and a number of photoelectrons from TPB1 at a lower 13.4 V LED voltage ($n_{TPB}(T; 13.4)$).
 384 The LED voltage is lower for TPB1 because at the AVA1 voltage (13.7 V), pulses saturate the largest vertical
 385 range of the digitizer at low temperatures. To compare the relative light yields, we want the ratio for the same
 386 excitation (ie LED voltage): $\frac{n_{AVA1}(T; 13.7)}{n_{TPB1}(T; 13.7)}$. These are related to the measurements by:

$$\underbrace{\frac{n_{AVA1}(T; 13.7)}{n_{TPB1}(T; 13.7)}}_{\text{relative light yield}} = \underbrace{\frac{n_{AVA1}(T; 13.7)}{n_{TPB1}(T; 13.4)}}_{\text{measurement}} \times \underbrace{\frac{n_{TPB1}(T; 13.4)}{n_{TPB1}(T; 13.7)}}_{\text{correction}}$$

387 We measure the term $\frac{n_{TPB}(T; 13.4)}{n_{TPB1}(T; 13.7)}$ (correction factor) at three temperatures close to room temperature, and
 388 assume it does not depend on temperature. Numerical values of the correction factor are provided in Tab. A.1.

Temperature (K)	Light Yield @ 13.7 V (photoelectrons)	Light Yield @ 13.4 V (photoelectrons)	Correction Factor
300	171.2 ± 0.5	67.0 ± 0.3	2.556 ± 0.009
292	171.6 ± 0.5	67.5 ± 0.3	2.542 ± 0.009
273	173.4 ± 0.5	68.2 ± 0.3	2.542 ± 0.009
Average			2.547 ± 0.005

Table A.1: TPB1 correction factor calculation based on the light yields at the lower LED voltage used for the whole run at 13.4 V compared to the higher voltage used for select temperatures at 13.7 V.

389