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ORIGINAL ARTICLE

Incorporating strongly triboluminescent europium dibenzoylmethide triethylammonium into simple polymers

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As mankind continues to extend technological boundaries, sensors must be improved in order to keep pace. The current problem that engineers and scientists face is how to actively monitor structures for damage. One possible method is to embed a triboluminescent material into a composite structure. Nearby sensors would monitor these structures for structural failure or impacts. This paper reports on recently completed research that incorporated the strongly triboluminescent europium dibenzoylmethide triethylammonium (europium tetrakis) into a selection of polymers, such as poly(methyl methacrylate). Additional work was completed to determine if europium tetrakis could be mixed with Cytoseal 60 and 280 to form a durable triboluminescent polymer for small-area sensors. Using a custom-built drop tower, the triboluminescent light yield and decay times was measured for the newly created triboluminescent polymers.

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INTRODUCTION

There are a number of techniques that are currently being used for damage detection and monitoring of civil, aerospace, military structures, spacecraft/structures, and aircraft.[1] However, the major drawbacks of the current techniques are that they do not provide *in situ* and distributed sensing.[1–4] In addition, the associated cost resulting from the downtime required for periodic nondestructive inspections can be very high for aerospace structures like aircrafts and civil structures like bridges.[1]

Review of related research

In 1888, Wiedemann and Schmidt defined triboluminescence (TL) as the emission of light produced by mechanical action.[5–8] The emission of TL could be used as the active element for smart structural sensors.[9,10] TL-based sensor systems may be able to overcome current structural health sensor challenges as they have the potential for wireless, *in situ*, and distributed sensing that can enable real-time continuous monitoring.[1] In addition, TL-based sensor systems could allow for real-time monitoring of both the magnitude and the location of damage with respect to the host structure.[9,10] They can also be used as stress, fracture, and damage sensors.[7,11] If these sensors are to become reality, however, the TL emitted must be bright. Of the hundreds of known triboluminescent materials, only a few are bright enough to be seen in daylight.[12]

In 1999, Sage and Geddes used the property of TL to patent a design for a sensor capable of discerning the locations of impact.[10,13,14] Their design involved coating a material with a triboluminescent crystal or creating a composite triboluminescent object.[10,13,14] A sensor would then be embedded within the structure or mounted on its surface.[10,13,14] Impacts to the structure would produce light that would be recorded and analyzed to determine the location.[10,13,14] In addition, Sage *et al.*[10,13,14] proposed that several different triboluminescent materials could be used and arranged at various locations. The advantage of such an arrangement is that when an impact takes place, its location could be determined by the wavelength emitted.[10,13,14] For example, by placing two different triboluminescent materials at known distances from the detector, it is possible to determine the approximate location of the impact by measuring the emitted wavelength.

In 2000, Xu *et al.*[15–17] were the first to propose that zinc sulfide doped with manganese (ZnS:Mn) and strontium aluminate doped with europium ($Sr_{0.975}Al_2O_{3.985}$:$Eu_{0.01}$) could be used for mechanical stress sensors. They fabricated a film of ZnS:Mn on various ceramic substrates.[10,13,14] The substrates were then subjected to mechanical stress and various impacts. This caused the ZnS:Mn to emit a bright light clearly visible with the naked eye.[10,13,14] In experiments with $Sr_{0.975}Al_2O_{3.985}$:$Eu_{0.01}$, Xu *et al.*[16] applied a known stress to plastic objects with a 0.1-mm layer of the phosphor. Their results showed

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that the light output of the phosphors is proportional to the applied strain.[16,17]

In 2011, Fontenot *et al.* were the first to investigate the triboluminescent spectra of ZnS:Mn at ballistic velocities.[18,19] They modified several 9-mm and 30-caliber projectiles by machining a hole in the projectile.[18,19] The hole depths were 12 mm for the 9-mm and 10 mm for the 30-caliber projectiles.[18,19] The ZnS:Mn powder was then placed inside the projectile and the hole was covered using epoxy.[18,19] After the epoxy was cured, the 9-mm and 30-caliber projectiles were fired into an aluminum and steel target, respectively.[18,19] The triboluminescent spectrum was then recorded for each impact. Their results showed that there was approximately a 1-nm shift in the triboluminescent peak wavelength between the 30-caliber and 9-mm projectiles augmented with ZnS:Mn powder.[18,19] The higher energy 30-caliber projectiles had a peak wavelength that was about 1-nm longer (lower in energy) than the equivalent data measured for the lower energy 9-mm projectiles augmented with ZnS:Mn powder.[18,19] This research showed that ZnS:Mn could be used as a pressure sensor as well as an impact sensor capable of discerning the impact energy by investigating the triboluminescent wavelength emission.

In 2012, Dickens *et al.*[20] investigated the effects of ZnS:Mn in vinyl ester matrices to understand the relationship between applied stress and TL emissions in polymer matrices. Using samples of ArmorStar IVEX vinyl ester resin doped with 5, 10, 25, and 50 wt% ZnS:Mn samples, the authors were able to determine that the TL emissions occur mostly when the composite matrix fails. This in turn results in the straining or failure of ZnS:Mn and a triboluminescent emission.[18] In addition, the authors found that during relaxation of mechanical testing, excitation occurs at the elastic fracture point.[20] This property is beneficial for monitoring of matrix cracking as it would eliminate or reduce false alarms.

Recently, the authors began investigating the TL and photoluminescence (PL) properties of europium dibenzoylmethide triethylammonium (europium tetrakis or EuD_4TEA), which emits TL, with sufficient yield to be seen with the naked eye.[12,21–29] The authors showed that the organic EuD_4TEA has 206% of the TL yield compared with ZnS: Mn subjected to low-energy impacts.[12]

The first EuD_4TEA material synthesized by Hurt *et al.*[21] showed TL that was visible in daylight. However, it was observed that TL property was dependent on the concentration of the chloride ions present, with TL property increasing as the concentration of chloride ions was decreased by washing. Replacing the chloride salt with europium nitrate caused the triboluminescent light yield to increase by 82%.[23] Furthermore, doping EuD_4TEA with dimethyl methylphosphonate was found to increase the TL yield by nearly 200%, raising the potential for practical TL sensors.[30]

Base polymers used in this research

Cytoseal is clear and colorless and is formulated from high-quality advanced acrylic resins. It dries rapidly, does not become brittle and crack or discolor with age, and preserves original slide specimen quality almost indefinitely. Slides mounted with Cytoseal will not stick together, and if tissue requires remounting, it can be dissolved in toluene or xylene. Cytoseal is available in two viscosities: 60 for use with cover glass, and 280 for thicker coating or minimal spreading.

Poly(methyl methacrylate), or sometimes called PMMA, is a clear plastic used as a shatterproof replacement for glass.[31] The clear barrier that keeps hockey pucks from flying in the faces of hockey fans is made of PMMA. The chemical company Rohm and Haas makes windows from it and calls it Plexiglas. Ineos Acrylics also manufactures PMMA and calls it Lucite, which is used to make the surfaces of household items such as hot tubs, sinks, and one piece bathtub and shower units. PMMA is a member of a family of polymers that chemists call acrylates, shown in Figure 1, but the rest of the world calls acrylics.[31]

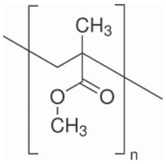

Figure 1 Chemical structures of PMMA.

EXPERIMENTAL PROCEDURE

Synthesis of EuD_4TEA for cytoseal mounting

The synthesis of EuD_4TEA was based on the procedures and methods described in Fontenot *et al.*[23] The synthesis began by dissolving 4 mmol of the europium nitrate in a warmed solution of 35 ml anhydrous denatured ethanol. Then 13 mmol of 1,3-diphenyl-1,3-propanedione also known as dibenzoylmethane and 14 mmol of triethylamine was added to the solution. The solution was then kept aside to cool at ambient temperature. The compound that formed was filtered and air dried at room temperature overnight.

Once the crystals were dried, 0.10 g was placed in the center of a one-inch Plexiglass drop tower slide. Cytoseal was then poured over the EuD_4TEA and left to dry for a week. Cytoseal is a clear colorless toluene-based mounting media formulated from acrylic resins that will not crack and discolor with age. For this experiment, Cytoseal 280 and 60 were used. Cytoseal 280 is a high-viscosity medium for application where minimum spreading is desired or in cases where a cover glass is not used. Cytoseal 60 is a low-viscosity medium that dries quickly and allows for a rapid even spreading, which nearly eliminates air bubbles. Pictures of the EuD_4TEA mounted in Cytoseal 280 and 60 are shown in Figure 2. It was observed that Cytoseal 280 creates a thick layer coating whereas Cytoseal 60 creates a very thin layer coating. At the same time the Cytoseal 60 coating still leaves the familiar powder feeling that is present for EuD_4TEA. In the case of Cytoseal 280, the layer was so thick that all that was felt was the Cytoseal coating.

Synthesis of EuD_4TEA and PMMA compounds

The synthesis of EuD_4TEA and PMMA was based on the procedures and methods described in Fontenot *et al.*[23] For these experiments, the PMMA (Sigma-Aldrich, St Louis, MO, USA, 182265) was crystalline and had an average molecular weight of 996 000. The first test synthesis began by dissolving 4 mmol of the europium nitrate in 25 ml of laboratory grade acetone. Then 13 mmol of dibenzoylmethane and 14 mmol of triethylamine were added to the solution. Then the EuD_4TEA solution was poured into a small ice tray with each section about half-way filled. Afterwards, PMMA was added until the EuD_4TEA solution was almost overflowing into the next section of the ice tray. This created about a 50% volume ratio of EuD_4TEA solution and PMMA. After each section was filled, the solution was left to dry over the next week. The ending product was a hard yellow object as shown in Figure 3a. This EuD_4TEA PMMA compound was extremely hard to break; however, when broken showed a quick flash of red light. In addition, this compound exhibited a strong luminescence as shown in Figure 3b. This was the same type of PL that was present in pure EuD_4TEA. Owing to its extreme hardness and large amount of energy required for fracture, no further testing was carried out. EuD_4TEA PMMA compound in this form would likely be a good candidate for use in hypervelocity impact conditions.

The synthesis of the second EuD_4TEA and PMMA test compound was prepared in a similar manner. For this synthesis, 4 mmol of the europium nitrate was dissolved in 25 ml of laboratory grade acetone. Then 4.0 g of PMMA and 13 mmol of dibenzoylmethane were added to the solution. Once dissolved, 14 mmol of triethylamine was added. The solution was then poured into the ice-tray sections and left to dry. The product that formed consisted of a brittle polymer with a yellow bottom and clear sides as shown in Figure 4.

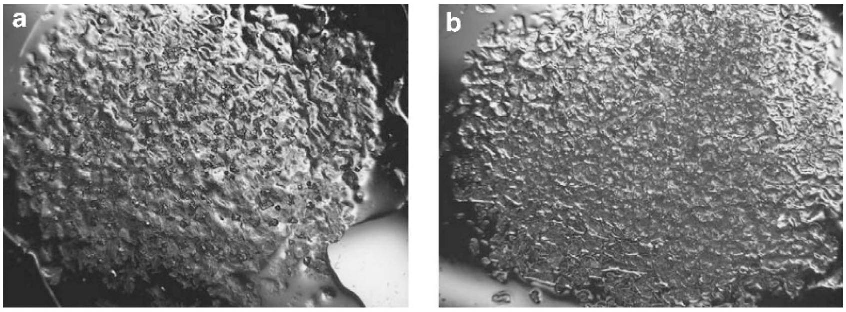

Figure 2 Close-up pictures of 0.10 g of EuD_4TEA mounted in Cytoseal (**a**) 280 and (**b**) 60. A full color version of this figure is available at *Polymer Journal* online.

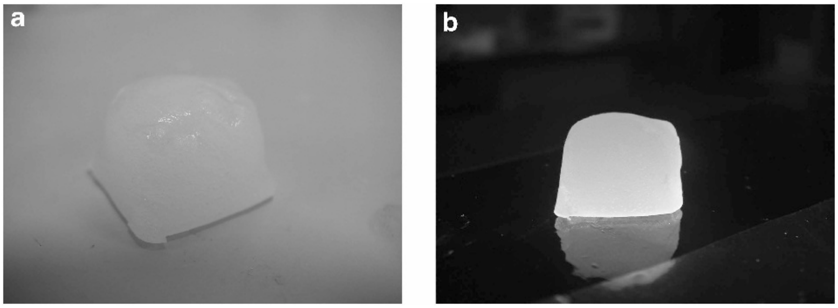

Figure 3 Picture of the first PMMA and EuD_4TEA sample taken using: (**a**) standard room light, and (**b**) ultraviolet irradiation. A full color version of this figure is available at *Polymer Journal* online.

Figure 4 Picture of the second PMMA and EuD_4TEA sample taken using natural light. A full color version of this figure is available at *Polymer Journal* online.

One interesting observation was that the clear sections that formed appeared to be a 110 μm thin coat that glowed bright red in sunlight. The yellow bottom of the compound had a thickness that ranged from 120 to 195 μm. This red glow was more pronounced and easily visible when brought outside around noon. Every noticeable clear section of the EuD_4TEA and PMMA compounds glowed bright red under sunlight and had no other forms of excitation. In addition, this compound yielded the same bright red triboluminescent flash as the plain EuD_4TEA.

In order to determine the effects of PMMA on the TL of EuD_4TEA, a final run was completed. It began by placing a varying amount of PMMA into the different sections of the ice tray. The amounts of PMMA used were 0.0096, 0.0148, 0.0203, 0.0408, 0.0524, 0.0999, 0.2044, 0.3006, 0.5012, and 1.0632 g. The solution of EuD_4TEA was doubled using 8 mmol of the europium nitrate, was dissolved in 50 ml of laboratory grade acetone with 26 mmol of DMB and then 28 mmol of triethylamine was added. Once the products were dissolved, 5 ml of the EuD_4TEA solution was poured into each of the sections of PMMA. The EuD_4TEA solution and PMMA were mixed until everything was dissolved and then left to dry over the course of a week.

The products that formed are shown in Figure 5. As the figure shows, PMMA has a significant effect on the structure of the finished compound. At low concentrations (<0.02 g), the final product is a pasty sticky yellow compound as shown in Figure 5a. As the PMMA concentration was increased, it started forming one solid layer. As shown in Figure 5b, there was not enough PMMA to keep the compound all together when it was removed from the tray. Instead, generally one solid block and a flaky compound formed. The mount of flakes reduced as the PMMA increased until 0.50 g was reached. At this concentration, a solid block compound was formed as shown in Figures 5c and d. This compound had a smooth side with internal pimples, shown in Figure 5c, produced by air bubbles and a rough uneven side as shown in Figure 5d. All of these materials exhibited PL and TL when excited.

PL testing

De-excitation by phosphorescence utilizes both the singlet- and triplet-excited electronic states.[32] For the europium complex, the ligand absorbs energy, undergoes intersystem crossing into a triplet state, and then transfers its energy to the Eu^{3+} ion.[32] The phosphorescence of each material was detected by excitation using an ultraviolet transilluminator manufactured by UVP, LLC (Upland, CA, USA). PL was recorded using an Avantes AvaSpec 2048 USB-2 spectrometer, which has a wavelength range of 445–680 nm and a resolution of 0.13 nm. The integration time was controlled using the AvaSoft software program. The integration time was increased by software until the photoluminescent emission spectrum reached its maximum that was just below the saturation limit of the spectrometer or until the background could no longer be completely subtracted due to large integration time. Once this was determined, 100 spectra were recorded and averaged.

TL testing

Using a custom-built drop tower designed and fabricated by the authors and described in Fontenot *et al.*,[24] the EuD_4TEA compounds were tested for their triboluminescent properties. The measurement began by placing the compound on a Plexiglass plate or the Cytoseal and EuD_4TEA on a Plexiglass plate in the drop tower. A 130-g steel ball was positioned on a pull pin at a set distance of 42 inches above the material. The pin was pulled

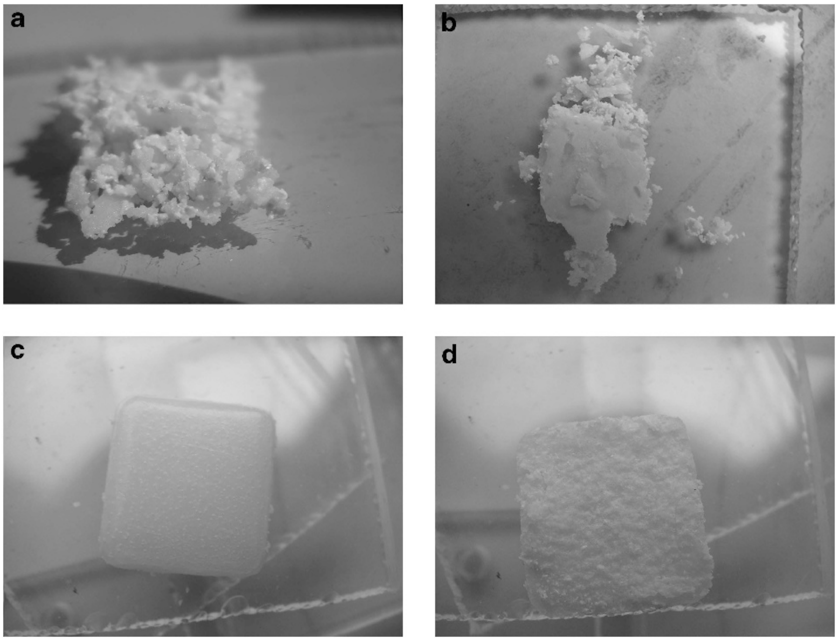

Figure 5 End product of the 5-ml EuD_4TEA solution with (**a**) 0.1048, (**b**) 0.0203, and (**c** and **d**) 1.0632 g of PMMA. A full color version of this figure is available at *Polymer Journal* online.

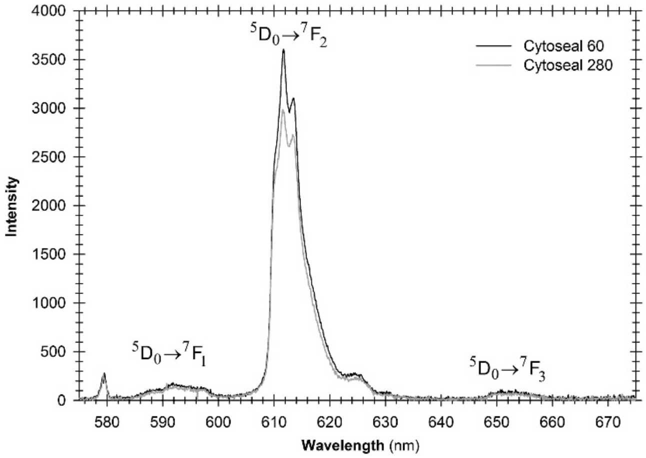

Figure 6 Measured photoluminescent spectra of EuD_4TEA and Cytoseal. The excitation wavelength was 365 nm. A full color version of this figure is available at *Polymer Journal* online.

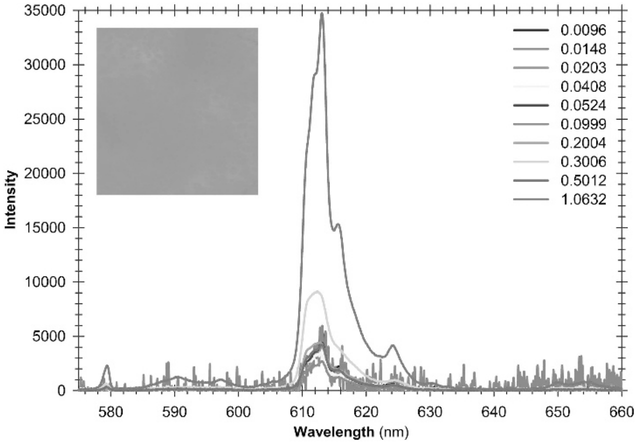

Figure 7 Selected measured photoluminescent spectra of EuD_4TEA polymers for the varying PMMA (g) precursor quantities. The orange-red inset is a picture of the photoluminescent emission produced by the EuD_4TEA polymers under ultraviolet irradiation. The excitation wavelength was 365 nm. A full color version of this figure is available at *Polymer Journal* online.

causing the ball to fall and impact the sample producing TL. After each test, the drop tube was removed, the ball was cleaned, and the sample compound was redistributed near the center of the target area.[24]

To determine the triboluminescent yield for a given sample, a United Detector photodiode was positioned under the Plexiglass plate 2.25 cm below the sample. A Melles Griot large dynamic range linear amplifier was used to increase the signal amplitude. A Tektronix 2024B oscilloscope records the signal in single sequence mode with a 500-μs measurement time. Once the signal was acquired, it was analyzed using custom LabVIEW program that integrated the area under the curve and calculated the decay time for the particular emission.[24]

RESULTS

Photoluminescent results

The measured photoluminescent emission spectra for EuD_4TEA compounds are shown in Figures 6 and 7, where the compounds are Cytoseal and PMMA, respectively. Notice that the orange-red photoluminescent spectra do not change when the quantities of PMMA are increased. The only slight differences between the spectra of the different media are due to some compounds having a lower PL. As a result, the lower probability transitions are buried in the noise. The spectra from all three compounds indicate that the luminescence from EuD_4TEA compounds comes from the typical Eu^{3+}-excited transitions from the $^5D_0$ levels to the lower $^7F_{0–4}$ levels. Owing to the high resolution of the spectrometer, multiple peaks were observed for each transition. The main emission occurred from the $^5D_0 \rightarrow {}^7F_2$ transition. In addition, the $^5D_0 \rightarrow {}^7F_4$ transition was not observed due to the transition occurring around 705 nm, which is outside of the limit of the Avantes spectrometer. This peak has been observed

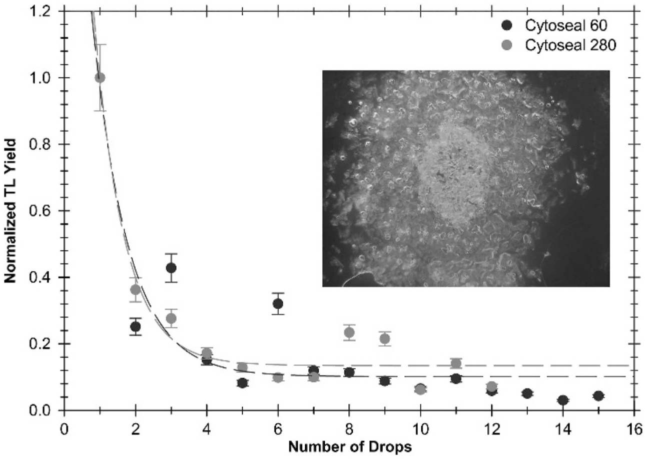

Figure 8 Plot of the normalized TL yield versus the number of drops for the two EuD$_4$TEA and Cytoseal formulations. The inset is a picture of the EuD$_4$TEA and Cytoseal 280 compound after 12 drops. Notice the damage in the center. A full color version of this figure is available at *Polymer Journal* online.

using an Ocean Optics S2000 spectrometer and PTI QuantaMaster^{TM} 14 Spectrofluorometer with a larger wavelength range and is reported in Fontenot *et al.*[26,33]

Triboluminescent results

Using the drop tower and LabVIEW VI tools as described above, the TL produced from each trial was analyzed. Owing to these measurements being a relative value, the data were normalized to a reference value. In the case of Cytoseal, the reference value was the first drop for each type of Cytoseal. The error in the triboluminescent yield in these experiments was estimated to be 10%. Figure 8 shows a plot of the normalized TL yield as a function of the number of drops for both Cytoseal formulations. It is apparent from Figure 8 that as the number of drops increase, the damage to the EuD$_4$TEA Cytoseal compound also increases. This causes the TL to decrease drastically, which is totally consistent with previous findings described in Fontenot *et al.*[25]

With the aid of the same LabVIEW, VI tools, the decay time for each drop was measured. The average triboluminescent decay time for the EuD$_4$TEA in Cytoseal 60 was 637.8 ± 66.9 μs. The error in this case was estimated to be the standard deviation of all the drops. This decay time is consistent with previous measurements for EuD$_4$TEA.[24–26] The average triboluminescent decay time for EuD$_4$TEA in Cytoseal 280 was 685.2 ± 70.2 μs. This measurement does fall within the error of previous measurements. The reason for the longer decay time is likely due to the fact that the TL is very dim for Cytoseal 280. As a result, the noise is increased when the amplifier has a large gain. This could cause an increase in the TL decay time.

The effects of PMMA on the TL of EuD$_4$TEA are shown in Figure 9. For these measurements, the data were normalized to the 0.1627 vol.% of PMMA and EuD$_4$TEA compound. The error in vol.% was estimated to be 5% and the error in TL yield was estimated to be 7%, which is the error from the synthesis process and drop tower.[34] As Figure 9 shows, the TL is dependent on the amount of PMMA used. The TL starts out small due to the elastic nature of the PMMA. Then it reaches a maximum TL yield at about 3.4% PMMA to EuD$_4$TEA solution. Once this concentration is reached the TL decreases rapidly. This is due to the fact that it is becoming harder for the ball to break the EuD$_4$TEA PMMA compound. In fact, when the concentration reaches about 8.5%, it becomes nearly impossible to break the compound. This was the case for the 18% PMMA. Here it took two drops just to break the compound. As a result, the amount of PMMA can be increased or decreased to optimize the impact energy under investigation. The decay time for the EuD$_4$TEA PMMA compound was 570.9 ± 39.6 μs, which is consistent with previous research results.[24–26]

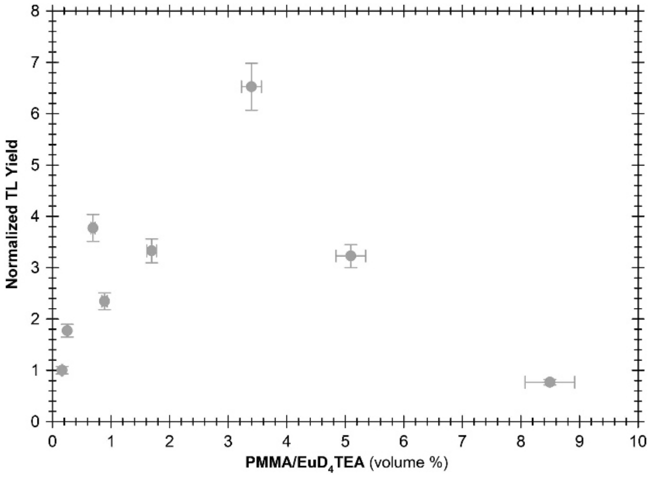

Figure 9 Plot of the normalized TL yield versus the quantity EuD$_4$TEA and PMMA compound. A full color version of this figure is available at *Polymer Journal* online.

CONCLUSIONS

In conclusion, it is apparent that EuD$_4$TEA can be incorporated into polymers or mounting media thereby making it a viable candidate for impact sensors. The best polymer for EuD$_4$TEA found in this research would have to be PMMA. The incorporation of EuD$_4$TEA into the polymer has demonstrated that by simply increasing the concentration of PMMA results in significant changes in the TL properties. At high concentrations, the PMMA can make a compound that is completely insensitive to low-velocity impacts. As a result, impact sensors can be designed so that they are only triggered above a given threshold. In addition, thin coats of EuD$_4$TEA and PMMA can emit a bright red light activated by sunlight and seen under bright light conditions such as noon day sun. Further research is underway to investigate other polymers and to create thin films of EuD$_4$TEA.

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