

Photochemical changes in absorption and fluorescence of DDM-containing epoxies



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ABSTRACT

Photochemical changes in the optical characteristics of solid polymers form the basis for many important technologies, but few examples are demonstrated in diamine-cured epoxy, one of the most important structural polymer systems. We have observed that diamine-cured epoxies containing the 4,4'-diaminodiphenyl methane (DDM) framework display changes in both absorption and fluorescence in response to UV light. The change from original “blue” to photo-activated “red” emission can be accomplished by illuminating samples of DDM-containing epoxy with photons of 254 nm or 370 nm wavelengths, followed by excitation of the newly-generated red-emitting fluorophore with 350–400 nm light. Studies of the monomer constituents and of many formulations of diamine-cured epoxy identify the DDM structure as the responsive moiety, both from the epoxy or diamine monomer. The fluorescence change is accompanied by the formation of orange and green chromophores; the orange chromophore is the fluorophore, with a broad 410 nm excitation and 607 nm emission. Our work shows the “blue-to-red” transition to be irreversible and independent of atmospheric oxygen; the fluorophore’s impermanence with time and its radical spectral signature identify it as a reactive intermediate rather than a photo-oxidation product. The central methylene radical of the benzoidal DDM structure is proposed as a red-emitting fluorophore/orange chromophore, with the green chromophore being a quinoidal methine resulting from the DDM radical.

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1. Introduction

Polymers that respond optically to environmental stimuli have many current and potential applications in the energy, medical, and structural engineering fields [1,2]. In most photo-responsive polymer systems a molecule transitions from an initial state to a final state of different optical characteristics. Polymers displaying photo-responsive changes in absorbance (color change) or emission (fluorescence change) or both have been well-documented. The nomenclature for photo-responsive molecules and polymers varies depending on whether the transition from one state to another is reversible (photochromism, photo-switching) or irreversible (photo-activation, light-activation) [3–10].

Photochemical reactions in polymers that are termed photochromic are generally reversible isomeric transitions in main-chain,

side-chain, or guest molecules caused by absorption of a photon of specific energy, usually ultraviolet (UV) light [1]. The back-reaction from final to initial state can occur in response to visible-light photons or heat [2]. Photochromic polymer systems have been commercialized in self-darkening windows and eyeglasses, and have been heavily studied as the basis for 3-dimensional optical data storage [11–15].

Molecules capable of undergoing irreversible photo-induced optical changes have been termed photo-activatable or light-activated [6,9,16,17]. Their activation via photons has also been described as the “unmasking” or “uncaging” of a chromophore or fluorophore. In “fluorogenic” systems, a photoactivatable molecule absorbs a photon of activation wavelength λ_{act} , causing a change from non-emissive to emissive behavior. In response to a second photon of excitation wavelength λ_{ex} , the emissive molecule can then emit fluorescent light of wavelength λ_{em} [9]. In these systems, a covalent bond is generally broken by λ_{act} , changing the optical characteristics of a molecule by removing a conjugation-

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blocking structure or opening a ring. Most of the photoactivatable fluorescent molecule systems in literature have been realized in liquid solution environments for the application of high-resolution bioimaging or nanoscopy, or for monitoring diffusion or flow rates in microfluidics applications [18,19]. Photoactivatable polymer systems have been demonstrated for biological process monitoring, deformation analysis, and drug release indication [20–23].

Photochemically induced optical changes in polymers have been demonstrated in many polymer classes including polyurethanes, acrylates, and siloxanes [2,24]. There have been relatively few demonstrated examples in the diamine-cured epoxies, however; this needs to be addressed as these epoxies are used in large quantities in the aerospace, automotive, and marine industries as the matrix material for fiber-reinforced composites, in the electronics industry as protective encapsulants, and in myriad industries as adhesives. The photochemical responses of diamine-cured epoxies have been studied mainly from the standpoint of understanding the photo-oxidative effects of environmental UV exposure, rather than development of stimuli-responsive systems [25–31].

Initially, diamine-cured epoxies are optically transparent and emit blue fluorescence in response to UV excitation. Many epoxies undergo photoinitiated radical oxidation reactions when exposed to prolonged UV illumination, beginning with photon-induced dissociation of covalent bonds, ultimately resulting in various carbonyl products. Often these carbonyls are chromophores which absorb in the UV, are non-fluorescent, and appear brown or yellow in color. A few epoxy formulations have been shown to form blue or green chromophores in certain atmospheres when illuminated with UV light. A common feature among those diamine-cured epoxies showing blue-green color formation is the presence of a diaminodiphenylmethane (DDM) molecular structure. This molecule is commonly used as the diamine monomer in the curing agents 3,3'- and 4,4'-diaminodiphenylmethane, as well as being at the core of the widely used epoxy monomer 4,4'-tetraglycidyl diaminodiphenylmethane (TGDDM). The green and blue chromophores generated photochemically from DDM-containing epoxy formulations are proposed as quinoidal forms of the DDM core structure which can be intermediates on the pathway to the final carbonyl products [25,30,31].

The relationship between mechanochemical and photochemical reactions is quite interesting - several mechanochemical reactions producing color change or fluorescence can also be accomplished photochemically. Researchers have demonstrated identical mechanochemical and photochemical reactions in polymer systems using cyclobutene, spiropyran-merocyanine, and lophine as active molecules [32–45]. Recently “radical-type” polymeric mechano-phores have been reported with green colored products after grinding or deformation [46–49]. The reaction we present here is believed to be a new radical-type mechano- and photo-active molecule.

In this paper we report the photochemical response of DDM-containing epoxies to UV light. Epoxies containing DDM from either the epoxy or curing agent display an irreversible “blue-to-red” change in fluorescent emission, along with generation of orange and/or green chromophores, in response to UV illumination. Our experiments show the “red” fluorescence results from the photochemically generated orange chromophore, which is a reactive intermediate that can turn to non-emissive forms including the green chromophore, a quinoidal methine. In a companion work to this report, we show that mechanical force delivered via uniaxial compression also produces these optical changes in DDM-containing epoxies.

2. Experimental

2.1. Materials

Molecular structures of the epoxies and diamine curing agents used in this study are shown in Fig. 1. The tetra-functional TGDDM epoxy used in this study was obtained from Huntsman under the product name MY720. The di-functional diglycidyl ether of bisphenol A (DGEBA) was obtained from Miller-Stephenson under the trade name Epon 828. The long-chain epoxy diluent diglycidyl ether of polypropylene glycol (DGEPPG) was obtained from Dow Chemical under the trade name DER 736. The DDM, diethylene-triamine (DETA), and 4,4'-methylenebis (2-methylcyclohexylamine) (MMCA) curing agents were obtained from Sigma Aldrich. The 4,4'-diaminodiphenyl sulfone (DDS) curing agent was obtained from Huntsman. The polyoxypropylenediamine (POPDA) curing agent was obtained from Dow under the trade name Epikure 3274.

2.2. Experimental methods

2.2.1. Sample fabrication

All three epoxies are liquid at room temperature; TGDDM is very viscous and was raised to 70 °C for pouring and weighing, but cooled to room temperature before mixing. The DETA, MMCA, and POPDA curing agents are also liquids at room temperature, so formulations involving these three curing agents were mixed with the epoxies at 1:1 epoxide:amino-H stoichiometry in 25–40 g batches and poured into aluminum molds to cure. The DDM curing agent was obtained in solid pellets, which were heated to melt then mixed into the epoxies as liquids. The DDM returned to solid form during mixing, so the mixture was gently heated until the DDM dissolved, then returned to room temperature. The DDS curing agent was obtained in powder form. The powdered DDS was stirred into the epoxy liquids which were gently heated until the DDS powder dissolved, after which the liquids were stirred and removed from heat.

The mixtures were cured at temperatures determined by dynamic differential scanning calorimetry of the mixtures. A typical procedure used a 24 h period after mixing at room temperature followed by a 1 h exposure at the temperature corresponding to the onset of the exothermic cure reaction peak. This cure procedure produced polymers that were capable of undergoing machining but did not necessarily produce complete cure or optimum mechanical properties. For example, the TGDDM-POPDA formulation discussed in this work was cured at room temperature for 24 h followed by 50 °C for 1 h; this resulted in 70% conversion of epoxide groups. This topic is covered in more detail in the companion work to this document. Examples of the scans used to determine cure procedures are included in the [Supporting Information](#).

Samples for optical analysis were machined from the casts into flat plates of approximate dimension 4 mm × 4 mm × 1.0 mm using a low speed saw with diamond wafering blade.

2.2.2. Optical imaging, photo-activation, and spectral analysis

Images of samples were collected using a Canon PowerShot ELPH 100HS digital camera mounted on a small tripod. Natural light images were taken in ‘portrait’ mode with no flash using a white ceramic plate as background. Fluorescence images were collected in ‘long shutter’ mode using a 15 s exposure in a darkroom using a black, nonfluorescent felt cloth as background. Illumination for the images came from a standard long wave UV bulb (λ_{\max} ~365 nm) mounted at 45° to the sample surface.

In systems where the fluorescent response of a molecule can be modulated by incident light, a distinction must be drawn between

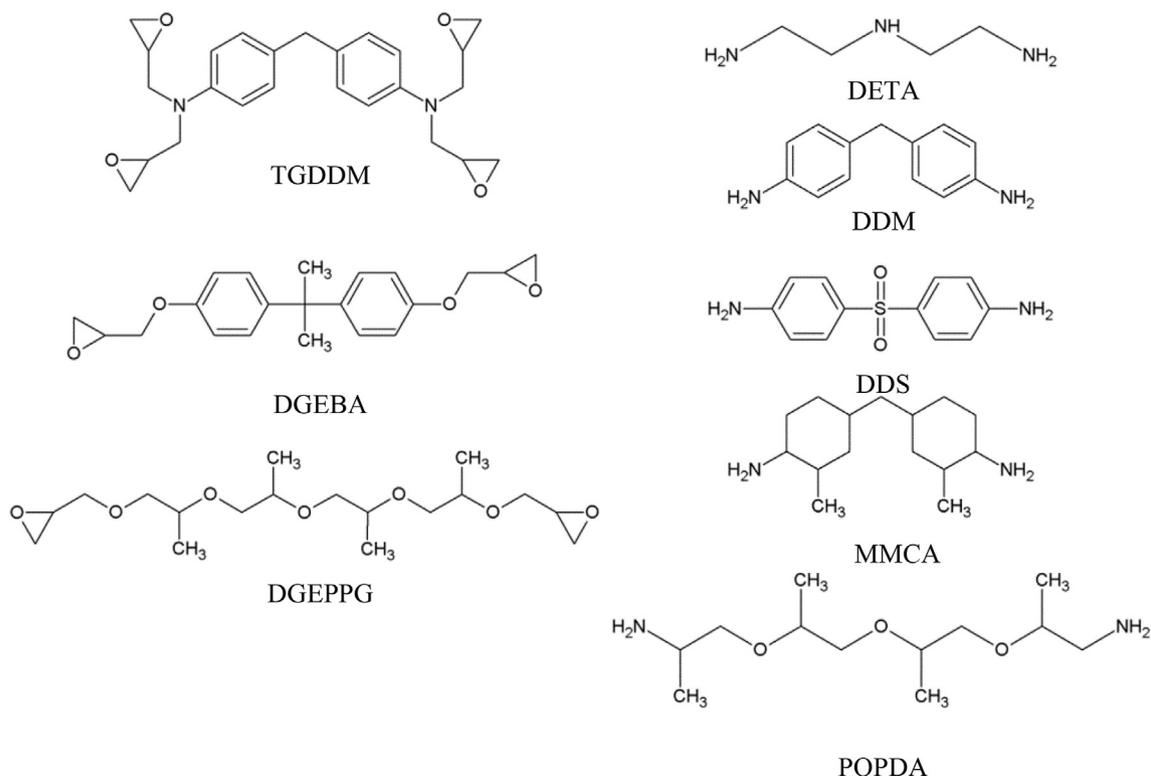


Fig. 1. Molecular structures of epoxy monomers and curing agents used in this study. Epoxies at left; diamine curing agents at right.

the light that causes the optical change and the light that stimulates emission from the changed molecule. Following Raymo's terminology, a responsive molecule absorbs a photon of activation wavelength λ_{act} , causing a change from non-emissive to emissive behavior. In response to a second photon of excitation wavelength λ_{ex} , the emissive molecule can then emit fluorescent light of wavelength λ_{em} [9]. Fluorescent excitation and emission spectra were collected from cured epoxy samples at room temperature in a Perkin Elmer LS-50B luminescence spectrometer. The solid polymer was machined as described above into 4 mm \times 4 mm \times 1 mm samples and mounted into a solid sample holding fixture. Spectra from photo-activated samples were collected after 30 min of illumination with 370 nm as λ_{act} .

Fluorescent emission spectra for this work were also collected with a Y-type 7-around-1 fiber optic fluorescence probe held at 45° to the sample surface and processed by a portable spectrometer (Stellarnet BLUE-Wave UVN 200). A 390 nm LED source (Stellarnet SL1-LED) was used as λ_{ex} . Measurements of changes in the fluorescent signal with time were collected using the spectrometer's episodic data capture function.

Measurements were most often collected at room temperature. To collect time-resolved emission spectra at temperatures above room temperature, samples were attached to the digitally controlled thermal stage of the GladiATR attachment (PIKE Technologies) to a Bruker Vertex 70 infrared spectrometer. Samples were brought into thermal equilibrium with the stage using a thin layer of thermally conductive paste (Arctic Silver) at room temperature; the stage was set to the desired temperature and measurements began when the target temperature was reached. Spectra were also collected from cryogenic samples. These samples were immersed in liquid nitrogen for several minutes to bring the samples to 77 K. Samples were rapidly mounted into the spectral analysis setup and data collection began immediately. Samples

were not temperature-controlled during the measurement, so for time-resolved measurements the sample temperature is rising towards room temperature during the collection.

The photoactivated fluorescence of epoxy samples was observed by first generating fluorescent intermediates using as λ_{act} photons from either a 15W, 120V CFL-15 UV-C mercury light bulb (254 nm) or the UV light source (370 nm) from a fluorescence microscopy set (Nightsea SFA-UV). Samples of epoxy of size 4 mm \times 4 mm \times 1 mm were illuminated at a stand-off distance of \sim 1 mm from the source, and exposures were timed. After exposure, emission spectra were collected using the portable spectrometer setup described above, with photons from a 390 nm LED as λ_{ex} .

Absorbance spectra were collected from solid samples using a transmittance method. A reflectance probe mounted into a 90° holder (Ocean Optics CSH) which isolated the probe and sample from ambient light was used to pass white light from a tungsten-halogen source (Stellarnet SL1) through the sample to a reflective aluminum foil tape layer. Light returning through the sample, having passed through the sample for a path length of twice the sample thickness, was collected by a spectrometer (Stellarnet Silver Nova). A white-light baseline value was collected with no sample in place, and absorbance spectra were determined by comparison. Absorbance spectra from liquid samples were collected using a Thermo Fisher Evolution 300 UV-Vis spectrophotometer. Liquid solutions of epoxy dissolved in dichloromethane were held in the beam path in quartz cuvettes, and compared to baselines of pure dichloromethane liquid.

Electron paramagnetic resonance spectra were collected from epoxy samples using a Bruker EMX EPR spectrometer with 1 mW of microwave (9.27138 GHz) power and a modulation amplitude of 1 G. A quartz sample tube was filled with sample of TGDDM-POPDA epoxy and illuminated with 370 nm light as λ_{act} for 30 min.

3. Results

3.1. “Blue-to-red” fluorescence change

Fig. 2 shows images of a sample of a TGDDM-POPDA formulation that demonstrates the “blue-to-red” fluorescence change. In Fig. 2a, incident photon of 370 nm wavelength serve as λ_{ex} for “blue” fluorescence from a TGDDM-POPDA sample at the onset of illumination; after 1 h of continuous illumination with 370 nm light at room temperature the sample emits a “red” fluorescence as shown in Fig. 2b. This “blue-to-red” emission change is the behavior we seek to understand further.

Fig. 2 shows that 370 nm light can serve as both λ_{act} for the generation of fluorophores and as λ_{ex} for the generated “red” emitters. By comparing samples before and after 370 nm UV illumination, excitation and emission spectra of the “blue” and “red” fluorescing species can be recorded and are presented in Fig. 3.

3.2. Excitation and emission spectra

Before UV illumination, using 390 nm as λ_{ex} , the “blue” emission of a TGDDM-POPDA epoxy sample exhibits two strong fluorescent emission peaks at 440 and 495 nm, and a weak emission peak at 611 nm. Fig. 3 shows excitation and emission spectra collected at room temperature from a TGDDM-POPDA sample. Fig. 3a shows the excitation spectra for these fluorescent peaks before illumination. Spectra were normalized to the peak intensity of the 440 nm peak, with 495 and 611 nm spectra then magnified for clarity as noted. The 440 and 495 nm emission seem to share common excitation peak features, a strong peak at 365 nm with shoulder at 290 nm. The excitation spectrum for 611 nm emission is broad and jagged, with a peak at 407 nm. The emission spectra in Fig. 3b show the “blue” state emission, with emission peaks at 440 or 495 nm depending on excitation wavelength. The 611 nm emission is barely detectable, being an order of magnitude weaker than the 440 nm emission. Fig. 3c shows the excitation spectra of “red” TGDDM-POPDA sample corresponding to the emission peaks after 30 min of 370 nm UV illumination. Spectra are normalized to the 611 nm peak excitation intensity, with 440 nm and 495 nm spectra then magnified as noted for clarity. After UV illumination, the excitation spectrum for 611 nm emission becomes much stronger than the 440 nm and 495 nm spectra. The emission spectra show a similar increase – the “red” emission at 611 nm becomes far stronger than the “blue” emission. In fact, the emission at 440 nm is almost undetectable; after UV illumination only the 495 nm emission remains of the original “blue” spectrum. At excitation wavelengths of 390–410 nm, it is apparent that the 611 nm emission is accompanied by a shoulder at ~660 nm.

3.3. Incremental activation with time

Fig. 3 shows that the three emission peaks of DDM-containing epoxies at 440 nm, 495 nm, and 611 nm can be excited using λ_{ex} of 350 nm–400 nm. As observed in Fig. 2, 370 nm illumination also can be used as the λ_{act} causing the “blue-to-red” transition. The changes in emission spectra can be observed over time during the transition using a strong 370 nm LED as source of both λ_{act} for the generation of red-emitting fluorophores and λ_{ex} for their emission. The results of this experiment are shown in Fig. 4. Fig. 4a shows the uncorrected emission spectra of a sample of TGDDM-POPDA epoxy at the onset of illumination (dashed line) and spectra collected at room temperature after intervals of illumination up to 25 min. The “blue” peaks appear at ~440 and ~490 nm in this setup; the “red” peak appears at 607 nm. It is clear that the “blue” emission peaks decrease in intensity as illumination progresses, while the “red” emission becomes much more intense. Fig. 4b shows the change in intensity of these peaks over time. The 440 nm and 490 nm values are normalized to their initial value, while the 607 nm peak is normalized to the maximum intensity which is reached after ~15 min of illumination. The “red” 607 nm intensity increases by nearly an order of magnitude in the first 15 min of exposure, after which it decreases, increases more slowly, then decreases again. The “blue” intensity of the peaks at 440 and 490 nm decrease rapidly and remain low throughout the exposure.

The decrease in “blue” emission over time may be due to the gradual formation of UV-absorbing photo-oxidation products on the sample surface. Other works have observed the formation of carbonyl compounds as photoinitiated radical oxidation products on the surface of various epoxies, with an increased absorbance in the UV wavelengths that extends into the visible over time [25,26]. The excitation-emission spectra in Fig. 3 make it clear that the “blue” emission would be affected most strongly by growth of a UV-absorbing oxidation surface layer, while the “red” emission would only be prevented if such a layer’s absorbance extended well into the blue wavelengths. The gradual decrease of the “red” emission over many hours may be explained by the extension of the oxidation layer’s absorbing wavelengths into the visible region as it thickens.

3.4. Irreversibility and transience of emission after activation

It is important to determine if the “blue-to-red” change in fluorescence observed in certain epoxies after illumination with UV light is reversible or not. If reversible, the most common means of recovering the initial behavior is with application of broad-spectrum light or heat. Reversibility would suggest an isomeric change as the mechanism of the fluorophore generation. Fig. 5 has the results of experiments comparing the spectrum of “red”

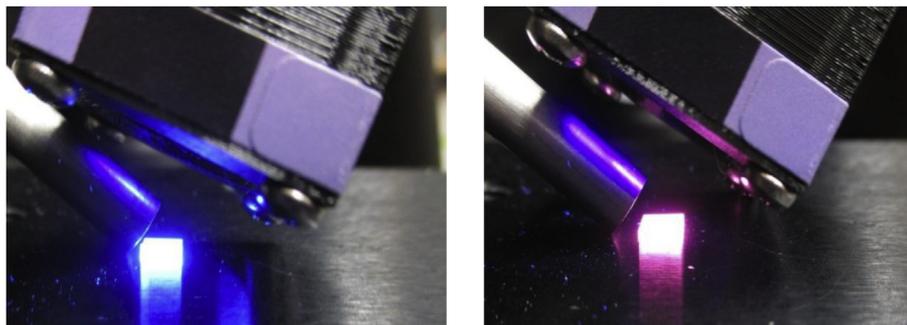


Fig. 2. sample of TGDDM-POPDA under 370 nm illumination. a) At onset of illumination. b) after ~1 h.

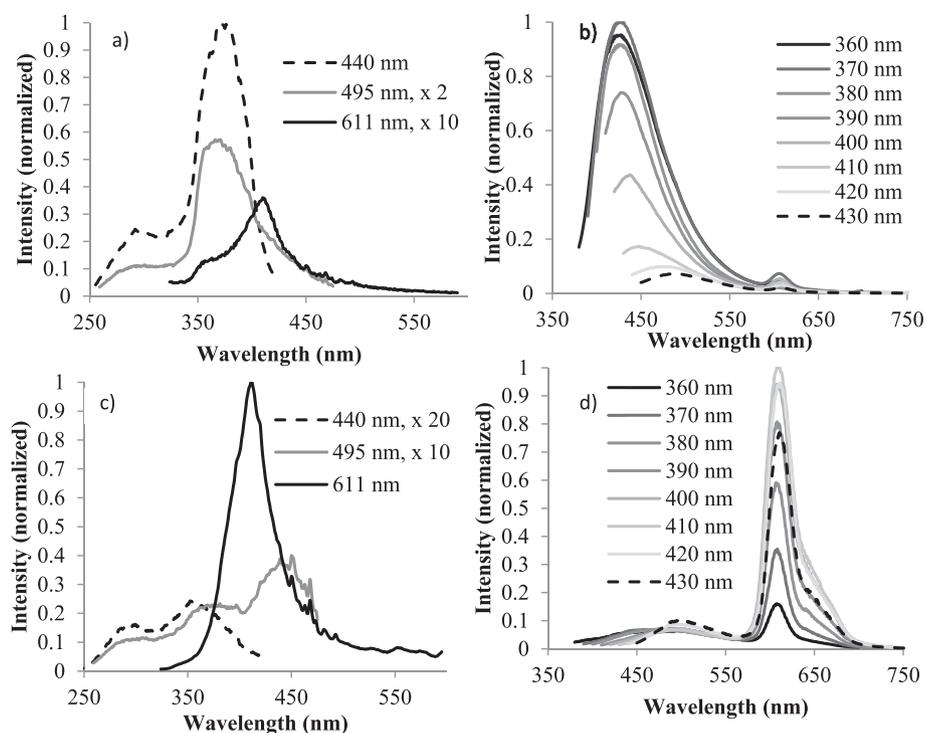


Fig. 3. Excitation and emission spectra from TGDDM-POPDA sample before and after 30 min exposure to 370 nm UV light. A) Excitation spectra before exposure. B) Emission spectra before exposure. C) Excitation spectra after exposure. D) Emission spectra after exposure.

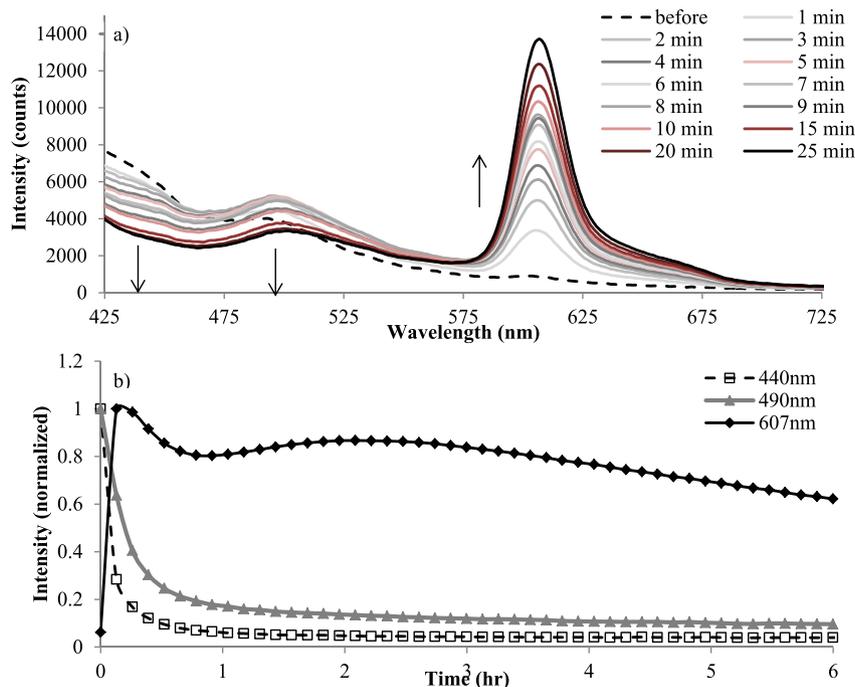


Fig. 4. top - spectral changes of TGDDM-POPDA under illumination over time. Bottom - plot of intensities of 3 fluorescence peaks over time.

samples of TGDDM-POPDA under exposure to white light and elevated temperatures. The “before” spectrum is of a sample in “blue” state. The “initial” spectrum is collected from a sample in “red” state, after 30 min of 370 nm exposure. Samples were then exposed to different environments: 60 min of dark at room temperature; 60 min at room temperature under white light; 60 min of

dark at 50 °C; and 30 min of dark at 75 °C. Spectra were collected at 5 min intervals during this period using 390 nm LED as λ_{ex} ; the intensity of the 607 nm “red” emission is normalized to the “initial” value and plotted in the inset of Fig. 5.

Exposure to white light and to elevated temperature, while they caused the 607 nm “red” emission intensity to decrease, did not

cause a reversion to “blue” emission as the 440 nm peak did not increase. This is inconsistent with photochromism, where the original emission should be recovered. But it does suggest that the photo-activated fluorophore is an intermediate state which eventually transitions to some other non-emissive form. The decrease in 607 nm intensity is slow at room temperature in the dark; the rate of decrease is faster at elevated temperatures and under white light illumination. At 75 °C the 607 nm intensity is nearly indistinguishable from its original intensity after 30 min of exposure.

Fluorescent emission in many fluorophores can be ‘quenched’ by elevated temperatures due to the increased rate of non-radiative transition processes from the excited state back to ground state [50]. Since these measurements were collected at elevated temperatures, the possibility exists that the “red” fluorescent emission decreased due to quenching rather than the conversion of emitting species to non-emitting species. This possibility was ruled out by recording the emission spectra of a sample after 30 min of 75 °C exposure, then cooling to room temperature. The 607 nm “red” emission, which disappeared during the 75 °C exposure, did not return when the sample was cooled, indicating 607 nm intensity decrease is due to conversion to non-emitting state. The 490 nm “blue” emission did show evidence of quenching as it was more intense after cooling to room temperature.

3.5. Wavelength and atmosphere effects

An important question is whether λ_{act} can be varied, as it may be inconvenient in some applications to have spectral overlap between λ_{act} and λ_{ex} or λ_{em} . Fig. 6 shows the results of using a 2 h illumination of a TGDDM-POPDA sample at room temperature with a 254 nm source as λ_{act} compared to a 370 nm source. It is clear that 254 nm also serves to photo-activate the “blue-to-red” transition in these epoxy samples – the “red” emission is at identical wavelength for either λ_{act} , suggesting that 254 nm or 370 nm cause the same transition. The spectra shows that 254 nm does not cause as much decrease in the “blue” emission, although the increase in “red” emission is similar.

Based on previous work in epoxy photo-degradation studies, the atmosphere in which samples were exposed to UV illumination had significant effect on the reactions produced [25,26,30,31]. Photo-oxidation was common in oxygen-containing atmospheres, and

several works observed different optical changes in samples illuminated in inert gas atmospheres compared to air or oxygen. With this in mind, we have determined if samples exposed to UV illumination in argon atmosphere also displayed the “blue-to-red” fluorescence change. Fig. 7 shows the emission spectra from DGEPPG-DDM samples after illumination with 370 nm λ_{act} for 40 min in an argon glove box or in ambient atmosphere at room temperature. Both samples exhibit the “blue-to-red” fluorescence change; The difference in “red” emission intensity between samples exposed in air and in argon is attributed to differences in sample size and experimental variation. The important result is that since “red” fluorescence develops at similar magnitudes in an argon environment as in an ambient environment, the “blue-to-red” transition does not need atmospheric oxygen to proceed. Inset to Fig. 7 is a photo of the sample emitting red fluorescence after 40 min of illumination; as in Fig. 2 this shows that 370 nm can serve as both λ_{act} and λ_{ex} regardless of atmosphere.

These experimental results show that the “blue-to-red” fluorescent emission change is not dependent on oxygen. Previous work has identified pathways for photochemical reactions in epoxies involving photoinitiated oxidation of a radical with the ultimate product being chromophores with carbonyl groups in epoxies; the multiple step processes begin with photochemical dissociation of a covalent bond producing reactive radical intermediates which react with atmospheric oxygen to form carbonyls [25–28,51–53]. These reactions result in brown or yellow colors in similar fashion to thermo-oxidation. Photo-oxidation reactions are not generally known to produce new fluorophores; in fact oxidation layers on epoxy samples tend to prevent fluorescent emission by absorbing UV excitation light before it reaches the fluorophores or color centers [54]. While the photo-oxidation reaction may occur and may contribute to the gradual decrease in emission strength under illumination observed in Fig. 4, it is not the reaction that produces the “red” fluorophore. From these results we can draw a distinction between the non-oxidative, fluorophore-producing “blue-to-red” reaction we observe here and more commonly observed photo-oxidative processes producing carbonyl compounds.

3.6. Monomer origin of “red” fluorescence

The origin of the fluorescence in 607–611 nm can be initially explored by determining the contributions to the solid polymer spectra of the original monomer species. The fluorescence of diamine-cured epoxies in monomer and polymer form has been

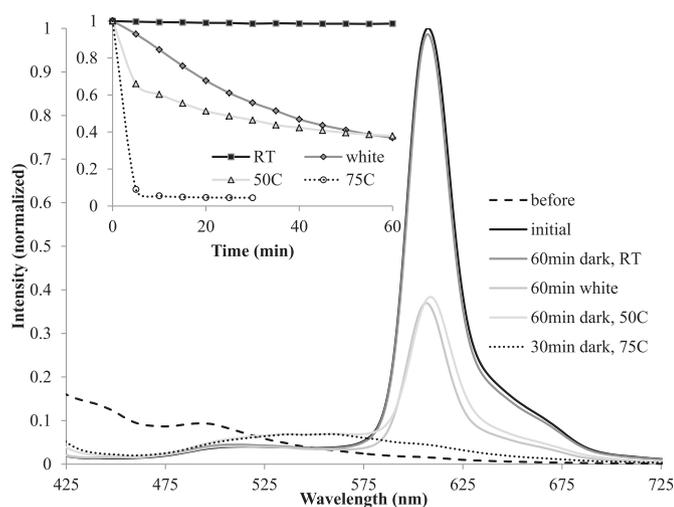


Fig. 5. Emission spectra of TGDDM-POPDA samples before UV illumination, after 15 min of 370 nm illumination, and after illumination then exposure to white light or elevated temperatures. Inset - 607 nm intensity over time for samples during exposure to white light or elevated temperatures.

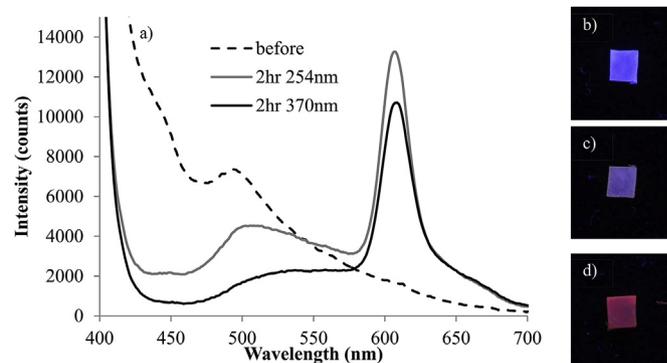


Fig. 6. a) Emission spectra of samples of TGDDM-POPDA before and after UV exposure. b) Image of a sample before exposure (long wave UV as λ_{ex}). c) Image of a sample after 2hr 254 nm illumination (long wave UV as λ_{ex}). d) Image of a sample after 2hr 370 nm illumination.

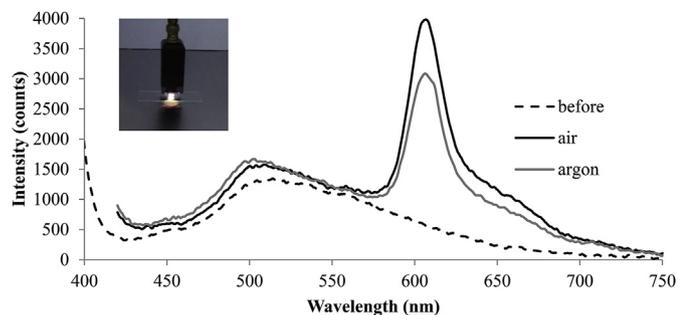


Fig. 7. Comparison of fluorescent emission spectra of DGEPPG-DDM samples after 40min 370 nm exposure in argon atmosphere and air atmosphere. Inset - photo of sample fluorescing in glove box.

studied in several works [53,55–58]. Using 450 nm excitation, Levy and Ames observed emission at 463 nm and 606 nm from uncured TGDDM monomer liquid. After curing with several diamine curing agents, the 463 nm intensity remained active in the solid and could be strongly influenced by absorbed water, viscosity, and cure conditions. George and Schweinsberg used 350 nm excitation to observe that the emission spectrum of uncured TGDDM monomer liquid showed a single emission peak at ~430 nm; after curing with DDS into polymer solid the emission spectrum showed two peaks at 430 nm and 510 nm [58]. Allen et al studied many commercial DGEBA epoxies in dilute solutions along with several amine-based curing agents including POPDA in liquid form; they found that the DGEBA epoxies were non-emissive while the amines displayed UV-excited fluorescence [53]. In particular the POPDA they studied showed a 350 nm peak excitation wavelength and 424 nm peak emission, which remained active during mixing and curing in a DGEBA-POPDA formulation; they also suggested that longer-wavelength emission from an excimer complex of aromatic species. These works suggest that both the TGDDM monomer and the diamine monomer may contribute to the observed “blue” fluorescence in diamine-cured epoxy solid samples, but that “red” emission is likely to originate only within the TGDDM molecule.

At room temperature, many of the epoxy and diamine monomers in Fig. 1 are liquids, while the behavior we observe in Fig. 2 occurs in the cured polymer which is a solid, glassy amorphous thermoset. Fluorophores often behave quite differently in a liquid environment compared to a solid environment, with emission often becoming more intense in solids due to restriction of molecular motion inhibiting vibrational or rotational non-radiative transition pathways. To correlate the emission of the monomers with the observed emission of the cured polymer, we felt it necessary to examine the monomer emission characteristics in solid state as well. This can be accomplished by freezing the monomer liquids rapidly into glassy solid form, similar to the “low temperature isolation matrix” technique used for studying optical properties of short-lived reaction intermediates [59]. The emission spectra from TGDDM and POPDA monomers in response to 370 nm as λ_{ex} in liquid form and frozen solid form are shown in Fig. 8.

Solid glassy TGDDM and POPDA both exhibit blue emission with two peaks at 440–450 nm, and 480–500 nm. The emission in liquid form is much lower in intensity for both species, with POPDA nearly undetectable. The contribution of the monomers to the spectrum from cured TGDDM-POPDA polymer is unclear. The peak position of TGDDM-POPDA emission is not necessarily indicative of either monomer, nor is the emission strength. The “blue” emission spectrum from cured TGDDM-POPDA will be treated as originating from either monomer species, or from excimers of aromatic network structures.

The “red” spectrum observed in cured TGDDM-POPDA samples develops over time during illumination with UV light, as shown in Fig. 2. This suggests an experiment where frozen monomer samples of TGDDM and POPDA are illuminated with UV light over a period of time. The results of this experiment are shown in Fig. 9, with Fig. 9a showing an image of frozen TGDDM fluorescence at the onset of illumination, Fig. 9b showing the spectra collected during the illumination, Fig. 9c showing an image of TGDDM fluorescence after ~10 min of illumination, and Fig. 9d showing the normalized intensity of 611 nm emission as time increases. After ~400 s of UV illumination, the frozen TGDDM monomer begins to emit a red fluorescence at 611 nm, which increases in intensity until ~600 s of illumination then begins to decrease. The change in emission color can be easily observed in the images. The frozen POPDA sample shows a decrease, then a general increase in intensity across the entire emission spectrum, followed by a permanent general decrease; no new peaks developed during the exposure.

The observed development of “red” emission from frozen TGDDM monomer is the same as that observed in solid TGDDM-POPDA. The instrumentation used for this experiment did not allow maintenance of cryogenic temperature so the samples are returning to room temperature and eventually melting during the timed exposures. The decreases in intensity of both frozen TGDDM and POPDA toward the end of the timed exposures are due to the return of the sample to liquid form, where fluorescence is less intense. Since frozen POPDA does not develop any new emission peaks during UV exposure, it is not considered to contribute to the “red” emission. The observed intensity fluctuations in frozen POPDA over time are attributed to changes in illuminated surface area due to crack formation and ultimately melting of the solid.

Studies of liquid TGDDM and POPDA under UV illumination have supported the findings of studies of frozen solid TGDDM. When spread into a film at room temperature, TGDDM liquid shows very rapid development of “red” emission under UV illumination. Fig. 10 shows the time-resolved emission intensity of a film of TGDDM liquid after a 5 s illumination with 370 nm as λ_{act} and 390 nm as λ_{ex} . The intensity changes are identical to those observed in cryogenic TGDDM monomer and in TGDDM-containing solid epoxies. After the intense UV source is removed, the emission intensity decreases very rapidly with a half-life of ~50 s. This is much faster than the intensity decrease observed in solid diamine-cured TGDDM-containing epoxies (see Fig. 5).

3.7. Origin of fluorophores and chromophores in solid

To further explore the involvement of the DDM structure in the photo-activation of epoxies, we studied each of the fifteen combinations of epoxy and diamine presented in Fig. 1. Before illumination, samples are clear or pale yellow and show “blue” emission in long wave UV. Samples were illuminated for 2 h using 254 nm or

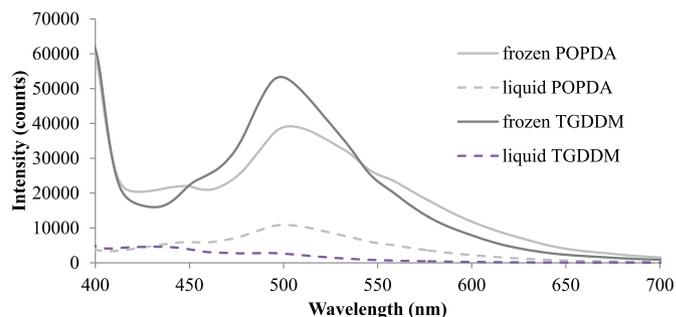


Fig. 8. Emission spectra of frozen and liquid monomer components of TGDDM-POPDA.

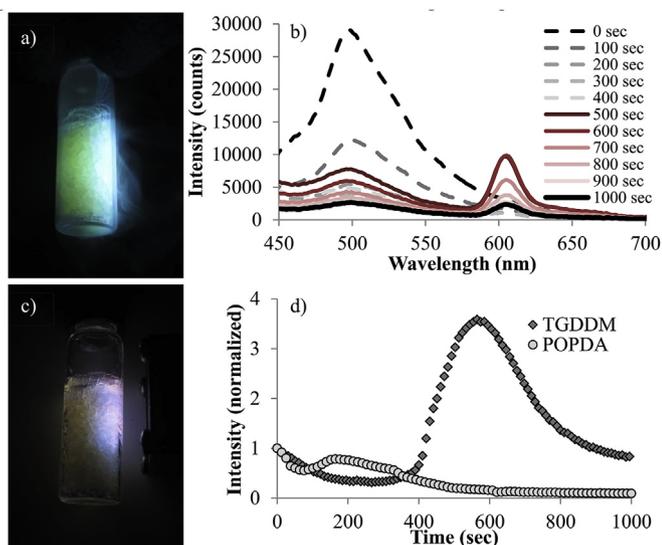


Fig. 9. a) Image of frozen TGDDM monomer, at onset of 370 nm illumination. b) Emission spectra from frozen TGDDM monomer collected at increasing times after onset of illumination. c) Image of frozen TGDDM monomer after ~10 min of illumination. d) normalized intensity at 611 nm of frozen TGDDM and frozen POPDA monomers.

370 nm as λ_{act} ; images were collected in ambient light and using long-wave UV as λ_{ex} . In Fig. 11, the ambient light images of the 15 formulations after 370 nm illumination are shown. It is clear that samples containing the core DDM structure, from either TGDDM as the epoxy or from DDM as the curing agent, show a color change while samples that do not contain DDM do not change color. The fluorescent images in Fig. 11 show that the samples containing DDM that change color also emit “red” fluorescence after activation, while those that did not change color emit the original “blue”. This clearly indicates the participation of DDM in the “blue-to-red” transition, and shows that color change is produced as a primary or secondary result of the same reaction. Illumination using 254 nm as λ_{act} produced similar results.

Interestingly, several of the samples in Fig. 11 show different color change but the same red fluorescent emission. A specific example is the TGDDM-DETA system and the DGEPPG-DDM system. After activation, the “red” fluorescence is present in both, but TGDDM-DETA is orange while DGEPPG-DDM is green. The absorbance spectra of these samples, collected via transfectance method, are compared in Fig. 12. Initially the samples absorb in the UV, consistent with “blue” emission as identified in Fig. 3. After activation, the orange TGDDM-DETA sample has strong absorbance

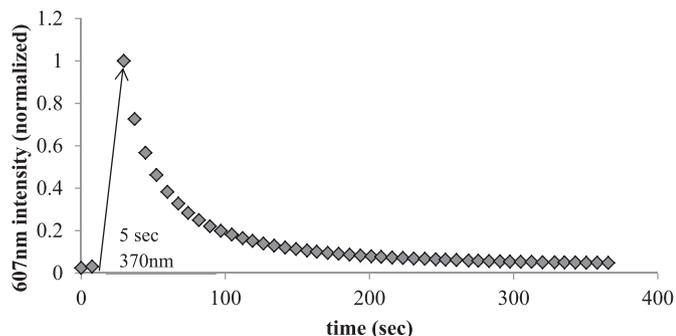


Fig. 10. Intensity of 607 nm emission of TGDDM film before and after 5 s 370 nm UV illumination.

at 410 nm. This is consistent with the red-emitting fluorophore identified in Fig. 3. The green DGEPPG-DDM sample has increased absorbance at 410 nm, but also a strong absorbance at 625 nm. This indicates that the orange-absorbing, red-emitting fluorophore is present in both samples, while the green chromophore is another species present only in DGEPPG-DDM. Studies of the other formulations support this conclusion.

Samples of certain DDM-containing epoxies have been observed in other works to form green chromophores in response to UV exposure [30,31]. The identity of the green chromophore can be investigated further by experiments in solution. A green chromophore can be produced from the TGDDM monomer dissolved in dichloromethane by addition of a few grains of iodine and brief sonication. Fig. 13 shows absorbance spectra from the green DGEPPG-DDM sample in Fig. 12, compared with a similar green color observed in a 5 wt% TGDDM solution in DCM after the addition of iodine. The samples have a strong absorbance peak at ~615–635 nm; a peak at 410 nm is observable in the solid samples but not in liquid, which has a small peak at 365 nm. The images inset to Fig. 13 show before and after ambient light images of the color change. When illuminated by 390 nm excitation, the solid sample was highly fluorescent while the liquid was not.

This experiment demonstrates the similarity between the chromophores produced via UV illumination in some solid DDM-containing epoxies, and the chromophores produced via interaction of TGDDM monomer with iodine in solution. The TGDDM-iodine chromophore is almost certainly a quinoidal methine, similar to those formed by aromatic amines in solution with iodine [60–62].

Atherton and later, Fulton proposed several mechanisms for generation of green chromophores in DDM-containing epoxies by exposure to UV photons [30,31]. These mechanisms involved oxidative dissociation of covalent bonds, resulting in generation of several radical intermediates; some of these would turn to the green quinoidal methine form responsible for the observed color. It is our hypothesis that the orange color and fluorescence observed in this work and the companion work on mechanochromic effects are due to one or more of these reactive intermediates formed at the central methylene of the DDM structure, and that the green color formed in some samples is due to the resulting quinoidal methine formed from the DDM intermediate.

3.8. Electron paramagnetic resonance spectroscopy

The hypothesis that a reactive intermediate is involved in the photo-activated fluorescence of DDM-containing epoxies may be tested using electron paramagnetic resonance (EPR) spectroscopy. Fig. 14 shows the EPR spectra of a sample of TGDDM-DETA collected before and after a 30 min illumination with 370 nm as λ_{act} . The spectral g factor of 2.005–2.008 from samples before and after illumination indicates the presence of organic radicals, with a large increase in radical concentration after illumination. The EPR spectrum of the compressed epoxy does not display hyperfine structure suitable for positive identification of the radical, however its general shape and features are quite similar to those observed by researchers creating radicals in epoxy using other stimuli [30,31,63–67]. The spectra are also indistinguishable from those of radicals created mechanochemically in the companion work to this one. This experiment demonstrates that organic radicals are generated in a TGDDM-DETA sample by illumination with 370 nm as λ_{act} .

3.9. Mechanism

Scheme 1 presents the original DDM structure, the reactive

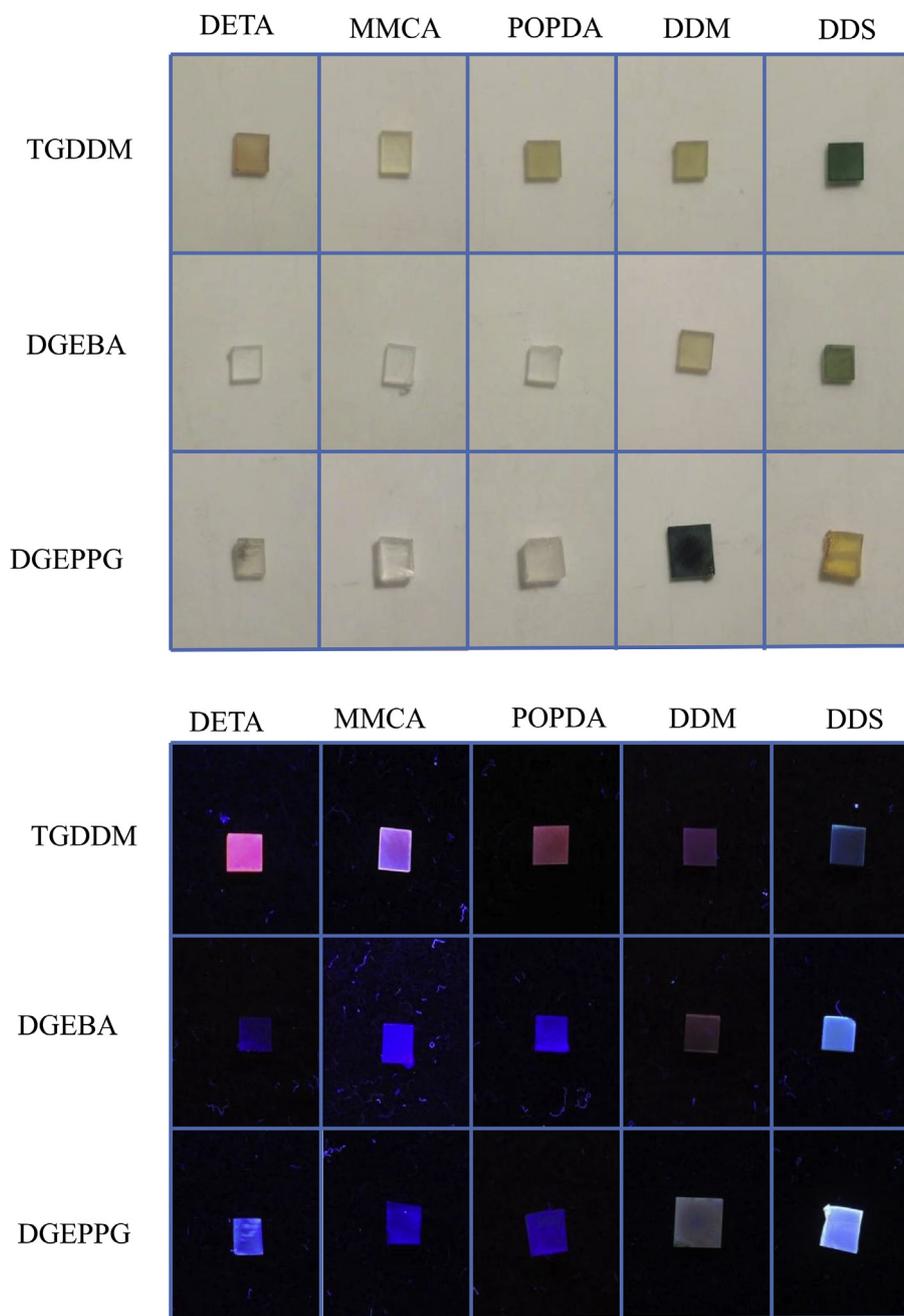


Fig. 11. Top: Ambient-light images of samples after 370 nm λ_{act} illumination. Bottom: Fluorescent emission of samples after 370 nm λ_{act} illumination, using long wave UV as λ_{ex} . Samples containing DDM show "red" fluorescence; others show "blue" fluorescence. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

intermediate structure, and the quinoidal methine structure, which are responsible for the color and fluorescence changes in DDM-containing epoxies. Radicals formed via UV photons in several positions may ultimately find a semi-stable position at the central methylene of the DDM structure, which can reduce its energy via resonance. Diphenylmethyl radicals similar to this proposed structure have been stabilized in cryogenic solvent glass, in host polymers, and in zeolite channels; in these stabilizing environments the radicals displayed similar absorbance and fluorescence characteristics to those observed from our DDM-containing epoxies [68–75]. A radical on the DDM structure in an amorphous glassy thermoset environment such as cured epoxy may be expected to have orange color, red fluorescence, and relatively long lifetime

consistent with our observations. As proposed by others to account for the green coloration observed, the quinoidal methine structure of DDM is a natural structure to form from the DDM with central methylene radical center. The selection of orange form or green form as the preferred structure for the different formulations will be studied in future works.

4. Conclusions

In this work we show the photochemical creation of orange and green chromophores and a red-emitting fluorophore in response to UV illumination of solid epoxy polymers containing the DDM structure. Spectroscopic analysis of the monomer constituents

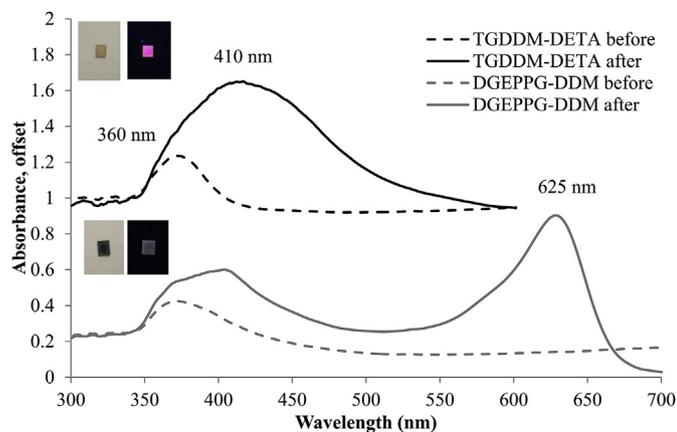


Fig. 12. Absorbance of samples after 370 nm illumination displaying similar fluorescence but different colors. TGDDM-DETA shows orange color and red fluorescence, while DGEPPG-DDM shows green color and red fluorescence. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

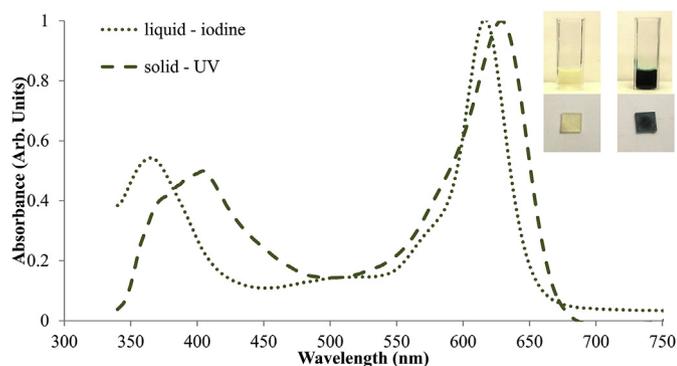
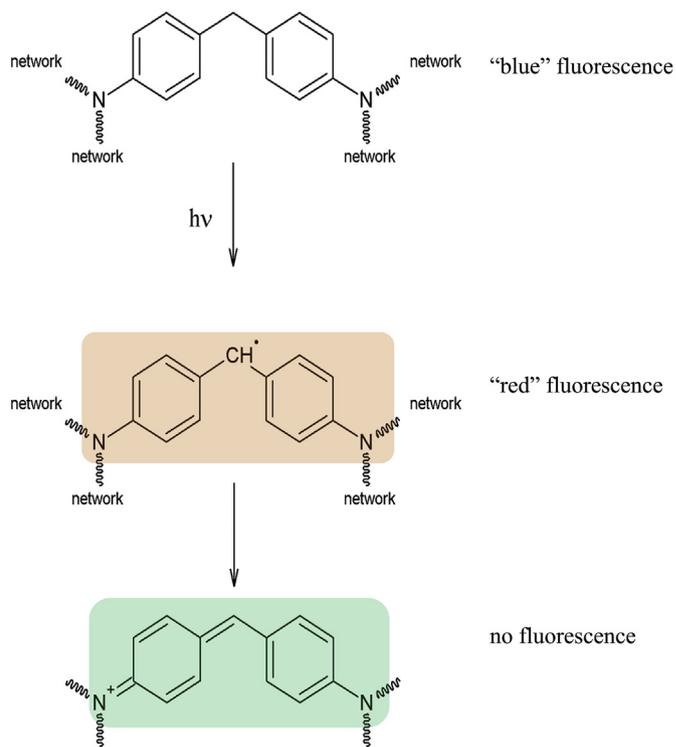


Fig. 13. Green color formation in DDM-containing epoxies, via photo-activation of DGEPPG-DDM solid, and TGDDM monomer in liquid solution via addition of iodine. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Scheme 1. Scheme for reactions creating orange and green chromophores and red fluorophore in DDM-containing epoxies.

shows that the DDM structure is the source of the red emission; analysis of the solid polymer shows that the orange chromophore is a reactive intermediate and source of the red emission, while the green chromophore is a quinoidal methine form of the intermediate. The creation of these chromophores and fluorophores is irreversible by white light or heat, and the red-emitting fluorophore ultimately transitions to some non-fluorescent state over time. The photochemical activation of fluorescence in cured

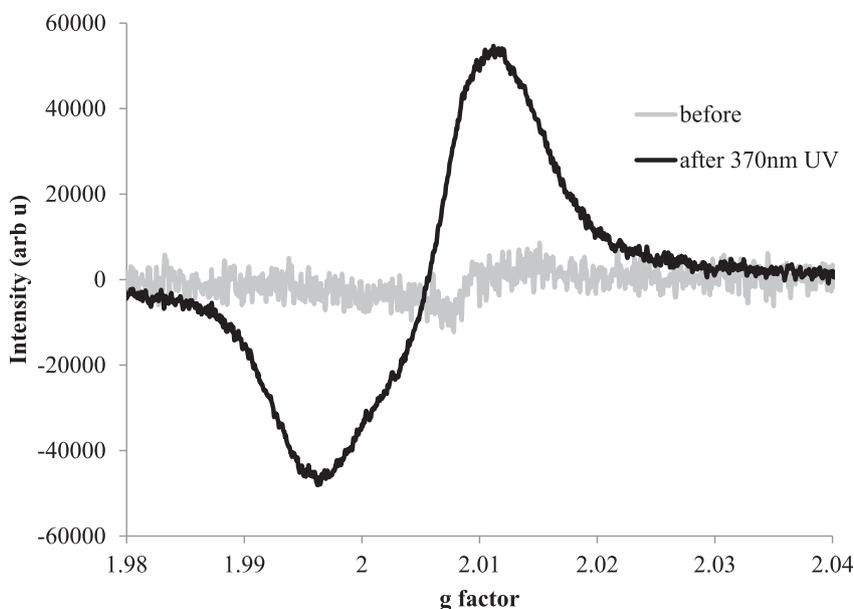


Fig. 14. EPR spectra of TGDDM-POPDA before and after 30 min illumination with 370 nm.

epoxies may have application in 3-D optical data storage or in light-emitting devices. The stability of fluorescent radicals at room temperature in cured epoxy may enable study of reactive radicals such as carbenes and nitrenes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.polymer.2018.03.015>.

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