

Thermal degradation of visible-light-cured thiol-methacrylate networks photoactivated with Camphorquinone



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ABSTRACT

This report describes the yellowing of visible light-cured thiol-ene networks formulated with Camphorquinone (CQ) as photoactivator. CQ displays an intense dark yellow color due to the presence of a conjugated diketone chromophore that absorbs at 470 nm. Irradiation of CQ with visible light produces an excited triplet state which interacts with oxidizable species, thus decomposing into colorless products. During the course of this study it was found that the color of thiol-ene networks changes from colorless to yellow after 4 months storage at 20 °C. This investigation was carried out to provide clarification of this issue. The yellowing in initially photobleached thiol-methacrylate networks was studied by UV–visible spectroscopy. The yellowing of the networks was apparent after 4 h at 50 °C, 1.5 h at 70 °C or 20 min at 110 °C. However, color changes were perceptible after 40 days at 20 °C. The change in color observed in the studied polymer networks is explained in terms of the regeneration of CQ through hydrogen transfer reactions between thiyl radicals and ketyl radicals. Results obtained in this research demonstrate that the yellowing displayed by thiol-methacrylate systems photoactivated with CQ jeopardizes the long-term stability of the derived films and bulk materials. Visible light photopolymerization offers many advantages over UV photopolymerization. However, in the particular case of thiol-ene resins photoactivated with CQ, the use of visible light is accompanied by undesired yellowing of the resulting polymers.

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1. Introduction

Thiol–ene polymerizations carry many of the attributes of “click” reactions [1–4]. These attributes include having rapid reaction rates with reactions occurring either in bulk or in environmentally benign solvents over a large concentration range, being insensitive to ambient oxygen or water. This exceptional versatility and its propensity for proceeding under even the mildest of conditions makes thiol–ene chemistry amenable to applications ranging from high performance polymer networks [1–4] to processes of bioorganic modification [5,6].

Initiation of thiol–ene polymerizations is achieved through the generation of radical centers, the most common method being photoinduced initiation [1–3]. In this study, Camphorquinone (CQ) was used as photoactivator for the visible light polymerization of thiol-methacrylate networks. CQ is excited under blue light irradiation ($\lambda = 470$ nm), to the excited singlet state which converts to

the reactive triplet state CQ^* via an efficient intersystem crossing [7,8]. Hydrogen abstraction from thiols by the CQ^* results in the formation of a thiyl radicals and ketyl radicals [8–10]. Once formed, the thiyl radical initiates the polymerization process by inserting into the carbon–carbon double bond to give a carbon-centered radical, thus initiating the radical-chain process [1–4].

CQ displays an intense dark yellow color due to the presence of a conjugated diketone chromophore that absorbs at 470 nm. During irradiation of CQ at 470 nm and reduction of one of the carbonyl groups, the conjugation is destroyed, causing loss of the yellow color, thereby resulting in colorless films and bulk materials [11,12]. On the other hand, pioneer studies by Stone and Cohen in 2-propanol and acetonitrile demonstrated that benzophenone is regenerated through hydrogen transfer reactions between thiyl radicals and benzophenone-derived ketyl radicals [13].

Yellowing in films and bulk materials is caused by photo-products from initiator residues and it is perceived as an undesirable color change [14–17]. In fact, a disadvantage of aromatic urethanes is that they can also cause yellowing of the coating itself [18]. This study was carried out in order to examine the

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regeneration of CQ in thiol-methacrylate networks and, therefore, to assess the color stability over time of the derived films and bulk materials. The regeneration of CQ in thiol-methacrylate networks was studied by means of UV–vis spectroscopy by monitoring the absorbance at 470 nm at different temperatures in the range 50–110 °C. Pentaerythritol tetra(3-mercaptopropionate) was used in combination with 2,2-bis[4-(2-methacryloxyethoxy) phenyl]propane and bisphenol A ethoxylate dimethacrylate.

To the best of our knowledge, this is the first report describing the regeneration of CQ in thiol-ene polymer networks.

2. Experimental

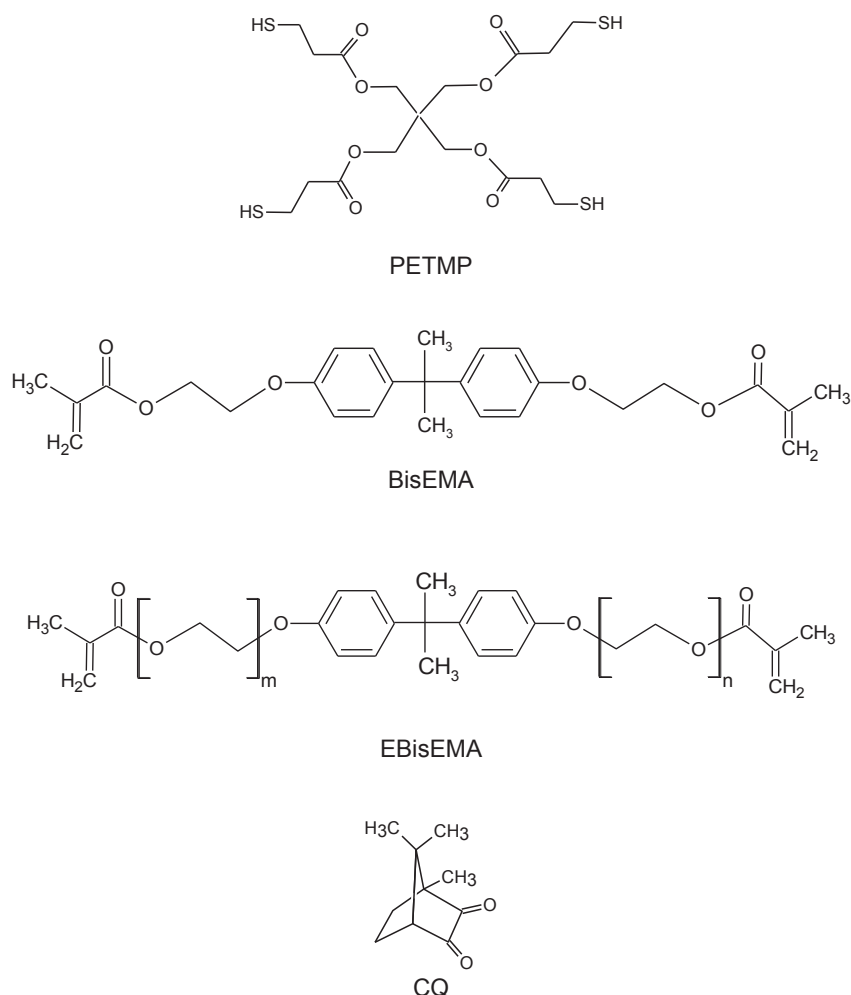
2.1. Materials

Pentaerythritol tetra(3-mercaptopropionate) (PETMP, >95%) and Camphorquinone (CQ, 99%) were from Sigma Aldrich, USA. The methacrylate resins were 2,2-bis[4-(2-methacryloxyethoxy) phenyl]propane (BisEMA, from Esstech, Essington, PA) and Bisphenol A ethoxylate dimethacrylate (E-BisEMA, Mn~1700 from Sigma Aldrich). The resins were activated for visible light polymerization by the addition of 1 wt % CQ. The light source used to photocure the resins was assembled from a 5W light-emitting diode (LED) with its irradiance centered at 470 nm (High power

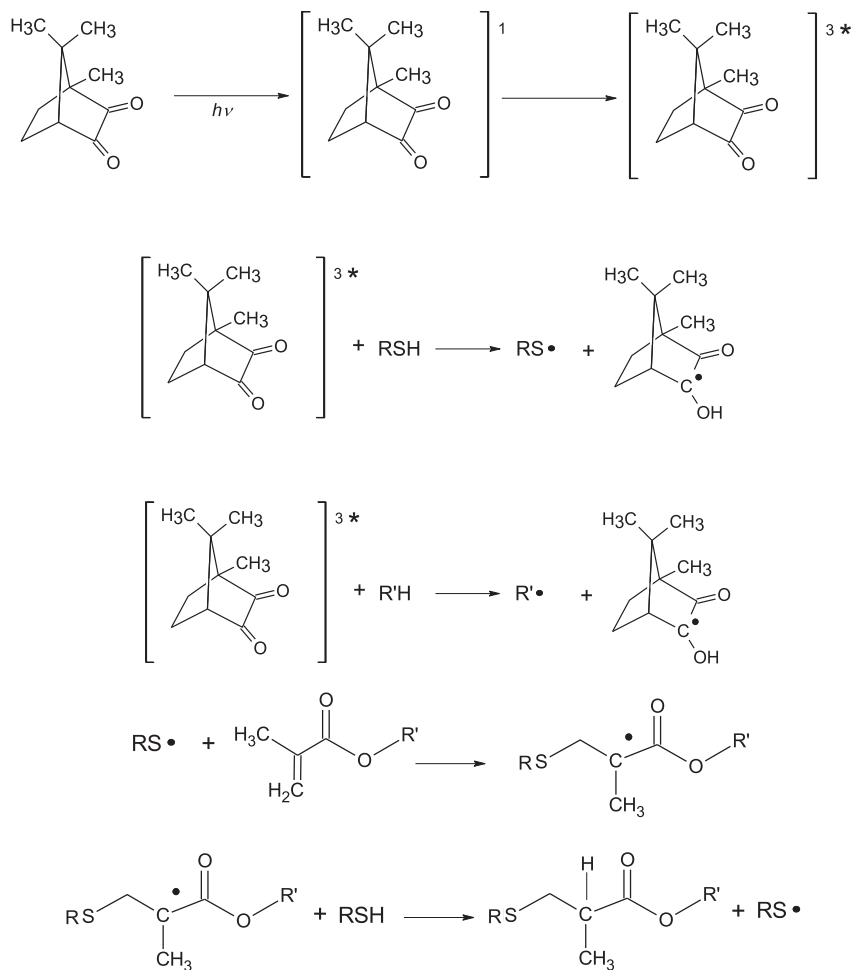
LED SML-LXL99USBC-TR/5 from Lumex, USA). The structure of the monomers and photoinitiators is shown in Scheme 1.

2.2. Photopolymerization

Measurements of conversion of methacrylate groups versus irradiation time were carried out at room temperature (20 °C) using near infrared spectroscopy (NIR) with a Nicolet 6700 Thermo Scientific. The NIR spectra were acquired over the range 4500–7000 cm^{-1} from 16 co-added scans at 2 cm^{-1} resolution. The resins were contained in a 10 mm diameter well constructed from a rubber gasket material sandwiched between two glass plates. The thickness of the samples was 3 mm. With the assembly positioned in a vertical position, the light source was placed in contact with the glass surface. The samples were irradiated at regular time intervals and the spectra were collected immediately after each exposure interval. These spectra were corrected with the background spectrum collected through an empty mold assembly fitted with only one glass slide to avoid internal reflectance patterns. The conversion of methacrylate groups was calculated from the decay of the absorption band located at 6165 cm^{-1} . Two replicates were used in the measurement of conversion. The peak corresponding to the S-H stretch of the thiol is located at 2568 cm^{-1} in the mid-IR region; however thiol absorbance was below detectable limits for the



Scheme 1. Structure of the monomers and photoinitiator used in this study.



Scheme 2. Photolysis of CQ under irradiation at 470 nm to produce initiating species for the polymerization of thiol-methacrylate.

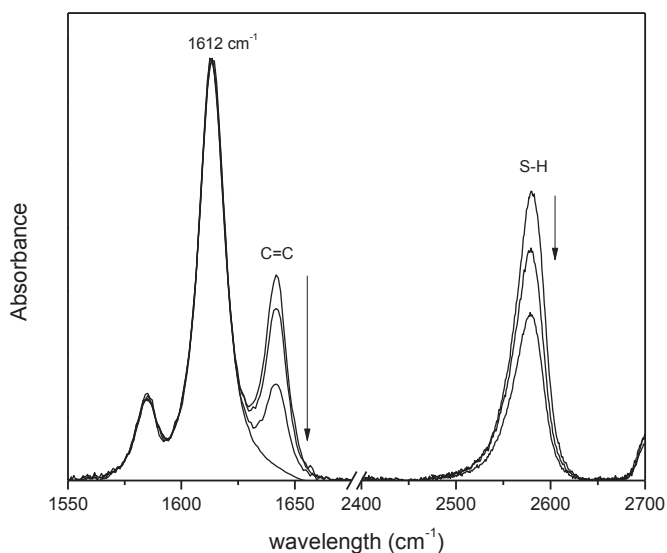


Fig. 1. Characteristic peaks in Raman spectra of thiol/methacrylate mixtures. The band at 2575 cm⁻¹ is assigned to the S-H group. The band representing the methacrylate double bond is located at 1642 cm⁻¹. The band at 1612 cm⁻¹, was selected as internal reference band.

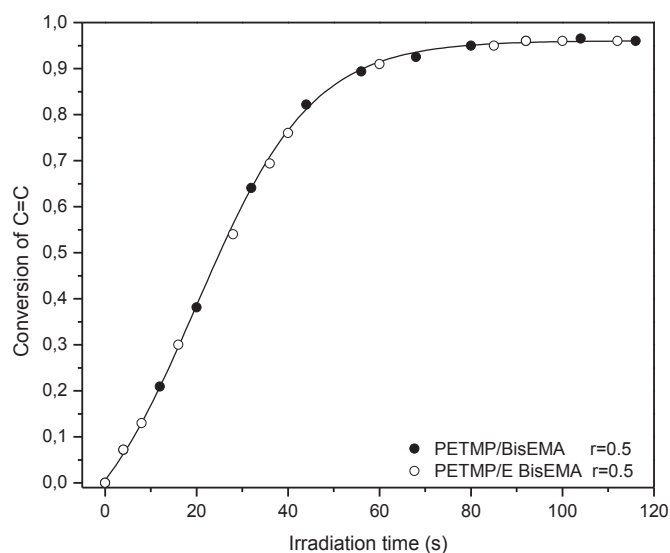


Fig. 2. Conversion of methacrylate groups versus irradiation time in PETMP-BisEMA and PETMP-EBisEMA. Samples containing 1 wt % CQ were irradiated at 470 nm. The specimens were 10-mm diameter and 3-mm thick. r is the thiol/methacrylate mol ratio.

Table 1

Conversion of thiol (SH) groups at 100% conversion of C=C groups in the prepared networks.

r is the PETMT:BisEMA or PETMT:EBisEMA molar ratio.

	SH conversion	T _g (°C)
PETMT-BisEMA r = 0.5	0.46	38
PETMP-BisEMA r = 1	0.26	8
PETMP-EBisEMA r = 0.5	0.48	-37
PETMP-EBisEMA r = 1	0.24	-41

formulation studied. Thus, the conversion of thiol groups was measured by Raman spectroscopy. These studies were performed at room temperature (c.a. 20 °C) with an Invia Reflex confocal Raman microprobe (Renishaw). A non-contact sampling objective (0.75 NA) with a 0.37 mm working distance was used and the excitation source was provided with the 785 nm emission line of a diode laser to the sample, thereby inducing the Raman scattering effect. The power of the laser was reduced to 10% to prevent damage by heating. At this power level, no thermal damage was observed. Raman spectra were taken averaging two acquisitions. The exposure time for each spectrum was 10 s. The spectra were collected in a Raman shift range between 400 and 1800 cm⁻¹ at a spectral resolution of 4 cm⁻¹. The irradiated spot on the sample surface was focused to a diameter of ~2 mm. Samples were sandwiched between a slide and a cover slip separated by a 1.5 mm thick rubber spacer with a 10 mm diameter circular hole. The circular hole of the assembly was filled with the reactive mixture and held using small clamps. Then, the assembly was introduced into the compartment of the Raman spectrometer for spectra collection. All spectra were collected at 300 mm below the surface of the cover-slip. Samples were irradiated at consecutive irradiation intervals of 4 s. After each exposure interval, the samples were transferred to the Raman sample compartment for the spectrum collection. The conversion profiles were calculated from the decay of the characteristic absorption band of each reactive group. The conversion of methacrylate C=C double bonds was followed by the decay of the band located at 1642 cm⁻¹, associated with the C=C stretching vibrations. The conversion of S-H group was assessed by the decay

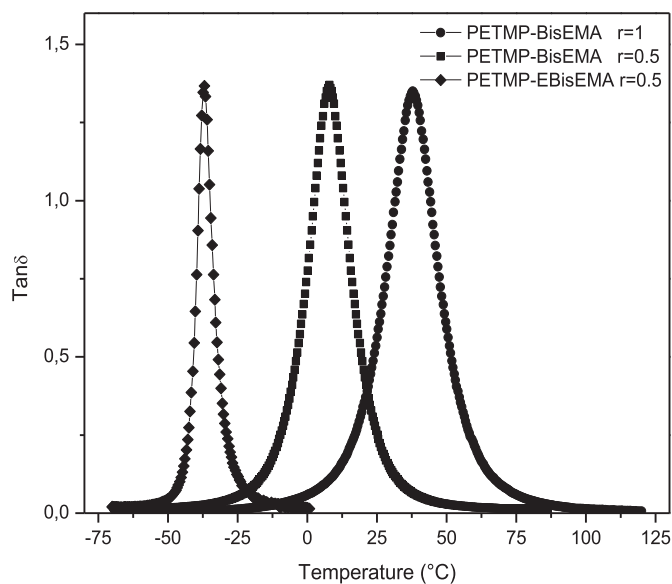


Fig. 3. Tan δ versus temperature for PETMP-BisEMA and PETMP-EBisEMA. r is the thiol/methacrylate mol ratio.

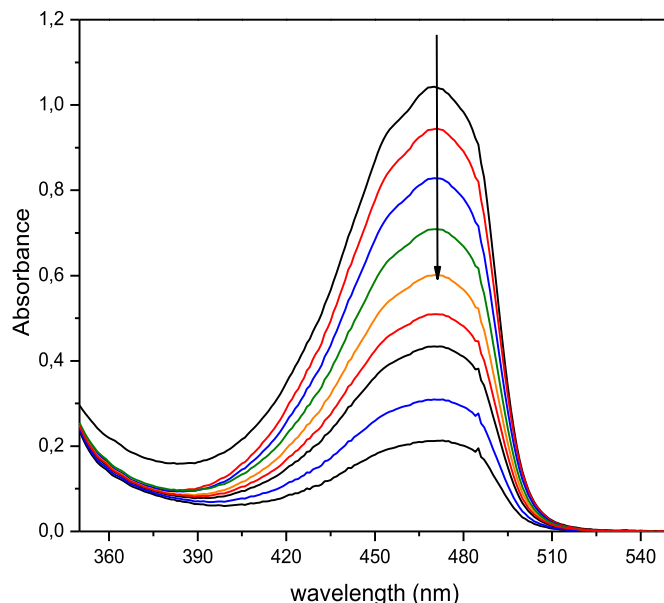


Fig. 4. Typical spectral changes showing the photobleaching of CQ. PETMP-BisEMA resin containing 1 wt % CQ during irradiation at 470 nm. The specimen was 10-mm diameter and 3-mm thick.

of the band at 2575 cm⁻¹. Two replicates of each of the resins were used in the measurement of conversion.

2.3. Characterization studies

The photolysis of CQ in thiol-methacrylate resins was followed using the changes in absorbance at the wavelength of its maximum absorption (470 nm). The absorption spectra were measured with an UV–vis spectrophotometer 1601 PC Shimadzu. The resins were contained in cells (3 mm) constructed from two quartz microscope slides separated by a PTFE gasket. An identical cell containing the monomer without CQ was used as the reference.

Changes in color in thiol-methacrylate networks when subjected to temperature changes were assessed by UV–visible spectroscopy. Samples photobleached previously were placed in the temperature-controlled sample holder of the UV–visible spectrophotometer. The absorbance at 470 nm was monitored as a function of time at 50, 70 and 110 °C.

Dynamic mechanical thermal analysis (DMTA) tests in torsion deformation mode were performed from -70 °C to 120 °C using the Rheometer MCR 301 (Anton Paar GmbH) equipped with fixture for rectangular bars (SRF92) and a temperature chamber (CTD600). Rectangular specimens with dimensions (ca. 40 ± 0.5 mm × 10 ± 0.05 mm × 1.5 ± 0.05 mm) (length × width × thickness) were tested. The frequency of oscillations was fixed at 1 Hz and the heating rate was of 5 °C/min. Previously, a strain sweep test in a representative sample was performed at 20 °C and 1 Hz in order to determine the linear viscoelastic range and select a strain value to apply in temperature sweeps. The selected strain value was 0.05%. A small axial force (around -0.5 N) was applied to the test specimen in order to maintain it under net tension.

3. Results and discussion

This section is divided into three parts concerned first with the polymerization of thiol-methacrylate networks photoinitiated with

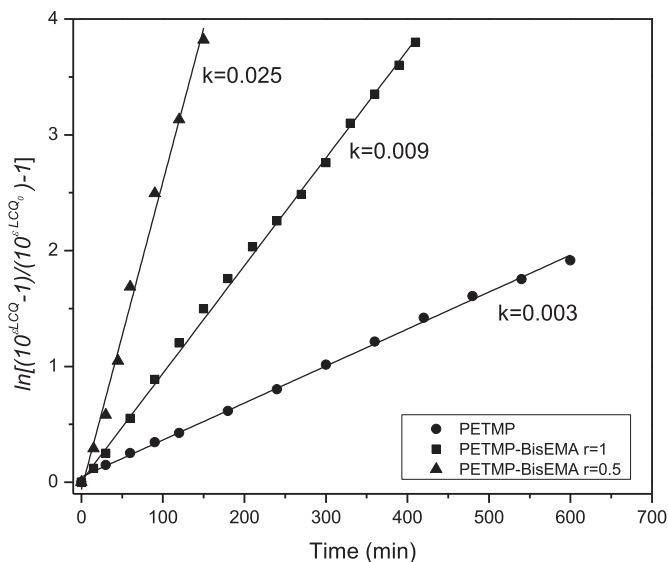


Fig. 5. Plots of Eq. (2) for PETMP-BisEMA, and PETMP. Resins containing 1 wt % were irradiated at 470 nm. The specimen was 10-mm diameter and 3-mm thick. The slopes of the lines (k) are shown for comparison.

CQ, followed by studies of photobleaching of CQ in the crosslinked networks. The last section shows results on change in color exhibited by the thiol-methacrylate networks during storage at different temperatures.

3.1. Photopolymerization

Thiol-methacrylate mixtures were photoactivated with 1 wt % of CQ and were photo polymerized with a 470-nm LED. CQ is excited under irradiation to the excited singlet state which converts to the reactive triplet state CQ^* via an efficient intersystem crossing [7]. Hydrogen abstraction from hydrogen donors such as alcohols, ethers and thiols by the CQ^* results in CQ-derived ketyl radicals and donor derived radicals [1,2,9]. Scheme 2 illustrates that the excitation of CQ followed by hydrogen transfer from the thiol results in a ketyl radical and a sulphur-centered thiyl radical [3,9,10]. Methacrylate monomers copolymerize with thiol functionalities through a mixed step-chain growth polymerization. In this polymerization mechanism (Scheme 2), while methacrylates readily homopolymerize through a chain growth mechanism, they are also capable of abstracting a hydrogen from the thiol monomers (chain transfer). Therefore, when a mixture of methacrylate and thiol monomers is polymerized, there are two possible reactions in which the methacrylate derived radical participates: propagation through another

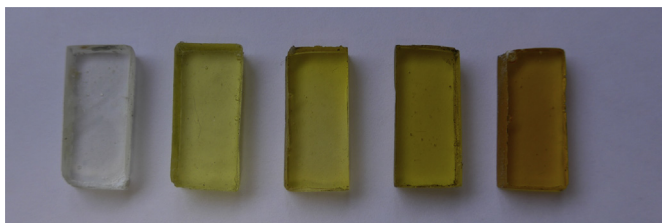


Fig. 6. Pictures of PETMP/BisEMA networks stored for 0, 10, 20, 30 and 90 min at 110 °C. The samples were first photobleached by irradiation at 470 nm for 10 min and then placed in the controlled temperature accessory of the UV–vis spectrophotometer.

methacrylate functional group and chain transfer to thiol. The thiyl radical, formed through the chain transfer step, further consumes the methacrylate groups by propagating through the C=C double bond. Termination occurs by radical-radical coupling.

The conversion values of C=C groups were calculated by NIR spectroscopy from the decay of the absorption band located at 6165 cm^{-1} . It is worth mentioning that the absorption band of the -SH group in the Mid-IR range (2572 cm^{-1}) had very low intensity; therefore, the conversion of thiol groups was measured by Raman spectroscopy. Fig. 1 shows representative spectra of a mixture thiol-methacrylate 1:2 mol ratio. The band located at 1642 cm^{-1} is associated with the C=C stretching vibrations. The band at 1612 cm^{-1} , which characterizes the aromatic ring, was selected as internal reference band. The conversion of thiol groups was calculated from the decay of the band located at 2575 cm^{-1} associated with the S-H stretching vibrations. Fig. 2 shows the conversion of C=C in PETMP-BisEMA mixtures photoactivated with CQ. It is seen that CQ is an efficient photoinitiator of the thiol-methacrylate systems studied in this research and confirms a good yield of initiating radicals. A great advantage of the use of CQ to initiate the polymerization of the thiol-methacrylate monomers shown in Scheme 1 is that no additional co-initiator is required. Table 1 shows the conversion of C=C and -SH groups in the prepared networks. The conversion of the methacrylate groups was 96% after 120 s of irradiation and it reached 100% after about 2 h in the dark due to the presence of free radical in the network after irradiation had ceased. While Raman spectra (Fig. 1) showed the disappearance of the band at 1642 cm^{-1} associated to the methacrylate groups, a fraction of thiol groups remained unreacted. This is attributed to homopolymerization of the methacrylate monomer. The ratio of homopolymerization through ene functional groups vs. thiol-ene addition has been studied by previous researchers [19–22]. Depending on the ene monomer used, the reaction proceeds with an equal consumption of both thiol and ene functional groups, or the ene functional group exhibits higher conversion than the thiol functional group because of homopolymerization. Bowman et al. found that for some thiol-ene systems the polymerization is representative of a true step growth polymerization

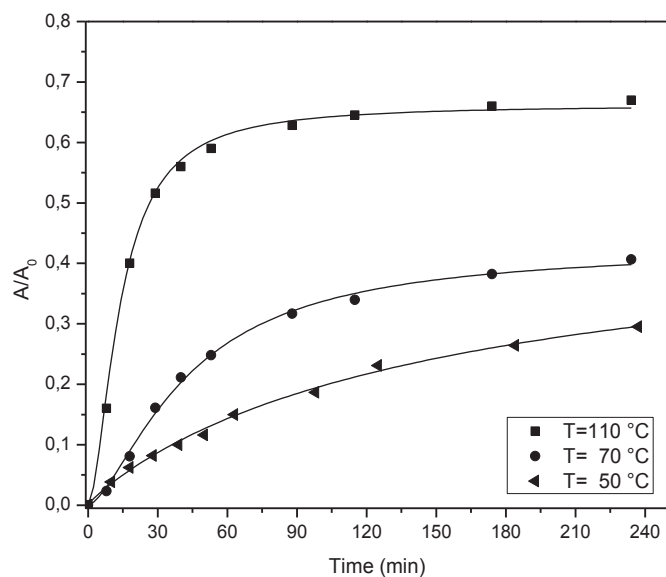


Fig. 7. Plots of absorbance at 470 nm versus time at different temperatures. 3 mm thick samples of PETMP:BisEMA at molar ratio equal to 0.5 were photobleached and then placed in the controlled temperature accessory of the UV–vis spectrophotometer.

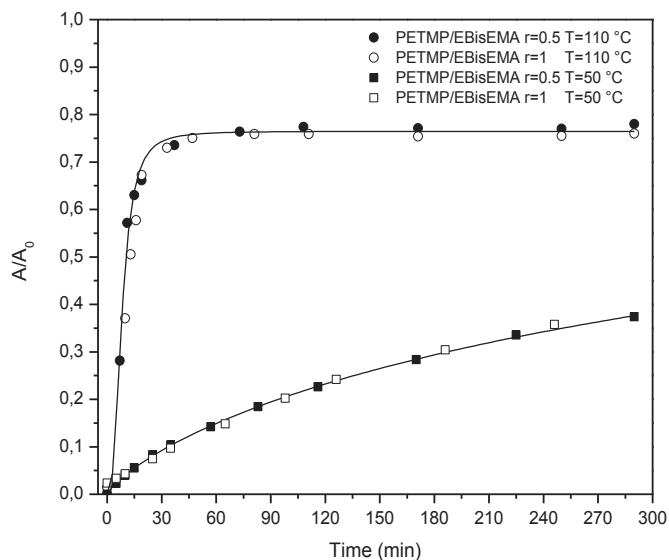
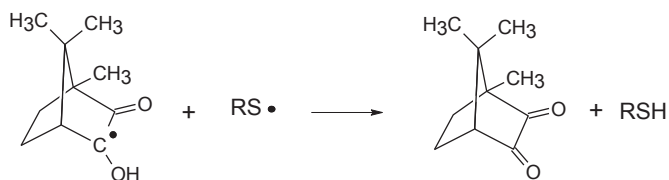


Fig. 8. Plots of absorbance at 470 nm versus time at different temperatures. 3 mm thick samples of PETMP:EBisEMA were photobleached and then placed in the controlled temperature accessory of the UV–vis spectrophotometer. No differences are observed between samples having $r = 1$ or $r = 0.5$.



Scheme 3. Regeneration of CQ and thiol by disproportionation of thiyl radical with ketyl radical.

with nearly equivalent consumption of the two functional groups [19,20]. Conversely for stoichiometric thiol–acrylate systems, the conversion of the acrylate functional groups was roughly twice that of the thiol functional groups [19,20]. Similarly, Lecamp et al. [21] showed that in a thiol–methacrylate system the methacrylate homopolymerization was faster than the thiol–ene addition so that the reaction was stopped because of the complete consumption of the methacrylate double bonds.

The glass transition temperature values (T_g) of the thiol–ene networks were assessed by dynamic mechanical thermal analysis (DMTA). Plots of $\tan \delta$ versus temperature and the T_g values are presented in Fig. 3 and Table 1 respectively. It is seen in Table 1 that the multifunctional PETMP in combination with BisEMA and EBisEMA results in polymeric networks with a wide variety of mechanical and physical properties. Both flexible elastomers and hard glassy polymers can be produced by varying the structure of the methacrylate monomer and the stoichiometry. The glass transition temperature is related to parameters such as the crosslink density, the average molecular weight between crosslinks, or the concentration of elastic chains. Table 1 shows that the T_g of BisEMA/PETMP systems is affected by its molar ratio (r). The lower T_g value in the BisEMA/PETMP when the thiol is in excess ($r = 1$) in comparison with the stoichiometric BisEMA/PETMP system ($r = 0.5$) is explained in terms of a lower concentration of elastic chains and the related lower crosslink density [23]. Concerning the E-BisEMA/PETMP system, its lower T_g values (Table 1) are explained in terms of a lower crosslinking density as a result of the higher molar mass

of E-BisEMA, and to the intrinsic flexibility of the chemical bonds present in E-BisEMA. Although the concentration of elastic chains is the most important structural factor affecting the glass transition temperature of rigid networks, its influence on flexible networks is less important [23]. This is possibly so because the relaxation of flexible networks preferentially occurs through “hinges” present in their chemical structures (i.e., the ether bonds of E-BisEMA), being much less affected by the concentration of crosslinking points. Therefore, the effect of changes in the molar ratio on T_g is much less significant for these networks.

Because of the presence of unreacted CQ, the thiol–methacrylate networks exhibited yellow color after polymerization. The photobleaching of the remaining CQ to give colorless polymers is described in the following section.

3.2. Photobleaching of CQ in thiol–methacrylate networks

During irradiation CQ absorbs visible light due to the n, π^* transition of the α -dicarbonyl chromophore to produce an excited triple state which interacts with oxidizable species, thus decomposing into colorless products [11,12]. Thus, the photodecomposition rate of CQ can be assessed by measuring the decrease in absorbance as a function of the irradiation time by UV–vis spectroscopy. Fig. 4 shows spectral changes during irradiation of CQ in PETMP–BisEMA showing a continuous decrease in absorbance with irradiation time. Irradiation of 3 mm thick samples containing 1 wt % CQ for less than 10 min resulted in a colorless network. The rate of decomposition of CQ is related to the quantum yield and the radiation absorbed [24]:

$$\frac{dCQ}{dt} = \frac{\Phi I_{abs}}{L} = \frac{\Phi I_0 (1 - e^{-\epsilon L CQ})}{L} \quad (1)$$

where CQ is the molar concentration of CQ, I_0 is the irradiance (in moles photons $s^{-1} cm^{-2}$) at the base of the sample, ϵ is the absorption coefficient of CQ, L is the thickness of the sample, and Φ , which is usually termed the quantum yield of the photoinitiator consumption, is the fraction of photoinitiator reduced per absorbed photon. Integrating Eq. (1) yields:

$$\ln \left[\frac{10^{\epsilon L CQ} - 1}{10^{\epsilon L CQ_0} - 1} \right] = -\Phi \epsilon I_0 t \quad (2)$$

where $(\Phi \epsilon I_0)$ is the CQ rate constant for the photobleaching of CQ and CQ_0 is the initial concentration of CQ. Typical plots of Eq. (2) are presented in Fig. 5. A satisfactory fit of experimental measurements of absorbance to a first-order kinetics for the decomposition of CQ in all the resins and polymers tested is observed. This trend is similar to that reported in previous studies on the photodecomposition of CQ/amine systems in methacrylate resins [7,11,12]. CQ is photobleached in the thiol–methacrylate mixtures due to the presence of labile hydrogen atoms in PETMP, BisEMA and EBisEMA. Hydrogen abstraction from thiol groups in PETMP and oxyethylene units in BisEMA and EBisEMA structures are competitively involved in the photoreduction of CQ. Consequently, the different rate constant values shown in Fig. 5 are attributed to the presence of different sources of abstractable hydrogen atoms.

It is worth mentioning that for a thick-section cure, it is advantageous to use photobleaching initiators in which light absorption by the initiator photoproducts is lower than that by the original photoinitiator molecule, thereby allowing more light to pass through the system [11,12,25]. UV–vis studies showed that photolysis products are transparent at the irradiating wavelengths, consequently the consumption of the CQ leads to an increase in light intensity in the underlying layers. The clean and rapid

photobleaching of CQ in the thiol-methacrylate networks makes it possible the photopolymerization of thick sections.

3.3. Color changes in photobleached networks

Thiol-methacrylate networks were photobleached at room temperature and then were immersed in the controlled temperature accessory of the UV–vis spectrophotometer. The thermal response of the samples was examined by monitoring the change in absorbance at 470 nm as a function of time and temperature. Fig. 6 is a picture showing typical changes in color in PETMP/BisEMA specimens under heating at 110 °C. Fig. 7 shows the increase in absorbance of CQ under heating of a thiol-methacrylate polymer having a molar ratio PETMP/BisEMA equal to 0.5. Fig. 8 shows the progress of the absorbance of CQ in PETMP/EBisEMA at molar ratios PETMP/EBisEMA equal to 0.5 and 1. As can be seen in Figs. 7–8 the rate of change in absorbance at 470 nm is markedly affected by the temperature of the medium. After 4 weeks at 20 ± 2 °C the absorbance at 470 nm in 3 mm thick specimens (not shown in Figs. 7–8) increased slowly to 0.2.

The changes in color observed during heating of thiol-methacrylate networks (Figs. 6–8) are explained in terms of reactions of hydrogen atom transfer of thiols with ketones [13]. It is well known that thiyl radicals participate in hydrogen atom transfer reactions which convert the ketyl radical intermediates back to starting materials, in competition with ketyl radicals coupling reactions to form pinacol [13]. Reactions of thiols with excited triplet benzophenones in 2-propanol and acetonitrile were studied by Cohen et al. [13]. In analogy with Benzophenone, Scheme 3 illustrates that the thiyl radical disproportionates with the ketyl radical thereby regenerating CQ and thiol. Regeneration of CQ was not observed in the absence of thiol. Samples of EBisEMA containing 1 wt% CQ were irradiated at 470 nm in order to produce complete photobleaching of CQ. Then, the colorless samples were placed in the controlled temperature accessory of the UV–vis spectrophotometer at 70 °C during 6 h. No change in color was observed during heating, which demonstrates that the ketyl radicals dimerized to form colorless pinacol and that reactions leading to recombination of CQ were absent. It is the remarkable property of thiyl radicals that participate in hydrogen transfer reactions which, in turn, result in regeneration of CQ from the initially photobleached thiol-methacrylate networks.

From results obtained in this study it emerges that the presence of reactions leading to recombination of CQ jeopardizes the long-term durability of films and bulk materials based on thiol-ene systems.

4. Conclusions

Thiol-methacrylate mixtures photoactivated with Camphorquinone (CQ) are efficiently polymerized by visible light irradiation. Photobleached thiol-methacrylate films show a marked yellowing over time as a result of CQ regeneration through hydrogen transfer reactions between thiyl radicals and ketyl radicals. The rate of regeneration of CQ is markedly affected by temperature in the range 20–110° C. The yellowing of thiol-methacrylate systems photoactivated with CQ jeopardizes the color stability of the derived coatings and bulk materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymdegradstab.2017.02.002>.

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