

# Use of curcumin and glycerol as an effective photoinitiating system in the polymerization of urethane dimethacrylate

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**Abstract** The objectives of this study were to verify the viability of the photoinitiating system using curcumin as a photoinitiator and glycerol as a coinitiator, to analyze the thermal and morphological features of the polymers produced, and finally evaluate the possibility of removing toxic Ethyl-*p*-dimethylaminobenzoate from the photoinitiating system. Curcumin, an orange–yellow dye extracted from the rhizoids of the plant *Curcuma longa*, is known to be a common photosensitizer, and the type II photoinitiating system consisting of a dye and an amine is long known to be effective. In recent years, the production of biodiesel has increased, and consequently, so has the generation of its main by-product, glycerol. Thus, it becomes necessary to study ways to incorporate glycerol into products. Using thermoanalytical methods (Thermogravimetry, Differential Thermal Analysis, and Differential Scanning Calorimetry), Middle Infrared Spectroscopy, and Scanning Electronic Microscopy, it was possible to assess the thermal and morphological characteristics of the polymers produced, and compare whether the presence or lack of tertiary amine, as well as the addition of different molar ratios of glycerol, had any significant impact on these characteristics. Results suggested that neither the

removal of tertiary amine nor the addition (in different proportions) of glycerol affected the thermal stability of the polymers. Also, removing the tertiary amine enhanced the total conversion degree of the polymers.

**Keywords** Photopolymerization · Curcumin · Thermal analysis · Glycerol · Conversion degree

## Introduction

In recent years, the area of polymer studies has become increasingly important to our society due to the broad range of materials that polymers can replace in the areas of engineering, pharmaceuticals, medicine, automobiles, and textiles [1]. In the case of photocurable polymers, that is, those that are hardened through photoinduction, for instance, polymers are useful as coatings, paints, adhesives, composites, holographic devices, and optical elements [2]. Equally important in this scenario are the economic and environmental advantages presented by polymers, particularly those synthesized from industrial wastes that would otherwise be left untreated, such as glycerol [1].

Photocuring techniques of polymerization are convenient because they provide fast curing, demand low energy, can be performed at room temperature, have low toxicity and are relatively inexpensive, when compared to the usual thermal methods of polymerization [1, 3]. In the 1970s, ultraviolet (UV) radiation began to be employed as a curing source in coating industries. On the following decades, however, there was an increasing urge to develop techniques of polymerization and photoinitiating systems (PIS) for use with visible light [2], as this spectrum is expected to be safer and more efficient than UV radiation [4]. Among the substances that work well as photoinitiators (PI) in the

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visible light spectrum are dyes and pigments [5]. Furthermore, the type II PIS of dye/amine has been widely acknowledged as an effective polymerization route [2]. As the area of polymer chemistry expands, it becomes necessary to search for novel and more efficient monomeric mixtures, and initiating systems [6].

Curcumin, an intensively yellow dye found in the rhizomes of *Curcuma longa*, has been previously reported as an effective PI for the copolymerization of styrene and methylmethacrylate [7]. Curcumin is also known to be an inexpensive multicolor photoinitiator with panchromatic light absorption [4, 8, 9]. The organic dye is nontoxic to the human health, being actually beneficial in a wide range of medical applications [10]. Considering what was exposed above, in the present study, curcumin was chosen as the photoinitiator in the polymerization of urethane dimethacrylate (UDMA), so that its functionality and effectiveness in a PIS could be further investigated.

In the Brazilian reality, glycerol (1,2,3-propanetriol) figures as one of the major by-products of the biodiesel production, with an estimate of 275,000 m<sup>3</sup> of glycerol produced in 2013 [11]. In addition, government incentive to the biodiesel production by means of the National Biodiesel Program (PNPB), which aims to increase the biodiesel percentage in fuels, will further increase the amount of glycerol by-product [11, 12]. Worldwide, the supply of glycerol exceeds its demand, resulting in economic and environmental concerns [11, 13]. The surplus of glycerol significantly reduces its market value and negatively affects the biodiesel production because of its disposal costs and the environmental impacts associated with its disposal [14].

Adding value to glycerol has become an attractive option in order to resolve the problems caused by its surplus. Applications of glycerol include production of chemicals and polymers [13–15]. In the field of polymers, glycerol can be applied as a monomer, both in the pure form and as glycerol carbonate and methacrylates, or as an initiator [15–18].

Acknowledging the need to add value to glycerol, this work sought to analyze the viability of employing it as a coinitiator in the presence of curcumin. Ethyl-*p*-dimethylaminobenzoate, a tertiary amine, is commonly used as a coinitiator with dimethacrylate monomer [4, 19]. However, tertiary amines are known to be toxic to the human health [20, 21]. In particular, a previous study conducted at the Thermal Analysis Laboratory at the Sao Paulo State University in Bauru, Brazil has shown that tertiary amines can be successfully substituted by polyalcohols (in specific glycerol), which are nontoxic, when camphorquinone is employed. Based on this finding, the study at hand aimed at verifying if this substitution would also be possible when curcumin is used *instead* of camphorquinone.

To verify the extent to which polymerization occurs when glycerol replaces tertiary amines in the presence of curcumin, Middle Infrared Spectroscopy (MIR) was used. Usual thermoanalytical methods, such as thermogravimetry (TG), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC), were conducted to compare not only the polymers without tertiary amines to those that contained it, but also to compare the impact of different molar ratios of glycerol in the polymer's thermal stability and other thermal events. Derivative Thermogravimetry (DTG) was applied to the TG curve to better observe the thermal events on the assays. Lastly, Scanning Electron Microscope (SEM) microscopy was performed to analyze the morphological aspects of the polymers.

## Experimental

### Preparation of the monomeric mixtures

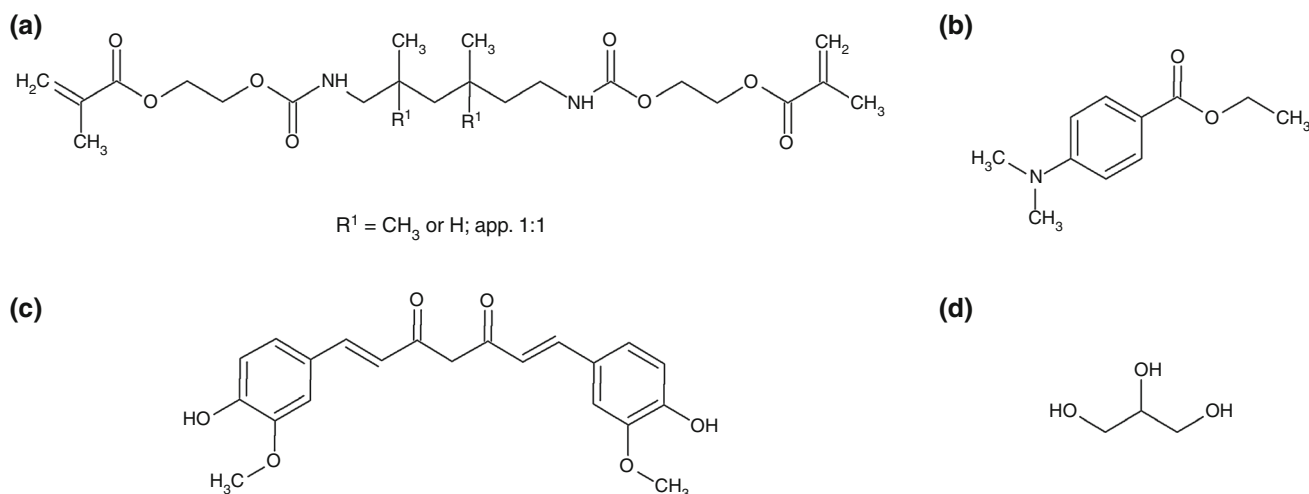
For the preparation of the monomeric mixtures, UDMA (Aldrich) was added to eight individual plastic containers, each with 0.01 mol of the monomer. Then, for two of these containers, 0.01 mol of glycerol (Merck) were added (1G); for other two, 0.03 mol were added (3G), while a third pair had 0.05 mol of glycerol added (5G). The remaining two containers had no glycerol added (NG). Afterward, these mixtures were separated into two categories (each with one of the NG, 1G, 3G, and 5G samples): Group I samples would have a tertiary amine, ethyl-*p*-dimethylaminobenzoate, as a part of their PIS, while Group II samples would not. Figure 1 shows the chemical structures of UDMA and glycerol.

### Preparation of the PIS

The photoinitiating solutions were prepared by dissolving curcumin (CUR) (Aldrich), and Ethyl-*p*-dimethylaminobenzoate were solubilized in acetone at a concentration of 20 mmol of each reagent and added to the reaction mixture in the proportion of 20% (mol) for Group I samples, whereas for Group II samples, no amine was incorporated. Figure 1 shows the chemical structures for CUR and the tertiary amine used in Group I polymers.

### Photopolymerization

The final mixtures containing monomers and PIS were photopolymerized using the light emission equipment D-2000 (DMC Ltd., São Carlos), which uses a LED to emit blue light in the range of 430–490 nm, as specified by the manufacturer. The mixtures were placed in a Teflon mold with 1.5 mm in depth and 3.0 mm in diameter, and were



**Fig. 1** Chemical structures of the substances used for the preparation of the monomeric mixtures: UDMA (a) and glycerol (d); and the substances used for the preparation of the PIS: curcumin (c) and ethyl-*p*-dimethylaminobenzoate (b)

polymerized for 400 s. After that, the cured polymers were washed with 70% alcohol to ensure all nonpolymerized monomers would be washed away, thus allowing for accurate characterization of the polymers while undergoing thermal analysis.

### Sample characterization

*Thermal analysis: Thermogravimetry (TG), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC)*

Simultaneous TG–DTA curves for each polymer were obtained using the thermal analysis system from Netzsch, model STA 449 F3. Approximately 10 mg of sample were measured and placed in a 70- $\mu\text{L}$   $\alpha$ -alumina open crucible. The parameters were set at a heating rate of 10  $^{\circ}\text{C min}^{-1}$ , and a flow rate of 50  $\text{mL min}^{-1}$  in a dry air atmosphere. The temperature range was from 25 to 800  $^{\circ}\text{C}$ .

DSC curves for each polymer were obtained with a Mettler-Toledo DSC1 Star<sup>e</sup> system. Approximately 10 mg of sample were placed in a 40  $\mu\text{L}$  closed aluminum crucible with perforated lid. The heating rate was of 10  $^{\circ}\text{C min}^{-1}$  and the flow rate was of 50  $\text{mL min}^{-1}$ . The environment used was dry air atmosphere. The cycle of heating/cooling began at room temperature (25  $^{\circ}\text{C}$ ). Then, the samples were cooled to  $-35$   $^{\circ}\text{C}$ , point at which an isothermal condition was kept for 10 min, and later heated to the temperature of thermal stability of the polymer with the smallest temperature of decomposition, which was 130  $^{\circ}\text{C}$ , as determined from TG curves. After that, the samples were cooled once again to  $-35$   $^{\circ}\text{C}$ , followed by an isotherm at this temperature, and heated to 130  $^{\circ}\text{C}$ . Finally, they were cooled back to room temperature.

### Middle Infrared Spectroscopy (MIR)

To calculate the degree of conversion for each polymer, a spectrophotometer from Bruker, model Vertex 70, was used. The equipment operated in the range 4000–400  $\text{cm}^{-1}$ . Monomeric mixtures were placed over the diamond crystal and polymerized while the transmittance ( $T\%$ ) of each sample was collected. Collection of data occurred every 10 s, and 60 measurements were taken for all samples. To quantify the degree of conversion for each sample Eq. 1, adapted from a formula vastly used in the literature [22–34], was used.

$$\text{DC (\%)} = \left[ 1 - \frac{T_{t=0}(\text{C}=\text{C})}{T_{t=x}(\text{C}=\text{C})} \right] \times (-1000) \quad (1)$$

Equation 1 provides the formula to calculate the percent of degree of conversion (DC) using the transmittance of double carbon bonds (C=C) present in the monomer.

Transmittance of the C=C bond can be observed near the wavenumber 1640  $\text{cm}^{-1}$ . At the initial time ( $t = 0$ ), a minimum of transmittance is observed at this wave number, as polymerization has not yet begun. At any other future time ( $t = x$ ), the transmittance is observed to increase, as polymerization takes place and double bonds are cleaved. With this input of data and applying Eq. 1, graphs of degree of conversion over time did plotted.

### Scanning electronic microscopy (SEM)

For the study of the polymers morphology, an EVO LS15 scanning electronic microscope from Zeiss was used. Preparation of the samples involved powdering them, placing them over a carbon adhesive, and finally plating them with gold. The voltage was set at 15 kV, and the

samples were magnified 300, 700, and 1000 times in a high vacuum environment ( $10^{-3}$  Pa).

## Results and discussion

### Photopolymerization

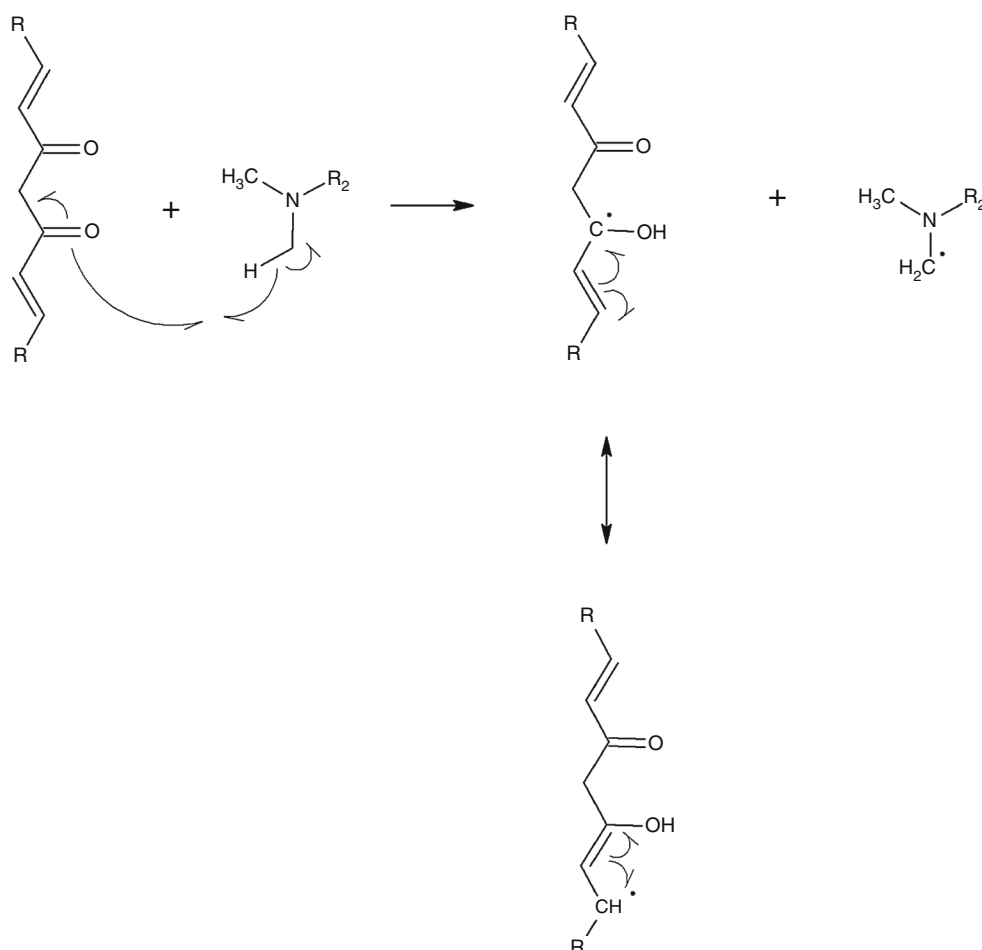
After polymerization, the fluid monomeric mixtures of all samples became thick and rigid, though still pliable. This hardening of the samples upon application of the blue light was the first indication that the samples tested were being polymerized. The mechanisms that explain how the polymerization occurred depend on whether the sample contained amine or not, and whether it contained glycerol or not. For Group I polymers, tertiary amine, Ethyl-*p*-dimethylaminobenzoate, was present in the PIS, and thus the type II dye/amine PIS could explain how polymerization took place. Curcumin, a photosensitizer, is excited by the blue light and extracts a hydrogen atom (H) from the tertiary amine, transforming it into a radical. Curcumin also had a radical in its structure; however, the resonance

structure that forms in it inhibits the colorant to continue the polymerization process on itself (Fig. 2). It is the radical structure in the tertiary amine ( $I_1$ ) that cleaves the double bonds (C=C) present on both extremities of the monomer's structure. After cleaving the double bonds, the  $I_1$  radical can bond with either the primary carbon, leaving the tertiary one with a radical (more stable), or the tertiary carbon, leaving the primary carbon with an unpaired electron (less stable), as seen in Fig. 3. This mechanism incorporates toxic tertiary amine into the polymers' structures [2, 4–7, 19].

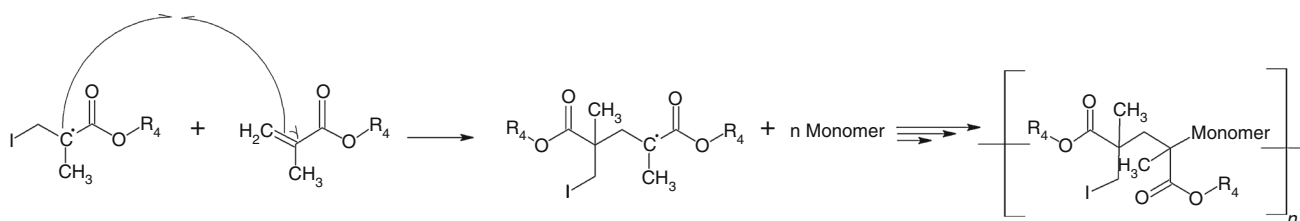
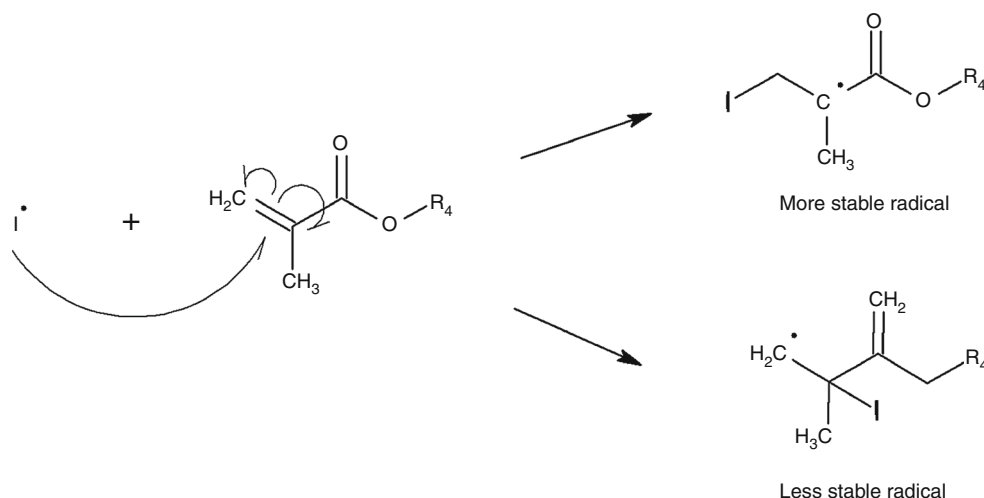
The radical left on the structure can then cleave another double bond, further propagating the polymerization reaction (Fig. 4). The polymerization terminates when the radical polymer reacts with another radical, or when the radical polymer reacts with another  $I_1$  radical.

For the polymerization of the Group I samples that contained glycerol, curcumin in an excited state could alternatively remove a hydrogen atom (H) from the alcohol, converting it into a radical ( $I_2$ ) that can cleave the double bond (C=C) on the monomer's structure, thus initiating the polymerization [19]. Again, the most stable form

**Fig. 2** Formation of  $I_1$  radical for the polymerization of all Group I samples



**Fig. 3** Initiation step: cleavage of the double carbon bond in the monomer's structure



**Fig. 4** Propagation step, where I could be any of the initiators mentioned

would be the one in which the radical  $I_2$  attacks the primary carbon of the monomer, leaving the tertiary one with the radical. This mechanism, shown in Fig. 5, incorporates glycerol on the polymers' final structures.

Propagation of this mechanism would involve radical species, either the  $I_2$  radical or the radicalized oligomer cleaving other double bonds. Termination would occur when two radical species, of any kind, react. The fact that polymers became increasingly whitish as the molar ratio of glycerol increased suggests that the polymerization mechanism changed as the alcohol was added. Hence, the mechanism presented in Fig. 5 is possibly a viable one.

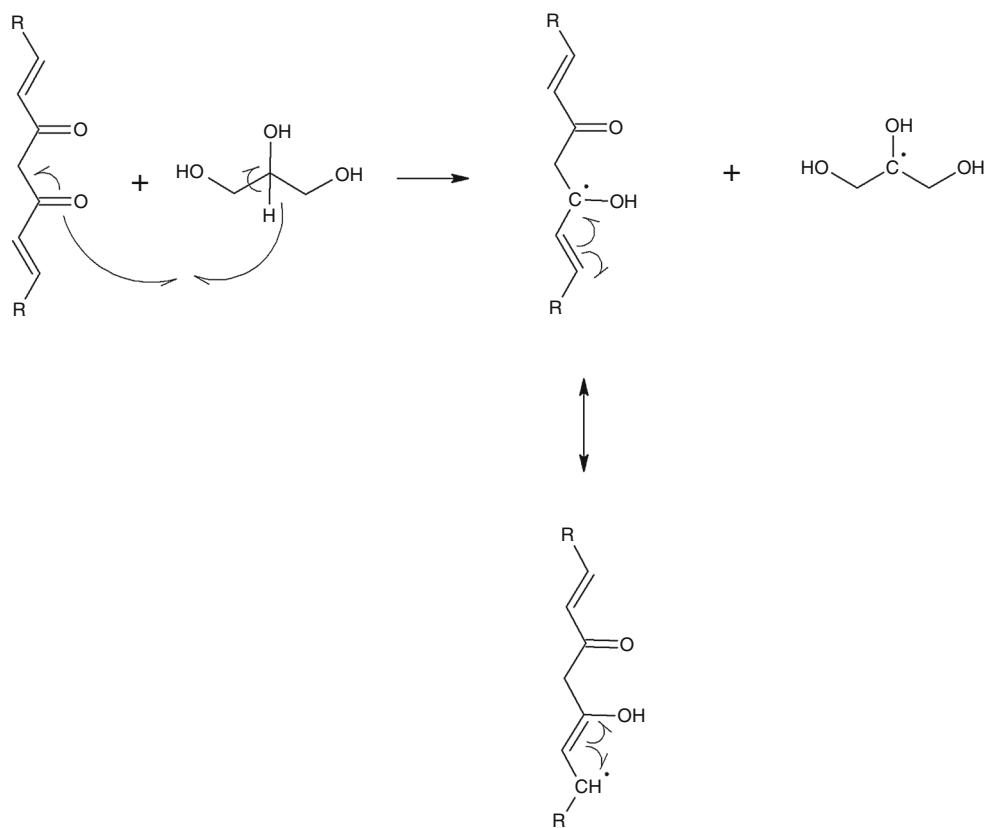
For Group II polymers that contained glycerol, the mechanism presented in Fig. 5 could be a viable one, since it does not depend on the tertiary amine in order to take place. As for the sample that had neither tertiary amine nor glycerol, photosensitized curcumin could form a radical directly on the monomeric structure (Fig. 6). This radical monomer would then carry on polymerization by cleaving double bonds ( $C=C$ ) on other monomers.

#### Thermal analysis: Thermogravimetry (TG), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC)

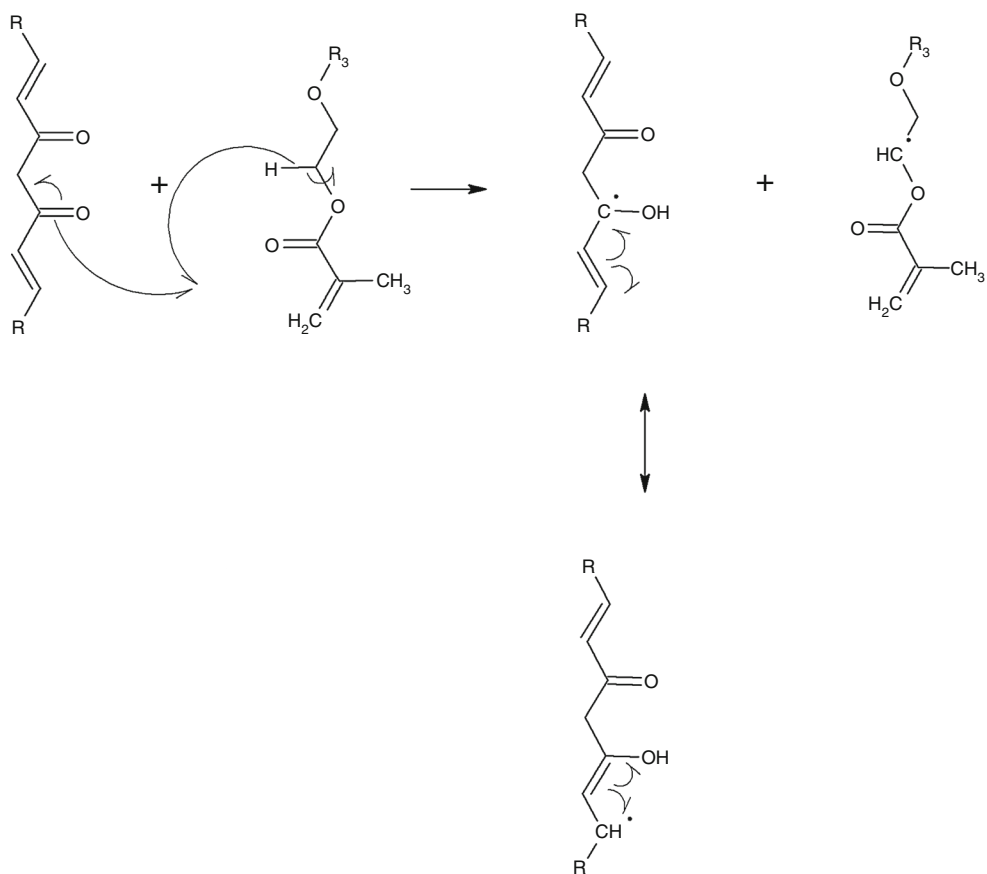
The TG–DTA curves of the polymers are presented simultaneously in Fig. 7 [Group I (a)–(d) and II (e)–(h)].

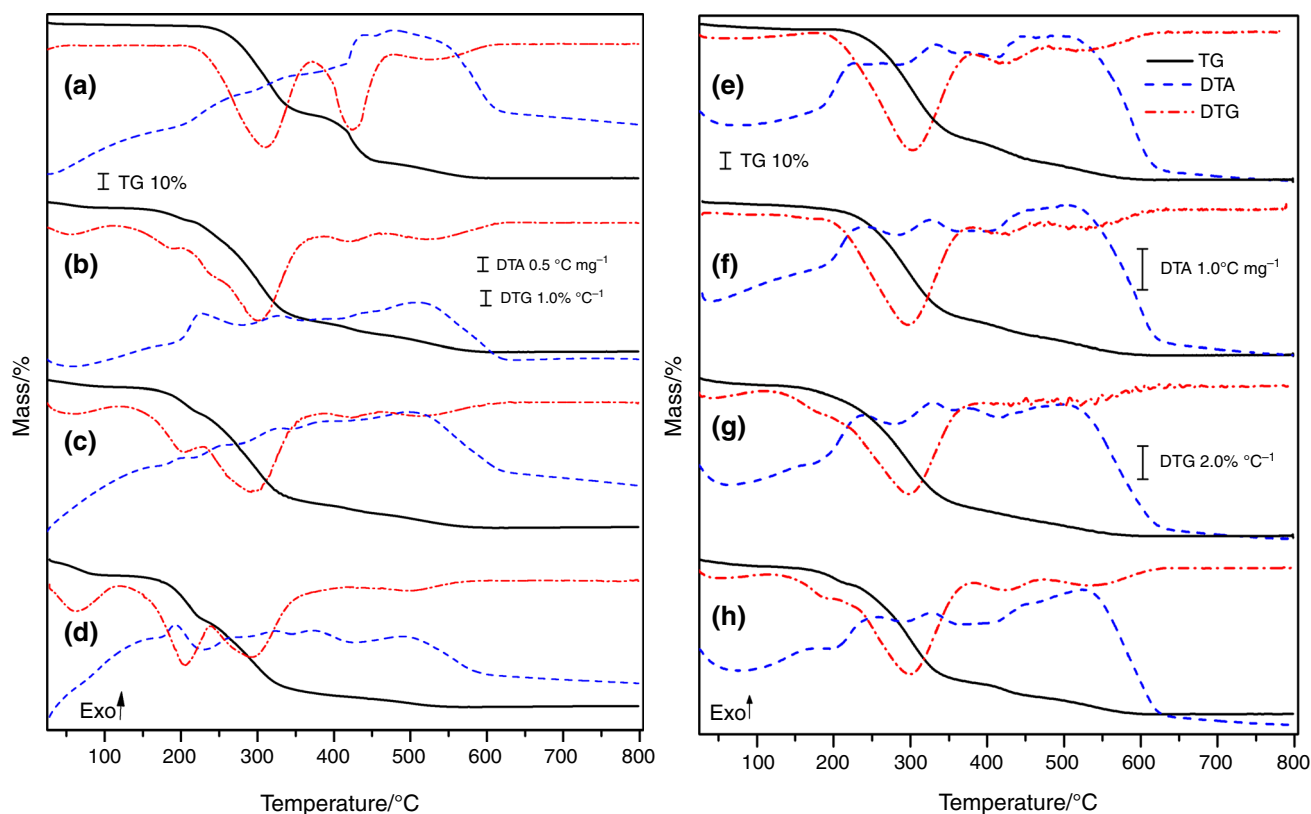
To better visualize the thermal events undertaken by each polymer, DTG was applied to TG curves and its curves are shown along with the TG–DTA curves. Table 1, shown below, summarizes these findings. Regardless of their PIS, all polymers exhibited four mass loss steps, namely volatilization of the solvent (1st Step), and thermal degradation (the remaining three steps). As seen in Table 1, these three steps of thermal degradation corresponded to regions in the DTA curve that were predominantly exothermic, as expected for a thermal degradation. The second step, however, was not as exothermic as the steps that followed it, which were mainly oxidative degradations. One of the reasons for this might be the volatilization of residual monomers, which is an endothermic process that could offset the exothermicity of the initial degradation. Another possible explanation is the depolymerization of the polymer, something that has been previously reported in methacrylate polymers [35]. No residual mass was expected to remain in the crucibles, as the carbonaceous residues from the second and third decomposition steps would in theory be completely oxidized in the fourth step. However, experimentally it was determined that the average residual mass was 2.76%. The average thermal stability for Group I (1G, 3G and 5G) polymers was 144.3 °C, with a standard deviation (SD) of 3.91, and that for Group II polymers (1G, 3G and 5G), 148.0 °C, with a SD of 3.95. The relatively small values of

**Fig. 5** Formation of the I radical for the polymerization of Groups I and II samples that contain glycerol



**Fig. 6** Formation of alternative radicals for the polymerization of Group II polymer without glycerol





**Fig. 7** TG and DTA curves for Groups I [(a) NG, (b) 1G, (c) 3G, (d) 5G] and II [(e) NG, (f) 1G, (g) 3G, (h) 5G] polymers

SD indicate that the addition of glycerol, even in different ratios, had little effect on the thermal stability of the samples. Also, the removal of tertiary amine for Group II polymers (1G, 3G and 5G) did not affect their thermal stability considerably when compared to the stability of Group I polymers (1G, 3G and 5G). Based on these findings, it can be suggested that the thermal stability of these polymers does not depend on their PIS.

In regard to the maximum rate of degradation of the second step, measured as the steepest negative inclination in the TG curve for the corresponding temperature range, or alternatively as the minimum point for the DTG curve, it was observed that removing the tertiary amine generally increased the rate, with the exception of the 3G polymers. It is important to note that even though Group II polymers achieved a greater maximum rate of decomposition, this did not translate to significantly lower thermal stabilities. The maximum degradation rates for Group I polymers were 0.737, 0.691, 0.639, and 0.623  $\text{mg min}^{-1}$ , for NG, 1G, 3G, and 5G polymers, respectively. Therefore, the addition of glycerol tended to decrease this rate in the presence of amine. For Group II polymers this same tendency was not clearly observed, as the rates went from 0.774  $\text{mg min}^{-1}$  for the NG sample, to 0.723, 0.602, and 0.736  $\text{mg min}^{-1}$ , for the 1G, 3G, and 5G samples,

respectively. Interestingly, the maximum rate for both Groups I and II polymers happened at around 290.0 °C, with the exception of Group I's 5G polymer's which was considerably lower (206.7 °C).

Due to the similarity of DSC curves for Group I and II polymers only curves for NG Group I are shown in Fig. 8. The DSC curves for other systems can be viewed in supplementary material (Figures S1–S7). For both Group I and II polymers no thermal events could be discerned for either the cooling or heating stages. In the first heating stage, however, endothermic events (average range between 11 and 125 °C for Group I polymers and 16–111 °C for Group II polymers) were observed. These events, which represent the volatilization of the solvent used (acetone), can be seen with greater or less intensity on the samples.

This finding indicates that the polymers created are thermoset, that is, are irreversibly set when heated, and cannot be fused when reheated. The chemical structure of the monomer employed, shown in Fig. 1a, has two double carbon bonds (C=C), which could lead to the formation of a reticulate, rather than linear, structure on the polymer. This reticulate configuration handicaps the fusion of the polymer, making it a thermoset, in agreement with the finding reported previously [36]. Considering that the polymers are thermoset, as indicated by the DSC analysis,



**Table 1** Summary of polymers' mass loss events ( $\Delta m/\%$ ). The temperature range in which each event occurred ( $\theta$  °C), and the temperature peak ( $T_p/^\circ\text{C}$ ) are also given

Polymers	1st step	2nd step	3rd step	4th step	5th step
Group I polymers <sup>a</sup>					
NG					
$\theta$ °C	25.0–121.2	215.7–371.8	371.8–467.5	467.5–625.6	–
$\Delta m/\%$	–3.56	–70.27	–16.12	–10.05	–
$T_p/^\circ\text{C}$	–	221.0–274.0 <sup>b</sup> , 308.0–360.6 <sup>b</sup>	420.0–459.9 <sup>b</sup>	511.9 $\uparrow$	–
1G					
$\theta$ °C	25.0–106.7	148.4–219.3	219.3–378.3	378.3–468.2	468.2–635.3
$\Delta m/\%$	–4.34	–8.88	–66.32	–8.76	–10.70
$T_p/^\circ\text{C}$	–	–	226.1 $\uparrow$ , 328.9 $\uparrow$	366.9–407.9 <sup>b</sup> 417.1–452.1 <sup>b</sup>	509.0 $\uparrow$
3G					
$\theta$ °C	25.0–115.1	143.9–228.5	228.5–366.1	366.1–462.8	462.8 – 637.1
$\Delta m/\%$	–4.53	–17.26	–58.04	–9.85	–8.62
$T_p/^\circ\text{C}$	–	180.1–224.8 <sup>b</sup>	231.3–280.6 <sup>b</sup> 288.0–347.5 <sup>b</sup>	363.3–440.5 <sup>b</sup>	496.5 $\uparrow$
5G					
$\theta$ °C	25.0–103.9	140.6–223.5	223.5–391.9	391.9–599.3	–
$\Delta m/\%$	–10.41	–26.36	–49.93	–7.74	–
$T_p/^\circ\text{C}$	–	192.5 $\uparrow$	245.2–286.5 <sup>b</sup> , 322.8 $\uparrow$ , 371.2 $\uparrow$	490.1 $\uparrow$	–
Group II polymers					
NG					
$\theta$ °C	25.0–108.9	198.6–379.8	379.8–464.7	464.7–621.7	–
$\Delta m/\%$	–2.81	–69.46	–12.95	–11.79	–
$T_p/^\circ\text{C}$	–	227.2 $\uparrow$ , 333.4 $\uparrow$	365.5–413.2 <sup>b</sup> 417.0–465.6 <sup>b</sup>	471.4–631.6 <sup>b</sup>	–
1G					
$\theta$ °C	25.0–106.2	152.1–364.2	364.2–446.2	446.2–627.1	–
$\Delta m/\%$	–2.26	–68.14	–10.37	–13.40	–
$T_p/^\circ\text{C}$	–	241.7 $\uparrow$ , 326.9 $\uparrow$	368.1–407.1 <sup>b</sup> 414.7–452.8 <sup>b</sup>	447.5–622.3 <sup>b</sup>	–
3G					
$\theta$ °C	25.0–99.8	147.8–217.9	217.9–366.7	366.7–631.0	–
$\Delta m/\%$	–4.39	–9.91	–64.89	–19.28	–
$T_p/^\circ\text{C}$	–	–	239.2 $\uparrow$ , 329.5 $\uparrow$ , 361.8–410.8 <sup>b</sup>	361.8–410.8 <sup>b</sup> 422.3–631.5 <sup>b</sup>	–
5G					
$\theta$ °C	25.0–107.0	144.2–224.3	224.3–381.7	381.7–470.4	470.4–628.8
$\Delta m/\%$	–4.15	–10.90	–61.58	–9.25	–10.66
$T_p/^\circ\text{C}$	–	144.2–203.3 <sup>b</sup>	212.8–291.1 <sup>b</sup> , 327.3 $\uparrow$	411.2–458.9 <sup>b</sup>	524.5 $\uparrow$

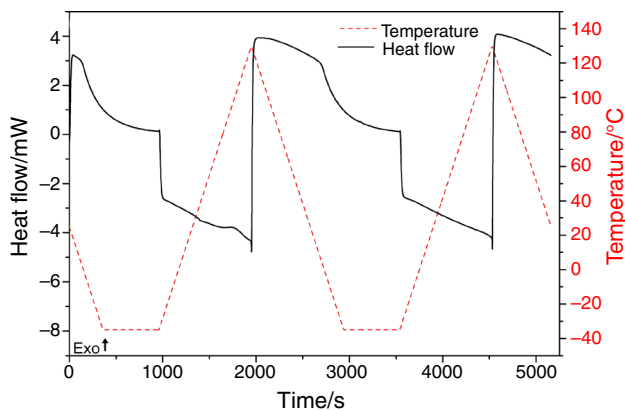
<sup>a</sup> Exothermic;  $\uparrow$  = Exo up<sup>b</sup> Group I polymers are those with tertiary amine, and Group II, those without it. The traces NG, 1G, 3G, and 5G indicate polymers in which the molar ratio of glycerol to UDMA is 0:1, 1:1, 3:1, and 5:1, respectively

and have a thermal stability around 118 °C, a probable application of the polymers would be in photocell sensors. Some commercial models [37] have operation temperatures that range from 0 to 75 °C, which is within the stability of the polymers. A previous study suggested that it is

possible to use dyes as sensitizers in photocells. Since the samples remained yellowish after polymerization, they still contained some unreacted curcumin (when in resonance curcumin does not reflect yellow). This remaining curcumin in the polymeric matrix could then possibly enable



the polymer to be employed as the organic component in the photocell structure. Additional luminescence and conductivity tests would have to be performed for each polymer to verify its applicability.

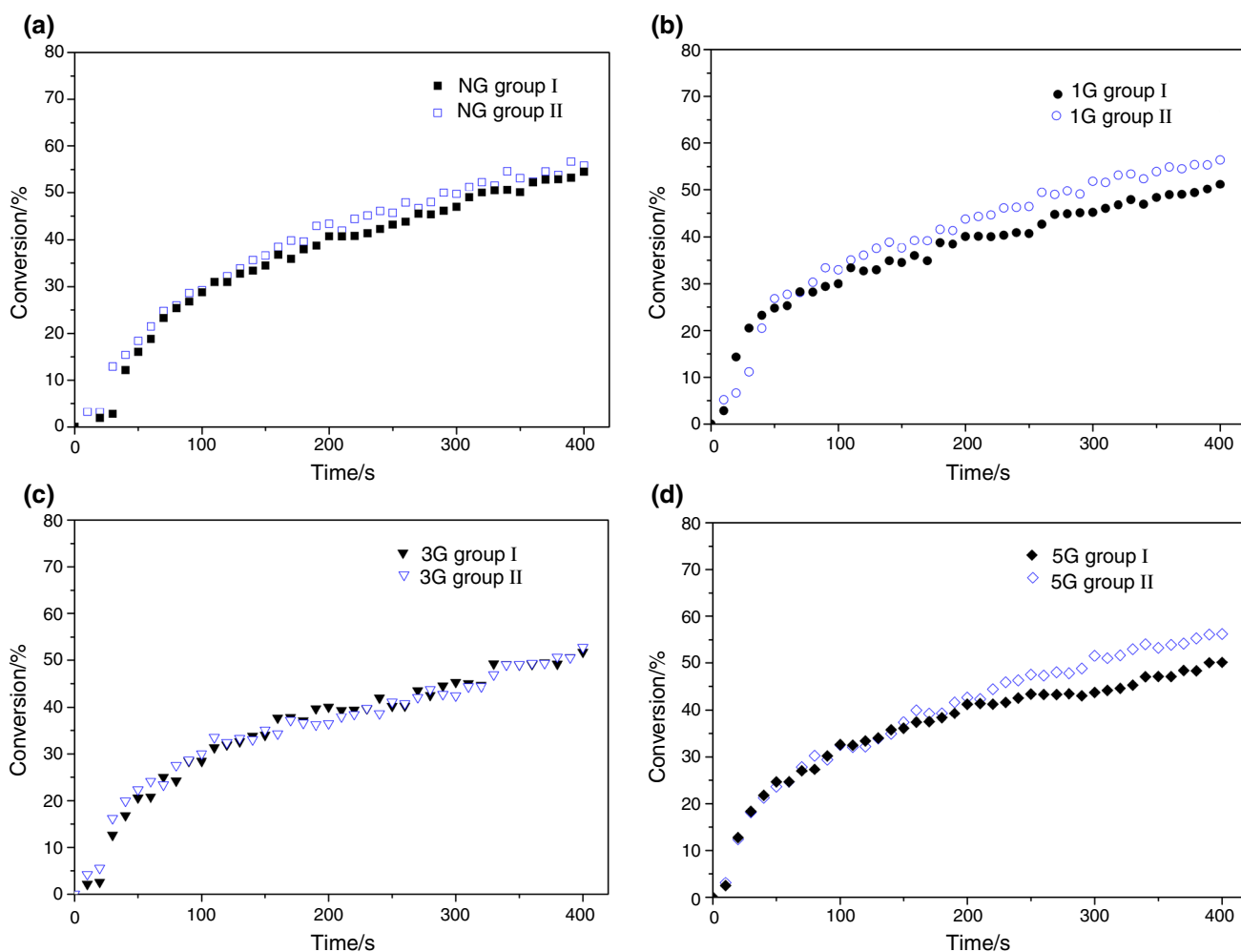


**Fig. 8** DSC curves for Group I NG polymer

### Middle Infrared Spectroscopy (MIR)

Using MIR and Eq. 1, it was possible to produce conversion degree curves for all polymers. Each of the four curves shown in Fig. 9 depicts the conversion degree for two polymers (one from Group I and the other from Group II) that have the same molar ratio of glycerol. In this way, it is possible to compare the effect that the tertiary amine or lack thereof has on the polymers' degree of polymerization. Table 2 shows the degree of conversion for all eight monomeric mixtures studied, for different moments during polymerization.

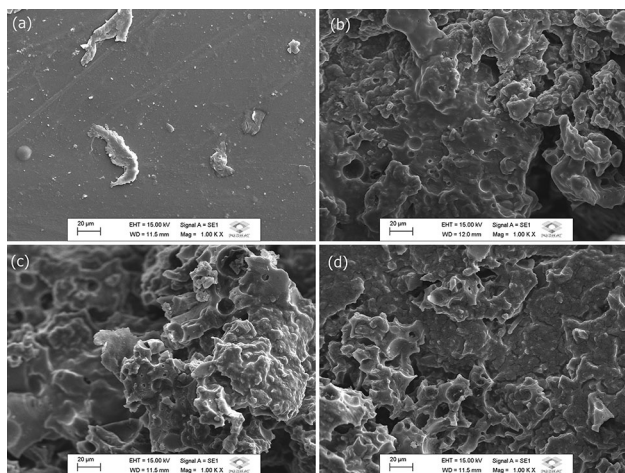
As seen in Table 2, all Group II polymers had a greater total conversion degree than their corresponding Group I polymers. Experiments have shown that Group II's percent increase in total conversion degree compared to that of Group I was of 2.39, 10.14, 1.89, and 12.15%, for NG, 1G, 3G, and 5G polymers, respectively. With the exception of 3G polymers, the addition of increasingly greater amounts of glycerol has widened the conversion gap between



**Fig. 9** Conversion degree curves for Groups I and II polymers without glycerol (a); with 1G (b); 3G (c); and 5G (d)

**Table 2** Conversion degree (%) for Group I and II polymers during polymerization

Polymers	10 s	20 s	50 s	100 s	200 s	400 s
Group I						
NG	0.74	1.91	16.06	28.80	40.71	54.50
1G	2.81	14.30	20.47	30.00	40.07	51.20
3G	2.13	2.54	20.63	28.49	40.06	51.80
5G	2.48	12.73	24.63	32.54	41.19	50.13
Group II						
NG	3.21	3.14	18.41	29.23	43.36	55.80
1G	5.19	6.64	23.25	32.99	43.76	56.39
3G	4.25	5.59	22.36	30.03	36.46	52.78
5G	3.09	12.39	23.63	32.54	42.62	56.22

**Fig. 10** SEM analysis with magnification  $\times 1000$  for Group I polymers: NG polymer (a); 1G polymer (b); 3G polymer (c), and 5G polymer (d)

Groups I and II samples. Figure 9 corroborates this idea. In Fig. 9a–c, the data points for Group II polymers (not shaded) are above those for Group I polymers (shaded) in the last measurements.

Another aspect to notice is that for Group I polymers the addition of glycerol reduced the total conversion, whereas the opposite was observed for Group II polymers. For Group I, the sample that did not contain glycerol (NG) had a total conversion of 54.50%, while the total conversion for polymers 1G, 3G, and 5G were observed to decrease: 51.20, 51.80, and 50.13%, respectively. In contrast, for Group II, the NG sample had a total conversion of 55.80%, and the final conversions for 1G and 5G polymers exceeded that of the NG polymer: 56.39 and 56.22%. The 3G polymer, however, deviated from this trend, and the total conversion decreased to 52.78%.

When it came to starting polymerization, overall, Group II polymers did not present an absolute advantage over Group I polymers. For NG and 3G samples, the polymers without tertiary amine (Group II polymers) had a significantly greater conversion degree after 20 s than those with the amine. In fact, a percent increase of 64.40 and 120.08% was observed for NG and 3G, respectively. For the 1G samples, the one containing tertiary amine had more than twice the initial conversion of the sample without amine. For the 5G samples, both polymers (with and without amine) had a similar initial conversion, namely of 12.73% for Group I's sample and 12.39% for Group II's sample.

Overall, Group II polymers had a better performance than Group I polymers, with greater total conversion degree for all samples, and a relative advantage when initializing the polymerization process. The significance of these findings is that the removal of tertiary amine, a substance that is known to be toxic to the human organism, from the PIS has optimized the polymerization process, by increasing the initial reaction speed of some polymers (NG and 3G) and augmenting the final conversion degree for all polymers. The tertiary amine radical is very reactive, and this could cause it to dimerize more easily than the glycerol radical. Dimerization of the radical extinguishes its initiating ability, and this could possibly explain why Group I polymers had a smaller conversion degree than Group II's. One last thing to consider is that the incorporation of glycerol to Group II polymers favored the polymerization of these samples by increasing the final conversion degree for all polymers, with the exception of the 3G polymer, while the addition of glycerol to Group I polymers worked against polymerization, reducing the final conversion degree. Thus, in the system where tertiary amine is not present (Group II), glycerol, a substance that needs to be removed from the environment, can be incorporated without hindering the system's polymerization process.

### Scanning electronic microscopy (SEM)

In regard to the morphology of the polymers, it can be said that for Group I polymers, the addition of glycerol imparted to the polymers a porous surface, whereas that of the NG polymer was particularly smooth. The number of pores and also their average diameter increased as the molar ratio of glycerol increased. Therefore, the incorporation of glycerol into the polymers' structures and the porosity that results can make the polymers applicable as filtration materials. The molar ratio of glycerol could be further investigated to yield filtering materials that can winnow out differently sized particles. Images of Group I polymers' morphology amplified 1000 times are shown in Fig. 10. SEM for Group II polymers had the same morphological behavior to that

observed for Group I polymers, due to the similarity the images can be viewed in supplementary material (Figure S8).

## Conclusions

The use of curcumin as a photoinitiator in the polymerization of UDMA proved to be effective, with an average conversion of 53.60% for all eight polymers studied. Another advantage is that curcumin is not toxic to humans and animals when compared to other commercial initiators. Polymers from Group II had, on average, a greater total conversion degree than did polymers from Group I. This shows that removing the tertiary amine from the PIS enhanced the polymerization process. Additionally, the removal of toxic tertiary amine did not affect the thermal stability of the samples. Likewise, the addition of glycerol onto the polymers' composition did not alter their thermal stability. Therefore, it is possible to add value to glycerol by incorporating it to the PIS for the photopolymerization of UDMA. The SEM analysis shown that the glycerol acted not only as a coinitiator on the samples that contained it, but also as a plasticizer, since it clearly altered the morphology of 1G, 3G, and 5G polymers. The alterations engendered by the addition of glycerol make the polymers potentially applicable as filtering materials.

All polymers analyzed are thermoset, and all contained some extent of unreacted curcumin. The presence of unreacted curcumin is evinced by the coloration of the polymers, which is slightly yellowish, with decreasing intensity as the molar ratio of glycerol added increased. Both of these factors would possibly allow the polymers to be used as the organic source in photocells. In the future, it is suggested that the applications proposed by this study be tested. In addition, verifying the reasons why the 3G polymer from Group II did not present the same increasing tendency in regard to total conversion degree as did the 1G and 5G polymers is encouraged.

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