Synthesis and characterization of triptycene type cross-linker and its use in photoinduced curing applications

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ABSTRACT

A novel triptycene type diacrylate cross-linker, triptycene hydroquinone diacrylate (THDA) was synthesized from the reaction of triptycene hydroquinone with acryloyl chloride and characterized. The photocuring behaviour and the reaction kinetics of the synthesized cross-linker were investigated by means of photo-differential scanning calorimetry (photo-DSC) experiments. Formulations containing monofunctional (meth)acrylate monomers, namely glycidyl methacrylate (GMA), 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), and 2-ethylhexyl methacrylate (EHMA), cross-linker, THDA and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator were irradiated. A conventional cross-linker without triptycene unit such as hydroquinone diacrylate (HDA) was used under the same conditions for comparison. The effects of the structure of the monofunctional monomer and triptycene moiety on the photopolymerization kinetics were evaluated and discussed.

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1. Introduction

The UV-induced polymerization of multifunctional monomers has been widely applied in various industrial fields mainly in the production of films, inks, and coatings on a range of substrates including paper, metal, and wood [1]. Moreover, variety of high-tech applications of photopolymerizations, such as the coating of optical fibers and the fabrication of printed circuit boards has been developed. This technology allows obtaining a quick transformation of a liquid monomer into a solid polymer having tailored physical–chemical and mechanical properties. The main advantage on using UV-radiation, to initiate the chain reaction, lies in the very high polymerization rates that can be reached under intense illumination, so that the liquid to solid change takes place within a fraction of a second [2–6]. Besides, the solvent- free formulation makes UV-curing an environmental friendly technique. Another distinct feature of light induced reaction is that polymerization will occur only in the illuminated areas, thus allowing complex relief patterns to be produced after solvent developments [7].

Multifunctional acrylates and methacrylates are the most extensively used monomers for photopolymerization [8–15]. Photopolymerizations of these multifunctional monomers were studied in detail by using various techniques such as differential scanning calorimeter, dilatometry, dynamic mechanical testing, and real-time IR spectroscopy [10,11,14,16–18]. Their polymerization is complicated due to several reasons such as; auto-acceleration, autodeceleration, incomplete conversion, trapping of radicals in networks, physical inhomogeneities in networks, and unequal reactivities of different functional groups [8,10,14,19–21]. Monomer structure (the type and the number of functional groups present, the distance and flexibility between functional groups, hydrogen bonding and liquid crystallinity, and the presence of heteroatoms) has significant effects on the reactivity of monomers [3,9,14,22–26]. Therefore, it is necessary to understand the effect of monomer structure on the photopolymerization reactivities.

Iptycenes are widely used in many applications because of their specific three dimensional scaffold in which arene rings are held together with a bicyclo[2,2,2]octane central unit [27]. In cases iptycene units are used in conjugated polymers, such polymers exhibit high stability and amplified fluorescent character playing a crucial role as a sensor for nitroaromatic explosives at gaseous phase [28]. Iptycenes are also utilized to produce low dielectric constant polymeric materials having improved thermal stability and high T_g [29]. Paddlewheel configuration of the three arene blocks brings high degree of internal molecular free volume (IMFV) to iptycene structure [30]. In LC (liquid crystal) applications by means of minimization IMFV, more proper and compact alignment of crystals occurs, because of decrease in aspect ratio (length/width) [31]. Discretely incorporation of triptycene (the simplest

iptycene) units into polymer backbone may enhance lateral interactions by virtue of occupation of triptycene cavities with neighboring polymer chain in order to minimize the free energy arose from IMFV of triptycene [32]. If a strain applies on polymer, adjacent chain begins to thread into the cavity till two opposite triptycene units meet and interlock (Scheme 1).

In this work, we herein report synthesis, characterization and photocuring behavior of a new cross-linker based on triptycene molecule. Photopolymerizations were performed with the formulations containing triptycene hydroquinone diacrylate (THDA) together with monofunctional monomers glycidyl methacrylate (GMA), 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), and 2-ethylhexyl methacrylate (EHMA), by using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoinitiator. Comparative photopolymerization studies were also performed by using structurally similar cross-linker, hydroquinone diacrylate (HDA) which does not possess triptycene unit. Photopolymerization kinetics was analyzed for different compositions of monofunctional monomers and cross-linked agents by using photo-differential scanning calorimeter (photo-DSC). Each monofunctional monomer was reacted with varied percentages of a difunctional monomer HDA and THDA respectively to observe the influence of triptycene based cross-linker on rate of polymerization.

2. Experimental

2.1. Materials

Glycidyl methacrylate (2,3-epoxypropyl methacrylate) (GMA, 97%, Aldrich), 2-hydroxyethyl acrylate (HEA, 96%, Aldrich), 2-hydroxyethyl methacrylate (HEMA, 97%, Aldrich) and 2-ethylhexyl methacrylate (EHMA, 98%, Aldrich) were used as purchased. 2.2-Dimethoxy-2-phenylacetophenone (DMPA, 99%, Acros) was also used without any additional treatment. Acryloyl chloride (96%, Aldrich), hydroquinone (≥98%, Fluka), hydrogen bromide (HBr, Merck) and quinone (≥98%, Fluka) were utilized without any purification. Anthracene (≥96%, Fluka) was purified via recrystallization from xylene.

2.2. Characterization

The ^{1}H NMR (250 MHz) solution spectra were recorded on a Bruker NMR Spectrometer using CDCl$_3$ with TMS as an internal reference. Fourier transform infrared (FT-IR) spectra were obtained using a Perkin–Elmer FT-IR Spectrum One spectrometer.

2.3. Preparation of cross-linkers

2.3.1. Synthesis of hydroquinone diacrylate (HDA)
Although hydroquinone diacrylate (HDA) is commercially available, it was simply synthesized by acylation of hydroquinone with acryloyl chloride [33]. (m.p. 87–88 °C) IR (cm^{-1}): 3000 (s, C–H),
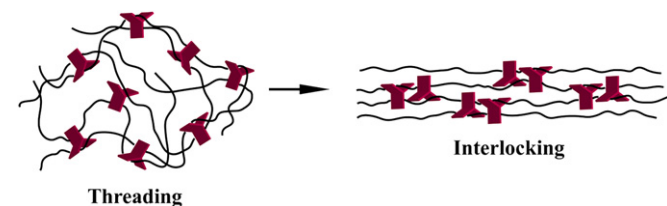
Scheme 1. Schematic representation of the steric interactions induced by triptycene units.

1740 (s, C=O), 1634, 1482 cm^{-1} (s, C=C). ^{1}H NMR: δ 7.1 (4H), 6.5–6.4 (2H), 6.1–6.0 (2H), 5.8–5.7 (2H).

2.3.2. Synthesis of triptycene hydroquinone (TH)
TH was prepared by following synthesis route described in the literature [27] At first step, anthracene (10 gr, 5.6×10^{-2} mol) recrystallized from xylene and dissolved with quinone (7 gr, 6.5×10^{-2} mol) in 150 mL xylene. Diels–Alder reaction taken placed in 250 mL round bottom flask at reflux temperature under nitrogen atm for 3 h. Pale yellow crystals collected and recrystallized from xylene. At second step 10 gr product of first step dissolved in 70 mL glacial acetic acid and 4 drops of 40% HBr was added to solution. Reaction was carried on for an hour at reflux temperature. TH crystals filtered and collected with high yield (93%). IR (cm^{-1}): 3400 (s, O–H), 3060 (s, C–H), 1635, 1480 (s, C=C), 1034 (b, C–H). ^{1}H NMR: δ 8.5 (2H), 7.3 (4H), 6.9 (4H), 6.3 (2H), 5.7 (2H).

2.3.3. Synthesis of triptycene hyroquinone diacrylate (THDA)
TH (2 gr, 7×10^{-3} mol) and 4 mL triethyl amine dissolved in 50 mL THF using 100 mL two necked flask. Acryloyl chloride (1.3 mL, 1.6×10^{-2} mol) added drop by drop and suddenly transparency of reaction mixture turns to cloudy white color. Reaction was continued for 3 h at room temperature under nitrogen atmosphere. Reaction mixture was taken to a separatory funnel. After work up, organic phase separated and THDA purified by using column chromatography. THDA was obtained as white crystals (mp: 195–197 °C) with 70% yield. IR (cm^{-1}): 3060 (s, C–H), 1736 (s, C=O), 1635, 1480 (s, C=C), 1034 (b, C–H). ^{1}H NMR: δ 7.3 (4H), 7.0 (4H), 6.8 (2H), 6.7 (2H), 6.6–6.4 (2H), 6.2–6.0 (2H), 5.4 (2H). Anal. Calc. for C$_{26}$H$_{18}$O$_4$: C, 78.67; H, 4.57. Found: C, 78.99; H, 4.30.

### 2.4. Preparation of formulations

Basically, formulations were prepared to investigate the effect of various components in the photopolymerizations. Molar percentage of cross-linkers in formulations was adjusted with respect to solubility of THDA in monofunctional monomers. For all formulations 1.0% molar ratio of DMPA was used. A typical formulation was prepared as follows: 1.0 mol% DMPA (0.020 g, 1.8 wt%), 1.0 mol% THDA (0.030 g, 2.7 wt%) and 98 mol% GMA (1.08 g, 95.5 wt%). The molar percentage of cross-linker was between 1 and 3, and the amount of monomer was altered accordingly so that the total molar percentage was 100.

2.5. Photocalorimetry (Photo-DSC)

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by means of a modified Perkin–Elmer Diamond DSC equipped with a high pressure mercury arc lamp. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 18.4 mW cm^{-2} by a UV radiometer covering broad UV range. The mass of the samples was 3 mg and the measurements were carried out in an isothermal mode at 30 °C under a nitrogen flow of 20 mL min^{-1}. The reaction heat liberated in the polymerization was directly proportional to the number of acrylate or methacrylate double bonds reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate or methacrylate groups (C) or the extent of the reaction was determined according to Eq. (1):

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \tag{1}$$

where ΔH_t is the reaction heat evolved at time t and $\Delta H_0^{\text{theory}}$ is the theoretical heat for complete conversion. $\Delta H_0^{\text{theory}} = 86$ kJ mol^{-1}
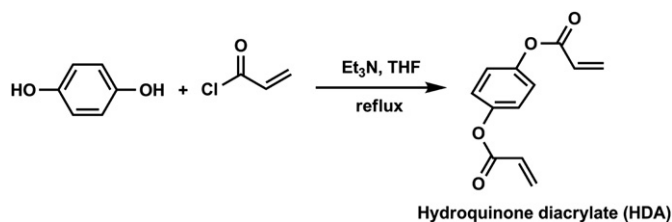
Scheme 2. Synthesis of hydroquinone diacrylate (HDA).

for an acrylic double bond and $\Delta H_0^{\text{theory}} = 56$ kJ mol^{-1} for a meth-acrylic double bond [25]. The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by Eq. (2):

$$R_p = dC/dt = (dH/dt)/\Delta H_0^{\text{theory}} \qquad (2)$$

2.6. Real-time infrared spectroscopy (RT-IR)

Real-time infrared measurements were performed on a Perkin–Elmer FT-IR Spectrum One-B spectrometer. The UV-radiation from a high pressure mercury arc lamp was introduced by a flexible optical fiber. The end of the optical fiber was positioned at a distance of 5 cm from the KBr disc to ensure the whole disc was irradiated by the UV light. The intensity of the light was measured as 16.8 mW cm^{-2} by a UV radiometer covering broad UV range. Measurements were performed in air. The spectra were recorded with a time resolution of 2.1 s and with a spectral resolution of 2 cm^{-1}. The curing reaction was followed by monitoring the decay of the intensity of the peaks at 810 cm^{-1} (alkene twisting vibration) by integrating the peak areas.

3. Results and discussion

The cross-linkers were synthesized by the acylation of the respective hydroquinone compounds with acryloyl chloride (Schemes 2 and 3).

Although hydroquinone diacrylate (HDA) was obtained by recrystallization from hexane, purification of triptycene hydroqui-none diacrylate (THDA) required chromatography on silica gel using hexane/ethyl acetate (9/1) mixtures. HDA and THDA were obtained as white solids with melting points of 87–88 °C and 195–197 °C, respectively. The reaction yields were 90% and 70%

after purification and the structures of cross-linkers were confirmed by spectral analysis. ^{1}H NMR spectra of HDA, TH and THDA are shown in Fig. 1.

The ^{1}H NMR spectrum of HDA showed characteristic peaks for acrylic protons at 5.6 ppm, 6.0 ppm and 6.4 ppm, and aromatic protons at 7.1 ppm. In the spectrum of THDA, while the signal at 8.9 ppm corresponding to –OH protons of the precursor TH completely disappeared, new signals originating from acrylic protons appeared at 6.1 ppm, 6.5 ppm and 6.7 ppm.

Photopolymerizations of several monomers using either HDA or THDA were followed by DSC under identical conditions of temperature (30 °C) and UV light intensity (18.4 mW cm^{-2}). Sche-matic representation of photoinduced cross-linking is shown in Scheme 4. As can be seen triptycene units are chemically incor-porated to the network after photocuring process.

Fig. 2 shows the time dependence of the polymerization rate (R_p) in GMA photopolymerization using HDA and THDA as cross-linkers.

It is well known that either cross-linking or linear polymer formation reaction takes place under control of diffusion. The main difference between the two systems is the suppression of trans-lational motions (center of polymer coils diffusion). In the cross-linking systems, such motions decrease drastically due to the network formation even at prior stages of the polymerization. This way molecular movement is restricted to only segmental diffusion and propagation of radical sites. As the cross-linking proceeds further, segmental diffusion is also suppressed and propagation becomes much faster, and dominates the reaction until maximum rate of polymerization is attained where the termination process becomes diffusion controlled [34]. On these bases, for both HDA and THDA with higher concentration of cross-linkers faster auto-accelerations and higher maximum rate of polymerization were achieved. As a consequence, the plateau regions observed before the onset of auto-acceleration became narrower especially in the case of the formulation containing 3 mol% THDA. Notably, THDA provides much faster rates then HDA (Fig. 3). The reaction proceeds under control of diffusion in earlier stages of the polymerization with THDA than HDA due to more pronounced lack of mobility of the coils. In other words, as THDA possess denticulate structure, both entangled or cross-linked ones induce formation of rough (barbed) coil networks provoking less translational diffusion then smoother ones formed with HDA.

As can be seen in Fig. 4, the effect of either cross-linker on the overall conversion is rather insignificant. Photopolymerizations
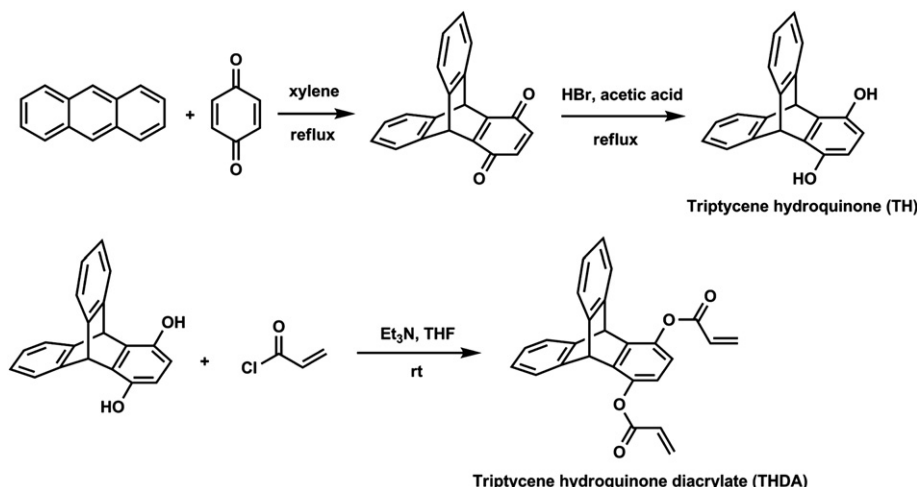
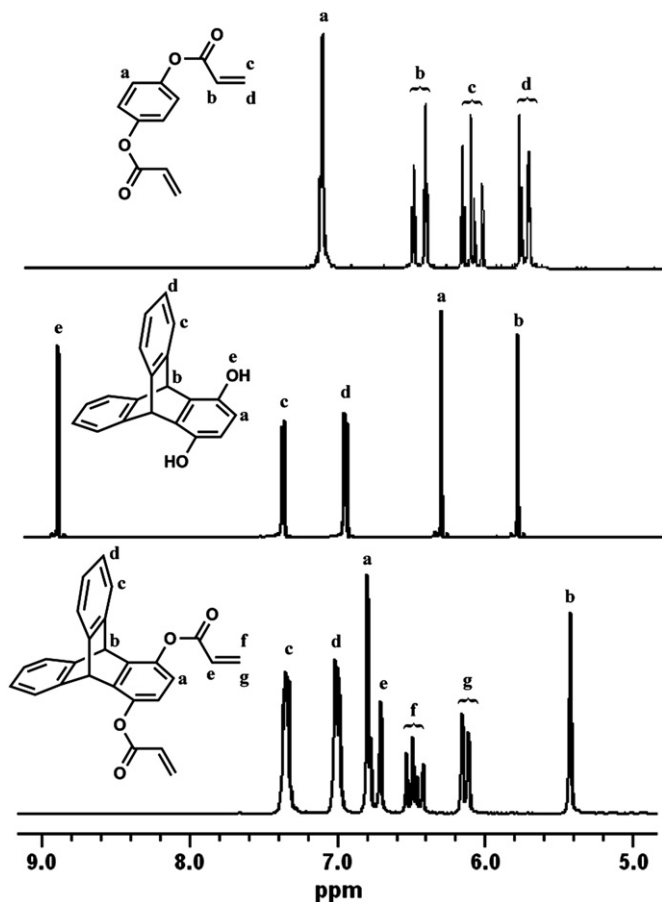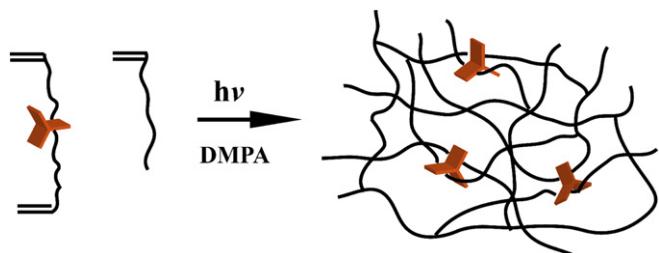**Scheme 3.** Synthesis of triptycene hydroquinone diacrylate (THDA).

Fig. 1. ^{1}H NMR spectra of hydroquinone diacrylate (HDA), triptycene hydroquinone (TH) and triptycene hydroquinone diacrylate (THDA) in CDCl$_3$.

with higher cross-linker contents could not be performed due to the limited solubility of THDA in the monomer, GMA.

Real-time infrared spectroscopy (RT-IR) is another excellent method used for investigation of kinteics of photopolymerization [35]. Therefore, we have also followed the photopolymerization of GMA using either HDA or THDA by RT-IR (Fig. 5). No significant effect was observed of either cross-linker for the overall conversion which was also in agreement with the previous findings using photo-DSC. However, the lower conversions attained from RT-IR measurements could be attributed to the inhibition effect of oxygen [36]. It is well known that the radicals generated during UV exposure are very sensitive to the presence of oxygen. The oxygen interrupts the chain formation resulting in lower conversions.

Apart from GMA, photopolymerizations with two other hydroxyl containing monofunctional monomers, namely 2-

Scheme 4. Schematic representation of photoinduced cross-linking of vinyl monomers using triptycene hydroquinone diacrylate (THDA).
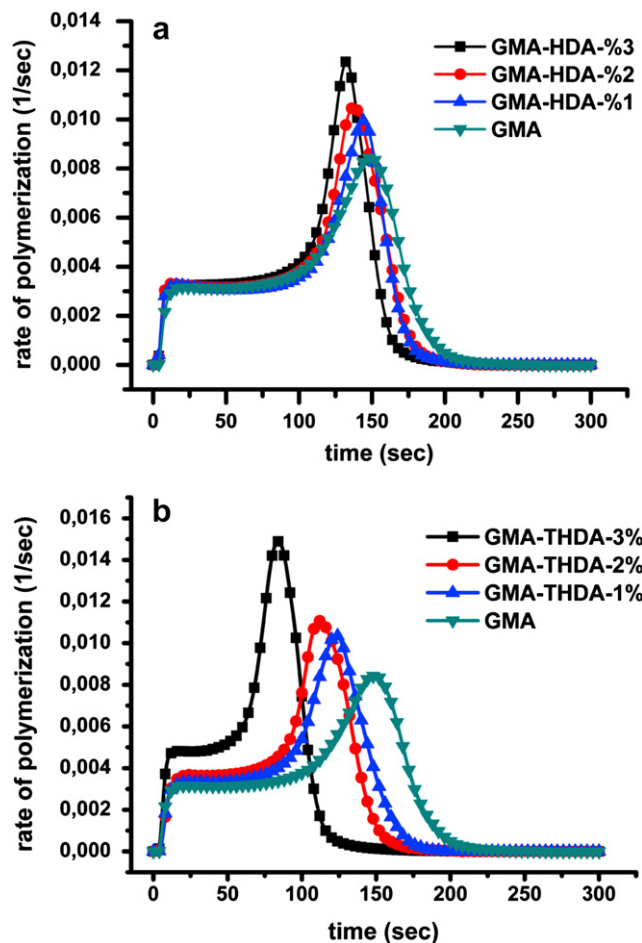

Fig. 2. Rate of photopolymerization of GMA in the presence of cross-linkers, HDA (a) and THDA (b) as a function of irradiation time at 30 °C.

hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) were also conducted. They were deliberately selected so as to investigate the photopolymerization behavior of monomers with simple alkyl chains with hydroxyl groups that are expected to form hydrogen bonding that effects the curing. However, the solubility of the cross-linker in these monomers was even lower than in GMA and therefore, photolymerizations of formulations containing up to
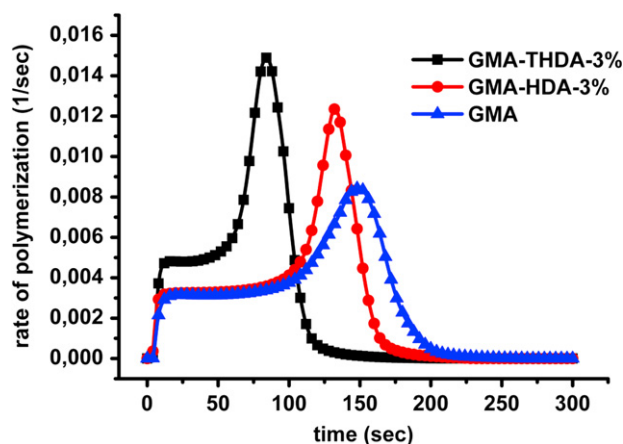

Fig. 3. Rate of photoinitiated polymerization of GMA in the absence and presence of cross-linkers, HDA and THDA.
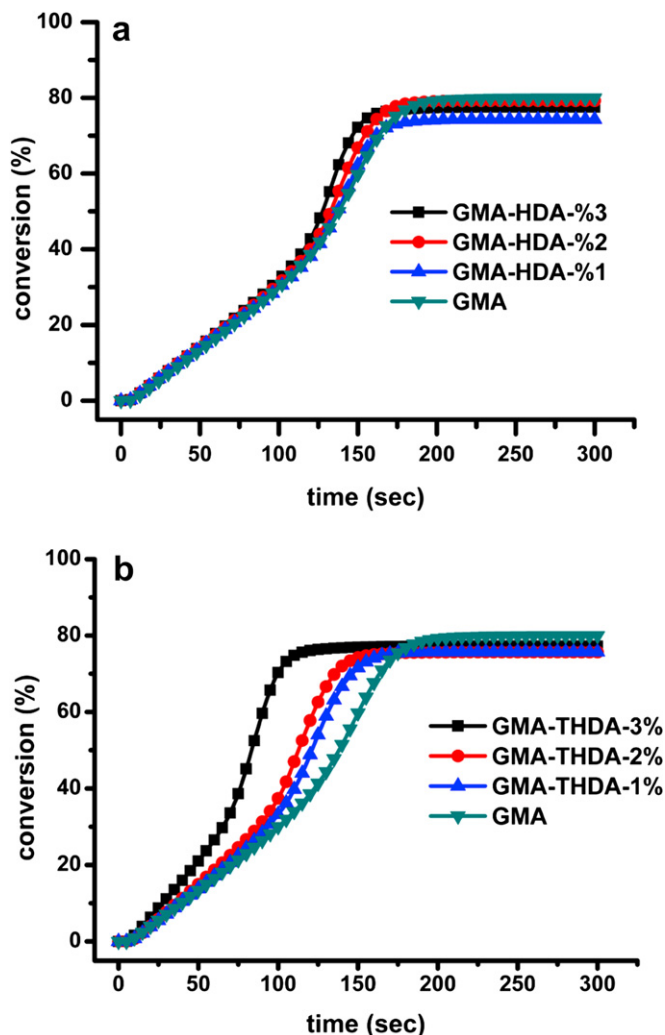
Fig. 4. Conversion-time plot for the photoinitiated polymerization of GMA in the absence and presence of cross-linkers, HDA and THDA.
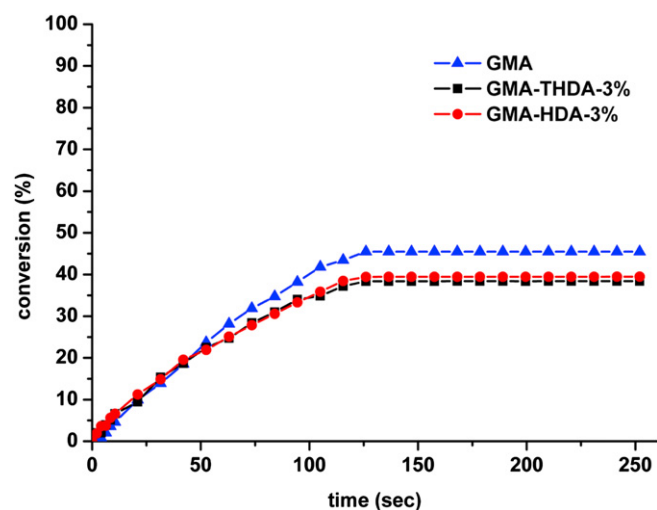

Fig. 5. Real-time infrared (RT-IR) kinetic profiles demonstrating the photopolymerization of GMA in the absence and presence of cross-linkers, HDA and THDA.

1 mol% cross-linker could be accomplished. As can be seen from Figs. 6 and 7, photopolymerizations with these monomers are faster than GMA. It is known that acrylates have higher rates of polymerization than comparable methacrylates. Therefore, with HEA monomer, no plateau region was noted. The rapid polymerization observed in this case may be due to the higher propagation rate constant of the acrylate monomer ($k_{pHEMA} = 1101$ L mol^{-1} s^{-1} [37], $k_{pHEA} = 2563$ L mol^{-1} s^{-1} [38]) and also due to the occurance of parallel reactions, like chain transfer. Although poly-HEMA is a glassy polymer and poly-HEA is a flexible polymer at room temperature, and the final double bond conversion is determined by system mobility, low double bond conversion was obtained for HEA polymerization which may be due to the very fast polymerization. Similar behavior was observed with various acrylate monomers [39].

It was clearly shown in GMA photopolymerization that the presence of pendant rigid triptycene units along the backbone of a polymer coupled with the occupation of triptycene cavities with portions of neighboring polymer chains reduces dramatically the molecular chain mobility by an increase of polymerization rate. However, in the case of HEMA and HEA such behavior was not observed which was attributed to the high k_p arising from H-bond interactions between monomer units. Therefore, we performed some more experiments using 2-ethylhexyl methacrylate (EHMA), structurally similar monomer without hydroxyl groups. Fig. 8
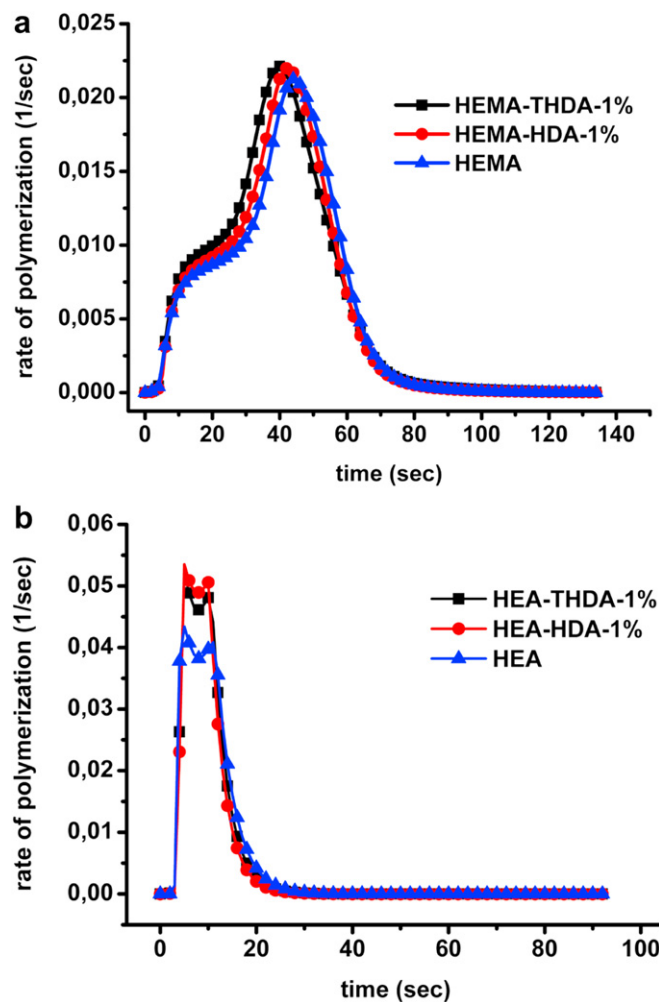

Fig. 6. Rate of photoinitiated polymerization of HEMA (a) and HEA(b) in the absence and presence of cross-linkers, HDA and THDA at 30 °C.
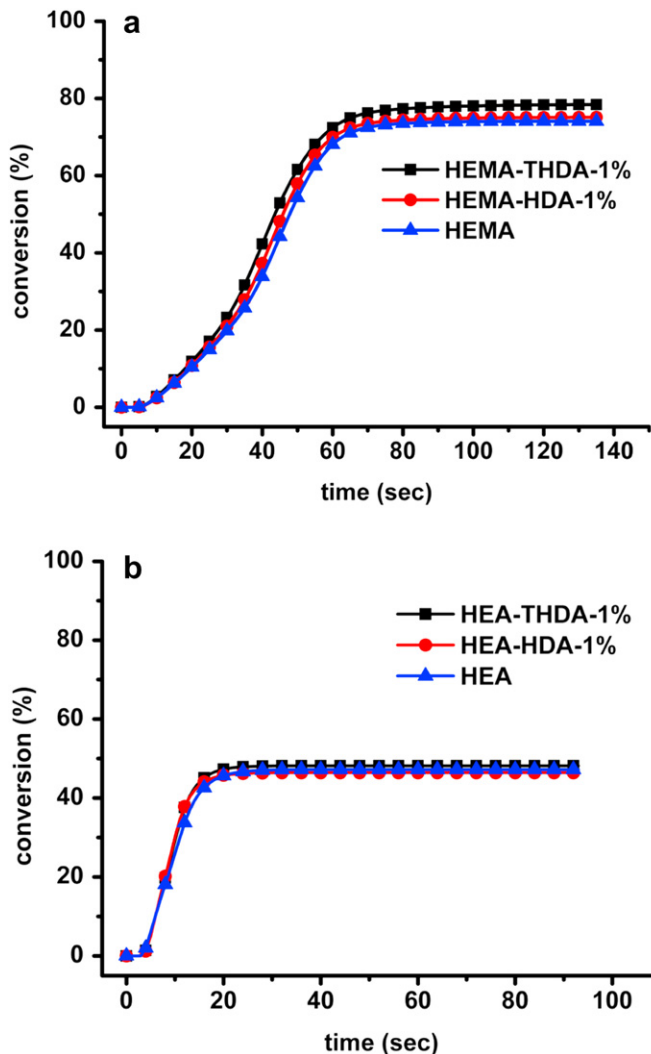
Fig. 7. Conversion-time plot for the photoinitiated polymerization of HEMA (a) and HEA (b) in the absence and presence of cross-linkers, HDA and THDA at 30 °C.

Fig. 8. Rate of photopolymerization (a) and conversion-time plot for the photoinitiated polymerization (b) of EHMA in the absence and presence of cross-linkers, HDA and THDA at 30 °C.

shows the time dependence of the polymerization rate and conversion-time plots of EHMA in the absence and presence of HDA and THDA. It is not surprising that EHMA displayed lower rate of polymerization compared to HEMA and HEA because of the lower k_p value ($k_{pEHMA} = 380$ L mol^{-1} s^{-1} [40]) pending from the absence of hydrogen bonding, favoring interaction of monomer units in the close proximity.

In conclusion, in this paper we reported synthesis of a new cross-linker possessing triptycene moiety in the structure and characterized. Moreover, its photopolymerization behavior in the UV curable formulations containing different monofunctional monomers was studied. Comparative kinetic studies revealed that the polymerization kinetics are governed mainly by the structure of the monofunctional monomer employed in the formulation and triptycene type cross-linker acts in a manner similar to the conventional cross-linkers. In the light of present study and the general behavior of triptycene molecules in polymer chains it is expected that cross-linked networks with enhanced properties such as ductility and stiffness can be obtained by photoinitiated free radical polymerization. Further studies on the investigation of the properties of the UV-cured products and comparison with those obtained by using conventional cross-linkers are now in progress and will be reported elsewhere.
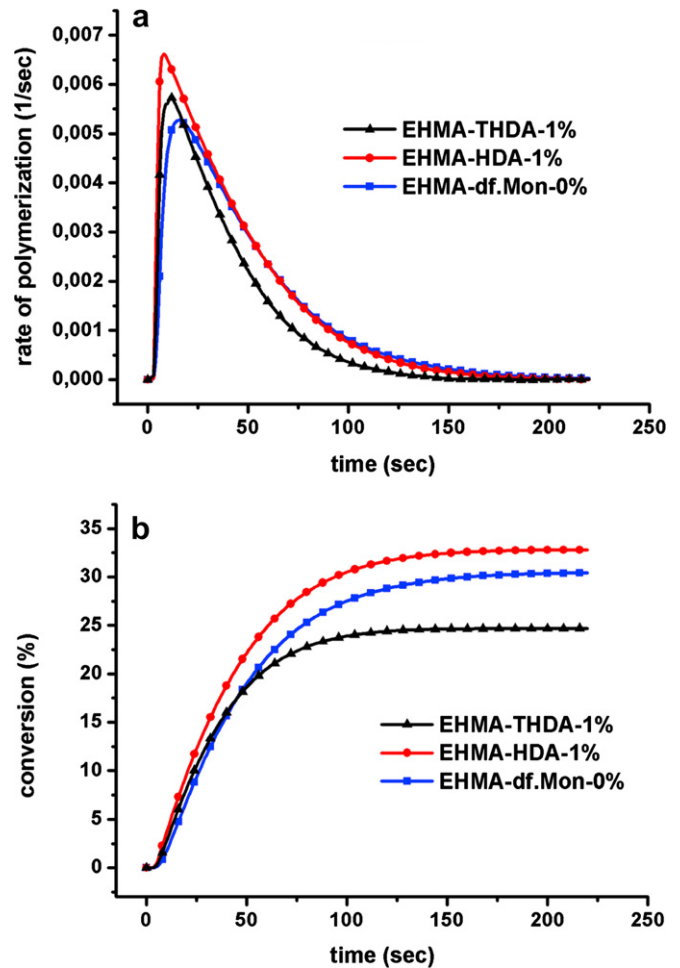
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