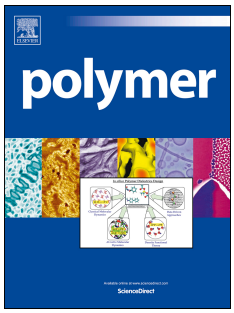
Accepted Manuscript



New allyl-functional catalytic comonomers for sequential thiol-Michael and radical thiol-ene reactions

Osman Konuray, Xavier Fernández-Francos, Xavier Ramis, Àngels Serra

PII: S0032-3861(18)30099-5

DOI: 10.1016/j.polymer.2018.01.073

Reference: JPOL 20333

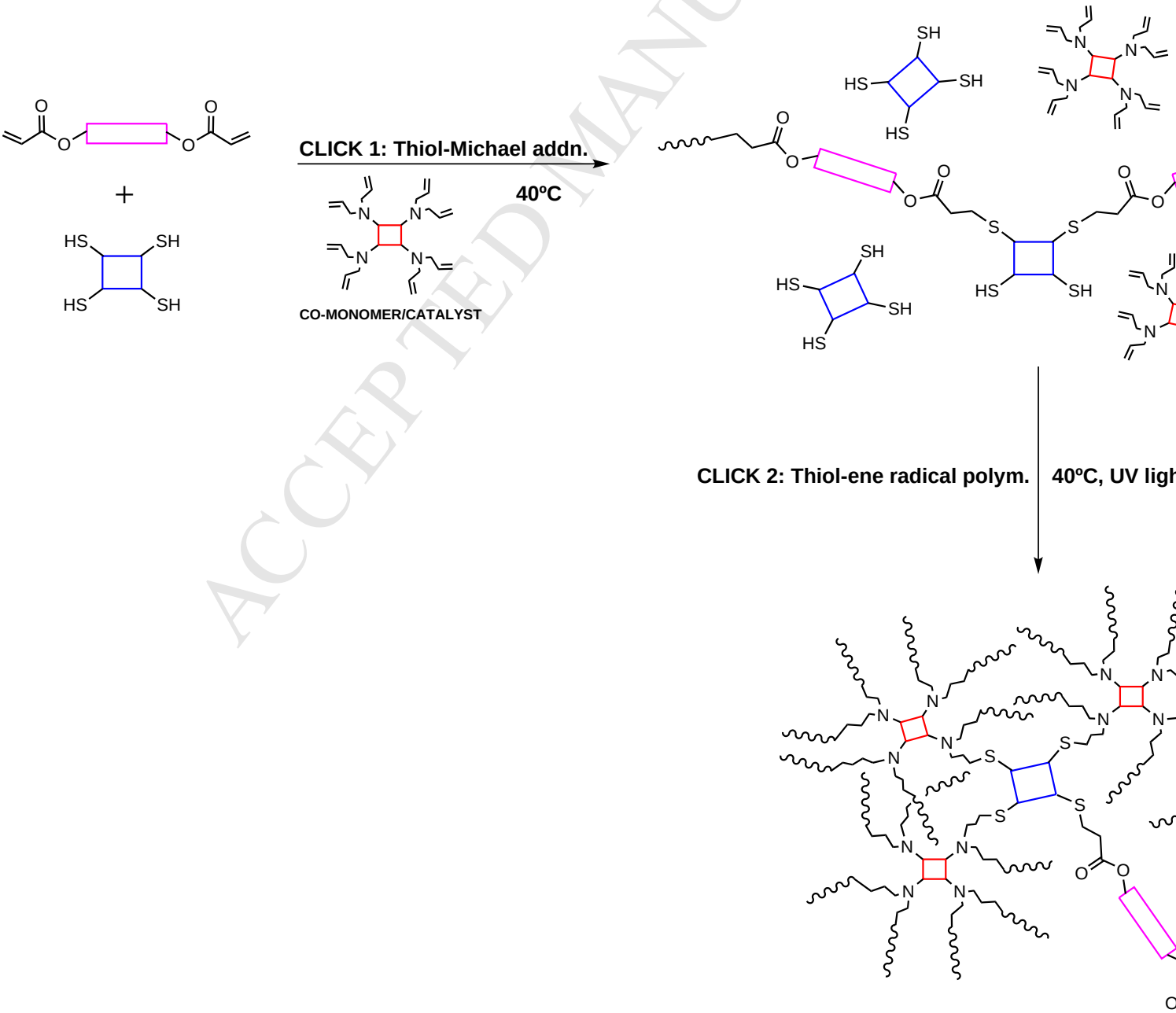
To appear in: *Polymer*

Received Date: 1 December 2017

Revised Date: 23 January 2018

Accepted Date: 27 January 2018

Please cite this article as: Konuray O, Fernández-Francos X, Ramis X, Serra À, New allyl-functional catalytic comonomers for sequential thiol-Michael and radical thiol-ene reactions, *Polymer* (2018), doi: 10.1016/j.polymer.2018.01.073.



New allyl-functional catalytic comonomers for sequential thiol-Michael and radical thiol-ene reactions

Osman Konuray[1*], Xavier Fernández-Francos[1], Xavier Ramis[1], Àngels Serra[2]

[1] Thermodynamics Laboratory, ETSEIB, Universitat Politècnica de Catalunya, Av. Diagonal 647, 08028 Barcelona, Spain
[2] Department of Analytical and Organic Chemistry, Universitat Rovira i Virgili, C/ Marcel•lí Domingo s/n, 43007, Tarragona, Spain.
*Corresponding author
E-mail: osman.konuray@mmt.upc.edu
Phone: +34 934016593
Fax: +34 934017389

ABSTRACT

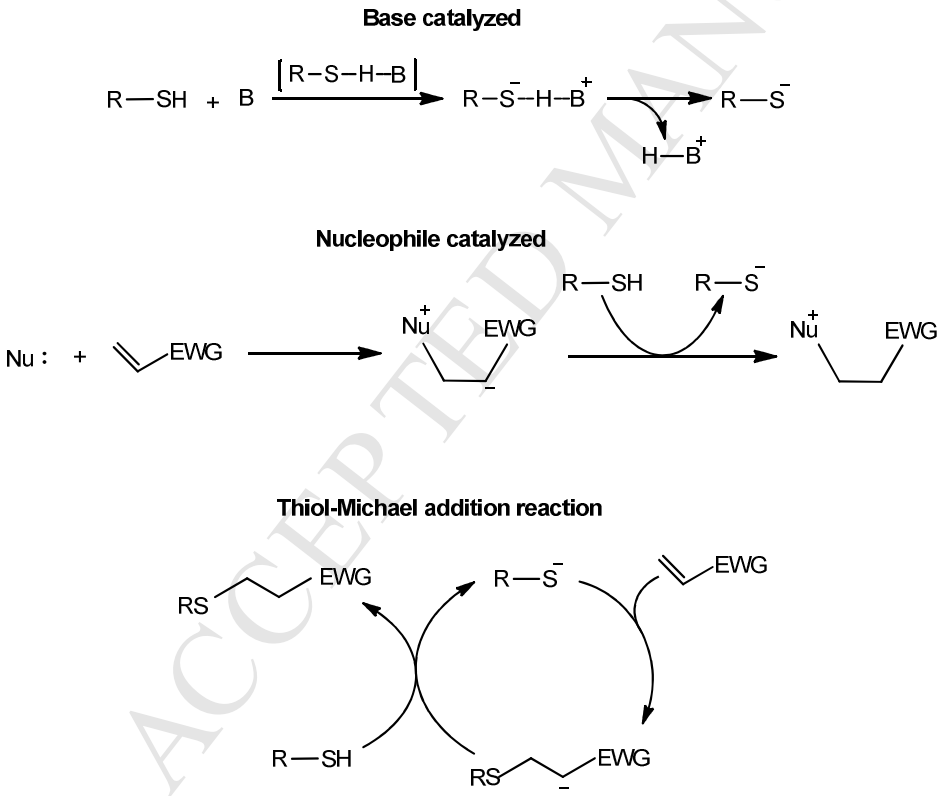
Soft poly(thioether) thermosets have been synthesized by employing a two-step curing procedure based on click chemistry. The first stage of curing is a thiol-Michael addition between acrylates (or methacrylates) and thiols in excess, catalyzed by a set of novel tertiary amine catalyst comonomers with allyl functionality. Subsequently, the pendant allyl groups of the comonomer get incorporated into the polymer network by undergoing thiol-ene UV photopolymerization with the remaining thiols. The strong catalysis by the high concentration of tertiary amine groups facilitates quantitative conversions at the end of the first stage. All remaining functional groups are depleted after a short period of UV irradiation. Final materials are clear, transparent, and exhibit homogeneous network structures with alpha relaxation temperatures in the range 3-25ºC. This sub-ambient relaxation temperature range suggests these materials may be suitable for coating applications where delicate substrates are involved such as plastic, wood and paper.

Keywords: Michael addition, dual-curing, thiol, acrylate, methacrylate, click reaction

1. INTRODUCTION

Recently, more and more research is directed towards environmentally benign processes for polymer preparation as health and environment related regulations become stricter all around the globe. In this regard, click chemistry [1] is of particular importance as it implies easy and efficient chemical routes to synthesize a great variety of polymers. Among these routes of obtaining crosslinked polymers, Michael addition reactions are interesting as they facilitate fast cure rates and high conversions and therefore are widely used in applications such as high performance coatings [2].

The thiol-Michael addition has been investigated and broadly utilized among others thanks to the ability of the S-H bond to easily undergo anionic or radical mediated polymerization reactions. These reactions can be initiated by a wide variety of precursor materials [3,4]. The thiol-Michael reaction may proceed through a base catalyzed or nucleophilic mechanism depending on the reaction medium. The two mechanisms are depicted in Scheme 1.



Scheme 1. The thiol-Michael reaction mechanisms. EWG: Electron withdrawing group. Scheme adapted from [5].

Although the nucleophile catalyzed route is faster, the by-product formed by the reaction between the nucleophile and the Michael acceptor is a drawback, since it reduces the thiol conversion [6,7]. Acrylates and methacrylates are commonly used as Michael acceptors as the

carbonyl group exhibits good electron withdrawing characteristics. Nair and co-workers presented a dual-cure procedure to synthesize a poly(thioether)-poly(acrylate) network. An off-stoichiometric mixture of thiols and acrylates in excess firstly undergo a thiol-acrylate Michael addition, followed by homopolymerization of the remaining acrylates. The intermediate materials after the first stage are soft, easy to manipulate and reactively stable. After the second curing stage, which is triggered by UV irradiation, the materials gain their ultimate properties required by the intended application [8,9]. It is also possible to design dual-curing systems involving more than two different functionalities. Recently, the authors of this paper presented an amine-acrylate-methacrylate ternary system which is cured by sequential aza-Michael addition of amines to acrylates, followed by methacrylate photopolymerization [10].

Dual-cure procedures make use of the orthogonality of the two curing reactions. In one such case, a mixture of vinyl sulfones and acrylates were reacted with thiols in a sequential fashion. Due to its higher reactivity, the vinyl sulfone reacts first with the thiol [11]. Other researchers used a combination of thiol-acrylate Michael addition followed by radical thiol-allyl reaction to obtain holographic materials [12], to control wrinkle formation [13], or for polymer functionalization [14]. It is also possible to combine nucleophilic thiol-ene reaction with radical thiol-yne [15,16]. In a recent work, our group proposed a dual system based on thiol-acrylate and acetoacetate-acrylate reactions where the difference in proton acidities of thiol and methylene unit of acetoacetate resulted in sequentiality [17].

Although less reactive than their acrylate counterparts, methacrylates could also undergo thiol-Michael additions in the presence of an adequate catalytic medium [6]. The efficiency of such a system was demonstrated by Xi et al. using a superbase catalyst to carry out thiol-Michael addition where the Michael acceptor was a methacrylate [18]. Methacrylates might also undergo photopolymerization at a later stage subsequent to Michael-type curing reactions and help increase the final glass transition temperature of dual-cure materials [10,19].

An elegant way to eliminate the need for added catalysts is to use a comonomer specially designed to exert a catalytic role that would participate at a certain stage in the polymerization. Among them, tertiary amine monomers with acrylate functionalities have been presented by a number of researchers [20,21]. In another paper, a hyperbranched polyamine (containing tertiary amines) was used as a catalytic comonomer in aza-Michael reaction [22].

In the present work, we have synthesized a novel set of tertiary amine comonomers with allyl functionalities, which exhibit a catalytic activity. We have used solvent-free and click based reactions carried out at eco-friendly conditions without any added catalyst to obtain practically pure comonomers with virtually 100% yield. Using these comonomers, we have synthesized poly(thioether) networks by employing a two-step procedure which is also based on click procedures. We first carried out a thiol-Michael addition of the thiols in excess to acrylates (or

methacrylates) (stage 1), catalyzed by our novel tertiary amine catalytic comonomers with allyl functionalities. The pendant allyl groups of the comonomer later underwent thiol-ene photopolymerization with the remaining thiols (stage 2) to yield the ultimate poly(thioether) product. The combination of sequential thiol-Michael and radical thiol-ene has been employed by other researchers for post-functionalization of polymers [23–25]. In our system, although stage 1 is expected to proceed mainly through a basic mechanism, there is also the possibility of nucleophilic initiation due to a small amount of primary amines remaining from comonomer preparation. These primary amine residues may also undergo aza-Michael addition to acrylates thereby getting incorporated into the final structure. We studied reaction kinetics of the two curing stages, and also intermediate and final material properties.

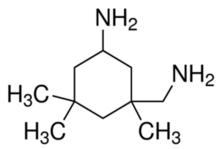
2. EXPERIMENTAL

2.1. Materials

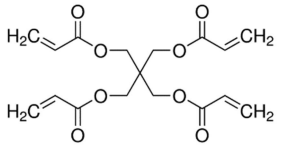
Diethylene triamine (DETA), 5-amino-1,3,3-trimethylcyclohexanemethylamine (IPDA), pentaerythritol tetraacrylate (PETA), allyl glycidyl ether (AGE), diallylamine (DAA), tricyclo[5.2.1.02,6]decanedimethanol diacrylate (TCDDA), triethylene glycol dimethacrylate (TEGDMA), pentaerythritol tetrakis(3-mercaptopropionate) (S4) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were supplied by Sigma Aldrich and used without further purification. Diglycidyl ether of Bisphenol A with an epoxy equivalent weight of 187 g/eq (coded as DG187) was supplied by Hexion Speciality Chemicals B.V. The structure of the chemicals used is depicted in Scheme 2.

2.2. Preparation of the allyl functionalized comonomers

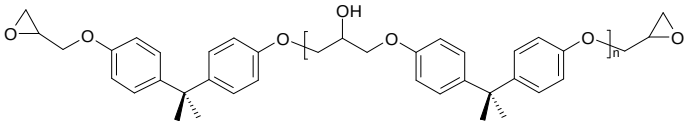
The preparation of the four tertiary amine catalytic comonomers with allyl functionality (hereafter will be referred simply as “comonomers”) was done by means of two click reactions: Aza-Michael and epoxy-amine. The structure of these compounds is shown in Scheme 3. The comonomers prepared were named according to the allylic compound used in their preparation and the final functionality: AGE4, AGE5, DAA4, and DAA8. Whereas click epoxy-amine reaction was employed to synthesize AGE4, AGE5, and DAA4, click aza-Michael reaction was used to synthesize DAA8.



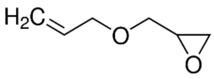
DETA IPDA



DETA



DG187

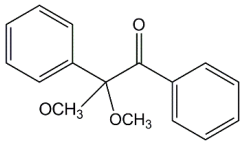


AGE

DAA

TCDDA

TEGDMA



S4

DMPA

Scheme 2. Chemicals used in the preparation of the materials

The synthetic procedures for all catalytic comonomers were similar. For a batch of 5 g, a stoichiometric mixture of allyl monomer (AGE or DAA) and its co-reactant (DETA, PETA, or DG187) was prepared by adding the required amount of both chemicals into a sealed 20 mL glass vial. The mixture was homogenized at room temperature using a magnetic stirrer, after which it was heated up to 40ºC and left under agitation at this temperature for 3 hours. The vial was then placed in an oven at 40ºC for 24 hours followed by an additional hour at 120ºC to ensure quantitative reaction. The vials were finally kept at 110ºC for 30 minutes under vacuum to eliminate volatile impurities. The purity of the product was analyzed by DSC and ^{1}H-NMR. No residual heat was observed in DSC, confirming completeness of the reaction.

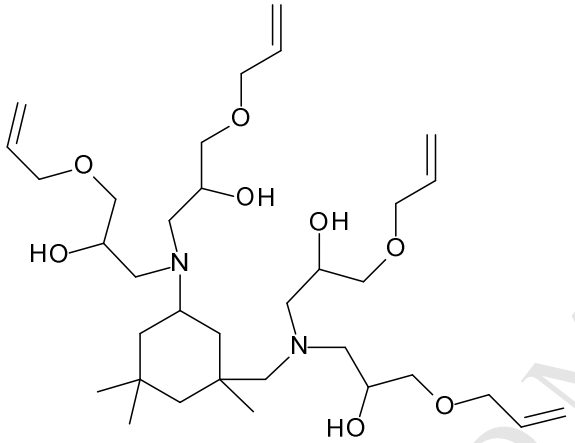
^{1}H-NMR assignment of AGE5 (δ in ppm in $CDCl_3$): 1.2-3 (m, -N- CH_2-, 18 H); 3.4 (t, -O-CH_2-, 10H); 3.8 (m, C<u>H</u>-OH, 5H); 3.9 (m, -C<u>H$_2$</u>-CH=CH_2, 10H); 5.2 (two dd, -CH=C<u>H$_2$</u>, 10H) and 5.8 (m, -C<u>H</u>=CH_2, 5H).

[1]H-NMR assignment of DAA4 (δ in ppm in $CDCl_3$): 1.6 (s, 6H, CH_3-); 2.6 (d, -CH_2-N, 6H); 3.2 (m, -C<u>H</u>$_2$-CH=CH_2, 8H); 3.9 (m, -CH_2-O, 4H); 5.1 (m, -CH=C<u>H</u>$_2$, 8H); 5.8 (m, -C<u>H</u>=CH_2, 4H), 6.8 (d) and 7.1 (d) (aromatic H, 4H + 4H).

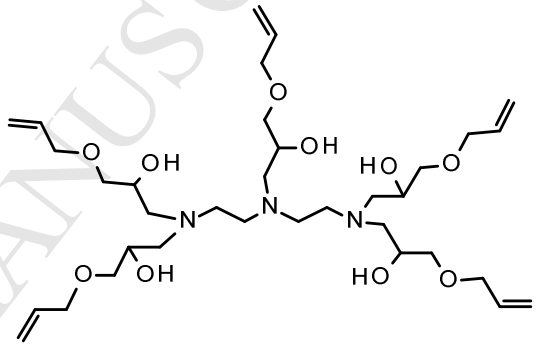
[1]H-NMR assignment of DAA8 (δ in ppm in $CDCl_3$): 2.5 (t, -N-CH_2-C<u>H</u>$_2$-COO-, 8H); 2.8 (t, -N-C<u>H</u>$_2$-CH_2-COO-, 8H); 4.1 (s, -O-CH_2-C, 8H); 5.1 (m, -CH=C<u>H</u>$_2$, 16H); 5.7 (m, -C<u>H</u>=CH_2, 8H).

[1]H-NMR assignment of AGE4 (δ in ppm in $CDCl_3$): 0.8-1.6 (m, 15 H); 2.1-3.0 (m, 13H); 3.3-3.5 (m, 10H); 3.7-3.9 (m, 4H); 4.0 (s, -C<u>H</u>$_2$-CH=CH_2, 8H); 5.1 and 5.3 (two dd, -CH=C<u>H</u>$_2$, 8H) and 5.9 (m, -C<u>H</u>=CH_2, 4H).

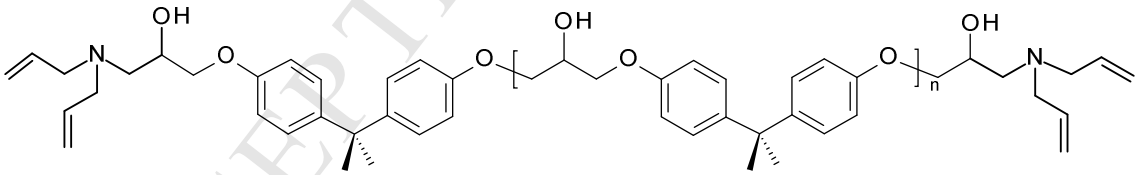
The assignments confirm the chemical structures of the different comonomers prepared. For space considerations, we only report the [1]H-NMR spectrum of DAA4 (Figure 1).



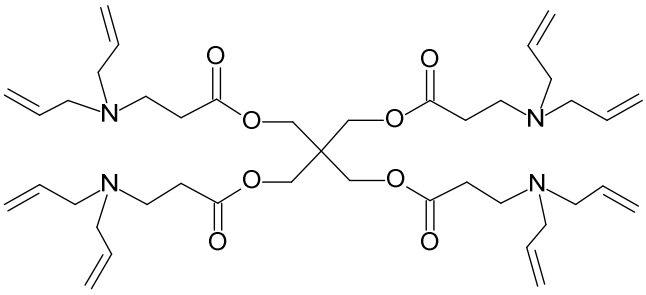
AGE4



AGE5



DAA4



DAA8

Scheme 3. Allyl functional catalytic comonomers synthesized

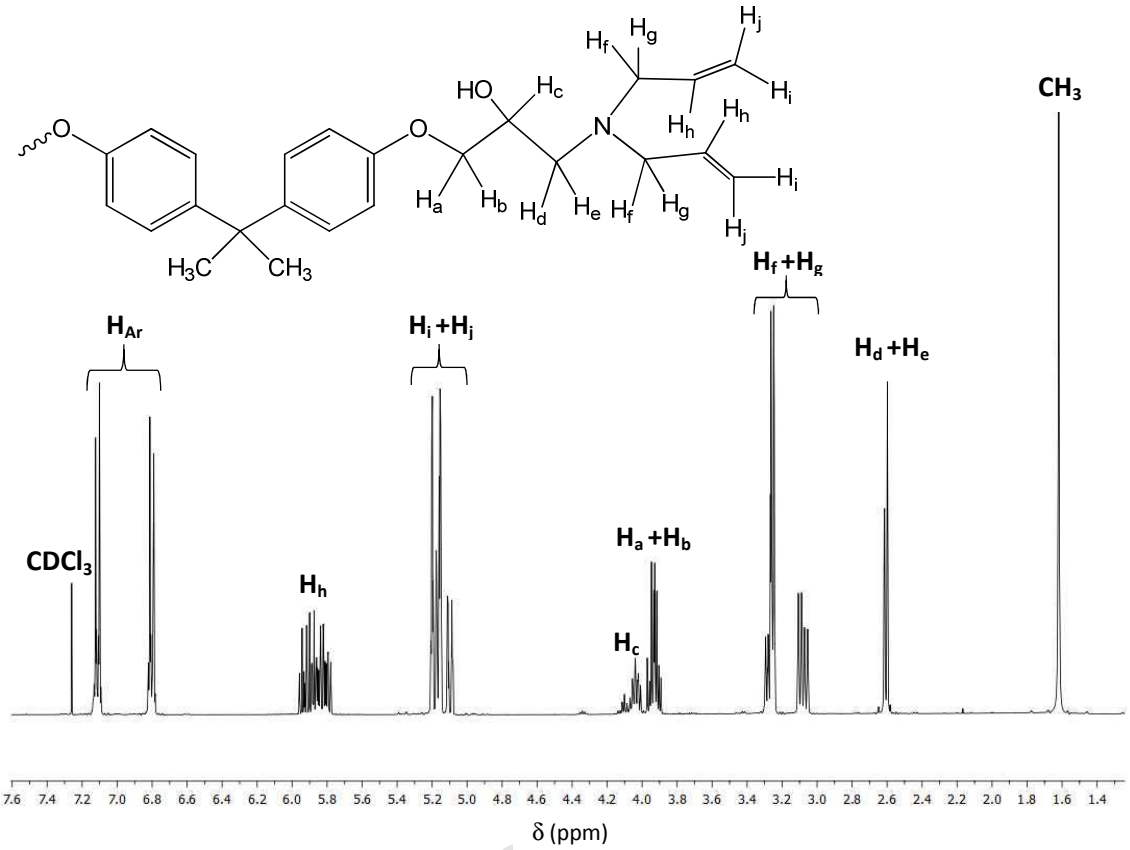


Fig. 1 ^{1}H-NMR spectrum of the DAA4 comonomer

2.3. Sample preparation

Based on our preliminary kinetic studies with a number of formulations using each comonomer, we chose two different Michael acceptors depending on the reaction kinetics of stage 1. For AGE4 and DAA8, we used a diacrylate: tricyclo[5.2.1.02,6]decanedimethanol diacrylate (TCDDA), whereas for AGE5 and DAA4, we used a dimethacrylate: triethylene glycol dimethacrylate (TEGDMA). Had we used the same diacrylate in formulations with AGE5 and DAA4, the thiol-Michael addition would have been extremely fast which in turn would have made sample preparation and analysis impractical. In all formulations, the thiol Michael donor used was the pentaerythritol tetrakis(3-mercaptopropionate) (S4). For the photopolymerization (stage 2) we used 2,2-dimethoxy-2-phenylacetophenone (DMPA) as Type 1 photoinitiator.

Double bond (Michael acceptor + comonomer): thiol (S4) molar ratio was stoichiometric. Michael acceptor was either TCDDA or TEGDMA. Weight percentage of photoinitiator DMPA was fixed at 0.5 % w/w. For a 1 g sample of each formulation, 0.5% w/w DMPA was dissolved in a mixture of the comonomer (AGE4, AGE5, DAA4, or DAA8) and S4 in their respective amounts in a 5 mL glass vial. The vial was kept at -20ºC in a freezer and was taken out just

before addition of the corresponding Michael acceptor. The mixture was stirred quickly for a few seconds in an ice water bath to delay the Michael reaction onset and was sent to immediate analysis. The formulations studied are collected in Table 1.

Table 1. Formulations used in the preparation of materials (per 1 g)

Formulation	TEGDMA		TCDDA		Comonomer		S4		Tert. N
	mg	mmol	mg	mmol	mg	mmol	mg	mmol	mmol/g†
AGE5-TEGDMA	269.8	1.90	-	-	262.3	1.9	467.9	3.8	1.17
DAA4-TEGDMA	269.8	1.90	-	-	268.8	1.9	461.4	3.8	0.95
DAA8-TCDDA	-	-	277.5	1.8	217.5	2.3	505.0	4.1	1.24
AGE4-TCDDA	-	-	277.4	1.8	281.0	1.8	441.7	3.6	0.90

†Based on total thiol-acrylate

2.4. Characterization

^{1}H-NMR spectra were registered in a Varian Gemini 400 spectrometer. $CDCl_3$ was used as the solvent. For internal calibration, the solvent signal at δ = 7.26 ppm, corresponding to $CDCl_3$, was used.

We used a Bruker Vertex 70 FTIR spectrometer equipped with an attenuated total reflection (ATR) accessory (GoldenGate™, Specac Ltd.) which is temperature controlled in order to monitor the thiol-Michael addition of acrylates (or methacrylates) to thiols and thiol-ene photopolymerization. Spectra were collected in absorbance mode with a resolution of 4 cm^{-1} in the wavelength range from 4000 to 600 cm^{-1} averaging 20 scans for each spectrum. Scans were performed at a rate of 5 s^{-1} using rapid scan mode for a duration of time sufficient to observe the highest achievable conversion in both stages. A Hamamatsu Lightningcure LC5 (Hg-Xe lamp) with one beam conveniently adapted to ATR accessory was used to irradiate the samples and to carry out thiol-ene photopolymerization. The spectral emission range of the UV lamp was 200-600 nm (high intensity around 365 nm). The irradiation intensity was approximately 4 mW/cm2 (measured at 365 nm). The conversion of functional groups is denoted as α and it is defined by Equation 1.

$$\propto = 1 - \frac{A'}{A'_0} \qquad (1)$$

where A' is taken either as the absorbance of the functional group under investigation and A_0' is the value of this absorbance at time 0, both normalized with that of the ester groups (1720 cm^{-1}) in the sample. Ordered in decreasing wavenumber, the absorbance peaks relevant to our analyses were at 3080 cm^{-1} (allyls), 2570 cm^{-1} (thiols), 1640 cm^{-1} (acrylates or methacrylates), 1407 cm^{-1} (acrylates), at 1300 cm^{-1} (double peak, methacrylates) 940 cm^{-1} (allyls), and 810 cm^{-1} (acrylates or methacrylates).

Calorimetric analyses were carried out on a Mettler DSC822e thermal analyser. DSC was either used to monitor residual reaction heats or to determine glass transition temperatures (T_g). The former was done to ensure quantitative yield after preparation of the comonomers, as well as to ensure complete reactive group conversion of poly(thioether) final products. Samples of approximately 5 mg were placed in aluminium pans with pierced lids and subsequently scanned at a rate of 10 ºC/min under nitrogen atmosphere. Intermediate samples (after stage 1) were irradiated in a Mettler DSC821 thermal analyzer using a Hamamatsu LC5 light source equipped with a Hg-Xe mid-pressure lamp conveniently adapted to the DSC by means of fiber optics probes. UV light intensity was 17 mW/cm^2 measured at 365 nm using a radiometer. Both analyzers were calibrated using an indium standard (heat flow calibration). The DSC822e calorimeter is equipped with a liquid nitrogen unit to allow working at cryogenic temperatures. T_g at the end of both stages of curing were taken as the temperature of the half-way point of the drop in heat capacity when the material changed from glassy to the rubbery state and the error is estimated to be approximately ± 1°C.

A thermo-mechanical analyzer Mettler TMA SDTA840 was used to determine the gel point during thiol-Michael addition (Stage 1) employing the method described in the literature [26]. A silanized glass fiber disc about 5 mm in diameter was impregnated with the newly prepared mixture and sandwiched between two aluminium discs. The sample was placed at 40ºC and subjected to an oscillatory force from 0.002 to 0.01 N with an oscillation frequency of 0.083 Hz. The gel time was taken as the onset in the decrease of the oscillation amplitude measured by the probe. The conversion of acrylate groups at the gel point, α_{gel}, was determined as the conversion reached in FTIR at the gel time.

The theoretical conversion of acrylate groups at the gel point, α_{gel}, during thiol-Michael reaction (Stage 1) was calculated assuming ideal random step-wise reaction, using the well-known Flory-Stockmeyer equation [27]

$$\alpha_{gel}^{\text{theor}} = \frac{1}{\sqrt{r(f-1)(g-1)}} \qquad (2)$$

where r is the acrylate:thiol molar ratio, f and g are the acrylate and thiol functionalities, respectively.

Fully cured materials were characterized using dynamic mechanical analysis (DMA). First, prismatic rectangular samples (ca. 1x12x20 mm^3) were prepared by injecting the liquid monomer mix into molds of the same size. Stage 1 curing was carried out under 40ºC for 24h to ensure complete acrylate conversion (thiol-Michael). The samples were then placed into a Vilber Lourmat UV oven equipped with 6 lamps emitting UV light at a wavelength 365 nm and 4 mW/cm^2 total light intensity. The samples were irradiated on both sides for stage 2 curing, and received a total dose of 11 J/cm^2 (radical thiol-ene). Complete cure was verified in subsequent

DSC scans. DMA was performed with a TA Instruments DMA Q800 device using single cantilever clamp at a frequency of 1 Hz and 0.05% strain at 3ºC min^{-1} from -40ºC up to a temperature sufficiently high for complete network relaxation. The peak temperatures of *tan δ* curves were taken as α-relaxation temperatures (T_a).

Fully cured samples were analyzed also for their soluble content. About 100 mg of each sample was placed in a 250 ml three-necked flask. To extract the soluble fraction, a sufficient amount of chloroform was added in the flask to ensure solubility of all soluble material. The mixture was boiled at 60ºC under atmospheric conditions for 24 h and was kept under constant reflux using a water cooled condenser. The flask content was then filtered to separate the soluble and gel fractions. Each filtrate was subjected to one-hour drying cycles at 70ºC in an electric oven. Weight measurements were performed between drying cycles and drying was continued until two consecutive weight measurements differed by less than 1%. The dry filtrate was weighed and noted as the (insoluble) gel fraction.

3. RESULTS AND DISCUSSION

3.1. Curing kinetics

As explained in the introduction, the proposed dual-curing procedure consists, of a Michael addition reaction of thiol groups to acrylates or methacrylates catalyzed by tertiary amine groups of the allyl comonomers, followed by a thiol-ene click reaction between the remaining thiols from the first stage and the allyl groups of the comonomers. Whereas the first reaction takes place thermally at 40ºC, the second is triggered by photoirradiation and is initiated by the photoinitiator DMPA. To shed light on the dual character of the proposed curing system , we first investigated the thiol-Michael addition stage by FTIR spectroscopy.

In generating the conversion-time plots in Figure 2 for the first curing stage, we analyzed the FTIR absorbance peak at 810 cm^{-1} (corresponding to the =C-H bending out of the plane) when the Michael acceptor was TCDDA and the peak at 1640 cm^{-1} (corresponding to the C=C stretching of acrylate group), when the Michael acceptor was TEGDMA.

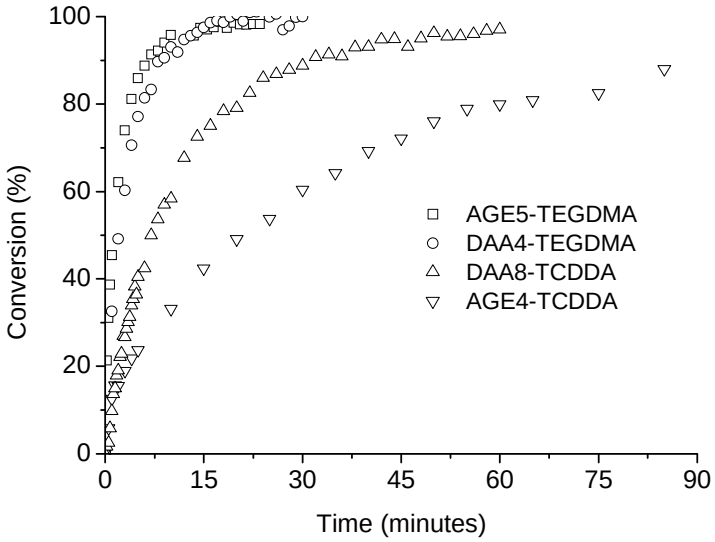


Fig 2. Stage 1 (thiol-Michael) acrylate/methacrylate FTIR conversions of all four comonomer - Michael acceptor pairs. Michael donor is pentaerythritol tetrakis(3-mercaptopropionate) (S4). Reaction is carried out at 40ªC.

In our preliminary experiments, we observed that AGE5 and DAA4 comonomers reacted extremely rapidly at 40ªC with TCDAA even before a homogeneous mixture could be obtained. On the other hand, DAA8 and AGE4 did not react with TEGDMA even after 24h. In all preliminary and final formulations, the concentration of tertiary amine groups was many orders of magnitude greater than in thiol-Michael reactions reported previously [7]. We believe that this was a direct factor causing the extremely fast reaction of our preliminary AGE5-TCDDA and DAA4-TCDAA formulations (not presented here). For these two comonomers, we therefore used the less reactive Michael acceptor TEGDMA in the final formulations. Even with this less reactive Michael acceptor, the AGE5 comonomer reacted fastest amongst all comonomers, followed by DAA4. The faster reaction of AGE5 may be explained by its higher concentration of tertiary amine groups (1.17 versus 0.95 mmol g^{-1} in Table 1). However, the tertiary amine concentration viewpoint fails to explain the fact that while DAA4-TEGDMA could cure in 1h, DAA8-TEGDMA (not shown here) was unreactive even after 24h. Despite its higher tertiary amine concentration and its more reactive Michael acceptor, even DAA8-TCDDA cured slower than DAA4-TEGDMA (See Table 1 to compare tertiary amine concentrations). This can be explained in part by the electron withdrawing effect of the neighboring ester group in the comonomer DAA8 (See Scheme 3) which would reduce its basicity. With a similar reasoning, one can argue that the less hindered tertiary amines in AGE5-TEGDMA could have contributed to the fast reaction (See Scheme 3) despite the less reactive Michael acceptor.

To clarify our postulations, we can mathematically analyze the reaction kinetics. As previously reported for Michael additions catalyzed by strong bases, the attack of the deprotonated Michael donor (anion) to the activated olefin (acrylate or methacrylate) follows pseudo-first order kinetics. This is because when a strong base is used, the reaction equilibrium for Michael donor deprotonation would lie to the right, so that the steady-state concentration of the resulting anion (which subsequently attacks the Michael acceptor) would be equal to the base concentration [28]. In such cases, the rate law appears as follows:

$$rate = k'[A] \quad (3)$$

where the apparent rate constant k' is a function of base concentration, and $[A]$ is the concentration of the Michael acceptor (acrylate or methacrylate). Although the Michael donor studied in the cited reference is an acetoacetate, the reaction follows the same rate law when the donor is a thiol. When weaker bases are used, the equilibrium constant for thiol deprotonation gets incorporated into the rate law and we get second order kinetics:

$$rate = k\, K_{eq} \frac{[B]}{[BH^+]} [thiol][A] \quad (4)$$

where K_{eq} is the reaction equilibrium constant for thiol deprotonation by the base, $[BH^+]$ is the concentration of the protonated base, and $[thiol]$ is the concentration of the thiol.

We can safely assume that when AGE5 and DAA4 was used, the thiol-Michael reaction followed the rate law in eq. 3. Although methacrylates generally perform poorly as Michael acceptors [2], the high concentration of the strong base compensated for it. Consequently, a high value for k' yielded the fast kinetics observed. On the other hand, due to the steric hindrance effects in DAA8 and AGE4, the reaction was more likely to follow the rate law given in eq. 4. When TEGDMA was used as Michael acceptor, both *k* and K_{eq} were small, and their product resulted in a small overall rate. Cure was only achieved when TEGDMA was replaced with TCDDA in which case the value of *k* increased, compensating the small K_{eq} to a certain extent. All formulations presented here achieved practically quantitative stage 1 conversions at the end of 60 minutes, except AGE4-TCDDA which reached completion after 2h.

For space considerations, we show the overall kinetic analysis of one formulation for each Michael acceptor (TCDDA or TEGDMA). The remaining formulations were omitted as they exhibited qualitatively similar results. In Figure 2, we present the relevant region of the FTIR spectra at different stages of curing of DAA8-TCDDA. Both curing stages were carried out at 40ºC. Observing the peaks characteristic to each functional group, we can verify the sequential nature of the overall curing reaction. The relevant peaks, ordered in decreasing wavenumber, are at 3080 cm^{-1} (C-H st, allyl group), 2570 cm^{-1} (S-H st, thiol), 1407 cm^{-1} (C=C st. acrylates), 940 cm^{-1} (out of the plane bending of =C-H of allyl groups), and 810 cm^{-1} (out of the plane bending of =CH of acrylate groups). For this formulation, the peak at 810 cm^{-1} was analyzed to generate

the conversion-time plot in Figure 1. Note how the sequential and click nature of the dual-curing process is corroborated by the inset graphs in Figure 3: All thiols and allyl groups remaining from stage 1 are totally consumed after stage 2 (radical thiol-ene). The duration of irradiation to reach complete conversion was 2 minutes. Samples were irradiated for 10 minutes nevertheless.

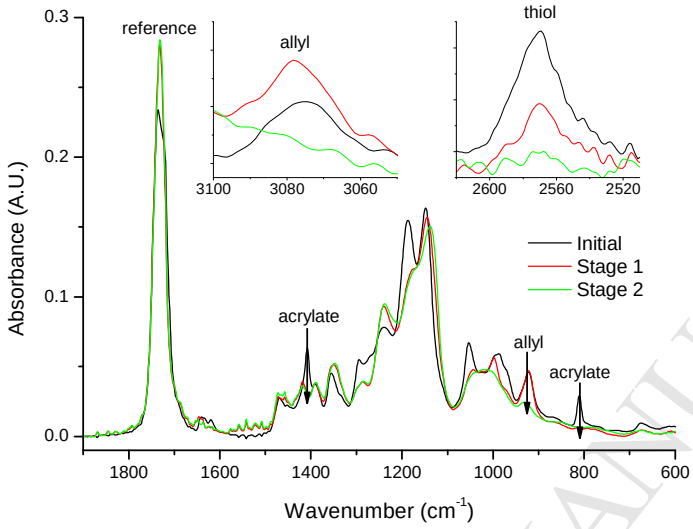


Fig 3. FTIR spectra after each curing stage of DAA8-TCDDA. Spectra normalized using carbonyl ester absorbance at 1720 cm^{-1}. Stage 1 is thiol-acrylate Michael addition; Stage 2 is radical thiol-ene photopolymerization. Both curing stages were carried out at 40ºC.

For AGE5-TEGDMA, as indicated by the absorbances at 1636 cm^{-1}, 1300 cm^{-1} (double peak) and 810 cm^{-1}, quantitative conversion of methacrylates is achieved by the end of stage 1 (See Figure 4). Upon a short UV irradiation, we observe the disappearance of the thiol peak at 2570 cm^{-1} as well as the allyl peak at 940 cm^{-1}. We also observe a low intensity allyl peak at 1646 cm^{-1} (see right-hand side inset of Figure 4) which disappears at the end of stage 2.

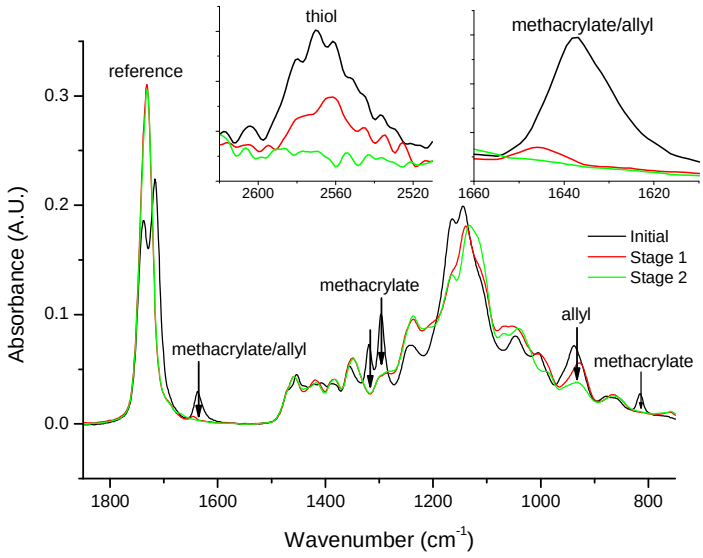


Fig 4. FTIR spectra after each curing stage of AGE5-TEGDMA. Spectra normalized using the carbonyl ester absorbance at 1720 cm^{-1}. Stage 1 is thiol-acrylate Michael addition; Stage 2 is radical thiol-ene photopolymerization. Both curing stages were carried out at 40ºC.

3.2. Gelation studies

As explained in the experimental section, gel points were determined using TMA. In Figure 5, the method is illustrated for the DAA8-TCDDA sample. Table 4 summarizes stage 1 gelling characteristics of all formulations. As can be seen, all experimental gelling conversions are higher than predicted by the Flory-Stockmeyer model (eq.2). This discrepancy has been encountered by other researchers for other systems such as amine-acrylate [22], or thiol-epoxy [29]. The most probable reason for the delay in gelation is intra-molecular cyclization [30,31] which would be more likely in formulations with TEGDMA as this molecule is more easily foldable than TCDDA. The rings in the structure of TCDDA make it a less flexible molecule. The higher values of $\propto_{gel}^{exp}$ in TEGDMA formulations corroborate this postulation. The Flory-Stockmeyer model assumes ideal step-wise polymerization where no such intra-molecular reactions are taken into account.

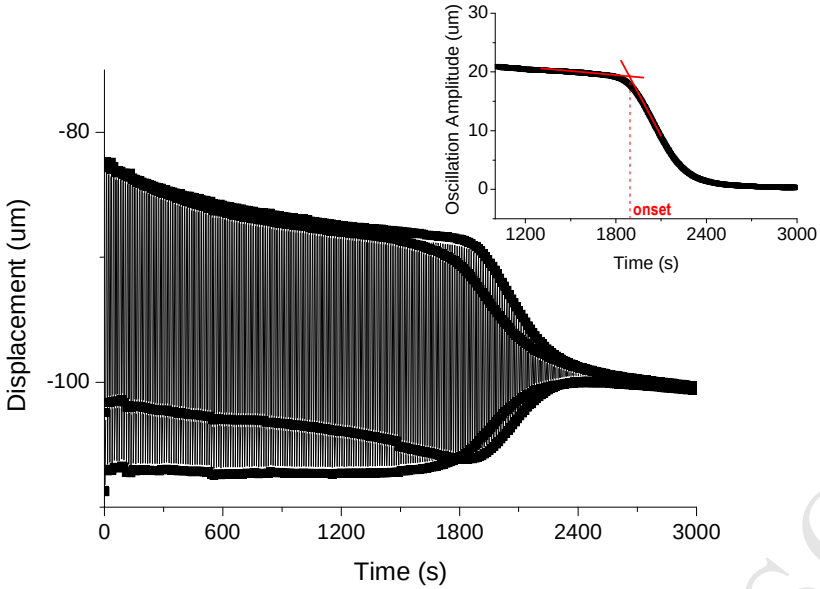


Fig 5. Determination of gel point using TMA data. Oscillation amplitude (inset) is calculated as the difference between the upper and lower envelopes of the TMA data. Gelling time is determined as the onset of oscillation amplitude decrease (the intersection of the two slopes shown in red). Sample is DAA8-TCDDA. TMA run performed at 40ºC.

Table 4. Stage 1 gel time and acrylate/methacrylate conversions at gel point.

Formulation	t_{gel} (min)	$\propto_{gel}^{exp}$	$\propto_{gel}^{theo\dagger}$
AGE5-TEGDMA	9	0.94[a]	0.82
DAA4-TEGDMA	17	0.99[a]	0.82
DAA8-TCDDA	32	0.90[b]	0.82
AGE4-TCDDA	102	0.90[b]	0.82

[†] Calculated using eq. 2; [a] Methacrylate conversion; [b] Acrylate conversion

3.3. Material properties

The final materials were characterized thermally. The amount of soluble material was also investigated using the method explained in the experimental section. In Table 5, we present T_g determined by DSC at each stage together with T_a determined by DMA. At the rightmost column, the gel fractions are given. Fully cured materials are clear, transparent and soft at room temperature. Storage moduli of formulations at the glassy region is typical of highly crosslinked polymers (i.e. 2-3GPa).

Table 5. Glass transition and alpha-relaxation temperatures.

Formulation	$T_{g,0}$ (ºC)[a]	$T_{g,int}$ (ºC)[b]	$T_{g,f}$ (ºC)[c]	T_a (ºC)[d]	*Gel. frac.*
AGE5-TEGDMA	-66.9	-42.3	-13.4	3.1	0.99
DAA4-TEGDMA	-69.8	-33.4	-5.7	8.8	1.00
DAA8-TCDDA	-63.4	-33.4	5.7	19.5	1.00
AGE4-TCDDA	-54.3	-17.6	12.4	24.8	1.00

[a] Initial T_g calculated using Fox equation [32] and $T_{g,0}$ of constituent systems (i.e. stoichiometric mixtures of AGE5-S4 and TEGDMA-S4); [b] T_g at the end of stage 1; [c] T_g at the end of stage 2; [d] Alpha-relaxation temperature

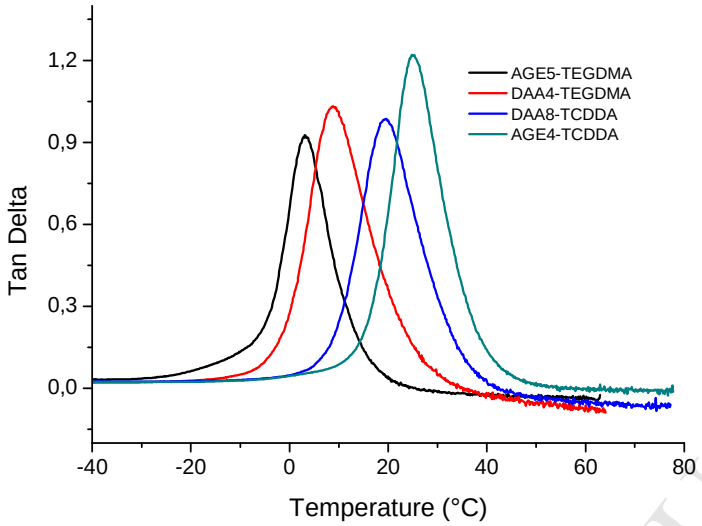


Fig 6. Tan delta curves of all formulations

The alpha-relaxation temperatures (T_α) span a range of 20ºC. As can be seen in Table 5, formulations containing TCDDA exhibited higher T_g and T_a. Monomers such as TCDDA and AGE4 which feature cyclic structures yield rigid polymers. Comparing AGE4-TCDDA and DAA8-TCDDA, one could expect DAA8-TCDDA to have a higher T_a since DAA8 has double the functionality of AGE4 and hence would result in denser crosslinks. Clearly, the rigidity of the AGE4 comonomer outweighs the effect of less dense crosslinks: AGE4-TCDDA is the most rigid polymer among all four. This dominance of monomer rigidity was observed previously [33]. Similarly, the incorporation of the TEGDMA, with its linear and flexible backbone, yielded polymers with lower T_g and T_a. Comparing AGE5-TEGDMA and DAA4-TEGDMA, we can note the slightly higher T_g and T_a as a result of the aromatic rings in DAA4. In all formulations, the alpha relaxations occur within narrow temperature frames indicating that our poly(thioether) materials have good network homogeneity (Fig. 6), as expected from the click character of the curing reactions at both stages.

4. CONCLUSION

We have shown an efficient procedure to prepare poly(thioether) thermosets starting from a set of clickable monomers. We first synthesize a set of tertiary amine comonomers through eco-friendly procedures based on click aza-Michael and epoxy-amine reactions. We incorporate these catalytic comonomers in several acrylate-thiol or methacrylate-thiolformulations to get a

final poly(thioether) structure through a dual-curing process. First, a thiol-Michael addition takes place between thiols and diacrylates or dimethacrylates, the choice of which depends on the extent of catalysis of the comonomer. This is followed by a radical thiol-ene UV photopolymerization of the remaining thiols and the allyl functional comonomer. Complete FTIR conversions were measured at the end of both stages showing true click behaviour. The fully crosslinked materials are soft, with T_a ranging between 3-25ºC. Thanks to this sub-ambient alpha-relaxation temperature range, we postulate that these materials could be used as flexible coatings for delicate substrates such as plastic or paper.

Furthermore, in contrast to base or nucleophile catalyzed conventional Michael-type systems, our formulations do not contain any low molecular weight catalysts, capable of migrating and contaminating substrates, and therefore the proposed system might be suitable for applications where very high purities are sought after. To obtain hard materials for different applications, one can use the same procedure but with more rigid and/or higher functional methacrylates involved, a stoichiometric excess of which would result in even harder materials after being photopolymerized at the final stage of curing.

The novel strategy proposed herein for preparing a new family of dual-curable thermosets is highly versatile, selective and energy efficient. Both curing stages take place with high yields at a mild temperature. Depending on the tertiary amine content and the molecular structure of the comonomer synthesized, curing kinetics and final material properties can be customized, allowing also the incorporation of methacrylates through rapid Michael-addition reactions.

ACKNOWLEDGEMENTS

The authors would like to thank MINECO (MAT2017-82849-C2-1-R and MAT2017-82849-C2-2-R) and Generalitat de Catalunya (2014-SGR-67 and Serra Húnter programme) for the financial support.

REFERENCES

[1] H.C. Kolb, M.G. Finn, K.B. Sharpless, Click Chemistry: Diverse Chemical Function from a Few Good Reactions, Angew. Chemie - Int. Ed. 40 (2001) 2004–2021.

[2] B.D. Mather, K. Viswanathan, K.M. Miller, T.E. Long, Michael addition reactions in macromolecular design for emerging technologies, Prog. Polym. Sci. 31 (2006) 487–531. doi:10.1016/j.progpolymsci.2006.03.001.

[3] C.E. Hoyle, A.B. Lowe, C.N. Bowman, Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis, Chem. Soc. Rev. 39 (2010) 1355.

doi:10.1039/b901979k.

[4] D.P. Nair, M. Podgórski, S. Chatani, T. Gong, W. Xi, C.R. Fenoli, C.N. Bowman, The Thiol-Michael addition click reaction: A powerful and widely used tool in materials chemistry, Chem. Mater. 26 (2014) 724–744. doi:10.1021/cm402180t.

[5] W. Xi, C. Wang, C.J. Kloxin, C.N. Bowman, Nitrogen-centered nucleophile catalyzed thiol-vinylsulfone addition, another thiol-ene “click” reaction, ACS Macro Lett. 1 (2012) 811–814. doi:10.1021/mz3001918.

[6] G.-Z. Li, R. Randev, A.H. Soeriyadi, G.J. Rees, C. Boyer, Z. Tong, C.R. Becer, D.M. Haddleton, Investigation into thiol-(meth)acrylate Michael addition reactions using amine and phosphine catalysts, Polym. Chem. 1 (2010) 1196–1204. doi:10.1039/c0py00100g.

[7] J.W. Chan, C.E. Hoyle, A.B. Lowe, M. Bowman, Nucleophile-Initiated Thiol-Michael Reactions: Effect of Organocatalyst, Thiol, and Ene, Macromolecules. 43 (2010) 6381–6388. doi:10.1021/ma101069c.

[8] D.P. Nair, N.B. Cramer, J.C. Gaipa, M.K. McBride, E.M. Matherly, R.R. McLeod, R. Shandas, C.N. Bowman, Two-Stage Reactive Polymer Network Forming Systems, Adv. Funct. Mater. 22 (2012) 1502–1510. doi:10.1002/adfm.201102742.

[9] D.P. Nair, N.B. Cramer, M.K. McBride, J.C. Gaipa, R. Shandas, C.N. Bowman, Enhanced two-stage reactive polymer network forming systems, Polymer (Guildf). 53 (2012) 2429–2434. doi:10.1016/j.polymer.2012.04.007.

[10] A.O. Konuray, X. Fernández-Francos, À. Serra, X. Ramis, Sequential curing of amine-acrylate-methacrylate mixtures based on selective aza-Michael addition followed by radical photopolymerization, Eur. Polym. J. 84 (2016) 256–267. doi:10.1016/j.eurpolymj.2016.09.025.

[11] S. Chatani, C. Wang, M. Podgórski, C.N. Bowman, Triple Shape Memory Materials Incorporating Two Distinct Polymer Networks Formed by Selective Thiol–Michael Addition Reactions, Macromolecules. 47 (2014) 4949–4954. doi:10.1021/ma501028a.

[12] H. Peng, D.P. Nair, B.A. Kowalski, W. Xi, T. Gong, C. Wang, M. Cole, N.B. Cramer, X. Xie, R.R. McLeod, C.N. Bowman, High performance graded rainbow holograms via two-stage sequential orthogonal thiol-click chemistry, Macromolecules. 47 (2014) 2306–2315. doi:10.1021/ma500167x.

[13] S.J. Ma, S.J. Mannino, N.J. Wagner, C.J. Kloxin, Photodirected Formation and Control of Wrinkles on a Thiol − ene Elastomer, ACS Macro Lett. 2 (2013) 474–477. doi:10.1021/mz400166e.

[14] U. Tunca, Orthogonal multiple click reactions in synthetic polymer chemistry, J. Polym. Sci. Part A Polym. Chem. 52 (2014) 3147–3165. doi:10.1002/pola.27379.

[15] J.W. Chan, C.E. Hoyle, A.B. Lowe, Sequential phosphine-catalyzed, nucleophilic thiol ene/radical-mediated thiol-yne reactions and the facile orthogonal synthesis of polyfunctional materials, J. Am. Chem. Soc. 131 (2009) 5751–5753. doi:10.1021/ja8099135.

[16] H. Peng, C. Wang, W. Xi, B.A. Kowalski, T. Gong, X. Xie, W. Wang, D.P. Nair, R.R. McLeod, C.N. Bowman, Facile image patterning via sequential thiol-Michael/thiol-yne click reactions, Chem. Mater. 26 (2014) 6819–6826. doi:10.1021/cm5034436.

[17] A.O. Konuray, F. Liendo, X. Fernández-Francos, À. Serra, M. Sangermano, X. Ramis, Sequential curing of thiol-acetoacetate-acrylate thermosets by latent Michael addition reactions, Polymer (Guildf). 113 (2017) 193–199. doi:10.1016/j.polymer.2017.02.072.

[18] W. Xi, H. Peng, A. Aguirre-Soto, C.J. Kloxin, J.W. Stansbury, C.N. Bowman, Spatial and temporal control of thiol-michael addition via photocaged superbase in photopatterning and two-stage polymer networks formation, Macromolecules. 47 (2014) 6159–6165. doi:10.1021/ma501366f.

[19] A.O. Konuray, A. Ruiz, J.M. Morancho, J.M. Salla, X. Fernández-Francos, À. Serra, X. Ramis, Sequential dual curing by selective Michael addition and free radical polymerization of acetoacetate-acrylate-methacrylate mixtures, Eur. Polym. J. 98 (2018) 39–46. doi:10.1016/j.eurpolymj.2017.11.003.

[20] A.K. Higham, L.A. Garber, D.C. Latshaw, C.K. Hall, J.A. Pojman, S.A. Khan, Gelation and cross-linking in multifunctional thiol and multifunctional acrylate systems involving an in situ comonomer catalyst, Macromolecules. 47 (2014) 821–829. doi:10.1021/ma402157f.

[21] C.O. Bounds, J. Upadhyay, N. Totaro, S. Thakuri, L. Garber, M. Vincent, Z. Huang, M. Hupert, J.A. Pojman, Fabrication and characterization of stable hydrophilic microfluidic devices prepared via the in situ tertiary-amine catalyzed Michael addition of multifunctional thiols to multifunctional acrylates, ACS Appl. Mater. Interfaces. 5 (2013) 1643–1655. doi:10.1021/am302544h.

[22] G. González, X. Fernández-Francos, À. Serra, M. Sangermano, X. Ramis, Environmentally-friendly processing of thermosets by two-stage sequential aza-Michael addition and free-radical polymerization of amine–acrylate mixtures, Polym. Chem. 6 (2015) 6987–6997. doi:10.1039/C5PY00906E.

[23] B.B. Uysal, U.S. Gunay, G. Hizal, U. Tunca, Orthogonal multifunctionalization of aliphatic polycarbonate via sequential Michael addition and radical-thiol-ene click reactions, J. Polym. Sci. Part A Polym. Chem. 52 (2014) 1581–1587. doi:10.1002/pola.27151.

[24] H. Durmaz, M. Butun, G. Hizal, U. Tunca, Postfunctionalization of polyoxanorbornene

via sequential Michael addition and radical thiol-ene click reactions, J. Polym. Sci. Part A Polym. Chem. 50 (2012) 3116–3125. doi:10.1002/pola.26098.

[25] I.I. Yilmaz, M. Arslan, A. Sanyal, Design and synthesis of novel “orthogonally” functionalizable maleimide-based styrenic copolymers, Macromol. Rapid Commun. 33 (2012) 856–862. doi:10.1002/marc.201200036.

[26] X. Fernández-Francos, X. Ramis, Structural analysis of the curing of epoxy thermosets crosslinked with hyperbranched poly(ethyleneimine)s, Eur. Polym. J. 70 (2015) 286–305. doi:10.1016/j.eurpolymj.2015.07.031.

[27] J.-P. Pascault, H. Sautereau, J. Verdu, R.J.J. Williams, Thermosetting Polymers, Marcel Dekker, Inc., New York, 2002.

[28] S.R. Williams, K.M. Miller, T.E. Long, Michael addition reaction kinetics of acetoacetates and acrylates for the formation of polymeric networks, Prog. React. Kinet. Mech. 32 (2007) 165–194. doi:10.3184/146867807X247730.

[29] A. Belmonte, X. Fernández-Francos, À. Serra, S. De la Flor, Phenomenological characterization of sequential dual-curing of off-stoichiometric “thiol-epoxy” systems: Towards applicability, Mater. Des. 113 (2017) 116–127. doi:10.1016/j.matdes.2016.10.009.

[30] K. Dušek, M. Dušková-Smrčková, Network structure formation during crosslinking of organic coating systems, Prog. Polym. Sci. 25 (2000) 1215–1260. doi:10.1016/S0079-6700(00)00028-9.

[31] Y. Tanaka, J.L. Stanford, R. Stepto, Interpretation of gel points of an epoxy-amine system including ring formation and unequal reactivity: Reaction scheme and gel-point prediction., Macromolecules. 45 (2012) 7186–7196. doi:10.1021/ma300984u.

[32] G.T. Fox, Influence of diluent and of copolymer composition on the glass temperature of a polymer system, Bull. Am. Phs. Soc. 1 (1952) 123. http://ci.nii.ac.jp/naid/10027041279/en/ (accessed October 30, 2017).

[33] A.O. Konuray, X. Fernández-Francos, X. Ramis, Curing kinetics and characterization of dual-curable thiol-acrylate-epoxy thermosets with latent reactivity, React. Funct. Polym. 122 (2018) 60–67. doi:10.1016/j.reactfunctpolym.2017.11.010.

- The novel allylic comonomers successfully catalyzed thiol-Michael reactions
- Depending on the their basicity, different reaction kinetics were observed
- They joined the polymer network later via radical thiol-ene reaction
- Soft, clear and insoluble materials were obtained by a dual-curing process