Elsevier Editorial System(tm) for Polymer
Manuscript Draft

Manuscript Number: POLYMER-17-201R1

Title: Sequential Curing of Thiol-Acetoacetate-Acrylate Thermosets by latent Michael Addition Reactions

Article Type: Research Paper

Section/Category: Synthesis and Chemistry of Polymers

Keywords: Michael addition
Thiol-acetoacetate-acrylate
Photobase

Corresponding Author: Professor Xavier Ramis, Professor

Corresponding Author's Institution: Universitat Politècnica de Catalunya

First Author: Ali Osman Konuray

Order of Authors: Ali Osman Konuray; Freddy Liendo; Xavier Fernández-Francos; Àngels Serra, Universitat Rovira i Virgili; Marco Sangermano; Xavier Ramis, Professor

Abstract: Thiol-acetoacetate-acrylate ternary dual-curing thermosets were prepared by a sequential process consisting of thiol-Michael addition to acrylates at room temperature followed by Michael addition of acetoacetates to acrylates at moderately elevated temperature. The curing sequence can be controlled with the help of the different acidities of the protons on thiol and acetoacetate groups, the favorable pKa of the base used as catalyst and the self-limiting character of Michael additions. The latency of the curing steps can be regulated by selection of the right catalysts, temperature and curing conditions. The properties of the intermediate and final materials can be tuned by changing the structure of the monomers and the contribution of both Michael addition reactions.

Cover Letter

Dept. de Màquines i Motors Tèrmics
UNIVERSITAT POLITÈCNICA DE CATALUNYA

Edifici de l'Escola Tècnica Superior
d'Enginyeria Industrial de Barcelona
Avgda. Diagonal, 647
08028 Barcelona
Tel./Fax: 93 401 73 89

Barcelona, February 21th 2017

Dear Dr. Axel H.E. Mueller
Editor of Polymer

We send the response to the reviewers' comments and the revised version of our manuscript entitled: **Sequential Curing of Thiol-Acetoacetate-Acrylate Thermosets by latent Michael Addition Reactions** to be submitted in Polymer.

Looking forward to hearing from you, I remain.

Yours sincerely,

Prof. Xavier Ramis

Response to Reviewers

We appreciate the reviewers' overall positive evaluation of the manuscript and the suggestions aimed toward its improvement. Taking into account the reviewers' comments, we have made corrections to the manuscript where convenient and highlighted them in red.

Referee: 2

Comments to the Author

It is pretty new and good idea to design this kind of thiol-ene sequential dual curing system, through the difference in Michael addition activity of different vinyl monomer and difference in pKa of different super base catalyst, especially the photo triggered latent base catalyst exhibited much better properties. This method can achieve controllability of two stage curing reaction in some degree and produce materials with wide range of Tg and thermo stability, even though the results were not totally satisfied in room temperature stability of first stage products.

The work was well designed and performed, the data were also well organized and analysized. It is recommended to be accepted to publish in this journal with a little revision.

In P19, l1, "Gelation during thiol-Michael reaction was studied by isothermal FTIR/TMA combined experiments at 30ºC for S3:AC:TMPTA formulations using 0.2% by weight of DMAP as catalyst and the results are summarized in Table 1." The data described in this sentence could not be found in Table 1, is there anything wrong? Is a wrong catalyst name written here?

As explained in page 14 (first paragraph) DMAP was selected for the determination of gel point conversion because of the slower reaction rate making it easier to prepare the samples and analyze them DBN and TBD could not be used because samples gel even before they are placed into the TMA Moreover in footnote d of Table 1 it is explained that gelation experiments were carried out using 0.2% by weight of DMAP instead of DBN as catalyst for all formulations.

Referee: 3

Comments to the Author

This work on the sequential thiol-Michael addition to acrylates by Michael addition of acetoacetates to acrylates is a valuable contribution. The work is well executed and the paper well written. I do have some suggestions for the literature review:

The concept of a thiol-acrylate reaction followed by another polymerization at higher temperature was first done by Binici et al. (Binici,B.; Fortenberry, D. I.; Leard, K. C.; Molden, M.; Olten, N.; Popwell, S.; Pojman, J. A. "Spherically Propagating Thermal Polymerization Fronts," J. Polym. Sci. Part A: Polym. Chem. 2006, 44, 1387-1395.)

Other work on thiol-acrylate polymerization that may interest the authors:

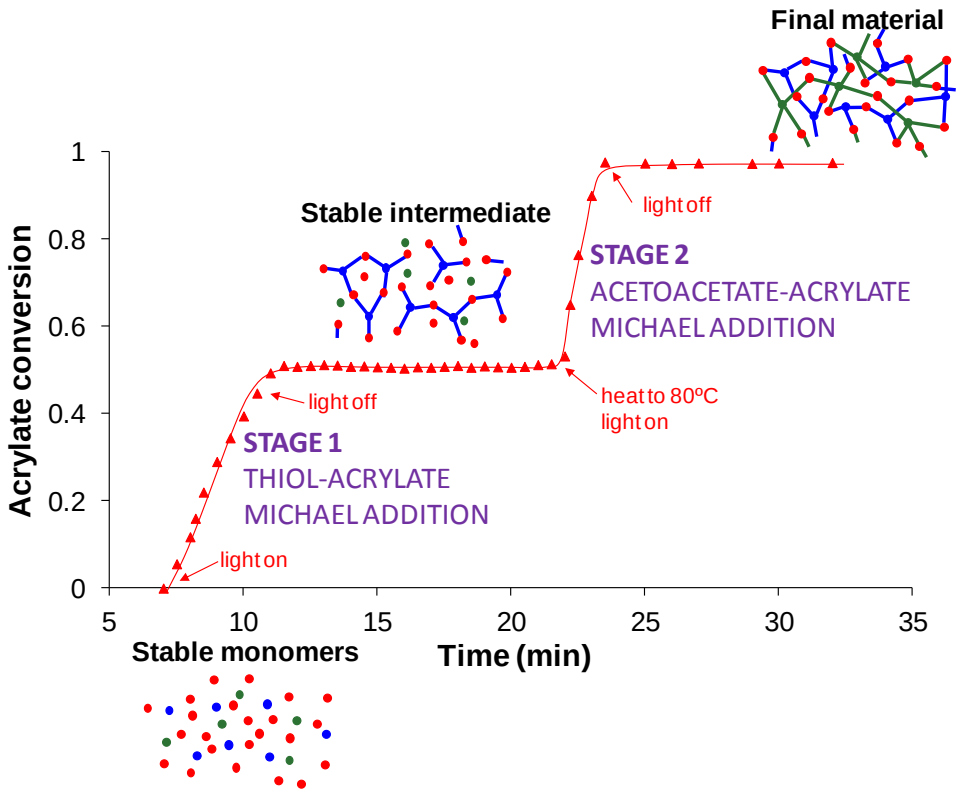
1) Bounds, C. O.; Goetter, R.; Pojman, J. A.; Vandersall, M. "Preparation and Application of Microparticles Prepared Via the Primary Amine-Catalyzed Michael Addition of a Trithiol to a Triacrylate," J. Polym. Sci. A Polym. Chem. 2011, 50, 409-422.

2) Bounds, C. O.; Upadhyay, J.; Totaro, N.; Thakuri, S.; Garber, L.; Vincent, M.; Huang, Z.; Pojman, J. A. "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 2013, 5, 1643-1655.
3) Garber, L.; Chen, C.; Kilchrist, K. V.; Bounds, C.; Pojman, J.; Hayes, D. "Thiol-Acrylate Nanocomposite Foams for Critical Size Bone Defect Repair: A Novel Biomaterial," J. Biomed. Mater. Res. Part A 2013, 101A, 3531-3541.
4) Higham, A. K.; Garber, L. A.; Latshaw, D. C.; Hall, C. K.; Pojman, J. A.; Khan, S. A. "Gelation and Cross-Linking in Multifunctional Thiol and Multifunctional Acrylate Systems Involving an in Situ Comonomer Catalyst," Macromolecules 2014, 47, 821-829.
5) Smoak, M.; Garber, L.; Chen, C.; Hayes, D.; Pojman, J. A. "Antimicrobial Cytocompatible Pentaerythritol Triacrylate-Co-Trimethylolpropane Composite Scaffolds for Orthopaedic Implants," J. Appl. Poly. Sci. 2014, 131, 41099.
6) Chen, C.; Garber, L.; Smoak, M.; Fargason, C.; Scherr, T.; Blackburn, C.; Bacchus, S.; Lopez, M. J.; Pojman, J. A.; Del Piero, F.; Hayes, D. J. "In Vitro and in Vivo Characterization of Pentaerythritol Triacrylate-Co-Trimethylolpropane Nanocomposite Scaffolds as Potential Bone Augments and Grafts," Tissue Engineering Part A 2015, 21, 320-331.

We agree that the work by Binici et al. is one of the first in dual curing research. They explore a sequential curing scheme using two reactions at different temperatures and as such, their work is relevant to ours. Therefore, we added a paragraph about this in our introduction section

Regarding the suggested references 1 to 6, we find the work by Higham et al. relevant to our discussion about gelation during thiol-acrylate Michael addition. The methods they used in calculating theoretical gel conversions are the same with our methods. Therefore we decided to add this work to our bibliography.

Graphical Abstract



Sequential Curing of Thiol-Acetoacetate-Acrylate Thermosets by latent Michael Addition Reactions

Ali Osman Konuray,[a] Freddy Liendo,[a] Xavier Fernández-Francos,[a] Àngels Serra,[b] Marco Sangermano,[c] Xavier Ramis[a,*]

[a] Thermodynamics Laboratory, ETSEIB Universitat Politècnica de Catalunya, Av. Diagonal 647, 08028, Barcelona, Spain

[b] Department of Analytical and Organic Chemistry, Universitat Rovira i Virgili, C/ Marcel·lí Domingo s/n, 43007, Tarragona, Spain.

[c] Dept. of Material Science and Chemical Engineering, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy

* Corresponding author: Tel.: +34 934016592; fax: + 34 934017389

E-mail address: ramis@mmt.upc.edu

Abstract

Thiol-acetoacetate-acrylate ternary dual-curing thermosets were prepared by a sequential process consisting of thiol-Michael addition to acrylates at room temperature followed by Michael addition of acetoacetates to acrylates at moderately elevated temperature. The curing sequence can be controlled with the help of the different acidities of the protons on thiol and acetoacetate groups, the favorable *p*Ka of the base used as catalyst and the self-limiting character of Michael additions. The latency of the curing steps can be regulated by selection of the right catalysts, temperature and curing conditions. The properties of the intermediate and final materials can be tuned by changing the structure of the monomers and the contribution of both Michael addition reactions.

Keywords

Michael addition, acetoacetate, acrylate, thermosets, photobase

1. Introduction

Dual-step curing systems that involve two controllable and sequential *click* reactions are of great interest because they provide easily tunable polymer networks that can be exploited in current and novel multi-stage technological applications [1].

A dual curing scheme involving thiol-acrylate Michael addition followed by a second curing reaction was first employed by Binici et al. [2] to carry out spherically propagating polymerizations. Recently, sequential dual curing procedures based on a single reaction mechanism but featuring monomers with different reactivity were developed [3-5]. In a recent study, nucleophile-catalyzed thiol-Michael addition was used to carry out sequential curing of vinyl sulfones and acrylates, where vinyl sulfones react selectively with thiols [3]. In a different paper [4], a mixture of two multifunctional thiols of different reactivity, an acrylate and a vinyl sulfone, were cured sequentially in consecutive steps at 22ºC (first stage of curing) and 90ºC (second stage of curing). In addition, the existence of two distinct networks led to a material with triple shape memory behaviour [4]. Bowman *et al.* [6] developed a new dual curing process based on sequential activation of thiol-acrylate and thiol-methacrylate reactions using a tertiary amine catalyst for the first stage and a photocaged superbase for the second stage. The use of photobase generators is a good strategy to ensure selectivity and latency but a radical inhibitor might be necessary in some cases [7].

In this study, we developed a novel methodology of sequential dual curing, based on two base-catalyzed Michael additions. The first is a thiol-Michael addition between thiol and acrylate groups (stage 1) and the second is a Michael addition of acetoacetate to acrylate groups (stage 2). Depending on the catalyst, monomers and thiol/acetoacetate/acrylate ratio, the stability period before both curing stages and the properties of the materials can be tuned. The participation of acrylate monomers in both stages of curing assures the covalent linkage between the two thermosetting networks.

2. Materials and methods

2. 1. Materials

All chemicals and reagents were purchased from Sigma-Aldrich and used as received unless noted otherwise. As Michael donors a trifunctional thiol crosslinker, trimethylolpropane tris(3-mercaptopropionate) M_w=398.56 g/mol (hereafter referred to as S3) (*p*Ka=9.3) [8], and a tetrafunctional acetoacetate crosslinker diethyl 3-oxopentanedionate M_w=202,20 g/mol (hereafter referred to as AC) ($pKa_{,1}$=12, $pKa_{,2}$=13) [9], were used. A difunctional 1,6-hexanediol diacrylate M_w=226.3 g/mol (HDDA) and a trifunctional trimethylolpropane triacrylate (TMPTA) were used as acrylate monomers (Michael acceptors).

Bases of different basicity (*p*Ka values) were used as catalytic systems: 1,5-diazabicycle[4.3.0]non-5-ene (DBN) (*p*Ka=13.5) [8], 4-(N,N-dimethylamino) pyridine (DMAP) (*p*Ka=9.2) [10], 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (*p*Ka=15) [11]. 1,5,7-triazabicyclo[4.4.0]dec-5-enyltetraphenylborate (TBD·$HBPh_4$) (*p*Ka=15) [11], synthesized as reported in the literature [12,13], was also used as a photobase generator. Isopropylthioxanthone (ITX) was used as a photosensitizer and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a radical inhibitor in formulations containing TBD·$HBPh_4$. **Figure 1** shows the chemical structure of the compounds used and the photo-generation of TBD from TBD·$HBPh_4$ as it is described by Sun *et al.* [12].

2.2. Sample preparation

The catalyst was added to thiol and stirred mechanically until the mixture became clear at room temperature. Then acetoacetate and acrylate were added in respective order to the aforementioned mixture followed by quick stirring and immediate analysis or

sample preparation**.** In formulations containing TBD·$HBPh_4$, ITX and TEMPO were added before the addition of acetoacetate and acrylate. Different formulations were prepared and coded as S3:AC:HDDA x:y:z or S3:AC:TMPTA x:y:z where x,y, and z stand for molar equivalents of thiols, acetoacetate hydrogens, and acrylate double bonds, respectively. Catalysts, ITX and TEMPO were added in parts per hundred (%) with respect to the total mass of mixture.

For proof of concept studies, three stoichiometric S3:AC:HDDA 1:1:2 formulations were prepared by adding: a) 0,5% DBN, b) 0,2% DMAP + 2% TBD·$HBPh_4$ + 1% ITX + 1% TEMPO and c) 2% TBD·$HBPh_4$ + 1% ITX + 1% TEMPO.

For the preparation of samples with tailor-made properties, S3:AC:TMPTA x:y:z formulations of different compositions were prepared by adding the minimum amount of DBN necessary to reach near complete curing. Fully cured samples for dynamomechanical, calorimetric and thermal analysis were prepared in a steel mold by isothermal dual curing in an oven at 30ºC for 2 hours (thiol-Michael addition) followed by 12 hours at 80ºC (acetoacetate acrylate Michael addition) and then postcured for 30 min at 200ºC.

2.3. Real-time conversion

A Brucker Vertex 70 FTIR spectrometer equipped with an attenuated total refection (ATR) accessory (Golden gateTM, Specac Ltd.) which is temperature controlled (heated single-reflection diamond ATR crystal) was used to monitor the evolution of acrylate groups during isothermal dual curing of the mixtures at 30ºC and 80ºC. Real-time spectra were collected at 30ºC or 80ºC in absorbance mode with a resolution of 4 cm^{-1} and a wavelength range from 400 to 4000 cm^{-1}, averaging 20 scans for each spectrum. A Hamamatsu Lightningcure LC5 (Hg-Xe lamp) with one beam conveniently adapted to ATR accessory was used to irradiate the formulations catalyzed with photobase

generator. The irradiation intensity was 17 mW/cm^2 (measured at 365 nm). Formulations containing TBD·HBPh$_4$/ITX/TEMPO were irradiated during both stages of curing, whereas formulations containing DMAP/TBD·HBPh$_4$/ITX/TEMPO were irradiated only during stage 2. A wire-wound rod was used to set a sample thickness of 25 μm.

The spectra were normalized using the area of the carbonyl ester group at 1720 cm^{-1}. The band at 1407 cm^{-1} (band of the CH_2 scissor deformation mode) [14] was used for the monitoring of acrylate groups and the conversion of these groups was determined by using the equation

$$\alpha_{acrylate} = 1 - \frac{A'_{1407,t}}{A'_{1407,0}} \qquad (1)$$

where A'_{1407} is the normalized area of the acrylate bands, and the subscripts t and 0 indicate the time t of spectra collection and initial time, respectively. The absorbance peak 2560 cm^{-1} was used to confirm qualitatively the complete conversion of thiol groups after stage 1 [4]. The low intensity of this band, in combination with the lower penetration depth at higher wavenumbers in ATR/FTIR spectroscopy, does not allow quantitative monitoring of thiol consumption.

2.4. Differential scanning calorimetry (DSC)

Calorimetric analyses were carried out on a Mettler DSC-822e thermal analyser. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium-zinc standard (temperature calibration).

Samples of approximately 10 mg were placed in aluminium pans with pierced lids and isothermally cured in the oven or in the FTIR as explained in sections 2.2 and 2.3. The glass transition temperatures (T_gs) of the obtained materials after both stage of curing were determined, by means of a scan at 10 ºC/min under nitrogen atmosphere, as the temperature of the half-way point of the jump in the heat capacity when the material

changed from glassy to the rubbery state and the error is estimated to be approximately ± 1°C.

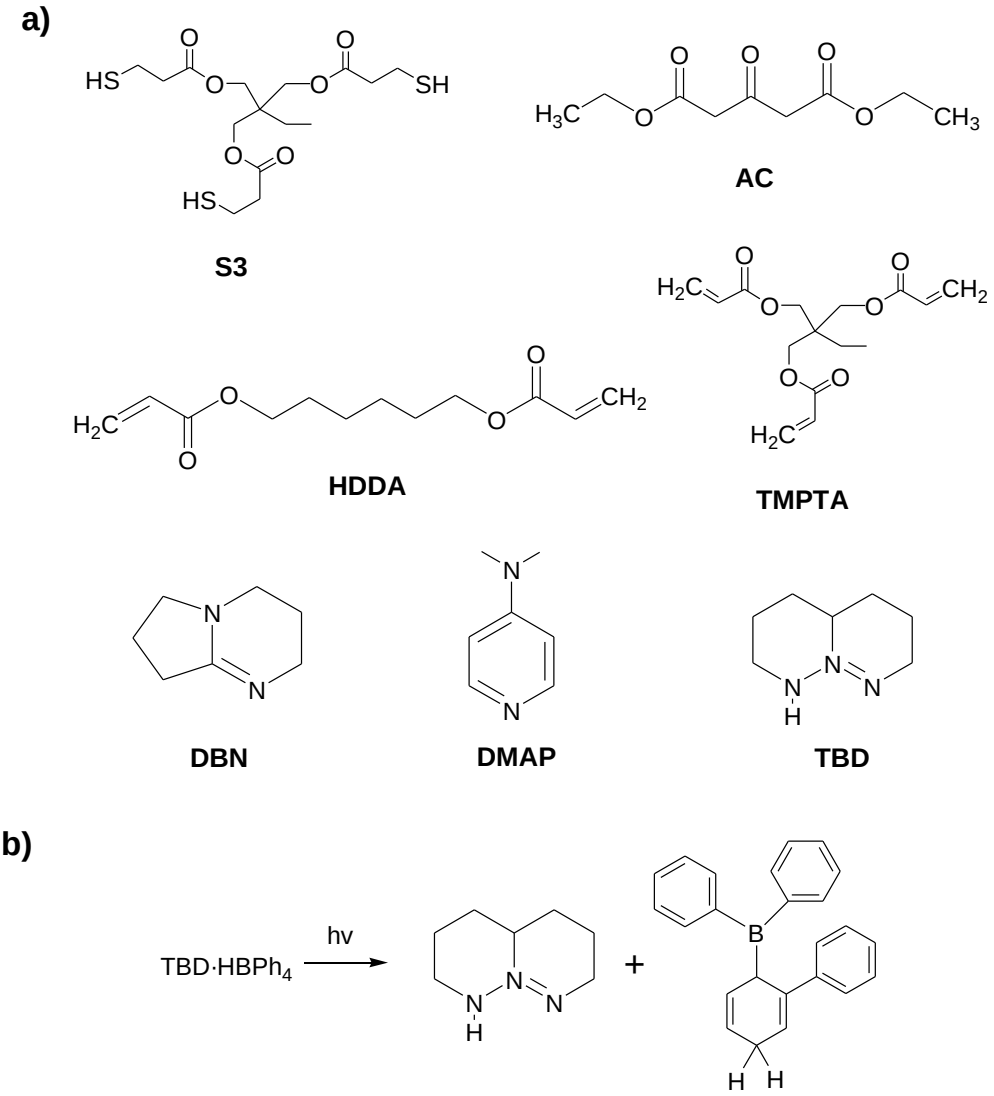


Figure 1. (a) Chemical structures of the compounds used in this study. (b) Photo-generation of TBD from TBD·$HBPh_4$.

2.5. Latency test

The latency tests were performed for S3:AC:HDDA 1:1:2 mixtures. After stage 1, samples were stored in a freezer and in an oven at controlled temperatures of -15 ºC and 30ºC, respectively. T_g's at different times of storage were measured by DSC, as explained in section 2.4, as an indirect way of measuring the conversion.

2.6. Gelation

A thermo-mechanical analyzer Mettler TMA SDTA840 was used to determine the gel point during thiol-Michael addition (stage 1) for S3:AC:TMPTA x:y:z formulations.

A silanized glass fiber disc about 5 mm in diameter was impregnated with the liquid formulation and sandwiched between two aluminium discs. The sample was placed at 30ºC and subjected to an oscillatory force from 0.005 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-Stockmayer equation [15-17]:

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

where r is the acrylate:thiol equivalent ratio, f the thiol functionality and g the acrylate functionality. For the formulations containing S3 and TMPTA, f and g are both equal to 3.

2.7. Dynamic mechanical analysis (DMA)

Fully cured materials were analyzed using a TA Instruments DMA Q800 device. Prismatic rectangular samples (ca. 1 x 13 x 20 mm^3) were analyzed by DMA using a single cantilever clamp at a frequency of 1 Hz and 0.05% strain at 3 ºC/min from -50 to 150ºC.

2.8. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out with a Mettler TGA/SDTA 851e/LF/1100 thermobalance. Fully cured samples with an approximate mass of 10 mg were thermally degraded between 30 and 800ºC at a heating rate of 10 ºC/min in a nitrogen atmosphere (50 cm^3/min measured under normal conditions).

3. Results and discussion

S3:AC:HDDA 1:1:2 formulations were chosen to demonstrate the potential of the proposed methodology for the preparation of a new family of thiol-acetoacetate-acrylate dual-curing thermosets, based on two sequential and self-limiting base-catalyzed latent Michael addition reactions (proof of concept).

The selection of the catalysts, DMAP, DBN, TBD/TBD·$HBPh_4$ (in increasing order of basicity) was made according to the acidity of the protons on thiol and acetoacetate groups and the *p*Ka values of thiol, acetoacetate and bases. TBD·$HBPh_4$ is a photobase generator capable of in situ generating TBD by irradiation (**Figure 1b),** that was selected as latent strong base. Release of TBD is facilitated by irradiation when desired.

The kinetic of Michael-addition reaction depends on the concentration of acrylate and also on the concentration of thiolate and enolate anions, formed by the deprotonation of thiols or acetoacetates, respectively. According to their *p*Ka values, S3 should react faster than AC, and DBN and TBD should be able to deprotonate both the S3 and acetoacetate, whereas DMAP would only deprotonate S3. A preliminary kinetic study revealed that the reaction of AC with HDDA did not take place at 30ºC within two hours with any of the catalysts tested. At 80ºC, AC:HDDA formulations reacted completely when DBN and TBD were used, but when DMAP was used, formulations barely reacted even after long reaction times. S3:HDDA mixtures reacted completely with all the catalysts at 30ºC, but the reaction, depending on the catalyst concentration, was very fast

with DBN and TBD, leading to significant polymerization and heating of the sample during preparation, making subsequent analysis impractical. Stoichiometric AC:HDDA and S3:HDDA formulations containing 2% (w/w) of TBD·$HBPh_4$ and 1% (w/w) of ITX reacted completely after UV-irradition with a Hamamatsu Lightning Cure LC5 (Hg-Xe) lamp and 17 mW/cm^2 intensity for 10 minutes at 30ºC and 80ºC, respectively. Acrylate homopolymerization took place in formulations with an excess of acrylate groups due to the formation of radicals during irradiation [7,18]. This could be avoided by using 1 % (w/w) TEMPO [7] as a radical scavenger and by limiting irradiation time and intensity.

Considering these preliminary results, S3:AC:HDDA 1:1:2 formulations were prepared using the following catalytic systems: a) DBN, b) TBD·$HBPh_4$/ITX/TEMPO and c) DMAP/TBD·$HBPh_4$/ITX/TEMPO. These formulations were sequentially cured (see **Figure 2**) starting from a temperature of 30ºC for stage 1 and 80ºC for stage 2 using the following three procedures:

a) Selective thermal activation of both stages using strong base catalyst, DBN.

b) Selective thermal and UV-activation of both stages using a strong photobase generator, TBD·$HBPh_4$.

c) Selective thermal activation of both stages using the weak base DMAP and TBD·$HBPh_4$/UV irradiation for the first and second stage, respectively.

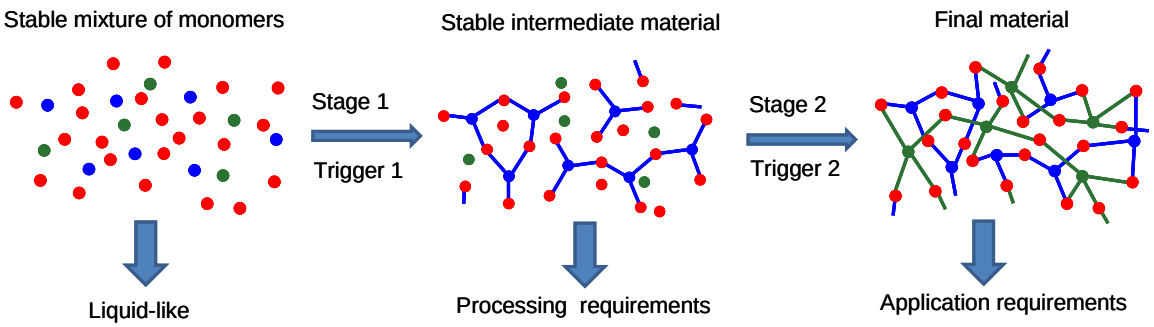


Figure 2. Schematic representation of the new dual-curing procedure. Red, blue and green circles are HDDA, S3 and AC monomers, respectively. Trigger 1 can be T=30ºC or/and UV-irradiation. Trigger 2 can be T=80ºC or/and UV-irradiation. Stage 1 is base-catalyzed thiol-Michael addition and stage 2 is acetoacetate-acrylate Michael addition reaction.

Figure 3 shows, the evolution of acrylate conversion during both curing stages, determined by *in-situ* FTIR/ATR monitoring, for the S3/AC/HDDA formulations studied**.** It can be observed that, for all procedures, an acrylate conversion of about 50% and 100% is reached at the end of stages 1 and 2, respectively. Although it was not possible to monitor the conversion of thiol groups with precision, FTIR/ATR spectra after stage 1 confirmed, albeit qualitatively, that all thiol groups were consumed. These results illustrate the sequential character of the curing process and the self-limiting character of thiol-Michael addition

In the formulation with 0.5% of DBN, stage 1 was very fast, whereas stage 2 was slower and a conversion plateau was reached. It is hypothesized that the amount of DBN was not enough to deprotonate completely the second hydrogen of AC, but increasing the amount of DBN is not recommended due to the high reactivity of the thiol-Michael reaction. Nevertheless, complete acrylate conversion was achieved by postcuring at 80 °C for 12 hours or at 200ºC for 30 min.

A more controlled system was obtained with DMAP and TBD·$HBPh_4$/ITX/TEMPO. stage 1 was slower due to lower basic character of DMAP. This system had a higher stability after stage 1, because acetoacetate-acrylate Michael addition does not take place

in the presence of DMAP at 30ºC. stage 2 was initiated only when the sample was UV-irradiated and heated up to 80ºC and was complete in approximately five minutes.

The formulation containing TBD·HBPh$_4$/ITX/TEMPO showed the most latent character, since no reaction started until the sample was irradiated. Moreover, stages 1 and 2, were completed in 4.5 and 1.5 min, respectively. It was necessary to limit irradiation during stage 1 to prevent free-radical homopolymerization of excess acrylates, even in the presence of TEMPO. Acetoacetate-acrylate addition required more base catalyst than thiol-Michael addition, making it necessary to be irradiated again during stage 2.

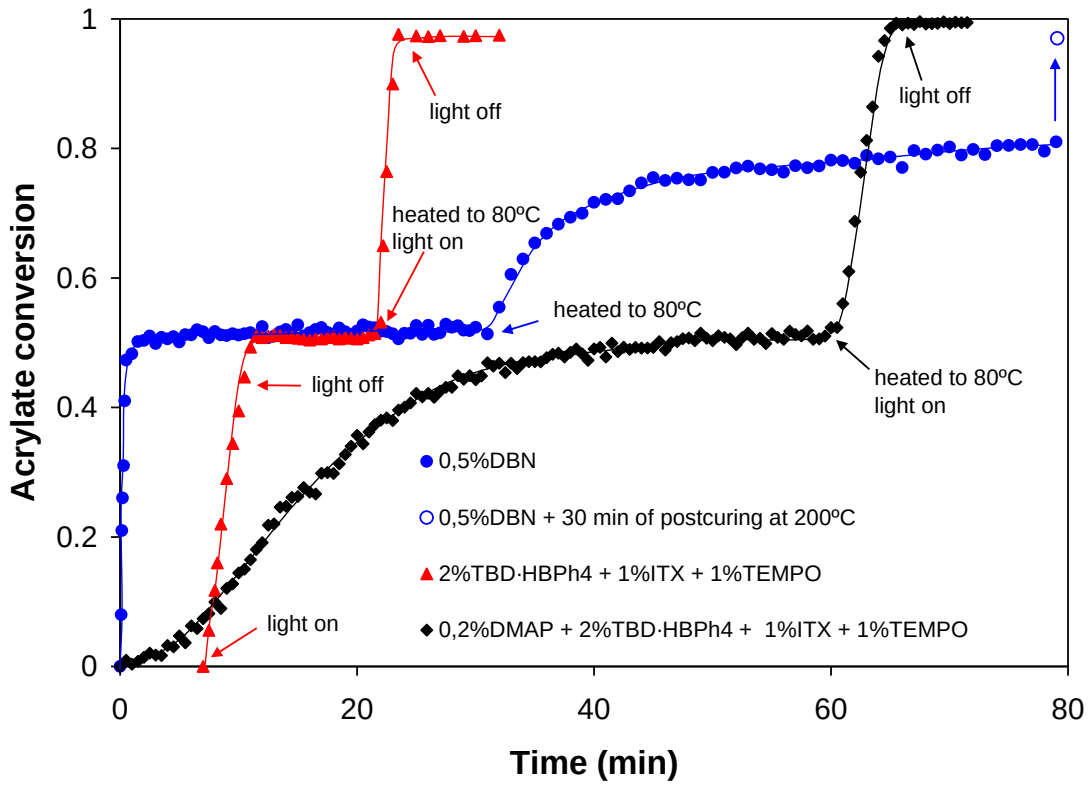


Figure 3. Acrylate conversion plots for the three dual-curing procedures, developed for S3:AC:HDDA 1:1:2 formulations. Reaction was started at 30ºC and when stage 1 is complete reaction mixture was heated up to 80ºC. Samples containing TBD·HBPh$_4$/ITX/TEMPO and DMAP/TBD·HBPh$_4$/ITX/TEMPO were irradiated with 17 mW/cm^2 using a Hamamatsu Lightning Cure LC5 (Hg-Xe) lamp. The blue hollow circles correspond to postcuring at 200 °C for 30 minutes and therefore the time scale is 110 minutes (80 min + 30 min).

The glass transition temperatures of the intermediate and final materials, obtained for the three dual-curing procedures, were almost identical, regardless of the catalyst used, with values averaging -70ºC and -25ºC after stages 1 and 2, respectively.

Storage stability after stage 1 was studied by calorimetry. T_g was measured to monitor the degree of curing, after prolonged storage at -15 and 30°C, as seen in **Figure 4**. All formulations stored at -15ºC showed extremely high latency, maintaining constant T_g during storage. When 2% of TBD·$HBPh_4$ was used, the material was stable at 30ºC, because the acetoacetate-acrylate reaction required extra UV exposure. Mixtures with DBN or DMAP/TBD·$HBPh_4$ showed an increase in T_g after two hours of storage at 30ºC, until they reached a plateau. Formulations containing only DMAP showed the same behavior as DMAP/TBD·$HBPh_4$ formulations. The activity of DBN can be rationalized on the basis of its high *p*Ka, which makes it possible to abstract the first acidic proton on the acetoacetate but not the second one. The unexpected activity of DMAP can be explained in terms of nucleophile-initiated anionic chain mechanism, similar to that proposed by Hoyle et al. [8,19]. In our system, the process could be initiated by nucleophilic attack of DMAP at the β-carbon of the acrylate C=C bond to give a strong enolate anion capable of abstracting the acidic proton of acetoacetate.

Having established these dual-cure procedures with a controlled curing sequence, we prepared and characterized a new family of sequential thiol-Michael/acetoacetate-acrylate Michael materials with a broad range of properties after both stages of curing, by replacing bifunctional HDDA with a trifunctional acrylate, trimethylolpropane triacrylate (TMPTA). Mixtures of S3:AC:TMPTA in different molar ratios and using DBN as catalyst were cured for 2 hours at 30ºC (thiol-Michael addition) followed by 12 hours at 80ºC (acetoacetate-acrylate Michael addition) and then postcured for 30 min at 200ºC. The amount of DBN used was the minimum required to achieve near complete conversion at the end of both curing stages, while at the same time making it possible to

facilitate sample preparation and ensure homogeneity at the beginning of the curing process. Photocured thick samples were not prepared for analysis because of the high amount of UV-irradiation is necessary and the impossibility of achieving homogeneous activation within all parts of the sample. DMAP was selected for the determination of gel point conversion because of the slower reaction rate, making it easier to prepare the samples and analyze them. DBN and TBD could not be used because gelation was reached quickly during TMA stabilization. **Table 1** shows the composition of formulations studied and results relevant to reaction kinetics and thermal characteristics at both curing stages..

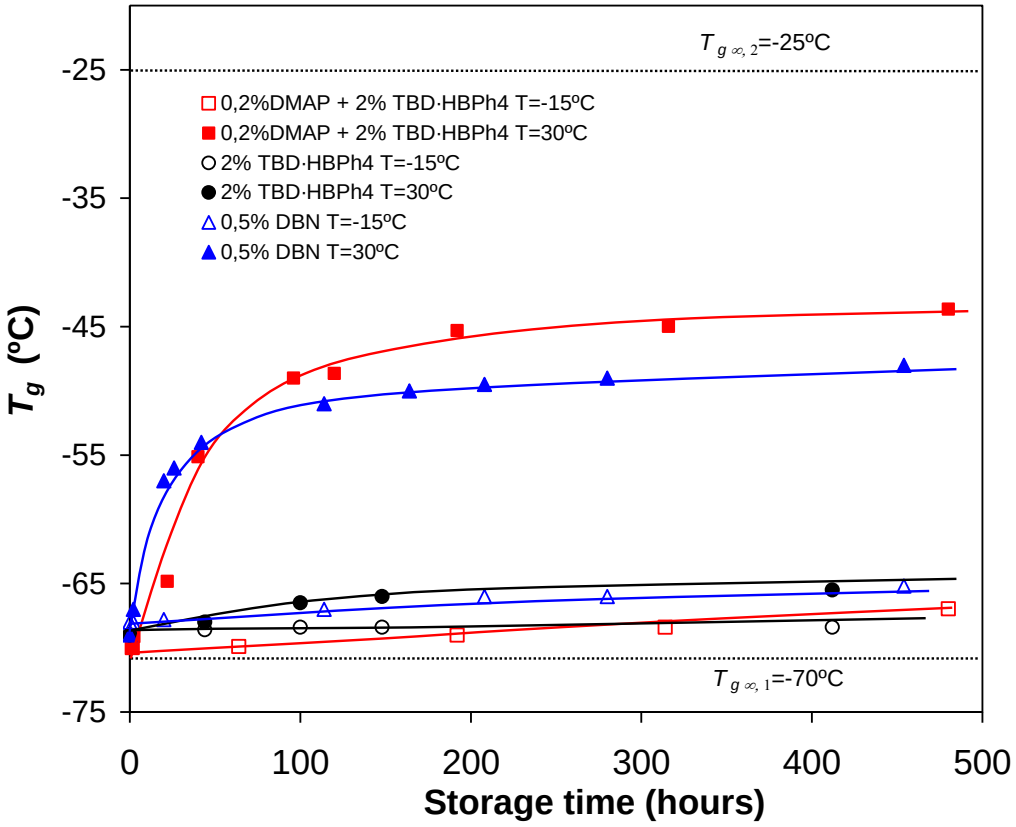


Figure 4. Glass transition temperatures at 10ºC/min of the different formulations as function of storage time after stage 1 which was performed under the same conditions of Figure 3. Final T_g after stage 2 are shown as dashed lines.

Table 1. Composition of S3:AC:TMPTA formulations used in this work. Acrylate conversions and glass transition temperatures after stage 1 and stage 2. Theoretical and experimental conversions at gelation. Thermal degradation data of the materials.

Formulation [a]	DBN [b] (phr)	S3 (wt%)	AC (wt%)	TMPTA (wt%)	Stage 1				Stage 2		
					Acrylate conv. (%)	T_g [c] (ºC)	α_{gel}^{exp} [d] (%)	α_{gel}^{theor} [e] (%)	Acrylate conv. (%)	T_g [c] (ºC)	$T_{5\%}$ [f] (ºC)
S3:AC:TMPTA 1:0:1	0.1	57.4	0.0	42.6	~100	-13	54	50	~100	-13	356
S3:AC:TMPTA 3:1:4	0.2	47.2	6.0	46.8	~75	-19	47	43	97	0	348
S3:AC:TMPTA 1:1:2	0.4	34.9	13.3	51.8	~50	-39	43	35	94	17	322
S3:AC:TMPTA 1:3:4	0.75	19.6	22.3	58.1	~25	-54	not gel	25	92	43	308
S3:AC:TMPTA 0:1:1	2	0.0	33.9	66.1	~0	-78	-	-	95	83	259

[a] Composition in molar ratio of SH:acetoacetate protons:acrylate double bonds. [b] DBN added in parts per hundred (phr) of the total weight of monomers. [c] Glass transition temperatures determined by DSC at 10ºC/min. [d] Experimental conversions of acrylate groups at the gel point, calculated as the conversions reached in FTIR at the gel times determined by TMA, using 0.2 phr of DMAP instead of DBN in all formulations. [e] Theoretical conversions of acrylate groups at the gel point calculated assuming ideal random step-wise reaction. [f] Temperature at 5% weight loss determined by thermogravimetric analysis at 10ºC/min in nitrogen atmosphere.

From **Table 1**, it can be observed that both curing stages proceed in an orthogonal fashion reaching near-complete conversions. Incomplete final acrylate conversion can be explained by the lower reactivity of the second acetoacetate hydrogen and by topological restrictions due to the high functionality and low equivalent weight of both TMPTA and AC, leading to a strongly hindered network structure. The T_g after thiol-Michael addition decreases with increasing AC content, due to the plasticizing effect of the acetoacetates and acrylates in excess. On the contrary, by increasing the content of AC, a significant increase in T_g after stage 2 is observed, related with the higher functionality and rigidity of AC in comparison with S3. For all formulations, a significant increase in T_g takes place after completion of stage 2 due to the reaction of acrylate and acetoacetato groups remaining after stage 1, leading to a significant increase in crosslinking.

The effect of acrylate structure can be demonstrated by comparing S3:AC:TMPTA 1:1:2 (**Table 1**) and S3:AC:HDDA 1:1:2 (proof of concept) materials. As it is expected, the T_g increases from -70ºC to -39ºC (stage 1) and from -25 to 17ºC (stage 2) when flexible HDDA with a functionality of 2 is replaced by less flexible TMPTA with a functionality of 3, leading to more densely crosslinked networks.

Figure 5 compares the tan δ and storage modulus of S3:AC:TMPTA final materials. In agreement with T_g's shown in **Table 1**, the relaxation curves are shifted towards higher temperatures with increasing AC content. The breadth of the tan δ peaks and the storage moduli at the relaxed state also increase accordingly, as commonly observed in thermosets with increasing crosslinking density. This was expected given the higher functionality and lower molecular weight of AC compared to S3. The shape of the tan δ becomes also somewhat bimodal with increasing AC content, suggesting some heterogeneity in the network structure of AC-TMPTA network.

Gelation during thiol-Michael reaction was studied by isothermal FTIR/TMA combined experiments at 30ºC for S3:AC:TMPTA formulations using 0.2% by weight of DMAP as catalyst and the results are summarized in **Table 1**. The theoretical conversion at gelation, α_{gel}^{theor}, and the experimental ones, α_{gel}^{exp}, follow the same trend, increasing with the S3 content, but α_{gel}^{exp} is higher than α_{gel}^{theor}. S3:AC:TMPTA 1:3:4 should have gelled at complete thiol conversion but did not. Intramolecular loop formation causing a delay in gelation could explain these discrepancies [20], as observed in off-stoichiometric thiol-epoxy formulations using S3 as thiol crosslinker [21].

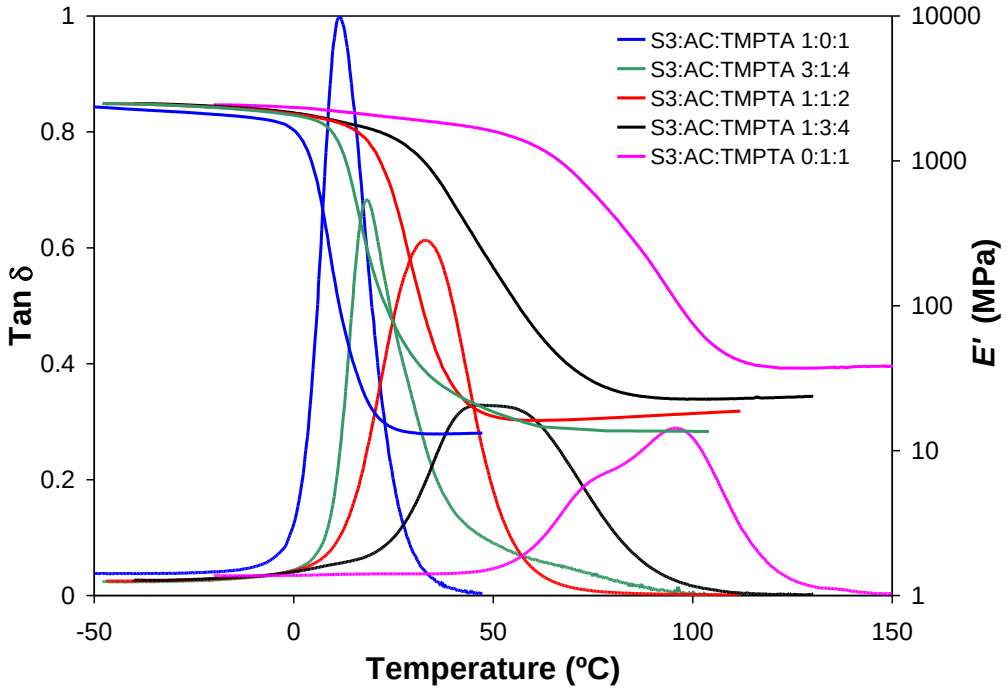


Figure 5. Storage moduli and tan δ curves as functions of temperature of dual cured S3:AC:TMPTA formulations using DBN as catalyst.

The thermal stability of the thermosets was studied by thermogravimetric analysis. **Table 1** shows that AC-rich materials degrade at lower temperatures possibly due to the loss of ethylene formed by β-elimination process of ethoxycarbonyl groups coming from the acetoacetates.

4. Conclusions

Three novel strategies for preparing a new family of thiol-acetoacetate-acrylate dual-curing thermosets, based on two sequential and self-limiting base-catalyzed Michael addition reactions, have been developed.

The curing sequence and the latency of the formulations at the beginning of both stages of curing can be overseen with the choice of catalysts, temperature and curing methodology.

Formulations containing a photobase generator are useful when latency is necessary and for UV cured coatings. Strong bases, such as DBN, can be used in applications where latency is not necessary, UV-irradiation is not available or thick parts are to be produced.

The resulting materials exhibit a wide array of properties depending on the relative contribution of the thiol-Michael and acetoacetate-acrylate Michael reactions and on the structure of the monomers, making them custom-tailorable and adaptable to a wide array of processing and application requirements.

Acknowledgments

The authors would like to thank MINECO (Ministerio de Economía y Competitividad) (MAT2014-53706-C03-01 and MAT2014-53706-C03-02) and the Comissionat per a Universitats i Recerca del DIUE de la Generalitat de Catalunya (2014-SGR-67). Xavier F.-F. acknowledges the Serra Húnter programme of the Generalitat de Catalunya.

References

[1] X. Ramis, X. Fernández-Francos, S. De La Flor, F. Ferrando, A. Serra, A. Click-Based Dual-Curing Thermosets in Thermosets, 2nd ed.; Guo, Q. Ed.; Elsevier, Amsterdam, 2017, Chap. 9

[2] B. Binici, D.I. Fortenberry, K.C. Leard, M. Molden, N. Olten, S. Popwell, J.A. Pojman, Spherically Propagating Thermal Polymerization Fronts, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 1387-1395.

[3] S. Chatani, D. P. Nair, C.N. Bowman, Relative Reactivity and Selectivity of Vinyl Sulfones and Acrylates Towards the Thiol-Michael Addition Reaction and Polymerization, Polym. Chem. 4 (2013) 1048-1055.

[4] 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.

[5] 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.

[6] 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.

[7] S. Chatani, T. Gong, B.A. Earle, M. Podgórski, C.N. Bowman, Visible-Light Initiated Thiol-Michael Addition Photopolymerization Reactions, ACS Macro Letters 3 (2014) 315-318.

[8] J.W. Chan, C.E. Hoyle, A.B. Lowe, C.N. Bowman, Nucleophile-Initiated Thiol-Michael Reactions: Effect of Organocatalyst Thiol, and Ene, Macromolecules, 43 (2010) 6381-6388.

[9] R.J. Clemens, F. Del Rector, A Comparison of Catalysts for Crosslinking Acetoacetylated Resins via the Michael Reaction, J. Coat. Tech. 61 (1989) 83-91.

[10] J. Shin, H. Matsushima, C.M. Comer, C.N. Bowman, C.E. Hoyle, Thiol-Isocyanate-Ene Ternary Networks by Sequential and Simultaneous Thiol Click Reactions, Chem. Mater. 22 (2010) 2616-2625.

[11] K. Kaupmees, A. Trummal, I. Leitoa, Basicities of Strong Bases in Water: A Computational Study, Croat. Chem. Acta 87 (2014) 385-395.

[12] X. Sun, J.P. Gao, Z.Y. Wang, Bicyclic Guanidinium Tetraphenylborate: A Photobase Generator and A Photocatalyst for Living Anionic Ring-Opening Polymerization and Cross-Linking of Polymeric Materials Containing Ester and Hydroxy Groups, J. Am. Chem. Soc. 130 (2008) 8130-8131.

[13] T. Rodima, I. Kaljurand, A. Pihl, V. Mäemets, I. Leito, I.A. Koppel, Acid-Base Equilibria in Nonpolar Media. 2.1 Self-Consistent Basicity Scale in THF Solution Ranging from 2-Methoxypyridine to EtP1(pyrr) Phosphazene, J. Org. Chem. 67 (2002) 1873-1881.

[14] N.B. Colthup, L.H. Daly and S.E. Wiberley, Introduction to infrared and Raman spectroscopy, 3rd ed., Academic Press, San Diego, 1990.

[15] J.P. Pascault, H. Sautereau, J. Verdu and R.J.J. Williams, Thermosetting polymers, Marcel Dekker, New York, 2002.

[16] G. Gonzalez, X. Fernandez-Francos, A. 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.

[17] 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.

[18] Y. Jian, Y. He, Y. Sun, H. Yang, W. Yang, J. Nie, Thiol-Epoxy/Thiol-Acrylate Hybrids Materials Synthesized by Photopolymerization, J. Mater. Chem. C 1 (2013) 4481-4489.

[19] 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) 5753-5751.

[20] Y. Tanaka, J.L. Stanford, R. Stepto, Interpretation of Gel Points of an Epoxy-Amine System Including Ring Formation and Unequal Reactivity: Measurements of Gel Points and Analyses on Ring Structures, Macromolecules, 45 (2012) 7197-7205.

[21] A. Belmonte, X. Fernàndez-Francos, A. Serra, S. De la Flor, Phenomenological characterization of sequential dual-curing of off-stoichiometric thiol-epoxy systems: Towards applicability, Mater. Des. 113 (2016) 116-127.

Highlights

- A new dual-curing procedure for thiol/acetoacetate/acrylate mixtures is proposed.
- Acetoacetate-acrylate and thiol-acrylate Michael additions are the curing stages.
- A photobase generator can be used when high latency is necessary.
- By changing the contribution of each curing stage, properties can be tuned