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## Towards two-step photopolymerization using aza-Michael click addition

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## ABSTRACT

Click reactions involving thiols and acrylates can be performed either through one-step thiol-ene photopolymerization or two-step thiol-Michael addition followed by photopolymerization. It is confirmed that the homopolymerization of acrylates prevents full completion of thiol-ene click addition, therefore leading to high amount of unreacted functional groups in the final material. By contrast, a two-step process consisting in off-stoichiometric thiol-Michael addition followed by photopolymerization of residual acrylates leads to full conversion of thiols. As a consequence, the overall polymerization efficiency is increased as well as the network homogeneity. Taking advantage of this two-step process, a third kind of polymer combining aza-Michael addition and photopolymerization was synthesized using amines instead of thiols. To assess the validity of such process, kinetic profiles and thermomechanical properties were investigated and compared to the ones obtained with thiols. It is found that the final network properties are very similar. This would afford more versatile polymer networks thanks to the large variety of commercially available amines.

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### 1. Introduction

UV-curable coatings are VOC-free systems leading to rapid ambient crosslinking, reduced energy consumption, and lower equipment space requirement. In most cases, the production of UV-curable coatings proceeds via free-radical photopolymerization of unsaturated polyesters and of acrylate functionalized oligomers [1,2]. Through this process, curing occurs via a radical induced chain growth polymerization which restrains the resin to undergo a rapid transition from a liquid state to a vitreous solid state [3–6]. Due to this mechanism, the polymerization yields highly cross-linked networks at low conversion resulting in a vitrification phenomenon [2]. This latter reduces molecular mobility, resulting in non-homogeneous cross-linked network, incomplete conversion and shrinkage [4,7,8].

To overcome these limitations, UV-curable coatings based on thiol-ene click reaction have been developed via a radical induced process involving step-growth polymerization which allows reaching high molecular weights or highly cross-linked networks at high conversion [2,9]. Therefore, these systems are able to stay in a viscoelastic state up to high conversion resulting in a shrinkage reduction [2]. Due to this enhanced molecular

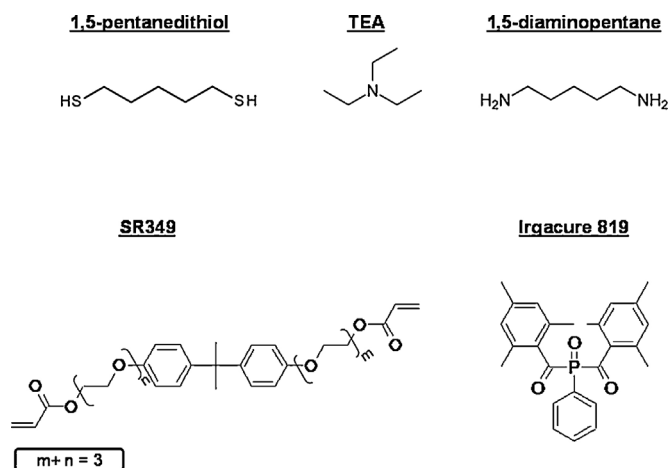
mobility, higher degree of monomer conversion, more homogeneous cross-linked networks, and improved substrate adhesion can be obtained [10]. Nevertheless, thiol-ene based coatings have poor mechanical properties (low stiffness and strength) and reduced thermal properties (low  $T_g$ ) in comparison to UV-cured acrylates [10].

To improve thermo-mechanical properties, thiol-ene step growth polymerization can be combined with radical chain polymerization, acrylates standing for enes (one-step thiol/acrylate strategy) [11,12]. However, in such case, acrylates can react through both chain growth mechanism (homopolymerization) and step growth mechanism by abstracting hydrogen from thiol monomers. This often results in incomplete thiols conversion [13]. To overcome this effect and reach a better control of reaction kinetics and properties [14–17], a two-step thiol/acrylate strategy [9,18,19] was proposed and combined the catalyzed thiol-Michael addition (step 1) and photopolymerization (step 2). The main thrust of this strategy is that off-stoichiometric Michael addition leads to full thiols conversion and partial consumption of acrylates. Residual acrylates are then able to photopolymerized. The final photopolymer thus results from the formation of two interlocking networks. By tuning stoichiometry or by changing thiol and acrylate structures, it is possible to access a wide variety of properties [15].

However, the limited choice of thiols restricts their use for a large scale operation [9]. For this reason, heteroatomic nucleophiles involving nitrogen, oxygen and phosphorus have to be considered

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**Scheme 1.** Chemical structures of the materials used in this study.

as viable alternatives [20]. Herein, we suggest a strategy using aza-Michael addition by replacing thiols by amines. Indeed, amines are widely marketed through epoxy and polyurethane technologies [21]. In addition, no catalyst is required as amines can act as both nucleophiles and bases [22,23]. In this study, we will first investigate the benefits of producing polymer via the two-step thiol/acrylate strategy compared to the one-step thiol/acrylate strategy. Then, two-step strategies involving either thiols or amines will be compared in terms of polymerization kinetics and thermo-mechanical properties.

## 2. Material and methods

### 2.1. Materials

Ethoxylated Bisphenol A Diacrylate (SR349) and Irgacure 819 (phenyl-bis(2,4,6-trimethylbenzoyl)-phosphine oxide) were obtained from Sartomer and BASF, respectively. 1,5-Diaminopentane (cadaverine), 1,5-pentanedithiol and triethylamine (TEA) were purchased from Sigma Aldrich (Scheme 1). All compounds were used as received.

### 2.2. Preparation of samples

#### 2.2.1. One-step strategy

Formulations were prepared by mixing ethoxylated bisphenol A diacrylate (SR349), 1,5-pentanedithiol and the radical photoinitiator Irgacure 819 (2.5 wt% relative to amount of thiol and acrylate).

#### 2.2.2. Two-step strategy (thiol)

Formulations were prepared by first mixing ethoxylated bisphenol A diacrylate (SR349), the catalyst trimethylamine (0.8 wt% relative to amount of thiol and acrylate) and the radical photoinitiator Irgacure 819 (2.5 wt% relative to amount of thiols and acrylates). Once it was dissolved, 1,5-pentanedithiol was added to the mixture according to the amount of acrylate C=C double bonds. After 300 min storage at room temperature in the dark (end of the thermal thiol-Michael addition, i.e. step 1), the mixture was finally photo-cured (step 2).

#### 2.2.3. Two-step strategy (amine)

Formulations were prepared by first mixing ethoxylated bisphenol A diacrylate (SR349) and the radical photoinitiator Irgacure 819 (2.5 wt% relative to amount of amines and acrylates). Once it was dissolved, 1,5-diaminopentane was added to the mixture. After 80 min storage at room temperature in the dark (end of the thermal

aza-Michael addition), the mixture was finally photo-cured (step 2).

#### 2.2.4. Film preparation

For DMA and DSC characterizations, mixtures were coated onto a polypropylene film and were finally light-cured using a 395 nm Firejet FJ200 LED from Phoseon placed on a conveyor belt (dose  $7 \text{ J cm}^{-2}$ , 395 nm). Regarding RT-FTIR investigation, mixtures were first spread between two polypropylene films and laminated between two CaF<sub>2</sub> pellets using a Teflon spacer (50  $\mu\text{m}$ ). Then, samples were cured using a Roithner LaserTechnik LED395-66-60-110 (395 nm) at  $70 \text{ mW cm}^{-2}$  during 2 min.

### 2.3. Differential scanning calorimetry (DSC)

Thermal properties of the different components were evaluated using Q200 from TA Instruments. Products were placed in hermetically sealed aluminium pans (between 5 and 10 mg) and heated from  $-80$  to  $30$  °C for Michael addition product (after step 1), and from  $-20$  to  $70$  °C for photopolymers ( $10$  °C  $\text{min}^{-1}$  ramp).

### 2.4. Real time Fourier transform Infrared spectroscopy (RT-FTIR)

Samples were laminated between two polypropylene foils and CaF<sub>2</sub> pellets using a Teflon spacer. The reactivity was monitored by RT-FTIR (Vertex 70, Bruker). Spectra were recorded with a time resolution of 0.261 s and with a  $4 \text{ cm}^{-1}$  spectral resolution. Disappearance of the acrylate C=C double bonds at  $1640 \text{ cm}^{-1}$  (stretching of C=C), thiol function at  $2510 \text{ cm}^{-1}$  (stretching of S-H) and amine function at  $3380 \text{ cm}^{-1}$  (stretching of N-H) were followed with irradiation time. Conversion of acrylate, thiol and amine was then calculated, respectively, according to:

$$\text{Conversion}(\%) = \left(1 - \frac{A_t}{A_0}\right) \times 100 \quad (1)$$

where  $A_0$  and  $A_t$  stand for the absorbance of the considered vibration band at time 0 and time  $t$ , respectively.

### 2.5. Dynamic mechanical analysis (DMA)

The dynamic thermo-mechanical properties of the UV-cured materials were investigated with a Q800 DMA (TA Instruments) in the tensile configuration. The samples were rectangular (12.8 mm  $\times$  5.3 mm  $\times$  0.070 mm) free films removed from polypropylene substrates. Temperatures ranged from  $-20$  to  $100$  °C and the heating rate was set at  $2$  °C  $\cdot$   $\text{min}^{-1}$ . The amplitude and frequency of the oscillatory deformations were adjusted to 15  $\mu\text{m}$  and 1 Hz, respectively.

## 3. Results and discussion

### 3.1. One-step thiol/acrylate strategy

The thiol-acrylate radical photopolymerization was first carried out for different thiol/acrylate molar ratios under 395 nm light. The initiating radicals formed from the irradiated photoinitiator are expected to initiate both the thiol-ene step-growth process and the acrylate free radical homopolymerization. As an example, 1:4 molar ratio FTIR kinetic is plotted in Fig. 1. Corresponding conversions and polymer glass transition temperatures ( $T_g$ ) are shown in Table 1.

In agreement with the literature [13], thiol conversion was found to be incomplete (between 39% and 53%) whatever the thiol/acrylate molar ratio used. This is merely attributed to the high efficiency of the acrylate homopolymerization. Differences between the kinetic constant of the acrylate propagation and the

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