



# Photocurable polythiol based (meth)acrylate resins stabilization: New powerful stabilizers and stabilization systems



Zakaria Belbakra <sup>a, b, \*\*</sup>, Zoubair M. Cherkaoui <sup>b</sup>, Xavier Allonas <sup>a, \*</sup>

<sup>a</sup> Laboratory of Macromolecular Photochemistry and Engineering, University of Haute-Alsace, 3b Rue Alfred Werner, F-68093 Mulhouse, France

<sup>b</sup> Huntsman Advanced Materials GmbH, Klybeckstrasse 200, CH-4057 Basel, Switzerland

## ARTICLE INFO

### Article history:

Received 14 August 2013

Received in revised form

15 September 2014

Accepted 17 September 2014

Available online 28 September 2014

### Keywords:

Photopolymers

Thiol-ene

Thiol-(meth)acrylates

Premature dark polymerization

Stabilization

## ABSTRACT

Photocurable thiol-ene formulations have tendency to undergo premature dark polymerization leading to a reduced pot-life and therefore only limited applications can be envisaged with these systems. New stabilizers and stabilization systems were experimented through thermal stability and photoreactivity studies. The experimental results highlighted their superior stabilization efficiency regarding photocurable thiol-(meth)acrylate resins. A stabilization system composed of lauryl gallate and triphenylphosphite showed excellent stabilization efficiency with enhanced photoreactivity of the thiol-(meth)acrylate resin and preserved thermo-mechanical properties of the photocured resin. Beyond the scope of stabilization of the target thiol-ene systems, lauryl gallate and triphenylphosphite can be envisaged as efficient stabilizers for other polymers against light ageing thanks to their friendly chemical nature. Origins and existing solutions in the art as regard to this stability issue are also discussed.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Radical photopolymerized (meth)acrylate systems provide on demand rapid cure which is a particular advantage of processing of thermosets. However (meth)acrylates are generally known to shrink when cured by UV light and present other disadvantages related to yellowing and surface tackiness (due to oxygen inhibition) [1–7]. Photopolymerized thiol-enes provide an excellent solution to the above mentioned problems. In fact, reported results have shown that thiol-ene photopolymerization suffers much less from the oxygen inhibition and showed an enhanced photoreactivity. Those effects are attributed to the generation of thiyl radicals which have a poor sensitivity toward the oxygen inhibition [8–11]. This particularity of thiols brought a lot of interest in the coating community. Actually, the use of polyfunctional thiols with (meth)acrylates enables the formation of highly cross-linked polymer networks which could be formed with high functional group conversion, high polymerization rate and with lower shrinkage (due to the delayed gel point) than conventional (meth)acrylate polymerization systems [12–18]. Indeed, when the average

functionality of thiol and “ene” components is higher than two, a three dimensional polymer network is created. New advanced materials with high mechanical properties could be designed using thiol-ene systems opening the door to many different applications such as dental resins, photo-curable coatings, adhesives, photore-sists, implantable biomedical devices (shape memory materials), ceramic materials for MEMS and microfluidic device, liquid-crystalline materials, adhesives and pressure sensitive adhesives, optical components, high performance thermosets and stereolithography [8,19–26].

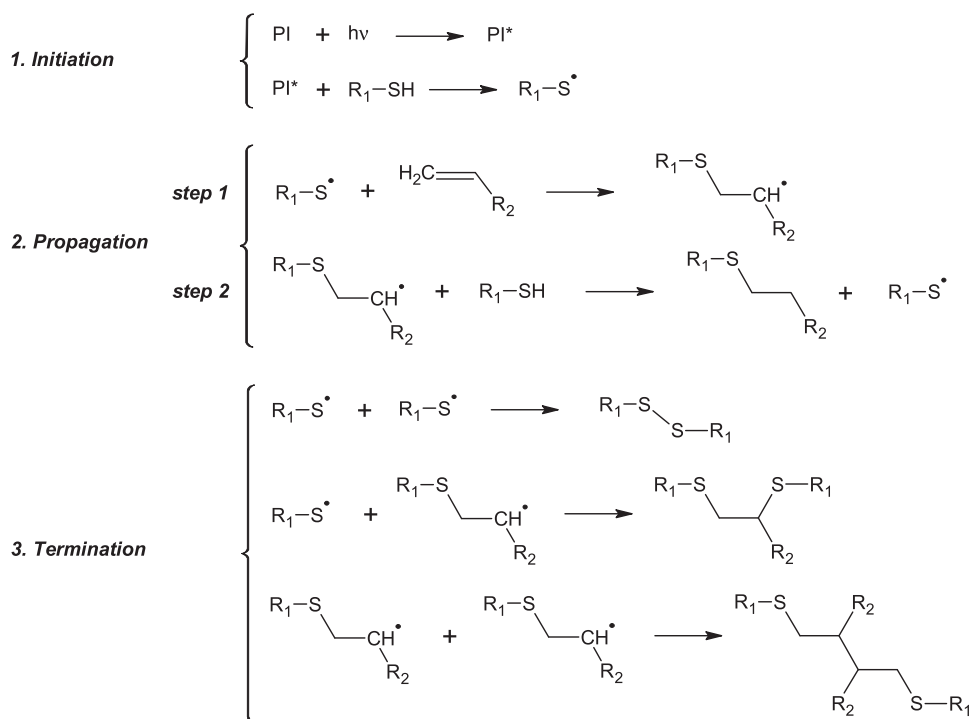
Thiol-olefine reactions were first described in 1905 [8,19,20,27]. The general thiol-ene polymerization mechanism depicted in Scheme 1, is described as a free radical step-growth mechanism involving two steps: an initial hydrogen abstraction of a thiol by a carbon centered radical to give a thiyl radical (step 1), and a subsequent addition of the thiyl radical to the carbon of another “ene” functional group (step 2). This two-step radical-chain process results in the addition of a thiol group onto an “ene” double bond [8,12,28].

It was shown that when specific monomer(s) which have tendency to homo-polymerize easily are used with thiol-enes (in binary, ternary or more thiol-ene mixtures), a more complex mechanism takes place. In the case of polymerization of (meth)acrylates and thiol mixtures, the strong homopolymerization tendency of the (meth)acrylate functional group results in a pseudo two-stage polymerization. The first stage is dominated by (meth)

\* Corresponding author. Tel.: +33 389 33 50 11.

\*\* Corresponding author. Huntsman Advanced Materials GmbH, Klybeckstrasse 200, CH-4057 Basel, Switzerland. Tel.: +41 61 29 92 382.

E-mail addresses: [Zakaria\\_belbakra@huntsman.com](mailto:Zakaria_belbakra@huntsman.com) (Z. Belbakra), [xavier.allonas@uha.fr](mailto:xavier.allonas@uha.fr) (X. Allonas).



**Scheme 1.** General thiol-ene photopolymerization mechanism.

acrylate homopolymerization and chain transfer, and the second stage is dominated by thiol-ene polymerization [9,12,13,29–31].

Despite of all these advantages, one important drawback is limiting the use of thiol-ene chemistry. Indeed, the dark premature polymerization giving rise to reduced pot-life of the thiol-ene resins is the main issue. Several solutions were proposed to overcome this difficulty but they are still not satisfactory because of their insufficient stabilization performance [32].

In the present paper, it is attempted to investigate other systems from which efficient stabilization of thiol-enes and more particularly of thiol-(meth)acrylate based resins at the level of industry requirement is likely to stem. At first it is intended to understand the origin of the premature thiol-ene polymerization. Then, some stabilizers are selected according to a specific analysis of the state of the art results on the thiol-ene resins stabilization in particular and oxidation stabilizers in general. All the investigated stabilizers have different molecular functions and do not act according to the same mechanism. Therefore, synergies between different types of stabilizers are of course in the scope of the present work. The selected stabilizers and stabilization systems are then tested over a polythiol-(meth)acrylate based resin (TMBR) and the stabilization results are discussed. Finally, the impact of the most efficient selected stabilizers on the photoreactivity of the photocurable TMBR and on the thermo-mechanical properties of the photocured TMBR will be discussed.

## 2. Materials and methods

The multifunctional (meth)acrylate based resin is composed of ethoxylated bisphenol-A di(meth)acrylate, an urethane diacrylate, trimethylolpropane triacrylate purchased from Sartomer and of Type I radical photoinitiators as 2,2-dimethoxy-1,2-diphenylethane-1-one (Irgacure 651) and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Lucirin TPO) purchased from BASF. The (meth)acrylate based resin was then

modified by adding 5 wt% of pentaerythritol tetrakismercaptopropionate (PETMP) purchased from Bruno Bock. This final resin constitutes the thiol-(meth)acrylate based resin called TMBR.

The different stabilizers used are shown in Scheme 2. The thermal stability of the thiol-methacrylate based resin (TMBR) with different stabilizers and stabilization systems was performed in dark.

The different samples were stored at room temperature during 60 days and an acceleration test was carried out by storing the samples at 60 °C during 31 days. In order to compare their relative stabilization efficiency, the same molar concentration of stabilizers was used for all the samples. Therefore, a total concentration of 23.5 mM for one component stabilizer was used for each sample. In the case of bi-component stabilizer systems, a concentration of 11.75 mM for each component was used and in the case of tri-component stabilizer systems, a concentration of 7.83 mM was used for each component. The viscosity of the different samples was monitored through the time using a Haake RS 80 rotational viscometer at 30 °C. The initial viscosity of the formulation was about 1130 mPa s. The error on the viscosity values was estimated to be ±1%.

Photoreactivity investigations were performed using the real time FT-IR technique using a Bruker Vertex 70 spectrophotometer equipped with a MCT detector (spectral resolution of 4 cm<sup>-1</sup>). The spectrophotometer was associated with a Xenon–Mercury UV source (Lighting Cure LC5 from Hamamatsu) equipped with an anti-calorific filter and an interferential filter at 366 nm. The lamp was calibrated to deliver an intensity of 30 mW/cm<sup>2</sup> ± 5% using an Ocean Optics USB4000 spectrophotometer. The photocurable viscous liquid formulation was applied onto a BaF<sub>2</sub> disk using a bar coater of 12 μm to obtain a 10–12 μm thickness. The initial absorbance of the IR band at 1410 cm<sup>-1</sup> was controlled before each measurement to be 0.7 ± 0.03. The decay of the (meth)acrylate double bond stretching vibration band at 1636 cm<sup>-1</sup> was monitored as a function of photo-curing time. The stable band at

Download English Version:

<https://daneshyari.com/en/article/5201664>

Download Persian Version:

<https://daneshyari.com/article/5201664>

[Daneshyari.com](https://daneshyari.com)