

# Efficient Stabilization of Thiol-ene Formulations in Radical Photopolymerization

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**INTRODUCTION** The thiol-ene reaction was first suggested by Posner in 1905,<sup>1</sup> but academic interest in this potential polymerization reaction remained fairly limited until the last two decades.<sup>2,3</sup> Interest in the thiol-ene reaction mechanism increased as distinct advantages over acrylate homopolymerization were discovered. The thiol-ene polymerization is unique in that it proceeds in general by a step growth radical polymerization. The simplified reaction mechanism of a photo-initiated thiol-ene step growth polymerization for an ene that cannot homopolymerize is well known and is presented in the Supporting Information.<sup>4–6</sup> Various researchers have shown that unlike (meth)acrylates, thiol-ene reactions have reduced oxygen inhibition<sup>7–11</sup> with significant lower shrinkage<sup>12–15</sup> providing materials with often better mechanical properties. In particular, addition of thiols to (meth)acrylate polymerizations contributes to significant improvement in impact resistance.<sup>16,17</sup> The thiol-ene step growth radical polymerization leads to a homogeneous crosslinked network with low volume shrinkage and delayed gelation, explaining the reduced brittleness. Because of the wide availability of monomers with different terminal ene groups, it is possible to tailor the physical and mechanical properties of the network structures to meet a diversity of applications.

Despite all these advantages, thiol-ene systems have serious drawbacks, such as limited shelf-life stability and bad odor of the thiol. This latter problem has been addressed by a number of high molecular multifunctional low-odor thiols that are now commercially available. The main issue now seems to be the premature gelation of the formulations with shelf life stabilities varying enormously from a few seconds to not more than a few weeks.

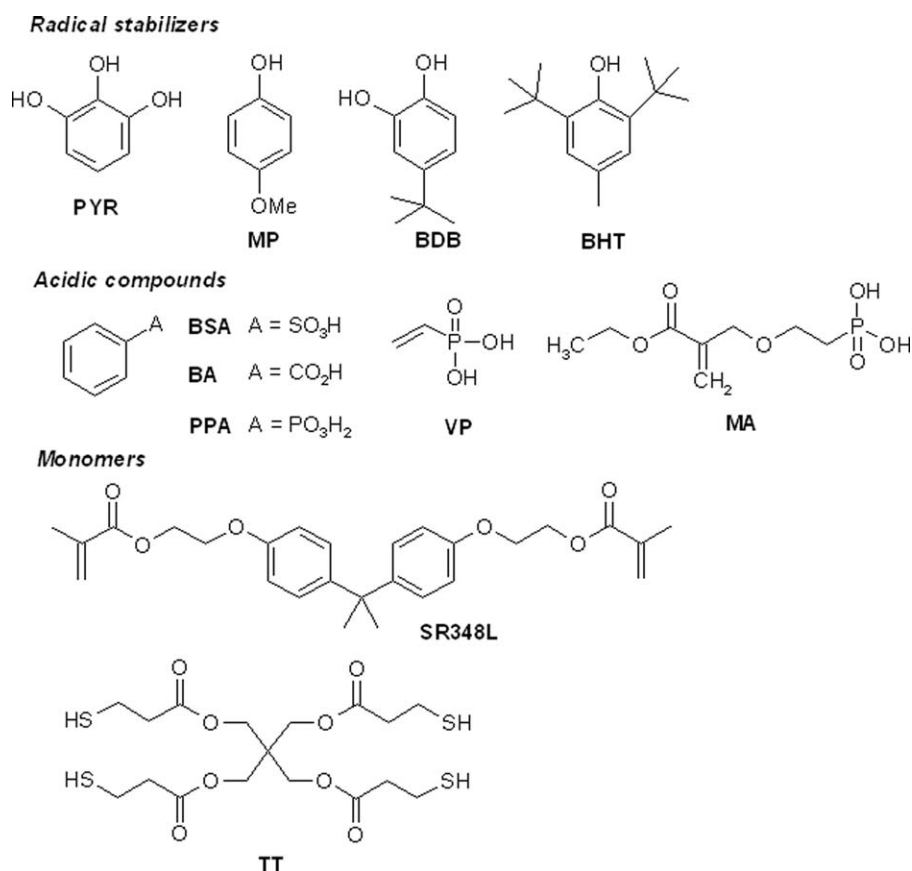
Several stabilizer systems have been proposed with the ability of extending the shelf life of thiol-ene mixtures and eliminating

premature polymerization at room temperature. In 1971, Stahly described the use of several radical scavengers, including triallyl phosphates.<sup>6</sup> In the early 1990s, Klemm and coworkers conducted an extensive program to evaluate thermal stabilizers such as pyrogallol (PYR), hydroquinone, and catechol as inhibitors of the premature gelation of thiol-ene mixtures at room temperature.<sup>18,19</sup> Of these thermal stabilizers, pyrogallol was found to be most successful. Several other stabilizers were also proposed such as: sulfur,<sup>20</sup> potassium iodide-iodine mixtures,<sup>21</sup> hindered phenolics,<sup>22–24</sup> aluminum or ammonium cupferronate (*N*-nitrosophenyl hydroxylamine) salts,<sup>25</sup> 3-propenylphenol,<sup>26</sup> triaryl phosphines and phosphites,<sup>27</sup> phosphonic acid,<sup>28</sup> and a combination of an alkenylphenol and cupferronate salt, to prevent thermal polymerization at ambient temperature. Davidson and Mead<sup>27</sup> reported that triphenyl phosphite was extremely effective in stabilizing mixtures consisting of multifunctional mercaptoesters with several multifunctional allyl ethers. Holy et al. reported that simple addition of aluminum cupferronate provides adequate stabilization against early gelation for acrylate-thiol mixtures for up to 1 week at 60 °C.<sup>28</sup> Christmas and coworkers<sup>29</sup> showed also that unstable acrylate mixtures containing thiols can be stabilized for longer than 30 days with aluminum cupferronate.

To determine an efficient stabilizer system, the mechanism of the thiol-ene dark reaction should first be considered. Holy reported that the limited shelf-life stability of thiol-enes may be caused by a variety of reasons such as: (1) the decomposition of peroxide impurities and subsequent initiation of a thermal free-radical reaction, (2) the reaction of hydroperoxide impurities to form thiyl radical intermediates that initiate polymerization, (3) thiol-ene reactions due to a base-catalyzed nucleophilic addition of thiol to the ene double bond, or (4) the spontaneous initiation of polymerization

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**FIGURE 1** Radical stabilizers and acidic coadditives screened for stabilizing thiol-ene formulations.

via the generation of radicals through a ground-state charge transfer complex formed between the thiol and the ene components in the mixture.<sup>30,31</sup>

Thus, the goal of this study has been to provide a stabilizer system capable of inhibiting any one of these different mechanisms leading to spontaneous gelation of the formulation. On one hand, acidic compounds should be applied to avoid nucleophilic addition, and on the other hand, the stabilizer system should contain classical radical stabilizers to inhibit the other mechanisms.

For this purpose, a screening study was first performed to identify a suitable radical stabilizer out of different classes of well known radical inhibitors. Then, the synergistic effect of the best stabilizer from the first study combined with an acidic coadditive was investigated in a thiol-ene formulation. The molecular structure for the monomers and inhibitors tested are given in Figure 1. The stability of the different thiol-ene formulations were evaluated by following the change in viscosity with time. Furthermore, the thermal stability and photoreactivity of the stabilized thiol-ene formulations was examined.

## EXPERIMENTAL

### Materials

All the thiol-ene formulations used were prepared as stoichiometric mixtures based on thiol and ene functional groups.

Pentaerythritol tetrakis(3-mercaptopropionate) (**TT**) and all stabilizers were purchased from Aldrich. Difunctional ethoxylated (2) bisphenol A dimethacrylate (SR348L) and trifunctional ethoxylated (3) bisphenol A diacrylate (SR349) were donated from Sartomer. Phosphonic acid monomer [4-(dihydroxyphosphoryl)2-oxo-butyl]-acrylic acid (**MA**) was kindly provided by Ivoclar Vivadent and Irgacure 184 by Ciba SC. Unless otherwise stated, all compounds were used as received.

### Methods

Viscosity was measured by using a Physica MCR 300 Modular Compact Rheometer from Anton Paar. A 0.1 mL sample was loaded in between a 25 mm cone-and-plate rheometer (1° angle; CP 25-1) at 25 °C. Measurements were taken at a constant shear rate of 100 Hz. Viscosity for each sample was measured in triplicate with SD < 5%. Thermal stability was estimated by differential scanning calorimeter (Shimadzu DSC-50). The temperature scale was calibrated using the standards In and Sn. Samples (~20 mg) were placed in open aluminum pans and heated under N<sub>2</sub> (20 mL/min) from room temperature to 200 °C at a ramp rate of 10 °C/min. An aluminum pan filled with (~20 mg)  $\alpha$ -alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) was used as a reference. Photo-DSC measurements were performed with a Netzsch DSC 204 F1 Phoenix on 10 mg samples containing 3 wt % of Irgacure 184 as photoinitiator. A filtered UV radiation source (280–500 nm Exfo Omnicure

**TABLE 1** Increase in Viscosity of a 2:1 Mixture of SR348L and TT in the Presence of Phenolic Stabilizers (90 mM or 9 mM) after 110 days at Room Temperature and at 65 °C

Radical Inhibitor	Viscosity at RT		Viscosity at 65 °C	
	Time for Gelation (h)	Increase after 110 days (%)	Time for Gelation (h)	Increase after 110 days (%)
None	45	Gel	6	gel
90 mM BDB	–	57	1,940	gel
90 mM MP	–	220	330	gel
90 mM BHT	–	180	140	gel
90 mM PYR	–	16	–	3,700
9 mM PYR	–	75	–	5,300

2001) was used with the aid of a light guide attached to the top of the DSC unit.<sup>32</sup> Intensity at the tip of the light guide was 3 W/cm<sup>2</sup>. Photo-DSC experiments were performed in triplicate with SD < 5%. Formulations with equimolar ratios of SR 348L and tetrathiol (TT) with stabilizers (90 mM 4-*tert*-butyl-1,2-dihydroxy benzene (BDB) and 90 mM MA) were assessed by NMR immediately after preparation and after 110 days stored at 65 °C. <sup>1</sup>H NMR spectra were measured with a Bruker ACE 200 FT-NMR-spectrometer using CDCl<sub>3</sub> as solvent.

## RESULTS AND DISCUSSION

### Assessing Phenolic Radical Inhibitors

The efficiency of different radical stabilizers (4-*tert*-butyl-1,2-dihydroxy benzene (BDB), 2,6-di-(*tert*-butyl)-4-methylphenol (BHT), 4-methoxyphenol (MP), and pyrogallol (PYR)) (Fig. 1) was evaluated by viscosity measurements of an equimolar mixture (based on functional group) of SR348L and TT. Each stabilizer was applied at concentration of 90 mM, and the formulations were stored at room temperature and 65 °C. To avoid photo-induced reactions, samples were stored in brown flasks. Table 1 shows the increase in viscosity of the thiol-ene formulation after 110 days storage time. The efficiency of the radical stabilizers decreased in the following order: PYR > BDB >> BHT ≈ MP. The best stabilization effects were found with addition of 90 mM PYR with an increase in viscosity of about 16% at room temperature and 3653% at elevated temperature after 110 days. Lowering PYR concentration by an order of magnitude (9 mM) still provided better stability than the other additives at 90 mM.

### Assessing Acid Costabilizers

To confirm the theory of a costabilization effect of acidic compounds, the influence of several acids with different pK<sub>a</sub> values such as benzenesulfonic acid (BSA), benzoic acid (BA), phenylphosphonic acid (PPA), vinylphosphonic acid (VP), and-[4-(dihydroxyphosphoryl)2-oxo-butyl]-acrylic acid (MA) were investigated on the thiol-ene formulation by using viscosity measurements. At elevated temperature, formulations containing strong 90 mM BSA (pK<sub>a</sub> -0.6) gelled within 1 h and those with 90 mM weak BA (pK<sub>a</sub> 4.2) gelled within 7 h. Relative to the control thiol-ene formulation without acid that gelled within 6 h, BA provides little to no

stabilization at the used concentration. Although strong Bronsted acids are known to catalyze thiol-Michael additions,<sup>33</sup> no attempts were made to delineate the precise mechanism for fast gelation with BSA. Interestingly, thiol-ene formulations with moderately strong phosphonic acids (pK<sub>a</sub> 1.88–2.34) required 20 h at 65 °C to gel indicating a moderate buffering ability (Table 2). The buffering ability of phosphonic acids was then tested in combination of PYR radical stabilizer to determine ideal conditions for storage of thiol-enes. All the phosphonic acids provided significantly lower viscosity after 110 days at 65 °C relative to formulation stored with PYR alone.

As the stabilizer system containing the phosphonic acidic monomer MA and the radical stabilizers PYR has shown the best results, the synergistic effect of these stabilizer systems was then examined in more detail. Different temperatures and different amounts of the stabilizer PYR were used in these experiments. Higher amount of the acidic compound MA could be accepted as it does not interfere with the radical polymerization. On the other hand, too much radical inhibitor PYR could slow down or even stop the photo-induced polymerization. By comparison, the two component stabilizer systems provided a degree of stabilization effectively more than the sum of the stabilization effect of the single components. These systems showed stability with no viscosity increase at RT and an increase in viscosity of only about 90% at 65 °C after 110 days of storage (Table 2). NMR analysis (Figs. S2 and S3 in the Supporting Information) of a comparable phenolic-phosphoric acid stabilizer system based on BDB and MA provides some clarification to the relation between viscosity increase and extent of reaction. For methacrylate:thiol formulations with 90 mM BDB and MA, viscosity increase after 110 days at 65 °C was 215% and double bond conversion was 11% (as determined from the reduction in vinyl proton integrals).

The efficiencies of the different stabilizers to inhibit the thermal polymerization of the thiol-ene system with increasing temperature were examined by DSC. Figure 2 displays the DSC plots recorded during polymerization of an equimolar mixture of SR348 and TT without and in the presence of stabilizers. The formulation without inhibitor shows an onset temperature at about 80 °C. The addition of the acidic MA

**TABLE 2** Stability of a 2:1 Mixture of SR348L and TT With or Without Pyragallol and Different Acidic Coadditives (90 mM) after 110 days at 65 °C

Pyragallol	Acidic Additive	pK <sub>a</sub>	Time for Gelation (h)	Viscosity Increase after 110 days (%)
Without	None		6	Gel
9 mM	None	–	–	5,300
90 mM	None	–	–	3,700
Without	BA	4.20 <sup>34</sup>	7	Gel
9 mM	BA	–	–	900
Without	MA	2.34 <sup>a</sup>	19	Gel
9 mM	MA	–	–	90
90 mM	MA	–	–	91
Without	VP	2.11 <sup>34</sup>	20	Gel
9 mM	VP	–	–	100
Without	PPA	1.88 <sup>35</sup>	20	Gel
9 mM	PPA	–	–	100
Without	BSA	–0.60 <sup>36</sup>	1	Gel
9 mM	BSA	–	3	Gel

<sup>a</sup> Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02.

shows no effect below 70 °C, but above this it appears to catalyze the gelation process. Addition of **PYR**, a classical radical stabilizer, provided excellent thermal stability which is explained by the quenching of thermally formed radicals out of, for example, peroxide impurities. Although the mixture of **MA** and **PYR** gave excellent results in storage stability tests at room temperature and 65 °C, thermal gelation is readily induced at 150 °C. From this, it could be concluded that at lower temperature the acidic component efficiently prevents the nucleophilic attack, but at elevated temperature (>120 °C) it catalyzes the gelation process.

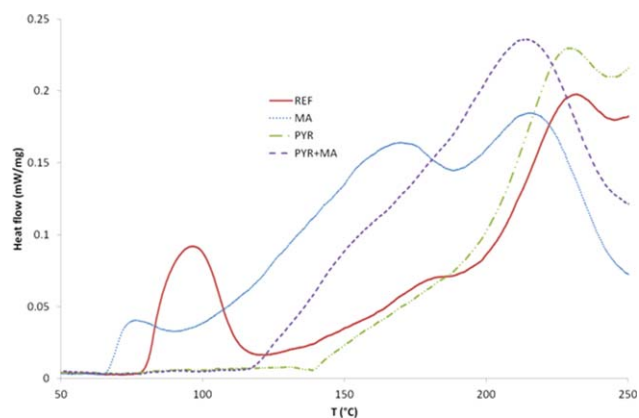
#### Photo Reactivity of Stabilized Thiol-ene Formulations

The effect of the stabilizer system on the photosensitivity of thiol-ene formulations was tested with the aid of photo-DSC. Photo-DSC allows simple and accurate determination of important kinetic parameters: the time to reach the maximum polymerization heat flux  $t_{max}$  (s), the heat of polymerization  $\Delta H_p$  (J/g) (the area under the peak), and the maximum heat flow corresponding to height of the peak  $h$  (mW/mg). From  $\Delta H_p$  and the maximum heat flow, the DBC and the rate of polymerization can usually be calculated. However, as a mixed thiol/methacrylate system was used based on two different and yet simultaneous modes of polymerization (methacrylate homopolymerization and thiol-ene step growth), direct calculation of rate and conversion is complicated.

In Table 3, the initial values of photoreactivity of the different thiol-ene formulations are compared. It is obvious that the presence of the acidic compound **MA** does not affect the photoreactivity of the thiol-ene formulation. By addition of a small amount of **PYR** as radical stabilizer, the initial values of the area, height and  $t_{max}$  remained practically unchanged compared with the formulation without stabilizer. By using

higher amounts of the radical stabilizer (90 mM), the height of the peak (corresponding to the rate of polymerization) and the area below the trace (corresponding to the monomer conversion) of the different formulations were only slightly reduced.

Although the combined use of acid buffer with radical stabilizer provided very good results with a 1:1 thiol methacrylate system, it was important to apply these conditions to other thiol-ene formulations. Namely, the tested formulation has been shown in prior work to be inherently more stable than formulations containing an excess of methacrylate or containing more reactive enes such as acrylates or vinyl ethers.<sup>37</sup> In further studies (see Supporting Information Tables S1 and S2), the synergetic effects of **PYR** in



**FIGURE 2** DSC plots of equimolar mixture of SR3482 and TT without stabilizer (RF), in presence of 90 mM MA comonomer, 9 mM PYR stabilizer, and a mixture thereof. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE 3** Photo DSC Data of a 2:1 Mixture of SR348L and TT in the Presence of Different Stabilizers

PYR (mM)	MA (mM)	$\Delta H$ (J/g)	Max Heat Flow (W/g)	$t_{\max}$ (s)
–	–	166	16.1	6.6
–	90	159	15.5	6.6
90	–	137	12	6.1
90	90	139	12.1	6.2
9	–	155	14.9	6.7
9	90	156	15.4	6.6

combination with phosphonic acid have also been successfully applied to more reactive industrial formulations based on a combination of multifunctional dimethacrylate and diacrylate monomers.<sup>38</sup> These mixed acrylate/methacrylate formulations are particularly interesting in stereolithographic processing where rapid cure in the presence of oxygen is desired. After 110 days, no change in viscosity was noted for the formulation stored at room temperature, while at 65 °C gelation was avoided with viscosity increasing only by a factor of 3.

The stabilizing efficiency of phenols and phosphoric acid coadditives was also applied to formulations with alternate ratios of thiol and methacrylate (see Tables S3 and S4 in the Supporting Information section). Using 0.1 wt % **PYR** and 1.8 wt % **MA**, viscosity was measured after storage at 65 °C for up to 80 days for formulations with methacrylate: thiol ratios from 1:1 to 12:1. Viscosity increase reached a maximum of 50% for a formulation with a ratio of 1.5:1 and dropped to only 17% for the 12:1 system. The stabilizing system is thus versatile and highly effective at preventing methacrylate polymerization.

Phenolic stabilizers with phosphoric acid coadditives were found also to stabilize formulations of thiols with ene monomers besides from (meth)acrylates. Two multifunctional allyl monomers (pentaerythritol allylether and triallyl triazinetrione) and one di-yne (1,7-octadiyne) were assessed by mixing with an equimolar concentration of **TT** and storing at 65 °C (see Tables S5 and S6 in the Supporting Information section). After 80 days, viscosity increase was highest for the thiol:yne system (260%) and lowest for the thiol:allyl ether system (130%). Although viscosity increase was greater than that of 1:1 thiol:methacrylate systems, gelation was avoided. These findings seem sure to broaden the industrial acceptance and application of thiol-ene based photoresins.

## CONCLUSIONS

In this article, we have presented an efficient stabilizer system for thiol-ene formulations with no increase of viscosity at ambient temperatures and a significantly improved stabilizer at elevated temperatures. The stabilizer system aimed to

interact with all possible modes of gelation and therefore contains a free radical scavenger and an acid with an appropriate  $pK_a$  value of about 2. The combination of these compounds displays a surprising synergistic effect, providing a stabilization which is more than the sum of the stabilization effect of the individual components of the stabilization system. The phenolic-phosphoric acid stabilizer system is both effective and versatile showing significant reduction in viscosity increase for formulations with thiols stored for extended periods with both an array of concentrations of methacrylates as well as alternate ene monomers (ynes and allyl ethers).

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