

Thiol-ene Chemistry: Past and Progress

Jon Scholte, PhD. Sartomer Americas

Jeff Klang, PhD. Saromer Americas

Abstract

Thiol-ene based click chemistry has been widely studied in academic circles for several years, but due to limitations of container materials and shelf stability they have yet to be widely applied in industrial coatings. In contrast to traditional acrylate photopolymerization, the unique chemistry and step-growth network formation allow by thiol-ene chemistry promote decreased oxygen inhibition and lower shrinkage stress. Moreover, these materials allow for the rapid polymerization of highly pigmented systems in applications such as graphic arts and personal care products. Herein, we report our recent advances in the use of and stabilization of several thiol-acrylate blends for use in various photocurable applications.

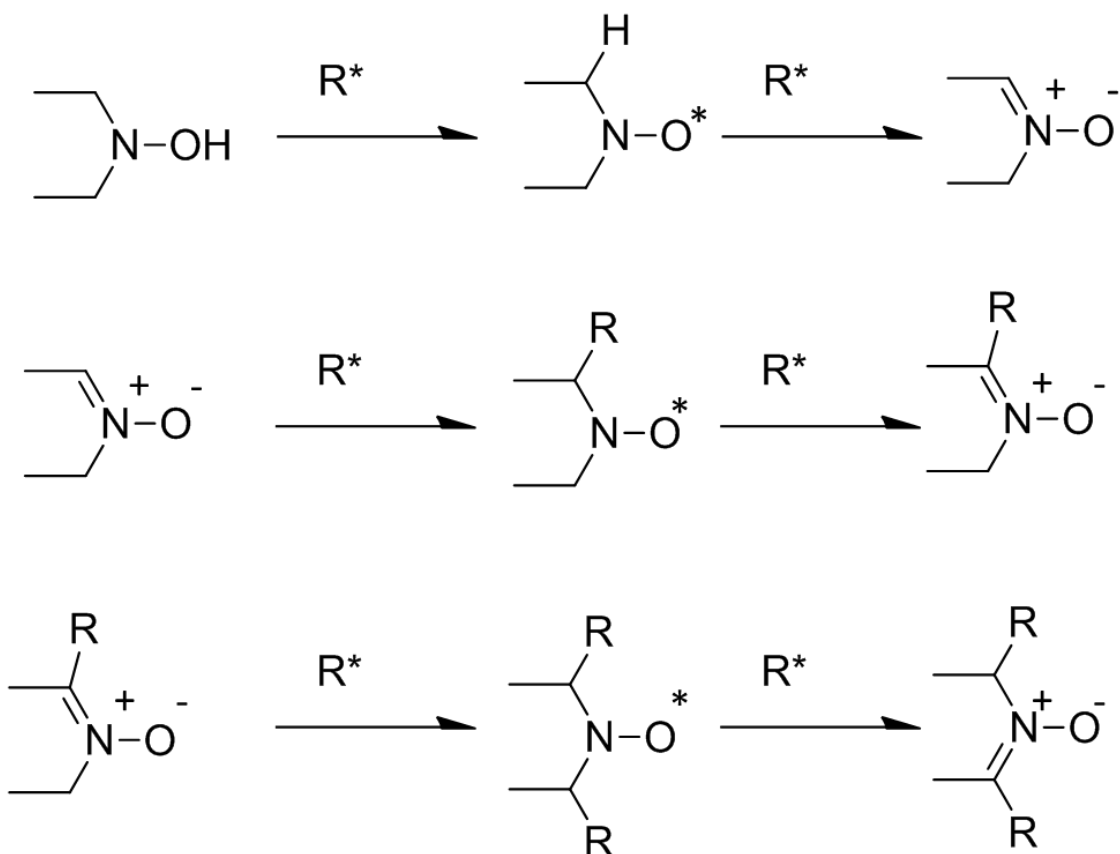
Introduction

Thiol-ene chemistry has been at the center of much academic and scientific research due to rapid reaction rates and multiple methods of initiation. Thiol-ene chemistry consists of the reaction of the labile hydrogen atom on mercaptan containing molecules and the reaction with any number of ene's including but not limited to acrylates and vinyl ethers.¹ The reaction between the thiol and ene is easily catalyzed and results in either chain transfer or when incorporated in stoichiometric amounts, results in a step growth polymerization. The change in polymerization mechanism results in networks with lower shrinkage which improves adhesion as well as more flexible films. The increased flexibility results from a decrease in microgels associated with (meth)acrylate homopolymerization.

While thiol-ene chemistry represents a unique method for overcoming oxygen inhibition while simultaneously increasing surface cure and flexibility; stabilizing these systems has presented some difficulty limiting their widespread adoption in industrial fields and applications. Herein we report our exploration of stabilization methods and benefits of thiol-acrylate chemistry.

Results and Discussion

Several methods of stabilizing the radical polymerizations are possible. One method that has been used is the incorporation of nitroxide or hydroxylamines. These compounds are capable of stabilizing several radicals per molecule making them invaluable additives in many acrylate chemistry applications. The mechanism by which these compounds can halt radicals is seen in scheme 1 below.²



Scheme 1 Diethylhydroxy amine radical stabilization/consumption mechanism.

As can be seen in scheme one a single diethyl hydroxylamine (DEHA) molecule can mitigate between 4 and 6 radical species. To see how DEHA would work as a stabilization agent in thiol-acrylate systems DEHA was added to diacrylate and tetrathiol photocurable resin. The change in viscosity and effect on cure can be seen in figure 1 below. Figure 1A shows the viscosity after 1 day and after 2 weeks at 60C as measured at 25C. We observe that due to the higher viscosity of the tetrathiol the initial viscosity of the 30% blend is almost double the 10 wt% oligomer. However, we observe that there is still a large build in viscosity suggesting that the DEHA is

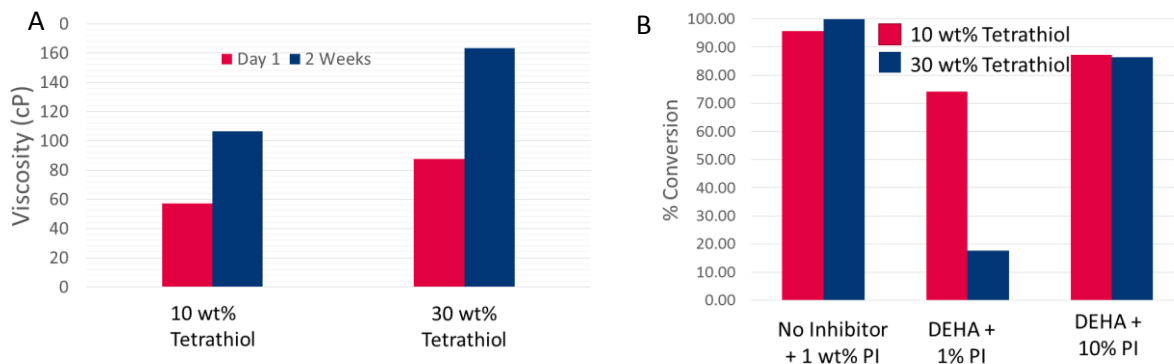


Figure 1 Viscosity as a function of time (A) and Conversion (B) of a diacrylate/tetrathiol blend stabilized with 0.1% DEHA.

allowing for some extent of polymerization. These results suggest that while DEHA can consume multiple radicals there is still opportunity for other species to potentially arise. Figure 1B meanwhile shows the limited conversion capable with DEHA as an inhibitor. As it is a very quick radical scavenger its ability to prevent polymerization once the photoinitiator is triggered becomes very obvious. We observe that for the formulation that does not have any additional inhibitor we observe very high conversions. However when 0.01 wt% DEHA and 1 wt% photoinitiator (Irgacure 4265) was initiated we observe very low yields, only 72% acrylate conversion for the blend with 10 wt% tetrathiol and 18% acrylate conversion. In order to get similar acrylate conversion to the non-DEHA containing formulation a 10 wt% photoinitiator package had to be included. This result indicates that there must be a large excess, in this instance roughly 100:1 initiator to stabilizer, to overcome the use of hydroxyl amines as stabilizers.

Stemming from these results and an exhaustive literature review we were able to identify blends of stabilizers that were capable of maintaining a low viscosity in thiol-acrylate blends. Figure 2A and 2B show a capability to stabilize blends with tri and tetra functional acrylates at tetrathiol content of up to 30 wt%. Both blends show less than a 30% viscosity build.

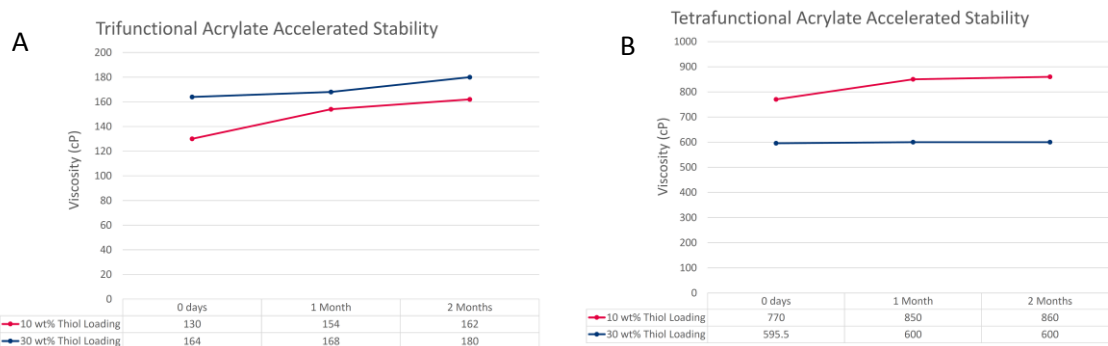


Figure 2 Accelerated aging of sample at 60°C for up to 2 months. Figure 2A shows triacrylate/tetrathiol blends with limited viscosity build with both 10 and 30 wt% tetrathiol. Figure 2B shows a tetraacrylate/tetrathiol blend with a viscosity build of less than 30% over 2 months.

One possibility that could cause these small viscosity builds would be the oligomerization of the thiol-acrylate blends. The formation of larger molecules would be consistent with small builds in entanglement or secondary interactions which would lead to a build in the overall viscosity of the blend. In order to detect for the formation of these oligomers we took gpc data from immediately after mixing and after the 2 months of accelerated aging. This data can be seen in figure 3 below for the trifunctional acrylate system. As we can see in figure 3a both species, the triacrylate and the tetrafunctional acrylate can both be observed within the blend immediately after mixing. Figure 3b meanwhile shows the gpc trace for the blend after 2 months with both the triacrylate and tetrathiol traces shown as well on the overlays. From this we can conclude that while there is some drift in the viscosity of these blends there is no observable oligomerization. The same conclusion was reached for the tetraacrylate tetrathiol blend, data not show.

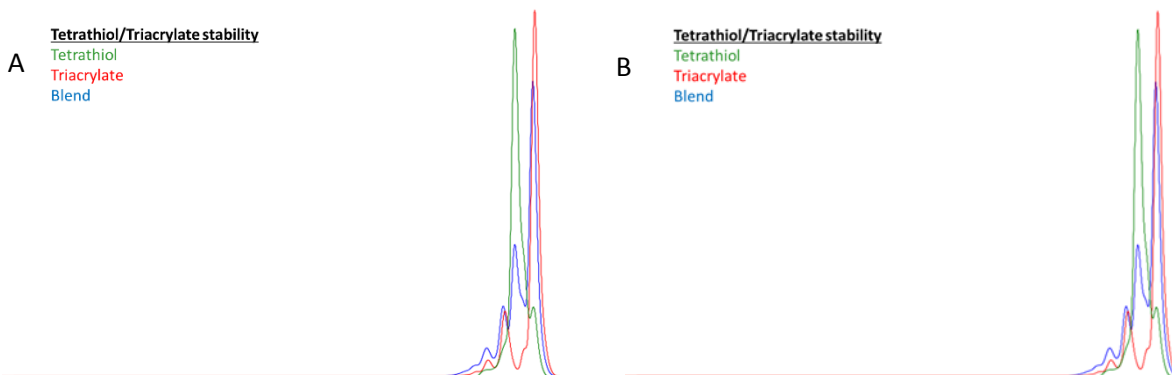


Figure 3 GPC traces of thiol acrylate blends. Figure 3A shows the GPC trace of a triacrylate/tetrathiol blend immediately after mixing showing. No peaks are observed indicating oligomerization. Figure 3B shows the same blend after 2 months of accelerated aging with all peaks in the blend being identified from either the tetrathiol or the triacrylate. The same trend was observed for a tetraacrylate/tetrathiol blend.

Conclusion

Herein we have identified a stabilization package capable of stabilizing both tri and tetra functional acrylates with tetrafunctional materials. These blends show little viscosity build and no oligomerization after 2 months accelerated aging at 60°C. Continued efforts will examine more functional acrylates as well as urethane and polyester acrylates.

References

- 1) Hoyle, C.E. and Bowman, C.N., "Thiol-Ene Click Chemistry" *Angewandte Chemie*, **2010**, *49*, 1540-1573
- 2) Abuin, E. , Encina, M. V., Diaz, S. and Lissi, E. A. "On the reactivity of diethyl hydroxyl amine toward free radicals." *Int. J. Chem. Kinet.*, **1978** *10* 677-686.