

Effects of Thiol-Functional Monomers on the Relative Reactivity and Shelf-Life Stability of Acrylate-Functional Monomer Blends

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Abstract

An earlier investigation (reported at RadTech 2002) was conducted to determine the effects on relative reactivity of adding trimethylolpropane *tris*-(3-mercaptopropionate) (a trifunctional-thiol) to UV-polymerizable, acrylate-functional systems. That initial work with formulations containing both oligomers and monomers resulted in severe shelf-life instability. It also failed to corroborate literature claims of significant increases in relative reactivity for these systems. In an attempt to isolate the causes for this instability and to resolve the issue of relative reactivity, several experiments have now been performed with oligomer-free systems containing only acrylate-functional and thiol-functional monomers, along with either a photoinitiator or a photosensitizer. The results of these more recent laboratory investigations are presented.

INTRODUCTION

During the decades of the '70s and '80s, W. R. Grace & Co.^{1, 2, 3}, Armstrong World Industries⁴, and other laboratories developed an ultraviolet (UV)-polymerization process that came to be known as "thiol-ene" chemistry. Their work indicated that these novel systems could be used in a variety of different applications. An excellent review of this technology, including discussions of various end-uses ranging from coatings and adhesives to imaging applications, has been written by Anthony F. Jacobine⁵.

Referring to a paper by R. W. Lenz⁶, Jacobine described thiol-ene chemistry as a process involving a step-growth addition mechanism that is propagated by a free-radical chain-transfer process. Thus, as reported by this laboratory in 2002, "...this [thiol-ene] technology represents aspects of both free radical addition and step-growth polymerization kinetics wherein thiyl radicals, **RS•**, are formed that subsequently add across a double bond, as in chain-growth polymerization processes. However, each new carbon-centered radical thus formed, very rapidly abstracts another hydrogen atom from the thiol-functional material(s) to form a new thiyl radical..."⁷. This newly formed thiyl radical subsequently adds across another double bond, establishing a sequential process that takes place in successive "steps," as in step-growth polymerization. Therefore, thiol-ene polymerization is a free-radical addition process that, ironically, follows step-growth polymerization kinetics.

Though this novel technology appeared to have significant commercial potential, interest in it seemed to wane in the early '80s. Perhaps this decline in interest was due to the odor of some of the thiol-functional materials, though the odor of the multifunctional thiols used in this laboratory and reported in this paper appears to be relatively low. Or perhaps this decline in

interest occurred because of a rapid increase in the development of a broad range of effective acrylate-functional materials during the 1980s. This increase in commercially available acrylate-functional oligomers and monomers may have diverted the attention of formulating chemists away from the thiol-ene technology and its perceived disadvantages. A third possibility for the observed decline is that when formulating chemists investigated the use of acrylates as the “-ene” in thiol-ene systems, they found the same shelf-life instability that was later observed and reported by this laboratory for such systems⁷.

Whatever the reason for the decline in interest in the early '80s, by the mid-1980s and early 1990s, according to Jacobine⁸, a resurgence of interest in thiol-ene systems began to take place. Jacobine speculated that this resurgence might have been fostered by a general increase in market interest at that time for **any** photopolymerization technology that did **not** involve the use of acrylates because of their real and perceived disadvantages. But this renewed interest does not appear to have been sustained. As recently as 1993, P. Dufour of Radcure Specialties SA stated that, “These [thiol-ene] systems do not represent an important share of the radiation-curing market due to the odour of polythiol compounds”⁹, thus, restating the hypothesis that odor was the major cause for a lack of interest in the materials. It would appear, then, that there was a temporary resurgence of interest in thiol-ene chemistry from a technical viewpoint but that such interest was never reflected in the commercial marketplace.

This interesting UV-polymerization technology is now, once again, under consideration in academic and industrial laboratories. Prof. Charles E. Hoyle at the University of Southern Mississippi (USM), for example, has reported renewed investigations into this important technology^{10, 11}. Personnel at USM have been able to prepare a variety of different formulations that, when polymerized in very thick sections, give a clear and colorless appearance while possessing substantial flexibility, impact resistance, hardness, and resiliency¹².

Prof. Hoyle seems to have been the “prime mover” in this latest resurgence. In fact, his outstanding work in this area served as the inspiration for the work now being done here in this laboratory. Prof. Hoyle “resurrected” the thiol-ene technology because of its apparent advantages, the most significant one being its versatility with respect to raw material selection. While much of the initial work of W. R. Grace & Co. and others involved allyl-functional materials¹³, it was known that thiol-functionality will react with literally **any** double bond, be it acrylate, methacrylate, vinyl, allyl, etc.; thus, the name “thiol-ene”.

Also, it turns out that the addition of multifunctional thiols to systems containing unsaturation allows for a significant reduction or perhaps even complete elimination of the relatively expensive photoinitiator system. In other words, functional oligomers and monomers capable of being polymerized with free radicals and containing effective amounts of thiol do not require typical levels of photoinitiator in order to polymerize. This is because the thiols function very effectively as “co-initiator” systems due to the fact that the –SH hydrogen atoms are very labile, having relatively high chain-transfer coefficients. Therefore, this technology has the potential to significantly enhance the product development chemist’s ability to formulate UV-polymerizable materials for a broad range of applications while reducing dependence on conventional photoinitiators and/or photosensitizers.

Ironically, it appears that much of the development of this technology has been focused on thiol-ene systems other than those containing the wide variety of commercially available acrylate-functional materials. A paper by D. P. Gush and A. D. Ketley of W. R. Grace & Co. published in 1978 discusses acrylate-based thiol-ene polymer systems¹⁶. More recently, N. B. Cramer and C. N. Bowman reported work to investigate the kinetics of thiol-acrylate photopolymerization¹⁷. Prof. Hoyle, et. al., also mentioned work with acrylates in their previously referenced publications^{10, 11}. However, it appears that little else has been reported specifically about these systems. This paucity in information may be indicative of the inherent instability encountered in this laboratory with such systems⁷.

Because of the apparent lack of significant studies of thiol-acrylate chemistry, a project was developed in this laboratory at the beginning of the new millennium that was designed to investigate the effects on stability, reactivity, and thermomechanical properties of adding multifunctional thiols to acrylate-functional UV-polymerizable systems containing little or no photoinitiator. Previously alluded to results of that work revealed a significant and apparently inherent instability in thiol-ene systems containing acrylate-functional oligomers and monomers⁷, an instability that could be overcome by addition of a suitable stabilizer¹⁸ but only at the cost of having a significant reduction in relative reactivity. In fact, even in the absence of the stabilizer, the relative reactivity of the thiol-acrylate systems investigated in that study, as measured using differential photocalorimetric (DPC) techniques, did not appear to be significantly better than the control systems that contained no thiol-functional monomer, apparently contradicting literature references^{10, 11}.

These unexpected results raised significant questions about the ultimate utility of these thiol-acrylate systems. What was the cause of the instability? In spite of literature references to the contrary, why were freshly made formulations NOT significantly higher in reactivity than similar systems with no thiol monomer added? What could be done to stabilize the systems? How could the contradictory results related to reactivity be resolved?

In an attempt to address one or more of these questions, a new investigation was initiated. This study was predicated on the idea that the unexpected results occurred due to the relative complexity of the formulations. After all, most of the formulations reported in the literature had consisted of oligomer-free, monomer-only systems of relative simplicity. Typically, these reported systems contained a single acrylate-functional monomer and a multifunctional thiol. The systems studied previously in this laboratory, by contrast, contained an acrylated aliphatic urethane oligomer, three different acrylate-functional monomers, a photoinitiator (PI) or photosensitizer (PS), and a tri-functional thiol. Perhaps one or more of these several components was enhancing the instability and/or precluding the observation of significantly higher relative reactivity.

With this in mind, the current study involved simple systems containing only one, two, or three acrylate-functional monomers, a PI or PS, and differing levels of trimethylolpropane *tris*(3-mercaptopropionate). The design of this experiment resembles closely a so-called "simplex" designed experiment involving three separate acrylate-functional monomers, three different binary blends of those monomers, and a single ternary blend of all three monomers. The purpose of this paper is to report the results of this investigation.

EXPERIMENTAL

Materials:

All materials utilized in this investigation were used as received from their supplier, without further purification.

Trimethylolpropane triacrylate (TMPTA), 1,6-hexanediol diacrylate (HDODA), and isobornyl acrylate (IBOA) - provided by UCB Chemicals Corporation.

Trimethylolpropane tris(3-mercaptopropionate) - obtained from Evans Chemetics.

1-hydroxycyclohexylphenyl ketone (Irgacure[®] 184) photoinitiator (PI) - provided by Ciba Specialty Chemicals Corporation.

Benzophenone photosensitizer (PS) - provided by Velsicol Chemical Corporation.

Equipment:

TA Instruments, Model Q100 Differential Scanning Calorimeter (DSC) w/photocalorimeter accessory (PCA) – This instrument (DPC) was used to determine the relative reactivity of the formulations. Both the reference and sample light guides contained 10 % neutral density filters. This reduced the light intensity experienced by the samples to approximately 56 - 65 mW/cm². Both “induction time” and the time required to reach the maximum in the exotherm curve were taken to be direct measures of the relative reactivity of a given formulation; the former representing the “initial reactivity” and the latter representing the overall average reactivity of the system.

Electronic Instrumentation & Technology's (EIT[®]) UV PowerMapTM radiometer – This was used to determine the UV-A dose (UV energy density) and peak irradiance experienced by the formulations as they were polymerized.

Procedures:

Preparation of Formulations – The procedures used to prepare and polymerize the formulations evaluated in this study were essentially the same as those reported previously^{14, 15, 16, 17} from this laboratory. In most cases the thiol-functional monomer and photoinitiator or photosensitizer were included as post-additions after the oligomer and monomers were uniformly mixed.

Relative Reactivity Measurements – An analytical balance was used to measure approximately 2 to 5 mg into the “lid” of a DSC sample pan. A lid was used because it provided a very flat surface for better contact with the thermoelectric “disk” or pedestal inside the sample chamber of the DPC instrument. An empty lid was used as the reference for these experiments.

Having properly calibrated the DPC, both sample and reference light guides were put in place above the sample and reference lids, respectively. The sample and reference were then exposed to a nitrogen purge at 50 mL/min, equilibrated at 25° C, and held isothermally for 0.5

minutes. At that point, the shutter on the DPC unit was opened, allowing the UV light to strike the sample and reference pans simultaneously. After a very short “induction time,” a sharp exotherm, as expected, was observed for each sample. The samples were exposed for a sufficient time to insure that the reaction had ceased, typically 2.00 minutes. The “end” of the reaction was determined by noting when the heat flow vs. time curve flattened out and ceased to drop further. The resulting curves were analyzed using the TA Instruments’ Universal Analysis software.

Experimental Plan:

Formulations containing only HDODA or TMPTA were prepared with PI or PS and varying levels of tri-functional thiol. No similar formulations containing only IBOA were prepared due to the lack of the ability to crosslink this monofunctional monomer. In addition to the two “single-monomer” formulations, three binary blends of the three acrylate-functional monomers were prepared with either PI or PS and varying amounts of thiol. Finally, a single ternary blend of equal masses of all three monomers was prepared. Thus, twelve (12) formulations were prepared and evaluated in this study. The compositions of these 12 formulations are given in **Tables 1 – 6**. Monomer blends containing TMPTA contained 0.5 pph PI or PS while the ones containing only HDODA or HDODA/IBOA contained 2.0 pph PI or PS.

**Table 1
HDODA Blend Composition**

Components	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6	Jar 7
HDODA	35.0g	35.0g	35.0g	35.0g	35.0g	35.0g	35.0g
Tri-functional thiol	3.5g (10pph)	7.0g (20pph)	10.5g (30pph)	14.0g (40pph)	19.5g (60pph)	28.0g (80pph)	40.0g (114 pph)

**Table 2
TMPTA Blend Composition**

Components	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
TMPTA	35.0g	35.0g	35.0g	35.0g	35.0g
Tri-functional thiol	3.5g (10pph)	10.5g (30pph)	19.5g (60pph)	31.5g (90pph)	47.1g (135pph)

**Table 3
HDODA/IBOA Binary Blend**

Components	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
HDODA	17.5g	17.5g	17.5g	17.5g	17.5g
IBOA	17.5g	17.5g	17.5g	17.5g	17.5g
Tri-functional thiol	3.5g (10pph)	7.0g (20pph)	10.5g (30pph)	14.0g (40pph)	40.0g (114pph)

Table 4
HDODA/TMPTA Binary Blend

Components	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
HDODA	17.5g	17.5g	17.5g	17.5g	17.5g
TMPTA	17.5g	17.5g	17.5g	17.5g	17.5g
Tri-functional thiol	3.5g (10pph)	10.5g (30pph)	21.0g (60pph)	31.5g (90pph)	44.15 (126pph)

Table 5
IBOA/TMPTA Binary Blend

Components	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
IBOA	17.5g	17.5g	17.5g	17.5g	17.5g
TMPTA	17.5g	17.5g	17.5g	17.5g	17.5g
Tri-functional thiol	3.5g (10pph)	10.5g (30pph)	21.0g (60pph)	31.5g (90pph)	34.8g (99pph)

Table 6
Ternary Blend Composition

Components	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
HDODA	11.67g	11.67g	11.67g	11.67g	11.67g
IBOA	11.67g	11.67g	11.67g	11.67g	11.67g
TMPTA	11.67g	11.67g	11.67g	11.67g	11.67g
Tri-functional thiol	3.5g (10pph)	10.5g (30pph)	21.0g (60pph)	31.5g (90pph)	34.8g (105pph)

RESULTS AND DISCUSSION

The shelf-life stabilities of the formulations are measured as the time required for the formulation to begin gelling. The blends are considered to be gelling when the viscosity of the formulations begins to increase significantly relative to the original viscosity. The shelf-life stability of the individual blends is recorded in **Tables 7** and **8** and in **Figure 1** below.

Table 7
Shelf-Life Stability in Days of the Blends Containing Photoinitiator

Concentration of Thiol (pph)	10	20	30	40	60	80	90	Equi-molar
HDODA	> 365	> 365	0.5	0.5	12	12		22
TMPTA	> 365		2-4		2-4		2-4	> 1
HDODA/IBOA	> 365	> 365	> 365	> 365				> 365
HDODA/TMPTA	> 365		1		> 1		> 0.5	> 0.25
IBOA/TMPTA	> 365		> 365		19		0.5	0.25
HDODA/IBOA/TMPTA	104		11		4		3	1

Table 8
Shelf-Life Stability in Days of the Blends Containing Photosensitizer

Concentration of Thiol (pph)	10	20	30	40	60	80	90	Equi-molar
HDODA	> 365	> 365	0.5	0.5	12	12		22
TMPTA	> 365		1		> 1		0.17	0.08
HDODA/IBOA	> 365	> 365	> 365	> 365				> 365
HDODA/TMPTA	> 365		> 4		1		> 1	2
IBOA/TMPTA	> 365		8		1		1	> 2
HDODA/IBOA/TMPTA	104		11		4		3	1

A convenient way to represent the overall shelf-life stability of the various blends is to use a “shelf-life stability triangle” where corners represent the individual acrylate monomers, the sides of the triangle represent the binary blends, and finally the center represents the ternary blend.

The IBOA containing an equimolar amount of thiol is shown to have the highest shelf-life stability; however, due to the lack of crosslinking capability, the sample was not tested for relative. Based on **Figure 1**, the shelf-life stability of the system appears to be proportional to the average acrylate functionality of the monomer blend. The average number of moles of acrylate in any given blend is determined by calculating the number of moles of each monomer present. These values are then multiplied by the functionality of the respective monomers and the sum of the results is calculated to give the total moles of acrylate in the blend. This value is utilized in calculating the moles of thiol functionality needed for the “equimolar” blends – those containing the maximum amount of thiol in each formulation.

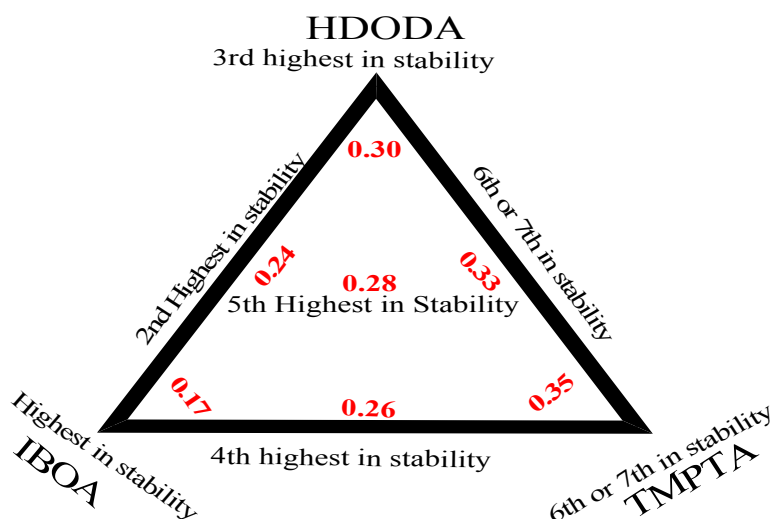


Figure 1
“Stability Triangle” for Monomer/Thiol
Blends w/PI or PS – Moles of Acrylate in Red

According to **Figure 1**, the blend with the highest shelf-life stability, as expected, is the blend that has the least number of moles of acrylate. In fact, the straight IBOA sample with its smaller number of moles of acrylate is shown to have the highest shelf-life stability. In contrast, the blend with the highest number of moles of acrylate is the least stable.

The observed effect of acrylate functionality on the stability of the formulations is a result of the increased concentration of acrylate double bonds with multifunctional monomers. Higher concentrations of reactive moieties would be expected to increase the reactivity and, thus, decrease the shelf-life stability of the system. Alternatively, one can consider that the difunctional and trifunctional monomers have two and three times, respectively, as many opportunities for reaction as does the monofunctional monomer. Thus, they tend to have lower shelf-life stability when blended with the trifunctional thiol.

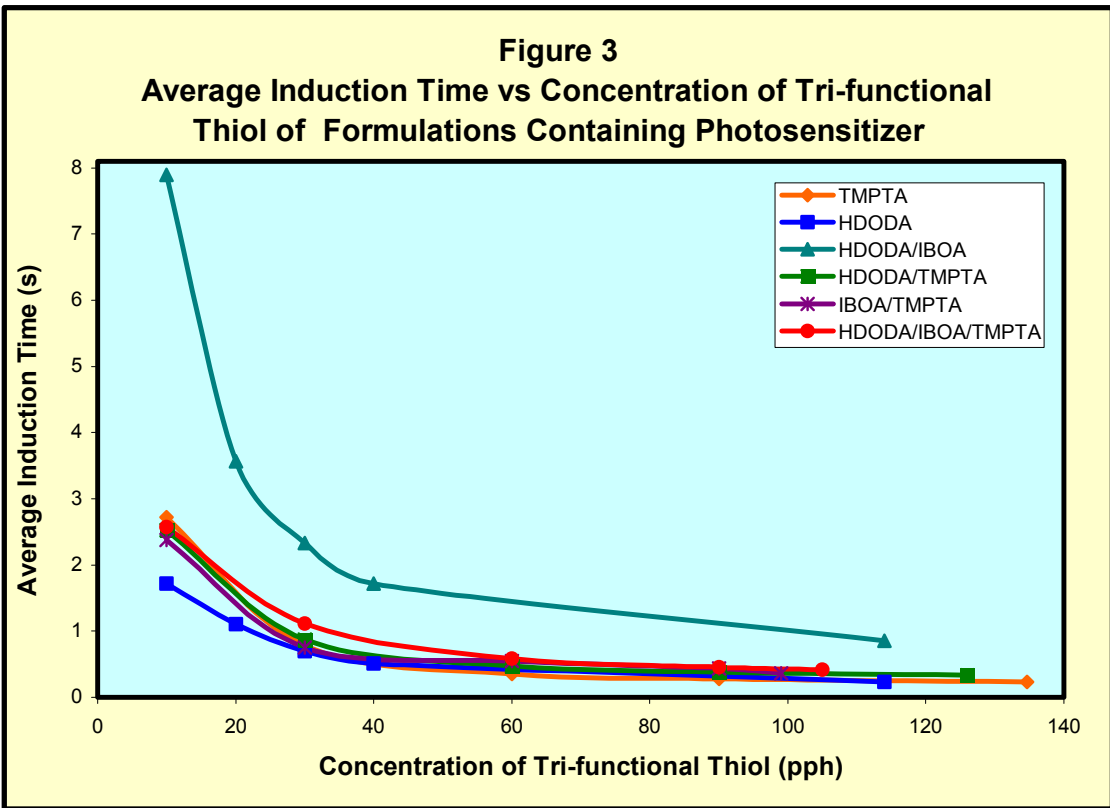
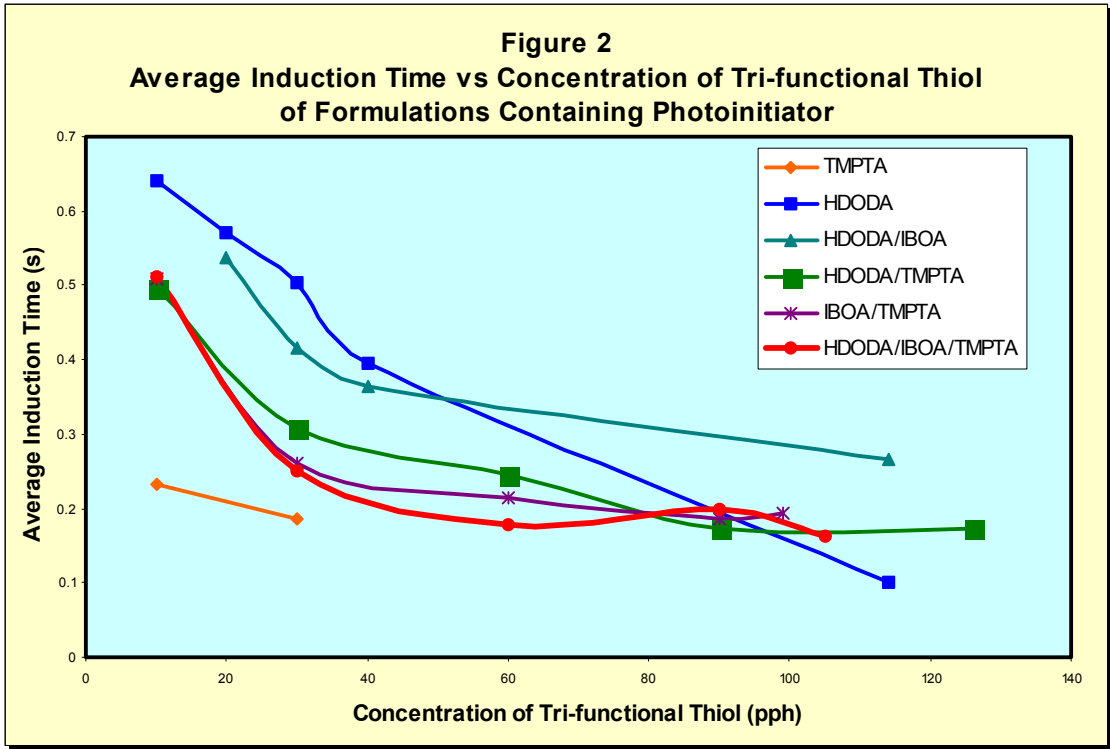
The relative reactivity of the individual blend is reflected in its induction time and peak max time, as measured using DPC. Induction time is the measured time interval between when the lamp's shutter is opened to expose the sample to UV light and when the reaction actually begins to occur as evidenced by a sharp increase in the slope of the exotherm curve. The induction time reflects the amount of inhibition that the system must overcome before actually beginning to polymerize and crosslink. It is strongly affected by the presence of inhibitors in the raw materials of the formulation, by the presence or absence of air during the reaction, by the intensity – more accurately known as the “peak power density” or “irradiance” - of the impinging UV light, and by the relative reactivity of the functional components. Thus, the induction time gives a good indication of the overall inhibiting effects of these parameters.

Peak max time is a second relative measure of the reactivity. Peak max time is the amount of time required to reach the maximum rate of energy output. Similar to the induction time, samples that experienced shorter peak max times have a relatively higher reactivity compared to samples that experienced longer peak max time. The graphs showing the effect of thiol concentration on the induction time for blends containing photoinitiator and photosensitizer are presented in **Figures 2 and 3**, respectively.

It appears in **Figure 2** that the thiol does have an effect on the induction time up to a level of about 40 pph for formulations containing PI. The largest effect is for the blends that have the two lowest amounts of acrylate functionality. Above about 40 pph, it appears that the thiol no longer has a significant effect. One should note on the y-axis, however, that the PI-containing formulations have very low induction times to begin with, relative to those containing PS.

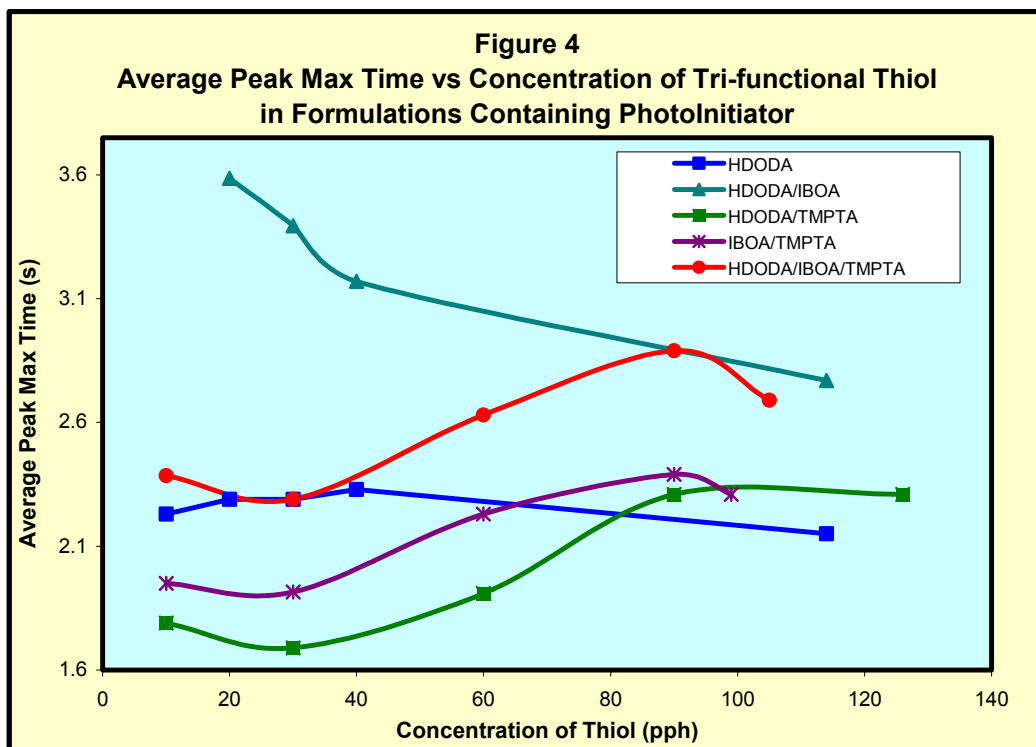
Figure 3 shows similar data for formulations containing PS. In this case, the effect of increasing the thiol concentration is more pronounced, particularly for the IBOA/HDODA blend, which has the lowest acrylate concentration. For the other blends, the effect is less pronounced, particularly for formulations containing more than about 40 pph thiol monomer. This more pronounced effect for blends containing PS is expected since without thiol, the blends would not be expected to polymerize and crosslink at all.

The effects of thiol concentration on the peak max times of the monomer blends containing PI and PS are given in **Figures 4 and 5**, respectively. **Figure 4** indicates that increases in thiol concentration have a negative impact on reactivity for all but the two lowest functionality



blends, particularly above about 30 pph thiol. The formulation with the least amount of functionality (IBOA/HDODA) does show some improvement in reactivity with increasing thiol and for the monomer mixture containing only HDODA, the thiol seemed to have no particular effect.

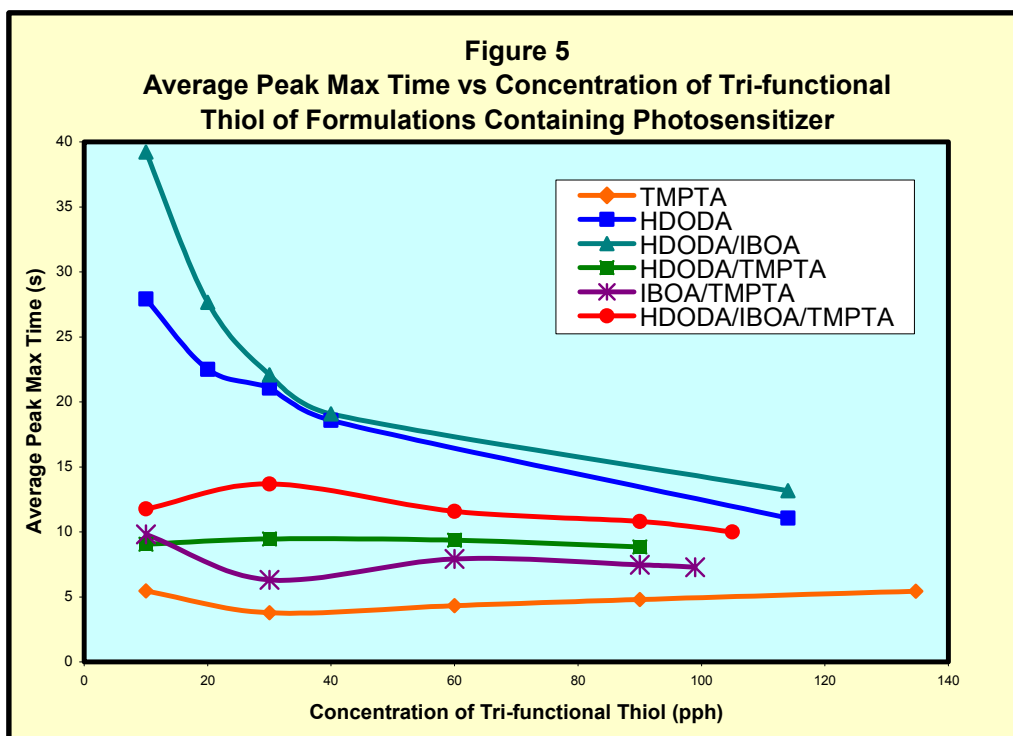
Figure 5 shows a similar effect of thiol on the reactivity of blends containing PS. The thiol seems to enhance reactivity (decrease the peak max time) for the blends with the lowest average acrylate functionality. For the higher functionality blends, there is no apparent effect. Thus, it appears that the thiol only enhances reactivity for formulations that contain the lowest average functionality, whether PI or PS is being used.



According to **Figures 2 - 5**, the binary blends of HDODA and IBOA, containing either photoinitiator or photosensitizer, seem to have the overall highest induction time and peak max time, which is indicative of lowest relative reactivity. This result is consistent with the results from the shelf-life stability. The binary blend of HDODA and IBOA demonstrated the best shelf-life stability and the lowest relative reactivity. The blends with the highest functionality tend to display higher reactivities and lower shelf-life stabilities, as might be expected. These are blends containing TMPTA, the highest functionality acrylate monomer.

SUMMARY AND CONCLUSION

The instability observed in this investigation upon addition of the tri-functional thiol is consistent with the previous work involving oligomer-based formulations. Many of the blends containing



tri-functional thiol have poor shelf-life stabilities, except those that contain either a small amount of thiol or that have a relatively low functionality. Thus, this investigation has demonstrated that acrylate blends containing thiols tend to have relatively low shelf-life stability, with or without the presence of an oligomer. The results also indicate that higher-functionality blends have less overall shelf-life stability than those with lower levels of acrylate.

As might be expected, the formulations that showed the least stability with respect to gelation, also showed the highest overall reactivity as indicated by the induction times and the peak max times. For the first time in this investigation, one acrylate-based formulation has shown good shelf-life stability at all levels of thiol monomer. The HDODA/IBOA blend had shelf life in excess of one year. However, it also had the lowest reactivity of any of the blends studied in this investigation. Thus, it appears that a balance between stability and reactivity can be struck by controlling the relative functionality of the acrylate monomer blend.

Acknowledgements

We would like to thank the Department of Natural Sciences of University of Houston-**Downtown** and the Robert A. Welch foundation for their continued support of the *Center for Applied Polymer Science Research*. We want to thank Surface Specialties UCB for providing the monomers and Ciba Specialty Chemicals Corporation for providing the photoinitiator used in this investigation. Finally, we want to express our gratitude to TA Instruments for providing technical guidance and a significant reduction in price that allowed us to obtain the differential photocalorimeter instrumentation used in this study.

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