Synthesis and Characterization of Novel Highly Functional Thiols

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Abstract

Comparable polymerization rates are observed with increasing thiol functionality for various thiol/triallyl ether photopolymerizations. Novel highly functional thiols synthesized by an amine-catalyzed thiol Michael addition reaction have been analyzed by proton NMR. Polymerization rates, measured by photo-DSC and real-time FTIR for reaction mixtures of 30 mol% thiol (f_{avg} = 3.3, 7.3) and 70 mol% 2, 4, 6-triallyloxy-1, 3, 5- triazine (TATA), indicate that rapid polymerization rates are attained with each thiol. Thin films produced by polymerization on a variety of substrates exhibit excellent adhesion to several substrates, along with good flexibility and high abrasion resistance.

Introduction

Photocuring of thiol-ene monomer mixtures provides many advantages over traditional acrylate-based polymerization including their ability to polymerization in air.[1,2] Thiol-ene polymerizations proceed by a step-growth, free-radical chain transfer mechanism in which the thiol acts as a chain transfer agent. The reduced oxygen inhibition in thiol-ene polymerization originates with the β-thioether carbon radical forming a non-propagating alkylperoxy radical that subsequently abstracts a hydrogen from a thiol group to form a thiyl radical, which then adds to a carbon-carbon double bond to continue the free-radical propagation sequence. An additional advantage of thiol-ene polymerization is its ability to polymerize in both the presence and absence of a photoinitiator at very fast rates. Additionally, the thioether bonds formed are very flexible, aid in adhesion to a variety of substrates, and serve as antioxidants.

DMA results of films show that the glass transition, T_g, and crosslink density decrease and polymer flexibility increases as thiol concentration increases in a trithiol:1,6-hexanediol diacrylate matrix.[1] T_g values drop from 90 °C to 20 °C for systems with 40% thiol while uniformity of the crosslink density improves. Thermodynamic studies confirm the reduction of crosslink density by analyzing photocrosslinking enthalpies for various dithiol/diacrylate polymers.[3] Despite the improvement in the uniformity of the crosslink density in typical thiol-ene based films and the accompanying improved physical/mechanical properties, there are only a few multifunctional thiols available commercially, and they are generally limited in functionality to four or less.

Synthesis of novel, highly functional thiols can improve polymeric characteristics of thiol-ene polymerizations since high thiol functionality should lead to increased glass transition temperatures and perhaps different film architecture. Previous work shows that polymerization rates increase only modestly with thiol functionality.[4]

Herein, we will report results for the synthesis and structural analysis of two multifunctional thiols with average functionality, f_{avg}, of 3.3 and 7.3 and the corresponding

polymerization rates for each thiol with 2, 4, 6-triallyloxy-1, 3, 5-triazine (TATA). NMR analysis confirms that thiol synthesis was successful using an amine catalyzed Michael addition of thiol to electron deficient acrylate bonds.[5] Kinetic studies using photo-DSC and real-time FTIR indicate that approximately equivalent polymerization rates and efficiencies are obtained for each thiol/ene system.

Experimental

Trimethylolpropane tris (3-mercaptopropionate), pentaerythritol tetrakis (3-mercaptopropionate), trimethylolpropane triacrylate, diethyl amine, and octyl amine were obtained from Aldrich Chemical Company, and 1,6-hexanediol diacrylate was obtained from UCB. All were used as received.

Synthesis of T_4 (Figure 1) and T_9 (Figure 1) monomers:

In general, synthesis was performed using a KDS 100 syringe pump from KD Scientific. A mixture of acrylate/amine catalyst (2 mol%) was added dropwise to excess thiol at a rate of 0.027 milliliter/minute with constant stirring. The amount of thiol used was based upon a 4:1 thiol:ene excess (based upon functionality) for the synthesis of the T_4 and 1.33:1 thiol:ene excess (based upon functionality) for the synthesis of the T_9 monomer. Elucidation of each monomer structure was performed on a Bruker 300 MHz NMR spectrometer.

An HDDA/diethyl amine mixture (0.022 mol/0.00044 mol) was added to trimethylolpropane tris(3-mercaptopropionate) (0.029 mol) to synthesize T_4. The average functionality calculated for the mixture of thiols formed was f_{avg} = 3.3. A trimethylol propane triacrylate/octyl amine mixture (0.0083 mol/0.0017 mol) was added to pentaerythritol tetrakis (3-mercaptopropionate) (0.038 mol). The average functionality calculated for the mixture of thiols formed was f_{avg} = 7.3.

Polymerization Kinetics

The kinetics studies for copolymerization of 2, 4, 6-triallyloxy-1, 3, 5-triazine (TATA) and T_4, and T_9, respectively, were determined by photo-DSC (nitrogen conditions) and real-time FTIR in order to compare the effects of thiol functionality on polymerization rates and crosslink density. Copolymerization of TATA and thiol involves a reaction of 70:30 molar mixture (based upon functionality) of TATA:thiol with or without photoinitiator (2 mol%). The photoinitiator used was 2, 2-dimethyl-2-hydroxy acetophenone (Darocur 1173 from Ciba Specialty Chemicals) which cleaves at the position α to the carbonyl group upon irradiation by UV light.

Exotherms were measured on a Perkin-Elmer DSC-7 modified with a medium pressure mercury lamp. Specially crimped aluminum pans were injected with 2-μL samples, giving a film thickness of 200 μm. Exotherms give direct information about photopolymerization rates. Real-time IR was performed on an IFS-88 Bruker spectrometer. From analysis of appropriate peaks, it was possible to obtain percent and actual mole conversions of thiol and ene groups versus time. Samples were placed between NaCl plates and irradiated by UV light filtered by a 2.0 neutral density filter.
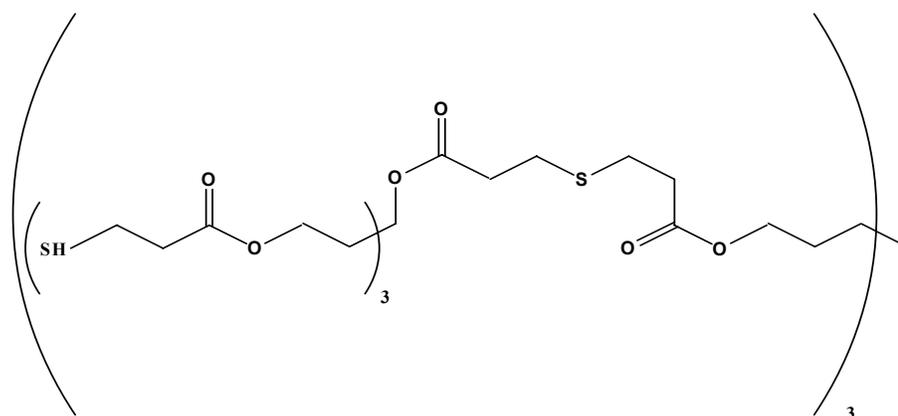
(a)
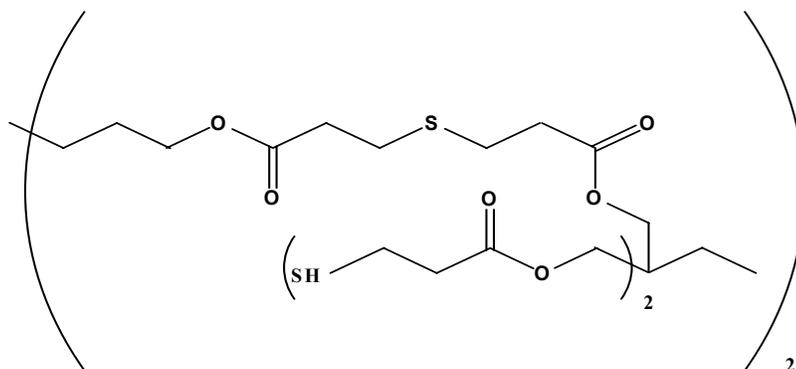
(b)

Figure 1. (a) Structure of T_4 monomer synthesized from 1,6-hexanediol diacrylate and 4:1 excess trimethylolpropane tris (3-mercaptopropionate); (b) Structure of T_9 monomer synthesized from trimethylolpropane triacrylate and 1.33:1 excess pentaerythritol tetrakis (3-mercaptopropionate).

Results and Discussion

Proton NMR results (Figure 2) confirm the formation of the thioether bond for each thiol synthesized. Upon reaction of 1,6-hexanediol diacrylate with trimethylolpropane tris (3-mercaptopropionate), the unsaturated acrylate double bonds groups are converted to saturated aliphatic groups. NMR results in Figure 2 show that the chemical shifts of the alkene protons change from δ6.4, δ6.2, and δ5.8 to δ2.6. The aliphatic (methylene) protons in the mercaptopropionate adjacent to the sulfide bond have chemical shifts at δ2.6 (a), thus providing evidence that the thioether bond is formed. The presence of thiol is indicated by the peak at δ1.6 (b). Similar results for T_9 monomer synthesized from the reaction of trimethylolpropane triacrylate and pentaerythritol tetrakis (3-mercaptopropionate) are shown in Figure 3.
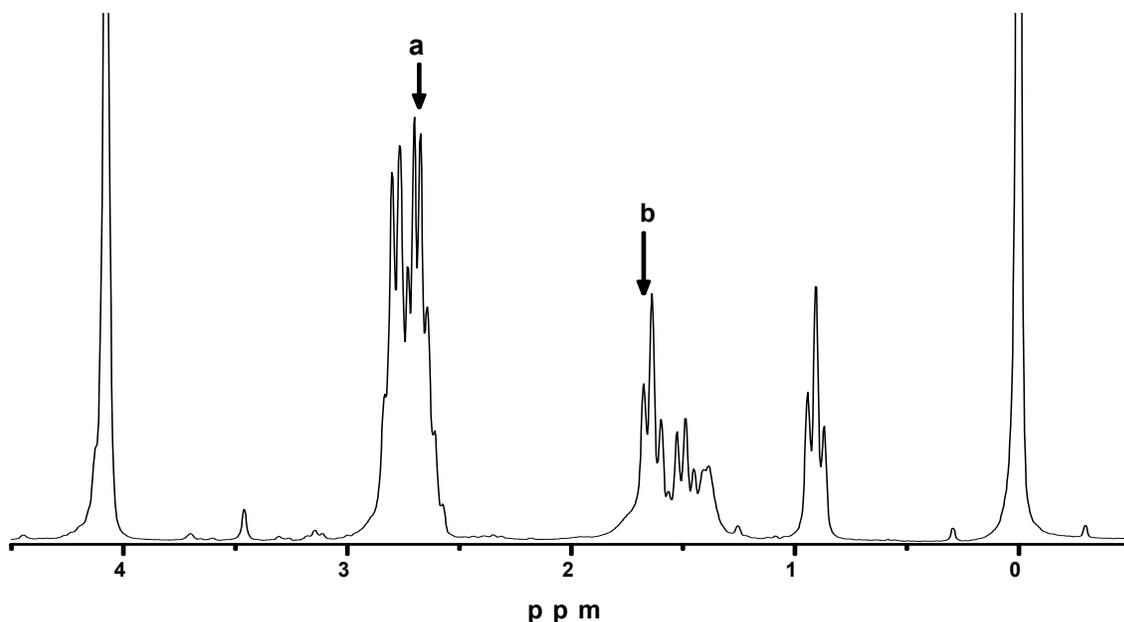
Figure 2. Proton NMR data. Structural analysis of T_4 monomer mixture.
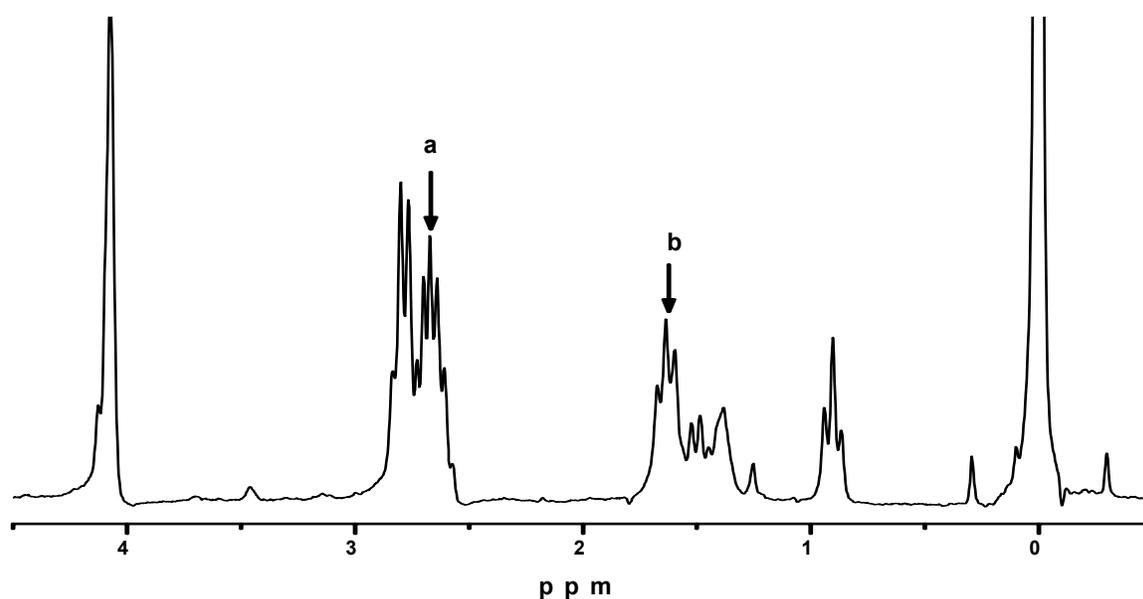

Figure 3. Proton NMR data. Structural analysis of T_9 monomer mixture.

For polymerization initiated with and without photoinitiator present, large differences in polymerization rates were not observed for polymerization of 30:70 molar mixtures of T_4 or T_9 and TATA (Figures 4 and 5). This suggests that the increase in thiol functionality from 3.3 to 7.3 has little effect on photopolymerization rates. Real-time IR data (Figures 5 and 6) confirm the results from photo-DSC in that the polymerization rates and final molar conversions (see Figure 6 for a direct comparison for moles converted versus time) are almost identical for the two systems.
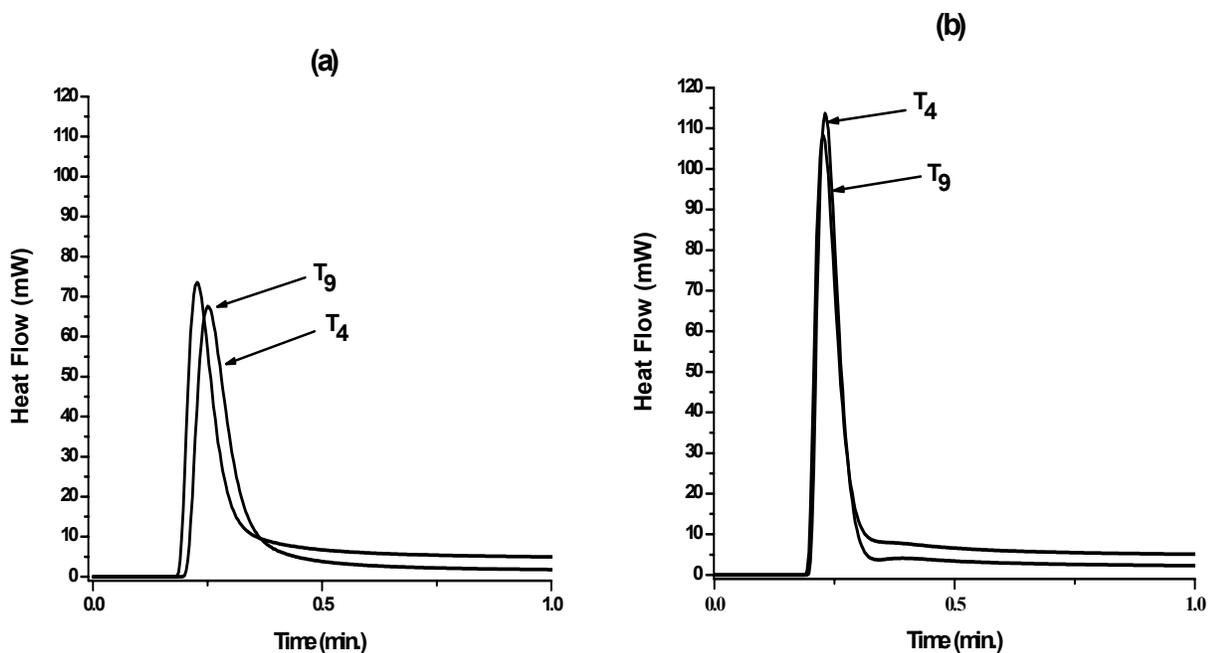
Figure 4. Photo-DSC exotherms. (a) Comparison of exotherms of photoinitiatorless reactions of T_9 (30 mol% thiol), and T_4 (30 mol% thiol) mixtures; (b) Comparison of exotherms of reactions of T_9 (30 mol% thiol) and T_4 (30 mol% thiol) mixtures with photoinitiator. Lamp source was medium pressure mercury lamp with irradiance of 88.96 mW/cm^2.
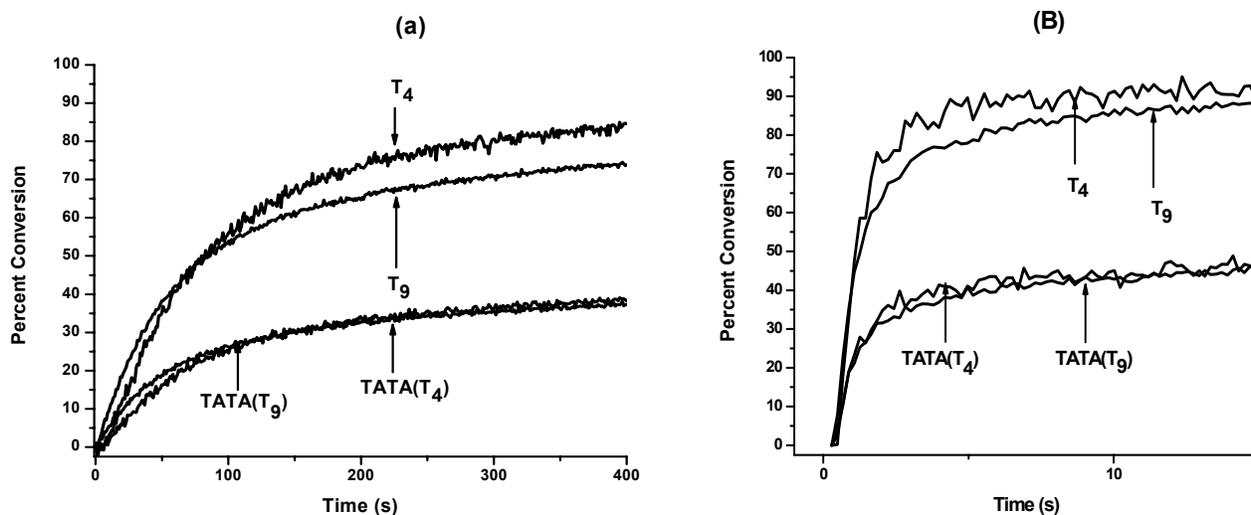

Figure 5. Real-time FTIR plot of Percent Conversion vs. Time. (a) Comparision of moles of thiol and ene converted in photoinitiatorless reactions of T_9 (30 mol% thiol, 70 mol% ene) and T_4 (30 mol% thiol, 70 mol% ene) mixtures; (b) Comparison of moles of thiol and ene converted in reactions or T_9 (30 mol% thiol, 70 mol% ene) and T_4 (30 mol% thiol, 70 mol% ene) mixtures with photoinitiator. Lamp source was a medium pressure mercury lamp with irradiance of 0.25 mW/cm^2.

This absence of differences in conversion and rate with thiol functionality is remarkable in view of expected differences in the conversion at which the gel point would be attained during the thiol-ene polymerization.[1]
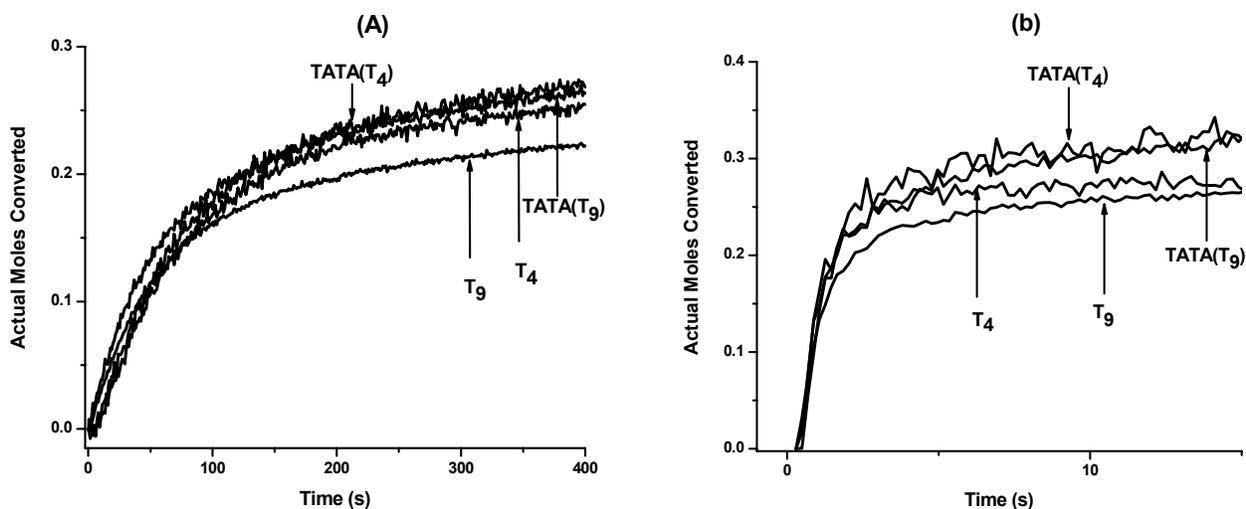

Figure 6. Real-time FTIR plot of Actual Moles Converted vs. Time. (a) Comparison of moles of thiol and ene converted in photoinitiatorless reactions for T_9 (30 mol% thiol, 70 mol% ene) and T_4 (30 mol% thiol, 70 mol% ene) mixtures; (b) Comparison of moles of thiol and ene converted in photoinitiated reactions for T_9 (30 mol% thiol, 70 mol% ene) and T_4 (30 mol% thiol, 70 mol% ene) mixtures with photoinitiator. Lamp source was a medium pressure mercury lamp with irradiance of 0.25 mW/cm^2.

Finally, thin films were made from 75 micron thick draw downs of 30:70 molar mixtures of each thiol-ene combination on paper, wood, glass, and metal substrates. The samples readily cured in air on a Fusion UV Systems curing line equipped with an H bulb. The films all exhibited outstanding adhesion to each substrate and excellent scratch resistance. Details of physical/mechanical property measurements will be forthcoming.

Conclusions

Proton NMR results confirm successful synthesis of highly functional thiols using a thiol-ene Michael addition reaction catalyzed by a primary amine. This synthetic method serves as a prototype for synthesis of additional highly-functionalized thiols. Based upon results from photo-DSC and real-time FTIR, an increase in thiol functionality was shown to have little tangible effect on photopolymerization rates for 70:30 TATA:thiol molar mixtures. An initial screening of films cast on a variety of substrates indicates that the films produced exhibit excellent physical and mechanical properties including good abrasion resistance and adhesion. This general synthetic method for producing thiols can be applied to the synthesis of a whole series of thiols with variation in functionality and chemical structure and thereby expanding opportunities for material synthesis of structures with a wide range of properties.

Acknowledgements

References

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3. Bowman, C. and Cramer N., *Mechanistic Studies, Advanced Characterization, and Novel Development of Thiol/Ene Reactions*, Radtech UV and EB Technology Expo & Conference 2002, Breckenridge, CO.

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5. Van Dijk, J. and Theodorus, M., *PCT*, WO 0064959 (2000) and previous references therein.