

# Photopolymerization of Several Novel Dendritic Systems

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**Abstract:** Photocurable multifunctional thiol-ene and dendritic acrylate based monomers were photopolymerized with varying concentrations of functional groups in order to study the final film properties of two different crosslinked networks. The mechanical and physical properties of the films were measured by dynamic mechanical analysis (DMA), a pendulum hardness tester and other instruments.

## Introduction

Photopolymerization of thiol-ene and acrylate based crosslinked networks has been the primary focus of many UV-curing studies for various applications. Thiol-ene systems polymerize by a free-radical step-growth process that forms a highly uniform crosslinked network with a very narrow glass transition ( $T_g$ ).<sup>1</sup> Shrinkage occurs to a great extent in the liquid state due to the high monomer conversion at the gel point of thiol-ene networks.<sup>1</sup> By contrast, early gelation in acrylate polymerization forms inhomogeneous high density regions.<sup>2-5</sup> It has been assumed that these high density “ball-like” structures coalesce and form more organized structures at high conversion.<sup>2,4-6</sup> Cramer and Bowman<sup>7</sup> showed that the addition of multifunctional thiols to multifunctional acrylates alters polymerization process and have a profound effect on the mechanical and physical film properties of the cured films due to the formation of more uniform networks.

Dendritic and hyperbranched molecules have attracted increasing attention both from fundamental viewpoint and for the great variety of expected applications in the last 15 years.<sup>8</sup> These systems have backbone structure with numerous branching points and a large number of end-groups that greatly affect their properties. Dendritic monomers with acrylate, vinyl ether, allyl ether or epoxy functional end groups have been studied as multifunctional crosslinking systems for use in UV cured coatings.<sup>9-11</sup>

Recently, the work in our group showed that polymerization of acrylate and thiol-ene mixtures forms a nano-structured morphology giving rise to very interesting and unique mechanical properties.<sup>12</sup> Since dendritic molecules have structure on the nano-scale, it should be very interesting to employ

multifunctional dendritic acrylates in UV curable ternary thiol-ene mixtures in order to determine the effect of dendritic structure on the morphology and mechanical properties of the final thiol-ene crosslinked network. Herein, we report the first example of a dual polymerization process involving thiol-ene and dendritic acrylate mixtures. The resultant mechanical properties of the cured thiol-ene/dendritic acrylate based hybrids were measured using DMA, pendulum hardness tester and other mechanical property measurement techniques.

## Experimental

All reagents were used without further purification. Allyl pentaerythritol (APE), trimethylolpropane tris(3-mercaptopropionate) (TriThiol) and dendritic acrylate (functionality=16, CN2302) was kindly supplied by Perstorp Specialty Chemicals, Bruno Bock Co. and Sartomer Co., respectively. 2, 2-Dimethoxy 2-phenyl acetophenone (DMPA) was obtained from Ciba Specialty Chemicals.

Thermal transitions of the films were recorded using a TA Q800 dynamic mechanical analyzer (DMA) by heating samples free standing films obtained by removing cured samples (see below) from glass substrates cured on a Fusion line from -100 to 300 °C at a rate of 3 °C/min and at frequency of 1 Hz in air. DMA was conducted under the shear sandwich mode for 10 x 10 mm square size samples with thicknesses of 150-200 µm.

Pendulum hardness was measured with a BYK Gardner Pendulum Hardness Tester. Cross-cut Tape test (adhesion) was conducted according to ASTM D3359-02, mandrel bend test (cracking and elongation) was conducted according to ASTM D522, and rapid deformation (impact) was conducted according to ASTM D2794-93. Thiol-ene mixtures were prepared by blending TriThiol with APE based on equal mole functional groups. CN2302 was added to the TriThiol-APE mixture (0, 20, 40, 50, 60, 80 and 100 acrylate mol%) to prepare seven different TriThiol-APE/CN2302 mixtures. The amount of UV initiator, DMPA, was 1 wt%. Films on glass plates (200 µm) and steel Q panels (125 µm) were UV cured on a Fusion curing line systems with an H bulb (400 W/cm<sup>2</sup>, belt speed of 10 feet/min).

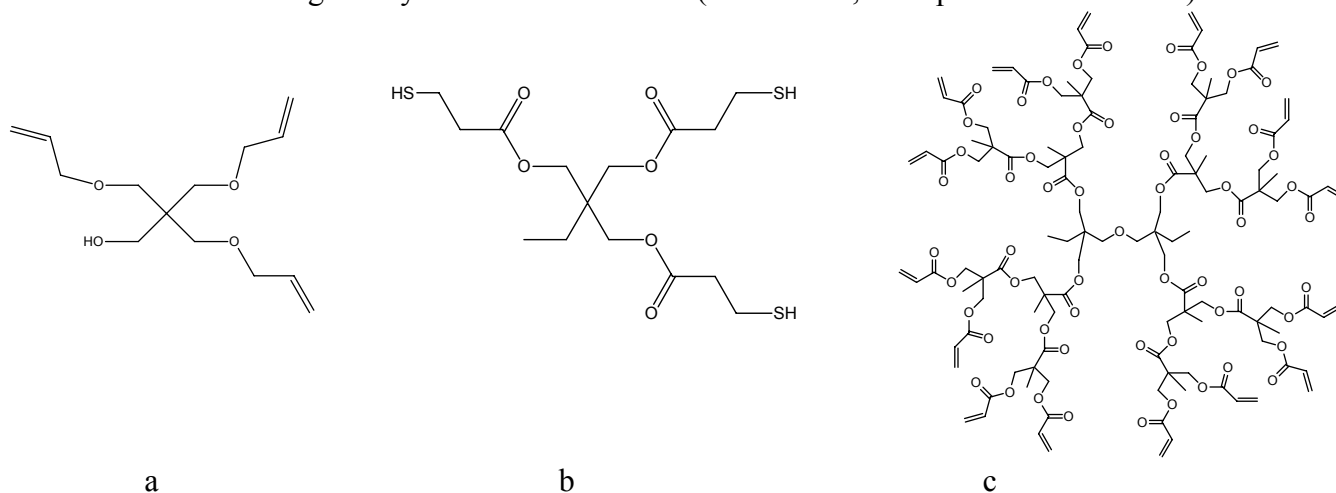
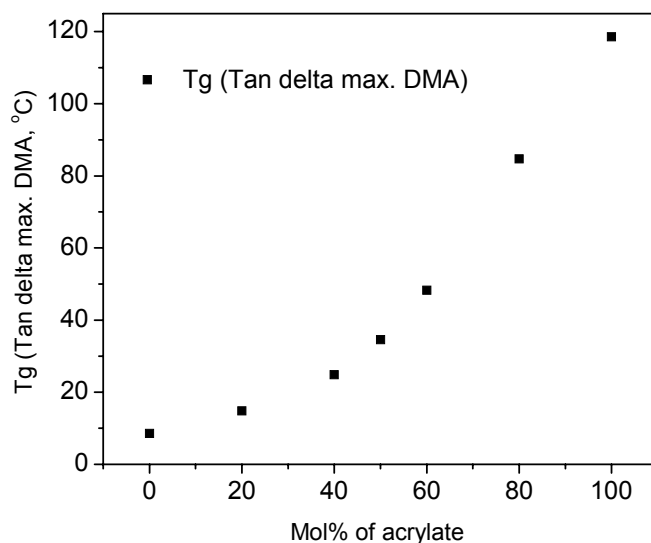


Chart 1 Chemical structure of APE (a), trithiol (b) and CN2302

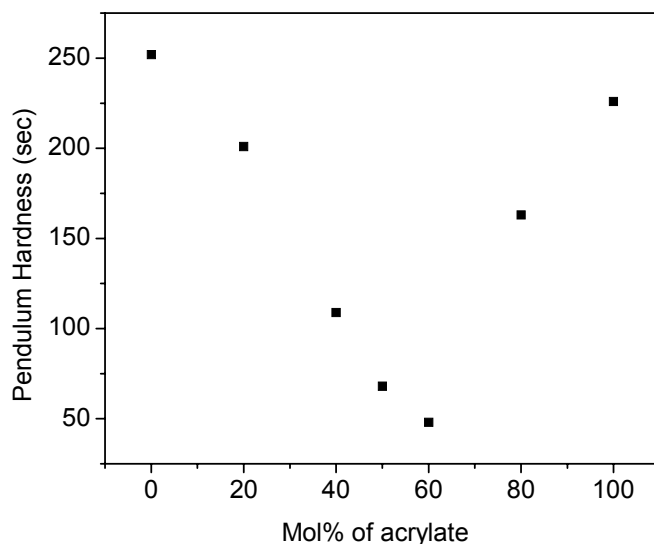
## Results and Discussion

The structures of all components used in this study are given in Chart 1. Photocuring occurred on a Fusion UV curing line, and the films subsequently removed from glass substrates. DMA analysis of the cured Trithiol-APE/ CN2302 films showed that the addition of increasing amounts of CN2302 (16 functional acrylate) to TriThiol-APE results in a film with an increasingly higher glass transition temperature as shown in **Figure 1**. The  $\tan \delta$  DMA plot (not shown here) of photocured pure CN2302 extends over a large temperature range extending to about 200 °C, indicative of a very inhomogeneous network. On the other hand, Trithiol-APE forms a uniform crosslinked network with a narrow  $\tan \delta$  plot (fwhm of about 20-25 °C). Interestingly, the polymerizations of mixtures of TriThiol-APE with CN2302 give  $\tan \delta$  plots with a single, narrow peak. This is indication of excellent mechanical coupling of any phase separated regions which are common for films fabricated thiol-ene-acrylate ternary systems.

Pendulum hardness measurements (Figure 2) of cured Trithiol-APE/ CN2302 films of glass substrates showed that with the addition of up to 60 mol% acrylate to TriThiol-APE, there is a sharp and continuously drop in the pendulum hardness with damping times decreasing from 252 seconds to 48 seconds. However, with addition of CN2302 concentrations of greater than 60 mol%, the pendulum hardness increases from 48 seconds to 226 seconds. The minimum in Figure 2 corresponds to a maximum in the energy damping found for the 60 mol% acrylate sample.



**Figure 1**  $T_g$  of UV cured Trithiol-APE/ CN2302 films measured by DMA (shear mode)



**Figure 2** Pendulum hardness of UV cured Trithiol-APE/ CN2302 films

**Table 1** Pencil hardness of UV cured Trithiol-APE/ CN2302 films

Mol% of acrylate	0	20	40	50	60	80	100
Pencil hardness	B	HB	2H	4H	4H	8H	8H

Finally, we note that, increasingly harder surface with the addition of acrylate to Trithiol-APE was observed by pencil hardness measurements of cured Trithiol-APE/ CN2302 films (see results in Table 1).

In order to complete the mechanical physical property evaluation of the ternary thiol-ene-acrylate, selected cured films were subjected to additional analysis. As shown in Table 2, films made from either the pure Trithiol-APE mixture or the 1:1 mole of TriThiol-APE/CN2302 dendrimer resulted in enhanced cross-hatched adhesion and reduced cracking propagation when subjected to a mandrel bending test. Especially interesting was the unexpected value for the front impact of the 1:1 mixture of the TriThiol-APE/CN2302 cured sample. We propose that this may result from a phase-separated morphology in addition to the fact that this sample has a maximum in the  $\tan \delta$  plot near room temperature. The impact measurements were made at room temperature, corresponding approximately to the peak in the  $\tan \delta$  plot; hence, the high energy absorbance as indicated by the enhanced impact value.

**Table 2** Mechanical properties of UV cured Trithiol-APE/ CN2302 films

	Trithiol-APE	50mol%Trithiol-APE/50mol% CN2302	CN2302
Adhesion	17.25% remained	12.7% remained	0% remained
Cracking (inch)	1.95	2.31	5.44
Front impact (pound)	42	60	28

## Conclusions

The thermal dynamic and mechanical properties of thiol-ene/dendritic acrylate based crosslinked networks were studied for varying concentrations of a dendritic acrylate monomer. The addition of dendritic acrylate into the thiol-ene mixture resulted in an increasing glass transition temperature and pencil hardness. The pendulum hardness showed a minimum corresponding to an enhanced impact value. Apparently, a sample with glass transition near room temperature has a higher propensity to absorb and dissipate energy without rupturing film structure. Additional results for films and thick plates fabricated from ternary thiol-ene-acrylate dendrimer mixtures will be presented at the conference.

## Acknowledgements

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