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Novel waterborne UV-crosslinkable thiol–ene polyurethane dispersions: Synthesis and film formation

Daniel B. Otts, Erik Heidenreich, Marek W. Urban*

School of Polymers and High Performance Materials, Shelby F. Thames Polymer Science Research Center, The University of Southern Mississippi, 118 College Drive # 10076, Hattiesburg, MS 39406, USA

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Abstract

A new class of water-dispersible polyurethane pre-polymers bearing pendant unsaturation was synthesized and used with polyfunctional thiol crosslinkers to prepare uniform aqueous colloidal dispersions capable of forming crosslinked films upon UV exposure at 254 nm. This novel approach to prepare UV crosslinkable, water-based polyurethane polymers offers numerous advantages over other similar systems. Photocuring behavior of films from such thiol–ene polyurethane dispersions (TE-PUD) was monitored using ATR-FTIR spectroscopy by following consumption of thiol and ene functionalities as a function of UV exposure time. Dynamic mechanical analysis (DMA) revealed a decrease of the glass transition temperature (T_g) with increasing thiol/ene ratios ranging from 0.5 to 1.1.

Keywords: Thiolene UV photopolymerization; NCO free polyurethanes; Film formation

While there have been significant interests in thiol–ene polymers [1–11], only limited knowledge pertaining to waterborne crosslinkable polyurethanes exists [12–15]. However, combining both chemistries offers a unique opportunity for the development of environmentally-compliant crosslinkable polymer networks. This communication reports the synthesis and preliminary data concerning film formation of novel waterborne UV-crosslinkable thiol–ene polyurethane dispersions (TE-PUD's). Specifically, the uniqueness of this approach is the synthesis of a low molecular weight polyurethane (PUR) pre-polymer (M_w = 2450 g/mol as determined by GPC) with terminal unsaturation and pendant acid groups which, upon combining with a polyfunctional thiol (M_w = 488.66 g/mol) in stoichiometric amounts ranging from 0.5 to 1.1 along with an appropriate neutralizing agent, is dispersed in water to form a uniform 'one component' (1K) colloidal dispersion with latent crosslinking ability. Due to its water insolubility, the polyfunctional thiol is emulsified by the water-dispersible PUR pre-polymer, and when such colloidal dispersion is applied to a substrate and water is allowed to evaporate, 254 nm UV irradiation results in a crosslinked network. While Fig. 1A outlines chemical reactions leading to the synthesis of such systems [16], Fig. 1B provides a schematic illustration of TE-PUD film formation. Other details concerning reagents used in this study are denoted in Table 1. It should be noted that the step-growth radical addition mechanism of thiol–ene systems facilitates development of a photopolymerizable system having significantly less oxygen inhibition than current UV crosslinkable urethane-acrylate based systems.

In an effort to characterize starting materials and their reactive components, ^{1}H NMR analysis was performed and Fig. 2, Trace A illustrates the spectrum of the PUR pre-polymer synthesized according to the scheme shown in Fig. 1A. For reference purposes, Traces B–E of Fig. 2 represent pentaerythritol allyl ether (PEAE), isophorone diisocyanate (IPDI), poly(neopentyl glycol adipate) pNGA, and *N*,*N*-dimethylolpropionic acid (DMPA) spectra, respectively. These starting materials were used in the PUR pre-polymer synthesis. As seen in Trace A, urethane N–H protons are detected in the 6.7–7.1 ppm region and terminal alkenyl protons due to end functionalization by PEAE are observed at 5.0–5.2 and 5.6–5.8 ppm. The same

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* Corresponding author. Tel.: +1 601 2666454; fax: +1 601 2665504.
E-mail address: marek.urban@usm.edu (M.W. Urban).

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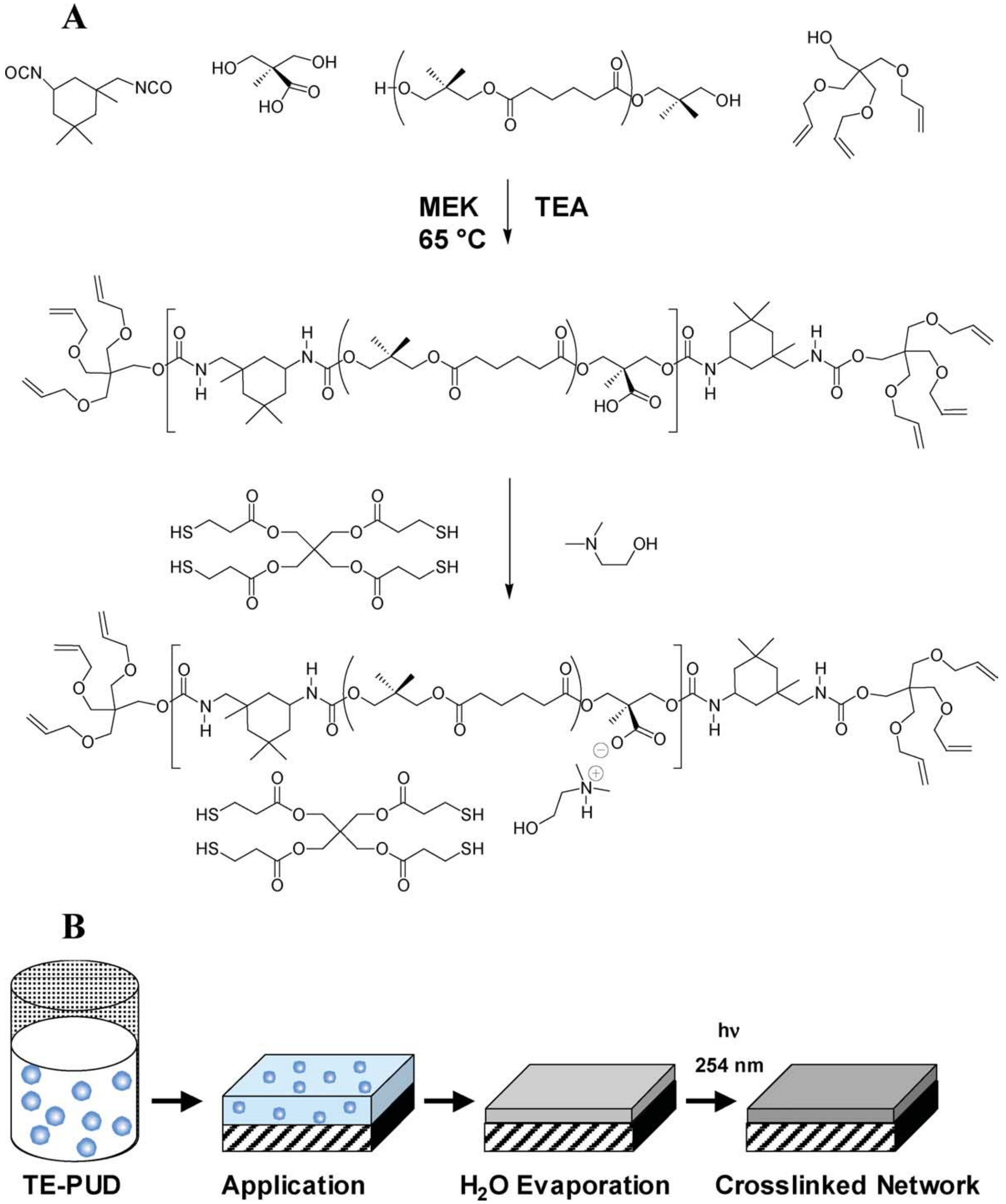

Fig. 1. A Reaction scheme for synthesis of polyurethane pre-polymer with unsaturated end groups followed by neutralization and mixing with PET3MP. B. Schematic illustration of TE-PUD film formation.

alkenyl functionality is also observed in the spectrum of PEAE in Trace B, thereby indicating that alkenyl functionality is present and preserved during the PUR pre-polymer synthesis. Further evidence of urethane formation is manifested by the presence of hydroxyl protons of PEAE observed at approximately 4.25 ppm in Trace B which are consumed during the reaction, and are consequently not detected in Trace A. Similarly, hydroxyl protons of pNGA are observed at 4.3 and 4.5 ppm in Trace D, but are not detected in Trace A. Incorporation of DMPA into the PUR pre-polymer backbone is evidenced by the disappearance of the resonance associated with hydroxyl α-methylene protons at 3.4 ppm in Trace E, again not observed in the spectrum of the pre-polymer (Trace A).

Preliminary studies concerning the presence of functional groups and photopolymerization of TE-PUD's are outlined below. Fig. 3, Trace A illustrates the ATR-FTIR spectrum of non-crosslinked TE-PUD

Table 1
Reagents and charges used in the synthesis of polyurethane pre-polymers

Component	Molar mass (g/mol)	Mole ratio	mmol	wt Fraction
Poly(neopentyl glycol adipate), pNGA	600.00	2.70	19.0	0.414
Isophorone diisocyanate, IPDI	222.28	6.40	45.0	0.364
Dimethylol propionic acid, DMPA	134.13	2.70	19.0	0.093
Pentaerythritol allyl ether, PEAE	242.15	2.10	14.8	0.130
Methyl ethyl ketone, MEK	72.11	n/a	n/a	n/a
Triethylamine, TEA	101.19	n/a	n/a	0.005
Total				1.00
Solids				27.5% w/w

film (SH/C=C ratio = 0.50). For reference purposes, Fig. 3, Traces B–E illustrate spectra of PEAE, pentaerythritol tetrakis(3-mercaptopropionate) (PET3MP), pNGA, and IPDI. While Traces C and D display strong bands due to ester C=O functional groups at approximately 1734 cm^{-1}, the carbonyl region of Trace A displays a band with a maximum at 1731 cm^{-1}, accompanied by a shoulder at 1700 cm^{-1} due to urethane C=O groups. Further evidence of urethane formation is provided by the presence of N–H bending modes of urethane linkages detected at 1530 cm^{-1} and shown in Trace A. Alkenyl functionality of PEAE is indicated by the out-of-plane C–H bending vibrations of alkene functional groups observed at 920 cm^{-1} in Trace B. The same band is also detected at 930 cm^{-1} in Trace A, indicating the presence of alkenyl functionality in the TE-PUD. Furthermore, the S–H groups of PET3MP are represented by an observable absorbance at 2566 cm^{-1}. The TE-PUD in Trace A also displays the band at 2566 cm^{-1}, which is highlighted by the inset in Fig. 3. The most pronounced spectral feature in Trace E is the intense band at 2253 cm^{-1} due to isocyanate C=O stretching vibrations of IPDI. This band is not observed in Trace A due to isocyanate consumption during urethane forming reactions. In summary, NMR and IR spectroscopic evidence demonstrates that both thiol and ene functionalities are preserved and are available for further crosslinking reactions in dried TE-PUD films.

Crosslinking reactions resulting from exposure to 254 nm UV radiation were also followed by ATR-FTIR and Fig. 4 shows spectral intensity changes associated with S–H and C=C groups [17] at 2566 and 930 cm^{-1}, respectively, for thiol–ene PUD films exposed to UV for up to 20 min using a SH/C=C ratio of 0.50. Upon irradiation, thiyl radicals may be generated by photolysis of the S–H bonds, which subsequently add to double bonds via a step-growth radical addition mechanism [2,7].

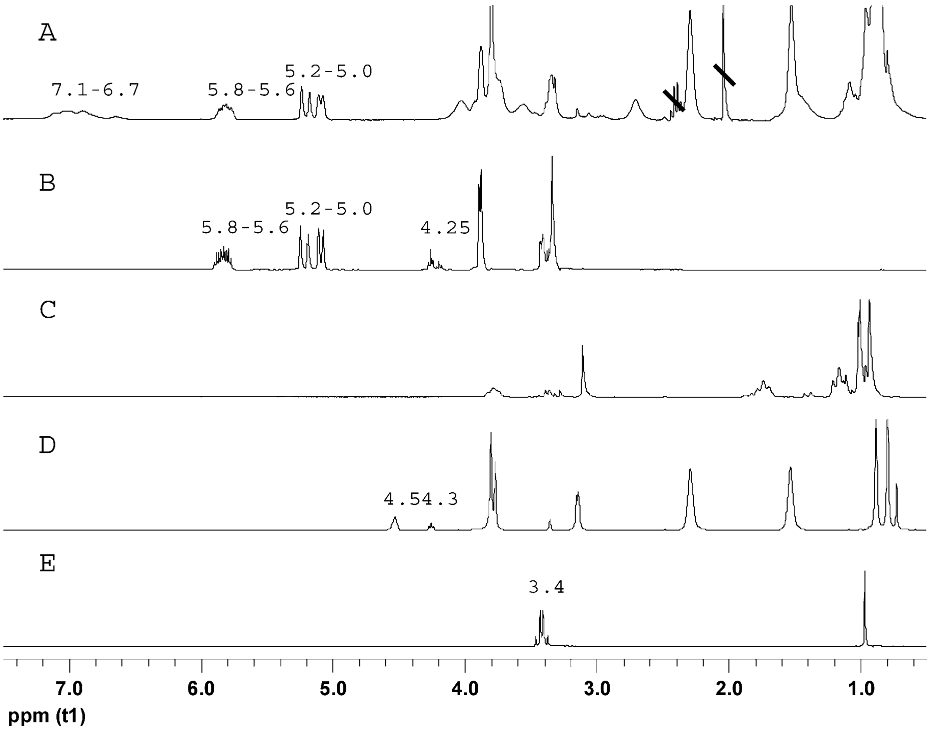

Fig. 2. 300 MHz ^{1}H NMR spectra of starting materials used in these studies. A. PUR pre-polymer; B. PEAE; C. IPDI; D. pNGA; E. DMPA. DMSO-d_6 was used as a solvent.

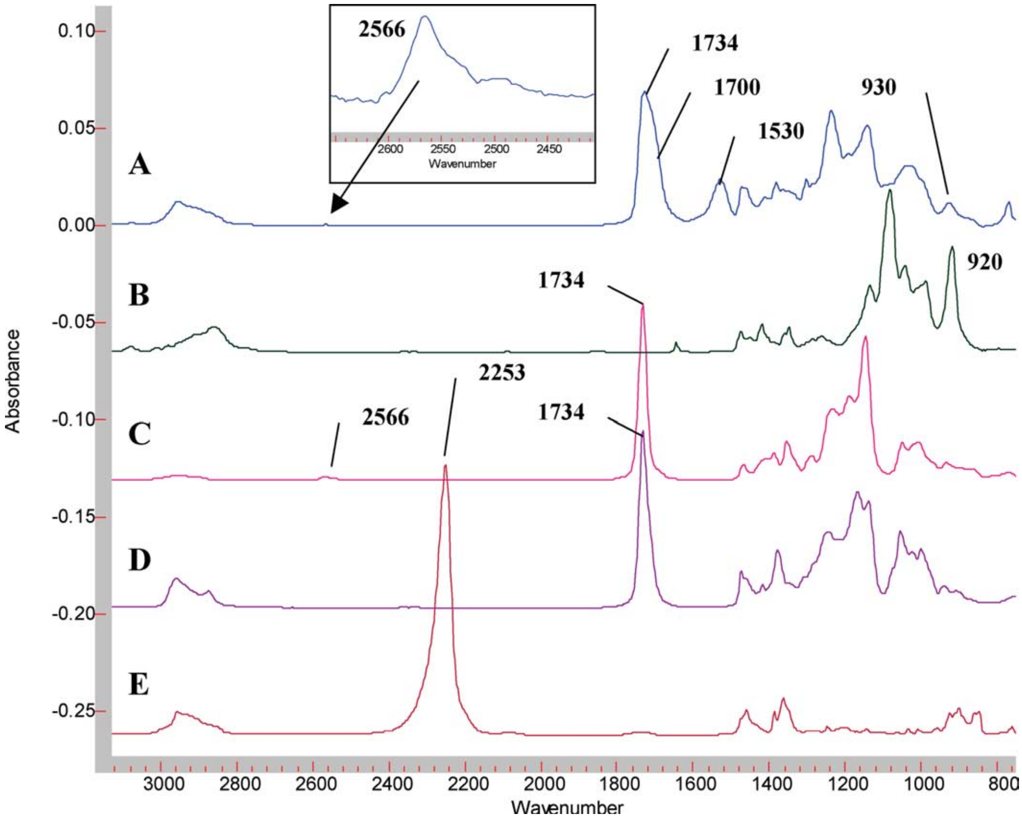

Fig. 3. ATR-FTIR spectra of materials used in these studies. A. Dried thiol–ene PUD; B. PEAE; C. PET3MP; D. pNGA; E. IPDI.

Consequently, crosslinking reactions may be monitored by observing the intensity decrease for the bands at 2566 and 930 cm^{-1}. For the data shown in Fig. 4 intensities were normalized to the C–H stretching region of the IR spectrum (i.e. 2800–3100 cm^{-1}). As seen, longer UV exposure times result in a rapid consumption of the S–H and C=C functionalities, indicating rapid reaction rates. However, the rates of conversion for such functional groups become limited by diffusion and concentration at extended UV exposure times [18].

As one would anticipate, exposure to 254 nm UV radiation also results in significant physical property changes. Specifically, non-crosslinked TE-PUD films exhibit a glass transition temperature (T_g) of approximately −9.0 °C as measured by DSC, which is attributed to a combination of the low molecular mass of the pre-polymer as well as plasticization effects of the polyfunctional thiol dissolved in the film. However, upon UV exposure in air, the T_g increases due to formation of a crosslinked network. Dynamic mechanical analysis (DMA) measurements [19] were performed on films photopolymerized for 20 min with SH/C=C stoichiometric ratios ranging from 0.50 to 1.10 and indicated that with increasing amounts of PET3MP (i.e. increased SH/C=C ratio), a decrease in the T_g is observed. Specifically, T_g's of 46, 43, 37, and 36 °C were observed for SH/C=C ratios of 0.50, 0.75, 1.00, and 1.10, respectively. Furthermore, the storage modulus (E') values in the rubbery plateau region of approximately 80–120 °C also increase with the increasing SH/C=C ratio, indicating increased crosslink density.

In summary, these studies demonstrate for the first time that thiol–ene radical addition is a viable crosslinking mechanism which can be utilized in 'one component' polyurethane aqueous dispersions with low/zero VOC levels. Such TE-PUD systems can be optimized to achieve desirable physical properties which can be adjusted by alterations of the S–H/C=C ratio as well as the PUR composition. Although concerns regarding the odor have been a concern, improved synthetic efforts have produced polyfunctional thiols with virtually no odor [7]. As a matter of fact specimens prepared during the course of these studies exhibit a slight odor immediately after crosslinking, which dissipated and was undetectable after a few days. In summary, TE-PUD's exhibit a great potential for the development of new PUR materials with low VOC levels and performance profiles that meet or exceed those of traditional solventborne polymers.

Acknowledgements

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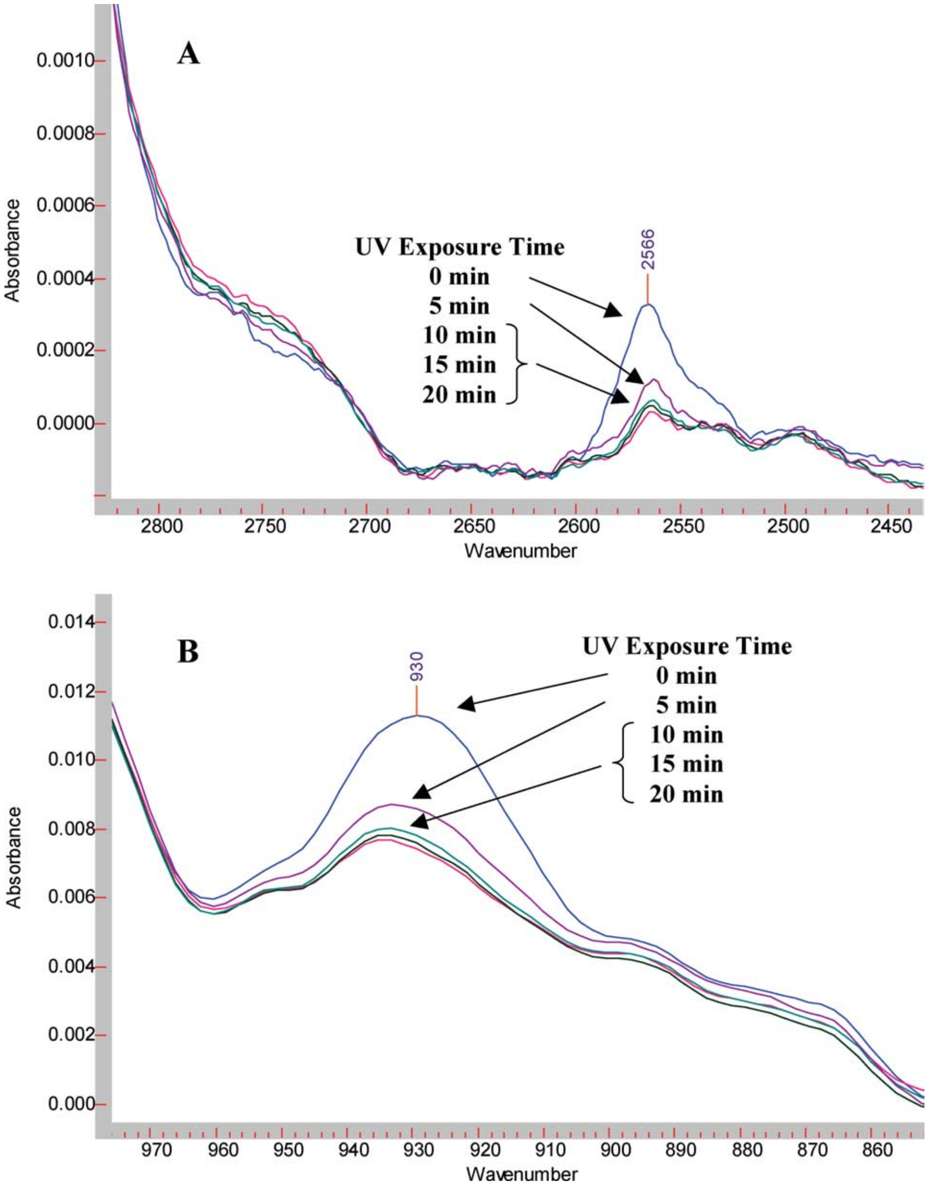

Fig. 4. ATR-FTIR spectra of thiol–ene PUD films prepared in these studies. Spectral regions shown illustrate consumption of A. R–SH functional groups at 2566 cm^{-1} and B. C=C functional groups at 930 cm^{-1} with increasing UV (254 nm) exposure time.

Appendix A

Poly(neopentyl glycol adipate) (pNGA, hydroxy end-capped, $M_n = 600$ g mol^{-1}), isophorone diisocyanate (IPDI, 98%, mixture of isomers), dimethylol propionic acid (DMPA, 97%), pentaerythritol allyl ether (PEAE, tech, 70%), *N*,*N*-dimethylethanolamine (DMEA, 99.5%), pentaerythritol tetrakis(3-mercaptopropionate) (PET3MP, 97. 4%), and triethylamine (TEA, 99.8%) were purchased from Aldrich Chemical Company. Methyl ethyl ketone (MEK, 99.8%) was purchased from Fisher Scientific, Inc. All reagents were used as received. Polyurethane pre-polymers with $M_w = 2450$ g/mol (GPC) bearing unsaturated end groups were prepared by reacting pNGA, IPDI, PEAE, and DMPA at 65 °C for 8 h in MEK using TEA catalysis (0. 5 wt% of total mass) and mild agitation. After 8 h, the reaction was completed as evidenced by the disappearance of the NCO band at 2265 cm^{-1}. The reaction mixture was then cooled to ambient temperature, yielding a clear, viscous liquid.

TE-PUD’s of the aforementioned PUR pre-polymers and PET3MP were prepared by dissolving PET3MP and a stoichiometric amount of DMEA (based on acid content of PUR pre-polymer) in MEK/PUR pre-polymer solutions followed by the drop-wise addition of water at 25 °C. Additionally, the thiol/ene (SH/C=C) stoichiometric ratio was adjusted to produce dispersions with varying levels of reactive groups. The MEK was subsequently removed by rotary evaporation at 60 °C, producing non-viscous TE-PUD’s having an average particle sizes of 56, 80, 110, and

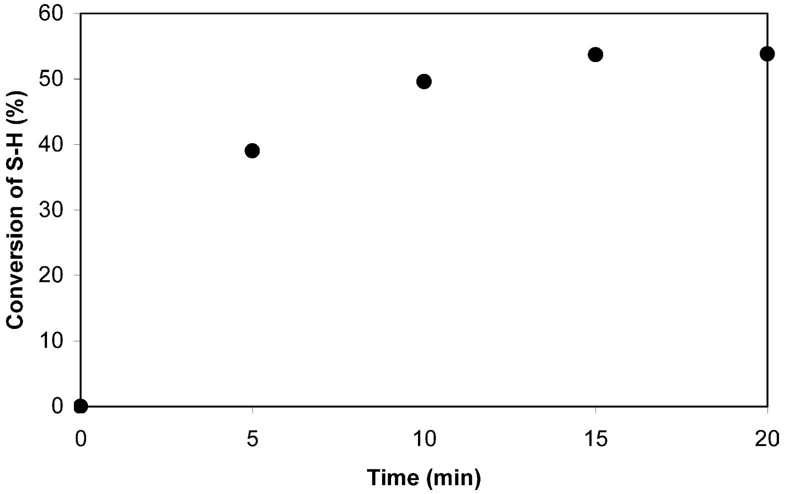

Fig. A1. Conversion of S–H functional groups as a function of UV exposure time for dried thiol–ene PUD films. SH/C=C ratio was 0.50.

126 nm for SH/C=C molar ratios of 0.50, 0.75, 1.00, and 1.10, respectively, which corresponds to 16.4, 22.8, 28.2, and 30.2 wt% PET3MP, based on solids. Solids contents of dispersions were approximately 20 wt% (based on total mass of pre-polymer and PET3MP). Such photocurable TE-PUD's were applied to glass substrates and allowed to dry at 30 °C for 30 min to obtain films of approximately 25 μm dried thickness. Additional films were prepared by casting TE-PUD's in polytetrafluoroethylene molds followed by drying at 30 °C for 2 h. All films were then photopolymerized by exposure to 254 nmHg lamp UV radiation for 20 min to form defect-free, clear, and mechanically stable solid films. Film thickness values of such specimens ranged from approximately 90–130 μm. The % conversion of S–H functional groups as a function of UV exposure time for dried thiol–ene PUD films is shown in Fig. A1.

Shear mode dynamic mechanical analysis (DMA) measurements of these films were performed using a TA Instruments DMA Q800 at 1 Hz with a 5 μm amplitude over the temperature range of −50–120 °C at 3 °C min^{-1}. Differential scanning calorimetry (DSC) was performed on dried, un-photopolymerized PUR pre-polymer using a TA Instruments DSC Q100 with a heating rate of 10 °C min^{-1}.

Gel permeation chromatography was performed using a Waters Alliance system (model 2695) equipped with a refractive index detector using a PLGel column (Polymer Laboratories, Inc.) calibrated with narrow polydispersity polystyrene standards. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic measurements were performed using a Digilab FTS-6000 spectrometer equipped with a fixed Ge single internal reflection element having an angle of incidence of 45° (Pike Technologies, Inc.) and a DTGS detector. A total of 200 scans were co-added and ratioed 200 background scans. When necessary, multi-point, linear baseline correction algorithms were applied to correct for baseline deviations. ^{1}H NMR measurements were made on a Varian 300 MHz spectrometer using eight scans, a pulse width of 3.55 μs, and relaxation delays of 1 s for monomers and 5 s for polymers. Samples for NMR analysis were dissolved in DMSO-d_6. Particle size distributions of TE-PUD's were performed on a Microtrac Nanotrac 250 particle size analyzer.

Storage modulus (E') and glass transition (T_g) values of thiol–ene PUD films photopolymerized for 20 min using 254 nm UV exposure with varying thiol:ene stoichiometric ratios are tabulated in Table A1. By increasing the SH/C=C ratio from 0.5 to 1.1, a decrease in the T_g is observed. However, the storage modulus (E') values in the rubbery plateau region of approximately 80–120 °C are also observed to increase with increasing SH/C=C ratio, indicating an increase in crosslink density. While these two findings may seem contradictory, since an increase in crosslink density might be expected to increase the T_g of a polymer, this phenomenon may be explained by a combination of the plasticizing effect of unreacted or partially reacted PET3MP that may remain in the film. Furthermore, by increasing the concentration of PET3MP in

Table A1
Storage modulus, T_g, and density measurements of thiol–ene PUD films after 254 nm UV exposure for 20 min

SH/C=C (ratio)	Storage modulus (Pa)	T_g (°C)	ν_e (mol/cm^3)	Density (g/cm^3)	M_c (g/mol)
0.50	5.89×10^4	46	1.90×10^{-5}	1.16	61,100
0.75	2.10×10^5	43	6.78×10^{-5}	1.15	17,000
1.00	3.62×10^5	37	1.17×10^{-4}	1.14	9770
1.10	4.23×10^5	36	1.36×10^{-4}	1.14	8360

The corresponding crosslink density and number average molecular weight of elastically effective network chains are also listed.

the system, the concentration of flexible thioether functional groups is increased while the concentration of urethane groups in the polymer is simultaneously decreased, therefore, hydrogen bonding and intermolecular forces in the polymer are reduced, thereby reducing the T_g.

Using the theory of ideal rubber elasticity, crosslink density, ν_e, and the number average molecular weight of elastically effective network chains, M_c, were calculated and are tabulated along with T_g's of thiol–ene PUD films with varying SH/C=C ratios in Table A1. As expected, crosslink density increases significantly with increased SH/C=C.

References

[1] Cramer NB, Bowman CN. J Polym Sci, Part A: Polym Chem 2001;39: 3311–9.

[2] Cramer NB, Scott JP, Bowman CN. Macromolecules 2002;35: 5361–5.

[3] Cramer NB, Reddy SK, O'Brien AK, Bowman CN. Macromolecules 2003;36:7964–9.

[4] Cramer NB, Davies T, O'Brien AK, Bowman CN. Macromolecules 2003;36:4631–6.

[5] Cramer NB, Reddy SK, Cole M, Hoyle C, Bowman CN. J Polym Sci, Part A: Polym Chem 2004;42:5817–26.

[6] Cramer NB, Reddy SK, Lu H, Cross T, Raj R, Bowman CN. J Polym Sci, Part A: Polym Chem 2004;42:1752–7.

[7] Hoyle CE, Lee TY, Roper T. J Polym Sci, Part A: Polym Chem 2004; 42:5301–38.

[8] Lee TY, Roper TM, Jonsson ES, Guymon CA, Hoyle CE. Macromolecules 2004;37:3606–13.

[9] Pojman JA, Varisli B, Perryman A, Edwards C, Hoyle C. Macromolecules 2004;37:691–3.

[10] Roper TM, Guymon CA, Joensson ES, Hoyle CE. J Polym Sci, Part A: Polym Chem 2004;42:6283–98.

[11] Roper TM, Kwee T, Lee TY, Guymon CA, Hoyle CE. Polymer 2004; 45:2921–9.

[12] Otts DB, Pereira KJ, Jarrett WL, Urban MW. Polymer 2005;46:4776.

[13] Otts DB, Urban MW. Polymer 2005;46:2699.

[14] Kaminski AM, Urban MW. J Coat Technol 1997;69:113.

[15] Urban MW, Allison CL, Finch CC, Tatro BA. J Coat Technol 1999; 71:75.

[16] Additional details pertaining to the synthesis and preparation of TE-PUD materials may be found in Appendix A.

[17] Silverstein RM, Webster FX. Spectrometric identification of organic compounds. 6th ed. New York: Wiley & Sons; 1997.

[18] This phenomenon is illustrated more clearly by Fig. A1 of Appendix A, which illustrates the conversion of S–H functional groups as a function of 254 nm UV exposure time. Conversion of S–H functional groups plateaus at approximately 15–20 min, resulting in an ultimate conversion of approximately 54%.

[19] Table A1 of Appendix A summarizes the results of DMA analysis.