

Supporting Information

Functional Dual-cure Latex Films from Thiol-Michael Addition Miniemulsion Polymerization

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Experimental section

Materials

Ethylene glycol bis(3-mercaptopropionate) (GDMP) and pentaerythritol tetra(3-mercaptopropionate) (PETMP) was donated by Bruno Bock. Neopentyl glycol diacrylate (NDA), trimethylolpropane triacrylate (TMPTA), 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO), butyl acetate, hexadecane (HD), 11-chloro-1-undecene, 6-chloro-1-hexanol and 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione (TATATO) was purchased from Sigma-Aldrich. IRGACURE® 2959, 651 (DMPA) was purchased from BASF. Divinyl sulfone (DVS) was purchased from Oakwood Products. 6-Azido-1-hexanol and 11-azido-1-undecene was synthesized by azido substitution from cross-bonding halide. Sodium dodecyl sulfate (SDS) was purchased from FLUKA. All chemicals were used as received without additional purification.

General miniemulsion polymerization procedure

To a mixture of 2.44 g PETMP (5 mmol), 1.98 g TMPTA (6.7 mmol), 0.18 g hexadecane (4 wt% to monomers) and 0.22 g TEMPO (5 wt% to monomers), 17.8 mL 0.875 wt% SDS aqueous solution was added. The mixture was then placed in an ice bath and was homogenized by a Branson sonifier 450 W/L (5 min, 1 min at a time with 1 min intervals, 70% amplitude). A stable emulsion was formed. The mixture was heated to 80 °C for 2h with magnetic stirring, unless noted elsewhere. The mixture appeared as stable emulsion after polymerization and no precipitation was observed. The combinations of thiol-acrylate monomers, the molar ratio of monomers and monomer loading in water may vary as noted.

Preparation of latex films

The emulsion was dried in a petri dish under ambient in air overnight and was ready for subsequent measurements. For dual-cure latex films, photoinitiator (I2959, 5 wt% to the mass of remaining unreacted acrylate) was dissolved in the latex before drying. The second stage curing was conducted by irradiating under a Black ray lamp (model B100AP, 8 mW/cm² at 365 nm) for 10 min.

Characterization

The polymerization kinetic measurements are obtained by real time Fourier transform infrared spectroscopy on Thermo Nicolet 6700. Before polymerization, the monomer mixtures were sandwiched between glass slides with a spacer of 100 μm. Then the sample was placed in a heating stage with temperature control (80±0.1 °C) and the series collection started right away. The conversions for thiol and vinyl groups were determined by the peak area around 2470-2600 cm⁻¹ and 3000-3150 cm⁻¹, respectively. Off-stoichiometric particles are harvested by centrifuge at 18000 rpm and washing with ethanol for three times. Spectra for dried particles were obtained by mixing KBr powder with particle dispersion, and the mixture was subsequently dried under

vacuum at 80 °C. A Thermo diffuse reflectance setup (DRIFT) is used to acquire spectra for powder samples. For latex films, the IR spectra were obtained by attenuated total reflectance Fourier transform infrared (ATR-FTIR) on Thermo Nicolet 6700.

Mechanical properties of latex films were studied by dynamic mechanical analysis (DMA) on a TA Instrument Q800. The dimensions of the polymer samples are 7 mm × 5 mm × 0.4 mm. The samples were tested with a frequency of 1 Hz with 0.01% strain. The T_g was determined by the highest point on the tan δ curve.

Imaging of nanoparticles was performed on a Tecnai biotwin T12 TEM. A drop of the diluted particle aqueous dispersion was let sitting on a copper grid for 10 s before the liquid was pulled away by a filter paper. For staining, a drop of 4 wt% osmium tetroxide aqueous solution was negatively casted on the grid and sat for 5 min.

Dynamic light scattering measurement was performed on a Brookhaven's NanoBrook 90Plus particle size analyzer. The miniemulsion dispersion was diluted in deionized water. A disposable cuvette containing 3 mL of diluted dispersion was placed in the analyzer and each sampling was averaged by a total of 3 minutes collecting. At least three runs were performed for each sample.

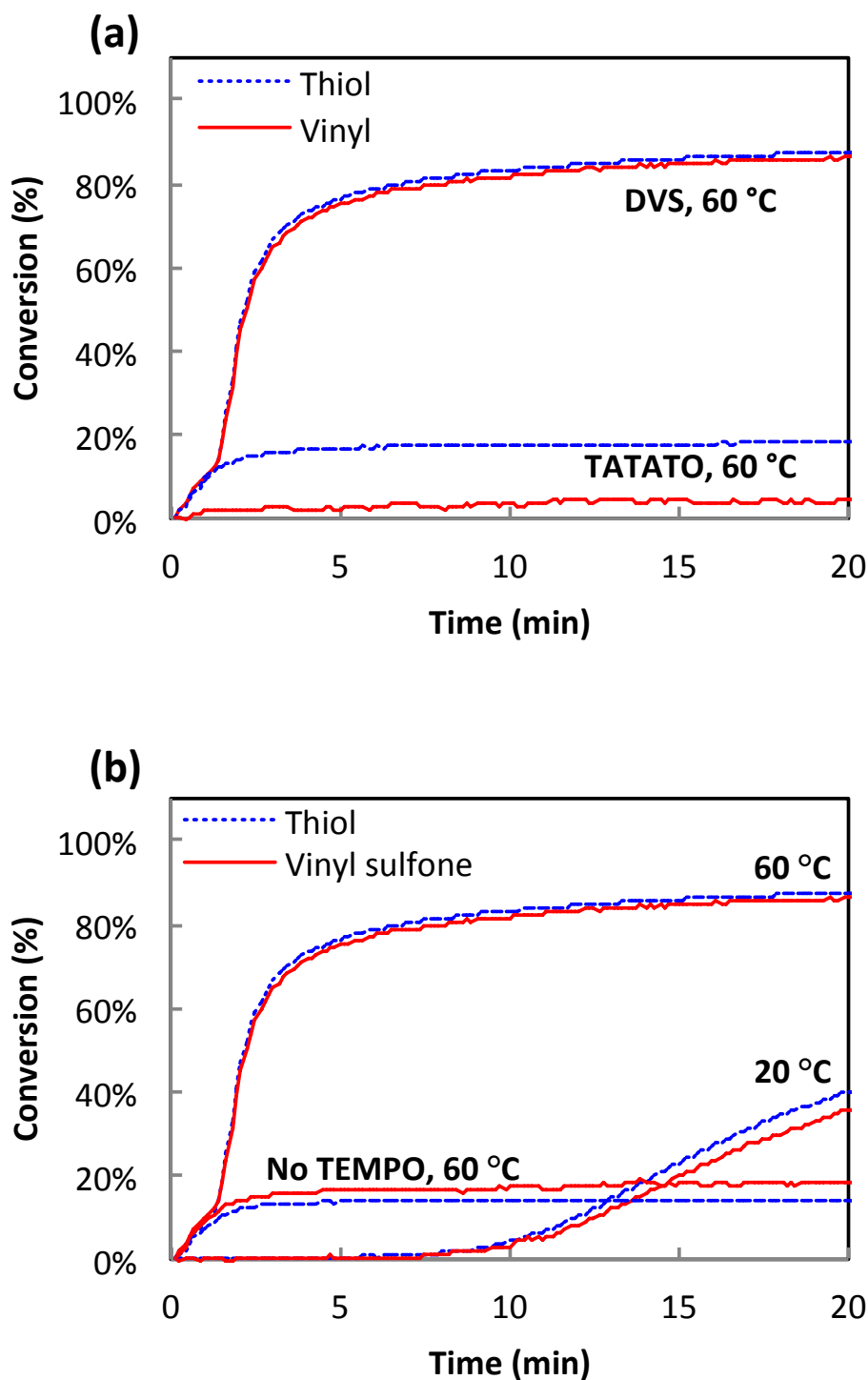


Figure S1. The kinetic of thermal initiation by TEMPO for various conditions: (a) PETMP-DVS and PETMP-TATATO, with 2 wt% TEMPO under 60°C. (b) PETMP-DVS with 2 wt% TEMPO under various temperatures, and PETMP-DVS without TEMPO under 60°C. The thiol/vinyl ratio is stoichiometric. Note that the samples are equilibrating from ambient to 60°C in the first 3 min.

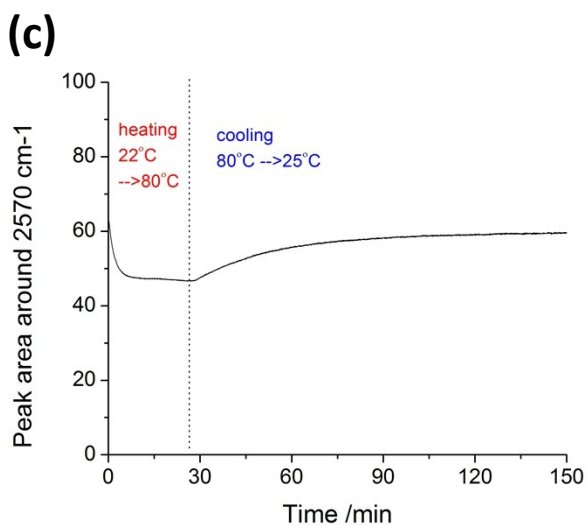
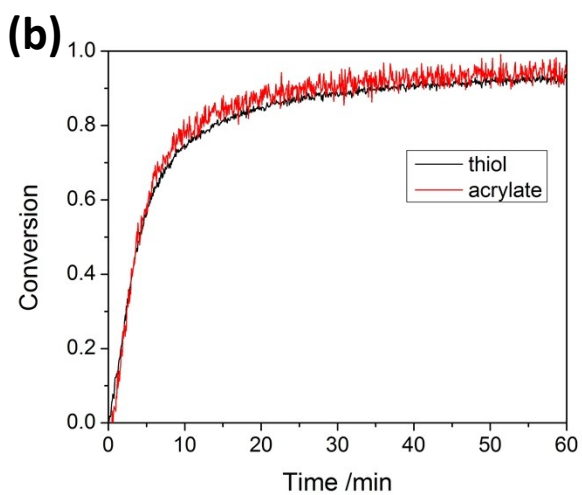
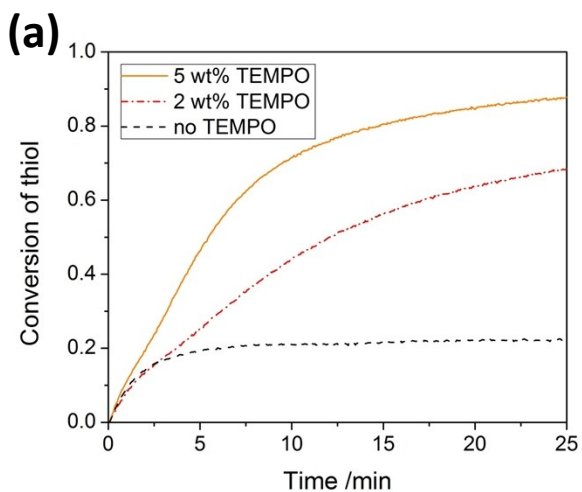


Figure S2. (a) The kinetic of thiol consumption in thermal initiation by various amounts of TEMPO for PETMP-TMPTA under 80°C. (b) The conversion profile of thiol and acrylate for

5wt% TEMPO. (c) Profile for peak area around 2570 cm^{-1} for PETMP-TMPTA under heating and cooling without the addition of TEMPO. Note that the samples are equilibrating from ambient to 80°C during the first 3 min. The thickness of IR samples is 0.25 mm. The peak around 2570 cm^{-1} is used for monitoring thiol, and that around 6150 cm^{-1} is used for monitoring acrylate.

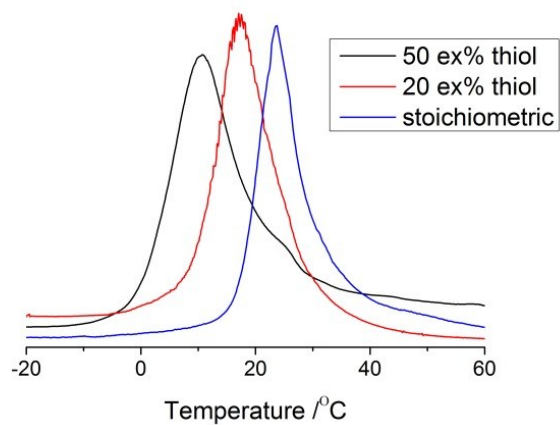


Figure S3. The glass transition temperatures for PETMP-TMPTA latex films, measured by dynamic mechanical analysis. The molar ratios of PETMP:TMPTA is 1:1.5 (black), 1:1.2 (red) and 1:1 (blue).

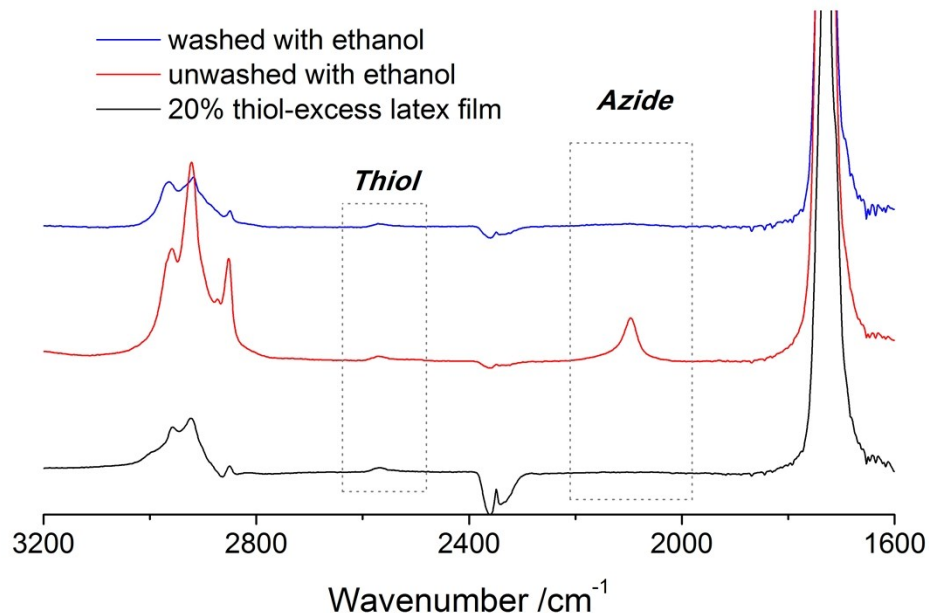


Figure S4. ATR-IR spectra for control experiments for surface functionalization by photo-induced thiol-ene reactions. Nonreactive 1-azidohexanol was used as a control for reactive 1-azido-undecene. Black line: latex film with 20% thiol excess prepared from PETMP and TMPTA; red line: irradiated latex film but not washed with ethanol; blue line: irradiated latex film which was washed three times with ethanol. Reaction conditions: A solution of 50 wt% 6-azido-1-hexanol in ethyl acetate (with 5 wt% DMPA) was applied to the surface of a latex film with 20% excess thiol. The film was exposed to UV light (8 mW/cm^2) for 10 min.