Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

Bringing *D*-Limonene to the Scene of Bio-Based Thermoset Coatings *via* Free-Radical Thiol–Ene Chemistry: Macromonomer Synthesis, UV-Curing and Thermo–Mechanical Characterization

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EXPERIMENTAL

Chemicals

R-(+)-limonene (or *D*-limonene) (Lim **1**, ≥97%, 136.24 g·mol^{-1}) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich (Stockholm, Sweden). Multifunctional thiols trimethylolpropane tris(3-mercapto propionate) (TMPMP **2**, 398.56 g·mol^{-1}), pentaerythritol tetra(3-mercapto propionate) (PETMP **3**, 488.6 g·mol^{-1}) and the monofunctional thiol *iso*-tridecyl 3-mercapto propionate (C13MP, 288.1 g·mol^{-1}) were kindly supplied by Bruno Bock Chemische Fabrik GmbH & Co (Marschacht, Germany). Photoinitiator 2,2-dimethoxy-2-phenylaceto-phenone (Irgacure 651®/DMPA, 256.3 g·mol^{-1}) was obtained from Ciba Specialty Chemicals Inc. (Switzerland). Thermal initiator 2,2'-azobis(2-methylpropionitrile) (AIBN, 164.21 g·mol^{-1}) was acquired from Fluka. Ethyl acetate (EtOAc, 99%) was obtained from Merck (Darmstadt, Germany). Deuterated chloroform ($CDCl_3$, 99.8%) was provided by CIL (Cambridge Isotope Laboratories, Inc., USA). All reagents and solvents were commercial products, used as received.

Instrumentation and Techniques

Fourier Transform Raman Spectroscopy. FT–Raman spectra were acquired using a Perkin-Elmer Spectrum 2000 NIR-Raman instrument with Spectrum software. Each spectrum recorded was based on 32 scans using a laser power of 1000 mW.

Nuclear Magnetic Resonance Spectroscopy. ^{1}H-NMR spectra of samples were recorded on a 400 MHz Bruker Aspect NMR spectrometer (Karlsruhe, Germany). ^{1}H-NMR spectra (128 scans) were acquired with a spectral window of 20 ppm, an acquisition time of 4 seconds, and a relaxation delay of 1 second. The samples were prepared by dissolving 8 mg of sample in 800 μl of deuterated chloroform ($CDCl_3$) containing 0.05% of TMS in a 5 mm diameter glass tube. Chemical shifts (δ) are reported in parts per million (ppm) relative to the tetramethylsilane reference signal (TMS, δ=0.00 ppm). Spectral analysis was performed using the Mestrec software.

UV-Light Source. Synthesis of limonene-based resins was performed by means of a hand held Blak Ray B-100AP (100 W, λ_{max}=365 nm) Hg UV-lamp delivering a constant irradiance of 25 mW·cm^{-2} as determined with an UVICURE Plus High Energy UV Integrating radiometer (EIT, USA), measuring UVA at $320 \leq \lambda \leq 390$ nm.

Macromonomer Precursors Syntheses. Organic syntheses of the multifunctional compounds **4** and **5** in the corresponding resins were performed either thermally or photochemically using two different stoichiometric compositions: in the first batch, stoichiometric thiol–ene mixtures based on (*R*)-(+)-limonene (diene, **1**) and TMPMP (trithiol, **2**) or PETMP (tetrathiol, **3**) with respect to individual monomer group functionalities (100% thiol and 50% enes in limonene; *i.e.*, thiol:ene = 1:0.5) were prepared by dissolving the comonomers in 50 wt.% ethyl acetate (EtOAc) with respect to the total amount of reactants. In the second batch, a 10-fold mole excess of limonene relative to the thiol functionality was introduced. The mass of limonene, m_{Lim}, required in the two batches was calculated from the expression: $m_{\mathrm{Lim}} = x \cdot f_{\mathrm{thiol}} \cdot f_{\mathrm{Mw}} \cdot m_{\mathrm{thiol}}$ (eqn. 1), where $x \geq 1$ denotes the number of moles fold increase of limonene, f_{thiol} represents the functionality of the thiol (multiplication factor), f_{Mw} is the quotient of molecular weights of terpene to multifunctional thiol, and m_{thiol} is the mass of thiol. All mixtures were supplemented with a small catalytic amount of initiator (~1.0 wt.% of total mixture) to accelerate the coupling reaction.

Thermal syntheses were carried out in 250-ml triple-neck round bottomed flasks in the absence of air for an extended period of 24-hours under constant magnetic stirring (300 rpm) and temperature kept between 67–70°C. The starting mixtures were initially degassed in ice-cold bath under stirring (350-rpm) and reduced pressure and then purged with argon gas to flush-out traces of dissolved oxygen and restore the headspace with an inert atmosphere. The ingress of oxygen was prevented by continuously feeding argon gas to the reaction system under moderate positive pressure.

Photochemical synthesis of resin 1 (TE-C1) was carried out according to details described in a previous report.[1] Synthesis of resin 2 (TE-C2) was conducted exactly in the same way as for resin 1 except by mixing limonene **1** with PETMP **3**. For monitoring the course of the reactions, small aliquot samples (800 μl) were taken periodically for conversion analysis using ^{1}H-NMR and FT–Raman spectroscopies after vacuum evaporation of the solvent. Diluting ethyl acetate (EtOAc) was removed *via* rotor-evaporation at 50–60°C followed by normal vacuum until most of unreacted limonene and traces of solvent were eliminated. All mixtures were prepared immediately before to each synthesis reaction in order to guarantee reproducibility of sample history.

Size-Exclusion Chromatography (SEC). DMF–SEC analysis was performed on a TOSOH EcoSEC HLC-8320GPC system equipped with an EcoSEC RI detector and three columns (PSS PFG 5 μm; Microguard, 100 Å and 300 Å) (MW resolving range: 300–1.0×10^5 Da) from PSS GmbH. Measurements were carried out at 50°C using DMF solvent supplemented with 0.01 M LiBr as mobile phase (isocratic elution, 0.2 $\mathrm{ml\cdot min^{-1}}$). A conventional calibration method was created using narrow linear poly(methyl methacrylate) standards. Corrections for flow rate fluctuations were made using toluene as an internal standard. PSS WinGPC Unity software version 7.2 was used to process and analyze the data. Analytes were dissolved in DMF/LiBr solvent (2.5 $\mathrm{mg\cdot ml^{-1}}$) and the resulting solutions filtered with a 0.45 μl teflon filter before analysis.

Resin Formulation, Coating Preparation and UV-Curing. Pre-cure thiol–ene resins were prepared by mixing in bulk equimolar amounts of thiol and ene functionalities of photo-chemically synthesized resins 1 (TE-C1) and 2 (TE-C2) as non-purified crude products containing compounds **4** and **5**, respectively; with the thiol crosslinkers **2** and **3**. Combination of equal-number functionality monomers (**2** + **4** and **3** + **5**) and different-number functionality monomers (**2** + **5** and **3** + **4**) afforded four distinct photocurable resins. The theoretical mass of thiol, m_{thiol}, per unit mass of ene-macromonomer, m_{ene}, required for an average 1:1 functional group stoichiometry was calculated according to the formula: $m_{\mathrm{thiol}} = f_1 \cdot f_2 \cdot m_{\mathrm{ene}}$ (eqn. 2), where f_1 is the group functionality ratio of macromonomer-to-thiol (*e.g.*, **2** + **5**, f_1 = 4/3 and **3** + **4**, f_1 = 3/4), and f_2 is the molecular weight quotient between thiol and ene-macromonomer. For mixtures of equal-number functionality monomers f_1 takes a unitary value. Non-purified crude resins were also mixed with non-balanced mole amounts of multifunctional thiol groups to give a second set of off-stoichiometric resins ranging from 1:1.10, 1:1.25 and 1:1.45 in ene:thiol mole ratios. All mixtures were supplemented with a small amount of UV-initiator (DMPA, ~2.0 wt.%) and thoroughly mixed under moderate heating for complete dissolution of the photoinitiator. The mild heating did not cause any detectable reaction as determined by ^{1}H-NMR. The liquid neat monomer mixtures were gently applied onto dried microscope glass slides and placed in the vacuum oven pre-set at 50ºC for 3 hours to remove any air bubbles trapped inside. Individual samples were cured under a low pressure mercury UV-lamp at an intensity of 25 $\mathrm{mW{\cdot}cm^{-2}}$ for 1 hour (final accumulated dose of 90 $\mathrm{J{\cdot}cm^{-2}}$). To ensure complete post-polymerization the resulting crosslinked films having 475 ± 67 μm thickness were dried in vacuum at 50ºC overnight and then stored in dark and dry environment for two weeks at room temperature before any measurements could be performed. The cured films were fully transparent and adhered strongly to the glass substrates.

Sol-content Determination. All crosslinked thiol–ene films were cut into small rectangular sections with approximate dimensions of 1.0 cm × 2.0 cm, dried in the vacuum oven at 50 °C for 1 hour, weighted and then soaked for a period of 48 hours in 5.0 ml of THF solvent under gentle stirring conditions (250 rpm). The films were subsequently washed (twice) with THF, cleaned with an absorbent paper to remove excess of solvent, weighted and placed again in the oven until all the residual solvent was evaporated. The process was repeated several times until complete leaching of the soluble portion was confirmed by constant weight after drying. Soluble fractions were determined from mass losses relative to initial dry mass according to the following expression:

$$\text{Sol content (\%)} = \left(1 - \frac{W_\text{f}}{W_\text{s}}\right) \times 100 \qquad \text{(eqn. 3)}$$

where W_S represents the initial dry weight of the film samples and W_f is the dry weight of the same film specimens after sol-extraction. Analyses were performed in triplicate from two independent UV-cured films and the results averaged.

Determination of Conversion. Conversions of thiol and ene functional groups were determined according to described in a previous reference.[1]

Dynamic Scanning Calorimetry (DSC). The thermal properties of the crosslinked thiol–ene networks were analyzed by DSC. The experiments were performed on a Mettler Toledo DSC 820 module equipped with a sample robot and a cryocooler. The DSC runs were carried out in closed sample aluminum pans hermetically sealed in air according to the following temperature program: first heating from 25 to 200°C, cooling from 200 to –40°C and then heating again up to 200°C. Isothermal segments of 5 min were performed at the conclusion of each dynamic segment. Cooling/heating cycles were performed at a constant rate of 5°C·min^{-1}. Thermal history was deleted with respect to the first heating ramp up to 200°C. The glass transition temperatures (T_g's) were determined from the second heating scan and taken at the inflection-point of the transition curve.

Dynamical Mechanical Thermal Analysis (DMTA). To examine the change in physical properties of the thiol–ene networks with temperature, DMTA measurements were conducted on a Q800 dynamic mechanical analyzer (TA instruments), equipped with a film fixture for tensile testing and gas cooling accessory. Dried film-specimens of rectangular geometry were processed from the original UV-cured samples and tightly clamped on the grips of the sample holder. The temperature was then decreased to a minimum of –70°C and held isothermally for a period of 5 minutes before measurements were started. Data were progressively recorded up to a temperature of 140°C following a heating rate increase of 5.0°C·min^{-1}. The tests were performed in controlled strain mode with a frequency of 1.0 Hz, oscillating amplitude of 15.0 μm, and a forcetrack of 125%. These settings were used for measurements of all samples. DMTA measurements provided values for storage modulus (E'), loss modulus (E''), loss factor (tan δ) and glass transition temperature (T_g) for the films presented in Table 1. The T_g values were taken as the maximum of the tan δ peak (E''/E' ratio).

Thermogravimetric Analysis (TGA). Measurements were conducted on a Mettler Toledo TGA/SDTA851 instrument equipped with a sample robot. Duplicate samples were heated from 40°C up to 500°C at heating rate of 10°C·min^{-1} under N_2 atmosphere (50 ml·min^{-1}). The mass amounts of sample 1 and 2 measured were 8.85 and 6.24 mg respectively. All thermal analyses were evaluated using STARe Software version 8.10. TGA profile is reported as the arithmetic mean of individual curves. Errors (SD) were less than 3.2%.

NUMERICAL SIMULATIONS

Photoinduced synthesis of resins 1 and 2 in organic solution were simulated numerically in the software package COPASI[2] for a running period of 6-hours. The kinetic model was built according to details outlined in a previous reference[1] accounting for primary and secondary coupling reactions. The results are displayed in Figure S1.

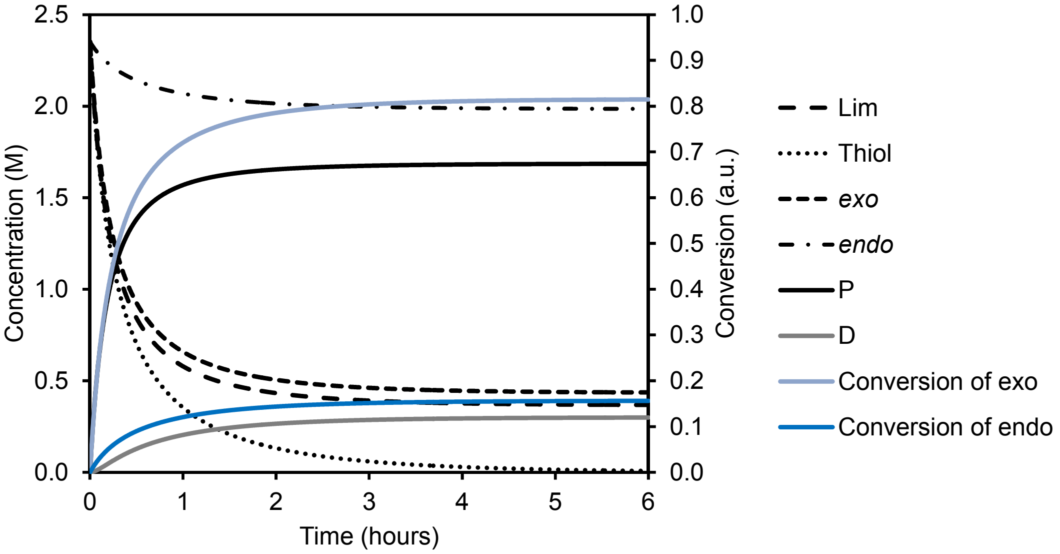

Figure S1. Kinetic output profiles from simulation with $k_t = 3.0 \times 10^9$ $M^{-1}\cdot s^{-1}$ for the thiyl self-termination reaction. ($[P]_t = [P_1]_t + [P_2]_t$; $[P]_f/[D]_f = 5.64$ and $C(\textit{exo})_f/C(\textit{endo})_f = 5.2$.)

TGA RESULTS

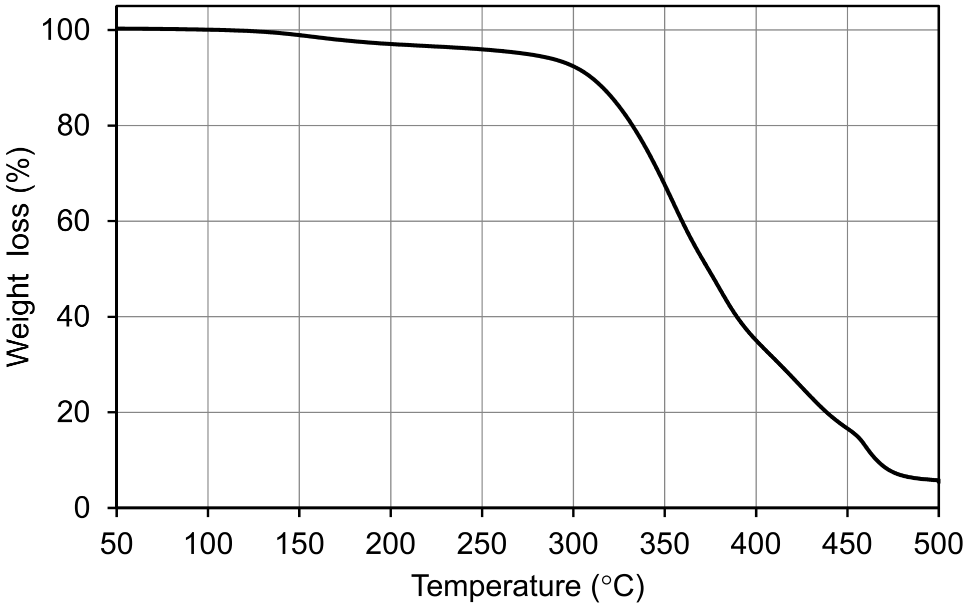

Figure S2. TGA curve showing the thermal degradation of thiol–ene network film M2+T4 (1:1). Main degradation region occurs from ~300°C onwards which is typical of organic polymeric materials.

REFERENCES

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