Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Recyclable and Repolymerizable Thiol-X Photopolymers

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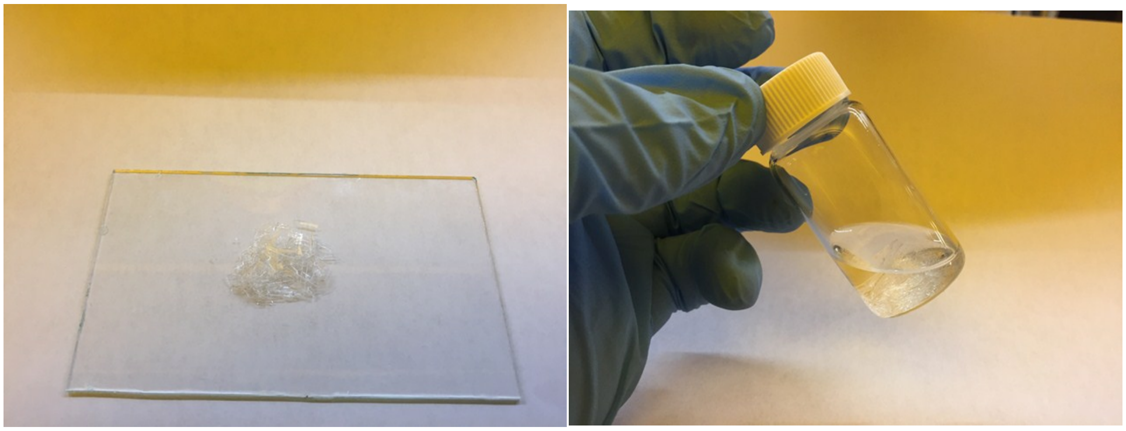
Experimental Section

Materials. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), methylhydroquinone and 3,3'-dithiodipropionic acid were purchased from Sigma-Aldrich. Dipentaerythritol hexa(3-mercaptopropionate) (Di-PETMP), ethoxilated-trimethylolpropan tri(3-Mercaptopropionate) (ETTMP 700 and ETTMP 1300), polycaprolactone tetra(3-mercaptopropionate) (PCL4MP) were donated from Bruno Bock. Irgacure 184 and Irgacure 651 (DMPA) were purchased from Ciba. Diallyl adipate was purchased from TCI. The silica microparticles (OX-50) was donated from Evonik Industries. A thioester di-allyl ether (TEDAE) was synthesized as previously reported.[1] All reactants and solvents were used as received.

Pristine photopolymer preparation. The UV-curable thioester containing thiol-ene resins were prepared by dissolving DMPA (2 wt% to monomers, 1.0 mol% with respect to alkene groups) in a combination of thiol and allyl ether monomers. The resin was casted between glass slides with 250 µm thick spacers and subsequently polymerized by irradiation with a BlackRay lamp (8 mW/cm^2 @ 365 nm) for 5 minutes. See the following picture for the reaction setup:

Recycling procedure. Polythioesters were recycled by degrading *via* thiol-excess thiol-thioester exchange reactions. Polymer samples were cut into ~ 20 cm^2 pieces, then mixed with a certain multiple equivalency of thiol monomers, an equal mass of reagent grade acetone and 20 wt% of TEA (50 mol% to thioestser groups) was added (both with respect to the total nonvolatile compounds). See the following pictures for the abovementioned reaction setup:



Particularly, oligomer 1, 2 and 3 (as listed in Table 1) were obtained from five, seven and nine equivalencies of additional PETMP. The mixture was stirred at ambient temperature with no precautions taken to guard the reaction from atmospheric oxygen or moisture. Generally, the thiol-ene polymers completely disappeared within 3 hours. The oligomers were purified by removing the volatiles, particularly, by rotary evaporation followed by high vacuum at 85^{o}C until the formation of bubbles had ceased.

Repolymerizing of the recovered oligomeric material. The reclaimed thioester containing thiol-ene resins were prepared by mixing the neat recycled oligomers with stoichiometric amount of the thioester diallyl ether monomer containing a pre-dissolved amount of DMPA (2 wt% with respect to the total of polymerizable materials). The mixture was polymerized under the same conditions as the pristine samples (8 mW/cm^2 @ 365 nm, 5 mins).

Composite preparation and degradation. Silica particles (~0.4 μm average diameter) were mixed in a stoichiometric PETMP-TEDAE monomer mixture (with 2 wt% DMPA) with varying weight fractions. The mixture was homogenized in a speedmixer (Flacktek DAC 150.1 FVZ-K) at 3000 rpm for 3 min. The mixture was sandwiched between glass slides with 250 μm spacers, and polymerized by irradiation with a BlackRay lamp (8 mW/cm^2 @365 nm) for 5 mins.

Photolithography procedure. Micro-features from both pristine and recycled monomers were prepared by contact liquid photolithography. Irradiation was performed by a collimated UV light (50 mW/cm^2 @ 365 nm) through a photomask (~100 μm circles separated by ~100 μm screening gaps). Pristine samples consisted of stoichiometric PETMP-TEDAE monomers with 0.5 wt% Irgacure 184 and 0.3 wt% methylhydroquinone, and were irradiated for 120 sec. Recycled samples consisted of stoichiometric recycled oligomers and TEDAE, with 0.5 wt% I184 and 0.3 wt% methylhydroquinone (both with respect to the unreacted moieties), and were irradiated for 80 sec. Immediately after irradiation, the unreacted compounds were thoroughly washed with ethanol.

Characterizations

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra and reaction kinetics were obtained on a Nicolet 670. Samples were placed between two glass slides (for thiol-ene systems) with 0.08 mm thick spacers. An Acticure 4000 lamp equipped with a 365 nm bandpass filter was used as light source. The conversions were determined by the decrease in peak area centered at 3085 cm^{-1} and 2570 cm^{-1} for the allyl ether and thiol, respectively.

Dynamic Mechanical Analysis (DMA). DMA experiments were conducted on a TA Instruments Q800. Samples were cut into strips with approximate dimensions of 10 × 6 × 0.25 mm. Temperature was ramped at 3 °C/min from -80 °C to 80 °C, at a frequency of 1 Hz. The glass transition temperature (T_g) was assigned as the peak of the tan δ curve. Tensile test was performed by ramping stress at 1.0 MPa/min.

Gel permeation chromatography (GPC). The molecular weight and distribution were obtained by gel permeation chromatography (Tosoh EcoSEC HLC-8320). Dimethyl sulfoxide was used as the eluting solvent at 0.35 mL/min at 50 °C. A refractive index detector was used, calibrated by PMMA standards.

Rheology. The viscosity of the recycled oligomer was measured on a TA instruments ARES rheometer. The liquid oligomers were placed between quartz plates (20 mm diameter, gap 0.1 mm). All oligomers behaved as Newtonian fluids in the detectable torque ranges.

Thermogravimetric analysis (TGA). The weight loss of polymer samples was obtained on a Perkin-Elmer Pyris 1. Sample filled platinum pans (~ 10 mg of samples) were heated from 55 to 800 °C at 10 °C/min under nitrogen flow.

Reference

[1] B. T. Worrell, M. K. McBride, G. B. Lyon, L. M. Cox, C. Wang, S. Mavila, C.-H. Lim, H. Corey, C. B. Musgrave, Y. Ding and C. N. Bowman, *Nature Communications*, in press

Table S1. Water swelling and stability tests in neutral deionized water at ambient temperature (~23°C). The thioester film was prepared from the stoichiometric polymerization of PETMP and TEDAE, while the control film was made from the stoichiometric polymerization of PETMP and diallyl adipate. Samples with dimensions of 40 * 5 * 1 mm were immersed in deionized water at ambient temperature and were weighed at various times.

	Weight increase after 1 day	Weight increase after 3 days	Weight increase after 1 week
Thioester film	0.9 % (±0.1 %)	0.8 %(±0.1 %)	0.7 %(±0.1 %)
Control film	0.8 % (±0.1 %)	0.8 % (±0.1 %)	0.6 %(±0.1 %)

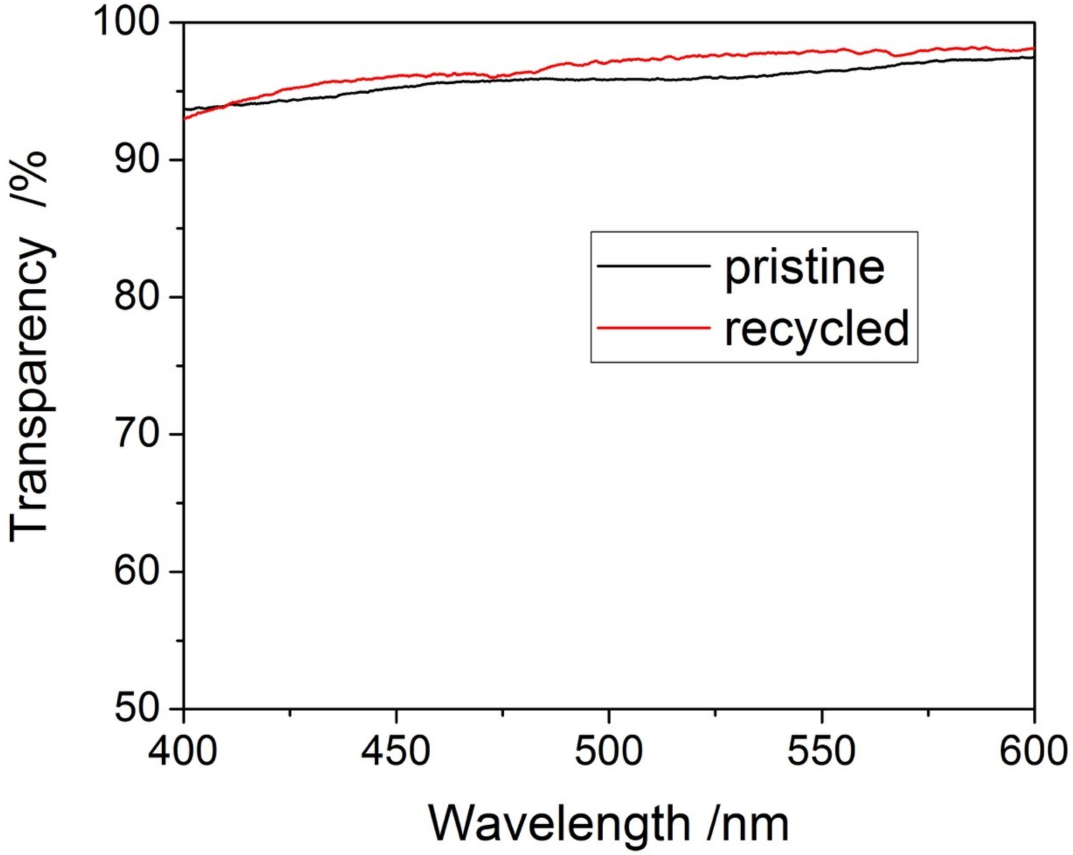


Figure S1. Transparency measurement of PETMP-TEDAE pristine and recycled films. The recycled film was obtained from Oligomer 2 in **Table 1**and stoichiometric amount of PETMP. A USB fiber spectrometer (Ocean Optics USB4000) setup was used to measure the optical transmittance of the transparent thioester films in the visible range (400 - 600 nm). The thickness of the samples was 0.25 mm.

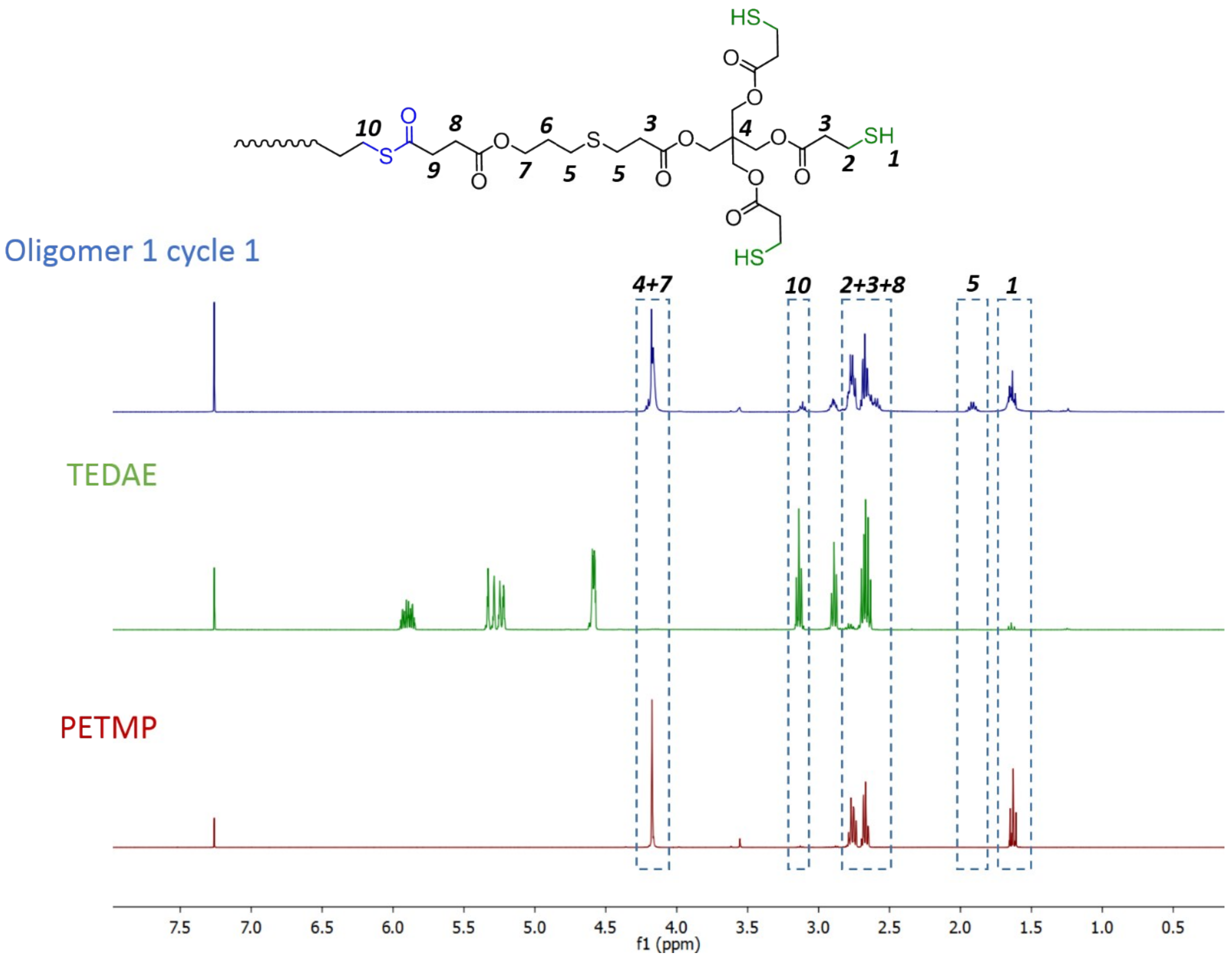


Figure S2. ^{1}H NMR spectra of recycled oligomer 1 as detailed in **Table 1** over various cycles. Oligomer was obtained by degrading with excess PETMP (with a stoichiometric number of 0.167) in acetone (equivalent mass to non-volatile compounds) with TEA (50 mol% to thioester groups), and subsequently dried under vacuum.

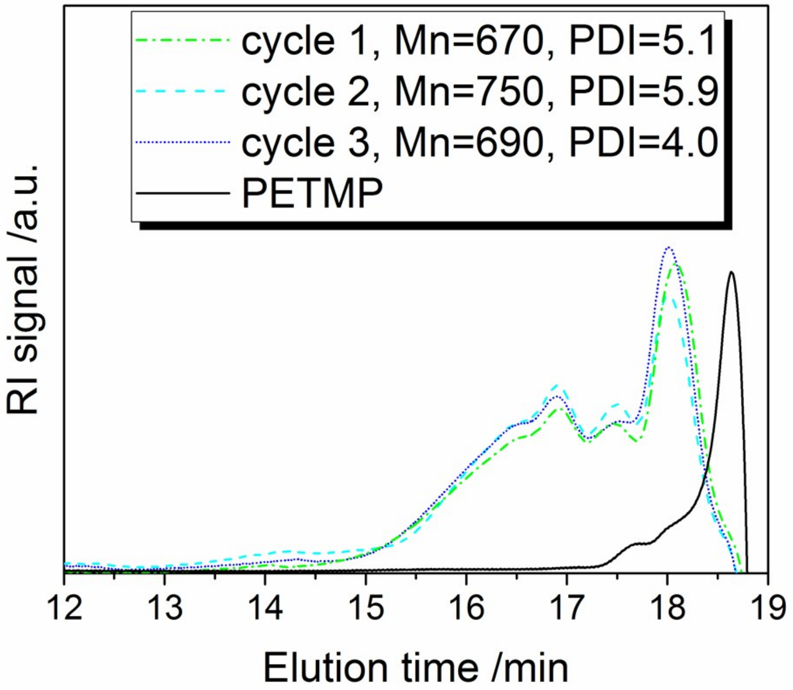


Figure S3. Refractive index profiles (obtained using gel permeation chromatography) of oligomer 2 as detailed in **Table 1** over various rounds of recycling. The oligomers were obtained by degrading in excess PETMP (with a stoichiometric number of 0.125) in acetone (equivalent mass to non-volatile compound) with a catalytic amount of TEA (50 mol% to thioesters) for 3 h, and subsequently dried under vacuum. Samples were prepared in dry DMSO with a concentration of 10 mg/mL, analyzed at 0.35 mL/min at 50 °C. Molecular weight and distributions were determined based on a calibration from standard PMMA samples.

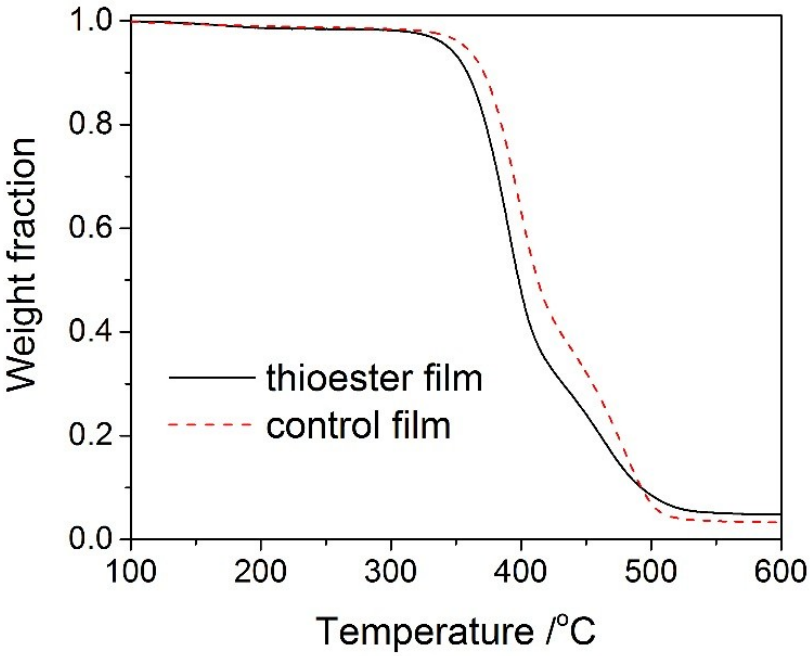


Figure S4. Thermogravimetric analysis of pristine PETMP-TEDAE and PETMP-diallyl adipate. The samples were ramped at 10 °C/min under N_2. Both the thioester and control group films were prepared from stoichiometric monomers with 2 wt% DMPA, irradiated under BlackRay lamp (8 mW/cm^2 @365 nm) for 5 minutes.

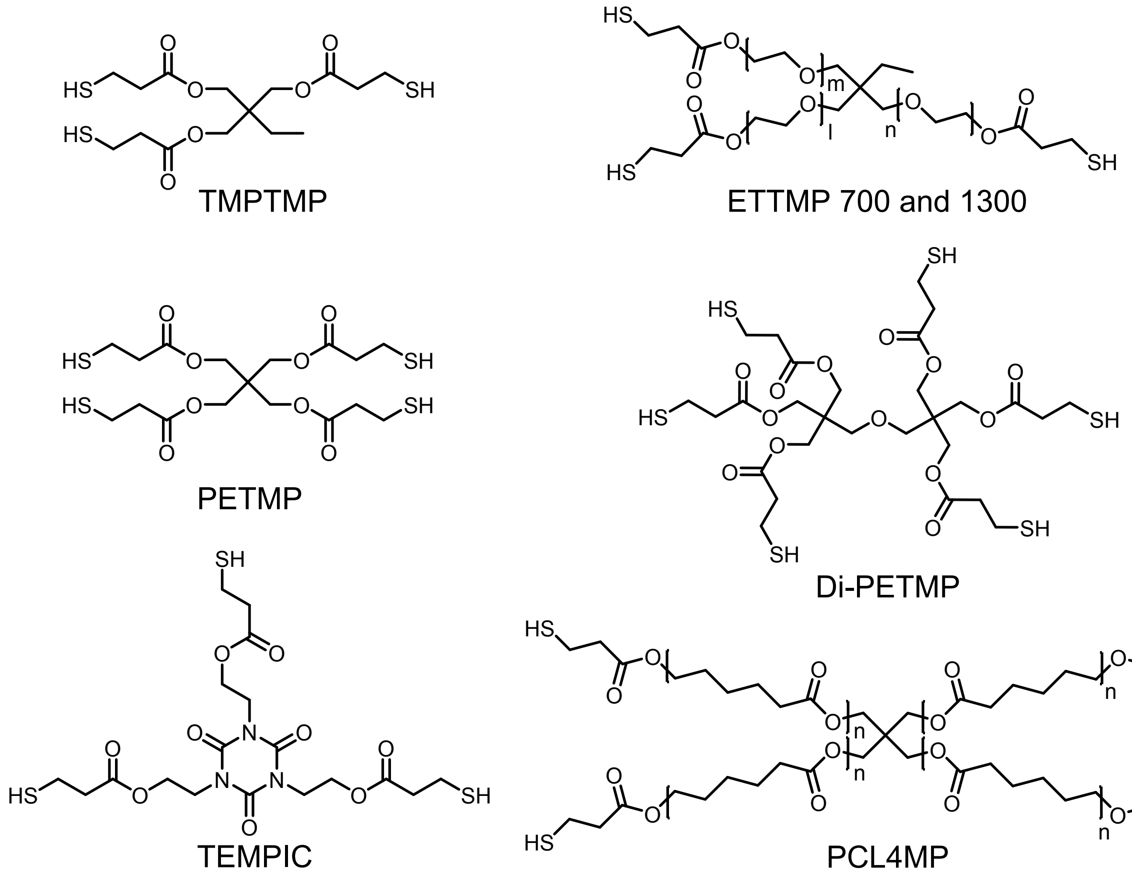


Figure S5. Various thiol monomers used in this work. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP); trimethylolpropane tris(3-mercaptopropionate) (TMPTMP); dipentaerythritol hexa(3-mercaptopropionate) (Di-PETMP); ethoxilated-trimethylolpropan tri(3-Mercaptopropionate) (ETTMP 700 and ETTMP 1300); polycaprolactone tetra(3-mercaptopropionate) (PCL4MP).

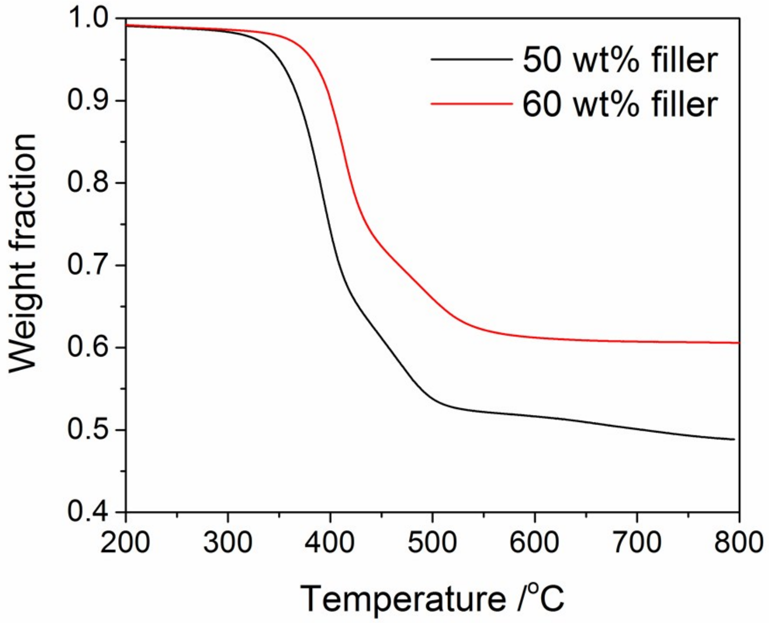


Figure S6. Thermogravimetric analysis of composite polymers with various silica particle loadings. Samples containing 50 wt% and 60 wt% silica particles (0.4 μm in diameter) were prepared from stoichiometric monomers with 2 wt% DMPA, irradiated under BlackRay lamp (8 mW/cm^2 @ 365 nm) for 5 mins. The samples were ramped at 10 °C/min under N_2.