Supporting Information for:

Elastomeric and Degradable Polyanhydride Network Polymers by Step-Growth Thiol-Ene Photopolymerization

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Experimental Section

Materials

4-Pentenoic anhydride (PNA), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), 3,5-dioxa-1,8-dithiooctane ("ethylene glycol-based dithiol", EGDT), 1-hydroxycyclohexyl phenyl ketene were all purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Tetrahydrofuran (THF) (JT Baker, AR Grade) and chloroform (JT Baker, AR Grade) were purchased from VWR International (Bridgeport, NJ) used as received. UV light was supplied by an Oriel 500 W Hg lamp.

Analytical Techniques

Gel permeation chromatography (GPC) was performed on a modular system comprised of the following: a Waters 515 high-pressure liquid chromatographic pump operating at room temperature, a Waters 717 autosampler, and a Viscotek LR40 refractometer. THF was used as a

continuous phase at a flow rate of 1.0 mL/min. The columns were calibrated with commercial linear poly(methyl methacrylate) standards. Polymer analyte solutions were prepared with 1.0-2.5 mg/mL, and sample injection volumes of 50 μl were used. ^{1}H NMR spectra of the polymers were obtained on a Bruker Avance 400 MHz spectrometer using 5 mm o.d. tubes. Sample concentrations were about 25% (w/v) in $CDCl_3$ containing 1% TMS as an internal reference. Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 at a scan rate of 2^{o}C/min and frequency of 1 Hz. The sample dimensions were 35 mm x 15 mm x 2 mm.

Synthesis Procedures

Approximately 1 ml solution of PNA, PETMP (and EGDT, if part of the formulation) was purged with N_2 for 3 minutes and then added to a 1 cm^3 teflon mold and exposure to UV light for 15 minutes yielded a crosslinked cube. Volumes for each component are given in Table 1 of the paper.

Degradation Study Procedures

After curing, the cube was removed from the mold, quickly weighed, and placed in a small glass vial with approximately 2 ml of phosphate-buffered saline (PBS) solution at pH = 7.4. At regular time intervals, the cubes were removed from the vial and the excess water carefully wiped off. For the more hydrophobic materials, the hydrolyzed outer layer was not fully soluble but was easily removed by gentle scraping. The sample was weighed and then returned to the PBS solution. The PBS solution was changed approximately every 12 hours.

Dynamic Mechanical Analysis Data

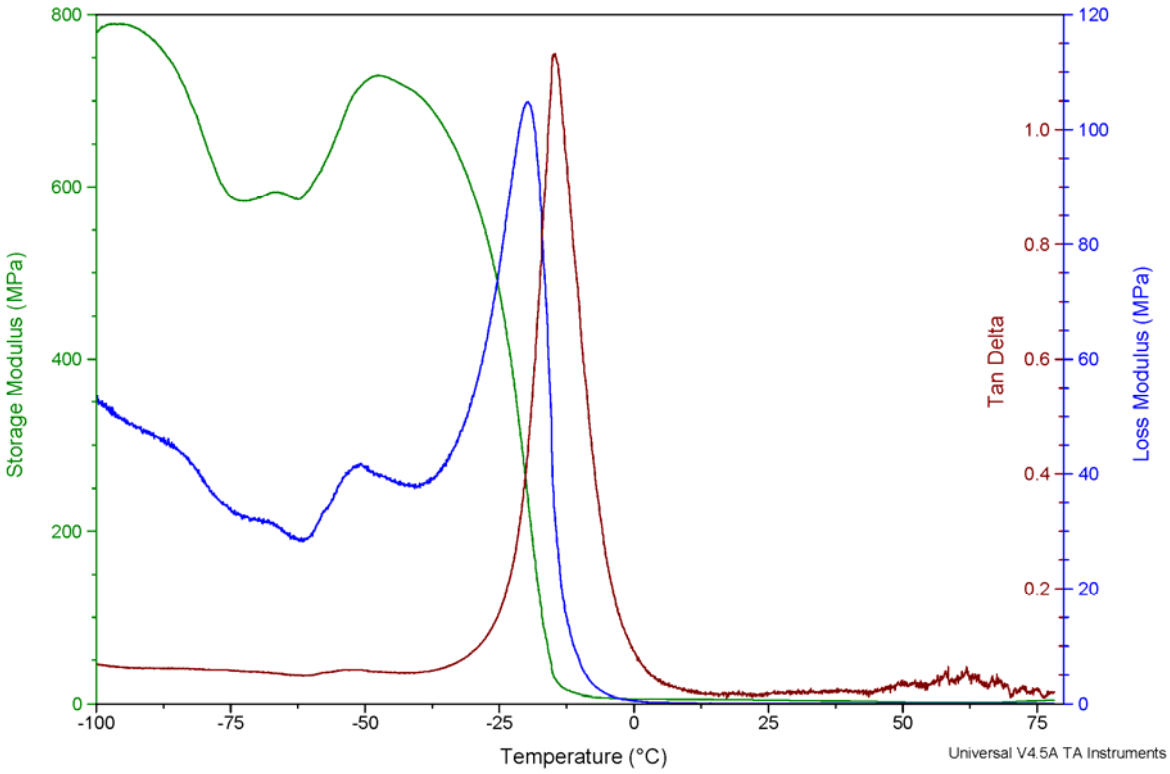

Figure S1. Storage and Loss modulus, and tan d, as a function of temperature obtained by DMA. Sample formulation: 1:1 mole ratio of PNA and PETMP, cured with 0.1 wt.% 1-hydroxycyclohexyl phenyl ketene as photoinitiator.