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Suppoting Information

High-Efficiency Self-Healing Materials Based on Supramolecular Polymer Networks

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Experimental Section

Materials

All chemicals were of the highest purity available and were purchased from Sigma-Aldrich (St. Louis, MO, USA). All solvents used for synthetic and chromatographic experiments were high-performance liquid chromatography (HPLC) grade and were obtained from TEDIA (Fairfield, OH, USA). Dimethylformamide (DMF) was distilled over calcium hydride prior to use.

Characterization

*Nuclear Magnetic Resonance (NMR)***.** ^{1}H-NMR spectra were measured on a Varian Inova-400 MHz spectrometer equipped with a Bruker magnet (9.395 T). The samples (approximately 15 mg) were analyzed at 25 °C in deuterated solvent.

Gel Permeation Chromatography (GPC). The weight-average molecular weight (*Mw*), number-average molecular weight (*Mn*) and polydispersity index (PDI; *Mw/Mn*) were measured using a Waters 410 GPC system controller equipped with a differential refractometer and three Ultrastyragel™ columns (100, 500 and 1000 Å) connected in series. The mobile phase was DMF at a flow rate of 1.0 ml/min. The system was calibrated with polystyrene (PS) standards of narrow polydispersity (Polymer Standards Service, MD, USA).

Differential Scanning Calorimetry (DSC). A TA Instruments (New Castle, DE, USA) Q-20 DSC was used to perform thermal analysis. Samples of ca. 5 mg were sealed in an aluminum pan, and then heated from -90 to 150 °C at a rate of 10 °C/min.

Small and Wide-Angle X-ray Scattering (SAXS and WAXS). SAXS data were collected using the BL17A1 wiggler beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The samples were sealed between two Kapton windows (thickness: 12 μm) and measured at room temperature. An X-ray beam with a diameter of 0.5 mm and wavelength (λ) of 1.1273 Å was used for the SAXS measurement (Q range: 0.015–0.3 Å^{-1}). The Q values of the SAXS profiles were calibrated using a polyethylene standard, Ag behenate, and tripalmitat. WAXS spectra of powders were obtained using a Rigaku D/max-2500 X-ray diffractometer. The radiation source was Ni-filtered Cu Kα radiation at a wavelength of 0.154 nm. The voltage and current were set at 30 kV and 20 mA, respectively. The sample was mounted on a circular sample holder; the data were collected using a proportional counter detector over the $2d$ range from 2 to 50° at a rate of $5°\ \text{min}^{-1}$. Bragg's law ($\lambda = 2d\ \sin\theta$) was used to compute the *d*-spacing corresponding to the complementary behavior.

Rheological experiments. Rheological characteristics were studied using a Physical MCR501 rheometer (Anton Paar Ltd, St. Albans, UK) with cone-plate measuring geometry. All measurements were carried out in a nitrogen atmosphere. Different strains were applied to obtain storage modulus (G') and loss modulus (G"). The gap distance was set to 0.049 mm. Samples were scanned from 50 to 160 °C at a rate of 3.0 °C/min, and the shear rate and frequency were fixed to 10 s^{-1} and 1 Hz, respectively.

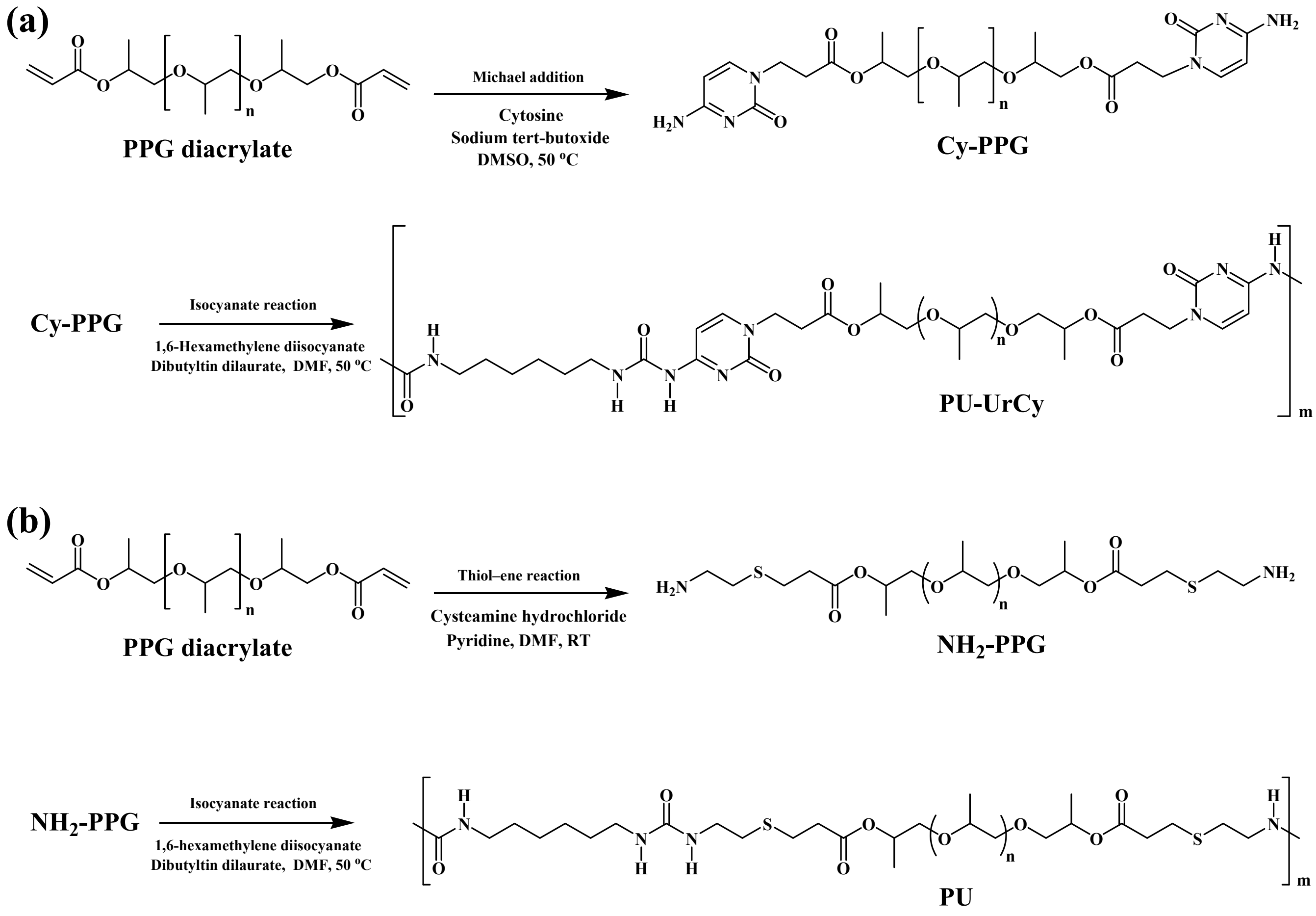
Dynamic Mechanical Analysis (DMA). DMA was carried out using a DSC DMA800 (TA Instruments Inc., New Castle, PA, USA) in tensile mode under the following conditions: frequency, 1 Hz; tensile preload, 0.01 N; and strain amplitude, 30 μm. The tests were heated at a rate of 3 °C/min from -80 °C to 100 °C, in an atmosphere of nitrogen gas.

Tensile tests. Tensile tests were performed using a universal tester (EZ-L; Shimadzu Corp, Kyoto, Japan) at a constant cross-head speed of 10 mm/min. All tests were performed under ambient conditions (20 °C, 65% relative humidity). Healing efficiency was calculated as the ratio of the tensile strength of the self-healed samples and original samples.

Scanning Electron Microscopy (SEM). The samples were sputtered with platinum and imaged using a field-emission scanning electron microscope (Hitachi S-4700, Tokyo, Japan) at an accelerating voltage of 15 kV. Test samples were prepared in DMF, the solutions were spin coated onto wafer substrates and the solvent was evaporated under vacuum at 40 °C. The healed samples were firmly fixed on silicon substrates before SEM.

Atomic Force Microscopy (AFM). AFM images were scanned in tapping mode on a NS4/D3100CL/MultiMode (Digital Instruments, Santa Barbara, CA, USA) using silicon cantilevers in air at 25 °C. All samples were spin-coated onto a silicon substrate and then dried under vacuum at 40 °C.

Syntheses



Scheme S1. Synthetic procedures for PU-UrCy and PU.

The synthetic route used to produce **PU-UrCy**, shown in **Scheme S1**, contained two steps, including Michael addition reaction and isocyanate reaction with high yield production (91%), and is described in more detail below.

(1) Synthesis of Cy-PPG

Poly(propylene glycol) diacrylate 800 (1050 g, 1.312 mol), cytosine (307 g, 2.760 mol) and Sodium tert-butoxide (0.3 g, 0.003 mol) were dissolved in 1000 mL of dimethyl sulfoxide (DMSO) in a flask and the reaction mixture was stirred at 60 °C for 48 h. During solvent evaporation, the crude product was dissolved in toluene (500 mL) and a hot solution was used to remove insoluble impurities.

Eventually, the solvent was evaporated, and then the product was dried under vacuum. Yield: 97% (1298 g).

(2) Synthesis of PU-UrCy

Cy-PPG (34.9 g, 0.034 mol) was dissolved in dry DMF (250 mL). An equimolar amount of 1,6-hexamethylene diisocyanate (5.72 g, 0.034 mol) and three drops of dibutyltin dilaurate were injected drop-wise via a syringe. The polymerization reaction was conducted at 50 °C under nitrogen. After 12 h of polymerization, an excess methanol (2.02 ml, 1.60 g, 0.05 mol) was added and the solvent was evaporated, then the residue was purified by pouring into acetone (200 ml) to generate a light yellow elastomeric solid. Yield: 85% (34.5 g).

Preparation of aliphatic polyurea as a control

(1) Synthesis of NH_2-PPG

Poly(propylene glycol) diacrylate 800 (56 g, 0.07 mol), cysteamine hydrochloride (18.2 g, 0.16 mmol) and pyridine (12.7 g, 0.16 mmol) were dissolved in 200 mL of anhydrous DMF, and the reaction was carried out at room temperature for two days in the dark. After evaporating the solvent, the crude oil sample was diluted with water (200 mL) and 20 mL of 10% aqueous sodium hydroxide solution was added. Subsequently, the aqueous phase was extracted with ethyl acetate (3 x 50 mL) and the combined organic layers were washed with saturated aqueous sodium chloride, dried over magnesium sulfate. After filtration, all of the solvent was removed under reduced pressure to yield the final product, a colorless viscous oil. Yield: 75% (49.8 g).

(2) Synthesis of PU

PU polymer was prepared as described for PU-UrCy, with the exception of replacing Cy-PPG with NH_2-PPG (32.4 g, 0.034 mol). The product was also purified by pouring into acetone to obtain a white powder. Yield = 74 % (28.2 g).

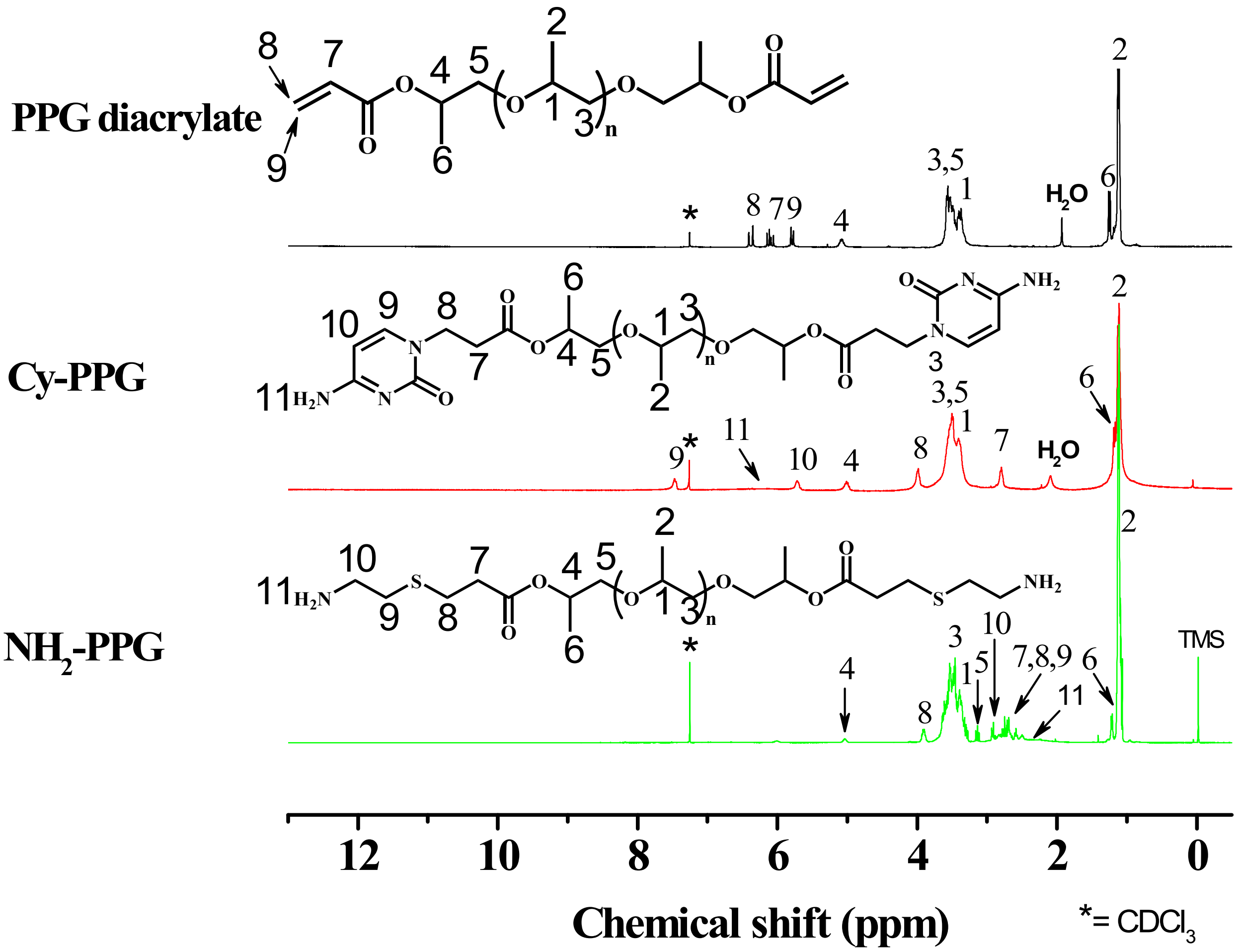


Figure S1. ^{1}H-NMR spectra of PPG diacrylate, Cy-PPG and NH_2-PPG dissolved in chloroform-d_1.

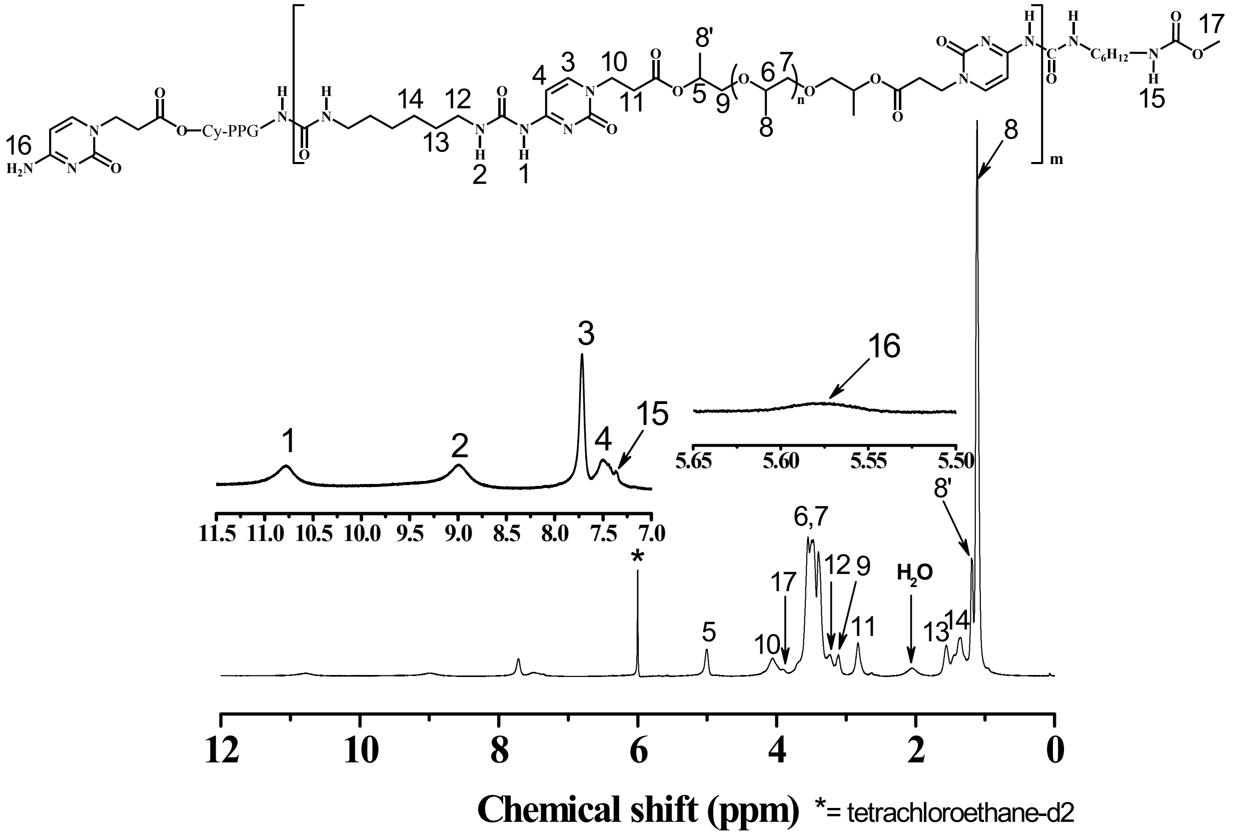
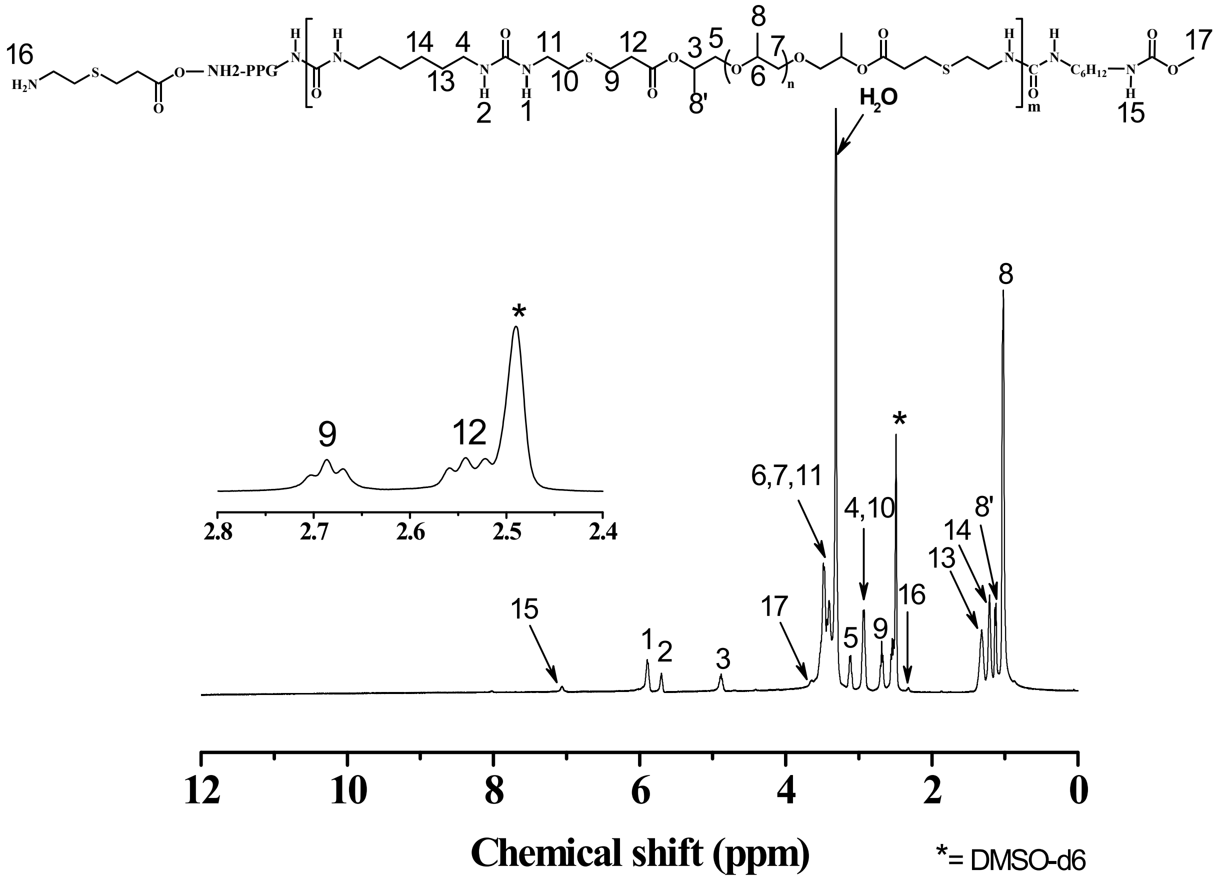


Figure S2. ^{1}H-NMR spectrum of PU-UrCy in tetrachloroethane-d_2.



Figures S3. ^{1}H-NMR spectrum of PU in dimethyl sulfoxide–d_6.

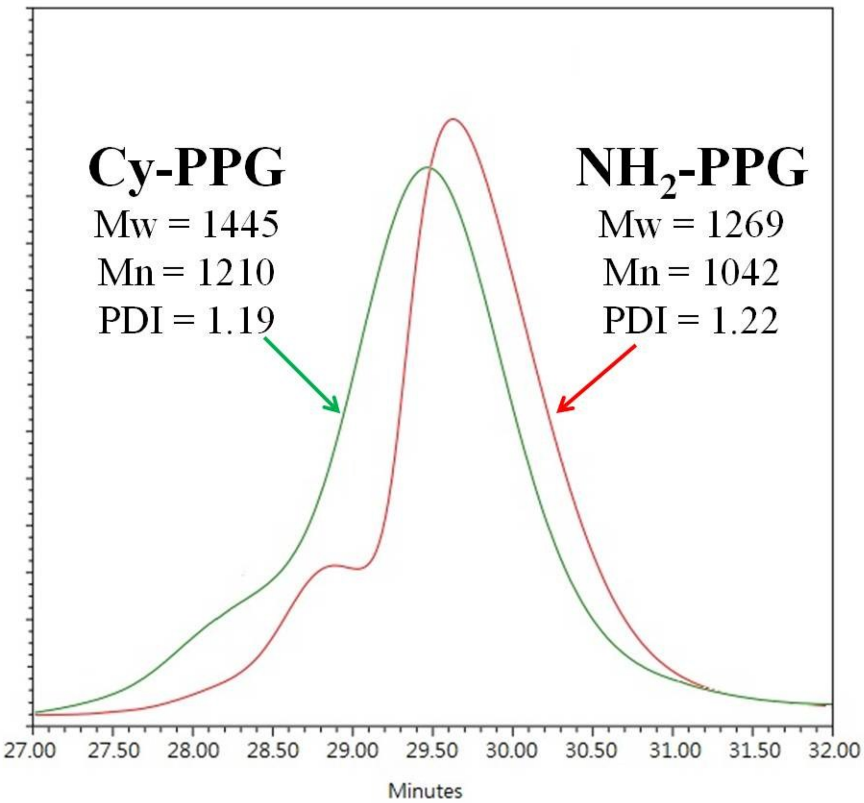


Figure S4. GPC traces for Cy-PPG and NH_2-PPG.

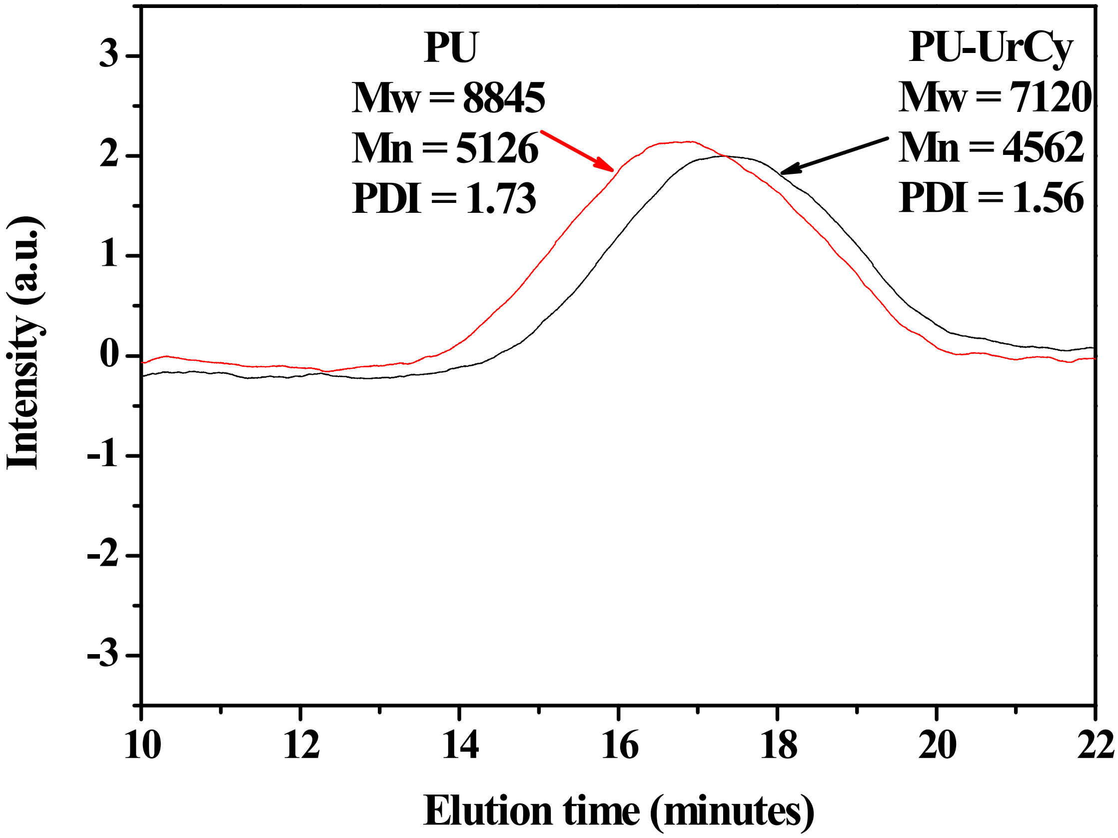
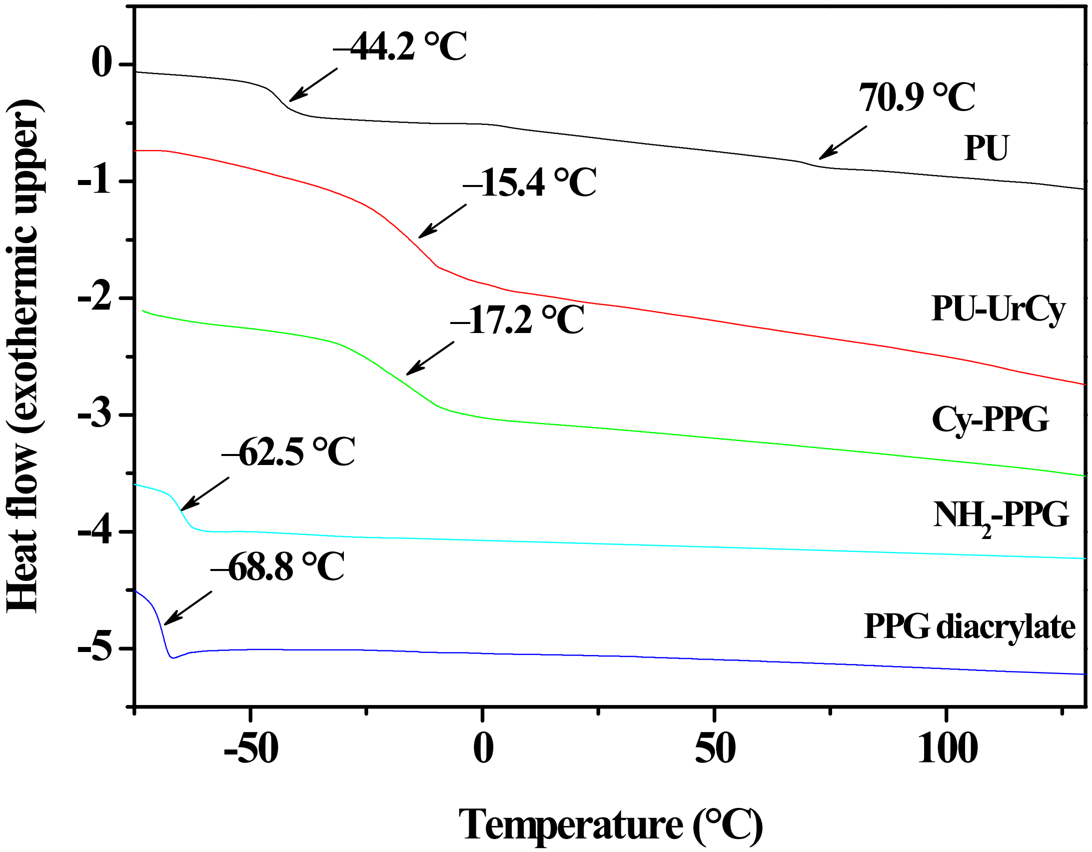


Figure S5. GPC traces for PU-UrCy and PU.



Figures S6. DSC curves for PU, PU-UrCy and related samples.

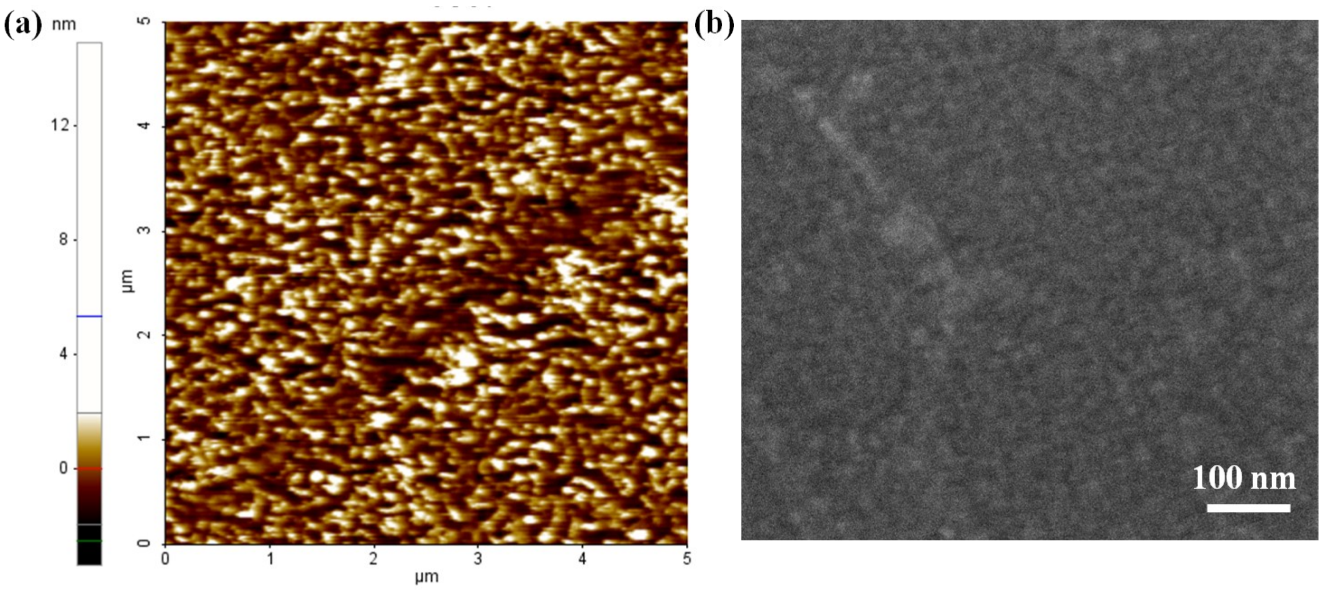


Figure S7. (a) AFM and (b) SEM images of the typical phase-separation morphology of annealed PU film.

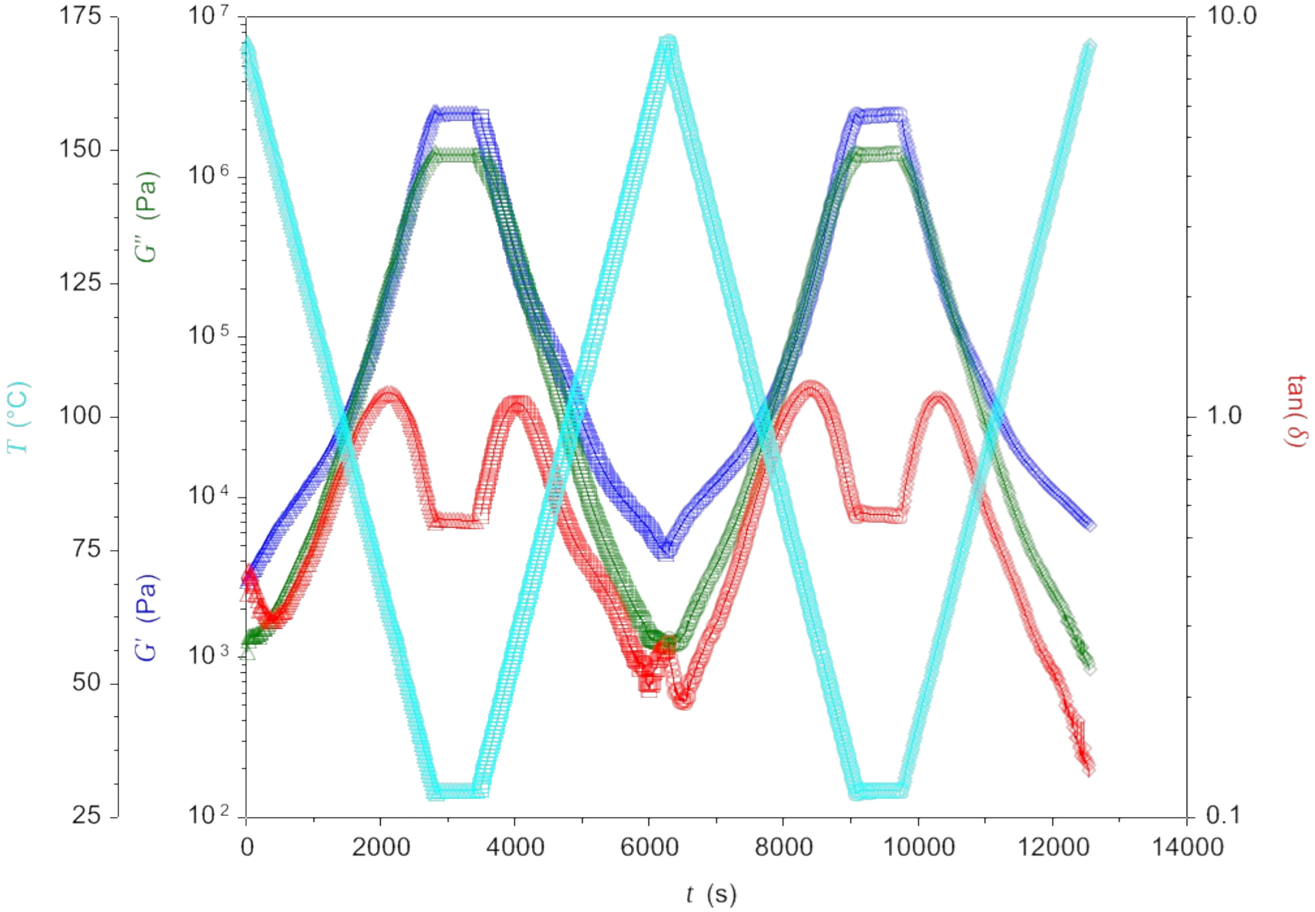


Figure S8. Temperature cycling rheology experiments for PU-UrCy: G', G'' (blue and green lines), with temperature (cyan line) and Tan δ (red line) variations are plotted versus time.

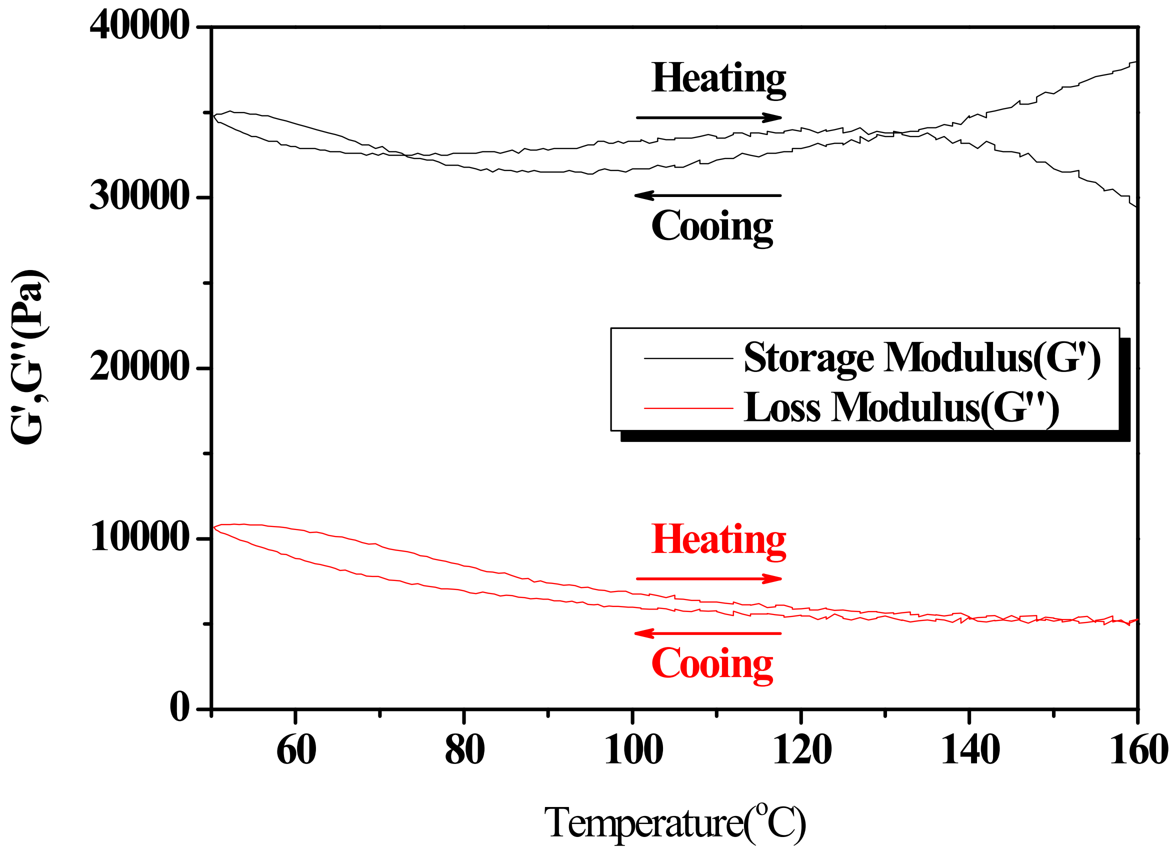


Figure S9. Rheology data for PU: **(a)** temperature stability sweep of storage modulus (G') and loss modulus (G'') from 50 to 160 °C.

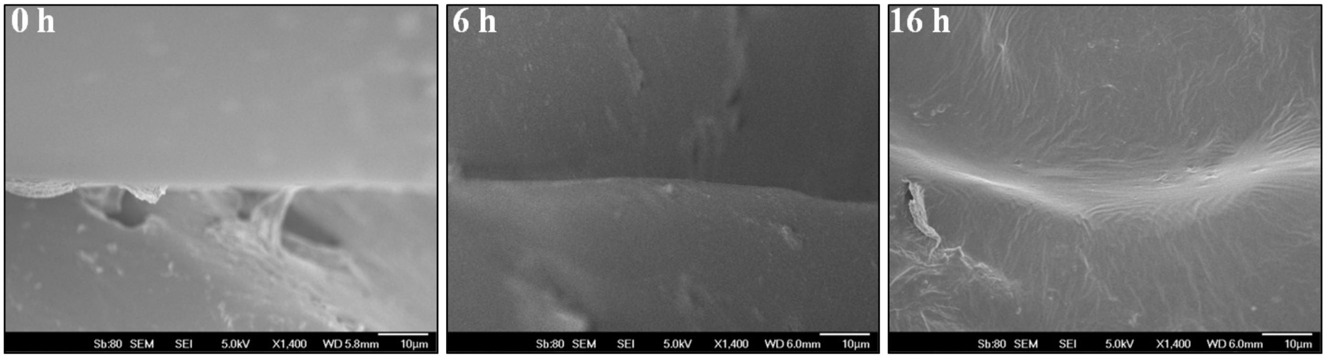


Figure S10. SEM images illustrating the change on the incision interface of PU-UrCy film over time at 25 °C.