Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Dynamic Supramolecular Self-Assembly: Hydrogen Bonding-Induced Contraction and Extension of Functional Polymers

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Experimental Section

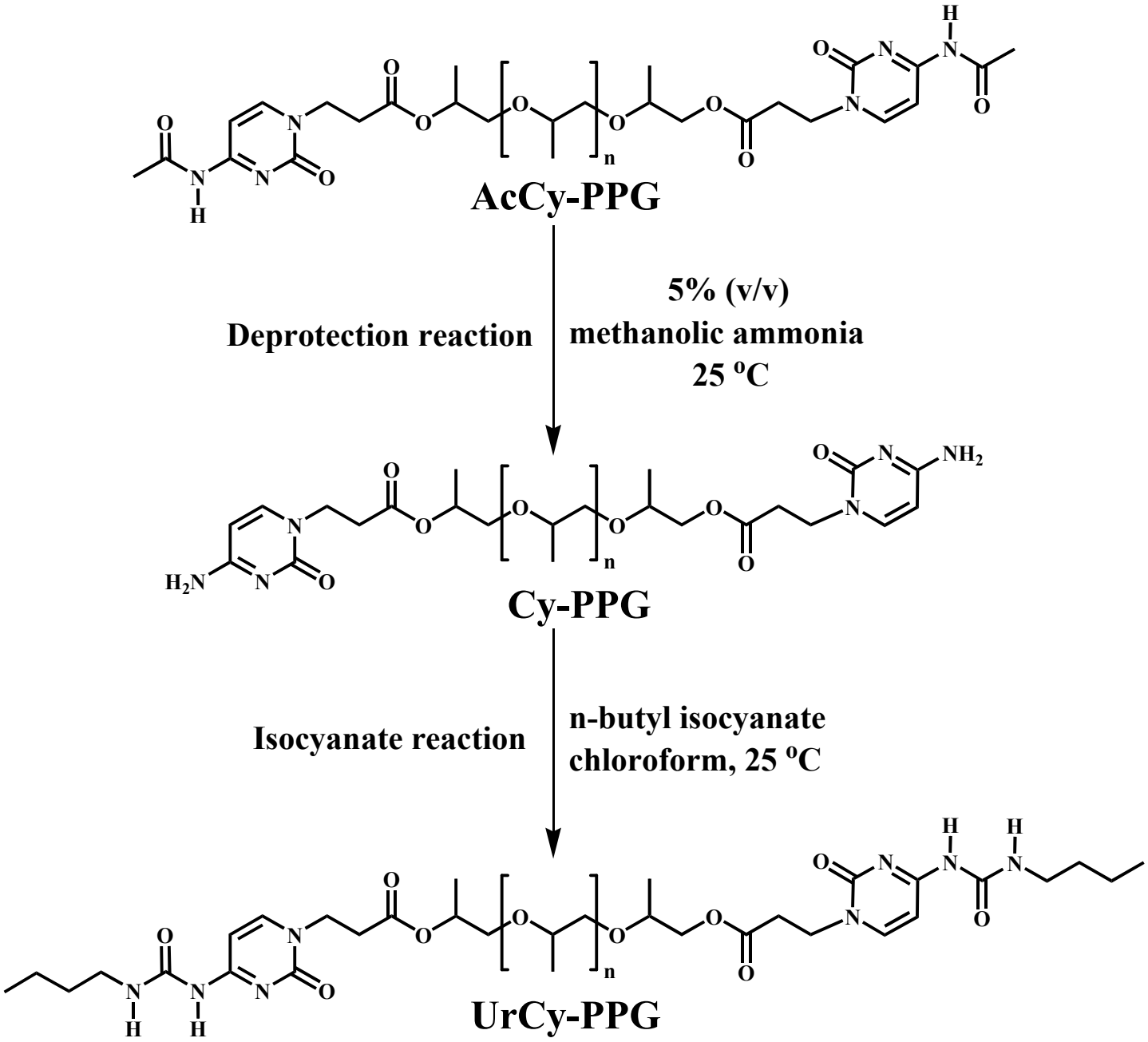
Materials

All chemicals and reagents were of the highest purity commercially available and were purchased from Sigma-Aldrich (St. Louis, MO, USA). High-performance liquid chromatography grade organic solvents were obtained from TEDIA (Fairfield, OH, USA).

Characterization

Proton Nuclear Magnetic Resonance (^{1}H-NMR). ^{1}H-NMR spectra were recorded using a Varian Inova Spectrometer equipped with a 9.395 T Bruker magnet and operated at 400 MHz. Samples (approximately 20 mg for ^{1}H NMR) in deuterated chloroform ($CDCl_3$) were analyzed at 20 °C. *Differential Scanning Calorimetry (DSC).* A PerkinElmer DSC 4000 instrument (New Castle, DE, USA) was used to measure glass transition, melting, and heat enthalpy. The DSC was operated under a dry nitrogen atmosphere at a scanning rate of 10 °C/min from -80 to 130 °C. The DSC second heating scans for all samples are shown in Fig. 1. *Small and Wide-Angle X-ray Scattering (SAXS and WAXS).* SAXS/WAXS data were generated using the BL17A1 wiggler beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Samples were sealed between two Kapton windows (thickness: 12 μm) and analyzed at room temperature. An X-ray beam with a diameter of 1.0 mm and wavelength (λ) of 0.113 nm was used (q range of SAXS: 0.1-5.9 nm^{-1}; q range of WAXS: 0.8-28 nm^{-1}). Variable temperature SAXS/WAXS analyses were performed at a heating/cooling rate of 1.0 °C/min in an air atmosphere. *Fourier Transform Infrared Spectroscopy (FTIR).* FTIR spectra were measured on a Spectrum Two FTIR spectrometer (PerkinElmer, Buckinghamshire, UK); 64 scans were collected at a resolution of 1.0 cm^{-1}. Temperature-dependent FTIR spectra were recorded over a temperature range of 30 to 110 °C at a scanning rate of 1.0 °C/min. *Rheological Studies.* The rheological characteristics of the samples were investigated using an Anton Paar MCR 501 rheometer (Anton Paar Ltd, St. Albans, UK) with cone-plate measuring geometry. All measurements were carried out in a nitrogen atmosphere. Different shear strains (γ) were applied to determine storage modulus (G'), loss modulus (G"), and complex viscosities. The gap distance was set to 0.05 mm. Samples were scanned from 70 to 120 °C at a scan rate of 1.0 °C/min; oscillation frequency and shear rate were 1 Hz and 10 s^{-1}, respectively.

Syntheses



Scheme S1 Synthetic procedures for AcCy-PPG, Cy-PPG and UrCy-PPG.

The synthetic route used to prepare UrCy-PPG contained three steps, including Michael addition, deprotection, and isocyanate reactions (Scheme S1). These procedures are discussed in more detail below.

(1) Synthesis of AcCy-PPG

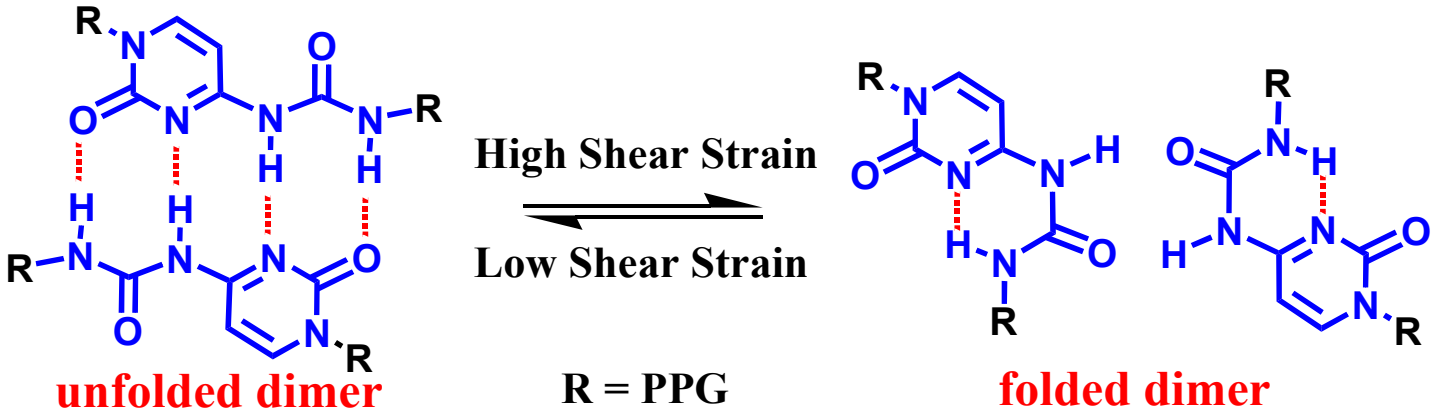
The synthetic procedure for AcCy-PPG has previously been described in detail.[26]

(2) Synthesis of Cy-PPG

AcCy-PPG (10 g, 9.06 mmol) was stirred with 5% (v/v) methanolic ammonia (50 cm^3) at 25 °C for 3 h. After removal of the solvent using rotary evaporation, the crude product was directly purified by flash column chromatography (silica gel, ethyl acetate) affording a pale-yellow liquid. Eventually, the sample was further isolated by precipitation in diethyl ether, filtered, and dried under vacuum; the product was a high viscosity liquid. Yield: 71% (6.58 g).

(3) Synthesis of UrCy-PPG

Cy-PPG (10 g, 9.78 mmol) was dissolved in dry chloroform (250 mL). An excess of *n*-butyl isocyanate (2.9 g, 29.35 mmol) was injected drop-wise via a syringe over 30 min. Subsequently, the reaction mixture was stirred at 25 °C under nitrogen. After 1 d of reaction, anhydrous methanol (1.1 g, 35.00 mmol) was added as a scavenger for unreacted *n*-butyl isocyanate, the solvent was evaporated, and the residue was purified by pouring into a large amount of diethyl ether (300 mL) to generate a light yellow solid. Yield: 93% (11.08 g).



Scheme S2 Possible shear-induced structural transition of the hydrogen bonding interactions within the UrCy-PPG system.

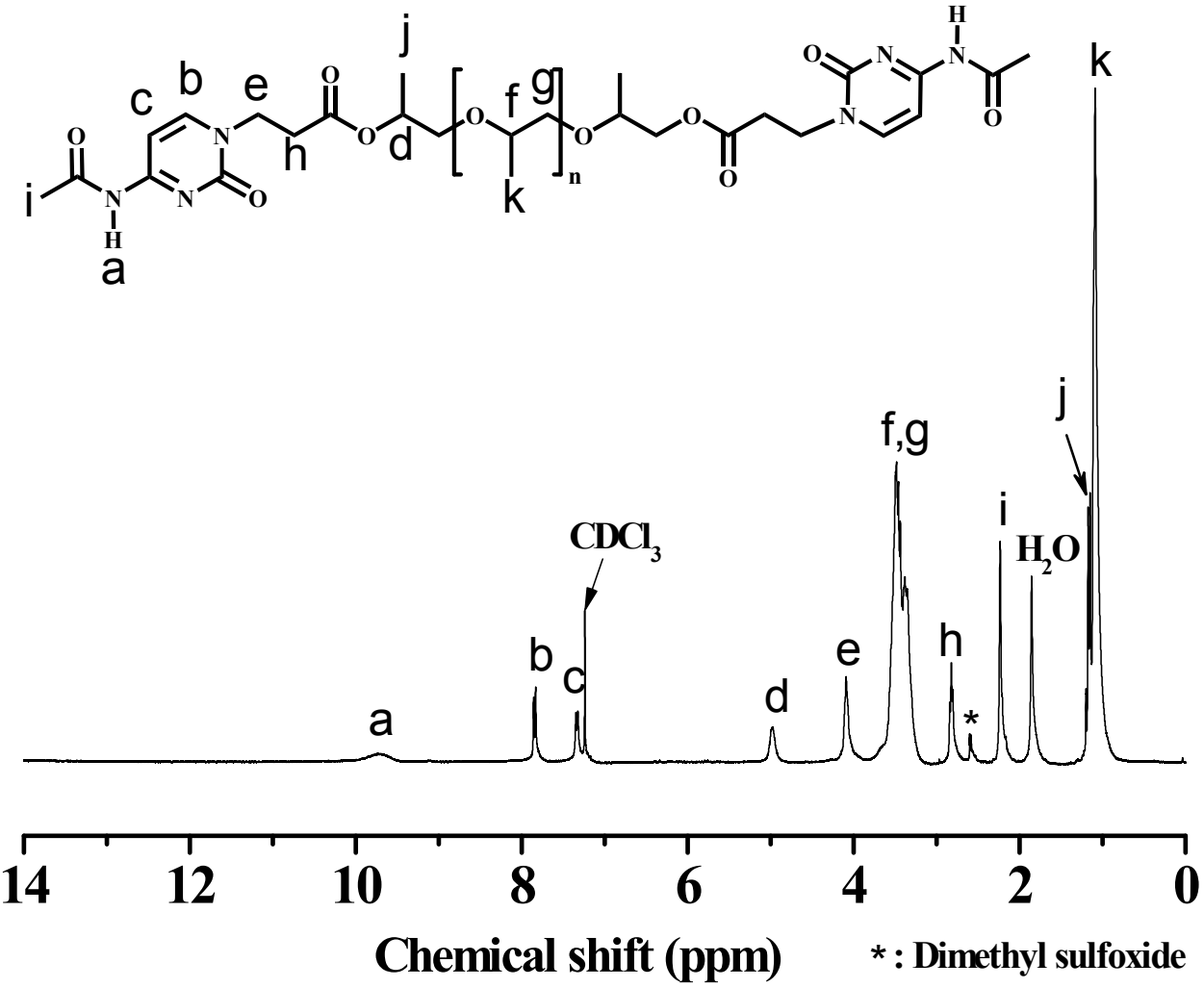


Fig. S1 ^{1}H-NMR spectrum of AcCy-PPG dissolved in deuterated chloroform ($CDCl_3$).

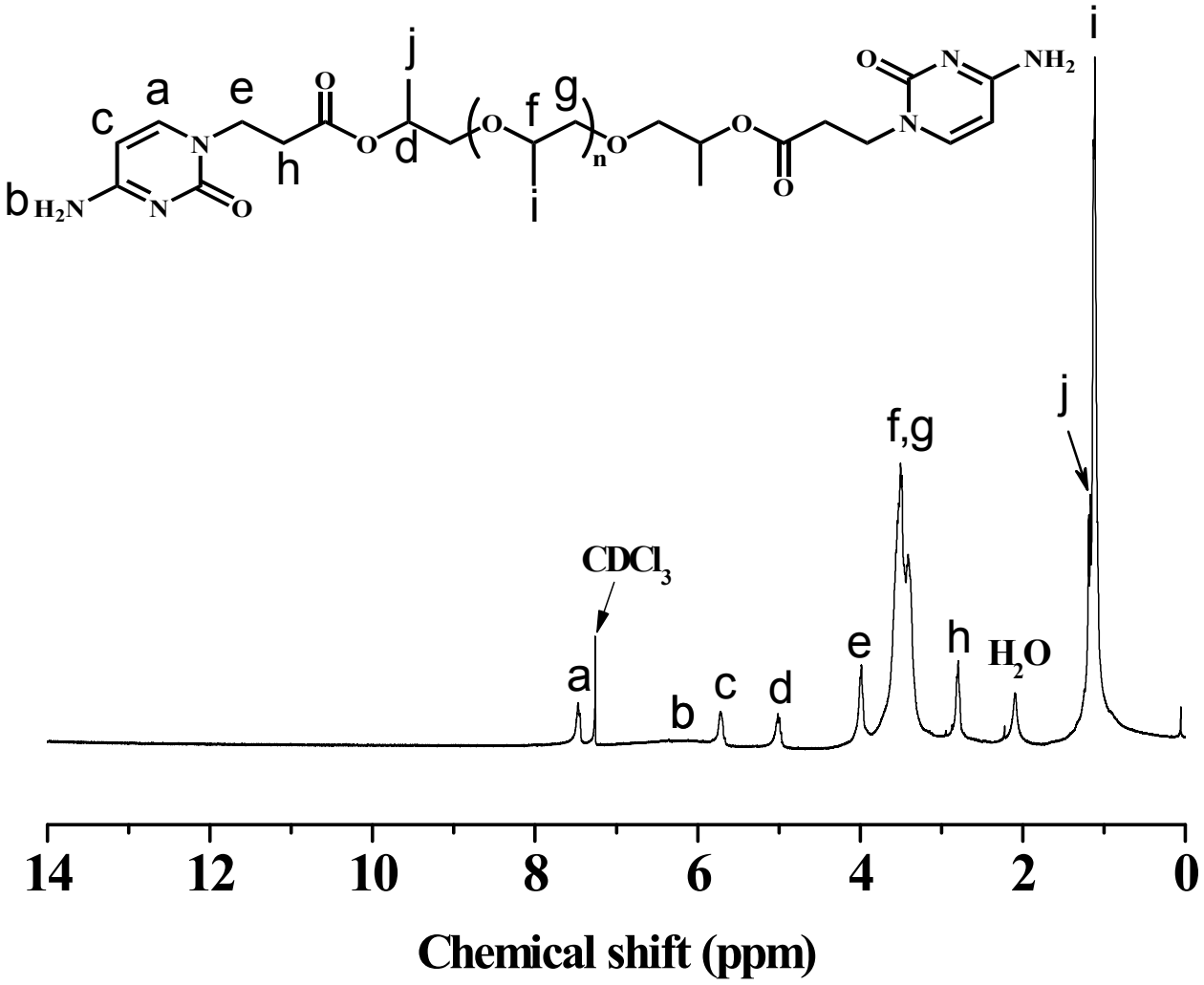


Fig. S2 ^{1}H-NMR spectrum of Cy-PPG dissolved in $CDCl_3$.

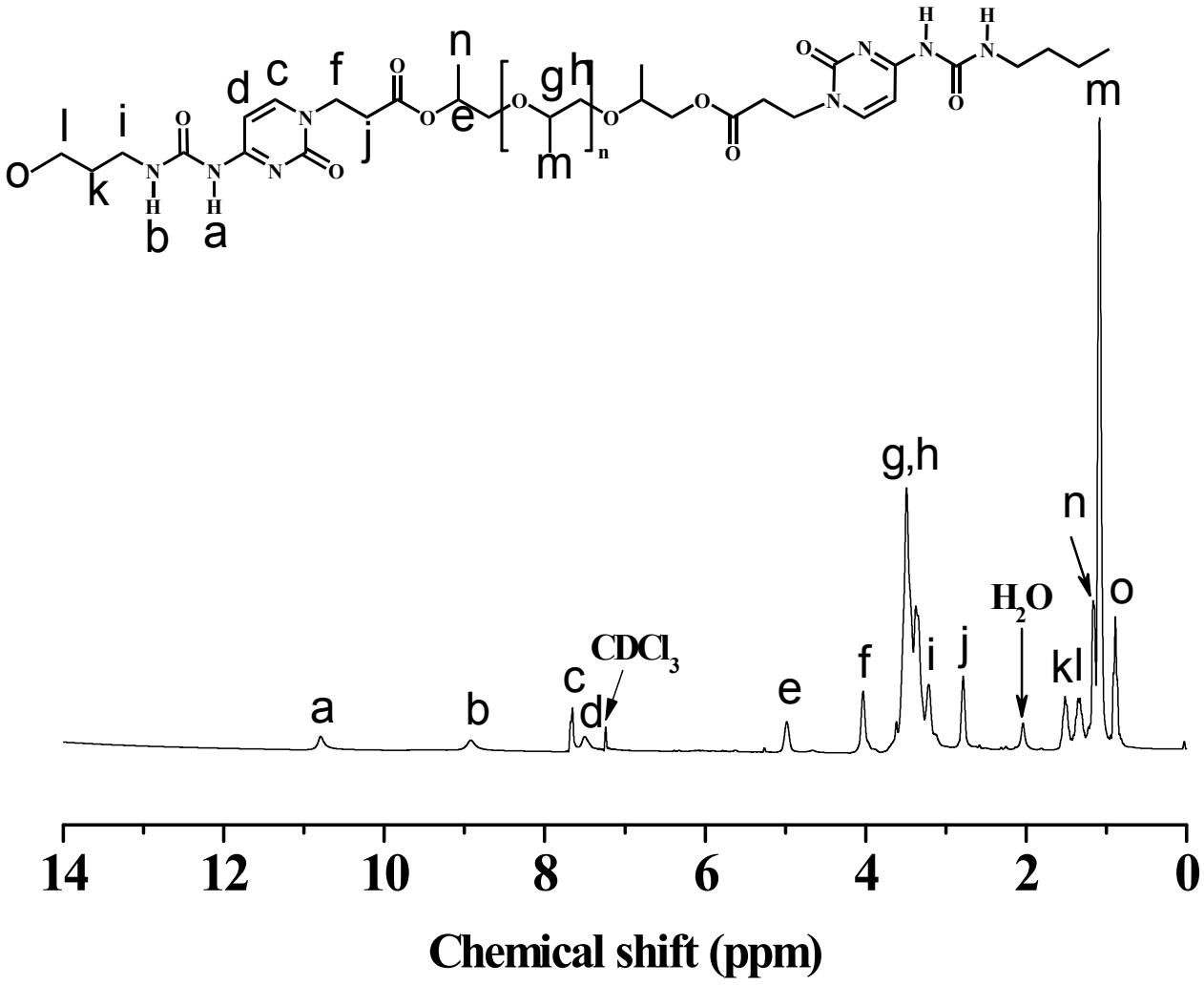


Fig. S3 ^{1}H-NMR spectrum of UrCy-PPG dissolved in $CDCl_3$.

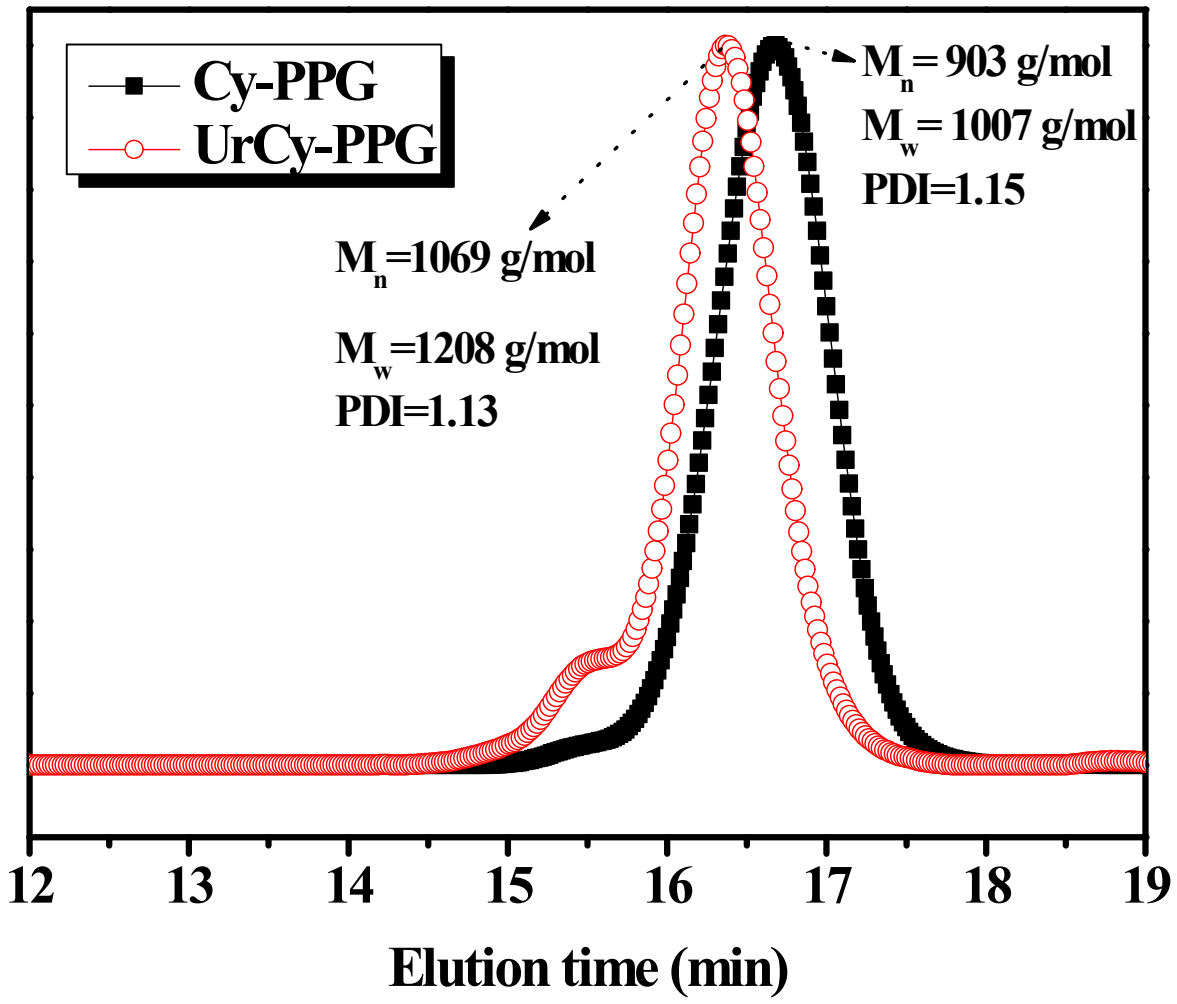


Fig. S4 Gel permeation chromatography traces for Cy-PPG and UrCy-PPG with tetrahydrofuran as the mobile phase.

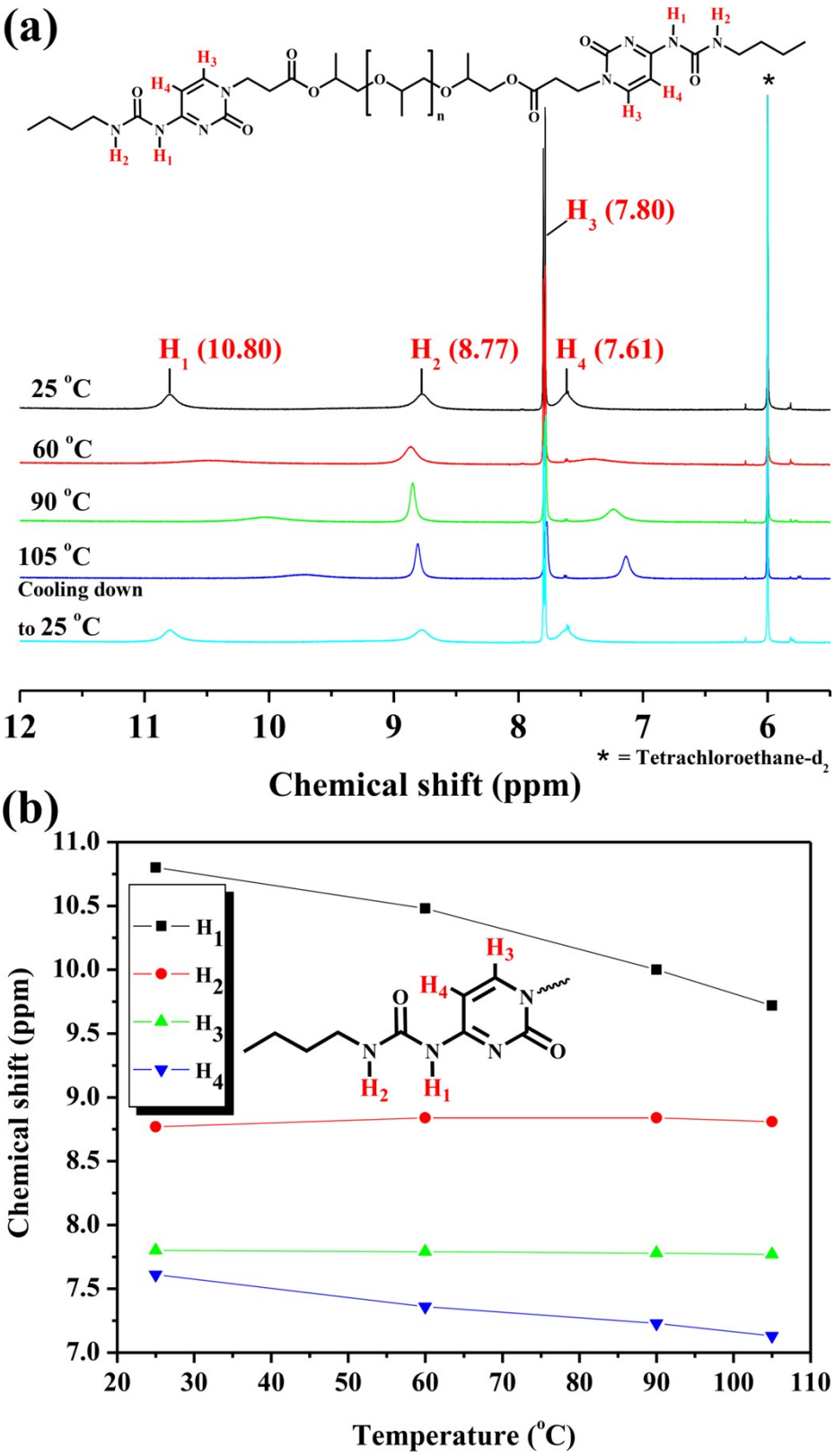


Fig. S5 (a) Variable-temperature ^{1}H NMR spectra of UrCy-PPG in tetrachloroethane-d_2 over the region 5.5–12.0 ppm. **(b)** Plot of the experimetal temperature dependence of the chemical shift differences (Δδ) between the UrCy protons in UrCy-PPG as determined from VT-NMR experiments recorded in tetrachloroethane-d_2.

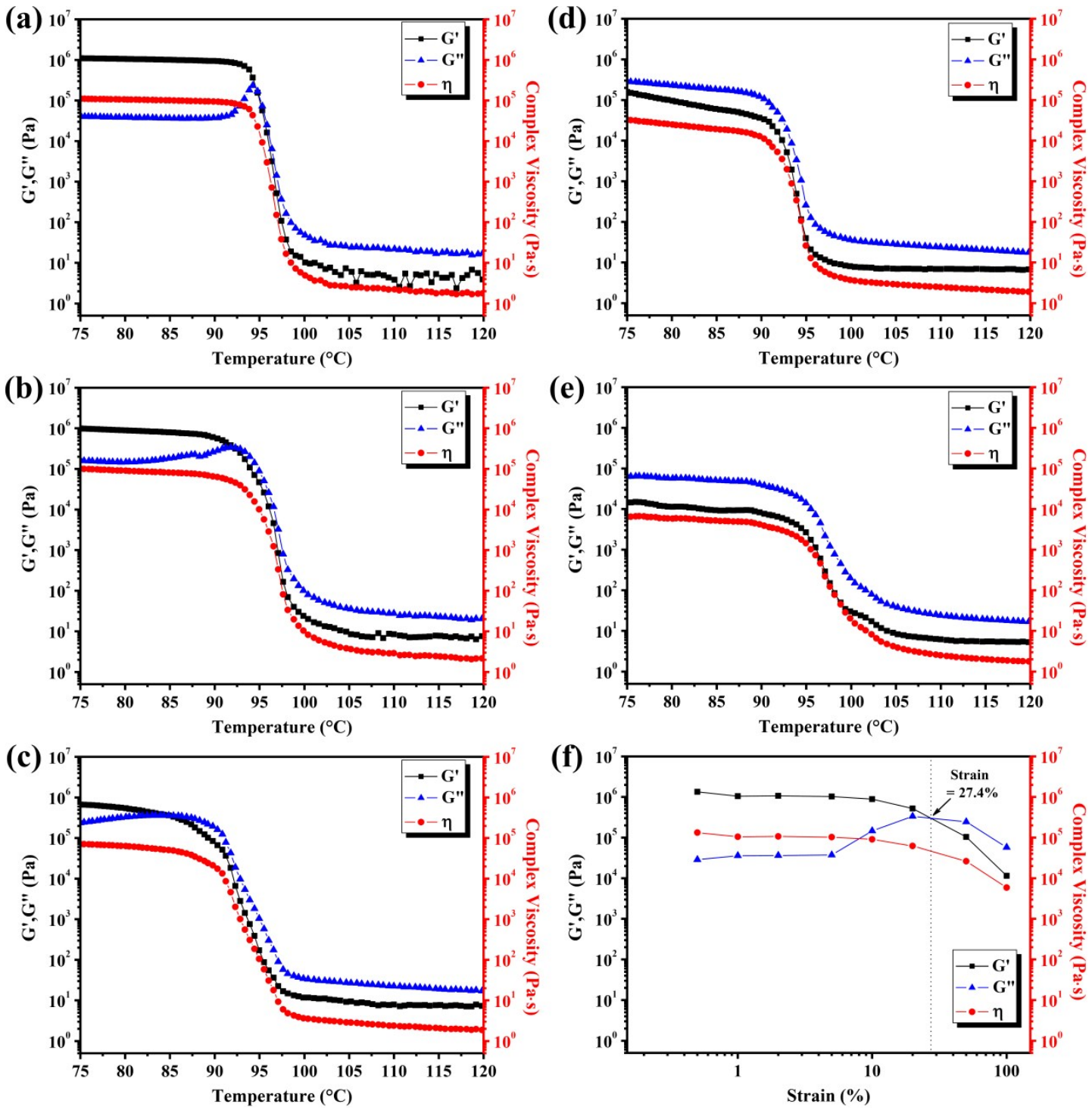


Fig. S6 Dynamic temperature sweep of storage modulus (G'), loss modulus (G"), and complex viscosity for UrCy-PPG at shear stresses (γ) of **(a)** 5%, **(b)** 10%, **(c)** 20%, **(d)** 50% and **(e)** 100%. **(f)** Rheology data for UrCy-PPG: G', G" and viscosity variations versus γ at 80 °C.