Designing Functionalizable Hydrogels through Thiol-Epoxy Coupling Chemistry

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Materials and Methods

Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), **1**, diglycidyl ether terminated poly(ethylene glycol) (PEG) (M_n = 1 kDa), **2**, diglycidyl ether terminated poly(dimethylsiloxane) (PDMS) (M_n = 0.8 kDa), TBAF-trihydrate, and pyrene-acid were purchased from commercial sources and used as received. Fluorescent dye functionalized gels were observed using a fluorescence microscope AX10Imager M1m (Zeiss, Germany). Images were taken with a low light-intensity CCD camera (PentaMax 12 bit CCD; Princeton Instrument Inc., Trenton, NJ).

Gelation Procedures

PEG (1kDa) Hydrogel: PETMP (**1**) (58.83 mg, 0.12 mmol) and TBAF.3H_2O (97%) (39.16 mg, 0.12 mmol) were dissolved in 225 mg of DMF, stirred for 5 minutes, and then added to an already prepared solution of PEG **2** (240.80 mg, 0.24 mmol) in 550 mg of DMF. This formulation was subjected to a vigorous stirring process to obtain a clear solution. This solution was heated to 70 ºC for 30 minutes. After cooling to the room temperature, the crosslinked material was washed thoroughly with ethanol and then water for several times and then used for further studies (yield = ~90%).

PEG/PDMS (80/20 mol%) Hydrogel: PETMP (**1**) (73.54 mg, 0.15 mmol) and TBAF.3H_2O (97%) (48.96 mg, 0.15 mmol) were dissolved in 225 mg of DMF, stirred

for 5 minutes, and then added to an already prepared mixture of PEG (**2**) (240.8 mg, 0.24 mmol) and PDMS (**3**) (48.16 mg, 0.06 mmol) in 550 mg DMF. This formulation was subjected to a vigorous stirring process to give a fine dispersion. This dispersion was heated to 70 ºC for 30 minutes. After cooling to the room temperature, the crosslinked material was washed thoroughly with ethanol and then water for several times and then used for further studies (yield = 88-91%).

PEG (2kDa) Hydrogel: PEG (2kDa) Hydrogel: PETMP (**1**) (18.32 mg, 0.038 mmol) and TBAF.3H_2O (99%) (11.96 mg, 0.038 mmol) were dissolved in 200 mg of DMF, stirred for 5 minutes, and then added to an already prepared solution of PEG 2kDa (150 mg, 0.075 mmol) in 100 mg of DMF. This formulation was subjected to a vigorous stirring process to obtain a clear solution. This solution was heated to 70 ºC for 1 hour. After cooling to the room temperature, the crosslinked material was washed thoroughly with ethanol and then water for several times and then used for further studies (yield = ~89%).

Mechanical Tests

The mechanical properties of the prepared hydrogels were measured by unconfined uniaxial compression tests using an Instron 5864 mechanical tester. Cylindrical-shaped hydrogel samples were prepared and immersed in distilled water until they reached equilibrium. They were compressed at a rate of 2 mm/min^{-1}. The compressive modulus was determined as the slope of the linear region in the strain range of the stress-strain curve.

Swelling Studies

Cylindrical-shaped hydrogel samples were immersed into distilled water and then freeze-dried. The initial mass of the samples was measured and then they were

immersed in distilled water. Swollen hydrogel were weighed (after removal of surface water using filter paper) at designed time intervals. Swelling was calculated according to the equation, $Q\ (\%) = [(W_s - W_d)/W_d] \times 100$, where, W_s is the mass of the hydrogel in the swollen state, W_d is the mass of the hydrogel in the dried state, and Q is the equilibrium-swelling ratio.

Gel Functionalization

The hydrogel network was freeze-dried, soaked in THF, and freeze-dried again. This dry sample was then immersed in dry DCM (0.5 mL). 8 mg pyrene-acid, 50 mg DCC, and 15 mg DMAP were then added. This reaction mixture was stirred at the room temperature for 12 hours. After this time, the hydrogel film was washed with DMSO, water, MeOH, and THF for several times, freeze-dried, and characterized.

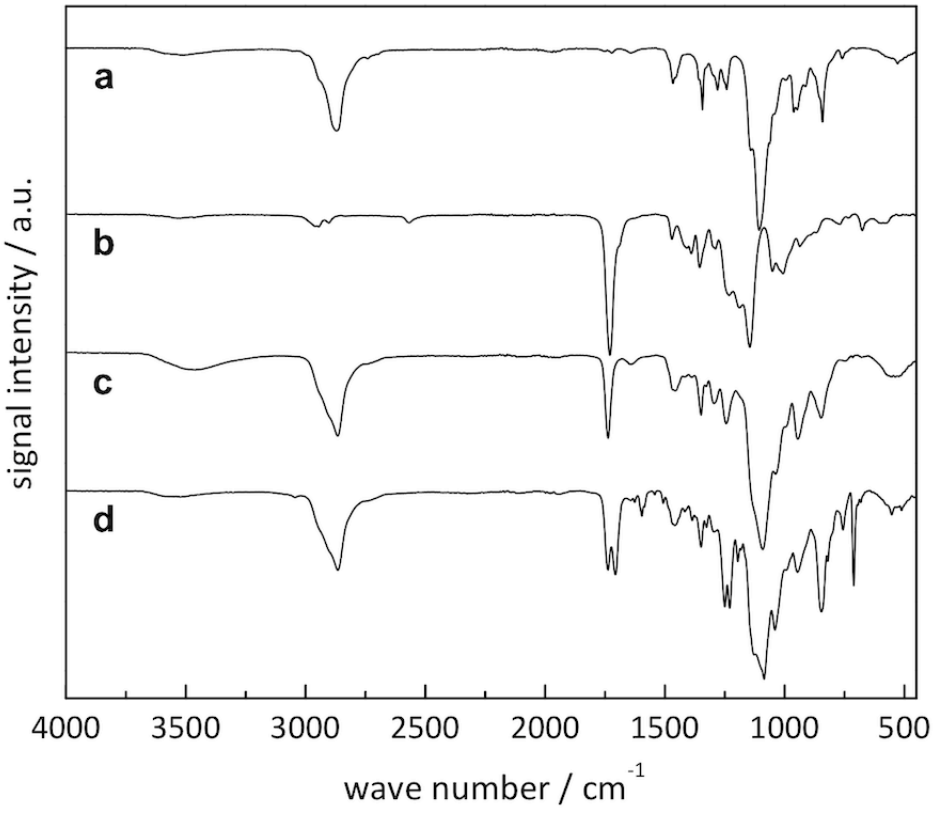

Figure S1. IR spectra of the gel precursors **1** (b) and **2** (a), PEG-hydrogel (c), and pyrene-functionalized hydrogel (d).

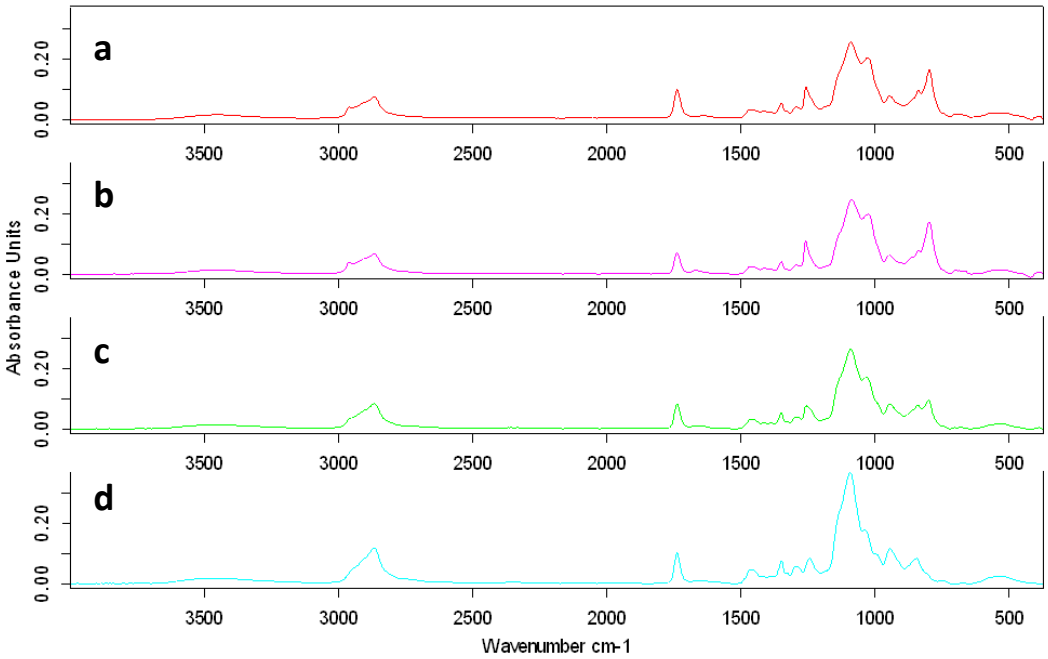

Figure S2. IR spectra of the prepared hydrogels. Entry 1 (d), entry 2 (c), entry 3 (b), and entry 4 (a) in Table 1 (27 wt% PEG **2**).