

Supporting Information

A rapid and facile preparation of novel macroporous silicone-based cryogels via photo-induced thiol-ene click chemistry

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Experimental section

Materials

Poly(vinylmethylsiloxane-*co*-dimethylsiloxane) copolymer (P(VMS-*co*-DMS), P1, VMS/DMS = 8/92 mol/mol %, $M_w = 28$ kDa, viscosity = 800-1200 cst) was obtained from Gelest, Inc. (Pennsylvania, USA) and used without further purification. The crosslinker 1,6-hexanedithiol (XL, > 97%) and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMAP, 99%) were purchased from Sigma-Aldrich (St Louis, Mo, USA) and used as received. AR grade chloroform (CHCl₃), toluene, methanol (MeOH), cyclohexane and other solvents were purchased from Chem-Supply Pty. Ltd. and used without further purification. Gasoline (unleaded #91) and diesel were purchased from Shell petrol station and used as received. Oil Red O dye was obtained from DIFCO Laboratories and used as received. The commercial non-woven polypropylene absorbent was obtained from Global Spill Control Inc., Victoria, Australia. A Milli-Q system (Millipore Inc., Milford, MA, USA) purified double distilled water was used for all the experiments.

Instrumentation

Attenuated total reflectance fourier transform infrared (ATR-FTIR) was performed on a Nexus 470 Fourier-Transform Infrared Spectrometer (Thermo Nicolet). Environmental Scanning electron microscope (E-SEM) images were acquired by using a FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini Sputter Coater prior to imaging. X-ray photoelectron spectroscopy (XPS) analysis was performed on A VG ESCALAB 220i-XL spectrometer under ultra-high vacuum (6×10^{-9} mbar) to reveal the surface composition of the gels. A fixed photon energy (Al K α 1486.6 eV) was used. A survey scan was performed between 0 and 1200 eV with a resolution of 1.0 eV and pass energy of 100 eV. High resolution scans for C1s (276 to 296 eV) and O1s (522 to 542 eV) were also conducted with a resolution of 0.05 eV and a pass energy of 20 eV. The contact angles of the cryogels were measured by Dataphysics OCA-20 Contact Angle Measuring Instrument. For emulsion separation measurements, the concentration of toluene was determined using a UV-Vis spectrophotometer (Shimadzu UV-1800). Compression testing measurements of the samples were carried out using Instron 5848 Microtester. A LED UV (600LED light strip ($\lambda_{max} = 395-405$ nm, 12V DC, 4.8W) activation apparatus was prepared utilizing the flexible and waterproof 600LED strip wrapped around a cardboard covering an area of 8cm x 8cm. This LED strip was then mounted to a foam support on either side of the LED square creating a raised platform (Fig. S1a-b) under which the reaction system was placed to start the reaction. (Fig. S1c). The open end of the LED strip was connected directly to a power pack and plugged in to the wall electricity socket.

Preparation of the cryogels

The photo-induced thiol-ene cryogelation reactions were conducted at -18°C or 0°C, respectively. These temperatures are below the freezing point of the reaction solvent cyclohexane which has a freezing point of 6.47 °C. Control samples (hydrogels) were also prepared at room temperature. The thiol-ene reactions were initiated by either UV or sunlight.

The mass loading was fixed at 10 w/v %. Briefly, PDMS (0.8 g, 0.029 mmol), XL (0.06 g, 0.400 mmol) and DMAP (0.004 g, 0.016 mmol) were dissolved in cyclohexane (8 mL). This homogenous reaction solution was transferred to a petri dish with a diameter of 5 cm (covered with aluminium foil during transfer to freezer to prevent any preinitiation of the reaction). This mixture was immediately frozen at -18 °C in the freezer for 30 min. Afterwards, the moderately frozen reaction system was placed under the LED UV activation apparatus (directly in the freezer) and the reaction was completed after 30 mins of UV exposure. The resulting cryogel was designated Cryogel-UV. For the sunlight initiated system, upon freezing for 30 min, the moderately frozen reaction system was removed from the freezer and whilst kept frozen at 0 °C in ice-water bath, the reaction was exposed to sunlight for 30 min. The cryogels resulting from this sunlight initiation were designated as Cryogel-Sun. The control samples prepared at room temperature were designated Hydrogel.

After completion of the thiol-ene-cryogelation process, the resulting samples were removed and thawed at room temperature. The cryogels were then immersed in toluene and complete replacement of the toluene solvent was carried out several times. For drying of the samples, the cryogels were first deswollen in methanol, and thereafter, were air dried at room temperature in a fume hood until a repeated constant weight measurement of the cryogel was achieved.

Oil Absorbance Performance Experiments

The absorption performance measurements were carried out for various organic solvents and oils with different densities. For these measurements, PDMS cryogels were placed inside the solvents or oils. Absorption occurred within 5 s and typically reached the saturation point. The weight of the PDMS cryogels before and after the absorption was recorded to calculate the absorption capacity. Weighing of the samples were carried out immediately to avoid the evaporation of the absorbed solvents and oils.

In order to investigate the emulsion separation ability of the cryogel, an oil (toluene) in water emulsion (5 % v/v) was prepared by adding 2.5 ml of toluene to 47.5 ml of water and then sonicated for 1 h. Thereafter, a piece of cryogel was inserted in the lower part of a 1mL syringe (Fig S5a). The emulsion was then immediately poured into the syringe. Drops of liquid were collected in a glass vial situated under the syringe. The concentration of oil in water present in the solution was determined by UV-Vis spectrophotometer at 268 nm (Fig. S5b). The concentration of toluene in the toluene/water solution was measured by preparing a calibration curve based on Beer-Lambert's Law (Fig. S5c).



Fig. S1 a-b) Images of the ‘OFF/ON’ LED UV activation apparatus. c) The thiol-ene click reaction set in dark under UV exposure.

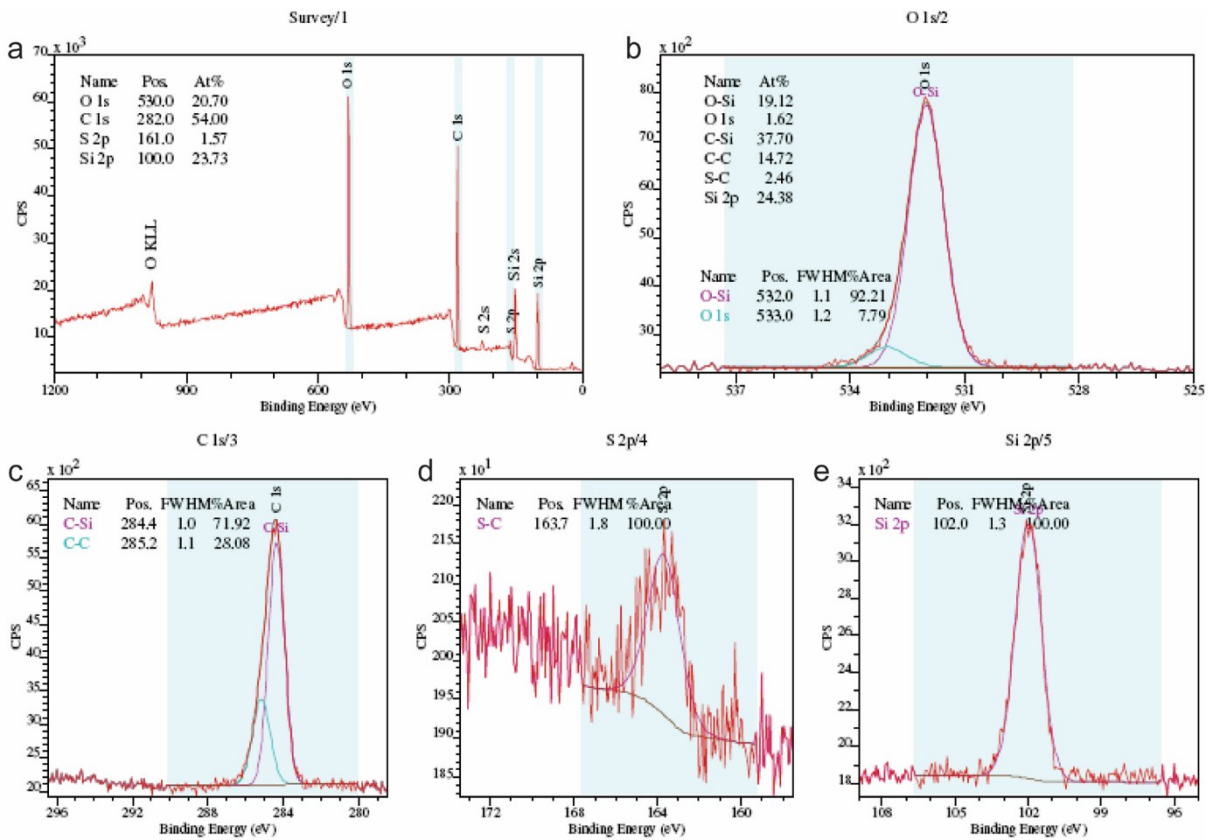


Fig. S2 XPS measurements of the PDMS Cryogel-UV formed. a) XPS wide scan spectra of the PDMS Cryogel-UV. b-e) High-resolution XPS O1s, C1s, S2p and Si2p spectra of the PDMS Cryogel-UV, respectively.

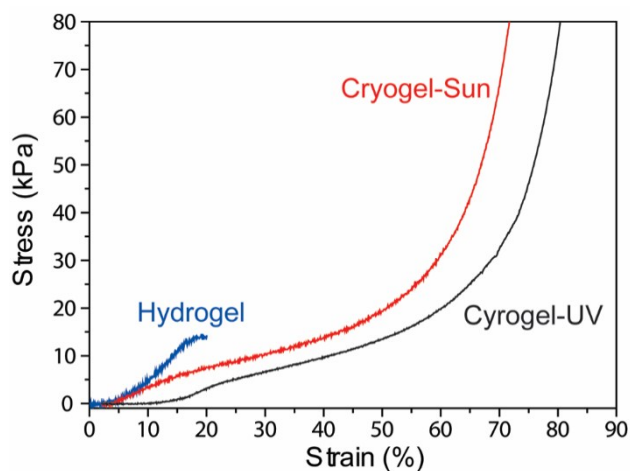


Fig. S3 Stress-strain curves for the 10 w/v % mass loading PDMS gels.

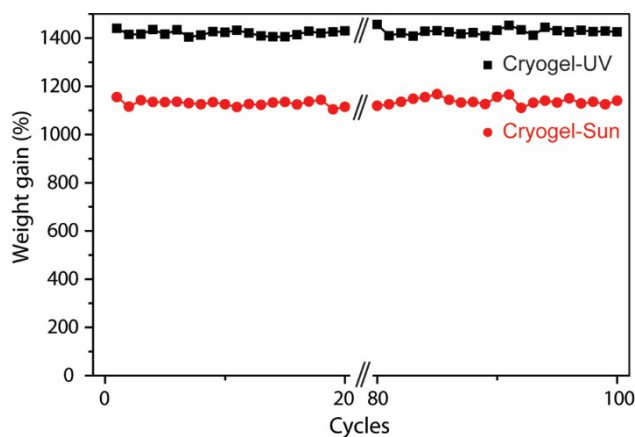


Fig. S4 Absorption capacity of the cryogels in toluene as a function of the recycling number.

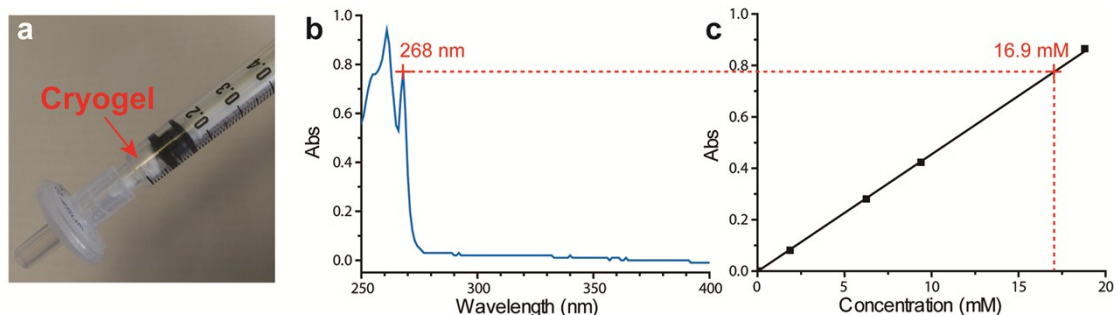


Fig. S5 a) A piece of cryogel inserted in a 1 mL syringe. b) The UV absorption curves of toluene in the toluene/water solution. c) The calibration curve prepared by measuring the absorbency of toluene in the toluene/water solution.

Table S1: The effect of exposing the cryogels for 24 h to harsh conditions on the toluene absorbency capacity (% weight gain) of the cryogels.

Condition	Absorbency (% weight gain)
200 °C	1423 ± 21
-80 °C	1401 ± 32
2M HCl	1435 ± 40
2M NaOH	1468 ± 31
Toluene	1417 ± 37
Non-exposed	1432 ± 25

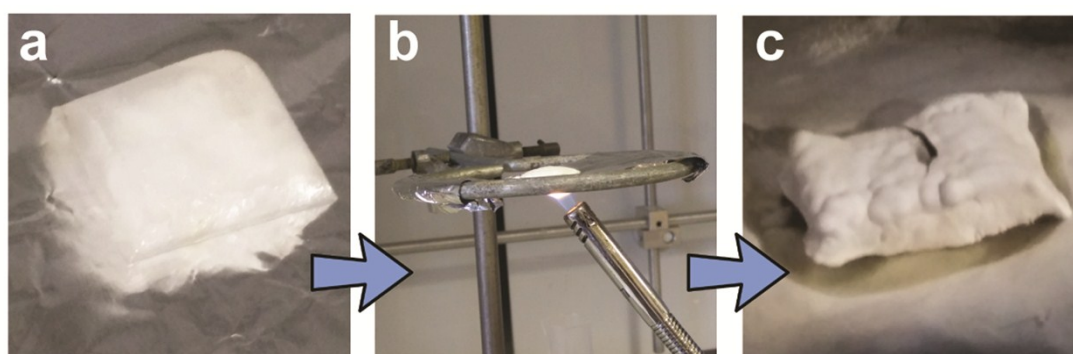


Figure S6: The flame ignition process of the cryogel a) A toluene absorbed cryogel sample placed on aluminium foil. b) Exposure of the cryogel sample to a flame. c) Image of the cryogel residue after exposure to the flame.