Supporting information

Thermoresponsive poly(ionic liquid) hydrogels

Bartosz Ziółkowski and Dermot Diamond*[a]

[a]CLARITY, The Centre for Sensor Web Technologies, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland.
E-mail: dermot.diamond@dcu.ie; Tel: +35317005405

Table of Contents

1. Materials

Tetrabutylphosphonium chloride ($[P_{4,4,4,4}][Cl]$) (Cyphos 443W) and tributyl-hexyl phosphonium chloride ($[P_{4,4,4,6}][Cl]$ were supplied by Cytec® (Ontario Canada) and used as received. Potassium 3-sulfopropylacrylate (SPA), sodium 4-vinylbenzenesulfonate (SS), poly(propylene glycol) diacrylate Mn 800 (PPO800), poly(ethylene glycol) diacrylate Mn 256 (PEG256) and 700 (PEG700), *N,N'*-methylenebisacrylamide (MBIS), 2-hydroxy-2-methylpropiophenone (HMPP) were all obtained from Sigma-Aldrich and used as received.

2. Synthesis of $[P_{4,4,4,4}]$[4-styrenesulfonate] (P-SS) and $[P_{4,4,4,6}]$[3-sulfopropylacrylate] (P-SPA)

7 g of phosphonium chloride was mixed with 10 g of water and 1.2 molar equivalents of the anion salt ([Na][4-styrenesulfonate] for $[P_{4,4,4,4}][Cl]$ or [K][3-sulfopropylacrylate] for $[P_{4,4,4,6}][Cl]$). The mixture was stirred at room temperature for 48 hours. The IL was extracted from the water phase by dichloromethane (DCM), the DCM phase was reduced by a rotary evaporator and the residual liquid was dried at high vacuum 0.1 mBar for 24 hours at room temperature. A final product yield of 97% was obtained.

.The obtained ILs were stored at 5 ˚C. Tetrabutylphosphonium 4-vinylsulfonate will be referred to as P-SS and the tributyl-hexyl phosphonium 3-sulfropropylacrylate will be referred to as P-SPA.

P-SS ^{1}H NMR, δ_H (400 MHz, $CDCl_3$): 0.82-0.85 (t, 12H, CH_3), 1.33-1.38 (m, 16H, CH_2), 2.07-2.74 (m, 8H, CH_2), 5.16-5.19 (d, 1H, CH), 5.65-5.69 (d, 1H, CH), 6.58-6.65 (q, 1H, CH), 7-27-7.29 (d, 2H, CH), 7.74-7.76 (d, 2H, CH) ppm.

P-SPA ^{1}H NMR, δ_H (400 MHz, $CDCl_3$): 0.75-0.79 (t, 3H, CH_3), 0.84-0.88 (t, 9H, CH_3), 1.19-1.22 (m, 4H, CH_2), 1.38-1.44 (m, 16H, CH_2), 2.07-214 (m, 2H, CH_2), 2.15-2.24 (m, 8H, CH_2), 2.75-2.79 (m, 2H, CH_2), 4.13-17 (t, 2H, CH_2), 5.68-5.71 (dd, 1H, CH), 5.93-6.00 (q, 1H, CH), 6.23-6.28 (dd, 1H, CH) ppm

3. Gel preparation

The monomeric IL (200 mg) was mixed with the desired amount (mol %) of crosslinker (MBIS, PEG 256, PEG700, PPO800) and 1 mol% photoinitiator HMPP. The mixture was stirred and poured into a PDMS mould containing 1 mm deep circular pits of diameters 5 and 10 mm. The gels were polymerised for 30 min in a UV curing chamber that produced 365 nm UV light intensity of 3.5 mW/cm^2. After the polymerisation the gels were placed for 1 hour in DI water for swelling. All analysis was done on the swollen gels.

4. Analytical Techniques

NMR spectroscopy

The NMR spectra were collected on a Bruker 400 MHz spectrometer at 25 ˚C. Samples were dissolved in deuterated chloroform. The spectra were analysed using Bruker TopSpin software.

Raman spectroscopy

Raman spectroscopy was performed using a Perkin Elmer® Raman Station 400F. Measurements were taken from 800 to 3200 cm^{-1} at 20 scans with 2 cm $^{-1}$. The samples were placed directly on a microscope slide covered with aluminium foil.

DSC

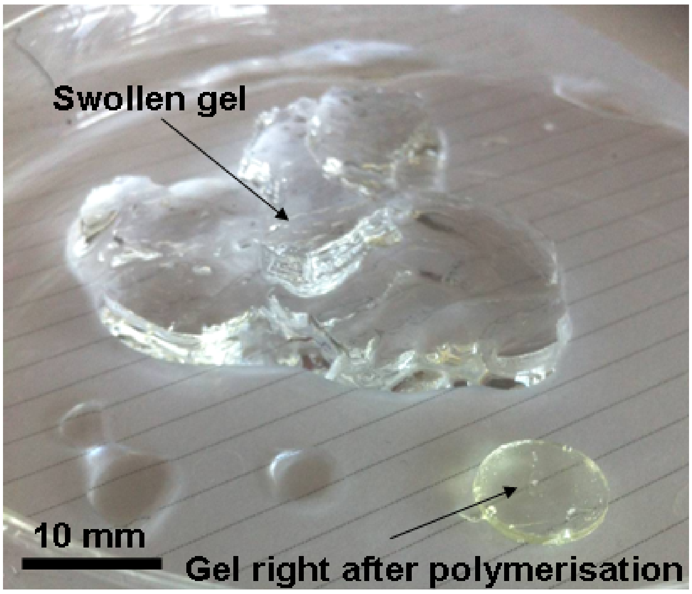
A Pyris 1 DSC was used to analyse the heat generated by the gels during the LCST transition. Thermal scans below room temperature were calibrated with the cyclohexane solid-solid transition and melting point at –87.0 °C and 6.5 °C, respectively. Thermal scans above room temperature were calibrated using indium, tin and zinc with melting points at 156.6, 231.93 and 419.53 °C, respectively. The water-swollen gels were placed on a tissue to remove excess DI water and cut into pieces ca. 10 mg. These were placed on aluminium DSC pans and sealed. The LCST values for these samples were determined by thermal scans at 10 ˚C/min with the following temperature program: Heat from 0 ˚C to 90 ˚C then cool from 90 ˚C to 0 ˚C. The LCSTs were determined as the endothermic peak during heating.

Temperature ramp microscopy.

The swollen gels were cut into squares roughly 3 mm in size. The imaging was performed using an Aigo GE-5 microscope with a 60x objective lens and the accompanying software. The gels were placed on an aluminium plate resting on a Anton Paar MCR 301 Rheometer peltier holder. The plate was filled with DI water and covered with a glass plate to avoid evaporation of water. The glass plate was also in contact with the filling water to avoid condensation. Temperature was controlled through the rheometer software and was ramped up from 20 ˚C to 70 ˚C by 5 ˚C steps. Each step the temperature around the sample was checked with a Fluke 62 Mini IR thermometer and gel size measurements were taken once the temperature stabilised.

5. Swelling behaviour of of P-SS and P-SPA gels

a



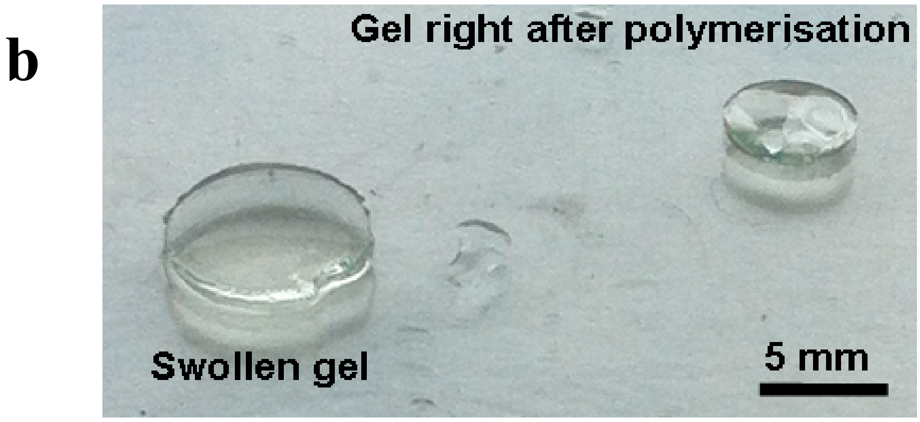


Figure S1. a) P-SS gel with 10% MBAAm right after polymerisation and after 2 hours of swelling in DI water at room temperature; b) P-SPA gel with 5 mol% PPO800 immediately after polymerisation and after swelling in DI water at room temperature.

6. Raman spectroscopy

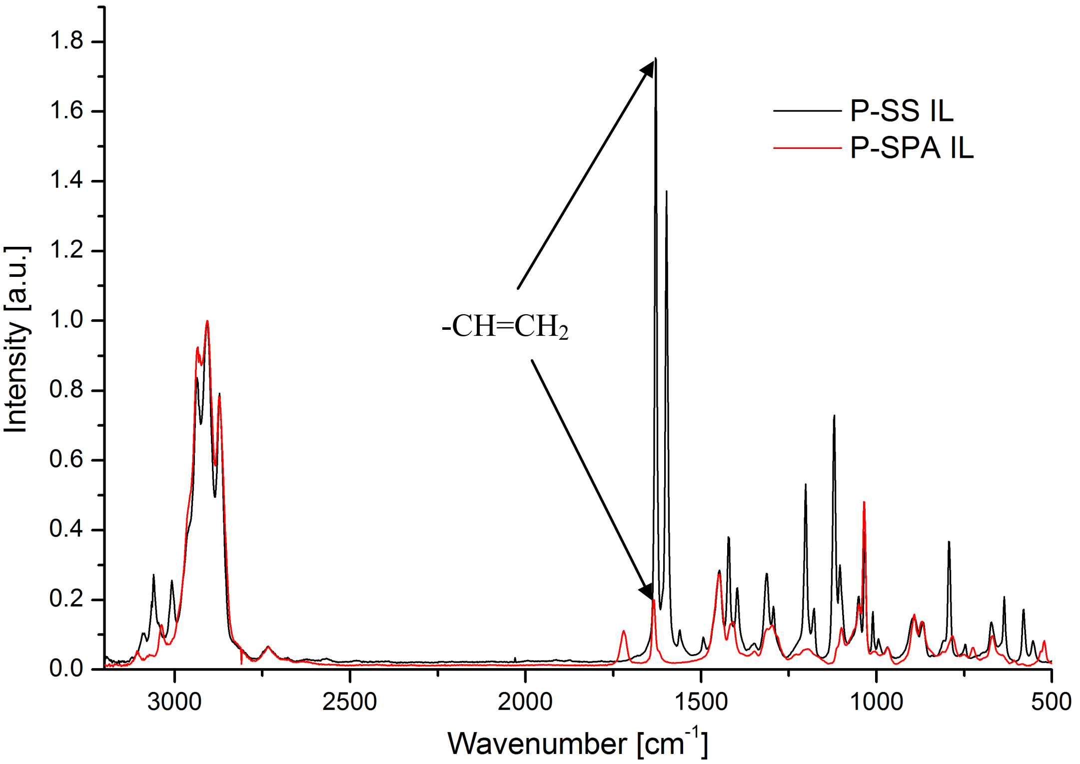


Figure S2. Raman spectra of P-SS and P-SPA monomeric ionic liquids. The 1630 cm^{-1} bands marked with the arrow represent the polymerisable vinyl C=C bond.

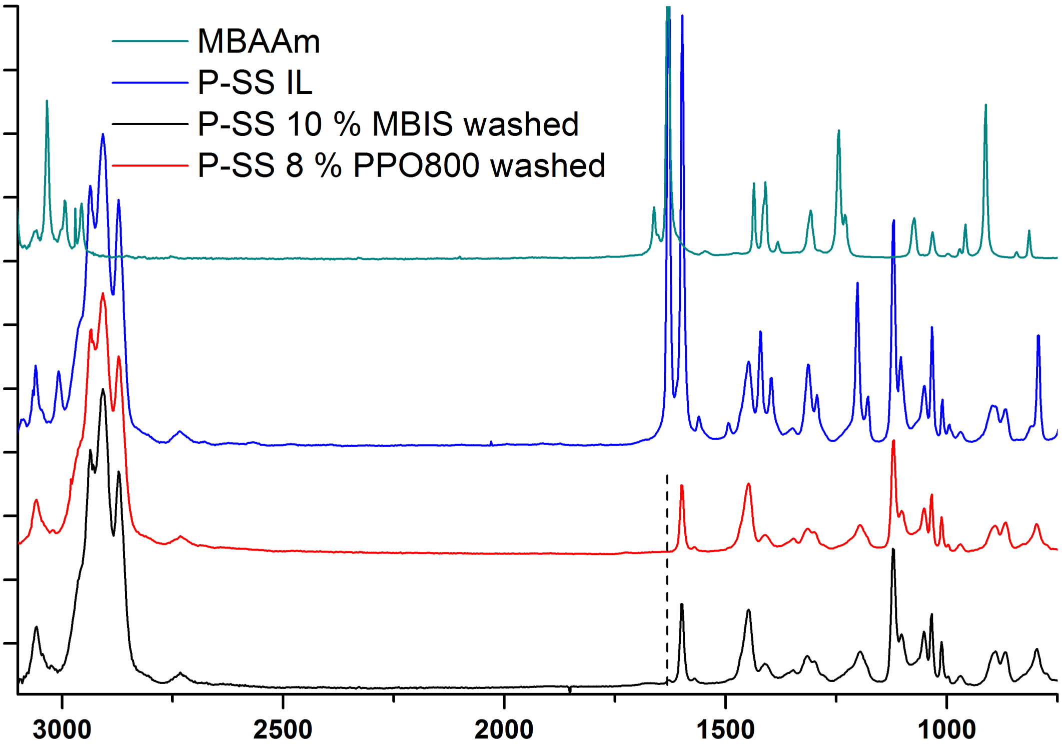


Figure S3. Raman spectra of the MBAAm crosslinker, monoeric P-SS IL and two washed gels: P-SS with 10 % MBAAm and P-SS with 8 % PPO800. The dashed line indicates 1630 cm^{-1} where the polymerisation active C=C band appears in the monomers.

7. DSC characterisation

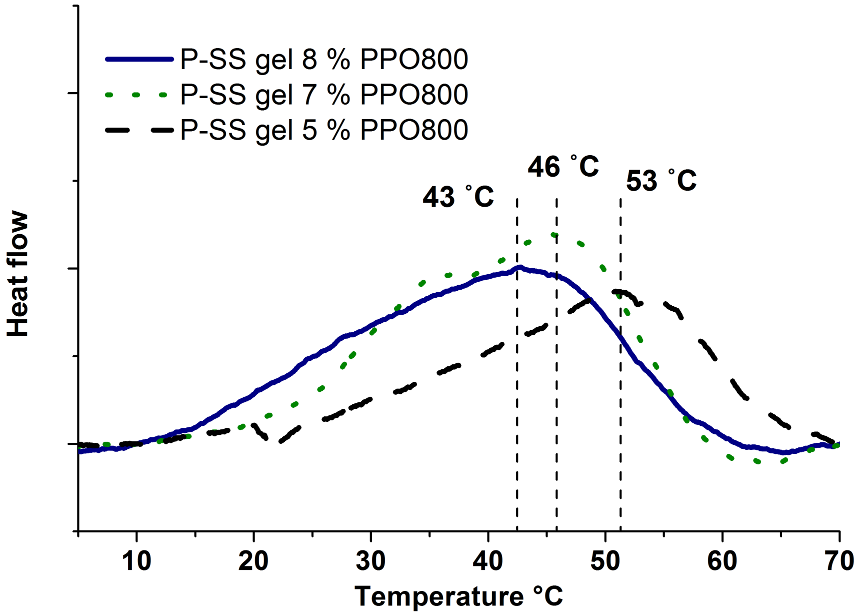


Figure S4. DSC scans of water swollen P-SS gels made with different amounts of PPO800 crosslinker.

Literature studies on polymerisation of poly(NIPAM) gels with chain transfer agents and RAFT agents have shown improved LCST behaviour.[1, 2] Therefore, we added 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid as a RAFT agent (monomer: RAFT ratio 50:1) to the P-SPA 5 mol% PPO800 system in order to investigate if similar improvements can be made in our thermoresponsive system. The resulting gels had the same broad DSC thermal characteristics as the gel without the RAFT agent (Fig. S5).

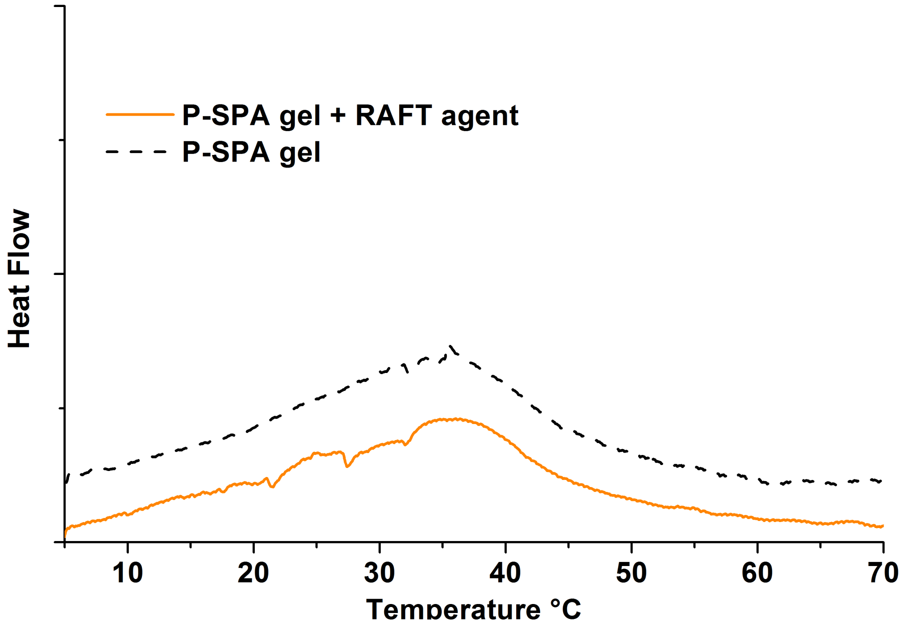


Figure S5. DSC scans of water swollen P-SPA gels made with 5 mol% PPO800 crosslinker. RAFT agent was used in 50:1 monomer-RAFT agent ratio.

References:

1. Liu, Q.; Li, S.; Zhang, P.; Lan, Y.; Lu, M., Facile preparation of PNIPAM gel with improved deswelling kinetics by using 1-dodecanethiol as chain transfer agent. *Journal of Polymer Research* **2007,** *14*, 397-400.
2. Liu, Q.; Zhang, P.; Qing, A.; Lan, Y.; Lu, M., Poly(N-isopropylacrylamide) hydrogels with improved shrinking kinetics by RAFT polymerization. *Polymer* **2006,** *47*, 2330-2336.