Supporting Information

Ionic Liquid modulation of swelling and LCST behavior of *N*-isopropylacrylamide polymer gels.

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I Analytical Techniques

Karl Fischer Titration Analysis

The IL and the water phases 1:1 wt %, were vigorously agitated in glass vials and allowed to reach the saturation equilibrium by the separation of both phases for at least 72 hours. This period, as well as in previous studies [1, 2] proved to be the minimum time required guaranteeing a complete separation of the two phases and that no further variations in water mole fractions occurred for longer periods.

The miscibility of water in the IL-rich phase was determined, where the samples were taken from the vials using glass syringes maintained dry and at the same temperature of measurements. All measurements of the miscibility of water with the ILs in question were performed at ambient temperature and pressure conditions, using a Mettler-Toledo® V20 Volumetric Karl Fischer Titrator.

Density

Densities were measured using a DMA-500 from Anton-Paar® (Australia). The density meter uses the “oscillating U-tube principle” [3] to determine the density of the liquid. Measurements were performed at atmospheric pressure from 20 to 60 °C for both neat and water-saturated ILs.

Viscosity

Viscosity measurements were performed at atmospheric pressure in the temperature range 20 to 60 °C on both neat and water-saturated ILs using an Anton-Paar® AMVn Viscometer, which employs a falling ball technique [4].

Differential Scanning Calorimeter

Differential Scanning Calorimetry (DSC) was performed using the Perkin Elmer® Pyris 1 Calorimeter. Individual scans were performed in the temperature range from

10 to 50 °C at a scan rate of 5 °C per minute. 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 156.60, 231.93 and 419.53 °C, respectively. Transition temperatures were taken from the peak maximum of the thermal transition.

Ionogel Diameter Measurements

Each polymerized ionogel was placed in de-ionized water at 20 °C for 24 hours and the swelling behavior recorded. Next, the gels were then placed in de-ionized water at 45 °C for 1 min. This temperature ensures the swollen hydrated ionogels undergo the LCST phase transition (as individually measured using DSC) [5].

All measurements were performed using a Mitutoyo® digital micrometer calibrated to a resolution of 1 μm.

NMR of Linear Homopolymers

^{1}H NMR spectra of purified linear polymers were recorded at 120 °C on a 400 MHz Bruker NMR in DMSO-d^6 solvent and are reported in parts per million (δ) from the residual solvent peak. The meso diad % of the polymer samples were calculated from the backbone methylene proton peaks of the homopolymers.

Rheometry

All measurements were performed on an Anton-Paar® MCR301 rheometer equipped with a steel bottom plate. Initially, all polymerized ionogels (12 mm diameter) were immersed in deionized water for 24 hours. The swollen gels were then analysed for changes in the loss and storage moduli through the LCST by using a temperature step program. All the swollen ionogels were analysed in oscillation mode with a parallel plate PP15 tool 15 mm diameter at 0.05 % strain and frequency of 10 Hz. The data points were collected every second and the following temperature ramp was applied: isotherm at 20 °C below the measured

LCST for 5 min, increase to 45 °C (20 °C /min) [5]. Because the water-swollen ionogels shrink during LCST transition, the instrument was set to adjust the gap according to 1N normal force on the sample. Therefore the smaller peaks in moduli present the plots are due to the instrument adjusting the pressing force of the sample [6, 7].

Infra-red Spectroscopy

Fourier transformed Infrared (FT-IR) measurements were taken with a Perkin Elmer Spectrum GX FT-IR System® instrument equipped with an attenuated total reflectance accessory in transmittance mode from 1000 to 3000 cm^{-1} at 20 scans with 2 cm^{-1} resolution. For solution samples, a droplet was transferred onto an ATR crystal, while ionogel samples were pressed into a KBr pellet.

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}.

Scanning Electron Microscopy

Ionogel and hydrogel were imaged using scanning electron microscopy (SEM) performed on a Carl Zeiss EVOLS 15 system at an accelerating voltage of 26.11 kV. Gold Sputtering of all gels was performed on a Polaron® SC7640 Auto/Manual High Resolution Sputter Coater. All gels were coated with a 10 nm gold layer, under the following conditions: Voltage 1.5 kV, 15 mA for 2 minutes at a coating rate of 5 nm/min.

II NMR of Ionic Liquids

1-Ethyl-3-Methylimidazolium EthylSulphate $[C_2mIm][EtSO_4]$

^{1}H NMR, δ_H (400 MHz; CD_3CN): 1.12-1.17 (t, 3H, CH_3), 1.32-1.37 (t, 3H, CH_3), 3.73 (s, 3H, CH_3), 3.9-3.99 (m, 2H, CH_2), 4.04-4.09 (m, 2H, CH_2), 4.69 (s, H, CH), 7.2-7.27 (d, H, CH), 7.32-7.33 (d, H, CH) ppm.

1-Ethyl-3-Methylimidazolium *bis*(trifluoromethanesulfonyl)imide $[C_2mIm][NTf_2]$

^{1}H NMR, δ_H (400 MHz; CD_3CN): 1.54 (t, 3H, CH_2CH_3), 3.93 (s, 3H, N-CH_3), 4.26 (q, 2H, N-CH_2), 7.52-7.67 (m, 2H, H, CH and H, CH), 8.88 (s, 1H, CH) ppm.

1-Ethyl-3-Methylimidazolium Dicyanamide $[C_2mIm][DCA]$

^{1}H NMR δ_H (400 MHz; CD_3CN): d 1.42 (t, CH_3), 3.84 (s, n-CH_3), 4.19 (q, N-CH_2), 7.67 (s, CH), 7.76 (s, CH), 9.10 (s, N-CH-N) ppm.

Trihexyltetradecylphosphonium Dicyanamide $[P_{6,6,6,14}][DCA]$

^{1}H NMR δ_H (400 MHz; $CDCl_3$): 2.0-2.3 (m, 8H, CH_2), 1.4-1.5 (m, 16H, CH_2), 1.2-1.3 (m, 32H, CH_2), 0.79-0.85 (m, 12H, CH_3) ppm.

III NMR of Linear Homopolymers

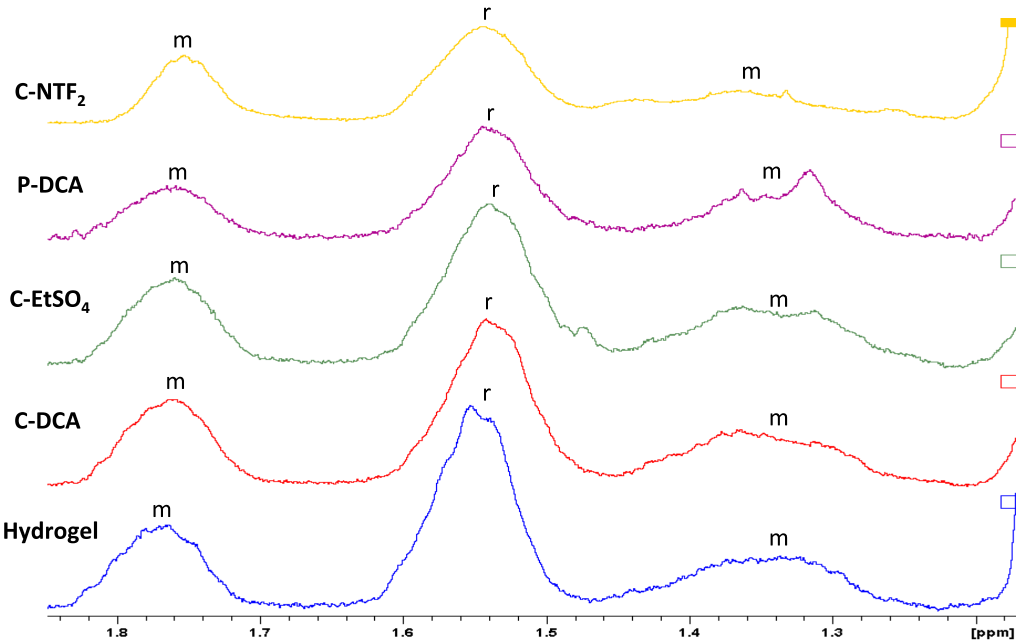

Figure S1. ^{1}H NMR (400 MHz, DMSO-d^6, 120 °C) spectra of linear pNIPAAM homopolymers prepared in various solvents. Shown are the meso (m) and racemo (r) dyads from the region of the backbone methylene protons at 1.2 - 1.8 ppm.

IV Vibrational Spectroscopy of Swollen Gels

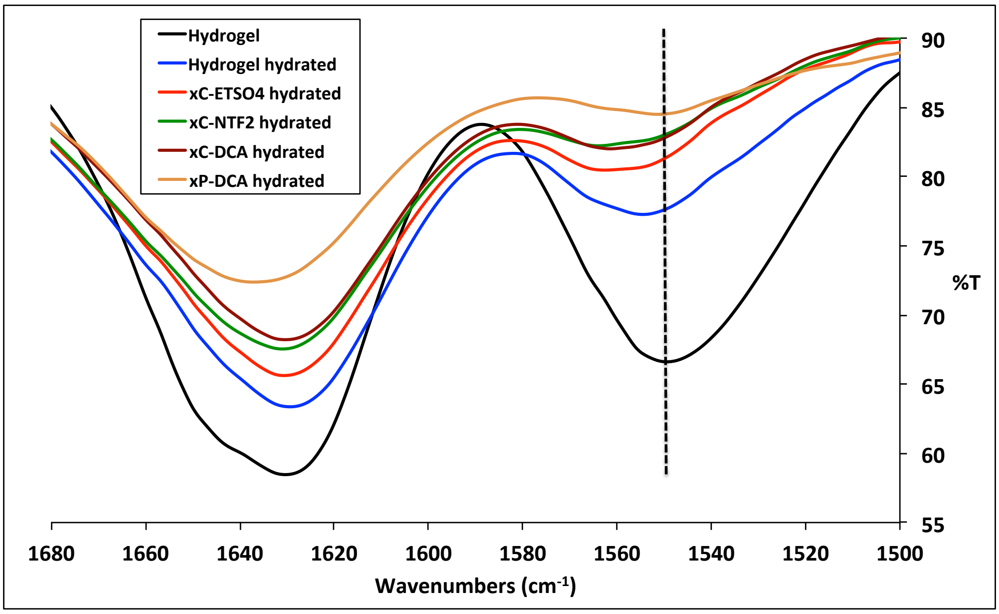

Figure S2. Infra-red spectroscopy recorded between 1500-1680 cm^{-1} of hydrogel (black), a hydrated hydrogel (red), and xC-NTf$_2$ hydrated (blue).

V Karl-Fischer Analysis of IL/Water Mixtures

Ionic Liquid	M_{IL}/g mol^{-1}	Mole Fraction (x_w)
$[C_2mim][EtSO_4]$	236.29	Miscible[5]
$[C_2mim][NTf_2]$	391.31	0.2156
$[C_2mim][DCA]$	177.21	Miscible
$[P_{6,6,6,14}][DCA]$	549.9	0.4284

Table S1. Experimental mole fraction solubilities of water (x_w) in Imidazolium- and Dicyanamide-based ILs at 20 °C.

VI Density and Viscosity of IL/Water Mixtures

Ionic Liquid	**Temperature (°C)**	Non-hydrated **Density (g/cm^3)**	Hydrated **Density (g/cm^3)**	Non-hydrated **Viscosity (mPa.s)**	Hydrated **Viscosity (mPa.s)**
C-EtSO$_4$[5]	20	1.2413	1.1754	93.6088	3.433
	30	1.2345	1.1114	74.6075	3.0444
	40	1.2277	1.1050	49.7062	2.4212
	50	1.221	1.0984	34.6231	1.9927
	60	1.212	1.0916	19.2359	1.7316
C-NTf$_2$	20	1.5154	1.4641	32.4902	23.9337
	30	1.5062	1.4534	27.3582	16.8197
	40	1.4965	1.4429	20.0407	12.7826
	50	1.4868	1.4327	15.1803	10.0548
	60	1.457	1.4226	12.2837	8.1369
C-DCA	20	1.0953	1.0478	15.9440	1.0474
	30	1.0887	1.0415	13.5997	1.0411
	40	1.0822	1.0351	10.5365	1.0347
	50	1.0757	1.0284	8.4365	1.0280
	60	1.0693	1.0214	6.9552	1.0211
P-DCA	20	0.8978	0.9012	330.6532	208.6054
	30	0.892	0.8952	252.8495	119.6639
	40	0.8863	0.8892	154.6302	74.5571
	50	0.8806	0.8832	99.7411	49.1904
	60	0.8759	0.8772	67.6314	34.1912

Table S2. Summary of density and viscosity values obtained for imidazolium- and dicyanamide-based ILs as a function of addition of water and increasing temperature.

VII Scanning Electron Microscopy

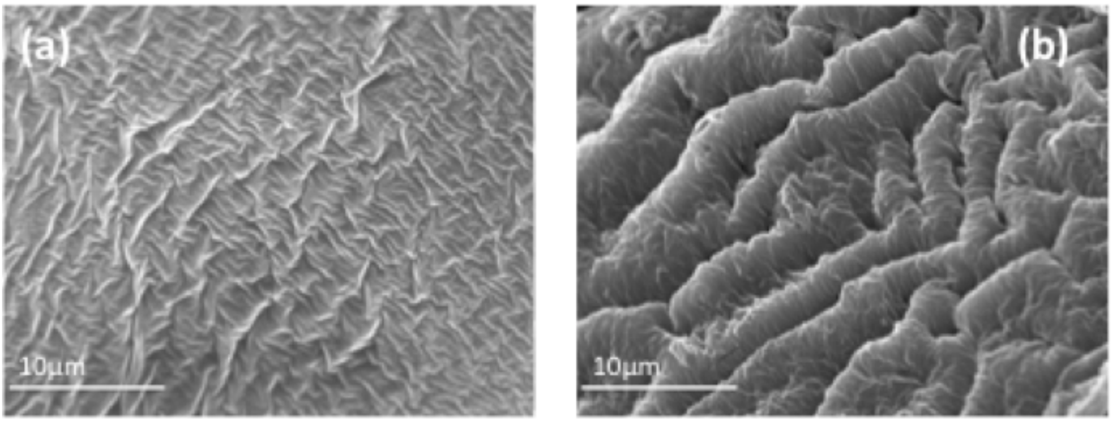

Figure S3. SEM images of pNIPAAM hydrogel, (a) after polymerization and (b) after swelling in deionized water [5].

VIII Rheometry of Actuating Gels

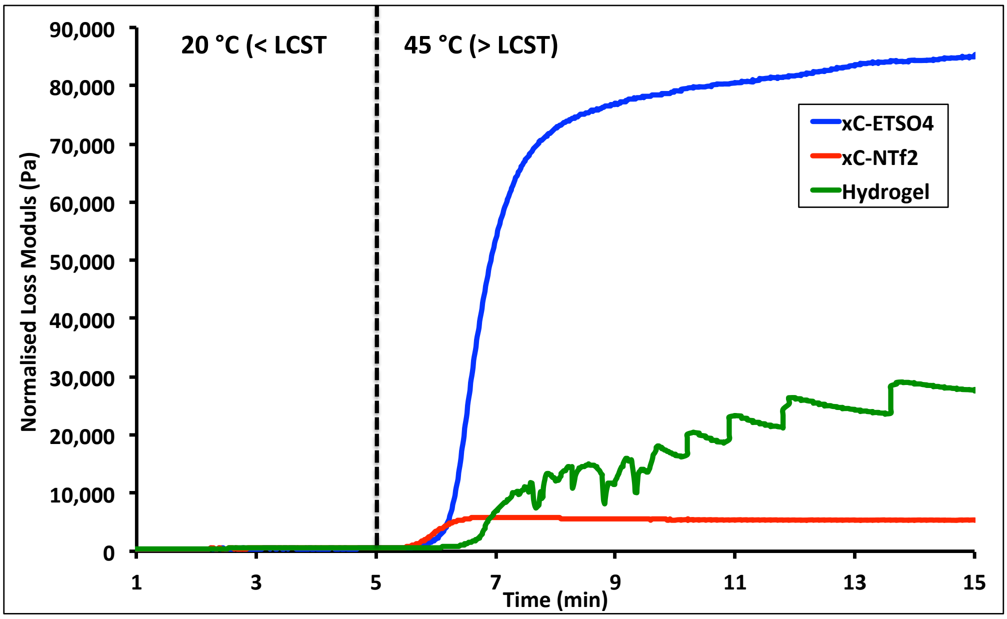

Figure S4. Loss modulus of **(red)** x-C-$EtSO_4$ and (**blue**) x-NTf_2 plotted against time during a temperature ramp from 20 ^{o}C to 45 ^{o}C at 20 ^{o}C / min.

IX Raman Spectroscopy of Ionogel Leaching

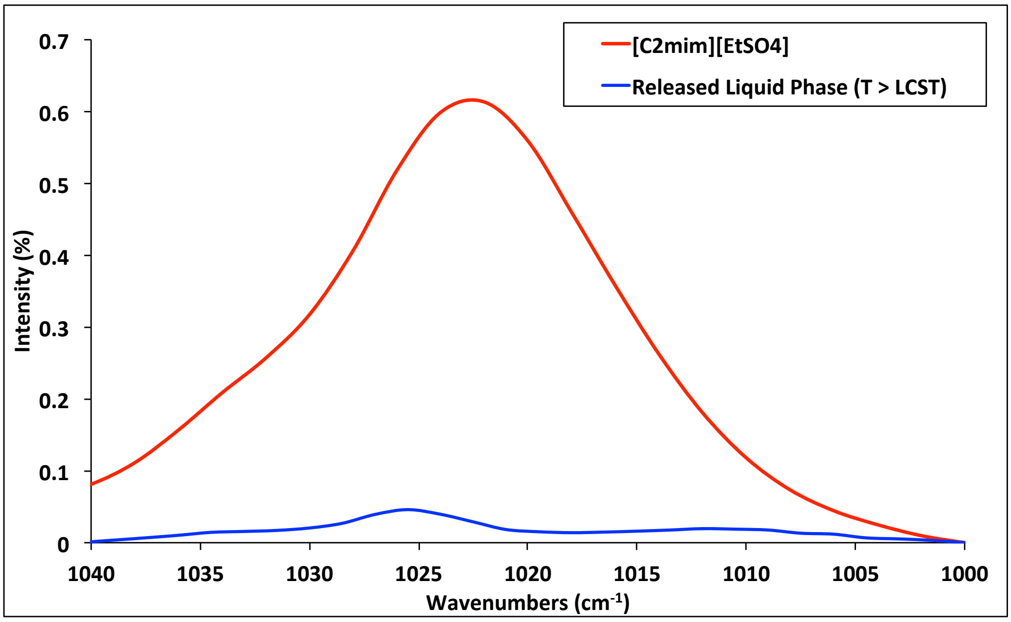

Figure S5. Raman spectra of symmetrical –SO_3- stretch found in (red) [C_2mim][$EtSO_4$] and (blue) aliquot of released liquid phase from xC-$EtSO_4$ above the LCST.

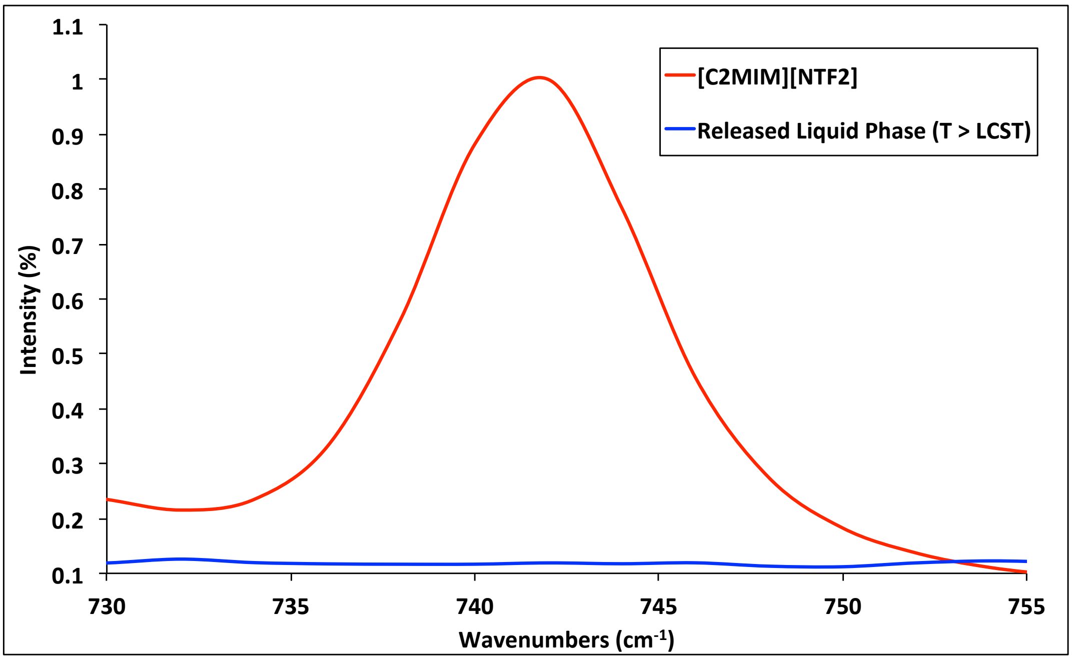

Figure S6. Raman spectra of symmetrical CF_3 bend found in (red) [C_2mim][NTf_2] and (blue) aliquot of released liquid phase from xC-NTf_2 above the LCST.

X References

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