Electronic Supplementary Information (ESI) for

Preparation of Thermoresponsive Hydrogels via Polymerizable Deep Eutectic Monomer Solvents

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Table S1. Elemental Analysis Results of Deep Eutectic Monomer Solvents

Sample	C %	H %	N %	C/N ratio
NIPAM:ChCl (initial ratio 3:1)	61.52	10.32	12.18	5.05
Predicted values:				
NIPAM:ChCl 3:1	57.65	9.88	11.69	5.03
NIPAM:ChCl 10.5:1	61.54	9.77	12.14	5.07
NIPAM:AcChCl (initial ratio 3:1)	58.84	9.68	11.15	5.27
Predicted values:				
NIPAM:AcChCl 3:1	57.64	9.41	10.76	5.35
NIPAM:AcChCl 4:1	58.72	9.47	11.04	5.31

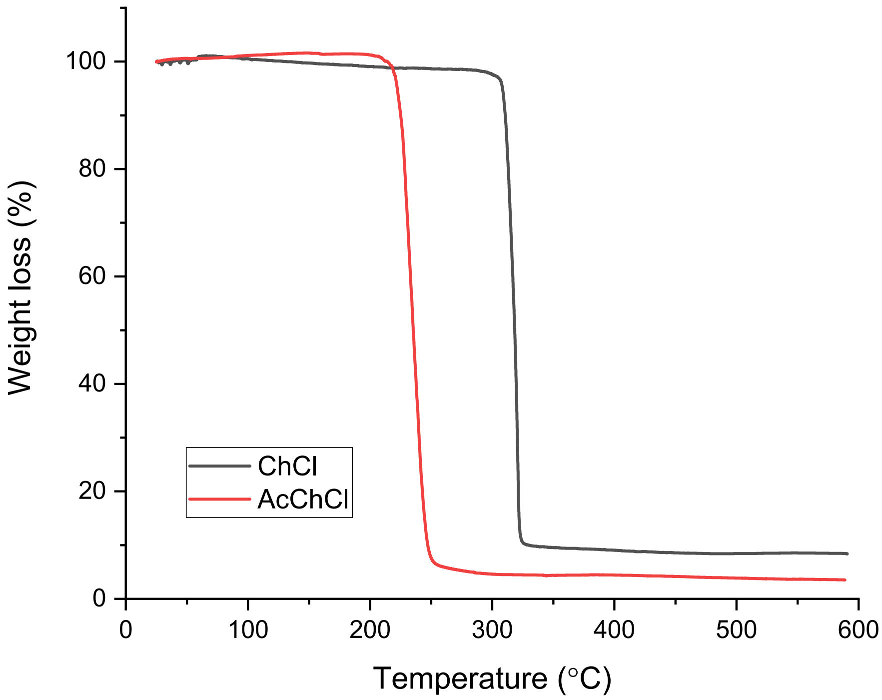

Figure S1. Thermogravimetric analysis (TGA) of choline chloride and acetylcholine chloride.

Table S2. Onset Temperature and Weight Loss Data from TGA Analysis.

Sample	T_{onset} **(°C)**	**Total Weight loss (%)**
NIPAM	160	98.55
ChCl	307	89.93
NIPAM-ChCl 3:1 eutectic	236	93.91
AcChCl	222	96.06
NIPAM-AcChCl 3:1 eutectic	178	93.11

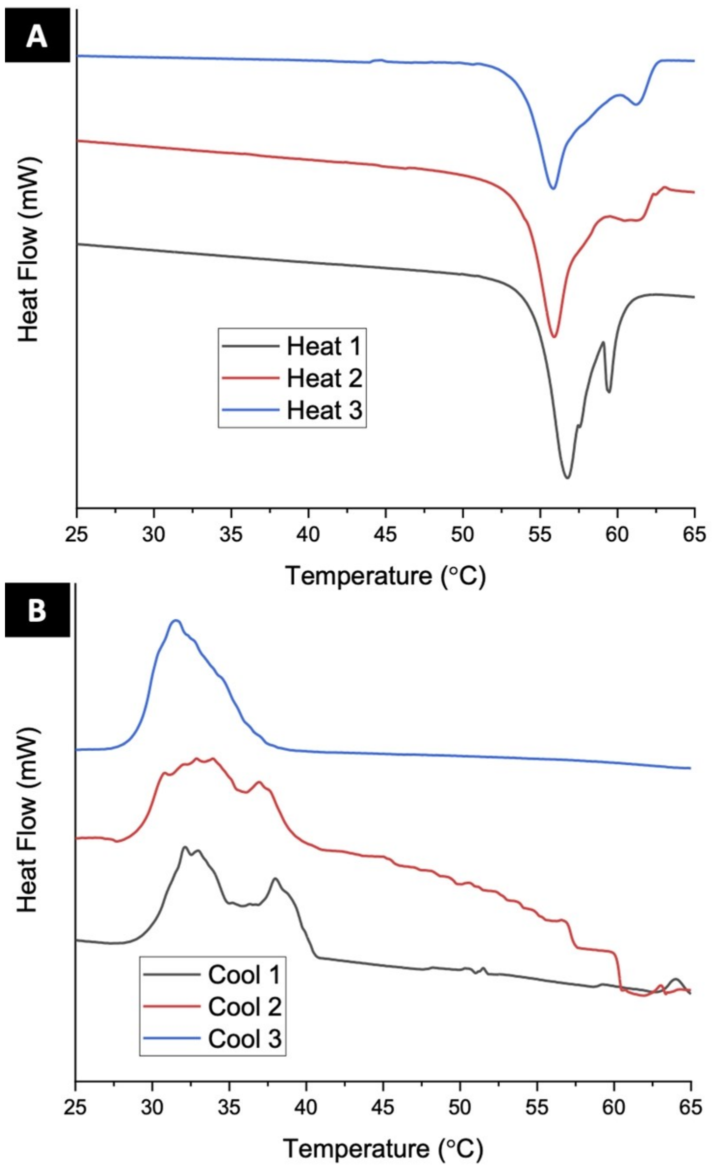

Figure S2. DSC analysis of NIPAM:ChCl 3:1 DEM systems and reproducibility of multiple heating (panel A) and cooling (panel B) loops. Heating/cooling rate = 5 °C min^{-1}.

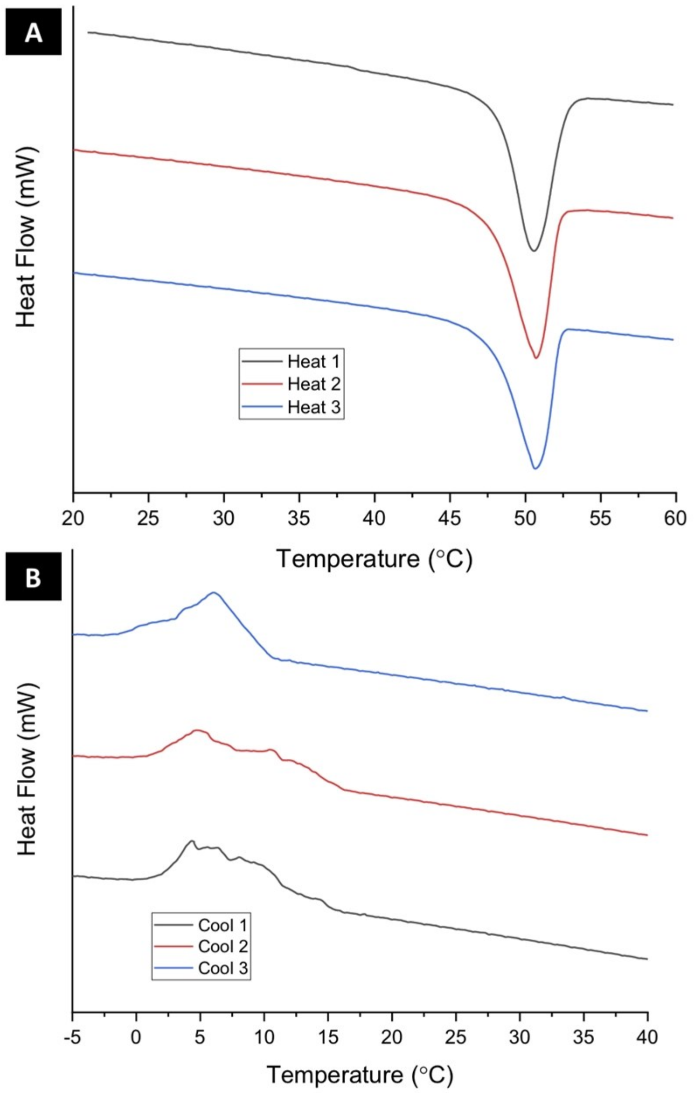

Figure S3. DSC analysis of NIPAM:AcChCl 3:1 DEM systems and reproducibility of multiple heating (panel A) and cooling (panel B) loops. Heating/cooling rate = 5 °C min^{-1}.

Table S3. DSC Analysis of NIPAM:ChCl 3:1 DEM systems (heating/cooling rate = 5 °C min^{-1}).

Cycle	T_{onset} (°C)	Mean	T_{max}(°C)	Mean	Δ*H* (J/g)
NIPAM:ChCl 3:1					
Heat 1	54.2	53.9 ± 0.3	56.5	55.9 ± 0.6	69.2 ± 3.4
Heat 2	53.8		55.7		
Heat 3	53.6		55.6		
Cool 1	40.4	39.1 ± 1.6	32.2	32.6 ± 1.4	– 67.1 ± 2.5
Cool 2	39.3		34.0		
Cool 3	37.5		31.6		
NIPAM:AcChCl 3:1					
Heat 1	48.2	48.0 ± 0.2	50.6	50.7 ± 0.1	79.1 ± 7.6
Heat 2	47.8		50.7		
Heat 3	48.1		50.8		
Cool 1	15.2	15.1 ± 1.2	4.4	5.1 ± 1.1	– 50.7 ± 3.0
Cool 2	16.3		4.9		
Cool 3	13.8		6.1		

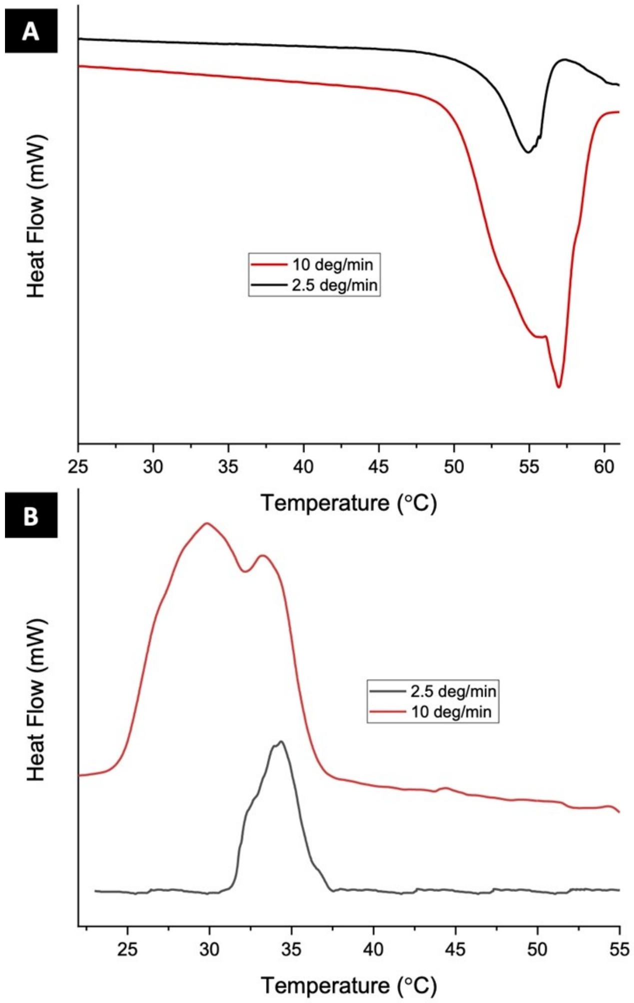

Figure S4. DSC analysis of NIPAM:ChCl 3:1 DEM systems as a function of DSC heating rate.

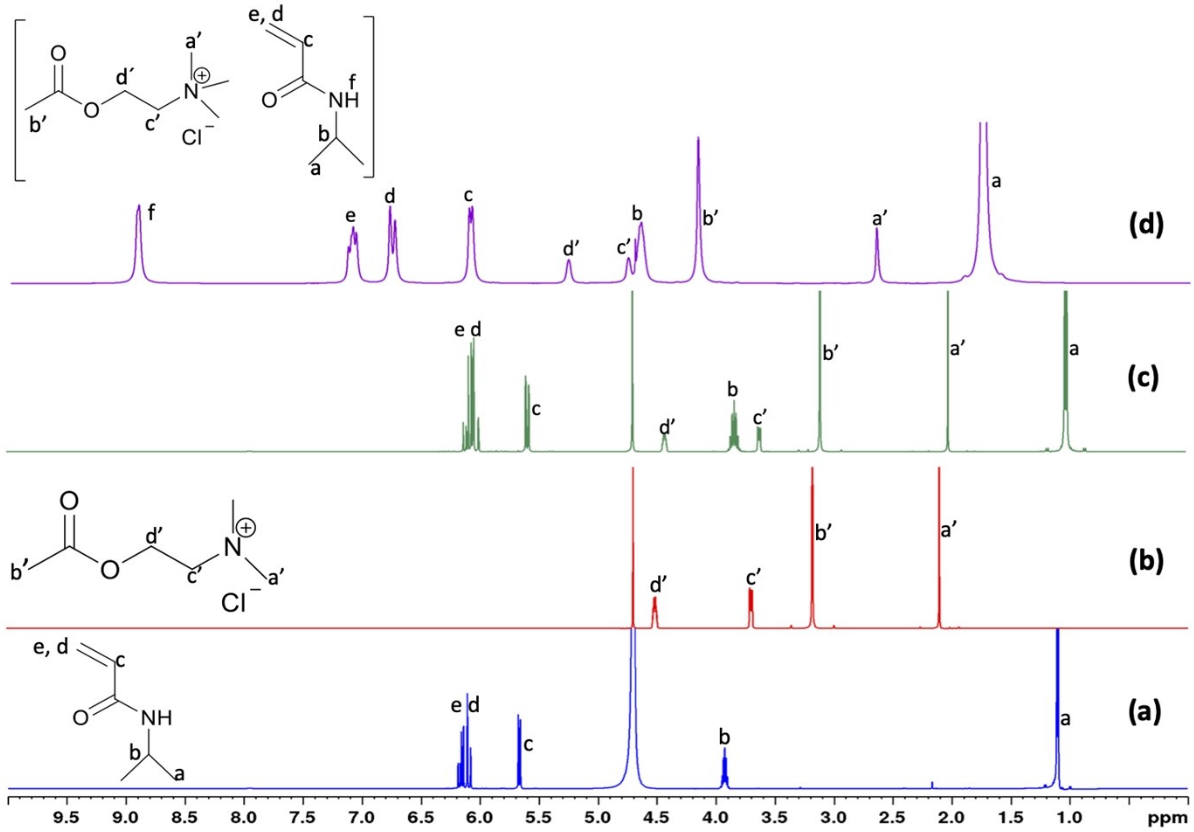

Figure S5a. ^{1}H NMR spectra a) NIPAM; b) AcChCl; c) a 3:1 mixture of NIPAM and AcChCl (all in D_2O); d) NIPAM:AcChCl DEM obtained by using a small capillary of D_2O placed in the sample.

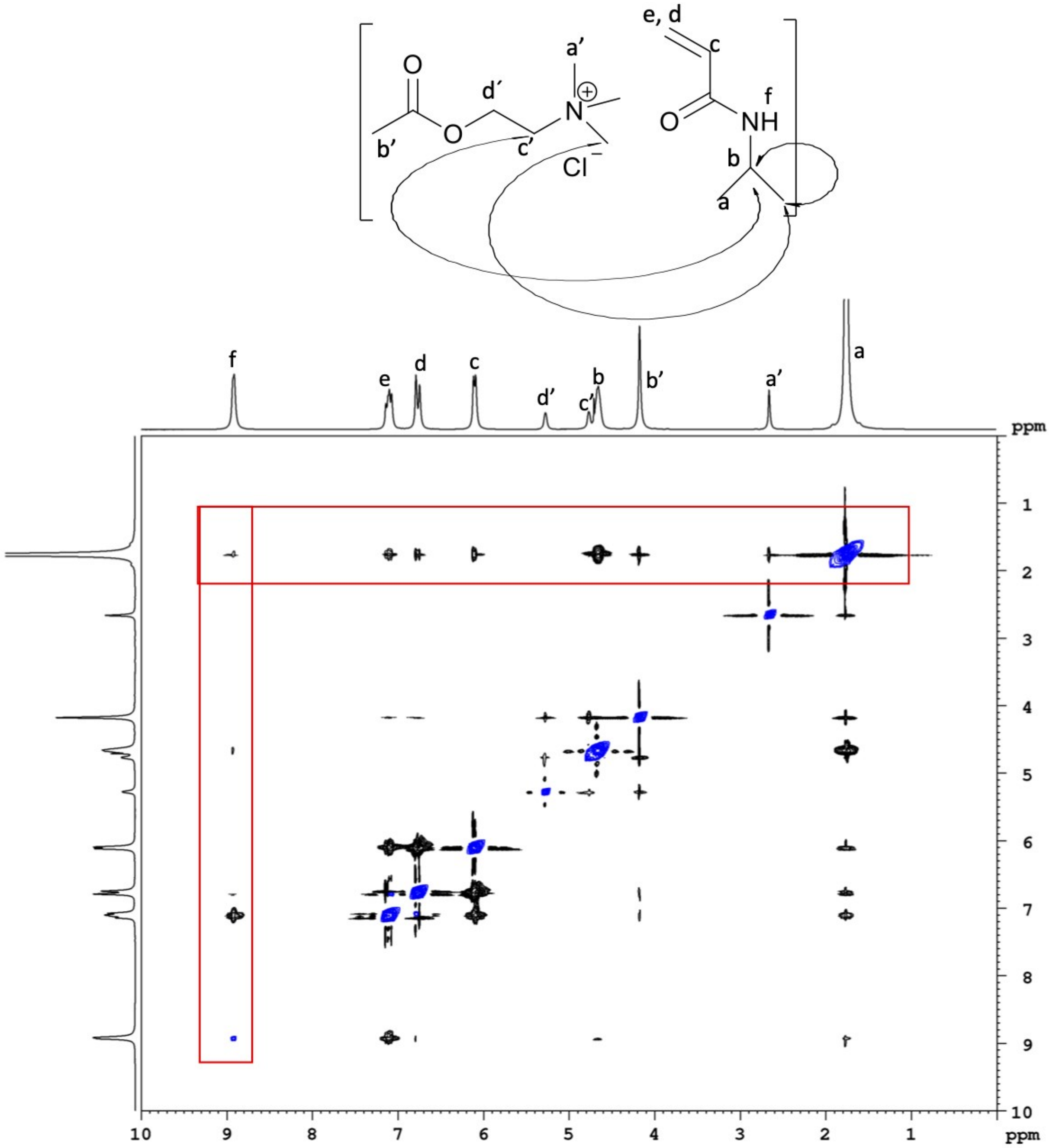

Figure S5b. ^{1}H-^{1}H ROESY spectrum of NIPAM:AcChCl DEM.

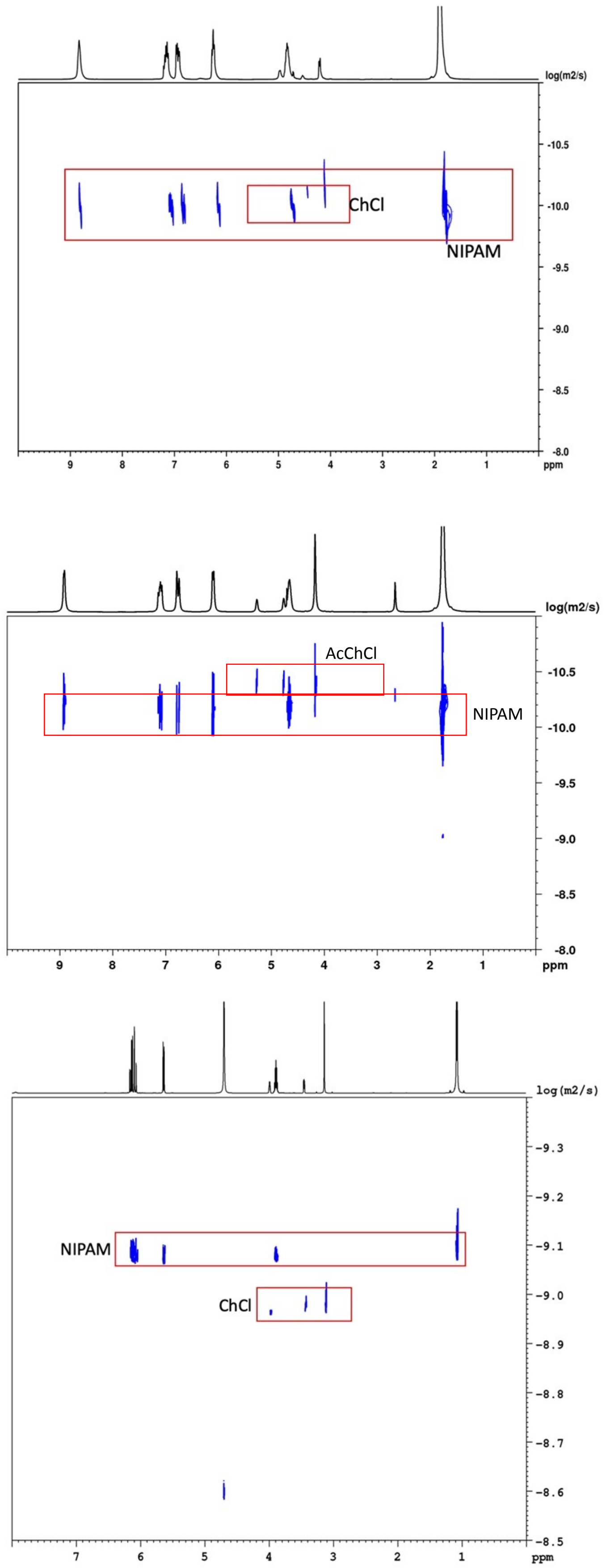

Figure S6. [1]H DOSY NMR spectra of (top) NIPAM:ChCl DEM; (middle) NIPAM:AcChCl DEM; (bottom) NIPAM and ChCl dissolved in D_2O.

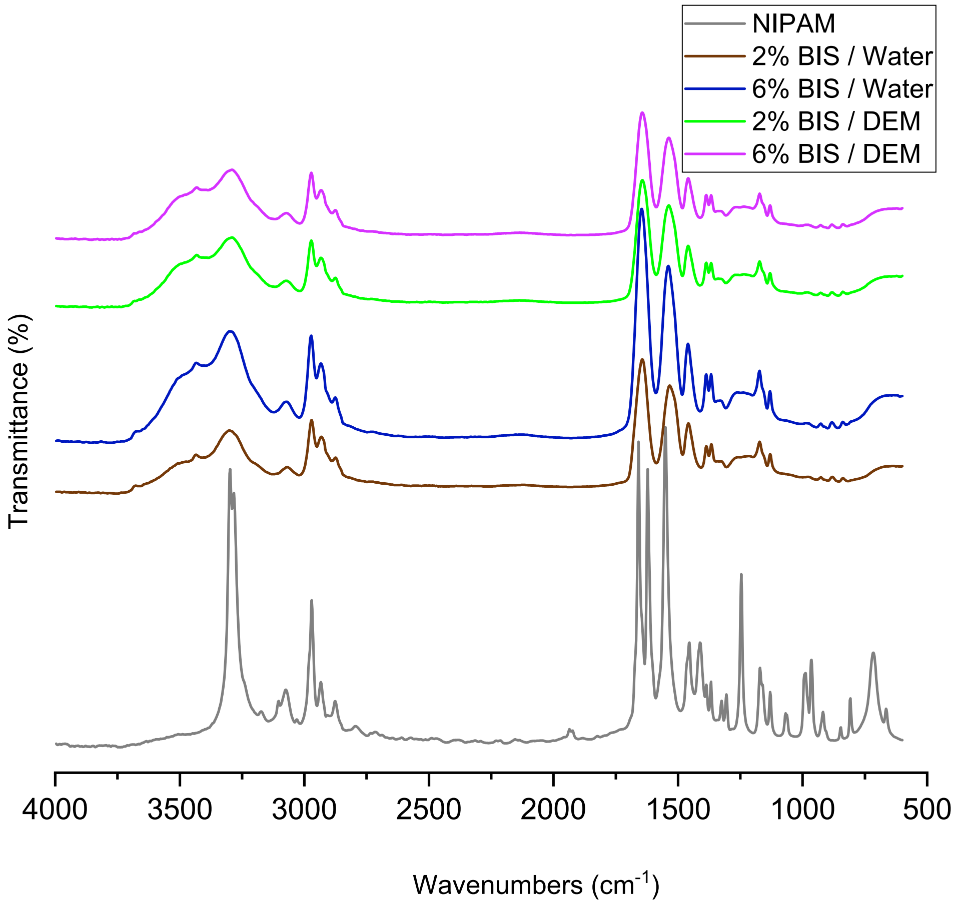

Figure S7. ATR-FTIR spectra of poly(NIPAM-co-BIS) hydrogels prepared in both DEMs and water.

The bands appearing at 2850 cm^{-1} and 2900 cm^{-1} are assigned to C–H stretching vibrations. The amide group N–H bending peak is also observed at 1550 cm^{-1}. The broad band at 3240 cm^{-1} is consistent with O–H and N–H stretching vibrations of carboxyl and amide groups. Additionally, the broad intense band in the range 800–1300 cm^{-1} can be assigned to C–O stretching and C–H bending vibrations.

Table S4. TGA Analysis of PNIPAM-BIS Hydrogels.

Sample	T_{onset} (°C)	**Weight loss T < 200 °C (%)**	**Weight loss 200 T < 600 °C (%)**
BIS 2% / DEM	346.9	10.48	80.68
BIS 6 % / DEM	346.3	7.87	86.87
BIS 2 % / water	362.2	2.45	92.73
BIS 6 % / water	345.3	4.88	91.72

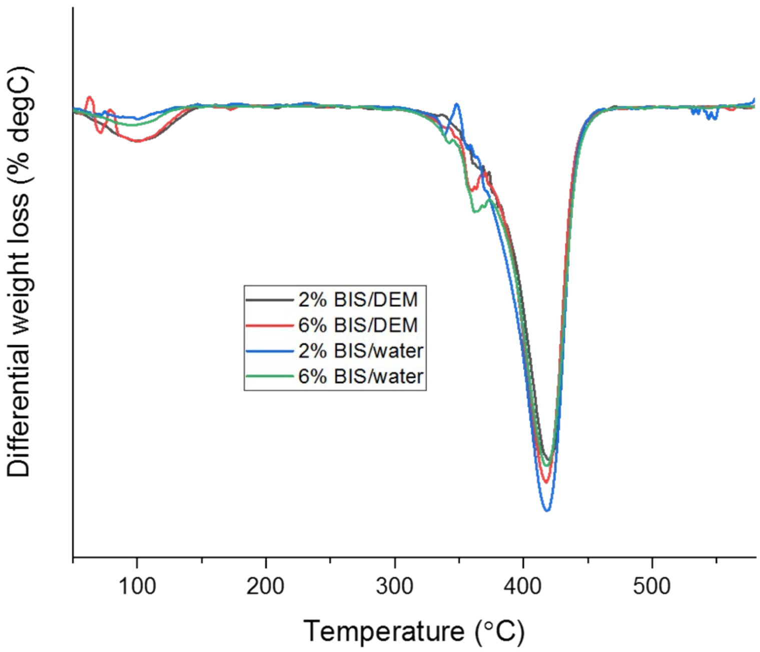

Figure S8. Differential TGA Analysis of PNIPAM-BIS Hydrogels.

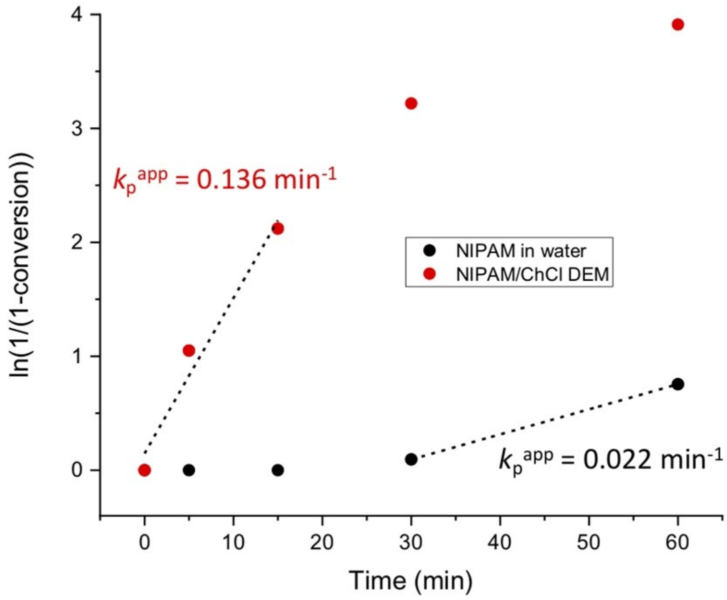

Figure S9. Plot of ln(1/(1-conversion) versus time for the polymerization of NIPAM in both a NIPAM:ChCl DEM system as well as in water.

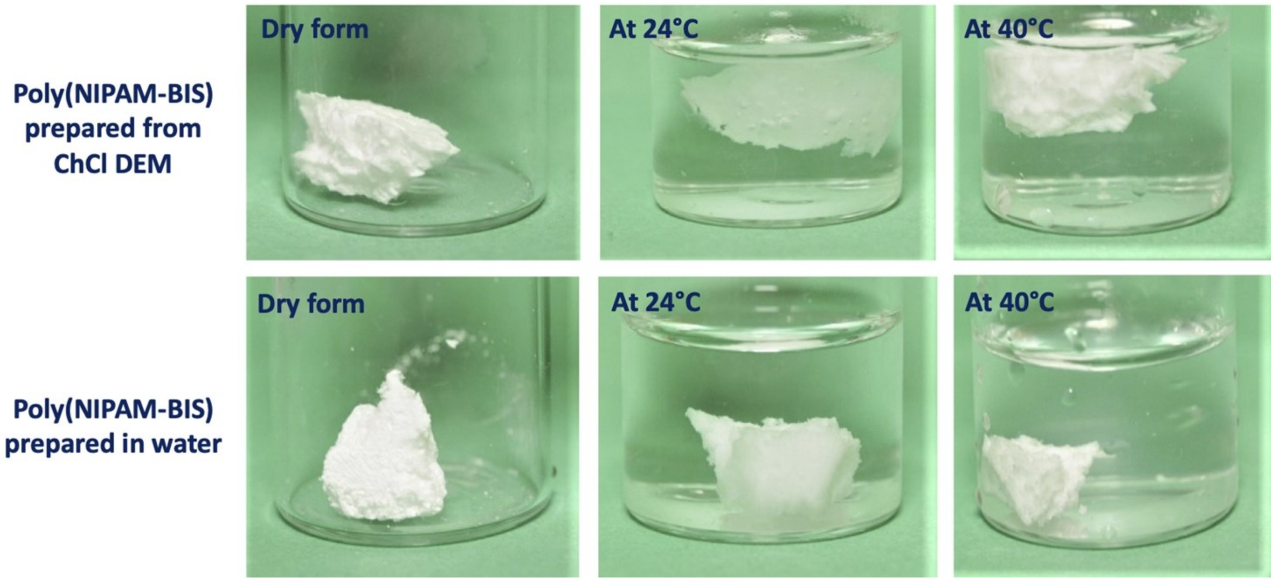

Figure S10. Photographs of freeze-dried hydrogels prepared by different methods.

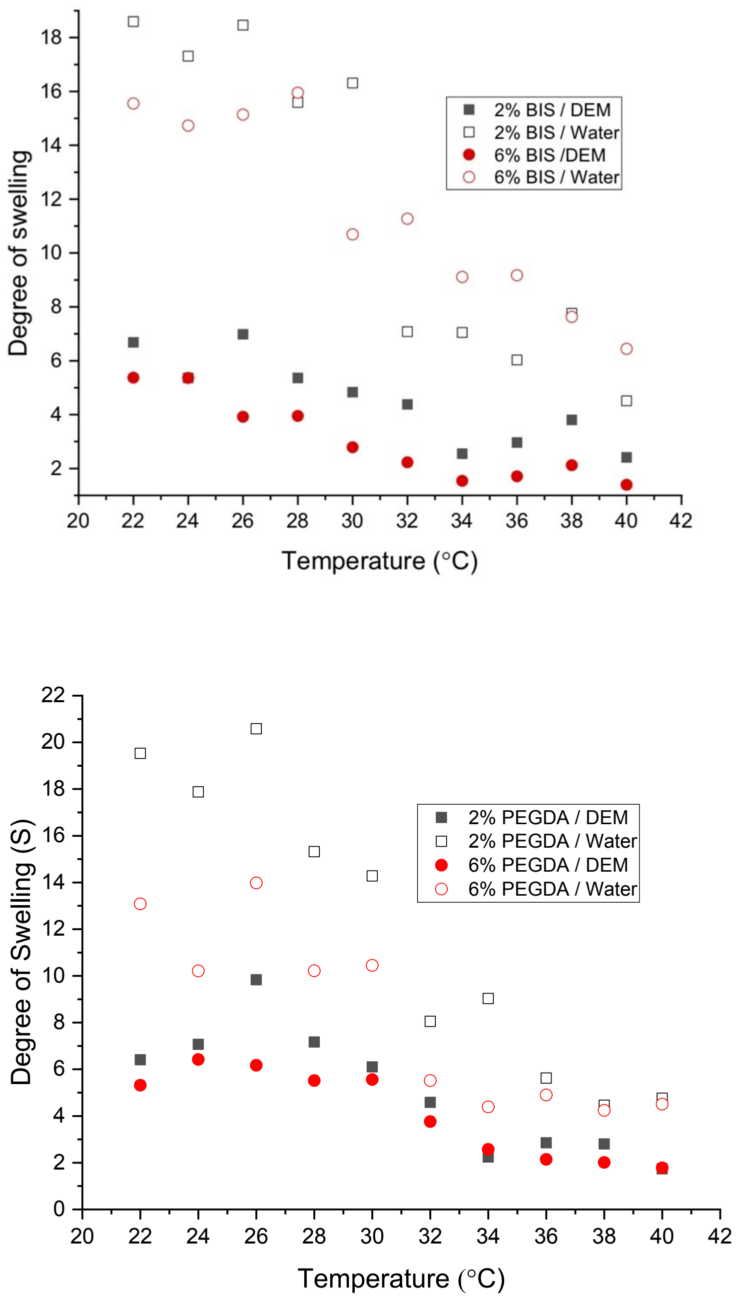

Figure S11. Degree of swelling (S) versus temperature for polyNIPAM-based gels prepared from ChCl DEMs (filled symbols) or water (open symbols). The crosslinker concentration was either 2 % (squares) or 6 % (circles) relative to NIPAM. Top panel: BIS as crosslinker; Bottom panel: PEGDA as crosslinker.

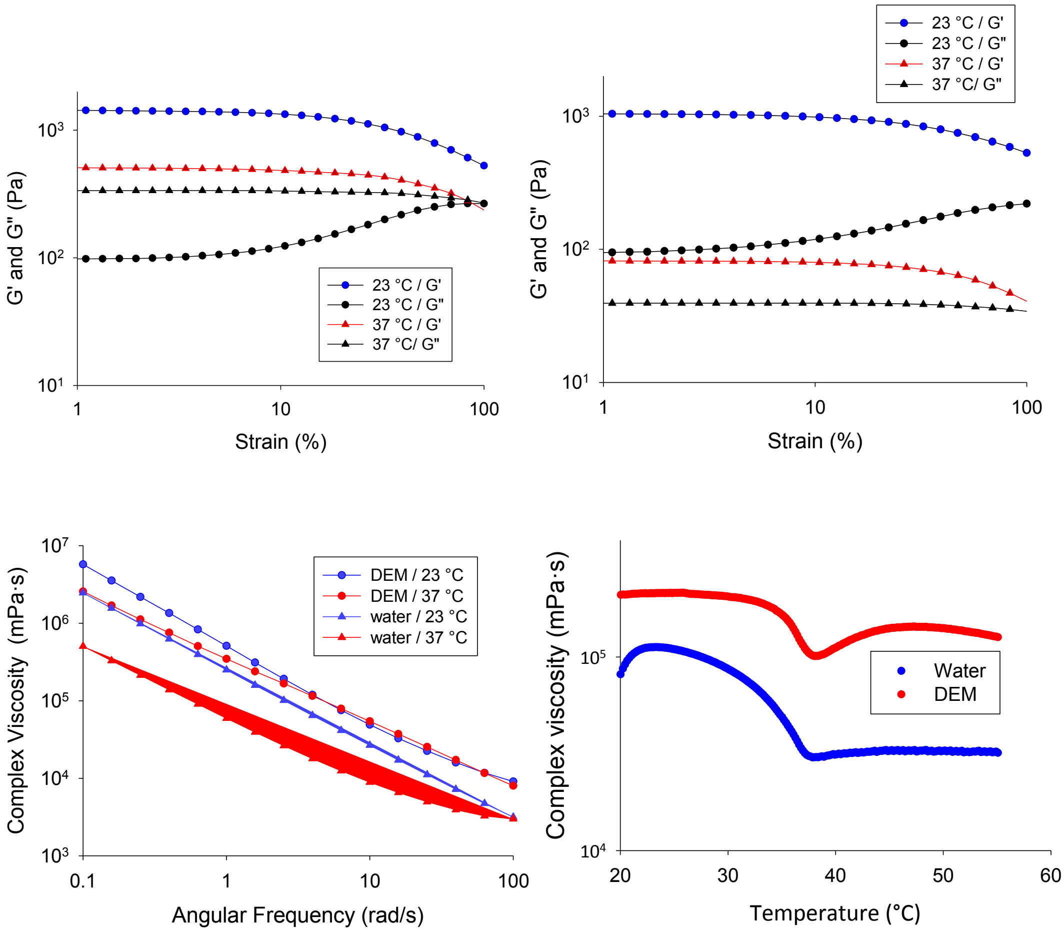

Figure S12. Rheological analysis of poly(NIPAM-co-BIS) gels swollen with water. (Top left): amplitude sweep of gels prepared from ChCl DEM. (Top right): amplitude sweep of gels prepared from water. (Bottom left): Frequency sweep comparison of the two gels. (Bottom right): Complex viscosity of the two gels as a function of temperature.

Flory-Rehner Analysis:

Flory-Rehner theory was used to determine the average molecular weight between crosslinks (M_c) based on the equilibrium degree of swelling (S_{eq}) of the hydrogels prepared in this work. The Flory-Rehner equation for an affine network model can be stated as:

$$\ln(1-\phi)+\phi+\chi\phi^2=\frac{d_p V_s}{M_c}\left[\left(\frac{\phi}{2\phi_0}\right)-\left(\frac{\phi}{\phi_0}\right)^{1/3}\right]$$

Where ϕ = polymer volume fraction in the gel, χ the Flory-Huggins parameter between the polymer and solvent, d_p the density of polymer, V_s the molar volume of solvent, M_c the average molecular weight between crosslinks, and ϕ_0 the polymer volume fraction of the gel in a reference state (see below discussion).

The following temperature and concentration dependence of χ was used:[1]

$$\chi=\frac{1}{2}-A\left(1-\frac{\theta}{T}\right)+C\phi+D\phi^2$$

Where θ is the theta temperature for NIPAM (303.6 K), and A, C and D are coefficients. Values of $A = -2$, $C = 0.32$, $D = 0.24$ were used based on recently published values,[1] however we acknowledge there are numerous functional forms (and values of these coefficients) reported in the literature.

The volume fraction of polymer ϕ was calculated from equilibrium swelling values via the following relation:

$$\phi=\frac{1}{1+\frac{d_p}{d_s}S_{eq}}$$

Where d_p and d_s are the densities of polymer and solvent respectively. The values of d_p and d_s used in this work for polyNIPAM and water were 1.1 and 1.0 g mL^{-1} respectively.

The volume fraction of polymer for each gel at different temperatures studied, in addition to the temperature and concentration-dependent value of the Flory-Huggins parameter, were used to determine the value of M_c that provided the best fit to experimental data. The value of M_c was then used to calculate the effective cross-linking density q_{eff}, which is defined as M_0/M_c where M_0 is the molar mass of a NIPAM repeat unit (113 Da).

There is significant debate regarding the value and interpretation of ϕ_0;[2] numerous authors define this quantity as the polymer volume fraction during gel preparation, however Lopez and Richtering[1] show that this often gives poor fit to data and ϕ_0 is typically much smaller (2 – 6 % of this value). In this work, ϕ_0 was allowed to be a free parameter in the fit to experimental data, and the following values were obtained:

Gel	$\boldsymbol{\phi_0}$
Water	0.020
ChCl DEM	0.056
AcChCl DEM	0.073

For the gel prepared in water, a value of ϕ_0 = 0.020 is comparable to the work of Lopez and Richtering,[1] whereas the DEM-based gels present higher ϕ_0 values, indicative of their different method of preparation.

Table S5. Swelling properties of poly(NIPAM-co-PEGDA) gels when immersed in water.

Method of gel preparation	**Temp (°C)**	$\mathbf{S_{eq}}$[a]	$\boldsymbol{M_c}$ **(Da)**[b]	$\boldsymbol{q_{eff}}$[c]
ChCl DEM	22	6.29 ± 0.17	4165 ± 190	0.0273
	40	1.64 ± 0.05		
Water	22	21.69 ± 0.53	23620 ± 980	4.82×10^{-3}
	40	3.65 ± 0.10		

[1] Lopez, C.G. and Richtering, W. *Soft Matter,* **2017,** 13, 8271
[2] Quesada-Pérez, M. *et al, Soft Matter,* **2011,** 7, 10536.