Supporting Information

Distinctly Different Solvation Behaviors of Poly(*N*,*N*-diethylacrylamide) Gel in

Water/Acetone and Water/DMSO Mixtures

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1. The Attribution of Free and Confined DMSO in PDEA-Water/DMSO Mixtures
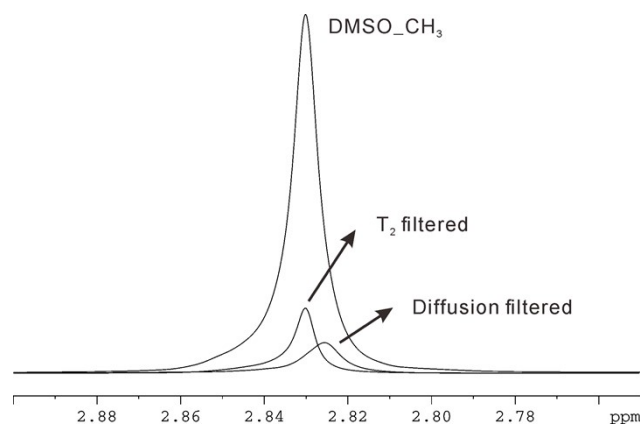
Figure S1 NMR peak of DMSO methyl protons in PWD2.5 at 313 K (a) normal; (b) T_2 filtered; (c) diffusion filtered. One component with longer T_2 and the other with larger self-diffusion coefficient are showed respectively.

Although DMSO shown only one peak in the high temperature collapsed gel network, the diffusion and transverse relaxation experiments demonstrate that such a DMSO peak consists of two overlapped signals. Herein, we show an example of PWD2.5 at 313 K in Figure S1. In Figure S1, peak a is the normal DMSO proton signal, peak b is the signal filtered with T_2 (the residual signal is mainly composed of free solvent) and peak c is the signal filtered with diffusion (the residual signal is mainly composed of confined solvent).
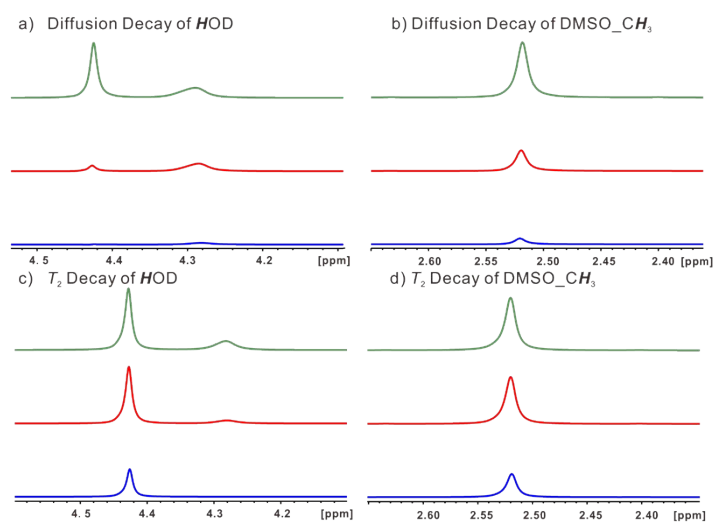

Figure S2 Diffusion decay and T_2 decay slices for water and DMSO protons in PWD2.5 at 313 K. The three slices of T_2 spectra correspond to three different tau and the three slices of diffusion spectra correspond to three different gradient field intensity.

For clarity of the free and confined solvent attribution, three slices are extracted from the

diffusion and T_2 relaxation spectra respectively. For water protons that split into two peaks, the left peak decays fast in diffusion experiment (see Figure S2 a) left peak) while slow in T_2 relaxation experiment (see Figure S2 c) left peak), was attributed to be the free water, while the right peak decays slow in diffusion experiment (see Figure S2 a) right peak) while fast in T_2 relaxation experiment (see Figure S2 c) right peak). Correspondingly, DMSO signals can be attributed into two components, the one with longer T_2 and smaller diffusion coefficient is attributed to be the free DMSO, while the one with shorter T_2 and larger diffusion coefficient is attributed to be the confined DMSO. Considering the T_2 fit function (I[t]= P_a*exp(-t/T_{2a})+ P_b*exp(-t/T_{2b}) in NMR experiment, the component ratio (P_a/P_b) of confined to free DMSO can be yielded by double exponential decay fitting, in which longer-T_{2b} and shorter-T_{2a} components represent the free DMSO and confined DMSO respectively.

2. Examples of Transverse Relaxation Time (T_2) Decay Fitting and Peak Deconvolution

Double exponential attenuation fittings of T_2 of acetone protons (in PWA2.5 and PWA5) and DMSO protons (in PWD2.5 and PWD5) are shown in Figure S3. For homogeneous comparison, two-component peak deconvolution of acetone protons in PWA2.5 and PWA5 at 318 K are shown in Figure S4. The acetone and DMSO composition (P_a/P_b) yielded from the above methods are listed in Table S1. The acetone contents in two different phases determined by above two methods are coincident very well. As for DMSO, the fitting of T_2 decay curve is of high accuracy. However, the two-component deconvolution of DMSO peak is very difficult, due to the complete overlap and unknown (possibly complicated) lineshapes of two DMSO components. Therefore we use T_2 relaxation method to determine the two DMSO components.
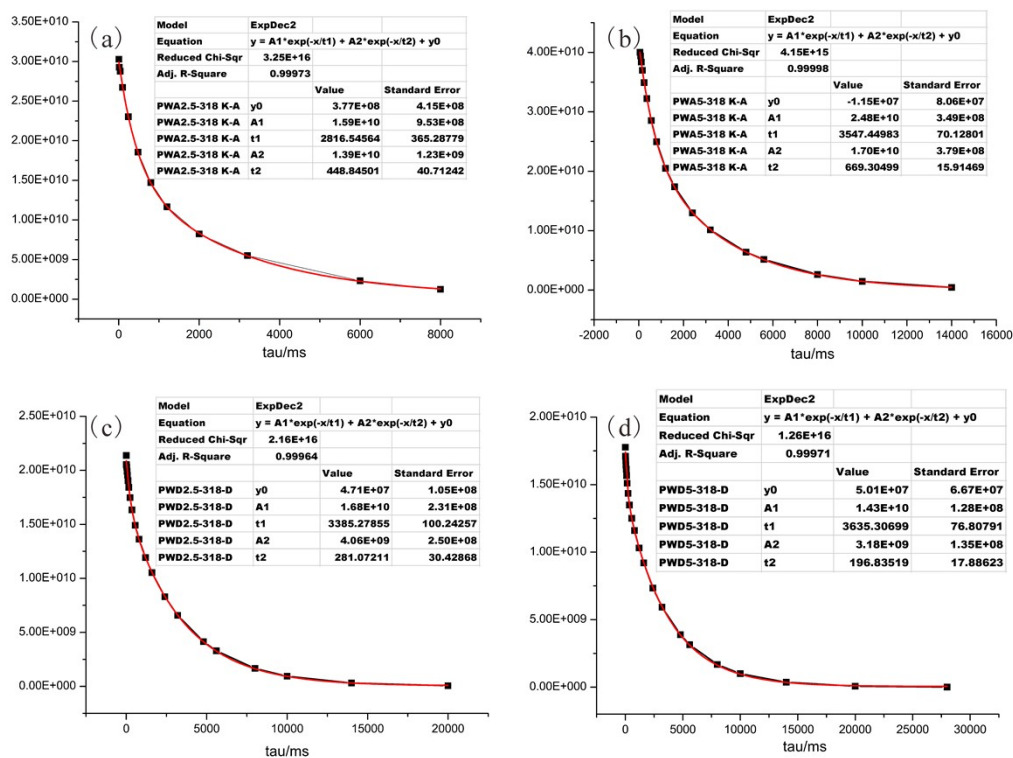
Figure S3 Exponential attenuation fittings of T_2 decay for acetone/DMSO protons in PWA2.5(a), PWA5(b), PWD2.5(c) and PWD5(d) at 318 K. The abscissa is tau, and ordinate is the corresponding area of peak integral. The value of t1 and t2 (in ms) are the transverse relaxation times (T_2) of the two component (confined and free): the smaller one (t2) is attributed to the confined solvent and the larger one (t1) is attributed to the free solvent. The coefficient A1 represent the content of free acetone or DMSO, and A2 represent the confined acetone or DMSO.
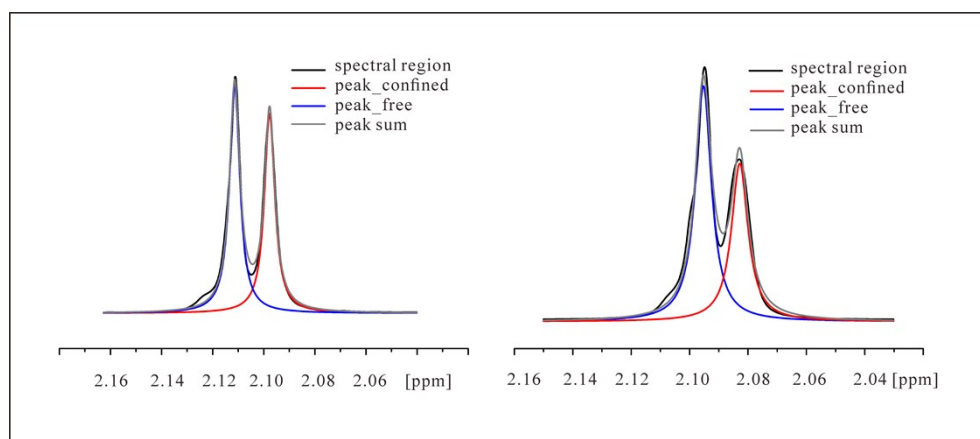
Figure S4. Peak deconvolution of acetone protons in PWA2.5 (left) and PWA5 (right) at 318 K.

**Table S1** The acetone and DMSO composition (P_a/P_b = A2/A1) obtained from T_2-decay fitting

and acetone composition from deconvolution.

	Deconvolution	T_2-fit
PWA2.5	0.88±0.04	0.87±0.09
PWA5	0.70±0.04	0.69±0.02
PWD2.5	-	0.24±0.02
PWD5	-	0.22±0.01

3. Aprotic solvent concentration measured by separating free solvent

To qualitatively confirm the validity of present NMR measurements for aprotic solvent concentration, the acetone and DMSO concentrations in free solvent mixtures of PWA5 and PWD5 induced by phase separation were measured independently. Two samples PWA5 and PWD5 were heated above 318 K at which the free solvents were expelled out of the gel network, and then these free solutions were taken out, weighted and transferred into NMR tubes. Liquid NMR measurement was carried on by adding a certain amount of ethanol into the solution as an internal concentration standard. The concentration of acetone and DMSO is calculated according to the integral ratio of the two CH_3 groups to ethanol CH_3 group (2:1). The free acetone concentration obtained is 1.50±0.05% for PWA5 and the free DMSO concentration is 6.64±0.13 % for PWD5, that is, the acetone concentration in free solvent mixture is lower than 5%, while the DMSO concentration in free solvent mixture is higher than 5%, confirming the preferential adsorption of acetone but exclusion of DMSO.

## 4. LCST of PNIPAM Linear Polymer in Water/Acetone and Water/DMSO Mixtures
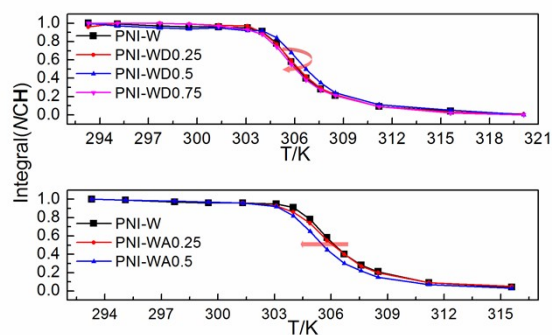
Figure S5. Temperature variation of the side chain methyne signals (*N*CH) integral of PNIPAM linear polymers in water/DMSO(up) and water/acetone(down) binary mixtures. The concentration of PNIPAM is 1% (w/w) and the concentration of DMSO and acetone are in molar fraction, i.e. WD0.25 means water DMSO=99.75:0.25.

Temperature variation of the side chain methyne signals (NCH) integral of PNIPAM linear polymers in water/DMSO and water/acetone binary mixtures are shown in Figure S5. It is found that the LCST of PNIPAM in 0.5% DMSO aqueous solution increases slightly compared to that in pure water, which is similar to the result measured by turbidimetry reported in the literature.[1]

5. LCST of PDEA Linear Polymer in Water/DMSO Mixtures

The LCST of PDEA linear polymer in 4 M DMSO aqueous solution and pure water are shown in Figure S6 for reference of the possible phase transition differences between gel network and linear polymer solution.
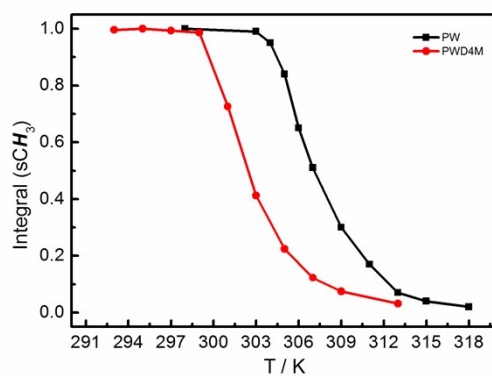
Figure S6. Temperature variation of the side chain methyl (sCH$_3$) signals integral of PDEA linear polymers in water/DMSO mixtures. The concentration of PDEA is 1% (w/w) and the concentration of DMSO in solvent is 4 M (~10% in molar fraction).

References

1.   H. Yamauchi and Y. Maeda, *J Phys. Chem. B*, 2007, **111**, 12964-12968.