



Supplementary Information

Thermo-reversible Sol-Gel Transition of Aqueous Solutions of Patchy Polymers

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Experimental

Synthesis

a) Synthesis of PCP [70:30 mol% of poly (DMA:AA)].

Into a 500 mL three-necked round bottom flask fitted with an overhead stirrer and an argon inlet were placed, *N,N*-dimethyl acrylamide (DMA, 26 g, 0.264 mol), acrylic acid (AA, 8.1 g, 0.112 mol) and deionized water (220 mL). The molar ratio of DMA:AA was 70:30. The pH of the solution was adjusted between 8 and 10 by addition of 1 M aqueous NaOH (20 mL). The homogeneous mixture obtained by stirring was de-aerated with Argon gas for 30 min followed by addition of ammonium persulfate (0.72 g, 0.0031 mol) and sodium metabisulfite (35 mg, 0.017 mol). Polymerization was allowed to proceed at 30°C for 90 min and the reaction was quenched by addition of 3 M HCl (10 mL). The resulting poly(*N,N*-dimethylacrylamide-*co*-acrylic acid), denoted in the manuscript as the precursor copolymer (PCP), was dialyzed against pure water for one week with intermittent replenishment of pure water and finally recovered by freeze-drying. The copolymer composition was determined by ¹³C NMR spectroscopy.

(b) Synthesis of HMCP. [70:20:10 mol% of poly (DMA:AA:DDA)]

Into a 500 mL two-necked round-bottom flask fitted with magnetic stirrer bar were placed PCP (6 g) and *N*-methylpyrrolidone (NMP, 200 mL) and reaction mixture was heated under stirring at 70°C for 24 h. To the reaction mixture, *n*-dodecyl amine, (1.22 g, 0.0066 mol, dissolved in 10 mL of NMP) and dicyclohexylcarbodiimide (DCC, 2.66 g, 0.0132 mol, dissolved in 10 mL of NMP) were added and the reaction was continued at 70°C for 12 h. The reaction mixture was allowed to cool to room temperature and the resulting polymer was precipitated into diethyl ether (3 L), filtered and dried at 50°C under vacuum. The polymer was purified by

dissolving it in chloroform (300 mL) and precipitating into diethyl ether (3 L). This process was repeated four times and the purified polymer was dried at 50°C under vacuum. Finally, the polymer was dissolved in deionized water containing 1 M NaOH (10 mL), which neutralized the carboxylic acid groups. The resultant hydrophobically modified copolymer (HMCP) solution was dialyzed against water and recovered by freeze-drying. The extent of hydrophobic modification in HMCP was determined by ¹H NMR spectroscopy.

Characterization

Gel Permeation Chromatography

Molecular weight of PCP was determined by gel permeation chromatography [Waters 2690] fitted with TSK GEL (7.5 x 300 mm) column and RI Detector. 1 mL/min flow rate of aqueous solution of NaNO₃ (0.1M) was used as the mobile phase. Polymer (10 mg) was dissolved in aqueous solution of 0.2 M NaNO₃ (10 mL) and the solution was filtered through a 0.45 μm filter before injection. Molecular weight of PCP was determined from the elution curve with reference to polyacrylamide standards.

Nuclear Magnetic Resonance Spectroscopy

The composition of PCP was determined by quantitative ¹³C NMR spectroscopy in DMSO-*d*₆ using a Bruker AV-500 spectrometer operating at a ¹³C frequency of 125 MHz with 10200 number of transients, 12.21 μsec of read pulse (p1), 10 sec of delay time (d1) 1.1 sec of acquisition time and inverse gated decoupling pulse sequence (zgig). The composition of HMCP was determined by ¹H NMR spectroscopy in CDCl₃ using a Bruker AV-500 spectrometer operating at a frequency of 500 MHz. All samples were allowed to dissolve for 4-5 days for homogenization before recording the spectra. Polymer concentrations used for ¹H and ¹³C NMR spectroscopy were 18 mg/mL and 85 mg/mL, respectively.

Differential Scanning Calorimetry

DSC experiments were performed using DSC Q100 (TA Instruments). Hermetic pans were filled with aqueous solutions of polymers of known weights (~5 mg). Dry N₂ gas was flowed through the cell at 10 mL/min. Temperature of the pans was ramped between 50°C and -50°C at 5°C /min. Data analysis was done using TA Advantage software.

Rheology

Specific viscosity measurements were carried out using Ubbelohde viscometers of three different capillary diameters under isothermal conditions by immersing them in a constant temperature water bath. Specific viscosities were measured over a temperature range of 4-25°C. Creep studies were performed with a drag flow rheometer (MCR301, Anton Paar) using cup and bob geometry (cup radius 9 mm, bob radius 8.33 mm) and Peltier temperature control fixture over the same temperature range of 4-25°C. Zero shear viscosities were calculated from the long time creep

compliance, and these were used further to calculate the specific viscosities.

Results and Discussion

Characterization

Three different mol% compositions of DMA:AA copolymers namely 60:40, 70:30 and 80:20 were synthesized using the procedure outlined in the synthesis section. Figure S1 shows results of the molecular weight determination of these copolymers using GPC. Figure S2 shows ^{13}C NMR spectra of different compositions of PCP recorded in $\text{DMSO}-d_6$. The peaks in the range 35-39 ppm correspond to methylene and methine protons of the backbone. The peaks at 173 ppm and 176 ppm, which are also shown in the inset, correspond to $>\text{C}=\text{O}$ of amide and acid, respectively. The various compositions of PCP were confirmed by integrated intensity ratio of carbonyl signals of amide and acid.

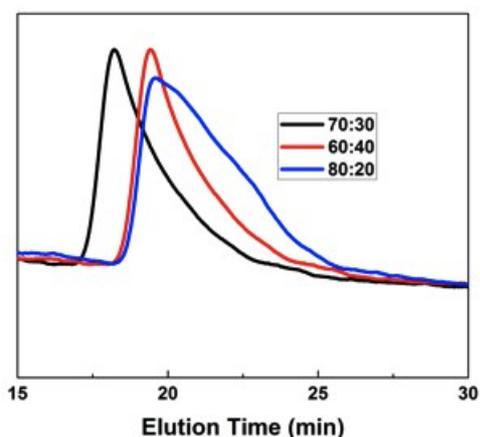


Figure S1: The molecular weights of different compositions of PCP were confirmed from the elution curve with reference to polyacrylamide standards.

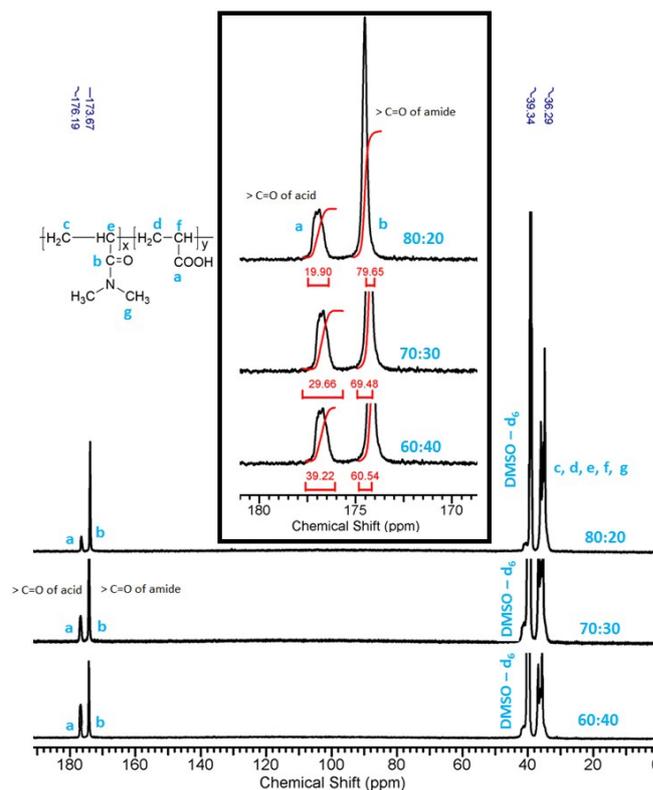


Figure S2 125 MHz ^{13}C NMR spectra of various compositions of PCP

10 mol% of AA units were coupled with DDA to make HMCP. Figure S3 show ^1H NMR spectra of various compositions of PCP and HMCP recorded in $\text{DMSO}-d_6$. The copolymer compositions of PCP were confirmed by comparing the areas under peaks at 2.81 and 1.0 - 2.4 ppm while the compositions of HMCP were confirmed by comparing areas under peaks at 0.87 and 2.81 ppm. The mol % of hydrophobic modification was calculated as follows

$$\text{Mol \% hydrophobic modification} = \frac{I_a \times \text{mol \% of DMA in backbone}}{I_b/2}$$

Here I_a & I_b respectively are the integrals of methyl protons of *n*-dodecyl chain and *N,N* dimethyl acrylamide units. From Fig 2, we have $I_a = 1$ and $I_b = 14$. The mol % DMA (70 %) in the sample of PCP was determined from ^1H and ^{13}C NMR spectroscopy. Hence, as determined from

$$\text{Mol \% hydrophobic modification} = \frac{1 \times 70}{7} = 10$$

Table T1 gives results of the solubility test of HMCP in water. It was found that HMCP of compositions 60:30:10 and 70:20:10 were soluble in water while 80:10:10 was insoluble in water. Thus, a critical hydrophilic-hydrophobic balance is necessary for dissolution of HMCP and exhibition of the abrupt sol-gel transition.

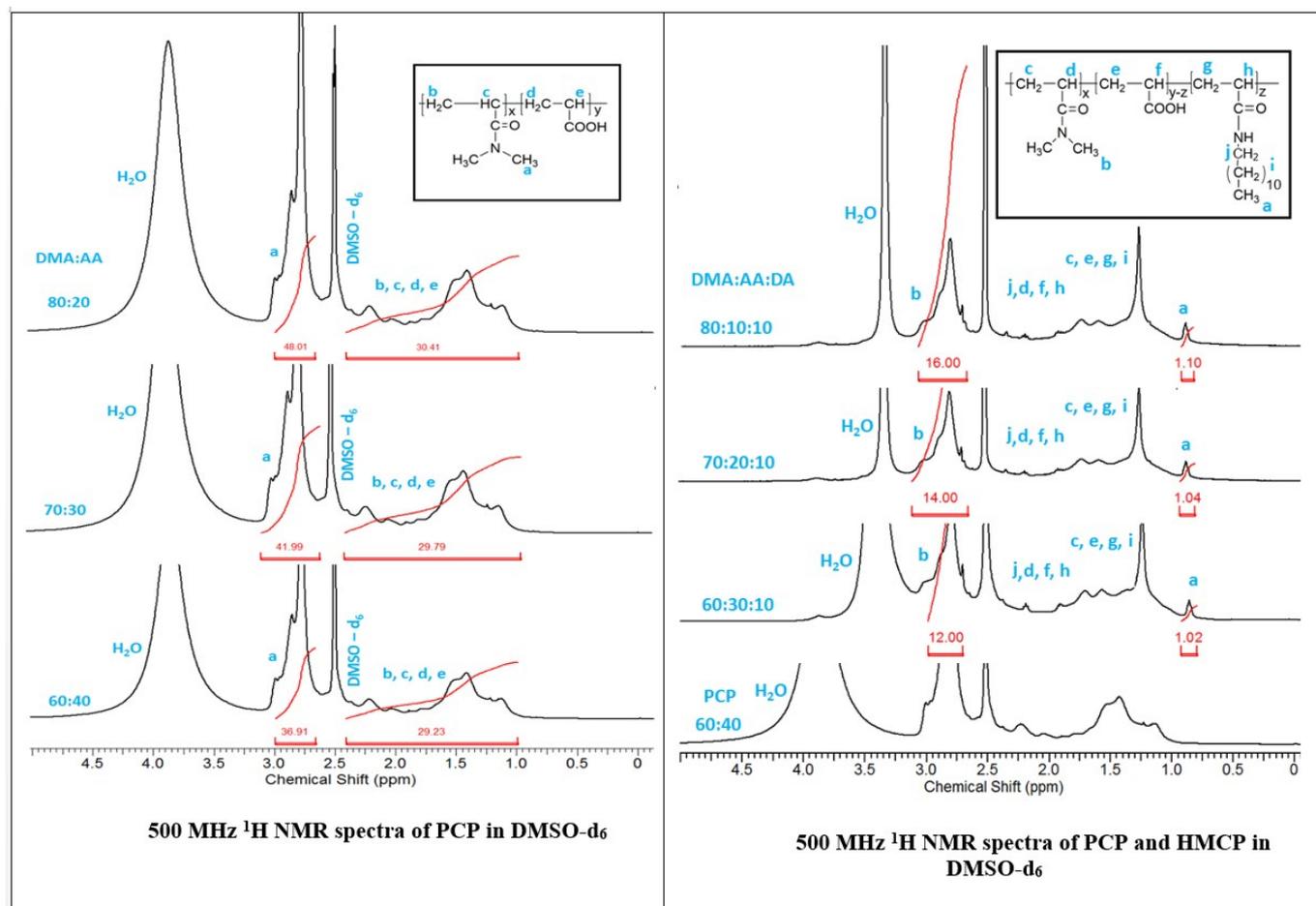
Figure S3: ^1H NMR spectra of various compositions of PCP and HMCP

Table T1: Conditions for preparation of PCP, molecular weights and solubility of HMCP in water at the tested concentration of 25 mg/mL

| Sr. No | Initiator (APS/SMBS) (w/w) | Monomer Feed ratio (DMA:AA) (w/w) | PCP (DM:AA) Mol% | HMCP (DMA:AA:DDA) | Molecular weight \overline{M}_w (gm/mol) | Solubility of HMCP in water at pH 8.5 | Remarks |
|--------|--------------------------------------|--|----------------------------|----------------------|---|---|---|
| 1 | 20.57 | 2.41 | 60:40 | 60:30:10 | 3.0×10^6 | Soluble, no thermothickening | Higher mol% of AA in PCP backbone renders the copolymer hydrophilic. |
| 2 | 20.57 | 3.21 | 70:30 | 70:20:10 | 5.0×10^6 | Soluble, abrupt thermothickening | Right balance of hydrophilic- hydrophobic character |
| 3 | 20.57 | 5.53 | 80:20 | 80:10:10 | 3.8×10^6 | Insoluble | Lower mol % of AA in PCP backbone renders the copolymer hydrophobic |

Rheology

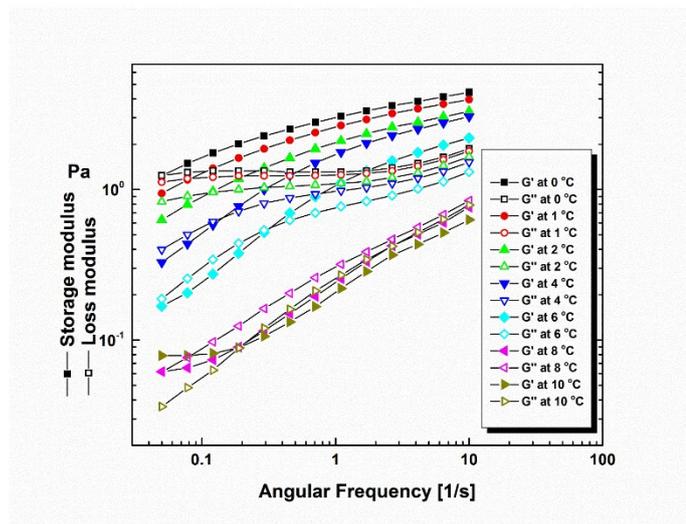


Figure S4(a): Angular frequency sweep experiment on HMCP solution of $C_p = 25$ mg/mL at different temperatures. At 25°C the solution shows predominantly viscous behaviour; the elastic modulus is too low to be measurable. This remains the case till about 8°C at which the elastic modulus becomes significant enough to be measurable but the viscous modulus is still dominant. A distinct cross-over of elastic and viscous modulus can be seen at temperatures below 6°C with an accompanying decrease in frequency dependence of the elastic modulus.

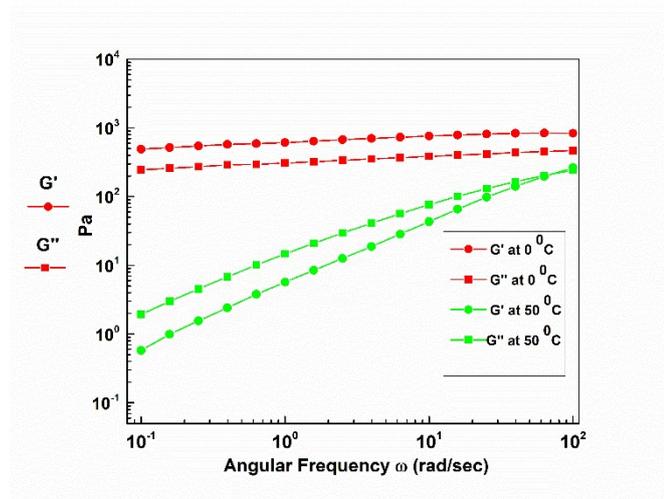


Figure S4(b) shows frequency sweep on HMCP solution of $C_p = 58$ mg/mL at representative temperatures of 0°C and 50°C. At 0°C the signatures of gel-like response namely, $G' > G''$ and frequency-independent moduli are clear. In contrast at 50°C, the moduli are

much lower, the elastic modulus is lower than the viscous modulus and both moduli have discernible frequency dependence indicating liquid-like behaviour. This data suggests that HMCP solutions are in liquid state at higher temperature and in gel state at lower temperature.

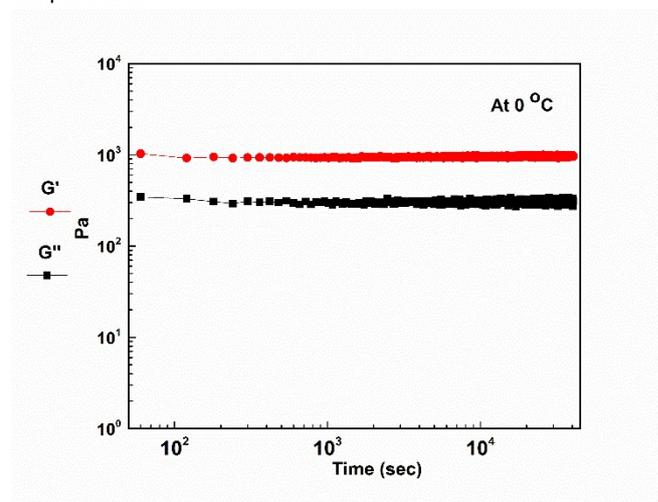


Figure S5: Oscillatory time sweep experiment on HMCP of $C_p = 58$ mg/mL at 0°C. The data shows that the HMCP gel is stable for the 10 h test duration.

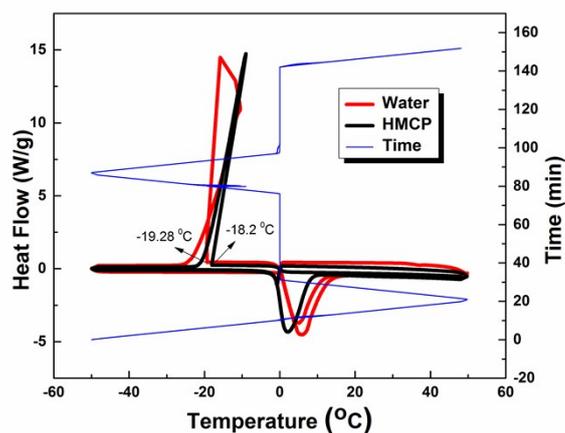


Figure S6: DSC curves showing heat flow during cooling and heating HMCP solution of $C_p = 25$ mg/mL between 50°C and -50°C at 5 °C/min. It was observed that the onset of freezing for both samples was close to -20°C. This was much lower than the temperature at which sudden viscosity increase was seen for this solution in rheological tests conducted at the same cooling rate.

Thus, the sol-to-gel transition at 6°C is not caused by freezing of the sol.

Dynamic light scattering:

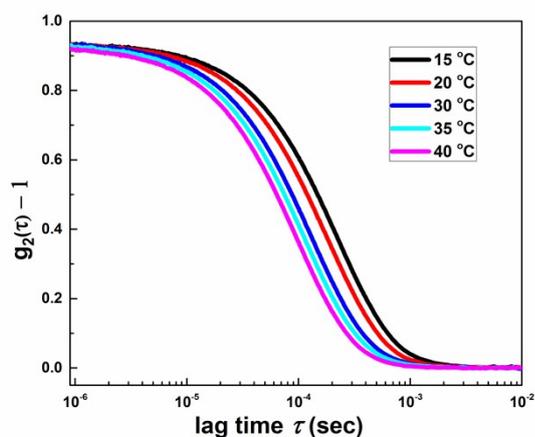


Figure S7(a): Decorrelation function $[g_2(\tau)-1]$ is plotted vs time lag τ for a dilute HPCM solution of concentration $C_p=0.2$ mg/mL in presence of 1 mM NaCl at four representative temperatures of 15, 20, 30, 35 and 40°C

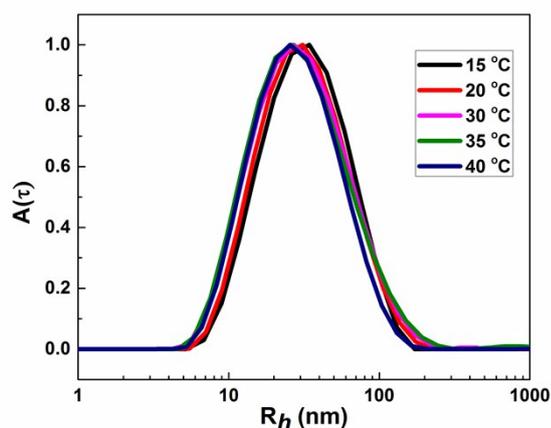


Figure S7(b): Relaxation time distribution at various temperatures shows single diffusive process in the aqueous solution.

Description of Video (SV1)

The video shows sol state of a 45 mg/mL solution of HMCP at 25°C, which turns into a self-supporting gel at 0°C when kept in an ice-bath.