Supporting Information for

Thermo-Thickening Behavior and Its Mechanism of

Chitosan-graft-polyacrylamide Aqueous Solution

Yonggang Shangguan^{*a}, Mingguo Liu^a, Mengjie Wang^a, Lei Jin^a, Zhengke Wang^a, Qiang Wu^b and Qiang Zheng^{*a}

^aMOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, PR China.

^bSchool of Engineering, Zhejiang A&F University, Hangzhou 311300, PR China

Elemental analysis (EA)

Table S1 shows the elemental analysis results of GPAM and calculated graft ratio.

The calculation process is shown as follows.

Calculation process:

Let the mass fraction $W_{CS} = x, W_{PAM} = y$ and the $W_{impurity}$ (the moisture and bonded water content of Chitosan) = z, and x+y+z=1, as equation(3). Equation(1) indicates the measured content of N(*N%*) and equation(2) the calculated O content, based on the theoretical content of Chitosan and PAM in Table S2. Then *x* and *y* are calculated from the equation set and final graft ratio equals to y/x.

Sample	N(%)	C(%)	H(%)	Graft Ratio(%)
GPAM	9.35	32.83	5.87	118
	13.28	40.14	6.74	316
	12.50	36.19	5.99	410
	14.10	36.69	6.29	563
	14.86	41.44	6.51	633

Table S1. The elemental analysis results of GPAM and calculated graft ratio.

Elements	Chitosan(CS)	PAM
N(%)	6.89	19.72
O(%)	34.16	22.54

 Table S2. The theoretical content of each element in the chosen chitosan and PAM.

$$\begin{cases} W_{CS} = x; \\ W_{PAM} = y; \\ W_{impurity} = z; \end{cases} \qquad \begin{cases} N\% = 7.41\% x + 19.72\% y.....(1) \\ 33.86\% x + 22.54\% y = 1 - (N + C + H)\% - z....(2) \\ x + y + z = 1....(3) \end{cases}$$
$$G\% = \frac{y}{x}$$

Rheological experiments

Figure S1 gives the evolution of complex viscosity of GPAM solutions at different temperature. FIgure S2 gives the steady shear results of the heated GPAM sample and the sample with the added NaCl. In according with the similar TEM results, both the two samples present the similar variations compared with that of the original sample. Figure S3 presents influence of GPAM concentration on complex viscosity of GPAM (G% = 316%) solution.

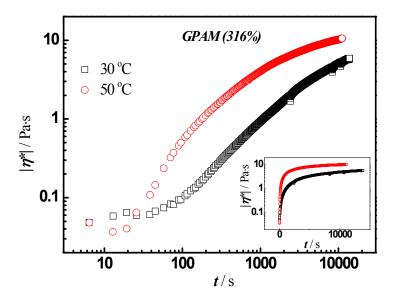


Figure S1. $|\eta^*|$ in the thickening processes of GPAM at 30 °C and 50 °C. The insert is the form with linear coordinates of time.

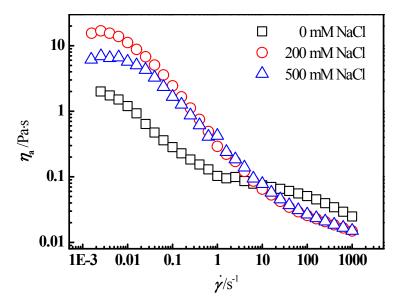


Figure S2. Comparison of the steady shear curve for the GPAM sample with the added NaCl and the original sample.

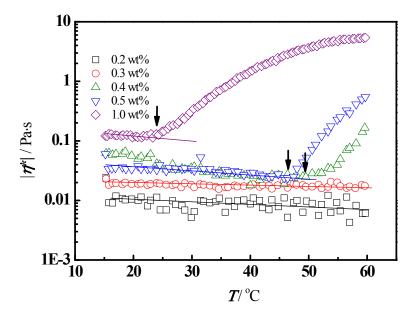


Figure S3. Influence of GPAM concentration on complex viscosity of GPAM (G% = 316%) solution. The strain is 0.2% and the oscillatory frequency is 6.283 rad/s. The heating rate of the samples is 5 °C/min.

Transmission electron microscope (TEM)

Figure S4 gives the comparison of TEM observations of the heated sample at 50 °C and the sample with the added NaCl at 20 °C. We found that both the two sample

displays smaller aggregate compared with that of the original GPAM sample. The reason of the transformation of the two samples lies in the hydrophobic aggregates when heating or adding NaCl.

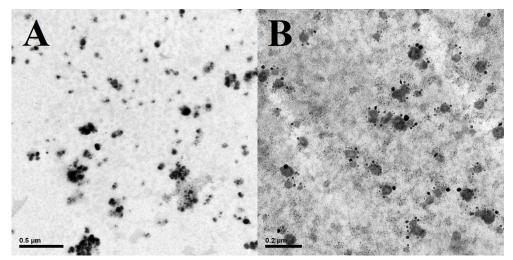


Figure S4. TEM observations of the (A) GPAM sample at 50 °C and (B) the sample with the sample added NaCl at 20 °C.

¹H-NMR observations:

Figure S5 and S6 give the ¹H-NMR spectrums of CS and GPAM respectively. The information of peaks and the reason that the peaks shift downfield with increasing temperature were discussed in our previous work (*Soft Matter* **2013**, 9, (6), 1835-1843.). FWHM is calculated using the software *MestReNova*, however, the difference of FWHM is too small to be present in the spectrums.

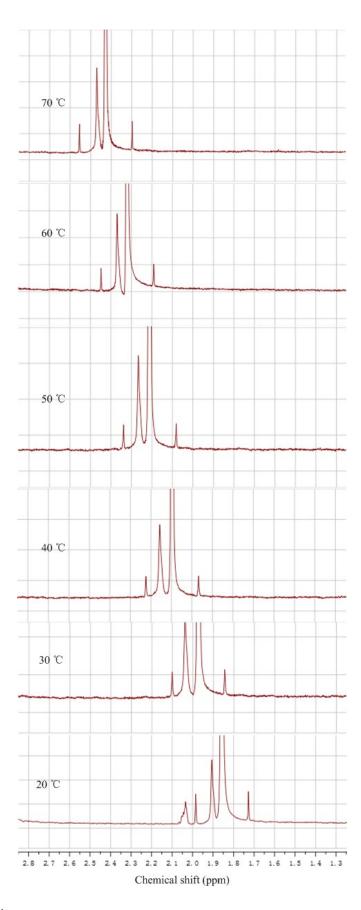


Figure S5. ¹H-NMR spectrums of 0.5 wt% CS solution at various temperatures.

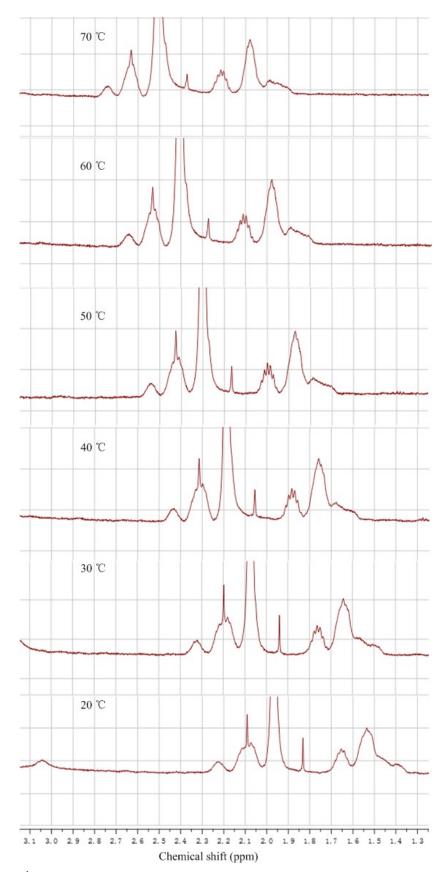


Figure S6. ¹H-NMR spectrums of 0.5 wt% GPAM (G% = 316%) solution at various temperatures.