

## Supporting information

### **Dielectric relaxations of poly(*N*-isopropylacrylamide) microgels near volume phase transition temperature: impact of cross-linking density distribution on volume phase transition**

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#### **1. The detailed preparation procedure of PNIPAM microgels with different cross-linking density**

**Microgels with a dense core and a loose shell (DC):** 0.6 g of NIPAM monomer and 0.03 g of MBA in 50 mL of deionized water were purged with nitrogen gas and preheated to 40 °C for 1 h to remove the dissolved oxygen. Then, 0.05 g of KPS was dissolved in 1 mL of deionized water and added to the reaction vessel with a syringe to initiate the polymerization. When the reaction mixture started to turn opalescent, the temperature was raised to 70 °C in 1 h. After this, 6 mL of a solution containing an extra 0.6 g of NIPAM was added with a syringe pump in 1 h. The reaction mixture was kept at 70 °C for 2 more hours.

**Microgels with a loose core and a dense shell (LC):** only 0.6 g of NIPAM monomer in 45 mL of deionized water was preheated to 40 °C and purged with nitrogen gas for 1 h. Then, 0.05 g of KPS was dissolved in 1 mL of deionized water and added to the reaction vessel to initiate the polymerization. When the reaction mixture started to turn opalescent, the temperature was raised to 70 °C in 1 h. Once the temperature reached 70 °C, 0.6 g of NIPAM and 0.03 g of MBA were dissolved in 5 mL of deionized water and added to the reaction vessel in 1 h using a syringe pump. Finally, the reaction mixture was stirred for 2 h more at 70 °C.

**Microgels with homogenous cross-linking density distribution (HOMO):** 0.9 g of NIPAM monomer was dissolved in 45 mL of deionized water and filtered to remove any solid impurities. The removal of dissolved oxygen was done similarly to the previous two syntheses. Then, 0.05 g of KPS was dissolved in 1 mL of deionized water and added to the reaction vessel to initiate the polymerization. Two minutes

after the initiation, 5mL of solution containing 0.3 g of NIPAM and 0.03 g of MBA was added in 1 h using a syringe pump. When the reaction mixture started to turn opalescent, the temperature was ramped to 70°C in 1 h. After all of the 5 mL comonomer solution was added, the reaction mixture was stirred for 2 h more at 70 °C.

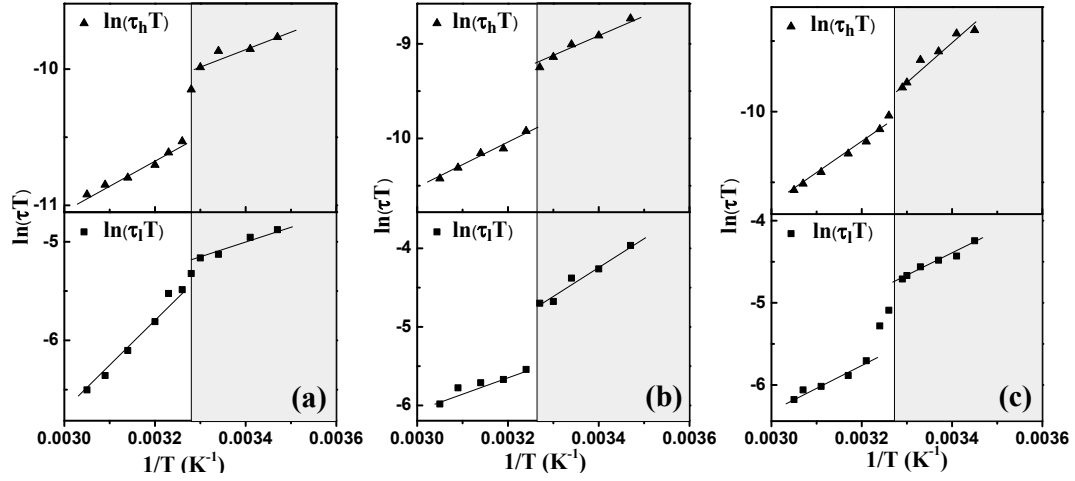
## 2. Thermodynamic analysis of relaxation processes

It is generally known that the temperature dependence of dielectric spectroscopy can provide a means of directly assessing the rate of the relaxation process, which is achieved by the relaxation time, giving a deeper discussion to the relaxation mechanism. Eyring has given the relationship between rate constant  $k$  of relaxation process (where  $k = 1/\tau$ , *i.e.*, the reciprocal of relaxation time) and thermodynamic parameters, such as activation enthalpy  $\Delta H$  and activation entropy  $\Delta S$ , as following:<sup>1</sup>

$$\ln \tau T = \ln\left(\frac{h}{k_B}\right) - \frac{\Delta S}{R} + \frac{\Delta H}{RT} \quad (\text{S1})$$

where  $h$  is the Planck's constant.

The  $\ln \tau T$  are plotted as a function of  $1/T$  for both the low- and high-frequency relaxation in Fig. S1. Obviously, both of the two relaxation processes show a good linear relation between  $\ln \tau T$  and  $1/T$  whether below or above the VPTT, but is divided into two parts around 32.5 °C, which indicates that a phase transition occurs similarly. Further, from the slop and intercept of the fitting line,  $\Delta H$  and  $\Delta S$  of the two relaxations for three types of PNIPAM microgels were estimated and the results are listed in Table S1 and S2, respectively. The positive enthalpy ( $\Delta H > 0$ ) implies an endothermic process of low- and high-frequency relaxation, and negative entropy ( $\Delta S < 0$ ) indicates the microgel systems undergo a processes in which the state of the systems from less ordered to ordered and associated with the cooperative changes in the environment.



**Fig. S1** Eyring plots of relaxation time of low- and high-frequency relaxation of three types of PNIPAM microgels with different cross-linking density distribution: (a) microgels DC, (b) microgels LC, (c) microgels HOMO.

**Table S1** Thermodynamic parameters for low-frequency relaxation estimated by eqn (S1)

Sample	$\Delta S$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )		$\Delta H$ (kJ·mol <sup>-1</sup> )	
	$T < VP_{TT}$	$T > VP_{TT}$	$T < VP_{TT}$	$T > VP_{TT}$
DC	-105.21	-12.77	14.94	42.76
LC	-56.1171	-96.71	31.25	16.91
HOMO	-86.2378	-79.49	21.96	21.82

**Table S2** Thermodynamic parameters for high-frequency relaxation estimated by eqn (S1)

Sample	$\Delta S$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )		$\Delta H$ (kJ·mol <sup>-1</sup> )	
	$T < VP_{TT}$	$T > VP_{TT}$	$T < VP_{TT}$	$T > VP_{TT}$
DC	-83.85	-61.73	9.36	14.73
LC	-53.50	-47.25	20.20	20.88
HOMO	-44.67	-53.53	21.96	18.44

Because the low-frequency relaxation is caused by the counterion polarization as discussed in section 3.3.2, in the whole measuring temperature range,  $\Delta H > 0$  means that the counterions will absorb energy from the environment to overcome electrostatic attraction and diffuse to the farther the distance. In contrast,  $\Delta S < 0$  shows the diffusion of counterions becomes more orderly with the increase of temperature. Moreover, the absolute values of  $\Delta S$  at  $T < VP_{TT}$  are higher than those at  $T > VP_{TT}$ . This is probably because at  $T < VP_{TT}$ , the counterions diffusing on the

surface of a swollen microgels shows a more disordered behavior, whereas at  $T > VPTT$ , the range of counterions diffusion limited in the collapsing microgels, leading to a reduction of the degree of order or the activation entropy.

As to the high-frequency relaxation originates from the contribution of two relaxation modes (micro-Brownian motions of PNIPAM chains and interface polarization) which were discussed in section 3.4.1, at  $T < VPTT$ , the micro-Brownian motions of side groups on PNIPAM need to absorb energy to overcome the constraint from the hydrogen bonds (see Fig. 9), resulting in  $\Delta H > 0$ , while at  $T > VPTT$ ,  $\Delta H > 0$  implies the fracture of hydrogen bond between the amide groups and water molecules. On the other hand,  $\Delta S < 0$  indicates that the structure of PNIPAM microgels tend to be orderly: when PNIPAM microgels are in a highly swollen state ( $T < VPTT$ ), the PNIPAM chain is in a stretching conformation as illustrated in Fig. 9(a), further, the hydrogen bonds formed between water molecules as well as water molecule and the hydrated PNIPAM. That is, the hydrogen-bond bridges between all the water molecules formed, which makes the structure of the microgels become more expanded. As temperature rises, some of hydrogen bonds fracture and the microgels become relatively compact. Similarly, at  $T > VPTT$ , the microgels become highly collapsed one and more orderly with the increase of temperature, because the PNIPAM polymer has formed intramolecular hydrogen bonds, as shown in Fig. 9(b). This is reflected by the activation entropy of  $\Delta S < 0$ .

## References

- 1 M. Davies and J. Swain, Trans. Faraday Soc., 1971, 67, 1637-1653.