

## Electronic Supplementary Information

# Unusual salt effect on the lower critical solution temperature of hyperbranched thermoresponsive polymers

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### Experimental Part

#### *Materials*

Isobutyric anhydride (98%) was purchased from Alfa Aesar and used without further purification. Hyperbranched polyethylenimines, HPEI1.8K (Polysciences,  $M_n=1800$ g/mol,  $M_w/M_n=1.04$ ), HPEI10K (Aldrich,  $M_n=10^4$  g/mol,  $M_w/M_n=2.5$ ) and HPEI25K (Hyperpolymers GmbH,  $M_n=2.5 \times 10^4$  g/mol,  $M_w/M_n=2.5$ ) were dried under vacuum prior to use. Benzoylated cellulose membrane (MWCO 1000g/mol) was purchased from Sigma. Triethylamine (A.R., TEA), Sodium chloride (A. R.), potassium chloride (A. R.) and anhydrous sodium sulfate (A. R.) were purchased from Tianjin University Kewei Chemical Company and used directly. Standard buffer solution (0.025M mixed phosphate, pH=6.86) was purchased from Shanghai Rex Co-perfect Instrument Company, which was diluted to the desired concentration before use. De-ionized water was distilled before use.

### *Characterization*

<sup>1</sup>H spectra were recorded on a Varian INOVA 500MHz spectrometer. The chemical shifts are given in parts per million (ppm). Light transmittance of the polymer solution was measured on a temperature-controlled Purkinje General (China) T6 UV/Vis Spectrophotometer at 650 nm, and the heating rate for polymer 2-4 shown in Table 1 is 0.1°C/3min and for polymer 1 is 1°C/5min. The LCST was defined as the temperature corresponding to the initial break points in the resulting transmittance versus temperature curve.

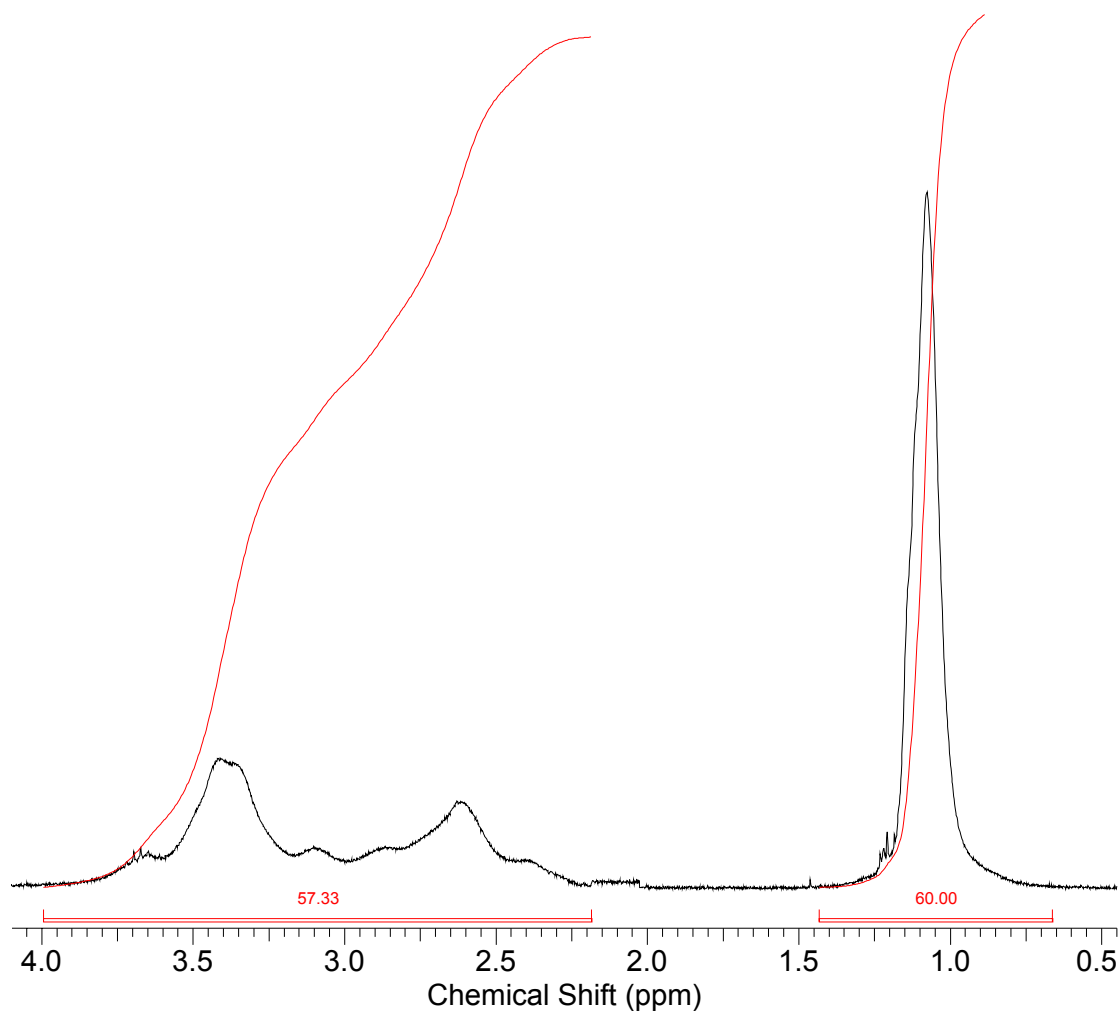
### *General procedure for the syntheses of IBAm terminated HPEIs*

The synthesis of IBAm terminated HPEI is exemplified for HPEI10K-IBAm<sub>0.95</sub>: Under nitrogen atmosphere, isobutyric anhydride (4.07g, 24.97mmol) was added dropwise to the mixture of HPEI10K (1.55g, 26.3mmol of terminal groups) and Triethyl amine (2.78g, 27.5mmol) in 20ml of chloroform at 0 °C with vigorous stirring. Subsequently, the reaction mixture was kept and carried out at room temperature for 24 h. Finally, the reaction temperature was raised to 65°C for 2h to finalize the reaction. After cooling down to room temperature, the produced salt was filtered off. The filtrate was washed with 10% sodium carbonate aqueous solution until basic aqueous solution was achieved, then washed with saturated brine until neutral. After removing the organic volatile under vacuum, the obtained residue was

dissolved in 10 ml of methanol and purified by dialysis against methanol using a benzoylated cellulose membrane (MWCO 1000g/mol) for 2 days in order to remove low molecular weight impurities. Finally, the methanol solvent was removed under vacuum, and the product was dried in vacuum for 24h.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.08 ( $(\text{CH}_3)_2\text{CHCON-}$ ); 2.20-3.90 ( $(\text{CH}_3)_2\text{CHCON-}$ , ethylene protons of HPEI polymeric backbone).

$$\text{Degree of amidation} = 60/6/[(57.33-60/6)/4]/0.73 = 116\%$$

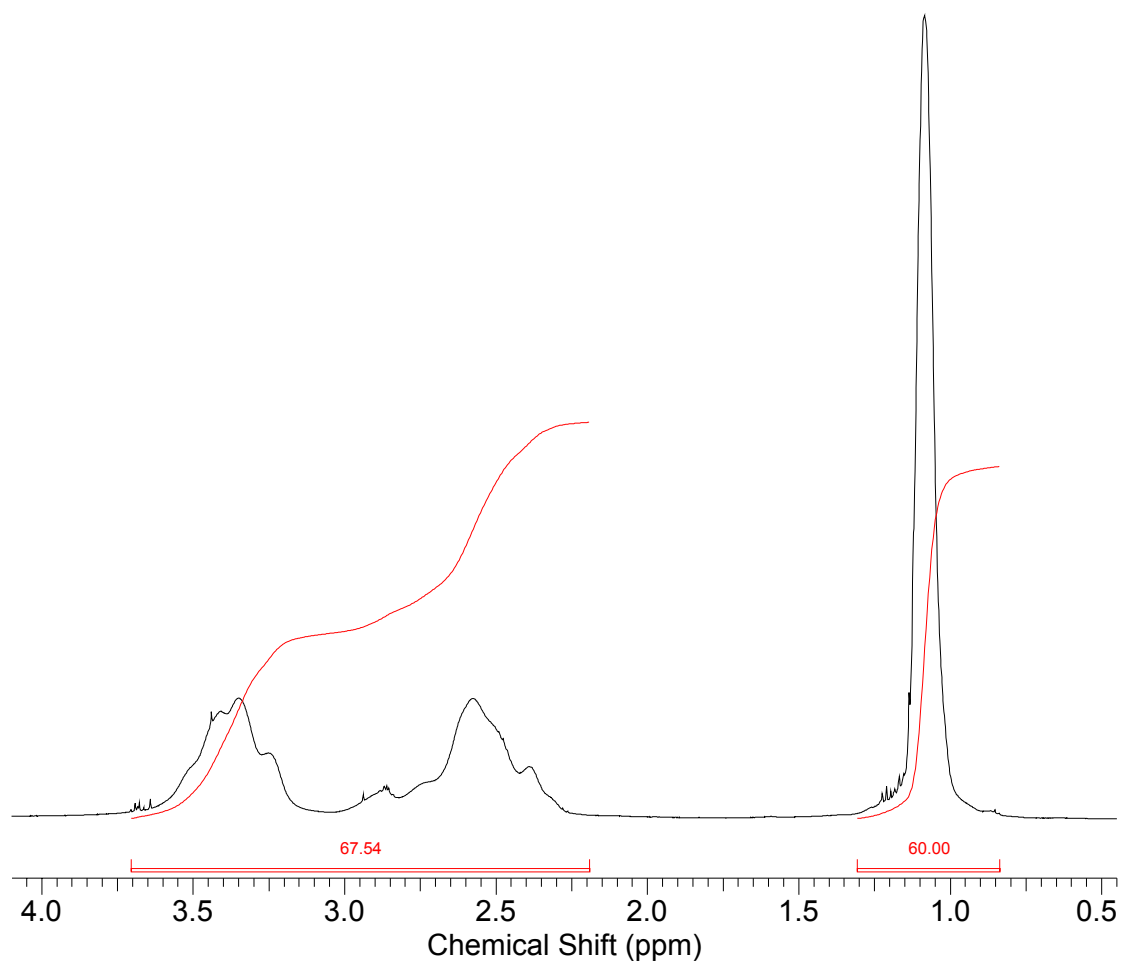


**Fig. S1**  $^1\text{H}$  NMR spectrum of HPEI-IBAm derived from HPEI10K and excess isobutyryl chloride

Supplementary Material (ESI) for *Soft Matter*

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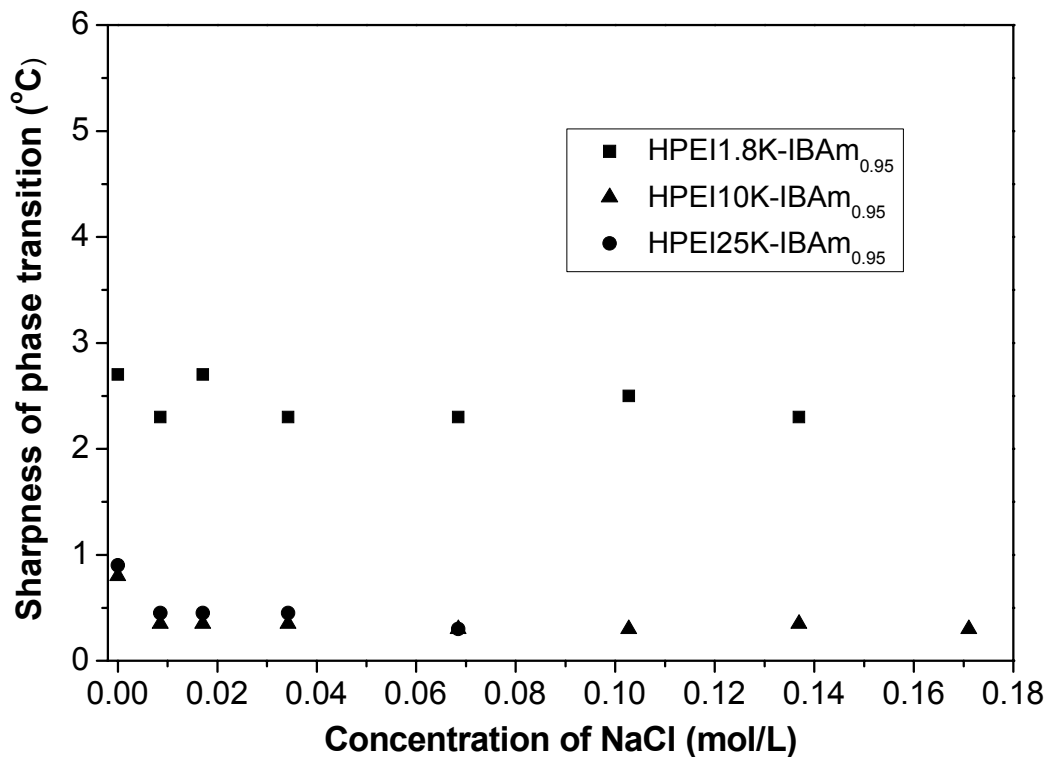
$$\text{Degree of amidation} = 60/6/[(67.54-60/6)/4]/0.73 = 95\%$$



**Fig. S2** <sup>1</sup>H NMR spectrum of HPEI-IBAm derived from HPEI10K and excess isobutyric anhydride



**Fig. S3** The typical photographs of thermoresponsive hyperbranched polymers (A) below the LCST, below room temperature (B) above the LCST, 30°C (HPEI10K-IBAm<sub>0.95</sub> at 2 mg/mL)



**Fig. S4** Effect of the concentration of NaCl on the sharpness of phase transition of IBAm terminated HPEI (■) Polymer 1, HPEI1.8K-IBAm<sub>0.95</sub>, (▲) Polymer 2, HPEI10K-IBAm<sub>0.95</sub>, (●) Polymer 3, HPEI25K-IBAm<sub>0.95</sub> (all the polymer concentrations are fixed at 2mg/mL)