

Supporting Information

Dynamic self-aggregation and disaggregation behavior of thermoresponsive hyperbranched polyethylenimine with peripheral NIPAM groups: an infrared spectroscopic study

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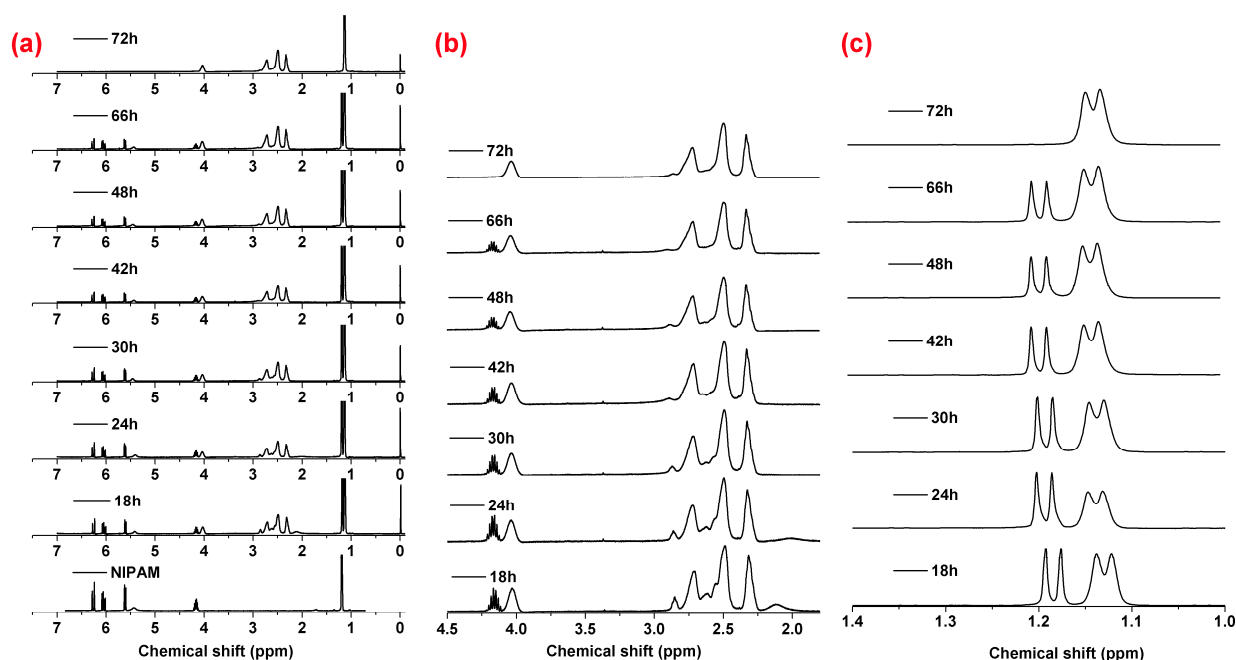


Fig. S1 ^1H NMR spectra of all aliquots as well as NIPAM in CDCl_3 in the region (a) 0-7.5 ppm, (b) 1.8-4.5 ppm and (c) 1.0-1.4 ppm.

Table S1 Integral area ratio of NIPAM monomers after and before reaction with different reaction time.

Time/h		18	24	30	42	48	66
Integral area	d/d'	2.14	1.52	2.35	2.72	2.68	3.00
ratio	e/e'	1.95	1.32	2.05	2.57	2.72	3.00

All samples with different reaction time were dissolved in CDCl_3 for ^1H NMR measurement.

For comparing NIPAM monomers before and after reaction, aliquots from 18 h to 66 h were used for ^1H NMR measurement without dialysis. However, for samples after 72 h, we performed dialysis

before freeze-drying for facilitating other measurements. Therefore, there are no signals for NIPAM monomers in the ^1H NMR spectrum of 72 h. From Fig. S1, it indicates that the contents of unreacted NIPAM monomers gradually decrease compared to NIPAM moieties in the periphery of HPEI with reaction. The resonances at 4.11-4.22 ppm, 3.95-4.11 ppm, 1.21-1.17 ppm and 1.17-1.11 ppm are denoted as d', d, e' and e, respectively. Here d and e are the signals of HPEI-NIPAM, while d' and e' are the signals of unreacted NIPAM monomers. The integral area ratios of d/d' and e/e' at different reaction time are listed in Table S1. As reaction proceeds, the integral ratios of reacted and unreacted NIPAM decrease except for the sample of 24 h, perhaps due to the inhomogeneous solution for extracting at 60 °C. Anyway, it reveals a trend of the increase of NIPAM contents on the periphery of HPEI.

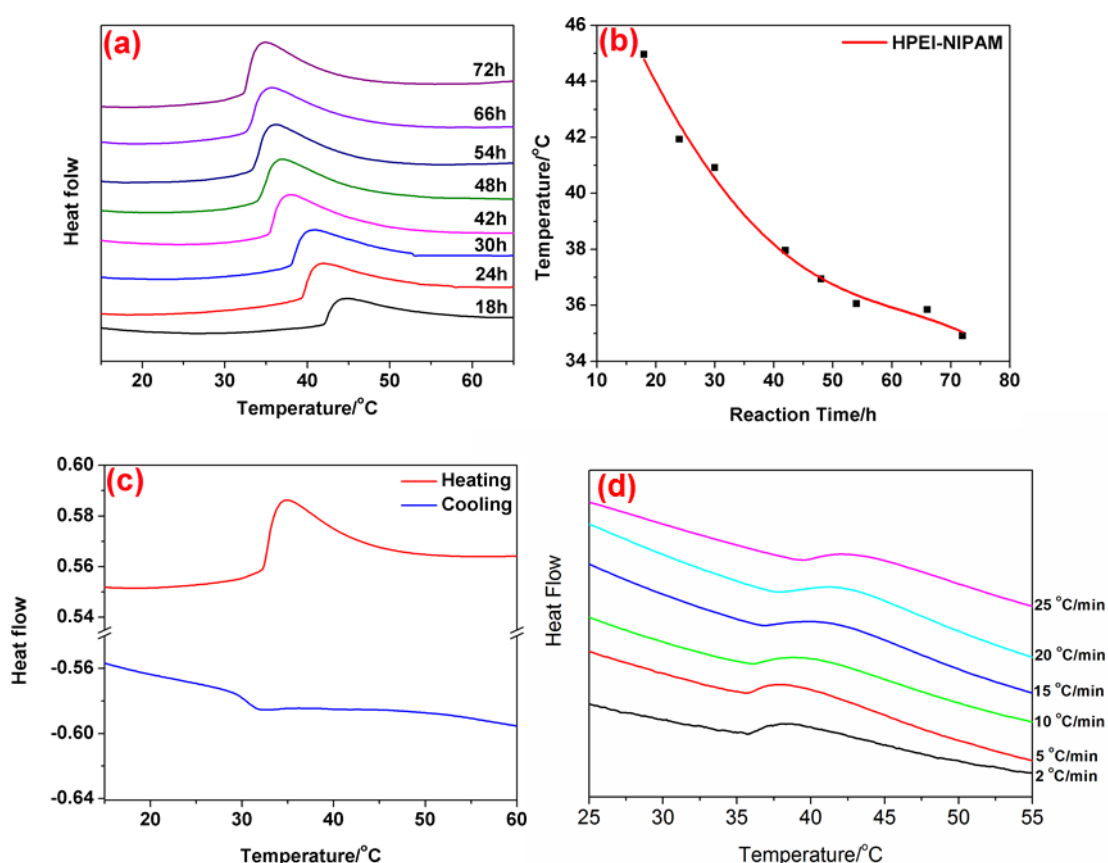


Fig. S2 (a) DSC curves of 10 wt% HPEI-NIPAM in H₂O with different reaction time. (b) Effects of reaction time on T_g derived from (a). Where, the solid line serves only as visual guides. (c) DSC heating and cooling curves of 10 wt% HPEI-NIPAM (72 h) at 10 °C/min. (d) DSC heating curves of 10 wt% HPEI-NIPAM (72 h) at different scanning rates.

All aliquots for DSC measurements were purified by dialysis and freeze-dried.

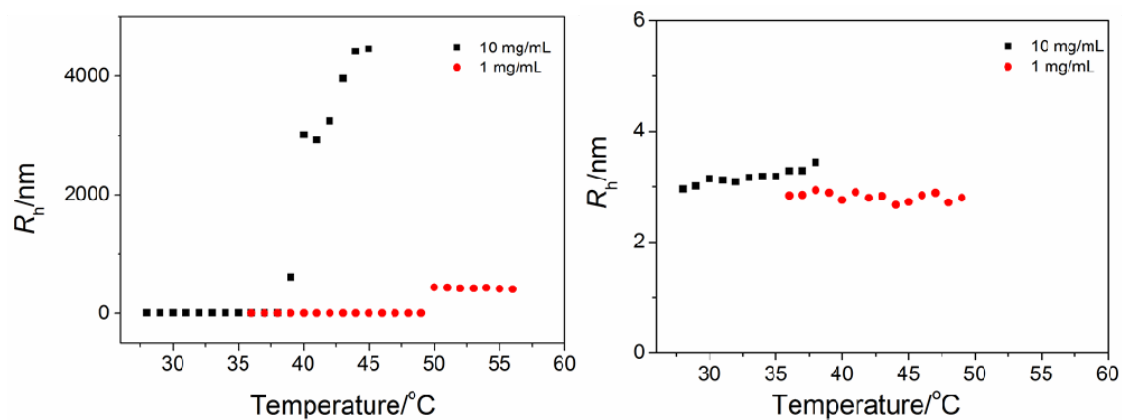


Fig. S3 Hydrodynamic radius (R_h) changes of HPEI-NIPAM aqueous solution (1 and 10 mg/mL) during heating.

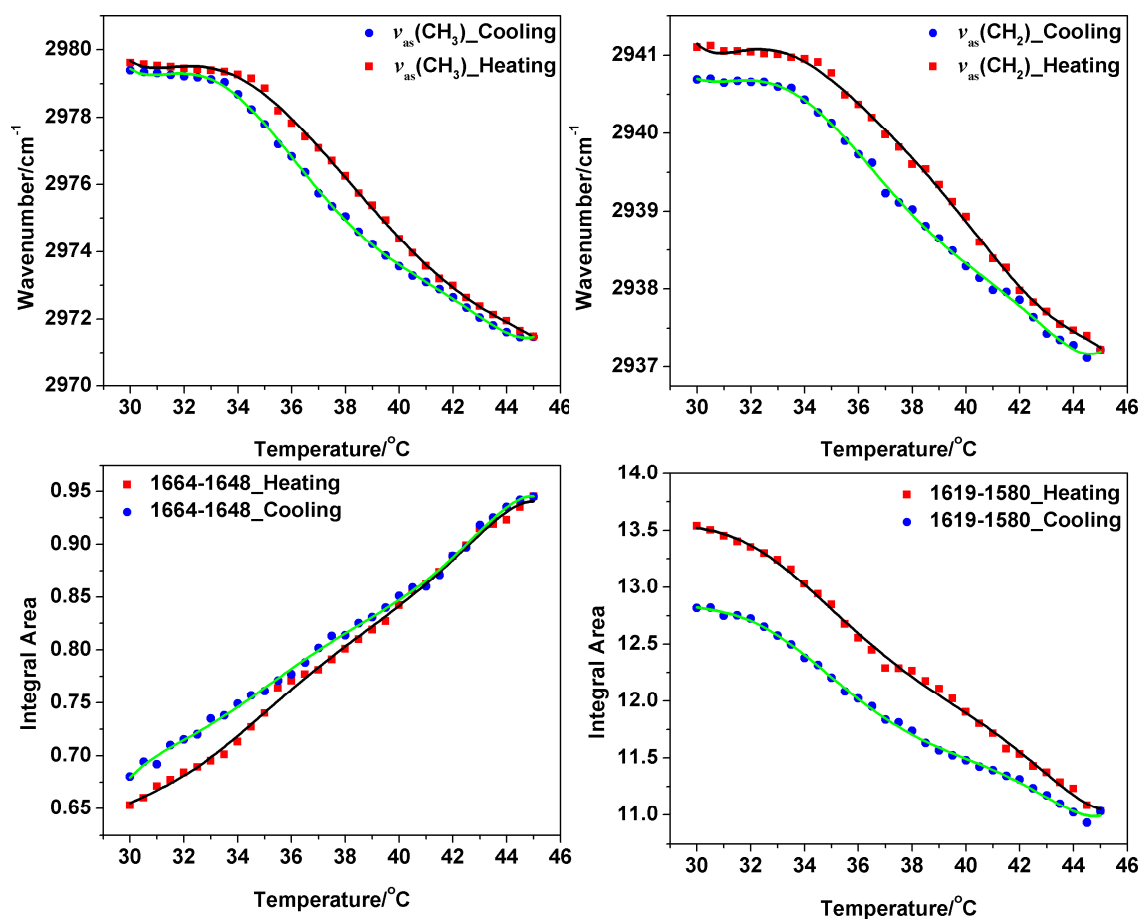


Fig. S4 Temperature-dependent frequency shifts of $\nu_{as}(\text{CH}_3)$ and $\nu_{as}(\text{CH}_2)$ as well as the integral areas in the regions $1664\text{--}1648\text{ cm}^{-1}$ and $1619\text{--}1580\text{ cm}^{-1}$ during heating and cooling, respectively.