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SUPPLEMENTARY INFORMATION

Mixtures of pH-responsive microgels and temperature-responsive star-like copolymers; from heteroaggregation to gelation

Somjit Tungchaiwattana[a], Ruixue Liu[a,b], Silvia Halacheva[a] Nur Nabilah Shahidan[a],

Andrew Kells[c] and Brian R. Saunders[a,*]

[a]*Polymer Science and Engineering Research Group, School of Materials,*

The University of Manchester, Grosvenor Street, Manchester, M13 9PL, U.K.

[b] *School of Material and Chemical Engineering, Zhengzhou University of Light Industry,*

Zhengzhou, 450002, P.R. China

[c]*Synthomer Ltd, 1½ miles Jalan Batu Pahat, 86000 Kluang, Johor, Malaysia*
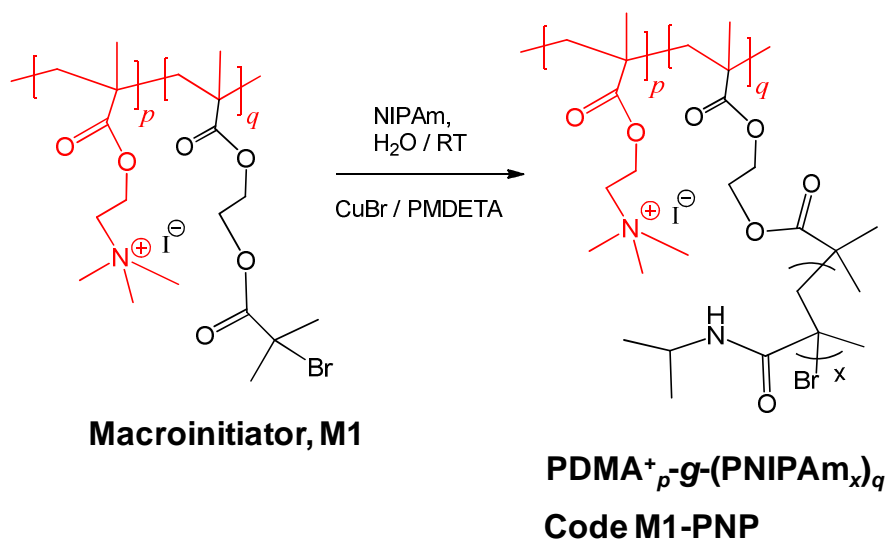
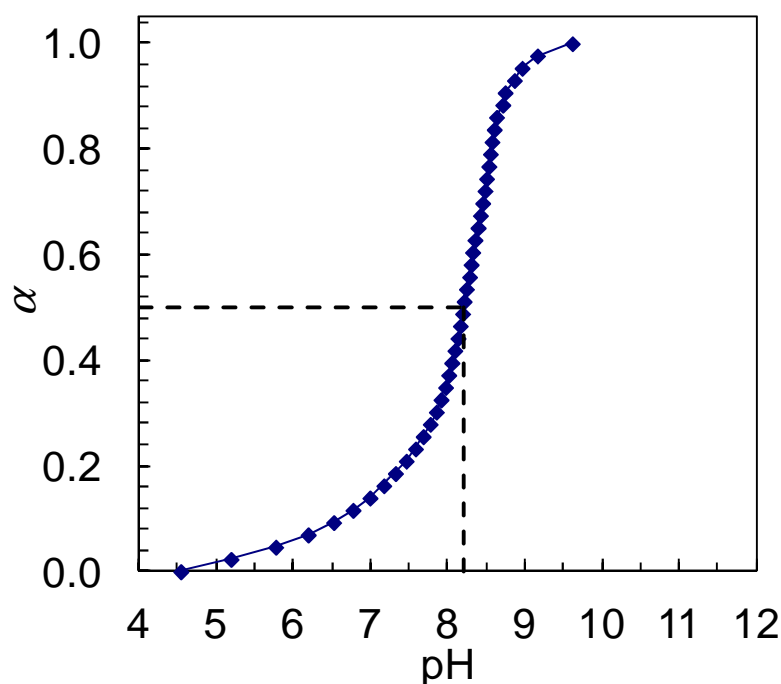**Scheme S1.** Preparation of temperature-responsive star-like PNP copolymers.

Fig. S1. Potentiometric titration data for the MG. α is the degree of neutralisation. The dashed line corresponds to the apparent pK_a.

M1-PNP copolymer compositions from ^{1}H NMR spectroscopy

The M1-PNP60 and M1-PNP100 copolymers were analysed using ^{1}H NMR spectroscopy. The spectra for both copolymers were similar and are shown in Fig. S2(a). For comparison, a spectrum of PNP is shown in Fig. S2(b). The ^{1}H NMR spectrum for the macroinitiator (M1) is shown for comparison in Fig. S2(c). The assignments for the NP protons (Fig. S2(a) and (b)) and the –N(CH$_3$)$_3^+$ protons are from Ray et al. [1] and Liu et al. [2], respectively. The spectra for M1-PNP60 and M1-PNP100 are dominated by PNP as can be seen from comparison to Fig. S2(b). This confirms that the side-chain degrees of polymerisation (x) were long compared to the backbone for both M1-PNP60 and M1-PNP100. Fig. S2(a) shows expansions of the –N(CH$_3$)$_3^+$ protons (labelled as f). The ratio of carefully integrated areas for these protons (A_f) to those for the –(CH$_3$)$_2$CH- protons (labelled as d) gave the value for x, using $x = 9(A_d/A_f)$. The analysis gave x values of 550 and 875 for M1-PNP60 and M1-PNP100, respectively.
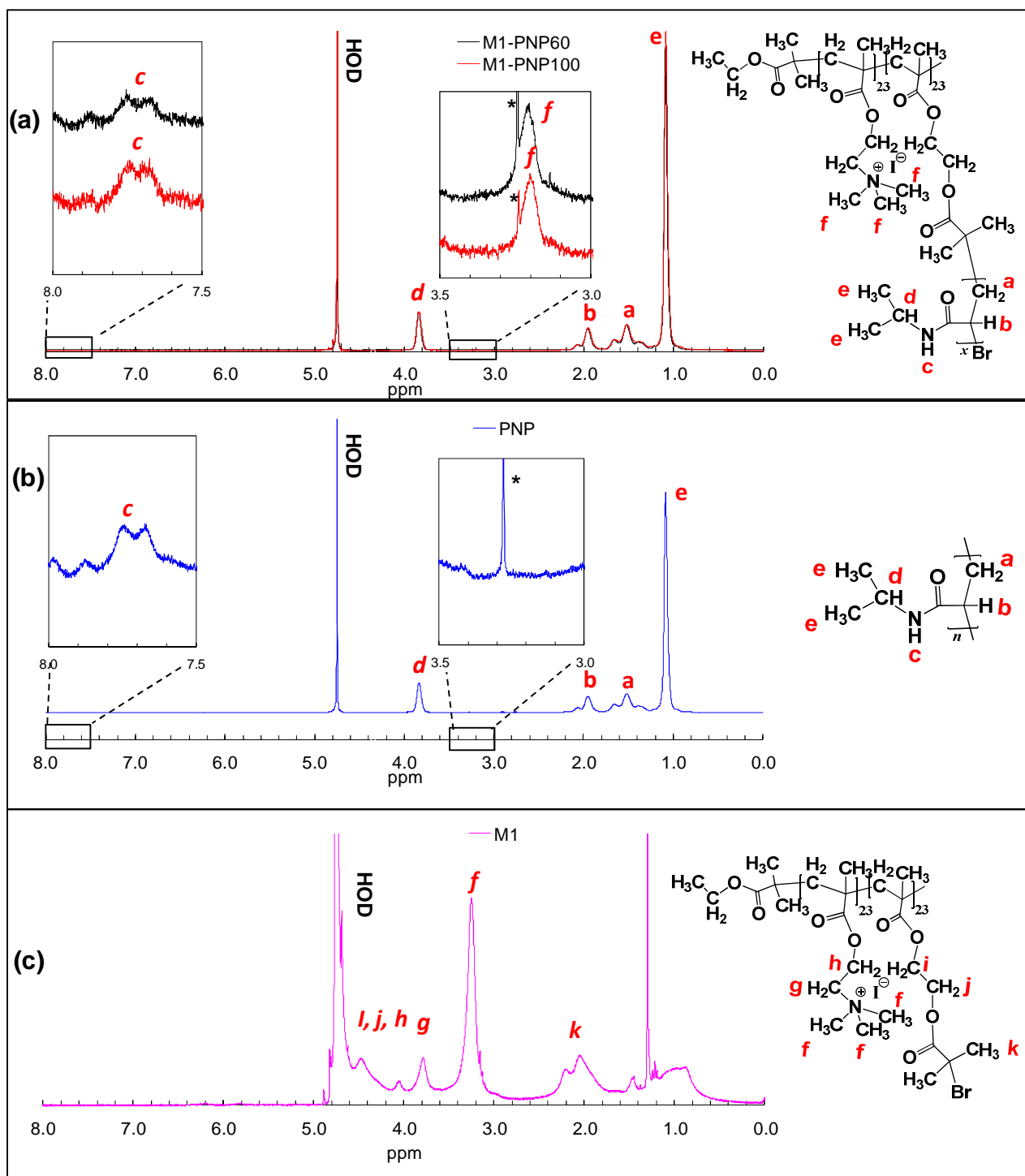
Fig. S2 ^{1}H NMR spectra of (a) M1-PNP60 and M1-PNP100 copolymers, (b) PNP and (c) M1. The spectra were recorded at room temperature in D$_2$O. The asterisks identify an impurity peak. The spectra in (a) have been offset vertically to make the magnified regions (insets) clearer.
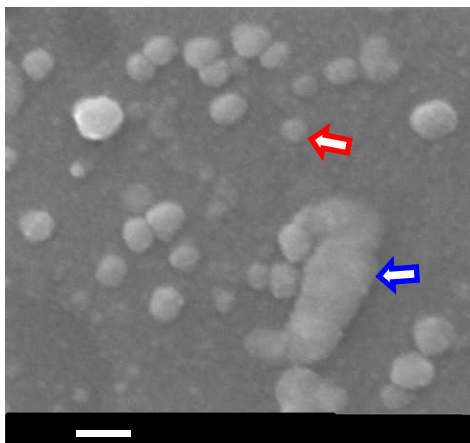
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Fig. S3 SEM image for deposited M1-PNP60. The red arrow shows a nanoparticle. The blue arrows identify a large nanoparticle aggregate. The scale bar is 200 nm.

References
[1] B. Ray, Y. Isobe, K. Matsumoto, S. Habaue, Y. Okamoto, M. Kamigaito, M. Sawamoto, *Macromolecules*, 2004, **37**, 1702.
[2] R. Liu, P. De Leonardis, F. Cellesi, N. Tirelli and B. R. Saunders, *Langmuir*, 2008, **24**, 7099.