

Direct synthesis of interface-decorated reactive block copolymer nanoparticles via polymerisation-induced self-assembly

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Electronic Supporting Information (ESI)

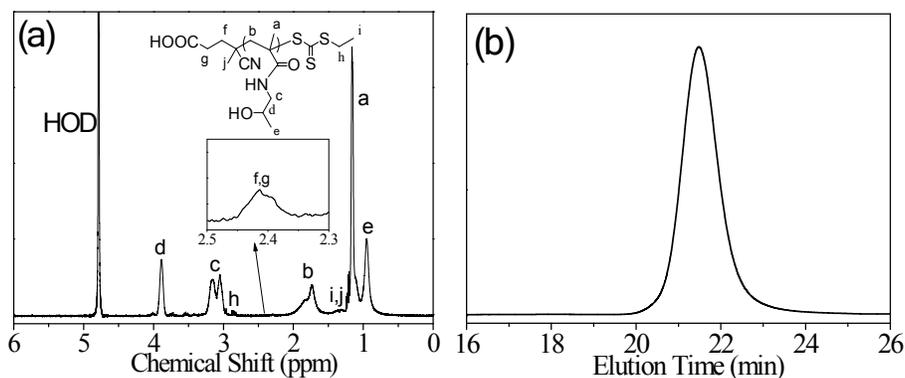


Fig. S1 (a) ¹H NMR spectrum and (b) SEC trace of PHPMA₁₆₆ that was synthesized via aqueous RAFT polymerization under visible light irradiation at 25°C.

As shown in **Fig. S1**, the ratio of integral signals $I_b:I_{a+e}:I_c:I_d$ equals 2:6:2:1 within analysis errors, which is consistent with the proton ratio of the targeted PHPMA polymer. More importantly, the signals *f* and *g* in CEP chain-ends (insert in Fig. S1a) are discernible, which were used to determine the degree of polymerization (DP_{HPMA}) according to Eq. S1, in which I_d and I_{f+g} are the integral signals $CH(CH_3)OH$ in HPMA units and CH_2CH_2COOH of CEP chain-ends, respectively. DP_{HPMA} value of 166 was thus assessed. The polymer was named as PHPMA₁₆₆ macro-CTA.

$$DP_{HPMA} = \frac{4 \times I_d}{I_{f+g}} \quad (S1)$$

As shown in **Fig. S1b**, the SEC trace is unimodal and symmetrical. SEC studies indicate a molecular weight (M_n) of 40.0 kDa, and a polydispersity index (PDI, M_w/M_n) of 1.13.

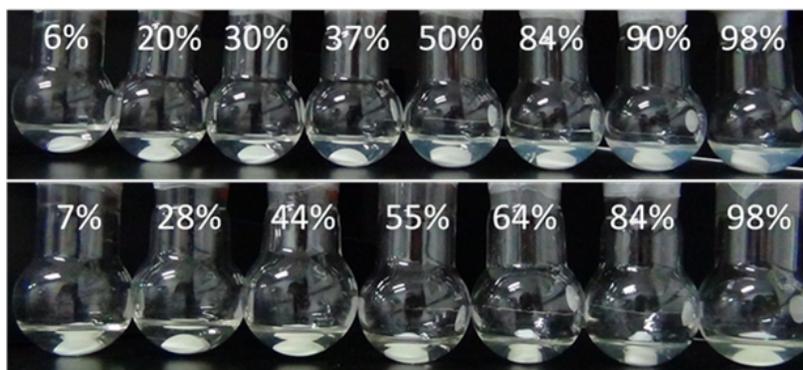


Fig. S2 Photographs of reaction solutions on polymerisation at different conversions at $[DAAM]_0 = 0.5$ M and $[DAAM]_0/[PHPMA_{166}]_0/[SPTP]_0 = 200/1/0.25$ (top) and 100/1/0.25 (bottom) under visible light irradiation at 25°C. Herein, the monomer conversions were determined by ¹H NMR in methanol-d₄.

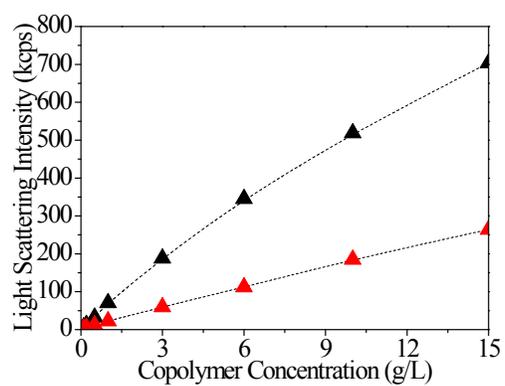


Fig. S3 The evolutions of light scattering intensities on diluting resultant solutions ($[\text{DAAM}]_0/[\text{PHPMA}_{166}]_0/[\text{SPTP}]_0=200/1/0.25$ (black) and $100/1/0.25$ (red), both at 98% conversions) with water from 15.0 to 0.10 mg/mL, in which laser was attenuated down to 20% of the original.

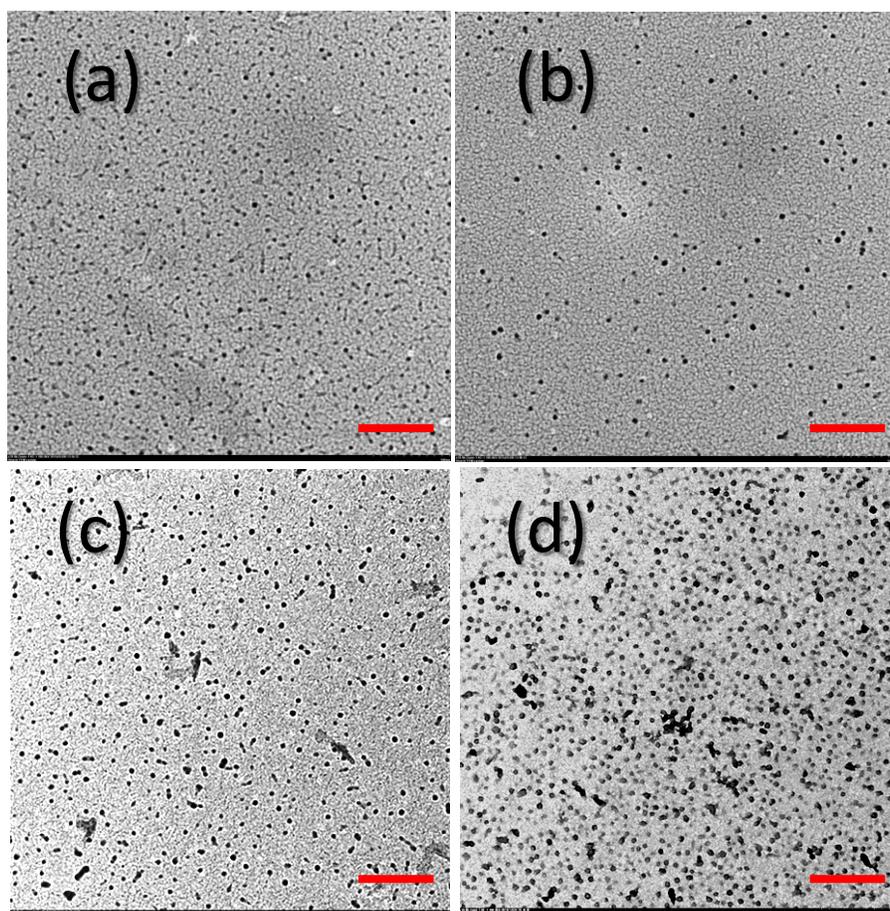


Fig. S4 TEM images of PISA-micelles formed upon polymerizations at $[\text{DAAM}]_0/[\text{PHPMA}_{166}]_0/[\text{SPTP}]_0=200/1/0.25$ to 50% (a), 84% (b), 98% (c) conversions; (d) those formed at a $[\text{DAAM}]_0/[\text{PHPMA}_{166}]_0/[\text{SPTP}]_0=100/1/0.25$ to 98% conversions. Scale bar: 500 nm.

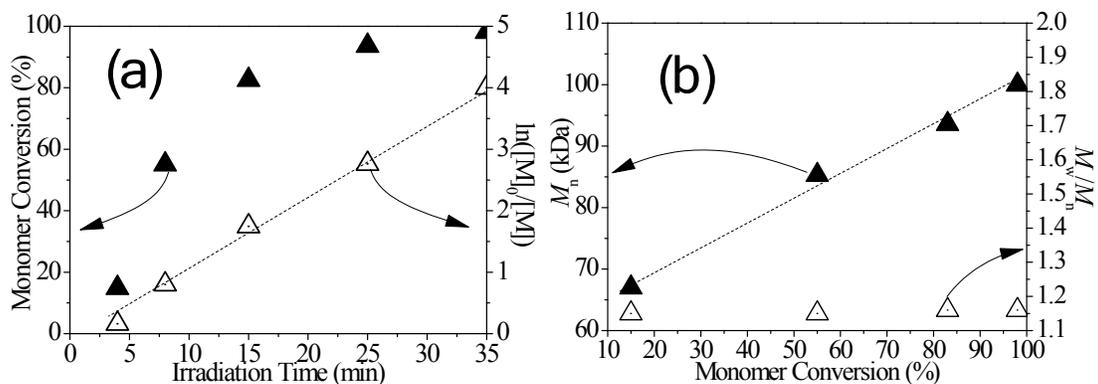


Fig. S5 (a) Kinetic plots of homopolymerisation of AEAM using PHPMA₁₆₆ macro-CTA in acidic water at $[AEAM]_0=0.5$ M and $[AEAM]_0/[PHPMA_{166}]_0/[SPTP]_0=200/1/0.25$ under visible light irradiation at 25 °C; (b) M_n and M_w/M_n vs. monomer conversions.

As shown in Fig. S5a, >98% conversions have been achieved on irradiation for 35 min, suggesting high reactivity of AEAM monomer under such mild aqueous conditions. The semilogarithmic plot evolved linearly with irradiation time, indicating the constant concentration of active growing-chain radicals during this radical polymerisation. Furthermore, as shown in Fig. S5b, the molecular weight increased linearly with conversions and the polydispersities were lower than 1.20 up to 98% conversions. These results demonstrate that this aqueous RAFT was rapid, efficient and well-controlled.

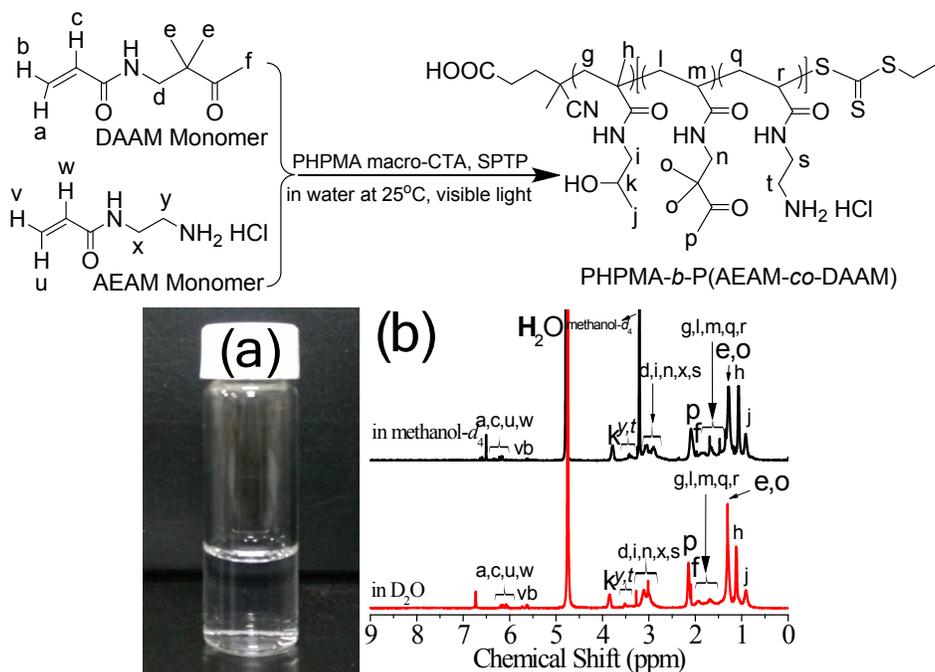


Fig. S6 (a) The photograph and (b) ¹H NMR spectra (in methanol-*d*₄ and D₂O) of reaction solution after copolymerization at $[AEAM]_0+[DAAM]_0=0.5$ M, $[AEAM]_0/[DAAM]_0=40/160$ and $[AEAM+DAAM]_0/[PHPMA_{166}]_0/[SPTP]_0=200/1/0.25$ under visible light irradiation at 25°C, in which 94% AEAM and 96% DAAM conversions were achieved. *Top*: Schematic illustration of the copolymerisation.

As shown in Fig. S6a, the reaction solution kept transparent up to 94% AEAM and 96% DAAM conversions. Moreover, as shown in Fig. S6b, the integral I_p/I_k ratios are equal in methanol-*d*₄ or in D₂O. These results demonstrate that the copolymerisation proceeded in the homogeneous solution to extremely high conversions.

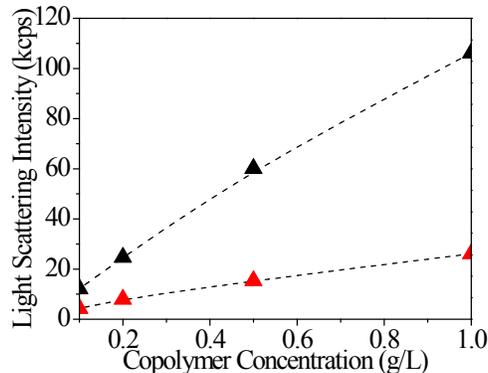


Fig. S7 The evolution of light scattering intensities upon dilution of the resultant solutions at $[\text{monomers}]_0/[\text{PHPMA}_{166}]_0/[\text{SPTP}]_0=200/1/0.25$ and $[\text{AEAM}]_0/[\text{DAAM}]_0=10/190$ to 46% AEAM and 93% DAAM conversions (*black*) and $[\text{AEAM}]_0/[\text{DAAM}]_0=20/180$ to 67% AEAM and 95% DAAM conversions (*red*) from 1.0 to 0.10 mg/mL, in which laser was attenuated down to 50% of the original.

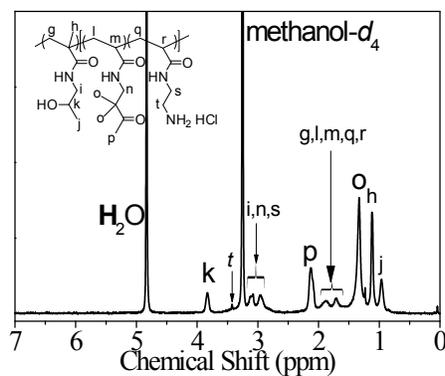


Fig. S8 ^1H NMR spectrum of the copolymer prepared by the copolymerisation at $[\text{AEAM}]_0/[\text{DAAM}]_0/[\text{PHPMA}_{166}]_0/[\text{SPTP}]_0 = 20/180/1/0.25$ to 95% DAAM and 67% AEAM conversions. ^1H NMR spectrum was recorded after dialysis, lyophilisation and then re-dissolving in methanol- d_4 .

As shown in Fig. S8, the proton signals k , t , p were used to determine DP values of AEAM and DAAM units according to Eqs. S2-S3, in which I_k , I_t and I_p are the integral signals $\text{CH}(\text{CH}_3)\text{OH}$ in HPMA unit, CH_2NH_3^+ in AEAM unit, and COCH_3 in DAAM unit, respectively; $\text{DP}=166$ of PHPMA macro-CTA assessed in Fig. S1 was used herein. Molecular structure parameters, $\text{DP}_{\text{AEAM}}=15$ and $\text{DP}_{\text{DAAM}}=176$ were assessed. Thus, this statistic-block copolymer was named as $\text{PHPMA}_{166}\text{-}b\text{-(AEAM}_{15}\text{-}co\text{-DAAM}_{176})$.

$$DP_{\text{AEAM}} = 166 \times \frac{I_k}{2 \times I_t} \quad (\text{S2})$$

$$DP_{\text{DAAM}} = 166 \times \frac{I_k}{3 \times I_p} \quad (\text{S3})$$

Imine conversion and Zn(II)-coordination of AEAM/PDCA compounds

AEAM (4.0 mg, 26.6 μmol), PDCA (3.85 mM in D_2O , 3.45 g, 13.3 μmol), ZnCl_2 (28.2 mM in D_2O , 0.173 g, 6.6 μmol) and D_2O (0.38 g) were dissolved in 10 mL vial. NaOD (0.02 mg/mL in D_2O) was added drop-wise to adjust the solution to pH 9.8. The reaction was equilibrated at 25°C for 24 h before ^1H NMR studies.

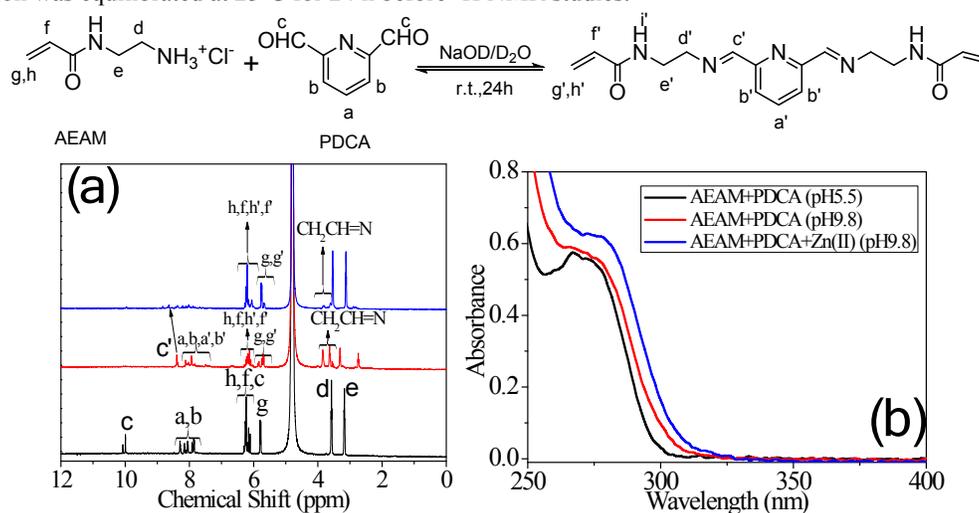


Fig. S9 (a) The variation of ^1H NMR spectrum of the solutions of AEAM and PDCA ($[\text{AEAM}]_0/[\text{PDCA}]_0=2$) at pH 5.5 (black) and pH 9.8 (red) and that after $\text{Zn}(\text{II})$ -coordination at $[\text{AEAM}]_0/[\text{PDCA}]_0/[\text{Zn}(\text{II})]_0=1/0.5/0.25$ at pH 9.8 (blue); (b) UV-vis spectra of as-mentioned solutions. Top: Schematic illustration for the imine conversion of AEAM monomer with PDCA in a basic solution.

As shown in Fig. S9a, signals at 6.1 and 10.0 ppm (CHO of PDCA) [Y. Packer, J. E. Meany, B. J. Nist, *J. Phys. Chem.*, 1967, **71**, 4509] are discernible at pH 5.5, suggesting negligible imine conversion. However, the signals disappeared on adjusted to pH 9.8. Moreover, CH=N signal c' at $\delta=8.37$ ppm appeared. The results indicate formation of imine bonds in basic solution at pH 9.8. CH=N signal at $\delta=8.37$ ppm remarkably attenuated and shifted to 8.6 ppm, and CH₂CH=N signals at $\delta=3.9$, 3.5 ppm were also decreased upon coordination with zinc ions. The formation of dative bonds was also confirmed by the red-shift of characteristic band of $\text{Zn}(\text{II})$ -coordinated ligand motifs (see Fig. S9b).