

The use of electrostatic association for rapid RAFT synthesis of histamine polyelectrolyte in aqueous solutions at and below 25°C

Tao Huang,^a Zhigang Cui,^a Yi Ding,^a Xinhua Lu^a and Yuanli Cai^{*a}

Electronic Supplementary Information

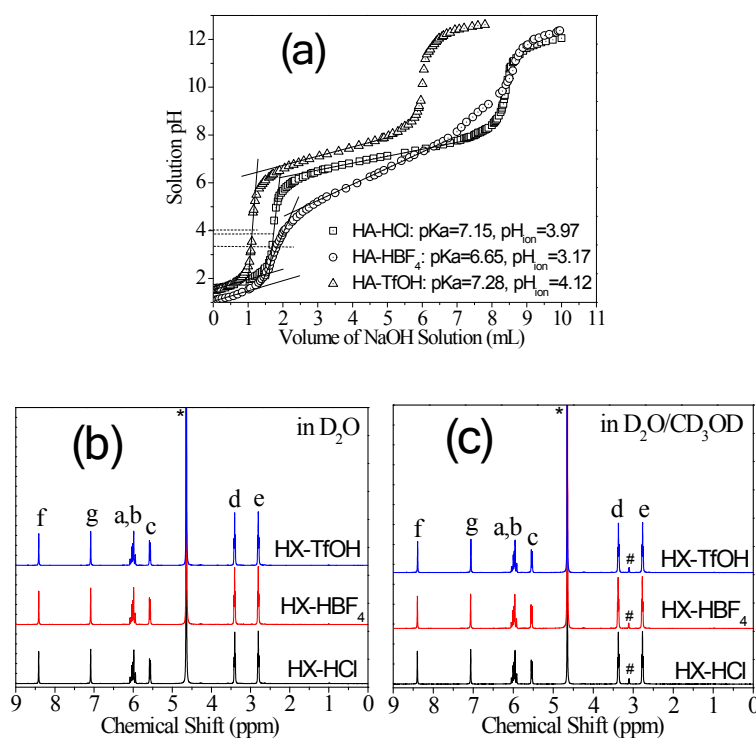


Fig. S1 Acid-base titration plots of the monomer salts (a), and ¹H NMR spectra of the as-lyophilized monomer salts in deuterium oxide D₂O (b) and in the mixture of D₂O and deuterated methanol (CD₃OD) at a $W_{D_2O}/W_{CD_3OD}=9$ (c).

The acid-base titration results (Fig. S1a) revealed the order of $pK_{a,HA-TfOH} > pK_{a,HA-HCl} > pK_{a,HA-HBF_4}$, which is in good agreement with the acidity order of TfOH > HCl > HBF₄. Moreover, the first transitions were determined at pH 4.12 for HA-TfOH, pH 3.97 for HA-HCl, and pH 3.17 for HA-HBF₄, below which the monomer was fully charged. Therefore, the critical solution pH value was termed as pH_{ion} . Accordingly, the reaction solutions were adjusted to pH 3.1 before irradiation, to ensure the complete ionization of the monomer into HA-HX monomer salts.

To elucidate solubility of these monomer salts, as-acidified aqueous solutions were separately lyophilized. One portion was dispersed in deuterium oxide (D₂O), another portion was dispersed in the mixture of D₂O and deuterated methanol (CD₃OD, $W_{D_2O}/W_{CD_3OD}=9$, which was equal to the $W_{water}/W_{methanol}$ ratios used in the reaction solutions as mentioned below). As shown in Fig. 1b, the proton signals of these salts are discernible with the integration ratios at an $I_{a+b}/I_c/I_d/I_e/I_f/I_g = 2:1:2:2:1:1$, within analysis errors. Moreover, these solutions are transparent, and the dynamic light scattering intensities of the solutions are roughly equal at *ca.* 1.5 kcps. These results demonstrate the excellent water-solubility of these ionized monomers. ¹H NMR (Fig. S1c) and laser light scattering results also confirmed the excellent solubility of these monomer salts in the mixture of water and methanol at a $W_{water}/W_{methanol} = 9$.

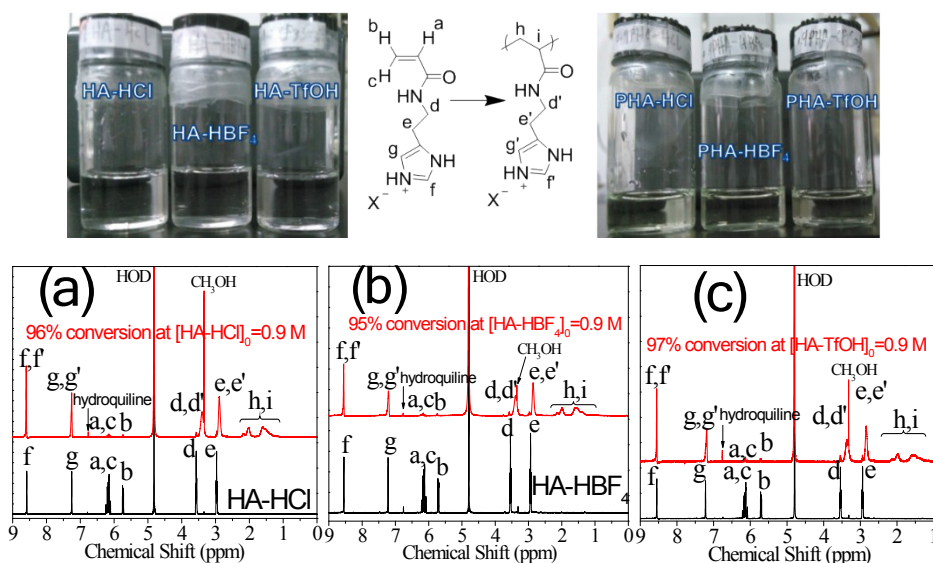


Fig. S2 ^1H NMR spectra of the monomer solutions, HA-HCl (a), HA-HBF₄ (b) and HA-TfOH (c), and the corresponding solutions after the visible light irradiations. *Top*: schematic illustration of the polymerisation and digital photographs of the solutions before and after irradiation.

As shown in Fig. S2, all the proton signals of the monomer salts and the corresponding ionic polymers are discernible. Moreover, these solutions are transparent, and the dynamic light scattering intensities of the resultant reaction solutions are roughly equal to those of the initial reaction solutions at *ca.* 1.5 kcps. These results reveal that both monomer salts and the corresponding polymers are molecularly dissolved in water. Accordingly, monomer conversions were assessed according to: $\text{conversion} = (I_{7.3} - I_{5.7})/I_{7.3} \times 100\%$.

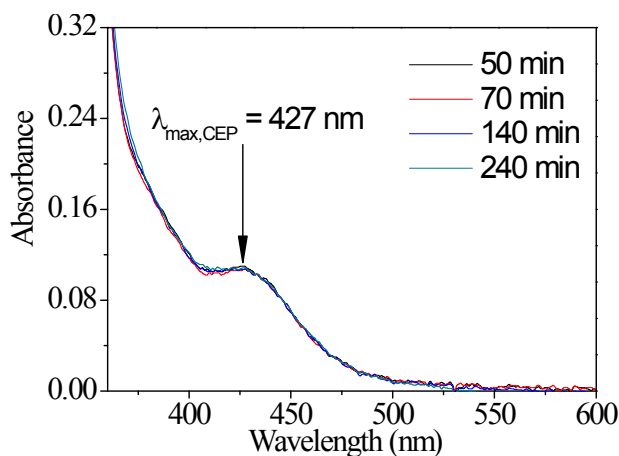


Fig. S3 UV-vis spectra of reaction solutions at $[\text{HA-HCl}]_0 = 0.6 \text{ M}$, $[\text{HA-HCl}]_0/[\text{CEP}]_0 = 300$ and $[\text{HA-HCl}]_0/[\text{SPTP}]_0 = 1200$ in the mixture of methanol and water (10:90, wt/wt) under visible light irradiation at 25°C.

As shown in Fig. S3, the absorbance of the characteristic band at $\lambda_{\text{max,CEP}} = 427 \text{ nm}$ was invariable over the whole duration of irradiation. These results demonstrate that the loss of RAFT chain-ends was negligible under such mild aqueous conditions.

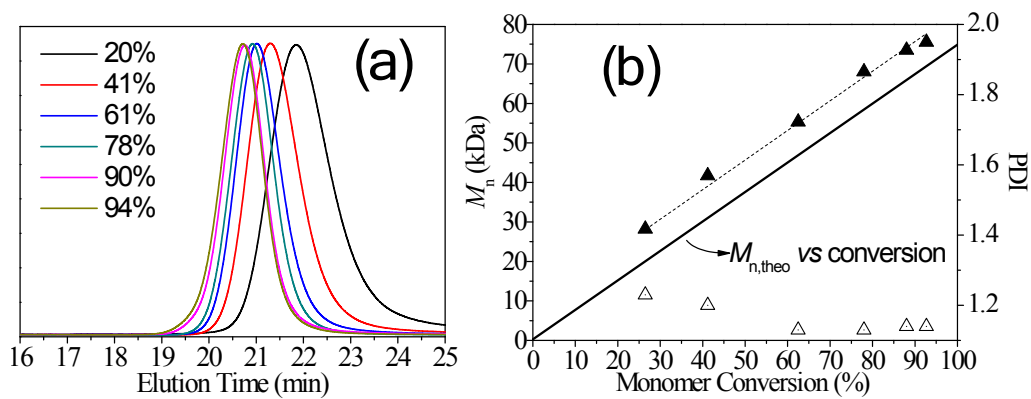


Fig. S4 (a) the shift of SEC traces, and (b) variation of molecular weight (M_n , ▲) and polydispersity index (PDI, Δ) with conversions in the reaction in 30:70 methanol/water at $[HA-HCl]_0 = 0.6$ M under visible light irradiation at 25°C.

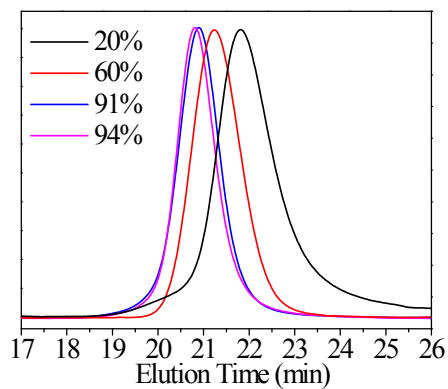


Fig. S5 shift of SEC trace with conversions in reaction in methanol/water (10:90, wt./wt.) at $[HA-HCl]_0 = 0.6$ M under visible light irradiation at 8°C.