Supplementary information

Synthesis of pH-responsive Amphiphilic Branched Macro-RAFT Agent and the Application in Surfactant-free Emulsion Polymerization

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In Fig. 1, the FTIR spectrum of the the PMA_{80}-b-$HBPtBA_{80}$ obtained by RAFT polymerization of tBA in presence of PMA_{80}-TTC as a RAFT agent, peaks at 1370cm^{-1} corresponded to tert-butyl group. After hydrolysis reaction between tert-butyl group and TFA, the band corresponded to tert-butyl group obviously disappeared and the bands at 3450 cm^{-1} corresponded to the characteristic in carboxyl group appeared in the FTIR spectrum of the PMA_{80}-b-$HBPAA_{80}$. It confirmed the success of hydrolysis reaction between tert-butyl group and TFA.

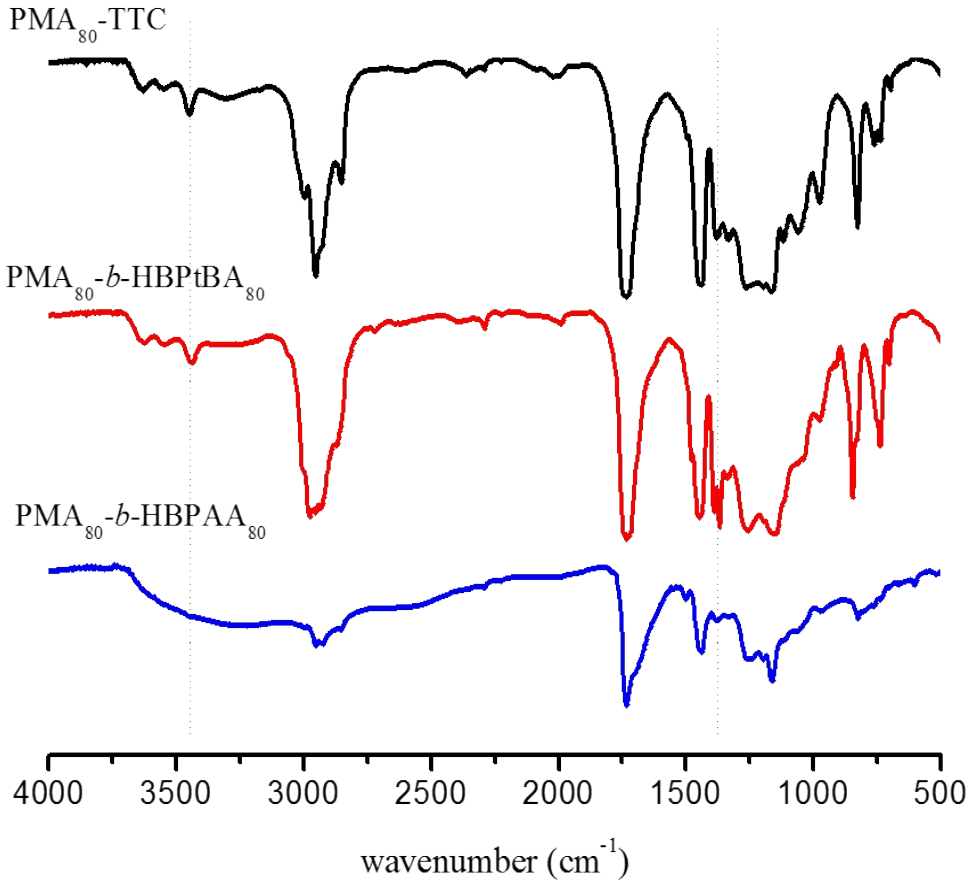
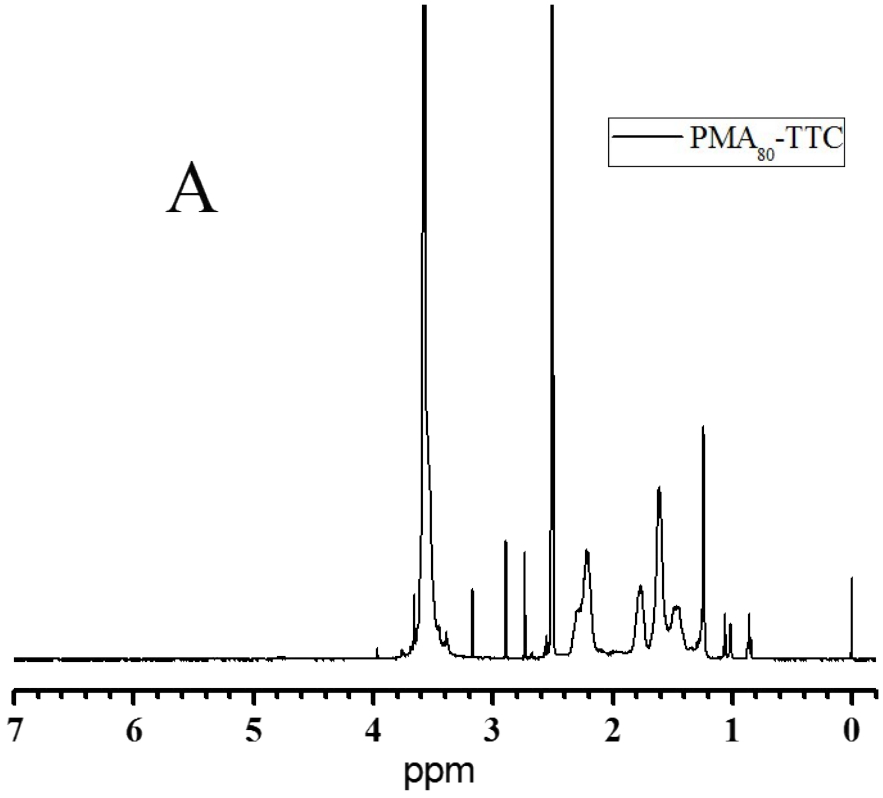


Fig. 1 FT-IR spectra of PMA_{80}-TTC, PMA_{80}-*b*-$HBPtBA_{80}$ and PMA_{80}-*b*-$HBPAA_{80}$.

The ^{1}HNMR spectra of PMA_{80}-TTC, PMA_{80}-b-$HBPtBA_{80}$ and PMA_{80}-b-$HBPAA_{80}$ were showed in Fig. 2, 1.44 ppm corresponded to tert-butyl group and δ

(TMS): 11.93 ppm and12.86 ppm corresponded to the characteristic in carboxyl group. It further proved the success of hydrolysis reaction between tert-butyl group and TFA. Through the above analysis, it is successful to acquire information on chain structures of macro-RAFT agents of PMA_{80}-TTC, PMA_{80}-*b*-$HBPtBA_{80}$ and PMA_{80}-*b*-$HBPAA_{80}$.



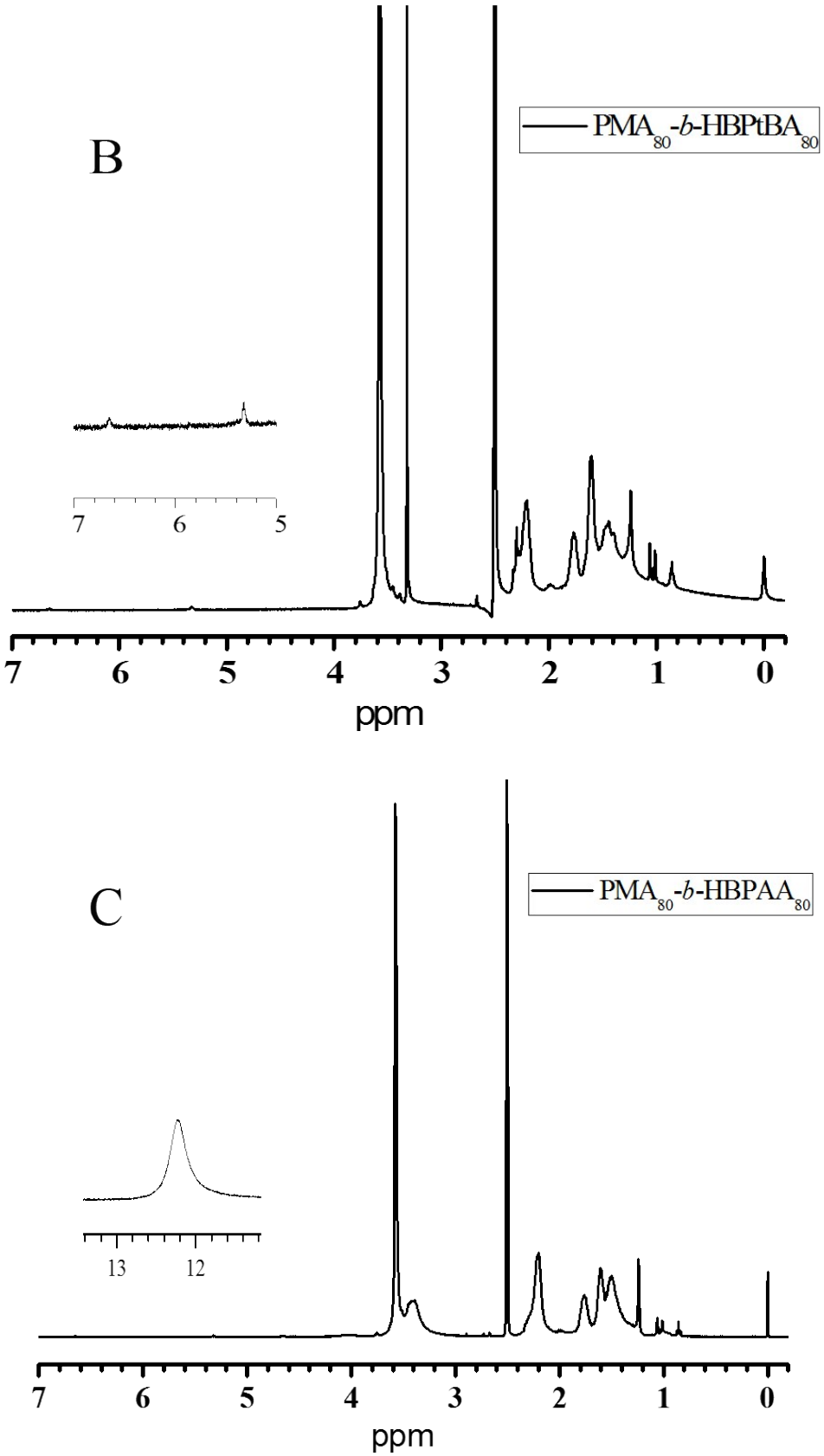


Fig.2 ^{1}H NMR spectra of (A) PMA_{80}-TTC, (B) PMA_{80}-*b*-$HBPtBA_{80}$ and (C) PMA_{80}-*b*-$HBPAA_{80}$.

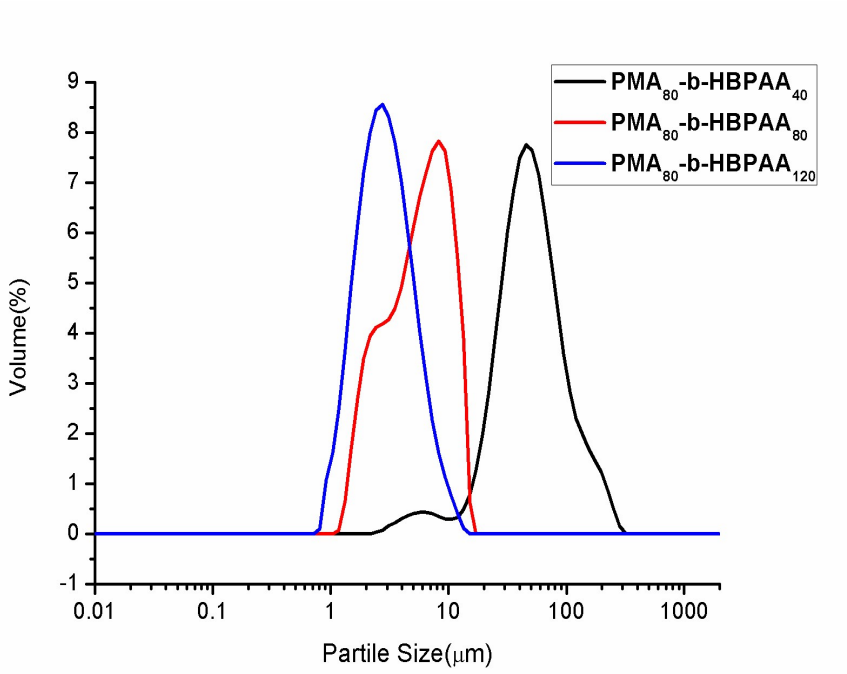


Fig.3.The particle size distribution in the emulsions prepared using (D1) PMA_{80}- b-$HBPAA_{40}$, (E1) PMA_{80}- b-$HBPAA_{80}$, (F1) PMA_{80}- b-$HBPAA_{120}$, at a fixed pH=3.0.

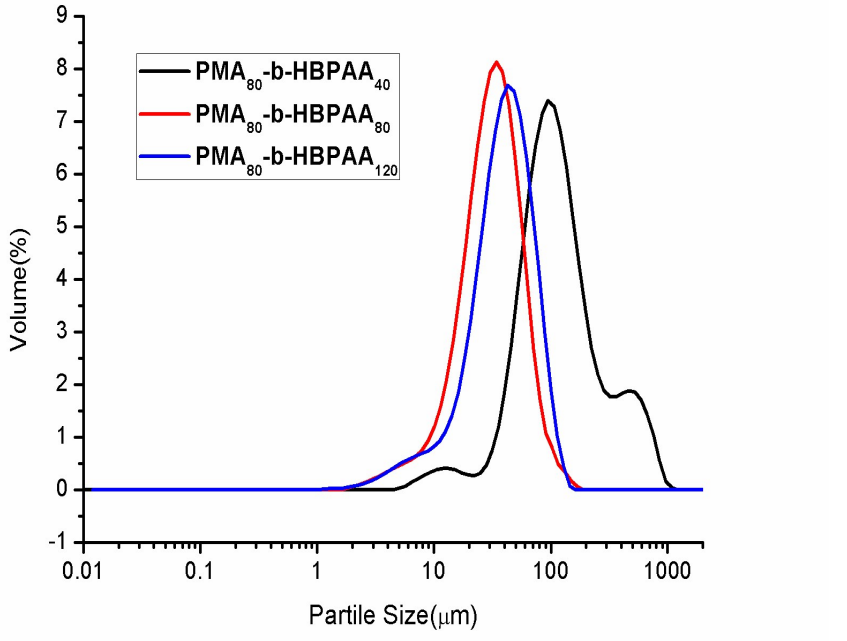


Fig.4.The particle size distribution in the emulsions prepared using (D2) PMA_{80}- b-$HBPAA_{40}$, (E2) PMA_{80}- b-$HBPAA_{80}$, (F2) PMA_{80}- b-$HBPAA_{120}$, at a fixed pH=12.0.

Table 1 [a] Uniformity of particles for toluene/water emulsions prepared using different branched copolymers.

pH	branched copolymers	Uniformity
3.0	PMA_{80}- b-$HBPAA_{40}$	0.443
	PMA_{80}- b-$HBPAA_{80}$	0.503
	PMA_{80}- b-$HBPAA_{120}$	0.559
12.0	PMA_{80}- b-$HBPAA_{40}$	0.372
	PMA_{80}- b-$HBPAA_{80}$	0.439
	PMA_{80}- b-$HBPAA_{120}$	0.431

a. Uniformity of particles was directly measured by Malvern laser particle size analyzer.

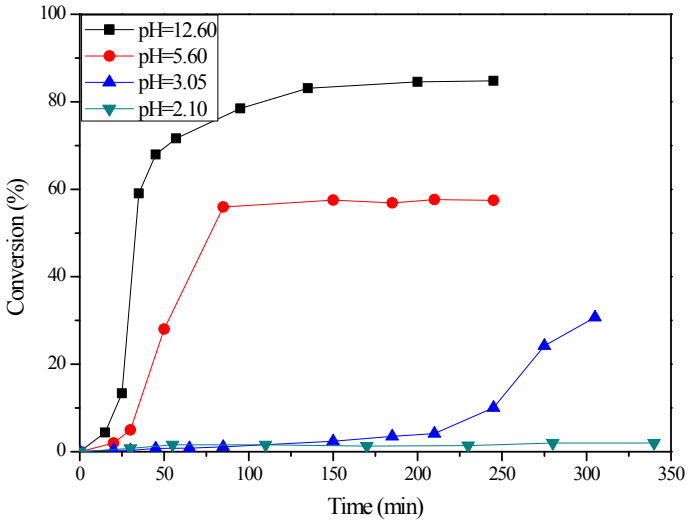


Fig.5. Evolution of monomer conversion versus time for the RAFT emulsion polymerizations of St mediated by PMA_{80}-*b*-$HBPAA_{120}$ at different pH with [St]/[PMA_{80}-*b*-$HBPAA_{120}$]/[ACPA]= 5400/7/2, [ACPA]/[$NaHCO_3$]=1/3.5, [St]=16.7wt%.

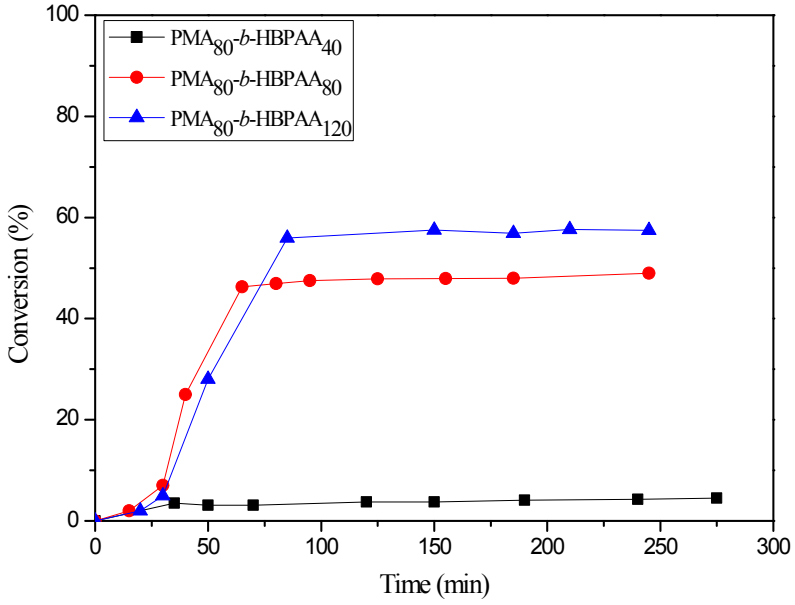


Fig.6 Evolution of monomer conversion versus time for the RAFT emulsion polymerizations of St mediated by PMA_{80}-*b*-$HBPAA_y$ with pH=5.5, [St]/[PMA_{80}-*b*-$HBPAA_y$]/[ACPA]= 5400/7/2, [ACPA]/[$NaHCO_3$]=1/3.5, [St]=16.7wt%.