# Supporting Information for *Langmuir* manuscript

## "Synthesis and Characterizationof Novel Polyacid-Stabilized Latexes"

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| Entry No. | Target DP | DP (¹H NMR) | Conv. % | Reaction time (h) | $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| 1 | 30 | 31 | 100 | 24 | 10,500 | 1.17 |
| 2 | 40 | 41 | 100 | 24 | 12,300 | 1.17 |
| 3 | 50 | 57 | 99 | 24 | 15,700 | 1.24 |
| 4 | 60 | 73 | 99 | 48 | 19,600 | 1.25 |
| 5 | 70 | 82 | 92 | 72 | 21,200 | 1.31 |

**Table S1.** Mean degrees of polymerization, monomer conversions and GPC molecular weight data for the homopolymerization of 2-hydroxypropyl methacrylate (HPMA) via ATRP in pure IPA at 50 °C (THF GPC calibrated with poly(methyl methacrylate) standards).
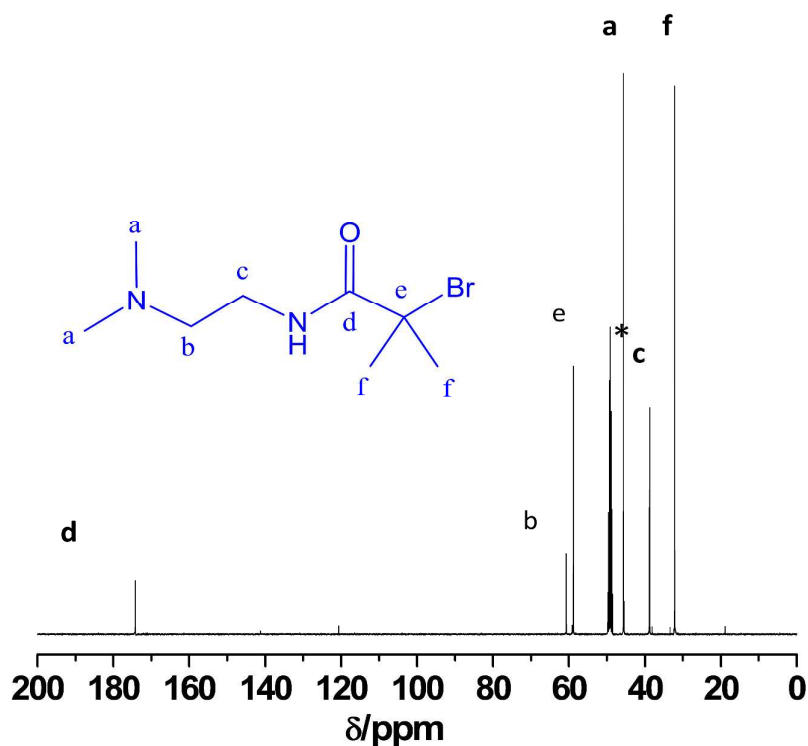


**Figure S1.** Assigned $^{13}$C NMR spectrum recorded in d$_4$-methanol for 2-(dimethylamino)ethyl-2-bromoisobutyrylamide ATRP initiator.
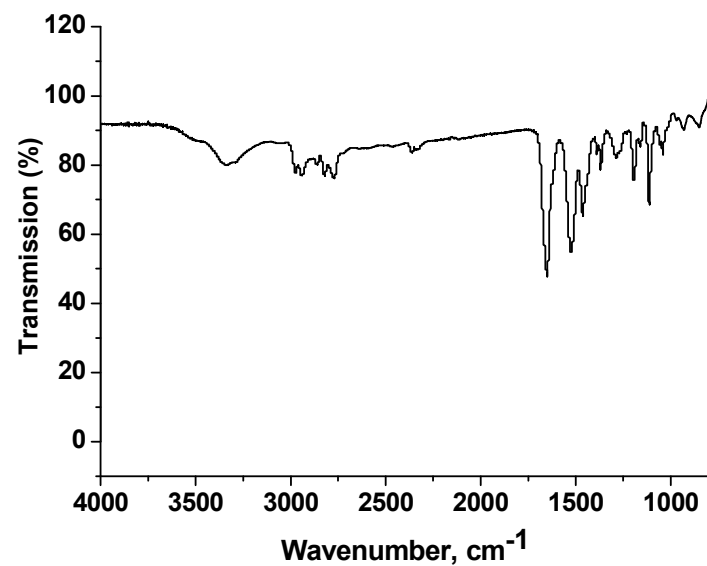
**Figure S2.** FT-IR spectrum recorded for dimethylamino)ethyl-2-bromoisobutyrylamide ATRP initiator.
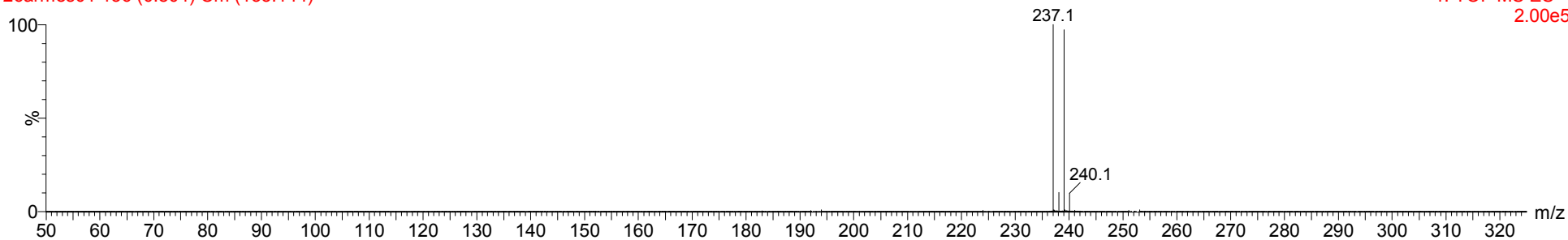
**Figure S3.** Mass spectrum recorded for 2-(dimethylamino)ethyl-2-bromoisobutyrylamide ATRP initiator. ESI-MS, m/z (M+H)$^+$ 237

Accurate mass (calculated), (M+H)$^+$: 237.0602 (237.0600) corresponding to an elemental composition of $C_8H_{18}BrN_2O$ ($C_8H_{18}BrN_2O$)
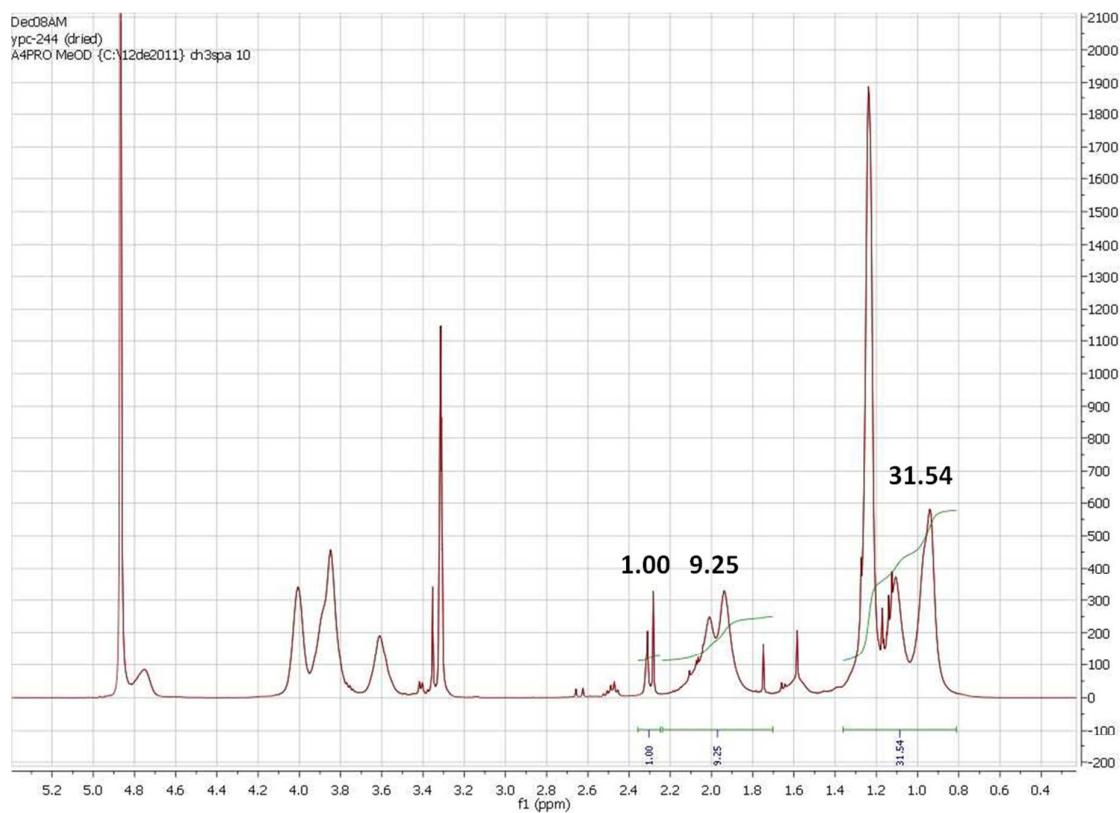
**Figure S4**. $^1$H NMR spectrum recorded in $d_4$-methanol for PHPMA$_{30}$ homopolymer precursor.

These peak integrals were used to calculate the mean degree of polymerization.
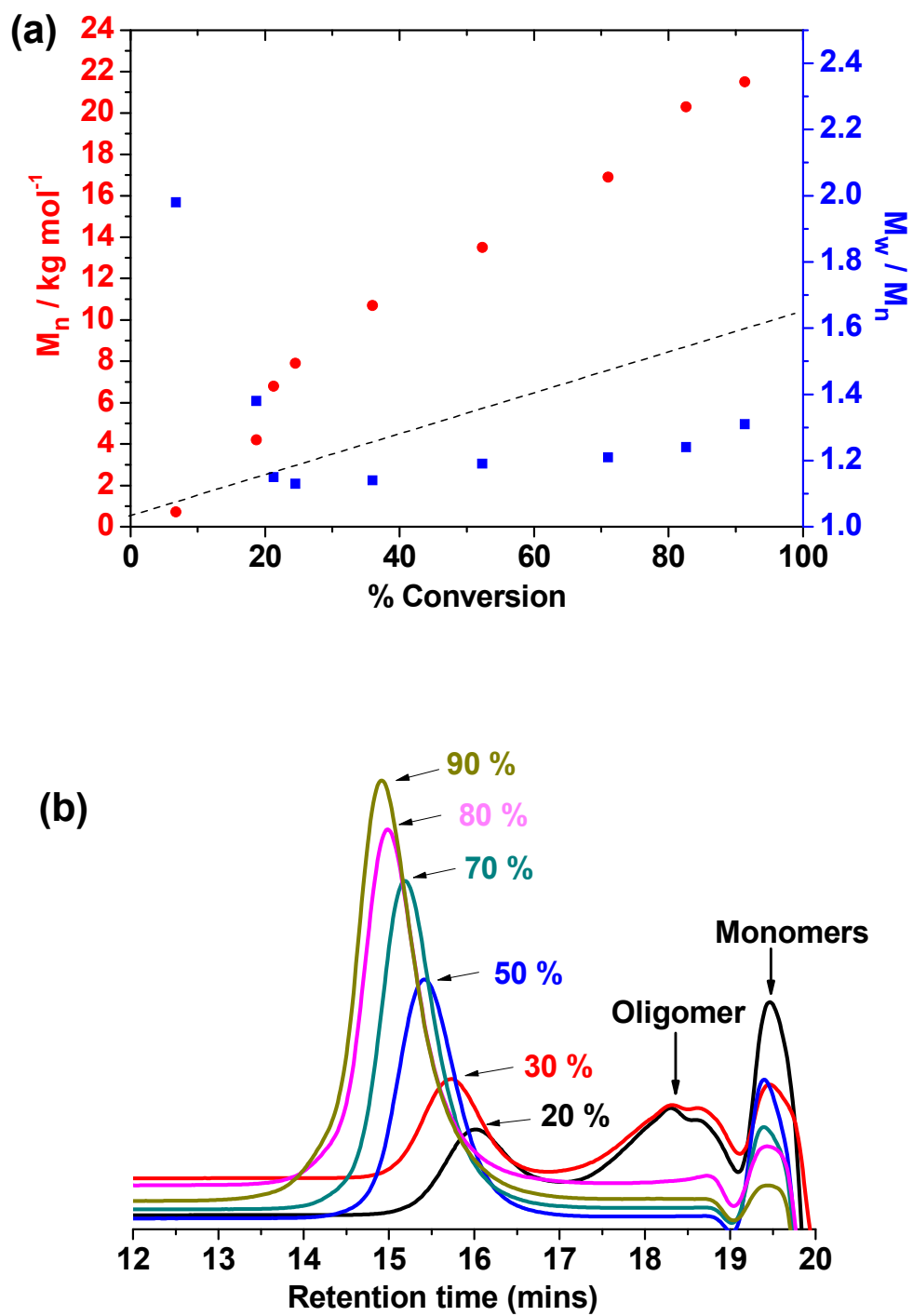
**Figure S5.** (a) Evolution of number-average molecular weight with monomer conversion and (b) THF GPC traces obtained for the ATRP synthesis of PHPMA$_{70}$ in pure IPA at 50 $^{o}$C. Relative molar ratios for initiator: Cu(I)Cl: bpy were 1:1:2. The dotted line represents the theoretical M$_n$.
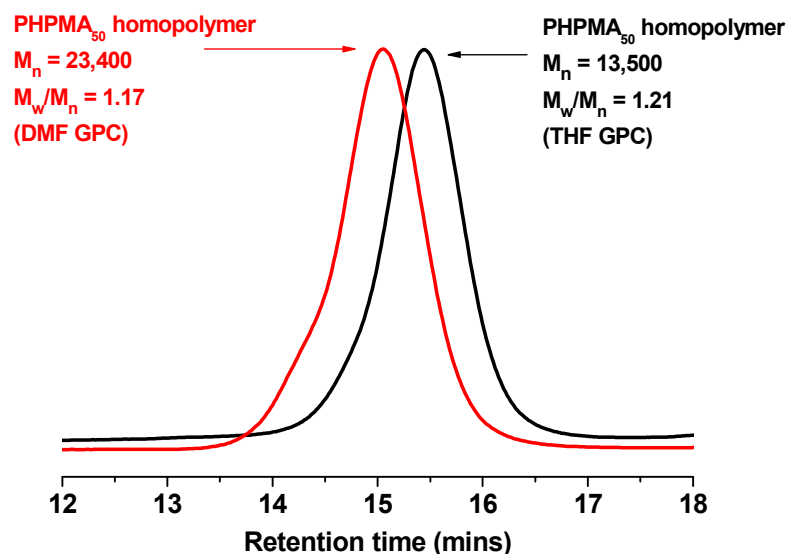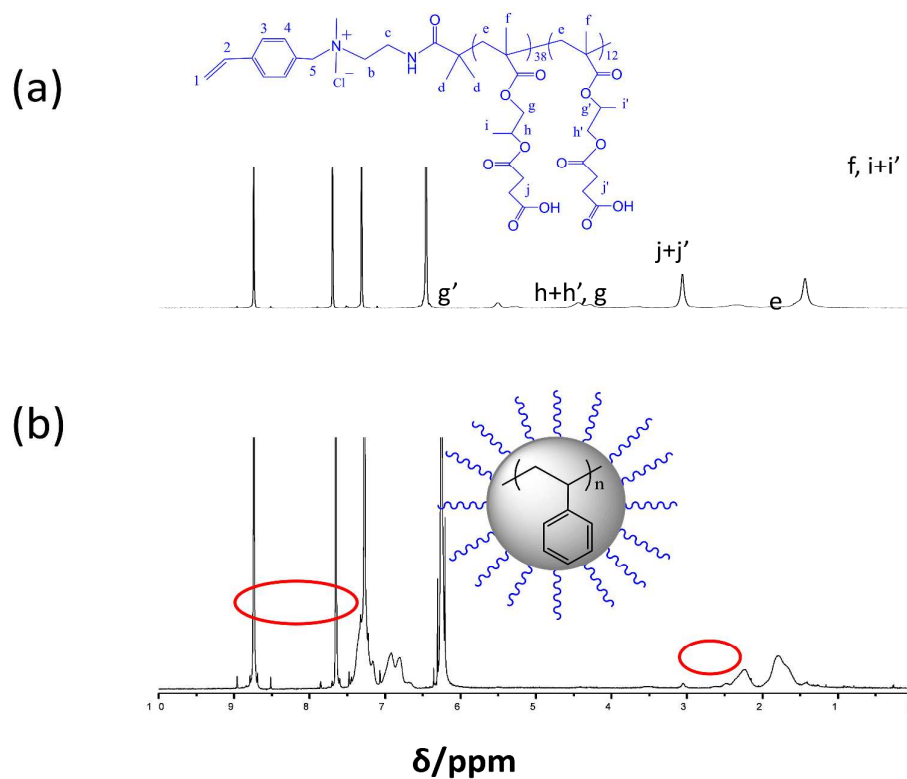
**Figure S6.** THF and DMF GPC traces obtained for PHPMA$_{50}$ homopolymer.



**Figure S7.** $^1$H NMR spectra recorded in d$_5$-pyridine for (a) PSPMA$_{50}$ macromonomer and (b) a dried PSPMA$_{50}$-PS latex prepared using 10 wt. % PSPMA$_{50}$ macromomer and a cationic AIBA initiator via aqueous emulsion polymerization. ( The red circles highlight the integrated signals that were used to determine the PSPMA stabilizer content. The signal at δ 3.0 is assigned to the four protons adjacent to the pendent carboxylic acid group on the PSPMA macromonomer, and the signals at δ 6.5-7.5 are assigned to the aromatic protons due to the polystyrene component).

**Example for calculating the stabilizer content of PSPMA-PS latexes**

For an $^1$H NMR spectrum recorded for dried PSPMA$_{50}$-PS latex prepared using 10 wt% PSPMA$_{50}$ macromomer and a cationic AIBA initiator (Figure S5), integrated signals at δ 6.5-7.5 (5H) are compared with signals at δ 3.0 (4H). This gives a PSPMA$_{50}$/PS **molar ratio (r)** of *30.87*

The molecular weight of styrene **M$_{sty}$ = *104.15 g/mol***

The molecular weight of a PSPMA$_{50}$ repeat unit **M$_{PSPMA}$ = *244 g/mol***

Therefore, the stabilizer content of this PSPMA$_{50}$-PS latex equals

$$\frac{M_{PSPMA}}{M_{sty} \times r} \times 100\% = \frac{244}{104.15 \times 30.87} \times 100\% = 7.60\%$$

**Example for calculating PSPMA stabilizer absorbed amount, Γ, in mg m$^{-2}$**

This calculation is based on the assumption that all the PSPMA macromonomer chains are located the polystyrene latex surface. For the PSPMA$_{50}$-PS latex prepared using 10 wt% PSPMA$_{50}$ macromomer and a cationic AIBA initiator (see entry 5, Table 2), the stabilizer content obtained from $^1$H NMR is **7.60 %** (see above sample calculation)

The density of polystyrene latex **ρ = 1.05 g cm$^{-3}$**

The diameter of this latex is estimated from its SEM image (see entry c, Figure 8) **d = 60 nm**

Therefore, the specific surface area **(A$_s$)** of **1 g** this latex can be calculated

$$A_s = \frac{3}{\rho(\frac{d}{2})} = \frac{3}{1.05 \times 10^{-6} \times (60 \times 10^{-9} \div 2)} = 95 \text{ m}^2$$

The value of A$_s$ is corrected **(CA$_s$)** for only a polystyrene core, assuming **1 g** of latex

$$CA_s = (1 - 7.60\%) \times A_s = 88 \text{ m}^2$$

For 1 g of latex there is 0.076 g (1 multiplied by 0.076) of PSPMA stabilizer, therefore **Γ =**

$$\frac{0.076 \times 10^3}{CA_s} = \frac{76}{88} = 0.86 \text{ mg m}^{-2}$$