Supporting Information

Polymerization-Induced Self-Assembly via RAFT in Emulsion: Effect of Z-Group on the Nucleation Step

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1.1. Synthesis and characterization of hydrophilic macroRAFT agents

Table S1 – Synthesis of hydrophilic macroRAFT agents via solution polymerization using RAFT agents with different Z-groups.[a]

MacroRAFT	RAFT agent	[Mon] (mol L^{-1})	[Mon]/ [RAFT]	[RAFT]/ [I]	X (%)/ t (h)[b]	$M_{n,th}$[c]	M_n /$Đ$[d]	*L (%)*[e]
$PMAA_{24}$-Ac	RAFT1	0.9	24	34	99/22	2380	2350/1.14	96.6
$PMAA_{40}$-Ac	RAFT1	1.0	44	39	99/22	4050	3830/1.13	97.2
$PMAA_{43}$-C4	RAFT2	1.0	43	40	98/24	3980	3930/1.13	96.8
$PMAA_{38}$-C12[f]	RAFT3	2.4	50	20	77/6	3712	4510/1.22	95.1
PAA_{43}-Ac	RAFT1	1.0	42	40	100/24	3320	2860/1.10	98.5
PAA_{40}-C4	RAFT4	1.8	40	38	99/22	3130	2940/1.10	98.5
PAA_{46}-C12[f]	RAFT5	3.0	48	20	96/6	3690	3370/1.15	97.5

[a]T = 80°C; Volume = 10-20 mL. [b]Conversion by ^{1}H NMR. [c]Theoretical M_n calculated according to equation 2. [d]Experimental number-average molar mass and dispersity determined either by SEC in THF based on conventional calibration using PMMA standards. [e]Livingness calculated according to equation 2. Water was used as solvent except for [f] performed in dioxane.

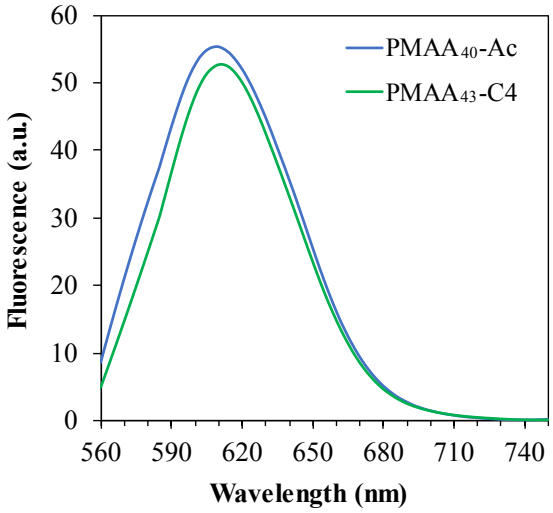

Figure S1 – Fluorescence spectra of PMAA-based macroRAFTs in aqueous solution at pH 3 using Nile red as solvachromatic dye with excitation wavelength at 550 nm. The excitation bandwidth was set at 3.0 nm and the emission bandwidth at 1.5 nm.

1.2. Additional PISA results

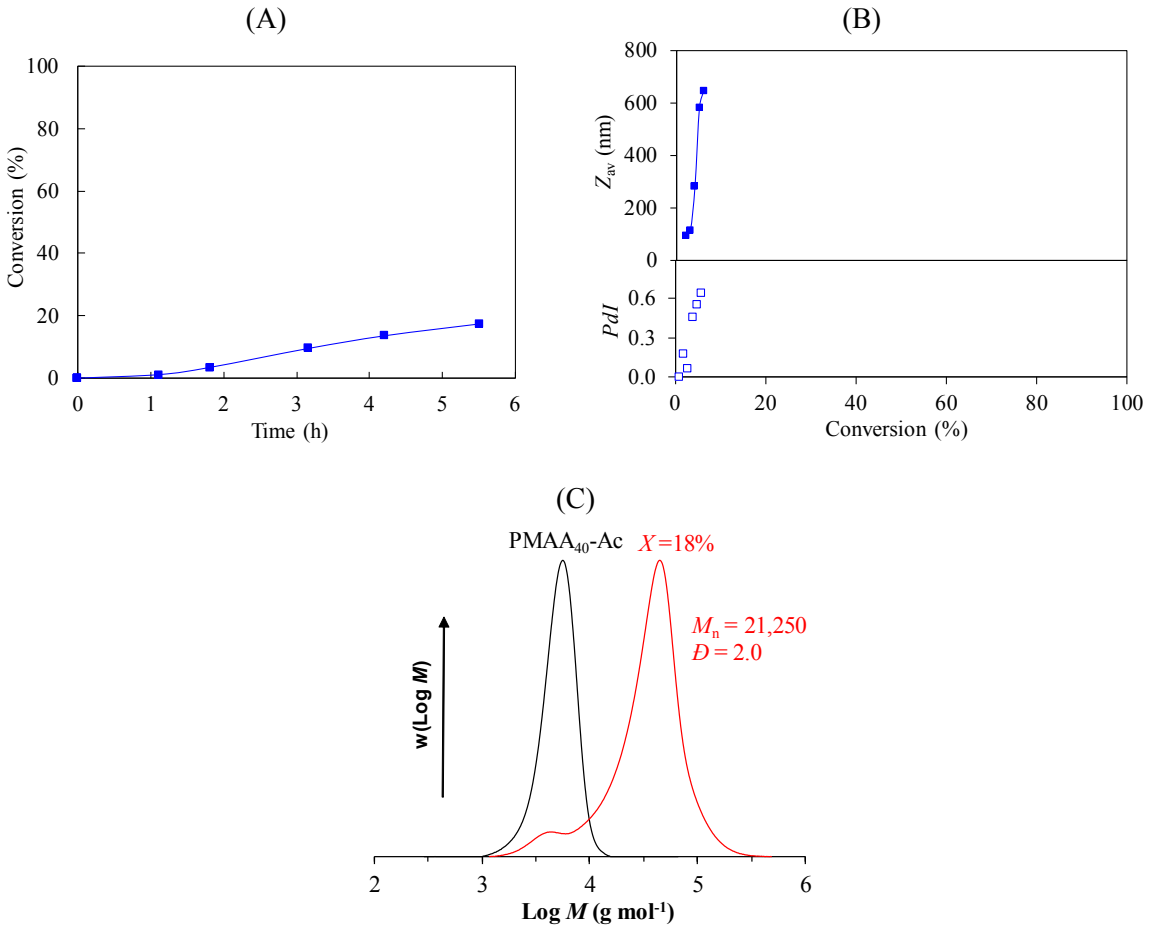

Figure S2 –PISA of styrene using $PMAA_{40}$-Ac macroRAFT and ACPA as initiator. (A) Conversion-time data plot, (B) intensity-mean average diameter (Z_{av}) and dispersity index (PdI) and (C) THF-SEC traces based on PS calibration curve. The formulation was based on Latex 2 but targeting a higher DP of 1200 and using ACPA as initiator. SC = 20%; T = 80°C; [RAFT]/[I] = 5; [Mon]/[RAFT] =1200; pH_0 = 2.5. $[NaHCO_3]$/[ACPA] = 3.5 was used to dissolve ACPA in water.

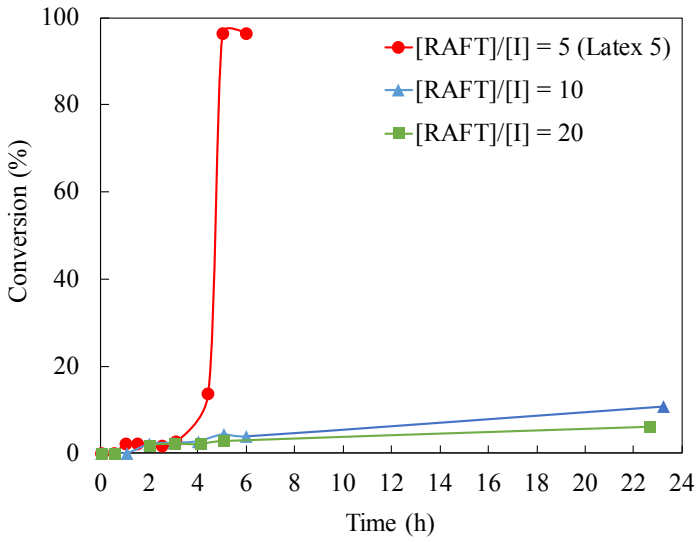

Figure S3 – Conversion-time data for PISA of styrene using PAA_{43}-Ac macroRAFT at different [RAFT]/[I] ratios. The formulations were based on Latex 5 but using a lower concentration of initiator at [RAFT]/[I] = 10 and 20.