

Supporting Information

Multiple Morphologies of PAA-*b*-PSt Aggregates throughout RAFT Dispersion

Polymerization of Styrene with PAA Macro-CTA

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3.1 Living features for RAFT Dispersion Polymerization of St.

To understand the mechanism of phase separation and morphology transition in polymerization-induced assembly, living features of RAFT dispersion polymerization in the present case should be firstly confirmed. Thus, the polymerizations of St (1.04 g) were carried out in different polymerization vials at 80 °C with PAA-DMP as macro-CTA and methanol (1.00 g) as the solvent. The feed molar ratio of St/PAA-DMP was kept at 1000:1. At the different intervals, one of the polymerization vials was taken out for the characterizations. Monomer conversion (*Con*) was determined gravimetrically and the composition of purified copolymer was determined with ¹H NMR spectrum in pyridine-*d*₅. ¹H NMR, pyridine-*d*₅, δ (TMS, ppm): 0.86 (m, 3H, -CH₃), 1.15-2.40 (m, -CH₂CH-), 3.32 (t, 2H, -CH₂S), 6.83-7.22 (m, -C₆H₅).

$$L_{\text{PSt}} = L_{\text{PAA}} \frac{I_{6.83-7.22}/5}{I_{1.15-2.40}/3 - I_{6.83-7.22}/5}$$

Equation 1

where $I_{6.83-7.22}$ and $I_{1.15-2.40}$ is the integral value of the proton signals at $\delta = 6.83\sim 7.22$ ppm and $\delta = 1.15 \sim 2.40$ ppm, respectively.

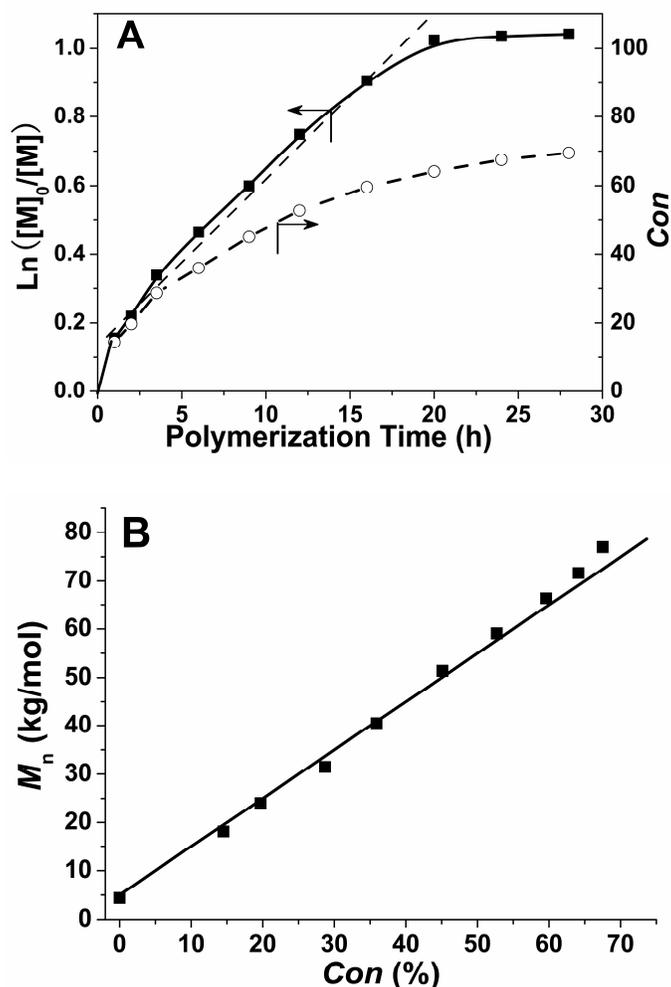


Figure S1 A: Kinetic plots of $\ln([M]_0/[M])$ - t and Con - t in RAFT dispersion polymerization; B: dependence of molecular weight of PSt block from ^1H NMR analysis ($M_{n\text{PSt,NMR}}$) on Con . PAA-DMP/St/AIBN = 10:10000:1 (in mole); St: 1.04 g; methanol: 1.00 g; 80 °C.

As shown in Figure S1-A, the linear dependence of $\ln([M]_0/[M])$ on polymerization duration (t) is roughly observed in the range of monomer conversion between 15-63%.

Within this duration, the transition of copolymer assemblies from spherical micelles, cylindrical micelles to vesicles occurred, as shown in Figure 2. Based on the data of Figure 1B, it is also found that $M_{n\text{PSt,NMR}}$ is proportional to Con below 63 % conversion.

Below the conversion of 15 %, polymerization rate was relatively larger. At this point of polymerization time (1 h), spherical micelles were formed. Above 63 % conversion corresponding to polymerization time of 16 h, polymerization rate was almost zero and large compound vesicles were produced. Moreover, $M_{n\text{PSt,NMR}}$ began to be greater than the expected value. These variation tendencies of polymerization rate and polymerization degree might be attributed to the morphology transition of copolymer assemblies.

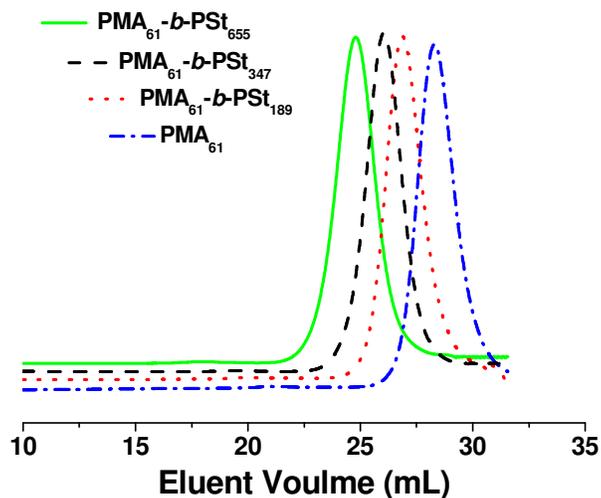


Figure S2. GPC traces of PMA-*b*-PSt from the esterification of PAA-*b*-PSt formed at different polymerization times.

To determine the molecular weight distribution of block copolymer obtained, PAA-*b*-PSt was converted into poly(methyl acrylate)-*b*-PSt (PMA-*b*-PSt). GPC traces

with THF eluent are demonstrated in Figure S2. The apparent molecular weight of PMA-*b*-PSt shows the continuous shift to higher molecular weight region with polymerization time and narrow distribution ($M_w/M_n < 1.20$). Above 63 % of *Con*, GPC traces become broader.