

File: Chundong Huang_v1.0-St, 4VP-PISA_20170702

**Adding Solvophilic Comonomer to Polymerization-Induced
Self-Assembly of Block Copolymer and Homopolymer: A
Cooperative Strategy for preparing Large Compound Vesicles**

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The ^1H NMR spectrum of the polymerization solution and the equations

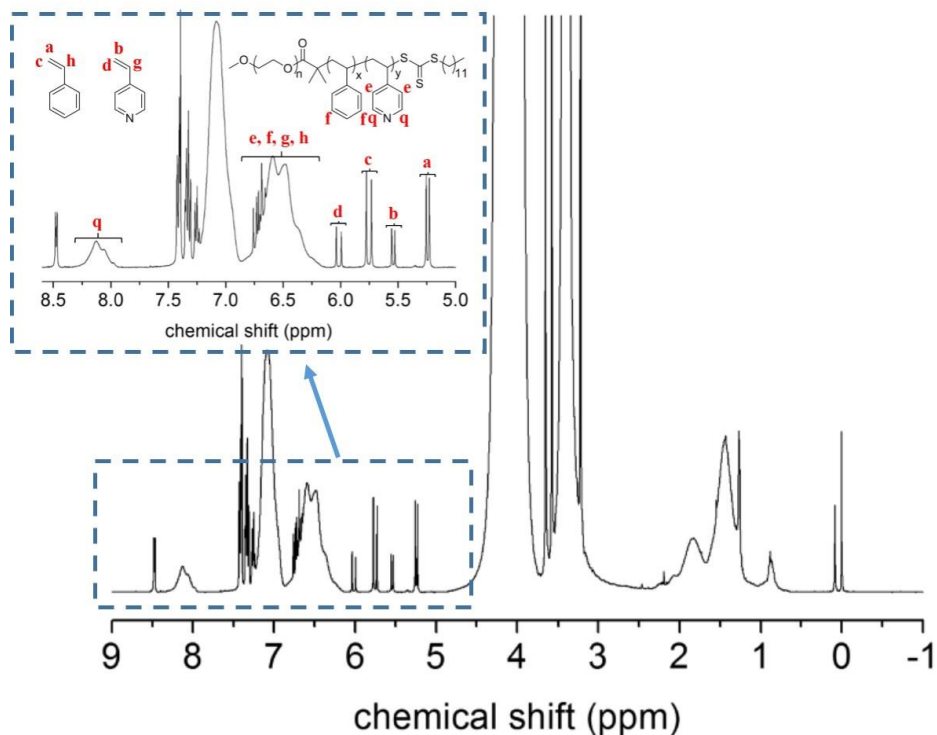


Figure S1. The ^1H NMR spectrum of the polymerization solution after the RAFT dispersion polymerization of 4VP and St mediated by mPEG₄₅-DDMAT and DDMAT in CDCl₃.

$$\text{Conversion}_{4VP} \% = \frac{I_{7.9 \sim 8.4}}{I_{7.9 \sim 8.4} + I_{5.97 \sim 6.06} + I_{5.5 \sim 5.58}} \times 100\% \quad (\text{S1})$$

$$\text{Conversion}_{St} \% = \frac{I_{6.1 \sim 6.85} - I_{7.9 \sim 8.4} - I_{5.97 \sim 6.06} - I_{5.69 \sim 5.82}}{I_{6.1 \sim 6.85} - I_{7.9 \sim 8.4} - I_{5.97 \sim 6.06} + I_{5.69 \sim 5.82}} \times 100\% \quad (\text{S2})$$

$$\text{Conversion}_{St/4VP} \% = \frac{n_{St} \times \text{Conversion}_{St} + n_{4VP} \times \text{Conversion}_{4VP}}{n_{St} + n_{4VP}} \times 100\% \quad (\text{S3})$$

in which, n_{St} and n_{4VP} are the initial molar quantity of the feeding styrene and 4-vinylpyridine, respectively.

Table S1. Summary of GPC data obtained for polymer nano-objects synthesized at 15% w/w solids via RAFT dispersion polymerization of St and 4VP in methanol/water (80/20, w/w) at 70 °C with $[m\text{PEG}_{45}\text{-DDMAT}]/[\text{DDMAT}] = 1/1$ at different $[\text{St}]_0/[\text{4VP}]_0$ ratios (DP of 200).

Exp.	$[\text{St}]_0/[\text{4VP}]_0$	final compositions	M_n (kg/mol)	M_w/M_n
1	6/1	mPEG ₄₅ -P(St _{133-co} -4VP ₁₈)/ P(St _{133-co} -4VP ₁₈)	13.6	1.10
2	5/1	mPEG ₄₅ -P(St _{124-co} -4VP ₂₀)/P(St _{124-co} -4VP ₂₀)	12.0	1.10
3	4/1	mPEG ₄₅ -P(St _{108-co} -4VP ₂₄)/P(St _{108-co} -4VP ₂₄)	11.1	1.12
4	3/1	mPEG ₄₅ -P(St _{93-co} -4VP ₃₁)/P(St _{93-co} -4VP ₃₁)	10.6	1.13
5	2/1	mPEG ₄₅ -P(St _{96-co} -4VP ₄₉)/P(St _{96-co} -4VP ₄₉)	12.0	1.14

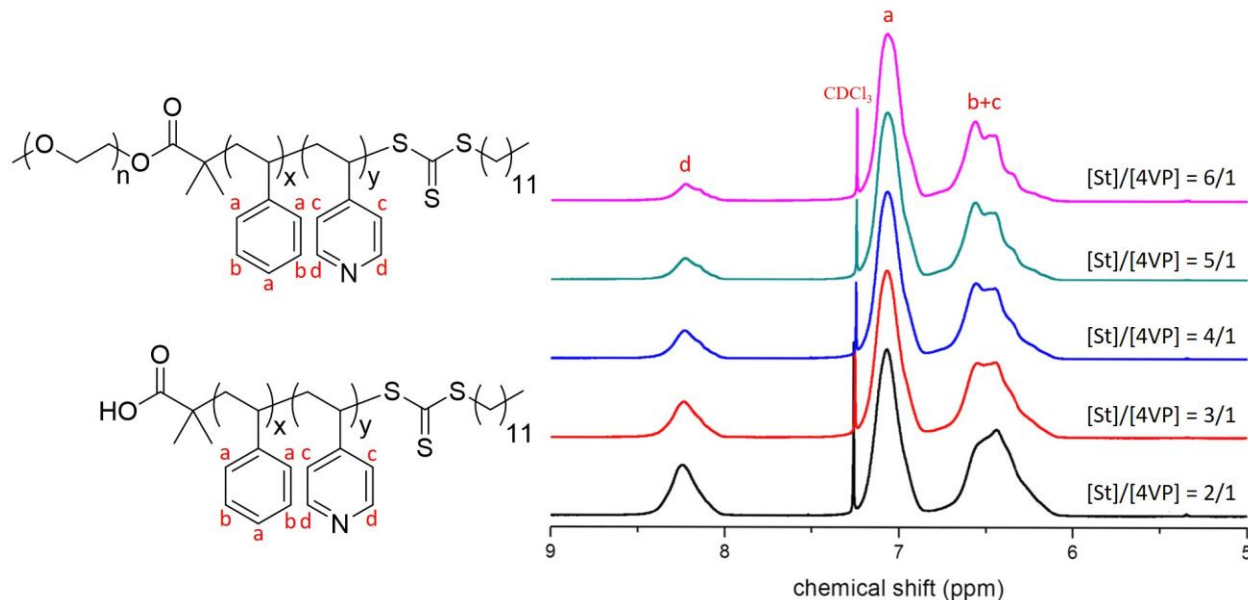


Figure S2. ^1H NMR spectra of mPEG₄₅-P(St-co-4VP)/ P(St-co-4VP) assemblies prepared via RAFT dispersion polymerization of St and 4VP with $[m\text{PEG}_{45}\text{-DDMAT}]/[\text{DDMAT}] = 1/1$ at different $[\text{St}]_0/[\text{4VP}]_0$ molar ratios in CDCl_3 .

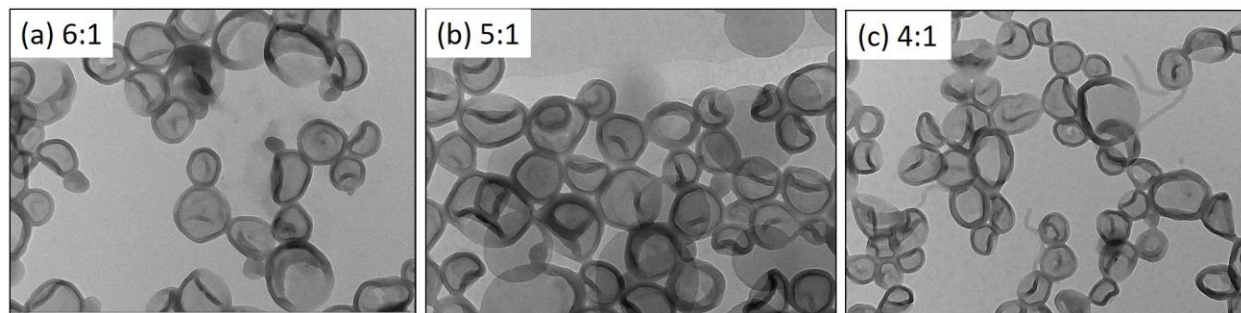


Figure S3. TEM images of polymer nano-objects prepared via RAFT dispersion polymerization of St and 4VP in methanol/water (80/20, w/w) at 70 °C mediated by mPEG₄₅-DDMAT at different [St]₀/[4VP]₀ ratios (target DP of 200).