Supporting Information

Dynamics of Soft and Hairy Polymer Nanoparticles in Suspension by NMR Relaxation

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1. CHEMICALS

Styrene (St), divinylbenzene (DVB), hexadecane, 2,2'-Azobis(2-methylbutyronitrile) (V-59), sodium dodecyl sulfate (SDS) methyl acrylate (MA), dimethyl formamide (DMF), dichloromethane (DCM), and DCM-d_2 were provided by Sigma-Aldrich. Anisole, n-hexane, tetrahydrofuran (THF), copper (II) bromide, Ascorbic acid, N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA) were purchased from Acros Organics. St, DVB, and MA were purified with a column of neutral alumina. Other commercially available chemicals were used as received. Polymerizable ATRP initiator (2-((2-(3-Methyl-2-oxobut-3-en-1yl)xy)ethyl)disulfanyl)ethyl 2-Bromo-2-methylpropanoate) was synthesized according to the method previously reported (Figure S1).[1]

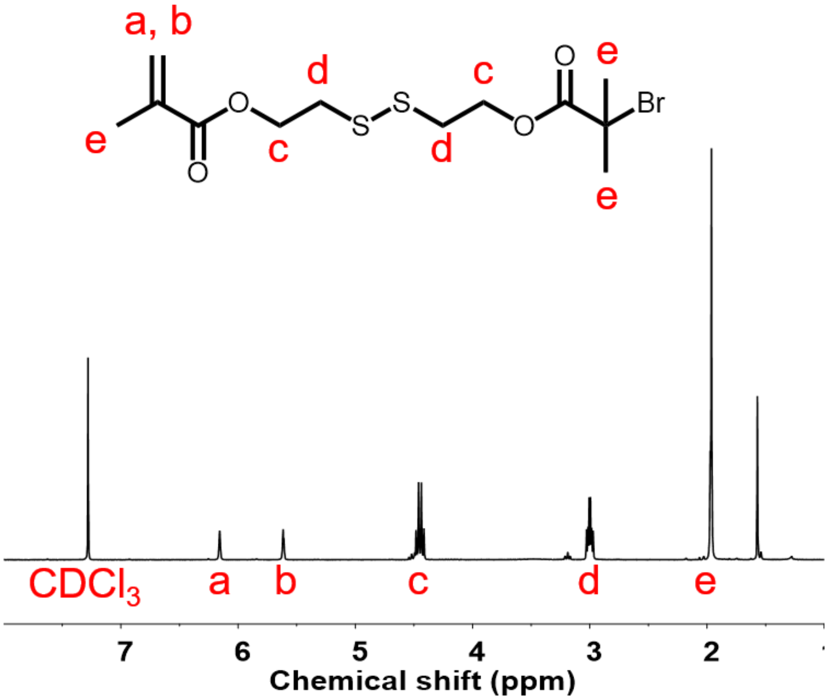

Figure S1. The ^{1}H NMR spectrum of polymerizable ATRP initiator (2-((2-(3-Methyl-2-oxobut-3-en-1yl)xy)ethyl)disulfanyl)ethyl 2-Bromo-2-methylpropanoate) in $CDCl_3$ as solvent.

2. SYNTHETIC METHODS

Synthesis of PS core NPs

The ATRP initiator functionalized PS NPs were prepared by miniemulsion polymerization followed by starve-fed emulsion polymerization. For the preparation of PS NPs cross-linked with 3 mol% of DVB (PS-DVB3), an organic phase composed of 25.3 mmol of St, 2.8 mmol of DVB, 0.14 mmol of V-59 and 1.1 mmol of hexadecane was combined to 24 mL of 0.3 wt% aqueous solution of SDS. The biphasic mixture was pre-emulsified by stirring for 10 min and then emulsified by ultrasonication (Branson Sonifier W 450 Digital equipped with a titanium solid extender tip, diameter of 1/2”). The solution was sonicated in an ice bath at 70% amplitude for 2 minutes in 10-seconds pulses followed 2-seconds pauses. The emulsified mixture was immersed in an oil bath at 80 °C to initiate free radical polymerization. Once the conversion reached 90%, 2 mL of 7.6 wt% SDS aqueous solution was added to increase the SDS concentration to 0.5 wt%. Then, an organic phase mixture of 5.8 mmol of St, 0.06 mmol of DVB and 0.03 mmol of V-59 containing 0.3 mmol of ATRP initiator was injected to the reaction vessel at a rate of 1.5 mL/hour. The reaction continued overnight under argon atmosphere. The resulting ATRP initiator-functionalized NP were purified by precipitation using methanol (3X) followed by redispersion in THF and precipitation in hexane (3 X) followed by redispersion in THF and then dried.

Synthesis of PS-PMA core-canopy NPs

ATRP was used to grow PMA chains from the initiator sites at the surface of the PS core. A stock solution of Cu(II)/PMDETA was prepared by mixing $CuBr_2$ (5 mg, 0.022 mmol) and PMDETA (48 µL, 0.22 mmol) with DMF (2.5 mL); a stock solution of ascorbic acid was made by dissolving ascorbic acid (40.5 mg, 0.23 mmol) with DMF (2.5 mL). A suspension of initiator functionalized PS NPs (0.1 g, 0.0078 mmol of initiator) in anisole (2 mL) was placed in a Schlenk tube with methyl acrylate (0.5 mL, 5.5 mmol). The mixture was purged with argon for 20 min. Then, 87.6 µL and 42.6 µL of Cu(II)/PMDETA and ascorbic acid stock solution were added to the Schlenk tube and the reaction was carried out in an oil bath at 70 °C. After different polymerization times, the polymerization was quenched, and the polymer functionalized PS nanoparticles were in hexane and washed by centrifugation then redispersed in DCM (3X).

Table S1. Grafting density and size of PS NPs in H_2O and in DCM.

DVB in PS Core (mol%)	**Grafting density in H_2O (chains nm^{-2})**	**Radius of NPs in H_2O (nm)**	**Radius of NPs in DCM (nm)**
0.5	0.81±0.06	45	92
3	0.86±0.07	51	92
10	1.08±0.08	69	81

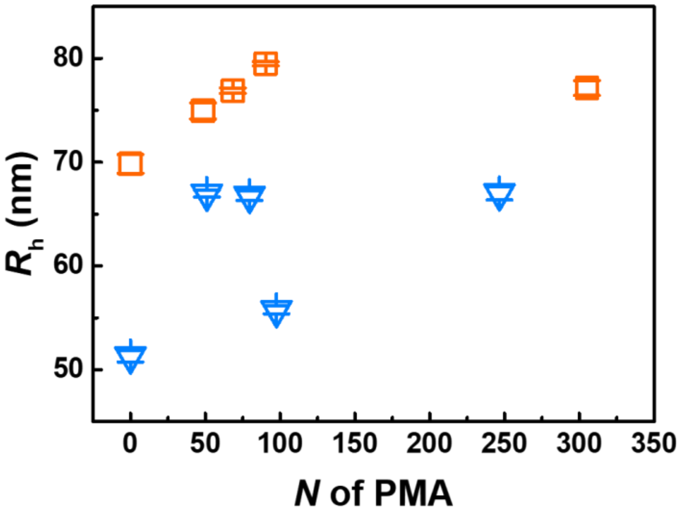

Figure S2. Hydrodynamic radius of PS-PMA NPs in water (in presence of surfactant) measured by dynamic light scattering for NPs prepared with 3 mol% of DVB (blue triangle) and 10 mol% of DVB (orange square) as cross-linker.

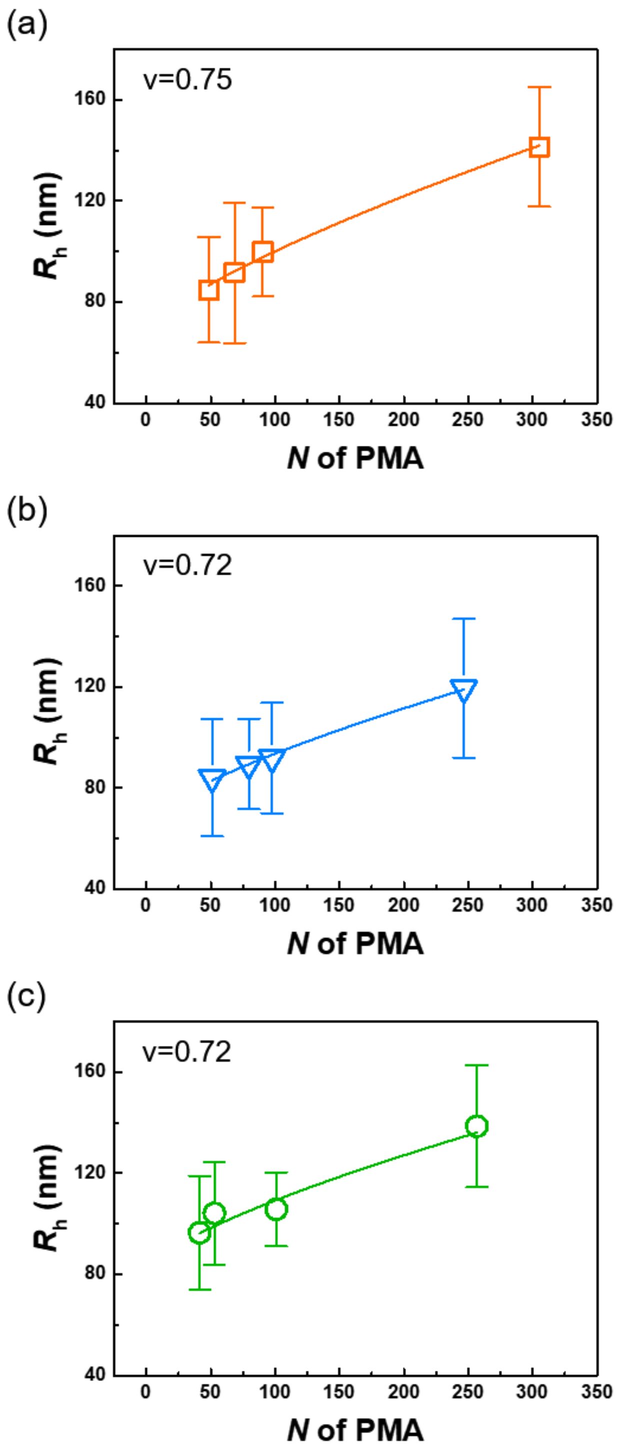

Figure S3. Radius of PS-PMA NPs with (a) 10 mol%, (b) 3 mol%, and (c) 0.5 mol% of DVB in DCM versus degree of polymerization (*N*) with the curve fit of $H \sim \mathrm{DP}^{\nu}+\mathrm{A}$.

3. NMR EXPERIMENTS

The PS-PMA core-canopy hairy NPs were dispersed in CD_2Cl_2 at a concentration of 16.7 mg·mL^{-1}. The relaxation experiments were performed on a series of NMR AVANCE spectrometers (Bruker) working at nominal frequencies of 500.13 MHz, 700.02 MHz and 850.27 MHz. The spin-lattice relaxation time constants (T_1) were measured using a standard inversion-recovery pulse sequence (180–τ–90–acquire). The recovery time (τ) was varied from 20 ms to 10 s and the temperature was set at 278 K, 288 K, 298 K and 308 K. The protons in the aromatic ring of PS (7.1 to 6.6 ppm) and in the methoxy group (3.7 ppm) were chosen for the analysis. The area of the NMR peak at each recovery time was fitted with a monoexponential decay (Eq. S1) to calculate the relaxation time T_1.

$$\frac{I(\tau)}{I(0)} = A \times (1 - 2 \times \exp(\frac{-\tau}{T_1})) \qquad \text{(S1)}$$

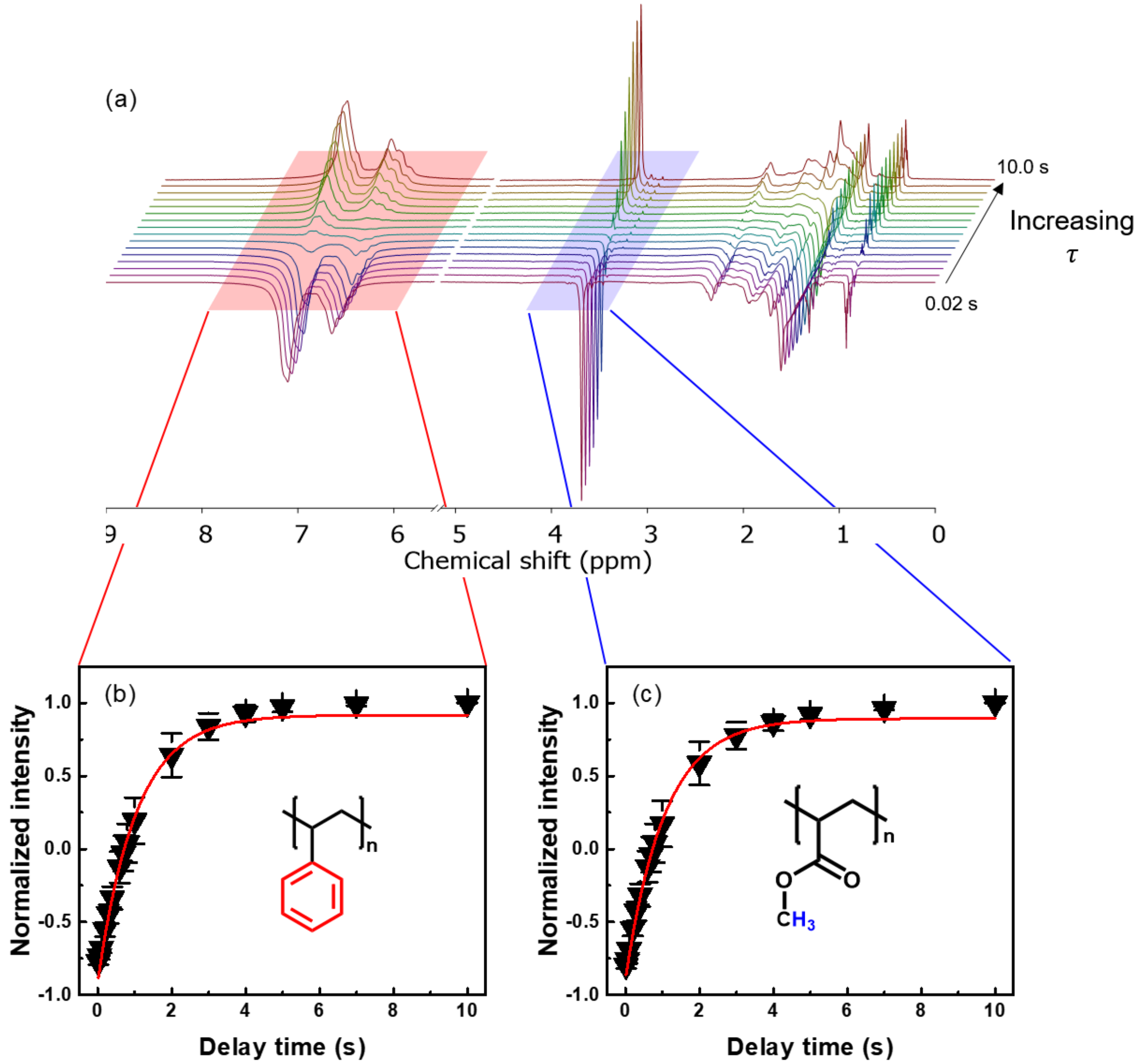

Figure S4. (a) Inversion-recovery NMR experiment of PS-PMA NPs at a Larmor frequency of 500.13 MHz at 298 K. ^{1}H magnetization recovery for (b) aromatic protons of PS and (c) methoxy protons of PMA in PS-PMA NPs fitted with eq S1

4. NMR RELAXATION

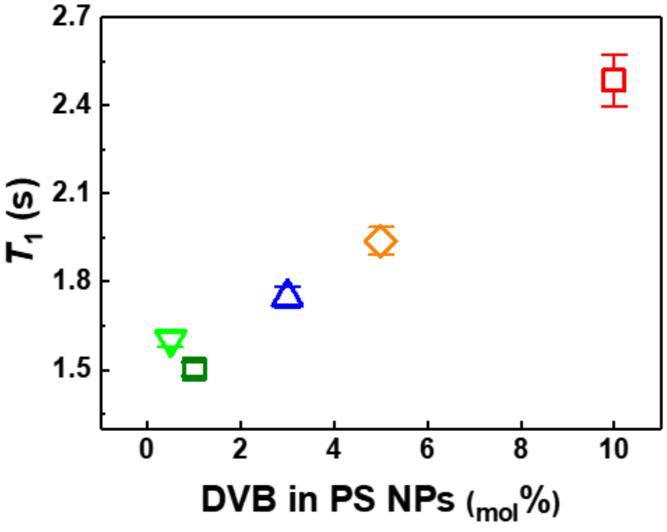

Figure S5. T_1 relaxation of PS aromatic ^{1}H in DCM-swollen naked PS NPs with different cross-linking densities, NMR at a Larmor frequency of 700.02 MHz at 298 K.

The correlation time (τ_c) was determined from the relaxation time T_1 measured at different magnetic fields with the Bloembergen-Purcell-Pound model. (Eq. S2)

$$T_1{}^{-1} = K\left[\frac{\tau_c}{1+\omega^2\tau_c{}^2} + \frac{4\tau_c}{1+4\omega^2\tau_c{}^2}\right] \tag{S2}$$

where $\omega = 2\pi\nu_0$ and ν_0 is Larmor frequency of the spin system, and K is the temperature-independent dipolar coupling constant given by:

$$K \propto \left(\frac{3\mu_0{}^2}{160\pi^2}\right)\left(\frac{\hbar^2\gamma^4}{r^6}\right) \tag{S3}$$

where μ_0 is permittivity of free space, γ is proton magnetogyric ratio, $\hbar$ is the reduced Planck constant, and r is the effective ^{1}H-^{1}H distance.

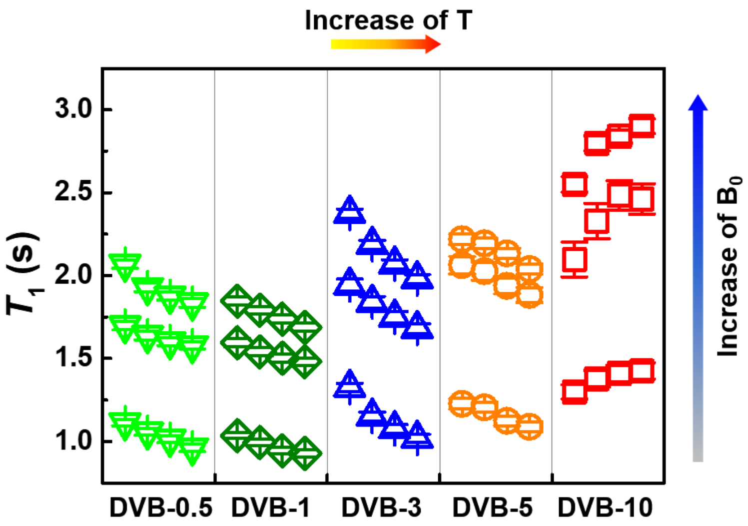

Figure S6. Temperature and magnetic field strength dependence of ^{1}H spin-lattice relaxation time of PS core NPs with different cross-linking density at Larmor frequencies of 500.13 MHz, 700.02 MHz and 850.27 MHz NMR at 278 K, 288 K, 298 K and 308 K

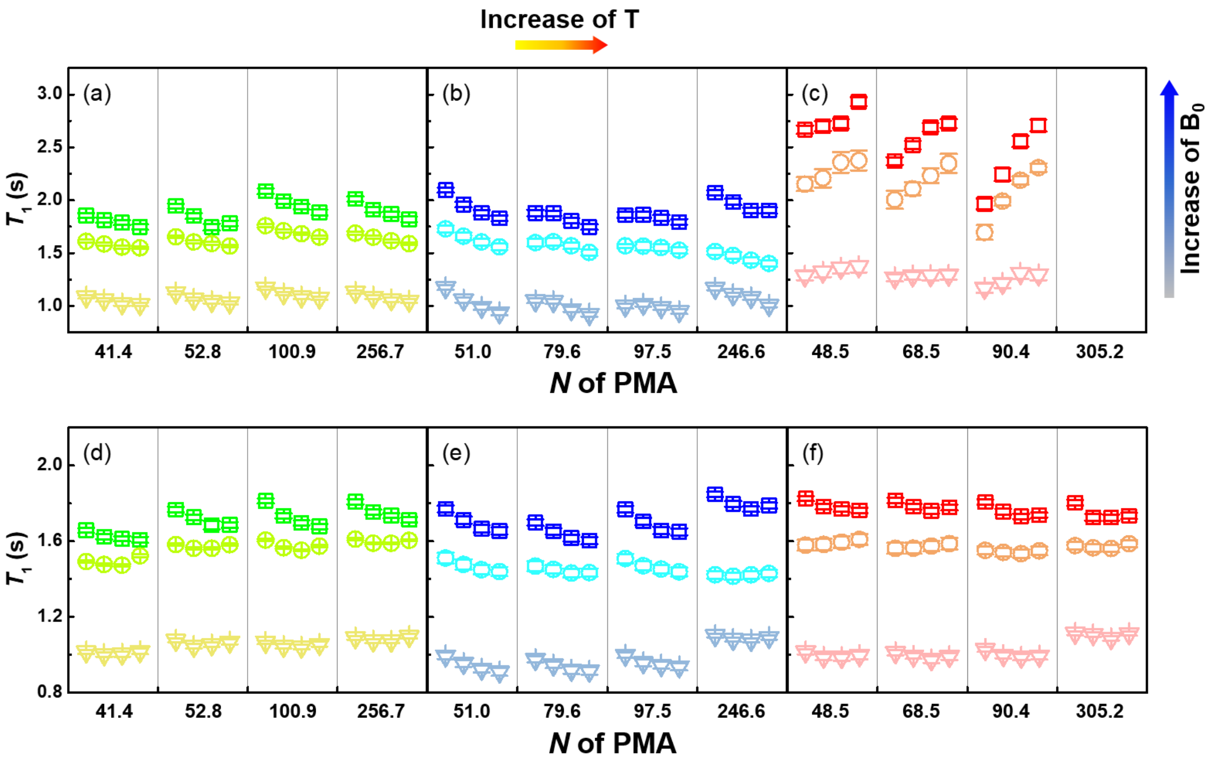

Figure S7. Temperature and magnetic field strength dependence of ^{1}H spin-lattice relaxation time of (a), (b), (c) PS core and (d), (e), (f) of PMA chains with DVB0.5, DVB3, DVB10 hairy NPs at Larmor frequencies of 500.13 MHz, 700.02 MHz and 850.27 MHz NMR at 278 K, 288 K, 298 K and 308 K. The magnetic field strength increases from the bottom set of T_1 to the above set. The temperature rises from the left (278 K) to the right (308 K) within one column.

5. THERMORESPONSIVE SWELLING BEHAVIOR OF PS-PMA NPs

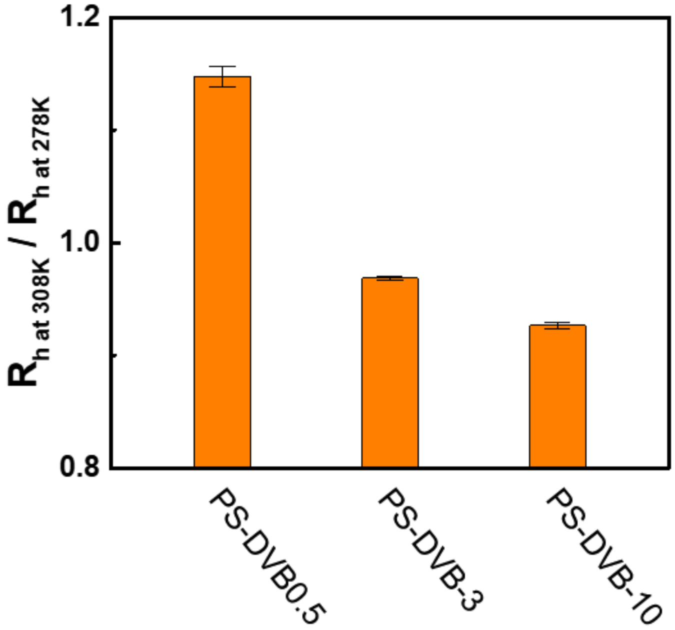

Figure S8. Normalized swelling of naked PS NPs in DCM at 308 K normalized by radii of NPs at 278 K.

6. REFERENCE

1. Graff, R. W.; Wang, X.; Gao, H. Exploring Self-Condensing Vinyl Polymerization of Inimers in Microemulsion to Regulate the Structures of Hyperbranched Polymers. *Macromolecules* **2015**, *48*, 2118-2126.