

Supplementary Materials

Table S1:

Summary of the molecular properties for PS nanoparticles prepared through nanoemulsion using divinylbenzene as the crosslinking agent, $K_2S_2O_8$ as the initiator, and dodecyltrimethylammonium bromide as the surfactant. Reactions were run at 65 °C at rates of addition of 1, 2, 10, 20, and 50mL/hr. Samples are categorized by the rate of addition of the styrene monomer and crosslinking density. Structural properties determined through small angle neutron scattering were measured using 1wt% solutions of nanoparticle in d_8 -tetrahydrofuran at 25 °C. The data was fit to Eq 1 using the fuzzy sphere form factor from Eq 2.

Rate of Add ^g (mL/hr)	χ^a mol %	Mw ^b 10 ⁶ g/mol	T _g (C)	R _g ^c (nm)	R _h ^d (nm)	PDI	R _g /R _h	R _c (nm)	τ^e (nm)	R _p (nm)	Ξ^f (nm)	σ^g
1	0.81	0.090	106	8.86	15.2	0.44	0.58	3.6 7	6.36	16.3 8	4.36	0.39
	1.91	0.167	113	8.43	17.0	0.43	0.50	3.3 0	3.76	10.8 1	8.03	0.34
	4.60	0.166	125	6.14	11.1	0.40	0.54	1.9 5	2.73	7.42	5.71	0.37
	10.7	0.386	157	6.21	10.0	0.17	0.62	3.5 1	3.44	10.4 0	3.27	0.33
2	0.81	0.238	108	10.1	16.2	0.37	0.62	3.4 6	4.62	12.6 9	3.40	0.36
	1.91	0.175	112	6.83	10.8	0.35	0.63	6.1 5	2.48	11.1 1	3.34	0.22
	4.60	0.419	120	7.00	12.5	0.35	0.56	6.0 0	1.40	8.80	3.52	0.16
	10.7	0.539	147	6.46	10.5	0.36	0.62	7.0 5	-	7.05	4.39	-
10	0.81	0.600	109	11.1	20.2	0.33	0.54	4.0 0	6.57	17.1 4	4.28	0.38
	1.91	1.079	113	10.0	19.7	0.33	0.51	8.5 3	5.47	19.4 6	5.13	0.28

	4.60	0.725	120	8.50	14.8	0.14	0.57	9.7 6	0.99	11.7 4	5.37	0.08
	10.7	0.834	144	7.70	12.5	0.35	0.62	4.9 9	-	4.99	5.18	-
20	0.81	1.189	109	12.8	24.3	0.33	0.53	2.3 3	5.01	12.3 5	10.98	0.40
	1.91	0.692	112	9.64	17.5	0.19	0.55	3.4 0	4.77	12.9 4	8.33	0.37
	4.60	1.763	121	10.8	20.9	0.28	0.52	7.4 0	1.02	9.43	1.49	0.11
	10.7	1.282	134	8.51	15.2	0.31	0.56	5.7 7	-	5.77	5.59	-
50	0.81	0.854	109	13.1	23.2	0.22	0.56	3.7 1	5.19	14.0 9	11.15	0.37
	1.91	1.232	113	11.2	20.2	0.34	0.55	4.8 5	6.33	17.5 1	4.66	0.36
	4.60	1.440	119	10.4	20.3	0.33	0.51	4.5 9	2.07	8.73	2.83	0.24
	10.7	1.326	137	8.46	14.9	0.33	0.57	8.3 3	-	8.33	5.36	-

^a mol% of DCB in total oil = $([DVB]_o/[S]_o + [DVB]_o) \times 100$

^b molecular weight calculated from forward scattering intensity at $q = 0$ ($I(0)$) from SANS using equation 4

^c Guinier radius determined from SANS

^d Hydrodynamic radius and PDI measured from DLS in THF

^e Half-width of fuzzy interfacial layer

^f Static correlation length from polymer crosslinks

^g Effective fuzziness of the nanoparticle = τ/R_p

Crosslinker		Mass (g)	Volume	Mole
-------------	--	----------	--------	------

(mol %)			(mL)	
0.81	Styrene	5.00	5.50	0.048
	Divinyl benzene	0.048	0.052	3.93×10^{-4}
1.91	Styrene	5.00	5.50	0.048
	Divinyl benzene	0.122	0.131	9.35×10^{-4}
4.60	Styrene	5.00	5.50	0.048
	Divinyl benzene	0.301	0.324	2.31×10^{-3}
10.7	Styrene	5.00	5.50	0.048
	Divinyl benzene	0.749	0.810	5.75×10^{-3}

Table S2: Composition of monomer mixtures for the crosslinking densities examined in this study.

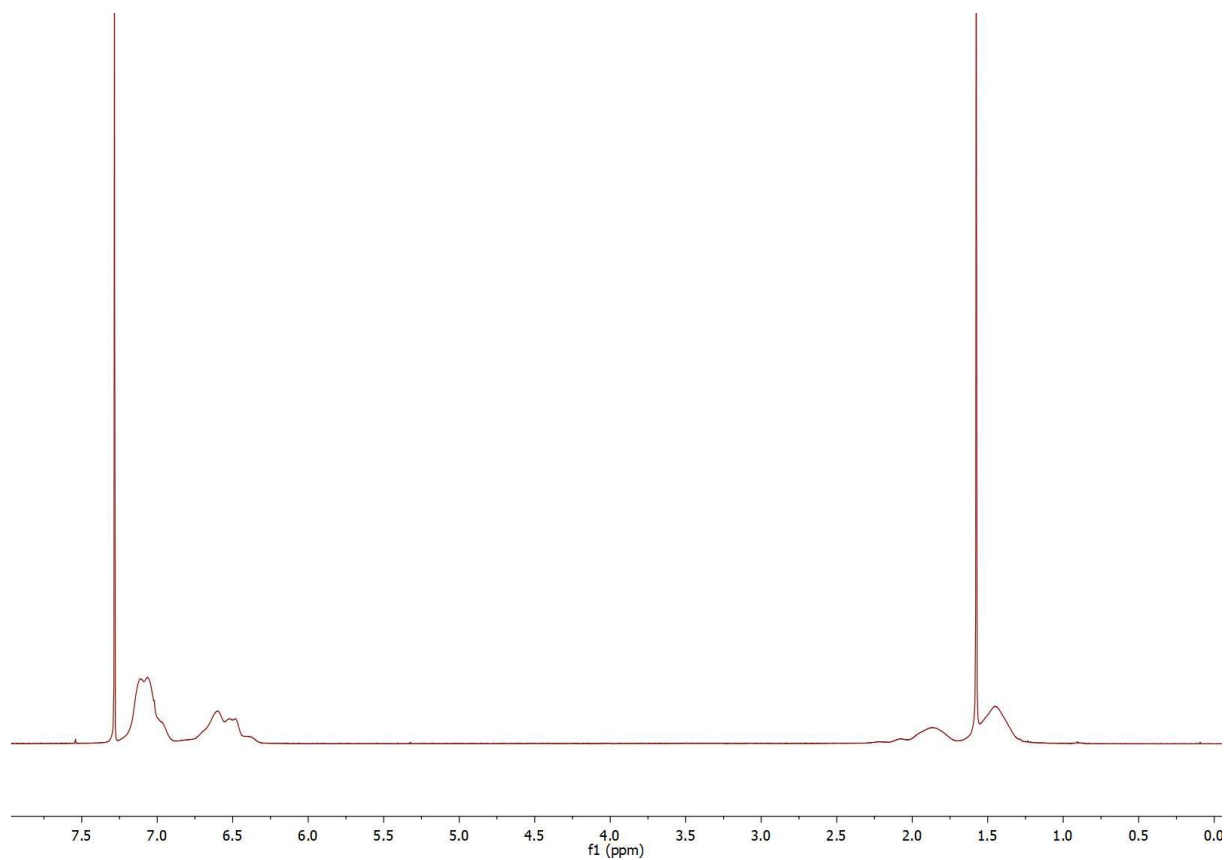
Measurements of Nanoparticle Density:

The mass of each nanoparticle sample was measured using a weight balance (Mettler Toledo NewClassic MF Model MS105DU) with an accuracy of 0.01 mg. A gas pycnometer (Micromeritics Accupyc II 1340) measured the volume of penetrable helium gas within the sample and sample cup (total volume 0.1cm^3) at room temperature ($20\text{ }^\circ\text{C}$) until the pressure did not vary more than 0.005psig/min during the equilibration period. The accuracy of the volume measurement is 0.0001 cm^3 . This cycle was repeated 5 times for reproducibility. The density was then determined from the mass to volume ratio, where the error of this measurement is less than 0.3%.

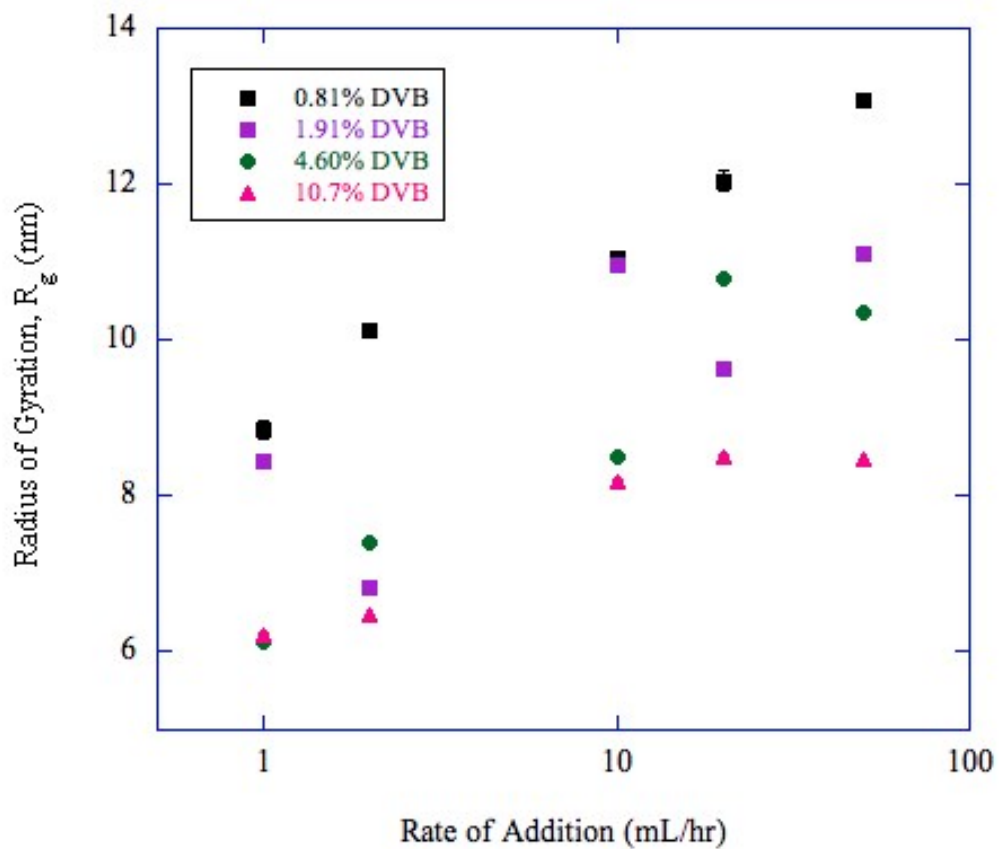
Rate of Addition (mL/hr)	χ^a (mol%)	Density (g/cm ³)	SLD (10 ⁻⁶ A ⁻²)
1	0.81	1.0519 ± 0.0006	1.394
	1.91	1.0783 ± 0.0014	1.464
	4.60	1.0783 ± 0.0007	1.440
	10.7	1.0710 ± 0.00022	1.449
2	0.81	1.0362 ± 0.0023	1.415
	1.91	1.0885 ± 0.0017	1.450
	4.60	1.0707 ± 0.0080	1.450
	10.7	1.0774 ± 0.0015	1.440
10	0.81	1.0700 ± 0.0012	1.439
	1.91	1.0745 ± 0.0015	1.445
	4.60	1.0976 ± 0.0009	1.476
	10.7	1.0788 ± 0.0018	1.451
20	0.81	1.0847 ± 0.0009	1.459
	1.91	1.1198 ± 0.0025	1.506

	4.60	1.1033 ± 0.0018	1.484
	10.7	1.1001 ± 0.0002	1.480
50	0.81	1.0883 ± 0.0014	1.464
	1.91	1.0971 ± 0.0016	1.476
	4.60	1.1301 ± 0.0010	1.520
	10.7	1.0897 ± 0.0007	1.466

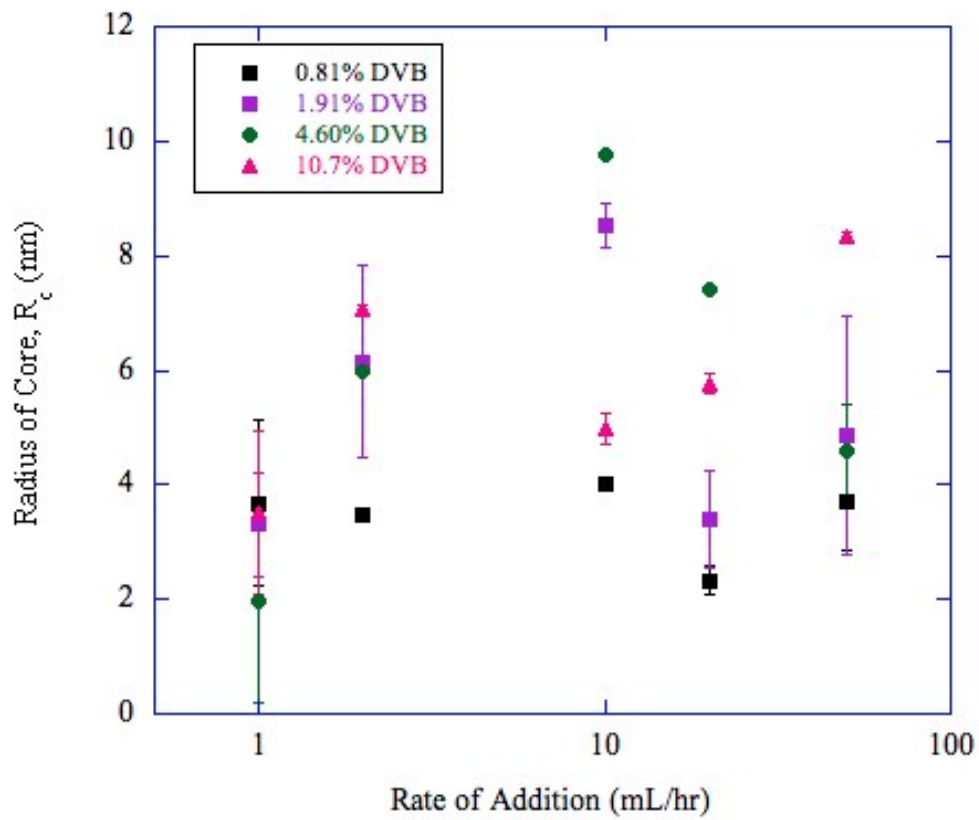
Table S3 2: Density of the PS nanoparticles as measured with pycnometry, as well as their scattering length density (SLD) determined based on the density. SLD values for each nanoparticle were obtained through the NIST SLD calculator.³⁹



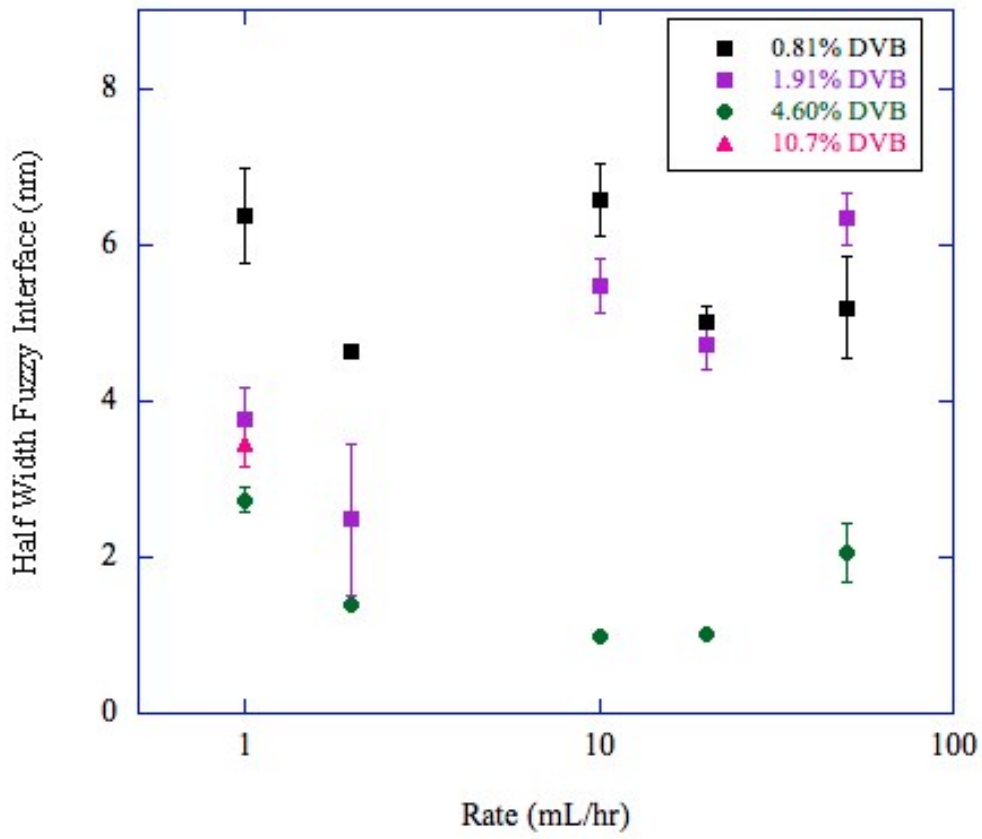
Supplemental Figure S1: ¹H NMR of soft PS NPs synthesized via 1 mL/hr rate of monomer addition with 0.81 mol% DVB crosslinker.



Supplemental Figure S2: Measured radius of gyration of PS nanoparticles as a function of monomer addition rate in d_8 -THF.



Supplemental Figure S3: Measured radius of the homogeneous core of the nanoparticle as a function of the monomer addition rate.



Supplemental Figure S4: Measured half width of the fuzzy interface in nanometers as a function of monomer addition rate.

