Supporting Information For:

Determination of Particle Size Distributions, Molecular Weight Distributions, Swelling, Conformation, and Morphology of Dilute Suspensions of Cross-Linked Polymeric Nanoparticles via Size-Exclusion Chromatography/Differential Viscometry

David M. Meunier,*[,†] John W. Lyons,[†] Joseph J. Kiefer,[†] Q. Jason Niu,[†] L. Mark DeLong,[†] Yongfu Li,[†] Paul S. Russo,[‡] Rafael Cueto,[‡] Nadia J. Edwin,[‡] Kevin J. Bouck,[†] H. Craig Silvis,[†] Christopher J. Tucker,[†] and Thomas H. Kalantar*[,†]

[†]Herbert D. Doan R&D Center, The Dow Chemical Company, Midland, Michigan 48674, United States

[‡]Polymer Analysis Laboratory, Department of Chemistry and Macromolecular Studies Group, Louisiana State University, Baton Rouge, Louisiana 70803, United States

Table S1. Summary of particle synthesis parameters.

Sample	Synthesis Process	Surfactant Type	Monomer: Surfactant (w:w)	Monomer (wt%, Rel. to Total Mixture)	Crosslinker Level (wt%, BOM[a])
1	Batch	Cu-Amine	1:2.4	7.8	4.3
2	Batch	Cu-Amine	1:3.2	6.0	4.4
3	Batch	Cu-Amine	1:2.4	8.9	8.8
4	Batch	Cu-Amine	1:2.4	7.4	16
5	Batch	Cu-Amine	1:2.4	4.9	16
6	Batch	Cu-Amine	1:2.4	5.4	12
7	Semi-Batch	Nonionic Ethoxylate	1:0.4	18.2	8
8	Batch	Ionic	1:3.4	4	19
9	Batch	Nonionic Ethoxylate	1:1.9	10.1	8
10	Semi-Batch	Nonionic Ethoxylate	1:2.1	8.6	8
11	Semi-Batch	Nonionic Ethoxylate	1:0.6	10.2	8
12	Semi-Batch	Nonionic Ethoxylate	1:0.9	17.9	19
13	Semi-Batch	Nonionic ethoxylate[b]	1:0.4	18.1	16
14	Semi-Batch	Nonionic Ethoxylate	1:1.8	9.8	24
15	Batch	Cu-Amine	1:4.0	6.3	16
16	Batch	Ionic	1:4.4	3.2	4.5
17	Semi-Batch	Nonionic Ethoxylate	1:0.4	18.2	8
18	Semi-Batch	Ionic	1:0.6	10	1.6
19	Semi-Batch	Ionic	1:0.6	10	1.6
20	Semi-Batch	Ionic	1:0.6	10	1.6
21	Semi-Batch	Ionic	1:0.3	20	1.6
22	Semi-Batch	Ionic	1:0.3	20	1.6
23	Semi-Batch	Ionic	1:0.1	40	1.6
24	Semi-Batch	Ionic	1:0.4	20	1.6
25	Semi-Batch	Nonionic Ethoxylate	1:13.2	1.8	50
26	Semi-Batch	Nonionic Ethoxylate	1:15.1	1.5	40
27	Semi-Batch	Nonionic Ethoxylate + Ionic	1:7.9	3.4	50

a. Based on Monomer

b. 70-ethoxylate

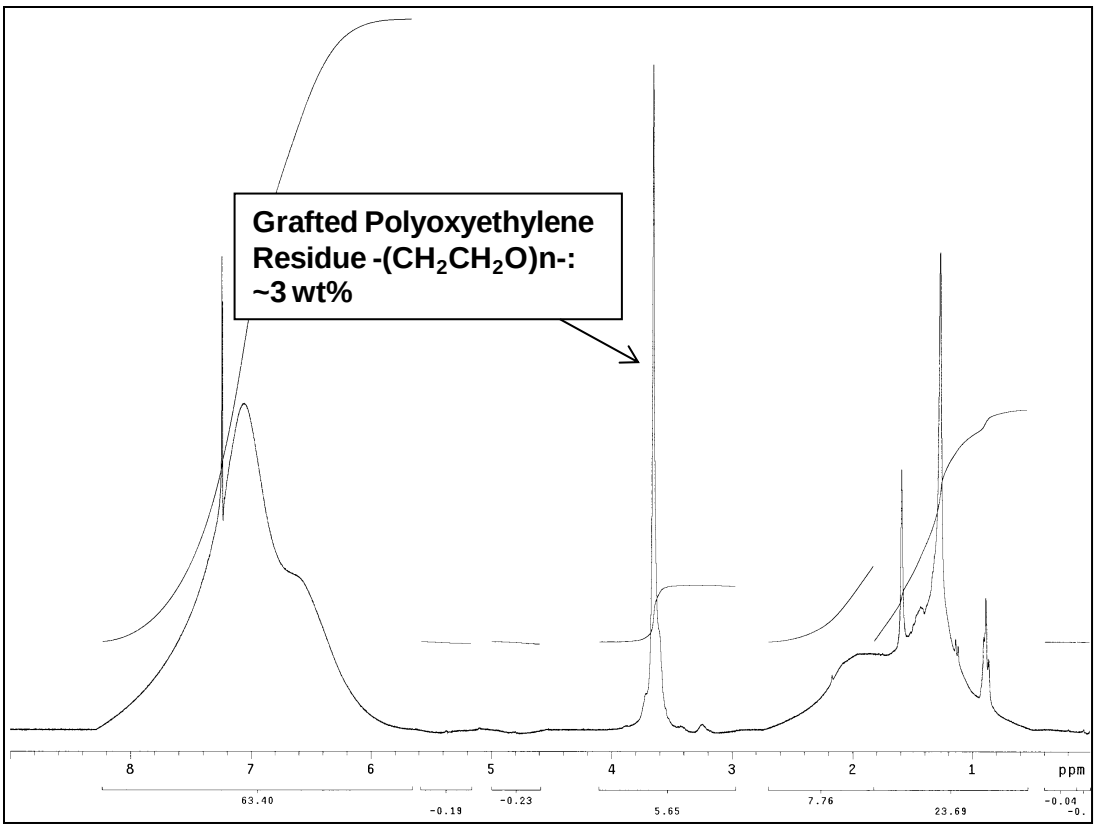

Figure S1. ^{1}H NMR spectrum of a typical PNP (sample **14**) illustrating the grafted polyoxyethylene moieties.

Typical DRI and DV signal strengths. DV and DRI signals for linear and spherical polymers: Concentration and differential viscometer chromatograms of a typical PNP sample are compared in Figure 3 to those obtained for a broad linear PS sample. Similar sample concentrations of comparable MW species were injected. Peak area response was the same for the concentration detector, as expected, but the DV response for the spheres is significantly smaller than that for the linear chains. Note that the expanded right-hand y-axis for the viscometer trace shows that the viscometer signal levels are much smaller for spherical PNPs versus linear-chain polymers of the same molecular weight, thus one has to be extremely careful to minimize any contributions to viscometer baseline noise. Although the DV signals for the PNP samples were low, the signal to noise ratio was more than adequate to make precise measurement of intrinsic viscosity at each elution volume increment.

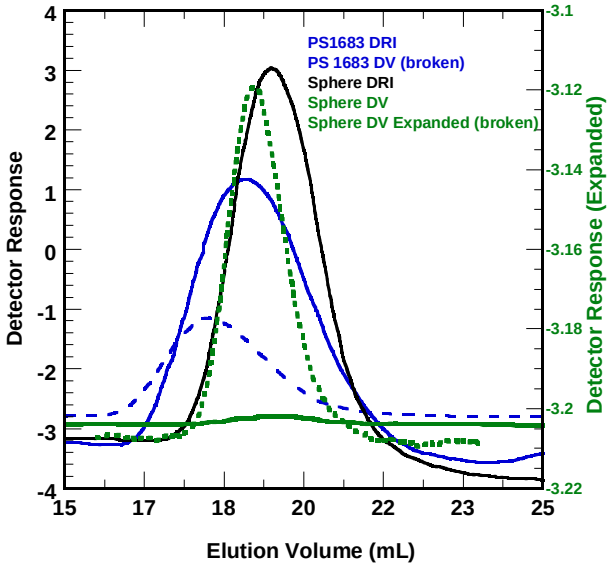

Figure S2. Typical concentration detector and viscometer detector chromatograms for a linear PS sample and for a spherical PNP sample. Solid blue trace: PS 1683 DRI signal; dashed blue trace: PS 1683 DV signal; solid black trace: PNP DRI; solid green trace: sphere DV; dashed green trace: expanded axis (green, right hand y-axis) sphere DV.

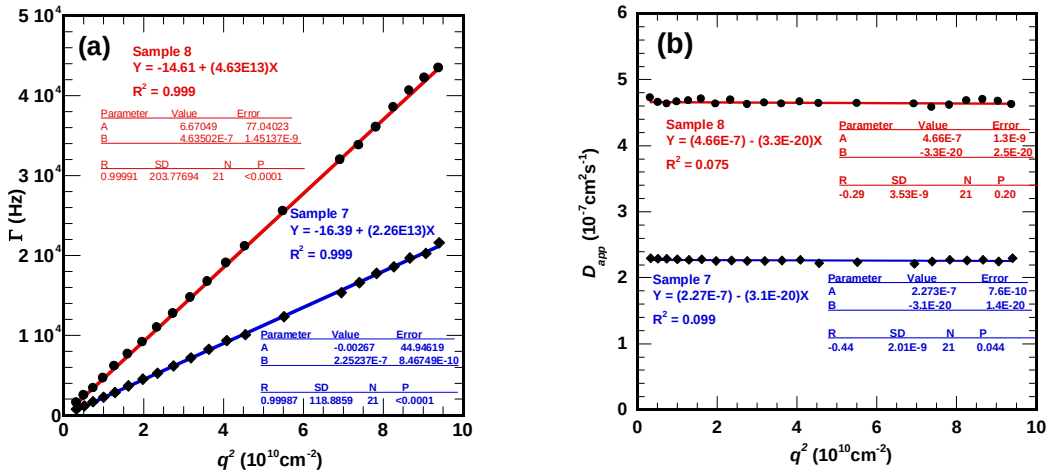

Figure S3. Detailed slope error analysis for Figure 3 in main text. (a) Decay rates (Γ) plotted against squared scattering vector (q^2), showing excellent particle uniformity for samples **7** (♦; line of best fit in blue) and **8**; (●; line of best fit in red); (b) Apparent diffusion coefficients (D_{app}) plotted against q^2 for samples **7** (♦; line of best fit in blue) and **8**; (●; line of best fit in red).

Table S2. R_g/R_h values for a series of PNPs.

Sample	R_g (nm)	R_h (nm)	R_g/R_h	VSF
7	16.0	21.1	0.76	2.41
8	6.7	10.4	0.64	1.95
9	11.8	16.6	0.71	3.56
10	12.9	17.8	0.72	2.17
11	17.3	22.7	0.76	2.39
13	16.6	22.6	0.73	1.69
15	5.1	6.5	0.78	2.12
16	18.3	28.3	0.65	4.74

Particles size data are summarized in Table S3.

Table S3. Apparent and absolute SEC/DV, DLS, SEC/LLS, and HDC particle size data for the synthesized PNP samples.

Sample	SEC Method	Apparent MW Data			SEC/DV Universal Calibration MW Data						SEC/SLS/MALS Absolute MW Data			SEC/DV	DLS (THF)	HDC (H_2O)
		M_n	M_w	M_w/M_n	M_p	M_w	d_p	d_w	IV (dL/g)	VSF	M_w (LLS)	d_w (LLS M_w)	R_g (MALS)	THF-Swollen d_w	d_h	Median d_v
15K PS STD[a]	ALPHA-3000	4,990	14,600	2.9	16,000	17,000	3.7	3.8	10.70	n.a.	16,400					
1683 PS STD[a]	ALPHA-M	98,600	254,000	2.6	260,000	271,000	9.4	9.5	78.97	n.a.						
1	Mixed B	72,189	122,000	1.7	720,000	851,000	13.2	13.9	10.00	4.00						
2	Mixed B	75,155	121,000	1.6	696,000	809,000	13.0	13.7	9.50	3.80						
3	Mixed B	42,934	79,000	1.8	646,000	758,000	12.7	13.4	6.00	2.40						
4	Mixed B	34,000	68,000	2.0	515,000	629,000	11.8	12.6	5.00	2.00						
5	Mixed B	43,000	67,900	1.6	464,000	534,000	11.4	11.9	5.50	2.2						
6	Mixed B	91,000	161,000	1.8	1,436,000	2,615,000	16.6	20.2	6.25	2.5						
7	ALPHA-M[b]				5,378,000	5,874,000	25.7	26.5	6.03	2.41				35.5	42.4	
7	Mixed C										8,060,000	29.5	16			
7	Phenogel series												15.3 ± 0.5			
8	Mixed B	65,300	85,100	1.3	721,000	879,000	13.2	14.1	4.88	1.95				17.6	20.8	
8	Phenogel series												6.7 ± 1.2[c]			
9	ALPHA-M				1,972,000	1,998,000	18.4	18.5	8.89	3.56				28.2	33.2	
9	Mixed C										2,929,000	21	11.8			
10	ALPHA-M				3,907,000	4,169,000	23.1	23.6	5.44	2.17				30.6	35.6	
10	Mixed C										5,234,000	25.5	12.9			
11	ALPHA-M				6,580,000	7,360,000	27.5	28.6	5.98	2.39				38.2	45.4	
11	Mixed C										10,410,000	32.1	17.3			
12	Mixed A	84,800	110,000	1.3	914,000	1,159,000	14.3	15.4	5.26	2.10				19.7	22.5	
13[d]	ALPHA-M				8,491,000	9,129,000	30.0	30.7	4.24	1.69				36.6	45.2	
13	Mixed C										12,270,000	33.9	16.6	39.5		
14	ALPHA-M	41,200	60,300	1.5	304,000	413,000	9.9	10.9	4.81	1.93	518,000	11.8		13.4	15.6	
15	ALPHA-M				157,000	238,000	7.9	9.1	5.31	2.12				11.7	13.0	
15	Mixed C										293,800	9.8	5.1[e]			
16	ALPHA-M				979,000	1,547,000	14.6	17.0	11.85	4.74				28.6[f]	56.6	
16	Mixed C										2,384,000	19.6	18.3			
17	ALPHA-M	280,000	355,000	1.3	7,385,000	8,125,000	28.6	29.5	5.18	2.07		0.0		37.6	39.8[g]	
17	Mixed C										>6,790,000	>27.7				
18	Mixed B	143,000	372,000	2.6	5,950,000	3,970,000[h]	26.5	23.2								31.1
19	Mixed B	203,000	391,000	1.9	5,970,000	4,250,000[h]	26.6	23.7								29.6
20	Mixed B	179,000	349,000	1.9	4,190,000	3,060,000[h]	23.6	21.3								26.3
21	Mixed B	332,000	601,000	1.8	11,370,000	9,390,000[h]	32.9	30.9								38.9
22	Mixed B	255,000	493,000	1.9	8,520,000	6630,000[h]	29.9	27.5								34.5
23	Mixed B	311,000	678,000	2.2	14,670,000	11,930,000[h]	35.8	33.4								44.7
24	Mixed B	187,000	464,000	2.5	9,020,000	6,050,000[h]	30.5	26.7								29.0
25	ALPHA-3000	9,350	11,600	1.2	22,000	25,000	4.1	4.3	5.78	2.31	26,500	4.4				
26	ALPHA-3000	10,300	13,000	1.3	26,000	27,000	4.3	4.4	6.02	2.41	32,500	4.7				
27	ALPHA-3000	9,850	12,800	1.3	19,000	23,000	3.9	4.2	6.17	2.47	32300	4.7				

Molecular weight data are reported in g/mol; particle diameter data are reported in nm.

a. Broad MW PS standard

b. ALPHA-M and ALPHA-3000 columns exhibited pure SEC elution to PS and PEO over the broadest sample range.

c. Reported size is near the limit of detection of this instrument.

d. 70-ethoxylate

e. $R_{h(z)}$ = 4.9 nm by SAXS; R_g/R_h = 0.76 (M. DeLong, unpublished results).

f. See main article for discussion.

g. R_h determined in GBL.

h. Low MW tail in all samples results in absolute $M_w < M_p$.