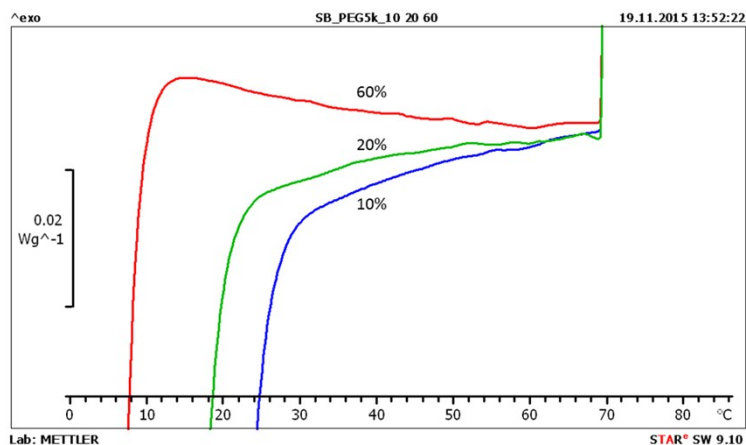
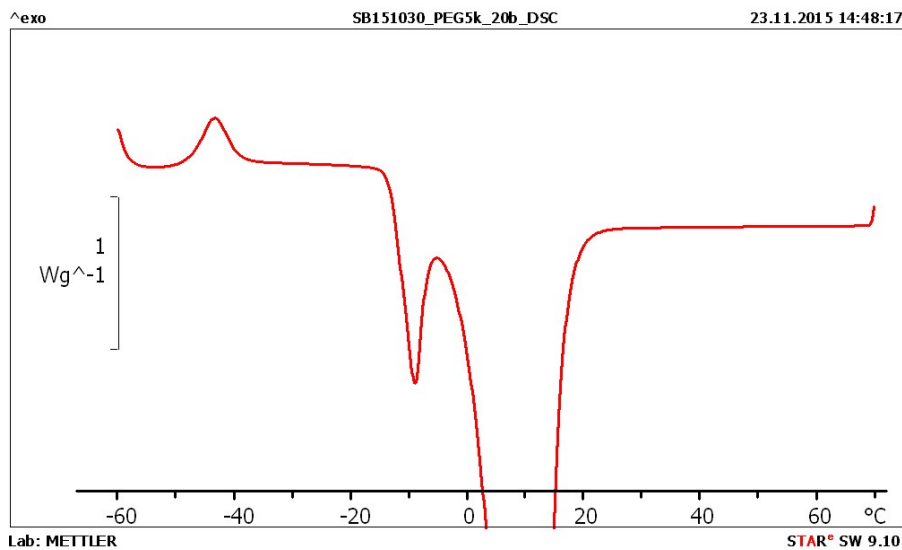


### Supplementary Information #1



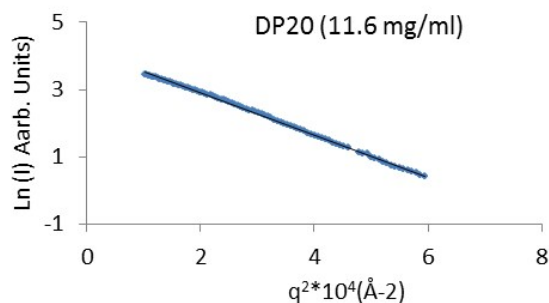
**Figure S1.** DSC scans of PEG<sub>5k</sub> at 10, 20 and 60% water contents showing the absence of any melting endotherm at 40 °C of the type seen in nanosphere dispersions.

### Supplementary Information #2

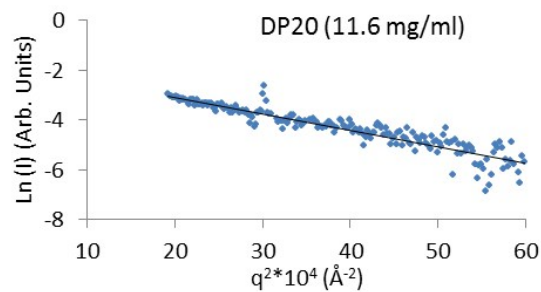


**Figure S2.** DSC scan of PEG<sub>5k</sub> that shows the endothermic transition due to bound water at -10 °C

### Supplementary Information #3



**Figure S3a.** Guinier plot of the inner part (low  $q$ ) used to determine total particle size.



**Figure S3b.** Guinier plot of the outer part (high  $q$ ) to determine the core size.

### Comparison of Guinier analysis and Irena simulation.

DP is the degree of polymerization. Low concentration: The values are average of measurements at 0.3 and 0.6 mg/ml for DP 4.6, and at 0.07, 0.15 and 0.29 mg/ml for DP 20.4. High concentration: The values are average of measurements at 2.3, 5.8 and 11.5 mg/ml for DP 4.6, and at 1.2, 2.3 and 11.6 mg/ml for DP 20.4.

DP	Concentration (high or low)	Core Dia. (nm)		Shell thickness (nm)		Total diameter (nm)	
		Irena	Guinier	Irena	Guinier	Irena	Guinier
4.6	High	12.8	9.8	6.5	9.1	25.7	27.8
	Low	7.6	5.4	8.8	11.0	25.2	26.6
7.9	High	13.2	8.0	5.0	9.6	23.2	26.7
	Low	N/A	6.6	8.8	10.2	23.7	27.1
20.4	High	21.2	11.6	5.5	12.0	32.2	35.1
	Low	11.4	7.8	8.5	13.2	28.3	34.3

**Observation:** Total size is smaller while the core radius is higher in Irena's analysis compared to Guinier analysis.

## Supplementary Information # 4

Compilation of the various changes in the characteristics of the nanospheres.  
The dimensions are in nm.

<b>Effect of DP</b>				
<b>High concentration (hc)</b>	DP5	DP20	Ratio DP20/DP5)	% Change
Core dia.	8.0	10.6	1.33	33
Total dia.	28.0	35.1	1.26	26
Shell thickness	10.0	12.2	1.23	23
Core volume	267	623	2.33	133
Total volume	11438	22625	1.98	98
Shell volume	11171	22002	1.97	97
Shell to core volume ratio	41.80	35.31	0.84	-16
% Core	2.337	2.754	1.18	18
Hydrodynamic dia.	40.700	67.800	1.67	67
Hydrodynamic vol.	35301	163188	4.62	362
<b>Low concentration (lc)</b>	DP 4.6	DP 20.4	Ratio (DP20/DP5)	% Change
Core dia.	4.4	5.3	1.21	21
Total dia.	26.9	34.2	1.27	27
Shell thickness	11.3	14.5	1.28	28
Core volume	44	79	1.79	79
Total volume	10176	20987	2.06	106
Shell volume	10132	20908	2.06	106
Shell to core volume ratio	230.64	266.27		15
% Core	0.432	0.374		-13
<b>Effect of concentration</b>				
<b>DP 4.6</b>	lc	hc	Ratio (hc/lc)	% Change
Core dia.	4.4	8.0	1.83	83
Total dia.	26.9	28.0	1.04	4
Shell thickness	11.3	10.0	0.89	-11
Core volume	44	267	6.08	508
Total volume	10176	11438	1.12	12
Shell volume	10132	11171	1.10	10
Shell to core volume ratio	230.64	41.80		-82
% Core	0.432	2.337		441
<b>DP 20.4</b>	lc	hc	Ratio (hc/lc)	% Change
Core dia.	5.3	10.6	1.99	99
Total dia.	34.2	35.1	1.03	3
Shell thickness	14.5	12.2	0.85	-15
Core volume	79	623	7.94	694
Total volume	20987	22625	1.08	8
Shell volume	20908	22002	1.05	5
Shell to core volume ratio	266.27	35.31		-87
% Core	0.374	2.754		

Effect of core-segment length: At higher concentrations, with increase in DP from 4.6 to 20.4, the diameters of the core, the nanosphere, the hydrodynamic shell, and the interparticle distance increase by 3, 7, 26 and 27 nm, respectively. At lower concentrations, the diameters of the core and the hydrodynamic shell (interparticle distance could not be measured) increase by 1, 6, and 27 nm, respectively. Thus, a small increase in the core size due to the longer core segments get amplified at larger radii. Less dense packing of the PEG segments with larger core diameter could increase corona diameter, increase the entrapment of water, and thereby the hydrodynamic volume and interparticle distance.