

Electronic Supporting Information

Role of block copolymer adsorption versus bimodal grafting on nanoparticle self-assembly in polymer nanocomposites

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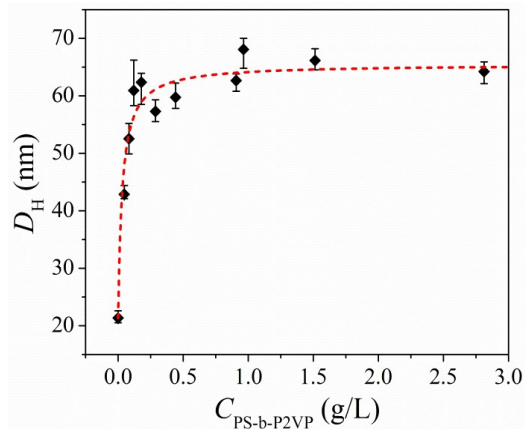


Figure S1. The apparent hydrodynamic diameter (D_H) of silica/PS-b-P2VP (110-b-12.5) dispersions as a function of PS-b-P2VP concentration ($C_{PS-b-P2VP}$). The dashed red line is a guide for the eye. Note that the saturation adsorption yields a grafting density of ~ 0.01 chains/nm².

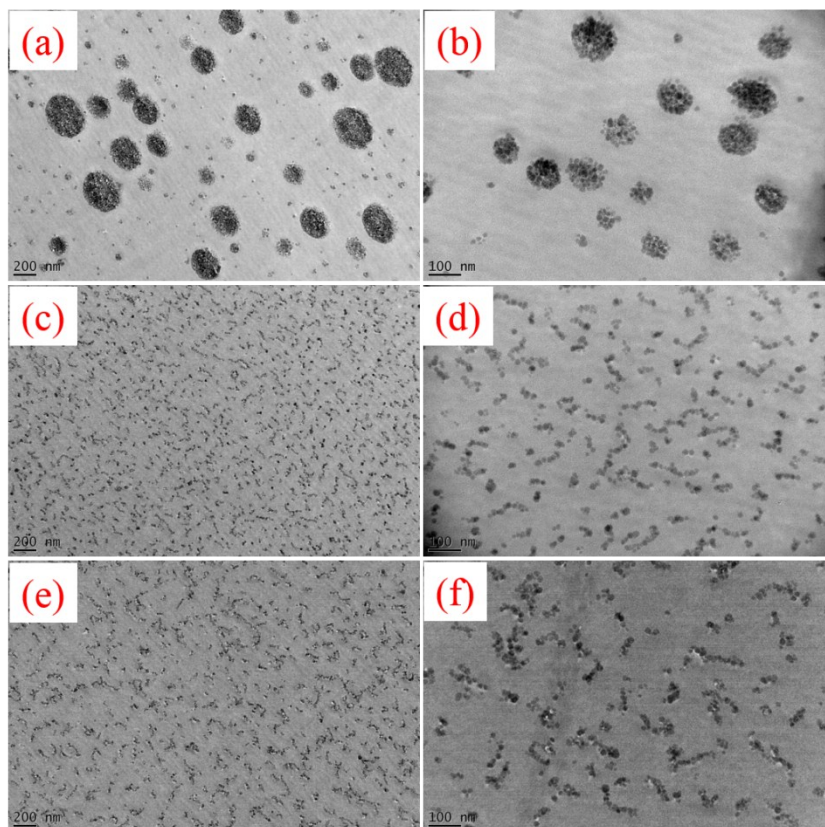


Figure S2. TEM micrographs for (a), (b) bare silica NPs in a 592 kg mol⁻¹ PS matrix; (c), (d) silica NPs fully adsorbed with 110-b-12.5 BCPs in a 106 kg mol⁻¹ matrix; (e), (f) silica NPs fully adsorbed with 110-b-12.5 BCPs in a 592 kg mol⁻¹ PS matrix. The images on the left column were photographed at a low magnification (40k) while the ones on the right column were obtained at a high magnification (110k).

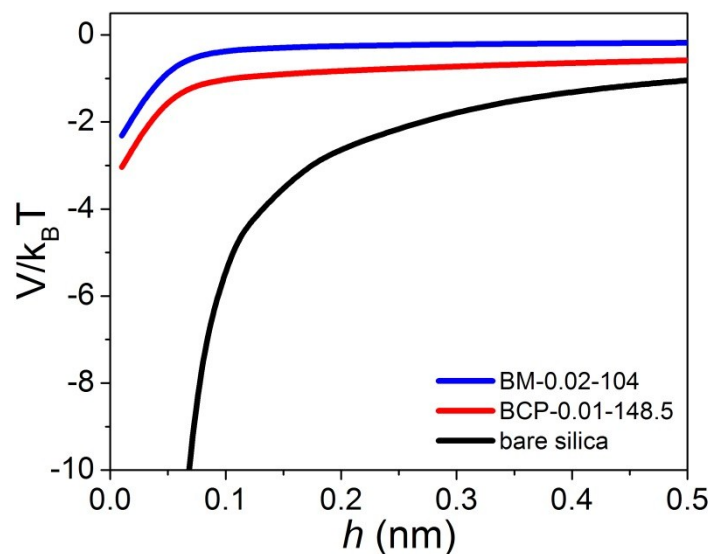


Figure S3. Van der Waals attraction potential ($V/k_B T$) as a function of the inter-particle separation (h) for bare (black), BCP-0.01-148.5 (red) and BM-0.02-104 (blue) silica NPs. Note that, for these calculations, we assume the P2VP chains are fully collapsed onto the silica surface.

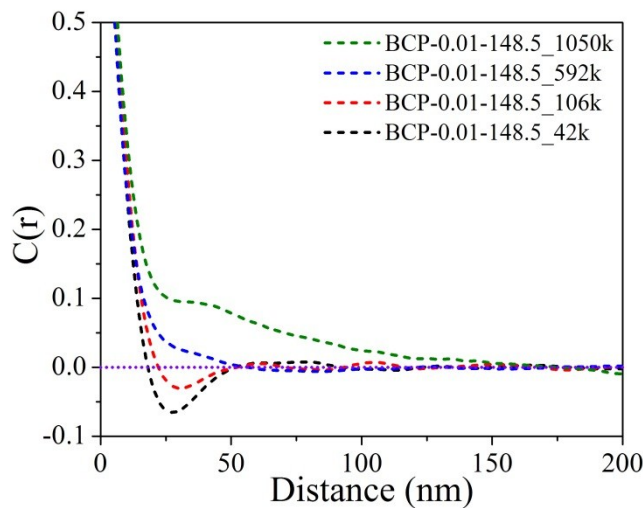


Figure S4. Pixel-pixel autocorrelation function $C(r)$ as a function of distance for TEM images of BCP (148.5-b-19) coated silica NPs in PS matrices with varying molecular weights, as indicated inside the graph.

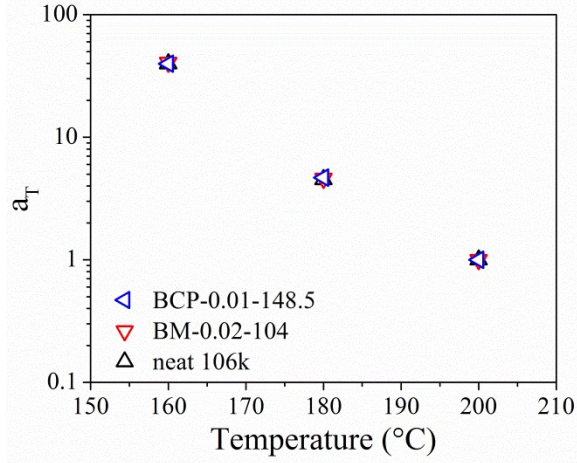


Figure S5. Time-temperature superposition shift factor as a function of temperature for neat 106 kg mol⁻¹ PS melts as well as those filled with 5 wt % bimodal grafted or BCP adsorbed silica NPs. The reference temperature is 200 °C.

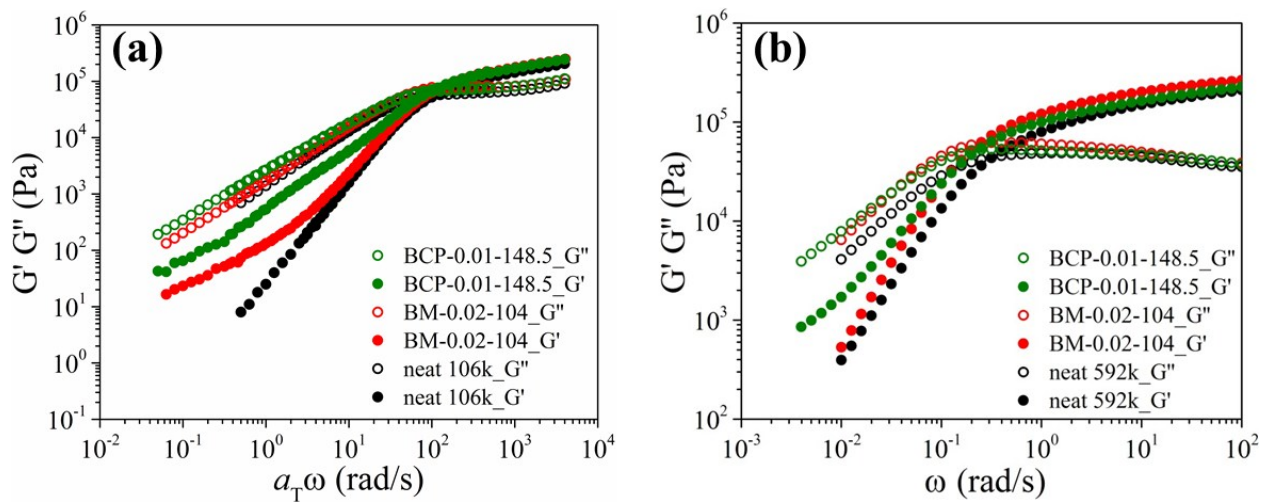


Figure S6. The storage (G' , closed symbols) and loss (G'' , open symbols) modulus as a function of angular frequency for (a) 106 kg mol⁻¹ and (b) 592 kg mol⁻¹ PS melts as well as their corresponding nanocomposites, as indicated inside the graphs. The reference temperature for (a) is 200 °C with the shift factors a_T shown in Figure S5. All the datapoints in (b) were collected at 200 °C. Also note that the nanocomposites have a silica core loading of 5 wt % and had been annealed for 5 days at 150 °C under vacuum before rheological tests.

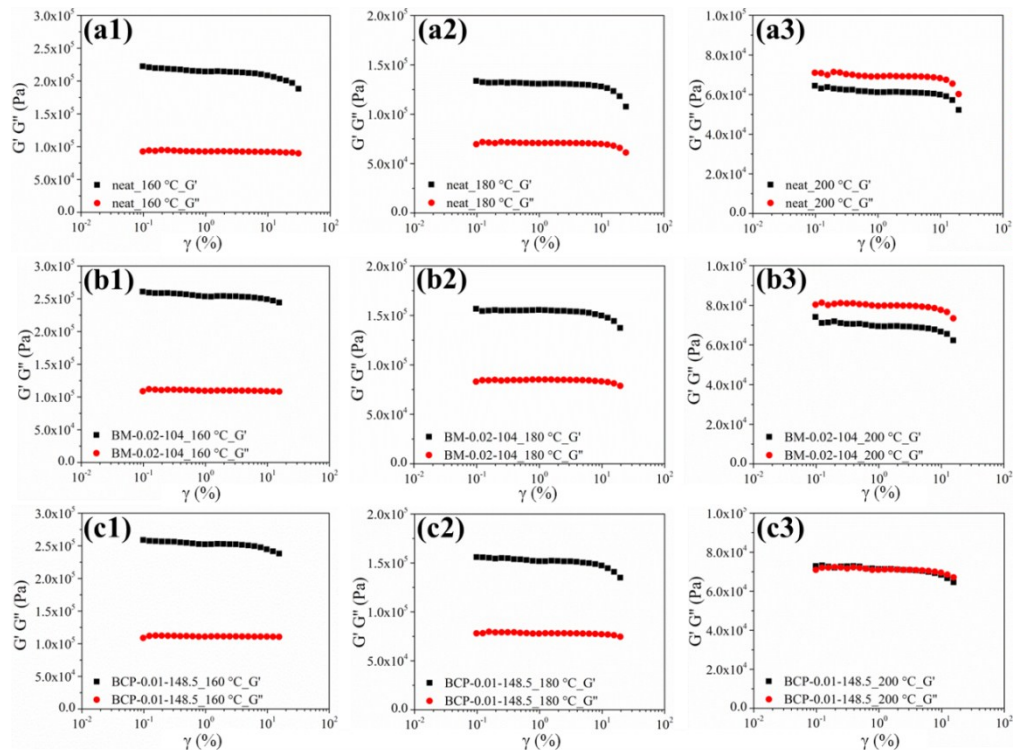


Figure S7. Strain sweep results for (a1-a3) 106 kg mol⁻¹ PS melts as well as those filled with 5 wt % (b1-b3) bimodal BM-0.02-104, and (c1-c3) BCP-0.01-148.5 silica NPs. All the measurements were conducted at an angular frequency of 100 rad s⁻¹. The temperature used for each experiment is indicated inside the figure.

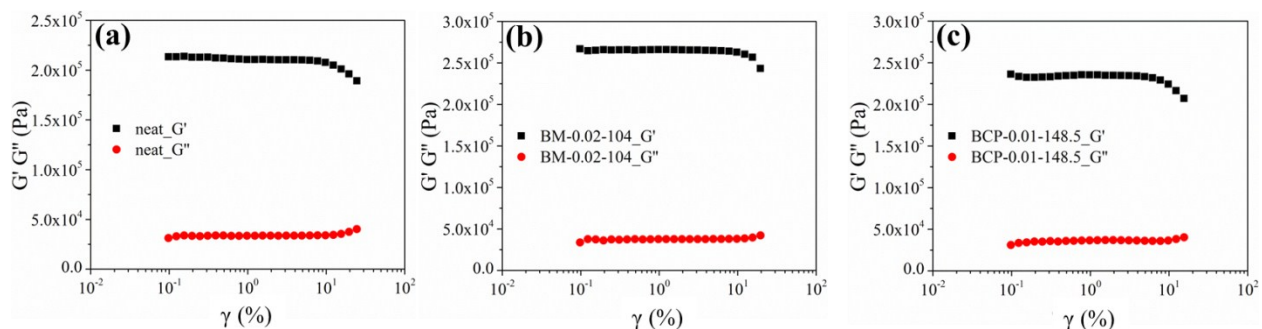


Figure S8. Strain sweep results for (a) 592 kg mol⁻¹ PS melts as well as those filled with 5 wt % (b) bimodal BM-0.02-104, and (c) BCP-0.01-148.5 silica NPs. All the measurements were conducted at an angular frequency of 100 rad s⁻¹ at 200 °C.