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Polymer-Grafted-Nanoparticle Surfactants

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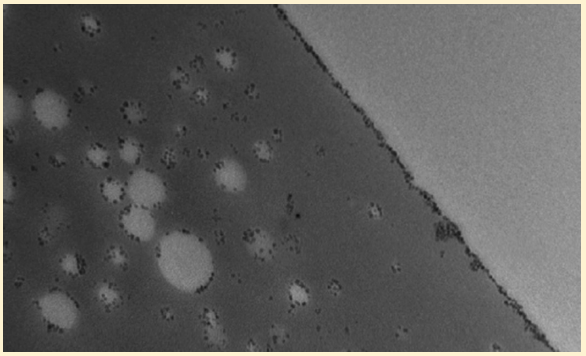
ABSTRACT: We have studied the surface behavior of nanoparticles, which are lightly grafted with polymer chains, when they are mixed with matrix chains of the same architecture as the grafts. We consider the particular case where the nanoparticle core and the grafted polymer chains energetically dislike each other and show that the extent of surface segregation of these "hairy" nanoparticles and their self-assembly into a variety of structures can be tuned by varying the number and the length of the grafted chains and the matrix chain length. These results unequivocally show that grafted nanoparticles in polymer matrices behave akin to block copolymers (or amphiphiles) in selective solvents, with readily controllable surface behavior.



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Controlling the dispersion of nanoparticles (NPs) into polymer matrices is the singular challenge in achieving the dramatic property improvements promised by polymer nanocomposites.[1] It is often difficult to achieve this goal since inorganic particles are typically immiscible with an organic phase.[2−4] One strategy to overcome this difficulty is to "shield" the particle surface by grafting it with the same chains as the matrix polymer.[5−17] While this "steric stabilization" methodology is operational in some cases, instead, more generally we have found that these grafted NPs self-assemble into a variety of structures.[18,19] Previously, we conjectured that this assembly occurs because the particle core and grafted polymer layer are immiscible with each other and thus attempt to phase separate. However, since they are constrained by chemical connectivity, they can only "microphase separate", as in the case of block copolymers and other amphiphiles, and assemble into a variety of morphologies. This conjecture is currently unproven, and we are driven to verify it so that we can utilize concepts already developed in the context of surfactants to the ordering of NP into structures of arbitrary complexity.

If these grafted NPs behave akin to surfactants, then they must be surface active and also assemble into structures at the surface. These effects should be tunable by varying the "head" to "tail" ratios of these amphiphiles. In this context, we point to the work of Green and his co-workers[20] who studied the phase behavior of gold nanoparticles *densely* grafted with polystyrene in thin film mixtures with tetramethyl bisphenol A polycarbonate (TMPC). These workers found that the particles were surface active, presumably because they behave akin to surfactants, but that they only displayed two states, phase mixed with the polymer matrix or phase demixed into large NP agglomerates. While these results can be rationalized by the relatively large grafting densities employed, no surfactant-like self-assembled structures were obtained. The analogy between these grafted nanoparticles and amphiphilic molecules therefore remains incomplete at this time. In this paper we consider the surface behavior of silica nanoparticles *sparsely* grafted with polystyrene chains mixed with a polystyrene matrix. In these cases we find that the nanoparticles both are surface active and also assemble spontaneously into a range of nanostructures which are the two-dimensional analogues of the three-dimensional structures seen previously.[18] The analogy between this class of "hairy" nanoparticles and surfactants is thus clearly established by this work.

Parenthetically, we point to many previous works that have found that bare particles preferentially segregate to the defects or the boundaries of a polymer sample.[21] This phenomenon is not driven by NP surfactancy, since, for example, the extent of their surface segregation can be tuned by power used to agitate the mixture (e.g., in the case of Pickering emulsions). Thus, the surface segregation of the NPs is not thermodynamically defined in these situations and, therefore, not easily controlled. In the same vein, bare nanoparticles do not typically assemble into nanostructures at surfaces.

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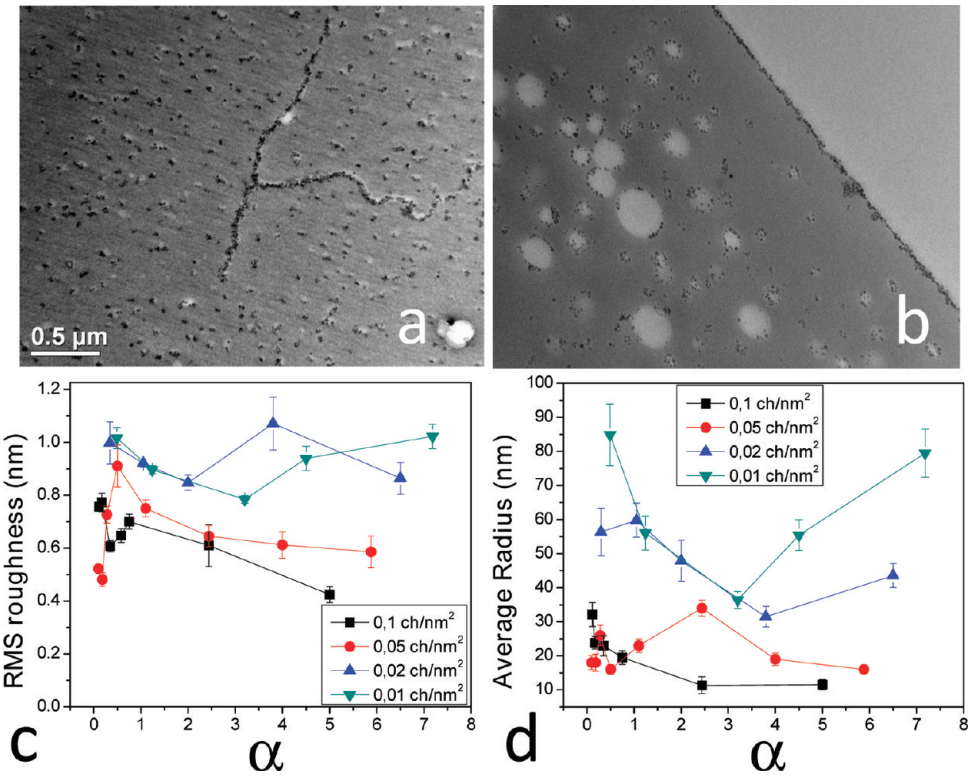

Figure 1. TEM micrographs of a thick sample composed of silica particles grafted with PS chains (σ = 0.02 chains/nm^2, 156 kg/mol) dispersed in a PS matrix (97 kg/mol) and annealed for 5 days at 150 °C under vacuum: (a) bulk of the sample; (b) surface of the sample. Evolution of root-mean-square roughness (c) and the average structure radius (d) as a function of α (the ratio of the grafted to matrix chain lengths) for σ = 0.1, 0.05, 0.02, and 0.01 chains/nm^2, respectively.

Experimental Details. To provide critical weight to the conjecture that grafted NPs behave analogously to surfactants, we examine the free surfaces of thin films of polymer grafted nanoparticles in a polymer matrix using atomic force microscopy (AFM) and a suite of other techniques. Polystyrene (PS) chains were grown from the surfaces of 14 nm diameter silica particles (Nissan Chemicals) using RAFT chemistry. These particles were mixed with free PS chains (matrix) to form the nanocomposites of interest. Four different grafting densities, σ, were investigated: 0.01, 0.02, 0.05, and 0.1 chains/nm^2 (6, 12, 31, and 62 chains per particle, respectively). The molecular weight of the grafted chain lengths varied from 34000 to 156000 g/mol, with maximum polydispersity (PDI) of 1.25. The particles and the PS matrix were mixed together in a good common solvent (benzene for NPs with σ = 0.01 and 0.02 chains/nm^2 and THF for σ = 0.05 and 0.1 chains/nm^2). The silica loading in the samples was fixed at 5 weight % of the core in all cases. The samples were sonicated and then spin-cast on cleaned Si substrates (p-type, single side polished (100) silicon wafers) using a P6700 spin coater system (Specialty Coating System. Inc.) to create ~100 nm thick films. These samples were studied either in situ or ex situ. For the ex situ studies, the films were annealed at 150 °C under vacuum and quenched to ambient temperature (below the PS glass transition temperature) for observation by AFM (Thermomicroscopes Autoprobe CP Research). For the in situ studies, the films were annealed directly inside the atomic force microscope (AFM, DI Multimode (JVH scanner) system from Veeco Instruments) to visualize any assembly processes. We also prepared thick samples (~10 μm in thickness) by solvent casting and annealed them under vacuum at 150 °C for various periods of time. These samples were embedded in epoxy, ultramicrotomed, and deposited on a copper grid (initially covered with a thin Formvar film) and then examined using a transmission electron microscope (Philips EM 430 at 100 kV).

Bulk Assembly. Figure 1 shows TEM micrographs of a thick sample. The grafting density is σ = 0.02 chains/nm^2, and the molecular weights of the grafted and matrix chains are 156 and 97 kg/mol, respectively. The sample was annealed for 3 days at 150 °C. The center of the film (Figure 1a), which can be considered as the bulk, exhibits well-defined self-assembly of the nanoparticles. Independent studies of several adjacent slices show the presence of the same structure, convincing us that the NPs spontaneously assemble into sheets. This behavior is in agreement with our previous results on bulk samples of similar nanocomposites.[18] We have previously presented results from theory and simulations which suggest that this bulk self-assembly reflects a balance between the energy gain when particle cores approach and the entropy of distorting the grafted polymers. In more detail, the inherent dislike between the (hydrophilic) silica cores and the (hydrophobic) polystyrene corona serves as the energetic driving force preferring core−core contacts. This is balanced against the accompanying corona distortion, leading to the formation of a myriad NP superstructures.

Surface Activity. Particle accumulation is visible near the free surface of the sample (Figure 1b) and around bubbles formed during the solvent evaporation process (Figure 1b). While this suggests that the particles are surface active, more persuasive evidence is presented in Figure 1c, which shows the rms roughness of the

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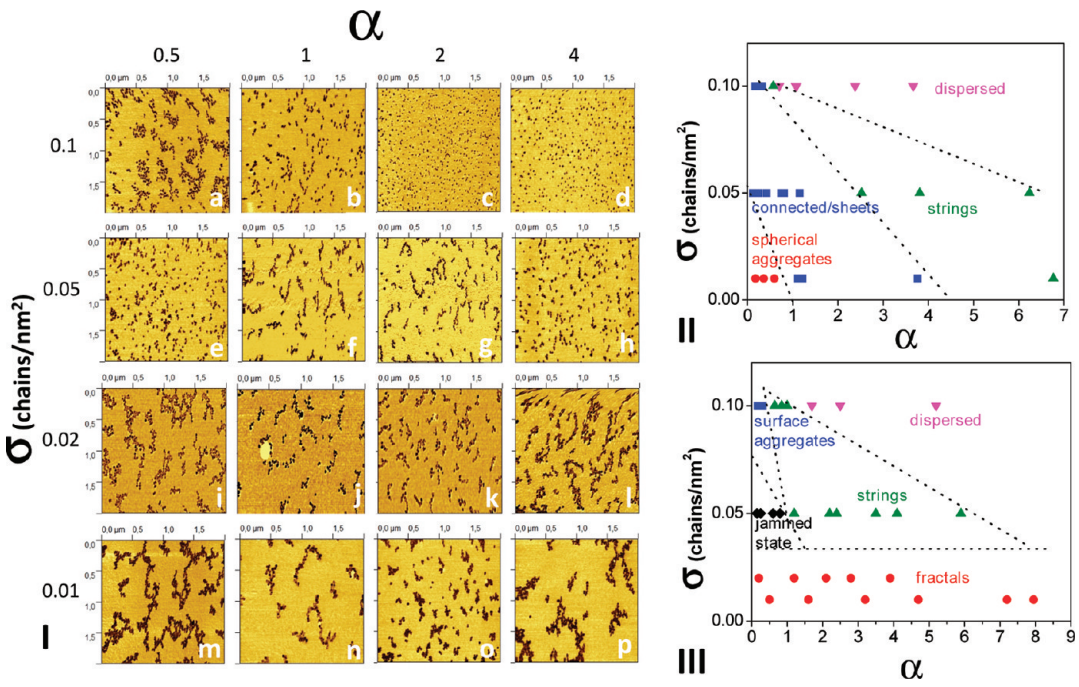

Figure 2. (I) AFM phase response micrographs of ~100 nm thick films of PS grafted silica particles dispersed in PS matrices of different molecular weights annealed for 3 days at 150 °C under vacuum. Each image is 2 × 2 μm in size. The samples had different values of α and σ: σ = 0.1 (a, b, c, d), 0.05 (e, f, g, h), 0.02 (i, j, k, l), and 0.01 (m, n, o, p) chains/nm^2, and α = 0.5 (a, e, i, m), 1 (b, f, j, n), 2 (c, g, k, o), and 4 (d, h, l, p). (II) Morphology diagram of the structures observed in the bulk samples after 5 days at 150 °C.[18] (III) Morphology diagram of the structures observed at the surface of 100 nm thick films annealed at 150 °C for 3 days.

air surface of a 100 nm thick sample. This figure clearly demonstrates that, in the limit of a large ratio of graft molecular weight to the matrix molecular weight (denoted by "α"), the surface roughness decreases with increasing PS grafting density on the silica particles. We focus on the large α limit where the polymer matrix chains wet the brush. In these situations the brushes are in good solvent and the only unfavorable interaction is between the particle cores and the polymers. In the opposite limit, where the α value tends to 0, the matrix chains dewet the brush autophobically.[22] There is now dislike between the polymers and the core, but also a dislike between the brush and matrix chains—this leads to trends that are more complex. (Many previous experiments have conclusively demonstrated that this crossover from wet to nonwet brush behavior occurs when $\alpha \sim 1$.[9,17,23−25]) We propose that the surface roughness behavior observed in Figure 1c at large α is definitive proof of the amphiphilic properties of the particles for the following reason: As one shields the particle with more PS grafts, the particles are less repelled from the matrix (steric stabilization) and hence the mixture becomes more thermodynamically miscible.[18] The surface segregation of the NP thus decreases with increasing σ as does the accompanying surface roughness.

Self-Assembly. We shall show here that the trends seen in Figure 1c for the rms roughness as a function of α are accompanied by the self-assembly of the particles at the free surface of the film. Figure 2 shows phase contrast AFM micrographs of 100 nm thick films of silica particles grafted with PS chains and dispersed in a PS matrix. Each film was annealed for 3 days. Since we perform AFM scans at room temperature on the surface of a glassy polymer, we are primarily sensitive to the free surface of the film. The four rows present different grafting densities and the four columns different α values.

Four clearly defined structures are visible; dispersed particles (Figure 2c,d), two-dimensional compact aggregates (Figure 2a), strings (Figure 2b,f−h), and large fractal structures (Figure 2i−p). While strings and fractals are somewhat similar in their structure, we define "strings" to be linear (not branched) and exactly one particle wide. Fractal structures are generally branched, interconnected, and several particles in width. Two-dimensional aggregates are almost circular in cross section. Figure 2(III) exhibits a "morphology" diagram derived from such data for the 100 nm thin films. The x axis in this plot, the ratio of grafted to the matrix chain length, α, is a measure of solvent quality as discussed for the bulk systems. This "morphology" diagram is qualitatively similar to the one obtained from three-dimensional bulk samples (Figure 2(II)). We propose that both the bulk and the surface assembly are driven by the surfactancy of the nanoparticles. However, some important points are emphasized: (1) Note that well-dispersed particles and strings are generally formed in both 3-d and 2-d for large grafting densities and good solvent quality (α > 1); this is a regime where the particles are sterically stabilized by the brush. We have monitored the kinetics of the growth of these structures (Figure 3) and find that the sizes of the structures in both cases remain constant over time. However, the area fraction of the surface that is covered by the strings increases with time, while the surface coverage in the dispersed phase is practically time invariant. Clearly, while the string sizes themselves seem to be fixed, more particles are blooming to the surface with time. Apparently, the sizes of the strings are dictated by system parameters and not due to kinetic factors, implying that these structures develop under thermodynamic control. (2) For poor solvent quality (small α) and large grafting density we see the formation of compact structures (spheres in 3-D vs circles in 2-D). These structures grow in time,

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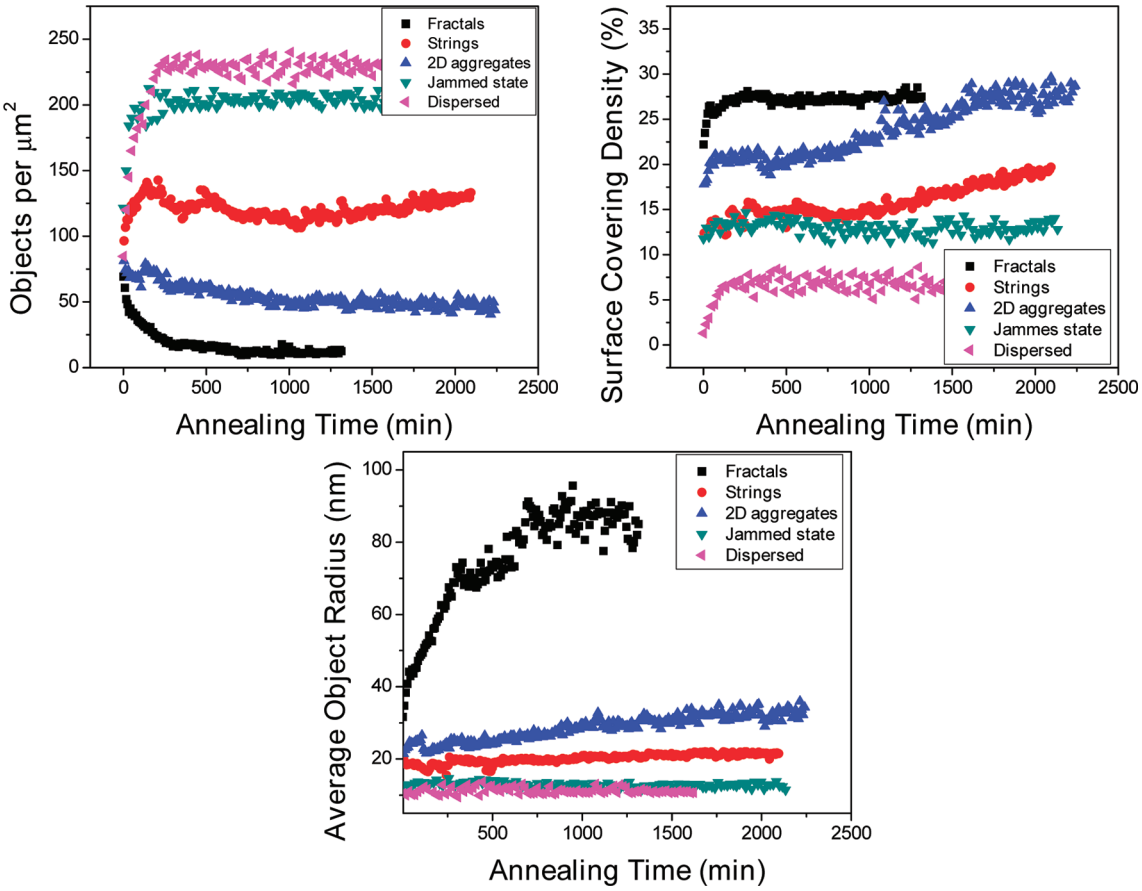

Figure 3. Evolution of the number of independent objects per μm^2, the particle surface covering density (%), and the average circular radius of the structures (nm) as a function of annealing time (min) at 150 °C for five characteristic samples, fractals ($\alpha = 7$, $\sigma = 0.01$ chains/nm^2), strings ($\alpha = 2$, $\sigma = 0.05$ chains/nm^2), two-dimensional aggregates ($\alpha = 0.1$, $\sigma = 0.1$ chains/nm^2), jammed state ($\alpha = 0.5$, $\sigma = 0.05$ chains/nm^2), and dispersed particles ($\alpha = 5$, $\sigma = 0.1$ chains/nm^2).

and their area fraction also increases in a power law fashion with time, implying that they are kinetically evolving and are probably a result of phase separation between the particles and matrix due to autophobic dewetting between the brush and the matrix. (3) In 2-D, all the low grafting density NPs yield fractally agglomerated structures. Following Langevin et al.,[21,26] we conjecture that the large NP−NP interaction strength dominates in the case of these poorly shielded particles and results in kinetically trapped states which do not readily evolve to equilibrium. Note that these structures grow, apparently by collisions between agglomerates; this is manifested by the fact that the net NP coverage of the surfaces is apparently independent of time, the sizes of the structures grow with time and hence their number decreases with time. These structures thus seem to follow kinetics reminiscent of diffusion limited aggregation, but we have not been able to establish this connection conclusively. (4) Another interesting new result we find is that in Figure 2e, for example, practically no structure formation occurs. We conjecture that the particles are shielded enough to not "stick" irreversibly to each other, but they are driven enough to the surface that they "fill" the surface and "jam". Proof of this conjecture comes from kinetic data which show that the surface coverages and sizes of the objects remain independent of time after an initial transient. Further, samples where we reduce the particle concentration yielded agglomerates, giving credence to our proposal that the NPs can jam due to increases in particle concentration.

Discussion. We now return to the unusual rms roughness values seen at a given graft density as the ratio of graft chain length to matrix chain length, α, was increased. At the highest graft density, as α increases, the particles are increasingly soluble in the matrix. This result has now been conclusively established by many previous experimental works, with the specific value of α at the transition point being $\sim$1.[9,17,23−25] Due to the increased miscibility of the particles in the matrix, they progressively go from forming spherical 2-D aggregates to strings and then dispersed particles with increasing α. Since the thermodynamics of mixing the particles and the matrix is thus becoming more favorable as we go from left to right in Figure 2(III), it is then clear that the surface activity of these NPs should also reduce. Substantiation of these underpinning ideas is presented in Figure 1d, where we see that the size of the NP clusters decreases monotonically with increasing ratio of grafted chain length to matrix length.

Similar results are seen in the intermediate graft density case (0.05 chains/nm^2) except in the limit where the particles jam ($\alpha <$ 1). Since these jammed states are not at equilibrium, it is hard to comment on these results here. In a similar manner the two lowest graft densities cannot be addressed in this framework since we believe that these are structures that evolve through irreversible agglomeration, e.g., diffusion limited aggregation (DLA).

Conclusion. We have conclusively shown that NPs grafted with polymer chains can behave akin to surfactants due to the

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dislike between the nonpolar organic grafts and polar inorganic NP cores. These grafted particles are surface active and their surface activity and self-assembly can be tuned by changing the number of grafted chains or by changing solvent quality (through the ratio of the grafted to the matrix chains, α). We find that strings and dispersed particles are apparently the only two "equilibrium" structures and that all other structures (jammed, 2-D agglomerates, and DLA like clusters) are nonequilibrium structures akin to gels. While the underpinning reasons for the creation of these gels, namely, packing, inter-NP attraction, and phase separation caused by the autophobic dewetting between the brush and matrix, are very different across the different cases, they yield nonequilibrium structures which evolve very slowly with time. Previously Langevin et al. had used bare nanoparticles, where inter-NP attraction dominates, to create long-lived foams. By extension, we believe that these decorated NPs may allow us to tailor the lifetimes of these foams with important consequences on applications.[21,26]

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