



Hierarchical self-organization of soft patchy nanoparticles into morphologically diverse aggregates



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ABSTRACT

We present a concise review of the large variety of self-assembly scenarios observed in solutions of diblock copolymer stars with a solvophilic inner block and a solvophobic outer block. A variety of modeling approaches and simulation techniques at different levels of detail reveals that individual molecules assume configurations akin to patchy colloids, but with a patchiness that depends on physical parameters and can adjust to external stimuli such as temperature and pH. These soft, patchy building blocks inter-associate at finite concentrations into micellar or gel-like solutions, including spherical and wormlike micelles, or they display macroscopic phase separation. The connections between single-molecule conformation and the structure of the concentrated solution are discussed, and coarse-grained strategies for these novel molecular entities are critically compared to one another.

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1. Introduction

Soft patchy nanoparticles are complex units at the nanoscale level that are characterized by soft and directional interactions. Examples of this class of particles can be mostly found in polymer-based systems: Janus-like polymer vesicles [1], patchy micelles emerging from the appropriate design of functionalised linear dendritic polymers [2], patchy nanoparticles with controllable symmetry resulting from the self-organization of block copolymer chains [3] or stars [4^{**}], block copolymer nanoparticles with microphase separation structures [5^{*}],

particles made of hydrophobic dendrimers with dynamic hydrophobic patches [6^{**}] or colloids grafted with poor-solvent polymer brushes [7^{**}] are just some examples. Also, some types of DNA-coated colloids [8^{*},9^{*}] and emulsions [10], as well as DNA nano-stars [11,12] are usually considered within the same class of systems.

The present paper focuses on star polymers with functionalised arms, known as Telechelic Star Polymers (TSPs), and presents an overview of the hierarchical self-assembly properties of these complex units. Experimental realizations of such macromolecules are, e.g., end-functionalized, zwitterionic polybutadiene star polymers [13^{**},14^{*}]. In particular, we consider TSPs whose arms are made of diblock copolymers – polymers made of two different blocks – composed of a solvophilic part, *A*, and a solvophobic part, *B*, where the latter is grafted

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onto a central core. The double nature of TSPs leads to a very rich assembly scenario when these macromolecules are exposed to selective solvents. Their ability to hierarchically self-assemble, first into soft patchy aggregates with different morphologies, and then into mesoscopic phases that are compatible with the functionalisation of the constituent units, makes TSPs excellent candidates as functionalised nanoparticles for smart materials.

At a single nanoparticle level, when exposed to a solvent, the intrinsic intramolecular interplay between entropic and enthalpic contributions leads to the formation of functionalised regions on the surface of the stars: when the density of solvophobic monomers is sufficiently high, either due to a high number of arms grafted on the anchoring point or to a high percentage of *A*-monomers per arm, the solvophobic regions tend to collapse on themselves forming patches, so that the contact with the solvent is minimized. While the solvophobic patches create a bonding pattern on the nanoparticle surface, the solvophilic core, due to the entropic repulsion between the *B*-monomers, acts as a soft substrate on which patches are distributed. The solvent quality, the temperature, the pH, the number of arms per star and the ratio between solvophobic and solvophilic monomers per arm are the key quantities that allow to fine-tune the single particle properties [4**,15*]. Once the physical and chemical parameters are set up, particles are either functionalised or not and the single particle properties are fully characterised.

At finite densities, when the nanoparticles interact with one another, the functionalised regions tend to coalesce creating an aggregation scenario where the single molecule properties are unaffected by the presence of other molecules [16*]. In other words, the faster and tighter intra-star association as compared to the inter-star association leads to systems composed of equilibrium patchy aggregates, which can possibly interact with each other while keeping, on average, a well defined internal structure. The peculiar features of such self-assembled patchy aggregates are the extremely soft interactions and the possible fluctuations in the patch position/size; for this reason they are referred to as soft patchy nanoparticles.

Soft patchy units emerging in TSP systems combine directional interactions and low bonding valence with soft interactions and mobile patches. In contrast, hard patchy units are usually characterized by a pre-defined and fixed patchiness: for this class of systems, the number, the size and the geometrical arrangement of the patches cannot fluctuate. Additionally, the patches are usually such that the single bonding condition (one bond per patch) is guaranteed or, at least, favored. Hence, in hard patchy systems there exists a correspondence between the patch number and the bonding pattern; such a correspondence is an important feature determining the properties and the structure of the macroscopic phases. For our soft patchy nanoparticles, the continuous fluctuations of the patch locations may lead to reversible modifications of the valence (patch number) and of the patch size; as a consequence the possibility of multiple bonding between the patches as well as the equilibrium patchiness at finite densities is controlled by the balance between the energy penalties associated to the distortion of the equilibrium patch arrangement and the energy gains due to the bonding between the patches.

In general, we can state that TSPs have a robust and flexible architecture and they possess the ability to self-assemble at different levels. At the single-molecule level, they first order as soft patchy colloids, which serve then as “soft Lego” for the emergence of larger structures. At the supramolecular level of self-assembly, the soft colloids assemble accordingly to their functionalities, spanning from gels, micellar structure up to complex crystal structures, such as for example diamond or cubic phases [4**].

2. Lattice models

Considerable progress in understanding the properties of TSPs and their concentrated solutions has been achieved by simulations

of lattice models; here, the pioneering work was that of Lo Verso et al. [17*], who employed a lattice model for individual polymers, *f* of which were anchored on a common center. Here, the model is built on a square lattice but sequential bonding between monomers is allowed not only along any of the 6 nearest neighbor directions but also along any of the 12 second neighbors and the 8 third neighbors, bringing the coordination of the lattice up to $z = 26$ and thus emulating a continuum case. Lattice sites are either empty (modeling the solvent molecules) or occupied by monomers, which are of two types: *H* for head or solvophilic and *T* for tail or solvophobic. Accordingly, each arm of the star has the architecture $H_m T_n$, with *m* and *n* denoting the number of repulsive and attractive monomers, respectively. The *f* arms are all anchored on a common, *H*-type central bead, creating thereby star diblock copolymers coded as $H(H_m T_n)_f$, in obvious notation. All monomers are subject to excluded volume interactions, i.e., lattice site occupancy is at most unity. This is also the only condition for the *H*–*H* and *H*–*T* interactions, whereas *T*–*T* interactions entail an attraction of depth $-\epsilon < 0$ as long as they find themselves within the coordination shell ($z = 26$) of one another.

Extensive, grand canonical Monte-Carlo simulations of $H(H_m T_n)_3$ -systems ($f = 3$) with $m + n = 10$ revealed the following scenario [17*]: for $n \geq m$, the system undergoes a macroscopic liquid-gas transition, terminating at a critical point with the critical temperature growing as the number of attractive end-groups increases. On the other hand, when $n < m$, the macroscopic phase separation disappears and the system forms micellar aggregates in which each TSP has collapsed its endpoints in one patch and several of such collapsed stars turn their patches into contact with one another, exposing their solvophilic parts to the solvent. This scenario has been fully confirmed by off-lattice simulations showing the collapse of each star to a single-patch configuration at sufficiently low temperatures [18,19,4**], as well as by recent simulations of micelle-like aggregates in the continuum, see Section 3.4. Upon further increase of the concentration, these spherical micelles begin to merge by fusing their attractive cores, forming thereby wormlike micelles, whose characteristics (length, stiffness, orientation) depend on the temperature as well as on the rigidity of the arms [20,17*]. The scenario has been confirmed also for the case of longer arms, $m + n = 20$ [21]. Moving on to higher functionalities, $f = 6$ and $f = 10$, the self-assembly scenarios become richer. Indeed, although the systems still show macroscopic separation for $n \geq m$, for the opposite case, $n < m$, the emerging structure now depends also on the ratio $\alpha \equiv n/(n+m)$, i.e., the fraction of attractive monomers. Whereas for $\alpha = 0.2$ again spherical micelles result, for $\alpha = 0.4$ the system spontaneously forms a percolating, macroscopic gel [21]. These findings are in full agreement with subsequent and independent off-lattice simulations (see the following section), which demonstrate that for $\alpha = 0.4$ the individual molecules adopt multipatch configurations, thus connecting into a macroscopic gel as concentration grows. On the other hand, for $\alpha = 0.2$ all arms collapse onto a single patch, promoting therefore the stability of micelle-like organization as that shown in Section 3.4. Finally, we point out the possibility of emergence of ordered structures for TSPs with $n < m$, provided the arms are sufficiently rigid [22].

3. Continuum models

Proceeding from lattice to continuum models allows on the one hand to move to more realistic representations of homopolymers, and on the other hand to move to a coarse-grained representation of the system, that will allow, through a multiscale methodology, to more comprehensively explore the phase diagram of TSPs. Continuum models, which are not hindered by the discrete nature that affects the lattice ones and thus allow for a finer tuning of the parameters, are better fit to assess the resulting phase space. However, simulations of continuum models are also inherently

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