Crystalline colloidal arrays from the self-assembly of polymer microspheres

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ABSTRACT

Various polymer microspheres have demonstrated their ability to form crystalline colloidal arrays in relatively concentrated suspensions. The behaviors of such structures are closely related to the characteristics and properties of the microspheres, which could be easily tuned with the choice of monomers and the polymerization procedure. Three commonly used kinds of microspheres are reviewed here: charged hard microspheres, microgels and core–shell particles with a hydrogel shell. The light diffraction displayed by the resulting crystalline colloidal arrays has triggered an increasing interest for potential applications such as optical switches and biosensors.

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1. Introduction

In search of advanced polymeric materials, polymer particles have been particularly popular, owing to the ease of synthesis and their interesting properties, for a wide variety of applications such as drug delivery [1,2], supported catalysis [3] or selective extraction [4,5]. One particular characteristic of some polymer particles is their ability to pack into crystalline colloidal arrays (CCAs), a phenomenon that has attracted much interest.

CCAs have been obtained from all kinds of particles uniform in size and shape. However, the ease for the formation of such arrays and the appropriate method are highly dependent on the particle properties. While many polymer particles self-assemble spontaneously above a certain concentration in solution or upon drying, some other particles such as silica may require more sophisticated techniques such as Langmuir–Blodgett deposition [6,7], vertical and horizontal deposition [8,9] or convective methods [10]. In most cases, only monolayers can be obtained and layer by layer depositions must be applied to form three-dimensional CCAs. The possible control over the number of layers may be an advantage but this method is less straightforward than a simple centrifugation.

Two main models have been used to understand the colloidal crystallization and the formation of CCAs: the "hard sphere" model and the "soft sphere" model. They differ from each other by the kind and the range of the interactions and by the shape of their resulting potential curves, leading to different phase diagrams. The "hard sphere" model describes correctly the behavior of non-charged particles in aqueous and organic solvents or charged particles in suspensions with high ionic strength, where only short-range interactions are involved. The crystallization of such particles is entropy-driven and results directly from the minimization of dead space. Therefore, it depends only on the volume fraction. The crystalline phase of hard spheres covers a very narrow range of volume fractions. The particles start to crystallize above volume fraction of 0.494 (freezing point), and between 0.494 and 0.545 the crystalline phase coexists with the fluid phase which disappears above 0.545 (melting point) [11]. Theoretically, the maximum volume fraction is 0.74 but such a value is not easily reached experimentally as the particles will start to pack randomly because of the high viscosity and movement restriction. The thermodynamically-favored crystalline structure is the face-centered cubic (fcc) but, because of the low difference in free energy between fcc and hexagonal compact (hcp), the hard spheres tend to form random hexagonal compact (rhcp) crystals [12]. The crystallization of colloids classified as hard spheres as well as the techniques to investigate it have been thoroughly described in reviews, notably by Palberg [13–15].

Ordered aqueous suspensions of polymer particles with low ionic strength usually belong to the "soft sphere" model because of the presence of surface charges and the resulting long-range repulsions, allowing the formation of CCAs over a wider range of volume fractions. Indeed, the freezing and melting points are quite different from those determined for hard spheres. The spontaneous self-assembly of polymer particles in solution is driven by many-body

interactions, the most prominent being the electrostatic interactions caused by the surface charges and the electrical double layer. The particles organize themselves to maximize the distance between them and their neighbors, and minimize the repulsions. Thus, while the volume fraction remains the most relevant parameter, contrary to hard spheres, other parameters such as the surface charge density and the ionic strength are also important parameters that dictate the formation of CCAs as illustrated in the phase diagrams for different "soft" particles. In addition, depending on the polymer and the surface properties, other forces may play a role in the balance such as steric and van der Waals interactions. As a result, the crystallization process and kinetics differ from hard spheres, even if the same three steps are also clearly identified: nucleation, growth and ripening. However, similarly to hard spheres, the most commonly observed structures with soft spheres are still close-packed lattices such as fcc and rhcp, depending on the crystallization kinetics. Fast crystallization favors the random stacking of hexagonal planes while a slow crystallization favors the most thermodynamically structure, i.e., the fcc lattice. Body-centered cubic organizations can also be obtained under certain conditions, typically low volume fractions, small amount of salt, high charge density or increased temperature or pressure, as enumerated by Okubo [16]. As a result of their periodic packing, CCAs diffract light, similarly to atomic and molecular crystals diffracting X-rays. Usually, CCAs diffraction is in the range from UV to IR depending on the interparticle distance. Diffraction in the visible range gives iridescent samples with an angular dependence of the color as stated by Bragg's law:

$$m\lambda = 2nd_{hkl} \sin\theta \tag{1}$$

where m is the order of diffraction, λ the wavelength of the diffracted light, n the refractive index, d_{hkl} the lattice spacing for the lattice plane defined by the Miller indices (hkl), and θ the angle between the incident light and the diffracting lattice plane.

CCAs formed by polymer particles have already proven to be of great interest for photonic materials and biosensors, taking advantage of their optical properties. To further improve the characteristics and properties and to meet the requirements for potential applications, a variety of particles has been investigated for the formation of CCAs. Concentrated suspensions of hard and charged spheres with polystyrene or poly(methyl methacrylate) have been extensively studied as model colloids to better understand the mechanism of the formation of CCAs. In a review published in 1993, Okubo detailed the formation, structure and mechanical properties of CCAs formed by charged hard particles in deionized suspensions [17]. Lately, these studies have been extended to soft spheres or microgels as they introduce new properties and tunable interactions. Lyon and co-workers reviewed thermoresponsive microgels and the CCAs thereof highlighting the effect of the volume phase transition and the potential applications of such dynamic systems [18,19]. More complex particles have been investigated to achieve better stability and specific properties, such as core–shell particles. In a review published recently on thermosensitive core–shell particles,