



# Stimuli-responsive colloids: From stratified to self-repairing Polymeric Films and Beyond



Marek W. Urban

Department of Materials Science and Engineering, Clemson University, Clemson, SC 29634, United States  
Center for Optical Materials Science and Engineering (COMSET), Clemson University, Clemson, SC 29634, United States

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## ABSTRACT

Although stratification in polymeric colloids and films has been known for a long time, its significance has not been recognized until surface-interfacial properties driven by mobility of dispersing agents became one of the key features that impact structure–property relationships. Learning from these studies, the last decade resulted in significant advances that have led to the development of a new generation of polymeric materials in general, and colloids in particular, that exhibit stimuli-responsive attributes. As significant as hydrophobic interactions are in biological systems, the abundance of these and other interactions can be found in colloids that are capable of recognition and dynamic responsiveness leading to life-like materials with significant technological applications. Recent advances in the development of stimuli-responsive colloidal materials are discussed in the context of surface and bulk responsive morphologies, from dynamic shape and color changing colloidal nanoparticles to expandable nanotubes and polymer-modified metal nanoparticles. Stimuli-responsive and signaling attributes of macromolecular segments of colloids along with dispersing components will play key roles during colloidal film formation. Concurrently, the development of heterogeneous functional objects that can exhibit dimensional change initiated by light or other environmental factors will form a new platform of amazing and sparkling technologies for the 21st century capable of producing on-demand self-repairing colloid-based materials.

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## 1. Introduction

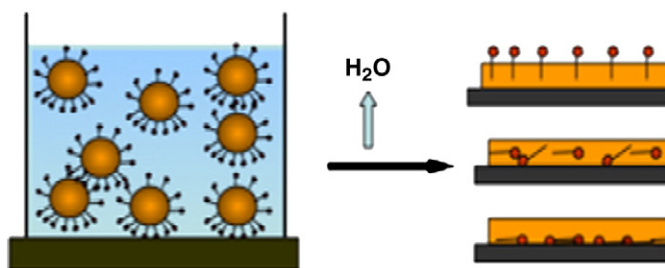
Before the turn of the 21st century there have been less than a handful of research articles dealing with stimuli-response materials. The majority of prior studies had directed their efforts toward functional materials and polymer colloids played a crucial role in these efforts. Regardless of chemistry, physics, or engineering focus, structure–property relationships were the main objective of the majority of these studies [1]. A decade or so later, realizing that polymers play a significant role in health, transportation, and energy, major research programs have redirected their focus on polymeric hybrid materials that are not only functional, but also offer unique attributes reflected in their internal and external responses. These may range from interfacial stratifications of individual components driven by surface and interfacial energy changes, to on-demand color changes or self-repairing attributes. There are many others. It is also important to realize that historically colloidal polymers were perhaps the first materials in which surfactants were observed to form independent and mobile heterogeneous entities capable of exuding on the top, or bottom and interiors of latex films [2], but their role on film formation and film properties was not recognized until later.

Considering that the essence of colloidal synthesis involves primarily only three components, monomer(s), solvent(s) (water and/or cosolvents), and dispersing agent(s) (if any), in principle, one would

not anticipate major complications. Nevertheless, the dynamics of interactions among these components plays a critical role during colloidal synthesis as well as their film formation. But if molecular building blocks contain stimuli-responsive components, another level of complexity is introduced, thus bringing new challenges as well as opportunities. Thus, recent advances in the development of stratification processes in colloidal films, communications among colloidal components, the role of heterogeneities in the context of stimuli-responsive behavior of colloidal nanoparticles, as well as their film formation are central themes that will pave new technological paths for colloidal science. This review attempts to bring recent advances in colloidal science in the context to these few ingredients that are required for colloidal synthesis and is divided into the following sections: stratification and signaling, stimuli-responsive colloidal nanoparticles, and engineered colloidal heterogeneities.

## 2. Stratification and signaling

Surfactant dynamics are quite intriguing; during coalescence these molecules may exude, followed by their appearance on the surface as individual molecules and/or as aggregates, growing in size, to vanishing into a film after certain coalescence times or under certain conditions. As depicted in Fig. 1, the displacement of surfactants can be driven by several processes that often compete



**Fig. 1.** Displacement of small molecular entities from particle surfaces and stratification during coalescence.

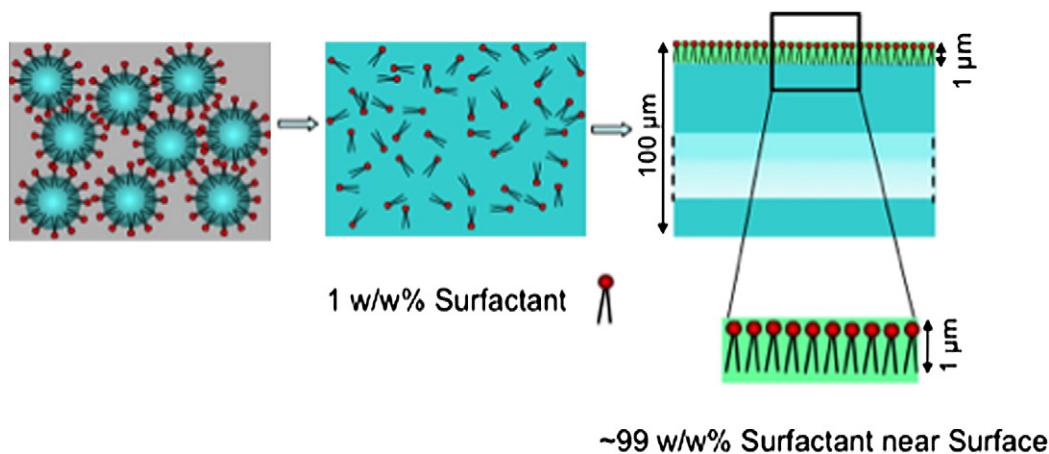
with each other: solvent evaporation and solubility, compatibility with colloidal particle matrix, surface tensions of the surrounding interfaces, temperature, and partial vapor pressure. In an attempt to quantify and sort out the role of each of these processes numerous studies have been conducted over the last two decades [3–5]. Although polymeric coatings at earlier times have been perceived as uniform materials, their multi-component content facilitated an opportunity for the development of property gradients across the film thickness, including glass transition variations as well as other properties. Going back to the early 90s, the development of stratification has led to a number of new and unique surface properties, but the complexity of interactions required orchestrated efforts in order to be functional in various environments. The main advantage of stratification studies was not only the development of polymer-specific stratifications in colloidal copolymer films [6], but was extended to new properties in epoxies [7], polysiloxanes [8], melamines [9], polyurethanes [10], and fluoropolymers [11].

A particular advantage of stratification is illustrated in Fig. 2, which schematically depicts a hydrophobic-to-hydrophilic transformation of initially hydrophobic polymer surface by the formation of perpendicularly oriented monolayer molecules with hydrophilic ends pointing upwards. As a result, the surface energy changes, thus facilitating hydrophilic interactions. This approach has found numerous biomedical applications, where typically hydrophobic polymer surfaces were temporarily and locally modified to obtain hydrophilic behavior. Since colloid particle morphologies play an essential role in coalescence and exhibit particular influence on interfacial regions near the film–air (F–A) and film–substrate (F–S) interfaces, formation of surface localized rafts that exhibit stimuli-responsive characteristics controlled by colloidal particle–phospholipid interactions as well as pH and temperature is of significant interest. These surface entities may resemble the natural phenomena of membrane lipid rafts that have significant implications for many advances leading to understanding the mechanistic aspects of cell–cell signaling, endocytosis,

and raft-raft cross-talk [12,13]. One of the intriguing biological phenomena is the ability of bio-active dispersing agents, such as phospholipids (PLs), to form well organized surface entities referred to as *surface localized ionic clusters* (SLICs). Interestingly enough, they form only during particle coalescence and are typically composed of PLs or a combination of PL and synthetic dispersing agents. Diffusion and mobility of phospholipid molecules are affected not only by their compatibility with colloidal particles, but also by electrolyte environments of colloidal dispersions [14]. When  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  counterions are added to MMA/n-BA aqueous colloidal dispersions stabilized with HSPC, and such films are coalesced, different degrees of diffusion of HSPC to the F–A interface exist, depending on the counterion, and conformational changes of HSPC result. Several mechanisms leading to stratification of these species were proposed [15,16], but it was not recognized until later that the neighboring methylmethacrylate (MMA) and n-butyl acrylate (nBA) units along the polymer backbone provide conducive environments to signal and attract amphiphilic groups of 1,2-dilauroyl-*sn*-glycero-3-phosphocholine (DLPC) PL, thus initiating SLIC formation [17]. Fig. 3 illustrates examples of the SLIC models resulting from interactions between copolymer components and DLPC molecules. As shown, the adjacent location of MMA–n-BA ester linkages plays an essential role in the formation of non-covalent bonding with SLICs. As much as noncovalent interactions play an important role in biological systems ranging from crystal interfaces to base-pairing, peptide and DNA recognition, and sensing, the abundance of these interactions can be found in colloids which are critical in many applications. As shown in Fig. 3, specific entities responsible for SLIC formation are selective noncovalent bonds of anionic phosphate and cationic quaternary ammonium segments of DLPC that interact with two neighboring carbonyl groups of nBA and MMA monomers of the p-MMA/nBA polymer backbone. While these fundamental studies offered new *vistas* in understanding of polymer–surfactant interactions as well as new synthetic approaches of copolymerizing hydrophobic monomers, they also played a significant role in the development of stimuli-responsive colloidal particles and films.

### 3. Stimuli-responsive colloidal nanoparticles

The concept of stimuli-responsiveness initiated over a decade ago [18] has significantly expanded [19] and has become a landmark of many studies. Since there are continuing needs for engineering new devices or objects that demand for materials to exhibit adaptive, self-regulating functions operating in an unprecedented and autonomous manner, this area of research is particularly potent. To achieve these properties, orchestrated micro, nano or smaller scale responsive regions within polymer networks must exhibit responsiveness to a given



**Fig. 2.** Exudation and alignment of surface-active molecules to the film–air interface.

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