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Adsorption of Pluronic block copolymers on silica nanoparticles

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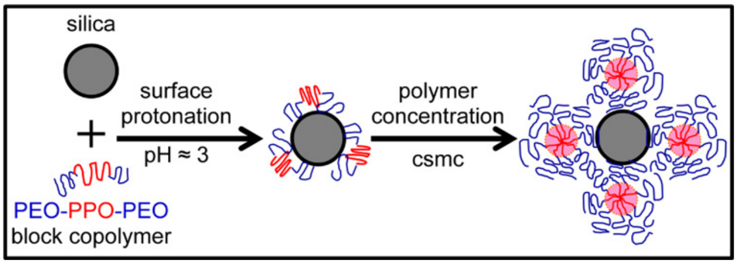
HIGHLIGHTS

- PEO–PPO–PEO block copolymers adsorb on protonated silica nanoparticles.
- Thick surface layer is formed above the critical surface micelle concentration (csmc).
- Above the csmc, adsorbed layer hydrophobicity is comparable to that of micelles.
- Below the csmc the adsorption of block copolymers is similar to that of homopolymers.
- csmc decreases with increasing particle surface concentration and temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymers on the surface of nanoparticles are of great scientific and technological importance since they dictate many important properties and functions of dispersed systems. We investigate here the organization of a representative poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymer on silica nanoparticles dispersed in water. Pluronic P105 ($EO_{36}PO_{56}EO_{36}$) adsorbs on protonated silica and starts forming hydrophobic domains above a certain bulk polymer concentration, called critical surface micelle concentration (csmc), which is lower than the critical micelle concentration (cmc) of Pluronic P105 in plain water. The csmc decreases with increasing particle concentration and decreasing particle size. Below its csmc, the PEO–PPO–PEO block copolymer adsorption on protonated silica nanoparticles is similar to the adsorption of PEO homopolymers. Above the csmc, the block copolymers form micelle-like aggregates on protonated silica nanoparticles, as suggested by the adsorbed layer thickness, adsorbed polymer amount, and presence of hydrophobic domains.

1. Introduction

The stability of colloidal dispersions often depends on the amount and thickness of the adsorbed polymer which, in turn, depend on particle–polymer interfacial interactions [1–3]. Particle–polymer interactions are very complex due to a delicate balance of various enthalpic and entropic contributions [1–2]. The organization of amphiphilic polymers at the solid–liquid interface is of fundamental interest due to their widespread applications such as lubrication, wetting, paint or food formulation, mineral processing, nanoparticle synthesis, drug delivery, bioprocessing [4–10].

Poly(ethylene oxide) (PEO) homopolymer and PEO-containing amphiphiles are popular systems for study because of their wide availability and commercial applications. The interactions between PEO or PEO-containing nonionic surfactants with silica surfaces, both flat and curved (colloidal particle), in aqueous solutions have been well studied [11–16]. The surface functionality of silica, temperature, and polymer molecular weight are found to influence the

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adsorption of PEO on the silica surface [17–18]. PEO homopolymer adsorbs on protonated silica (containing SiOH) surfaces but does not adsorb on deprotonated silica (containing SiO^-) surfaces [18–20]. PEO-containing nonionic surfactants adsorb on protonated silica and form micelle-like surface aggregates above a bulk surfactant concentration called critical surface micelle/aggregate concentration (csmc/csac) [21], which is lower than their critical micelle concentration (cmc) (i.e., the amphiphile concentration at which micelles start forming) in plain water [12,14–15]. Hydrogen bonding between PEO and SiOH has been considered responsible for the adsorption of PEO and PEO-containing nonionic surfactants onto silica surfaces [14].

The use of PEO-containing block copolymers for the adsorption and control of dispersion properties of nanoparticles is advantageous compared to that of PEO homopolymers [22]. Amphiphilic PEO–poly(propylene oxide)–PEO (PEO–PPO–PEO) block copolymers of the Poloxamer or Pluronic family are a natural choice because of their well studied solution properties and commercial availability with varying molecular weights and PEO/PPO compositions [23–25]. PEO–PPO–PEO block copolymers can adsorb from aqueous solution onto silica [26–30]. Interactions of PEO–PPO–PEO block copolymers with silica surfaces are complex and less understood compared to PEO homopolymers, and information about the adsorbed polymer layer structure [29] is lacking. For example, a recent AFM study described 1 nm thick, 20–30 nm diameter, globular shaped PEO–PPO–PEO (Pluronic P105) block copolymer layers absorbed on protonated silica surface as surface micelles, assuming a flat configuration of PPO blocks on the surface [30]. The understanding of adsorbed layer formation of PEO–PPO–PEO block copolymers is mainly based on adsorption isotherms which do not provide sufficient information on the polymer organization in the adsorbed layer. Moreover, the influence of PEO–PPO–PEO–silica surface interactions on the self-organization and structure of the adsorbed polymer layer has not been addressed properly.

The aim of this work is to examine how various parameters such as particle surface chemistry, size, concentration, and temperature influence nanoparticle–polymer interactions and control the self-organization and structure of the adsorbed polymer layer. We consider the interactions of the PEO–PPO–PEO block copolymer Pluronic P105 ($EO_{36}PO_{56}EO_{36}$) with silica nanoparticles (of different size and surface chemistry) dispersed in aqueous solution. A combination of the csmc and adsorbed polymer layer thickness has been used to provide insight on the polymer assembly onto the silica nanoparticles. First, we discuss the influence of silica nanoparticles on the csmc. Next, we discuss the adsorbed Pluronic P105 amount and structure on silica nanoparticles and compare with that of adsorbed PEO homopolymers. To the best of our knowledge this is the first report on how nanoparticle properties such as size and concentration influence the surface organization of PEO–PPO–PEO block copolymers.

2. Materials

2.1. Nanoparticles

Silica nanoparticles are suitable systems for study because of their commercial availability, wide industrial applications, well studied surface chemistry, and easily modifiable surface (protonated and deprotonated) [31]. Silica nanoparticles of three different sizes, Ludox® SM-30, HS-40, and TM-50 (denoted in the present work as SM, HS, and TM, respectively) dispersed in water at pH ~ 10 were obtained from Grace Davidson (Columbia, MD) as a gift. These particles are negatively charged (with a zeta potential of −70 mV [32]) and electrostatically stabilized. Some properties of the as received nanoparticles are presented in Table 1.

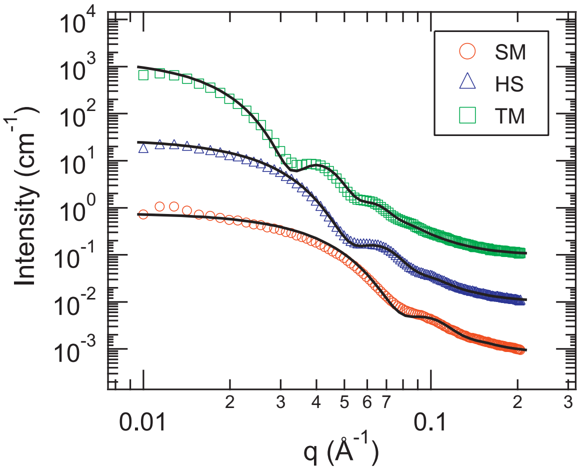

Fig. 1. Small angle X-ray scattering (SAXS) data from 1 wt% of (○) SM, (△) HS, and (□) TM silica nanoparticles dispersed in water. The data for the HS and TM particles are shifted vertically for clarity. The solid lines are fits to the polydisperse sphere form factor.

Small angle X-ray scattering (SAXS) data for 1 wt% dispersions of SM, HS, and TM particles in water are presented in Fig. 1. Fits of the polydisperse sphere form factor to these SAXS data indicate that SM, HS, and TM are spherical with nominal diameter 10.6, 16.6, and 26.0 nm, and polydispersity of 0.16, 0.15, and 0.15, respectively (Table 1). The structure factor is considered to be unity since the particle concentration is low and particle–particle interactions are negligible. We note that the size of the particles obtained from SAXS is close to the size that can be estimated from the nominal surface area (Table 1). The particle shape and sizes that we obtained from SEM images (not shown here) are in agreement with the SAXS data. FTIR spectra of dry SM-type particles confirm the presence of Si—O—Si, silanol (SiOH), and molecular water [33].

2.2. Polymers

The Pluronic P105 poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (obtained from BASF and used as received) has a nominal molecular weight of 6500 that corresponds to 56 PO and 2 X 37 EO segments. Poly(ethylene oxide) homopolymers (Fluka Chemika) of two different molecular weights, 6000 and 20,000 have also been used.

2.3. Sample preparation

Stock solutions of block copolymer have been prepared by dissolving Pluronic P105 in water into which nanoparticles have previously been dispersed. A requisite amount of either HCl or NaOH was added to adjust the pH to 3 or 10 and render the

Table 1
Properties of as received nanoparticle dispersions used in the present work (data obtained from the nanoparticle supplier, unless otherwise noted).

	Particle notation	Particle concentration (wt%)	Surface area (m^2/gm)	Particle diameter (calculated based on surface area) (nm)	Particle diameter (obtained from fit to SAXS data) (nm)
Ludox SM 30	SM	30	320–400	8.8–11.1	10.6
Ludox HS 40	HS	40	198–258	13.7–17.8	16.6
Ludox TM 50	TM	50	110–150	23.5–32.7	26.0