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Adsorption and emulsification properties of amphiphilic poly(styrene-*co*-octadecyl maleamic acid salt) with comb-like architecture

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ABSTRACT

Amphiphilic poly(styrene-*co*-octadecyl maleamic acid salt) (PS-*co*-ODMAS) with a comb-like architecture was synthesized employing a heterophase aqueous polymerization reaction. The side-chain comonomer from octadecyl maleamic acid salt exhibited hydrogelation characteristics and provided conditions for a controlled polymerization reaction. PS-*co*-ODMAS polymers consisting of 5 and 10 mol% side-chain monomer showed a high molecular weight on the order of 10^6 and narrow polydispersity index at 1.33 + 0.02. The polymer consisting of 10 mol% side-chain monomer was shown to exhibit properties that are significantly different from those with 5 mol%, and the control poly(styrene) synthesized using sodium dodecyl sulfate surfactant. The polymer consisting of 10 mol% side-chain monomer formed hollow spherical spheres of 30 nm size. It also showed close-packed structures of the side-chain monomer on the polymer surface. Detailed adsorption studies at the liquid/liquid interface were carried out to evaluate and understand the scope for modification in surface energy characteristics of polymers in the presence of additives drawn from simple surfactants. Triton X-100 was shown to undergo effective adsorption on the polymer consisting of 10 mol% side-chain monomer and thus could generate stable emulsions with different volume fractions of heptadecane. The results from electron microscopy studies and viscosity of emulsions are discussed.

1. Introduction

The organization of polymer particles at the liquid/liquid interface provides stable emulsion phase structures that are popularly known as Pickering emulsions. They have been known for a long time [1] and exhibit interesting properties. Pickering emulsions show a good shelf life owing to the high free energy of desorption of particles from the interface, enhanced viscosity, and mechanical strength [2]. The reports related to generation of Pickering emulsions using inorganic polymer species like SiO_2 and clay are well documented [3–11]. There is a growing revived interest in Pickering emulsions in view of the wide choice in design of particulate emulsifiers and the scope in design of novel functional materials. Kawaguchi and co-workers recently demonstrated the design of thermally sensitive Janus microgels with a unique morphology from poly(*N*-isopropylacrylamide) (PNIPAM) using Pickering emulsion methodology [12]. The application of Pickering emulsion in biomineralization was demonstrated, e.g., in the design of hollow spheres of TiO_2 [13]. Nanocomposite emulsifiers consisting of organic and inorganic polymers were successfully employed to design stable Pickering emulsions with interesting characteristics [14–16]. To cite some examples, polymer particles from 4-vinyl pyridine chloride stabilized using SiO_2 and the microgel derived from them were shown to provide Pickering emulsion that responded to the environment [17–19]. Latex or, in other words, organic polymer dispersions draw significant attention especially in the context of generation of Pickering emulsion with novel characteristics and smart behavior. This is possible because of the interesting physicochemical characteristics of monomers, and scope for design of polymers with different chemical architectures. Armes and co-workers demonstrated that poly(styrene) (PS) latex that was modified with a steric stabilizer from a diblock copolymer of polydimethylaminomethacrylate (PDMA)-*b*-polymethylmethacrylate (PMMA) could form smart Pickering emulsion [20–22]. Binks and Rodrigues showed that carboxyl group-coated PS particles formed high stable emulsions that could reverse from an oil/water to a water/oil type of emulsion as controlled by pH and electrolyte concentration [23]. The chemically modified PS through aldehyde/sulfonate functionalization was shown to perform as a good particulate emulsifier [15,24,25]. Dai and co-workers have shown that the Ps particles could be utilized to form high viscous emulsion of poly(dimethylsiloxane) in water [26] after functionalization with sulfate groups. Ngai and co-workers recently showed that stable high internal phase emulsion could be enabled using microgel particles from poly-*N*-ispropyl acrylamide (PNIPM)-*co*-polymethacrylic acid (PMAA) [27].

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Basically, it could be followed that different approaches are adopted to design polymers that show efficient adsorption at the liquid/liquid interface, smart behavior, and morphology. This is enabled through judicious choice of the monomers. Polymers consisting of segments drawn from long alkyl side-chain monomers classically provide comb-like structures that influence the organization at the interface. They display a high surface coverage in view of their capability of forming thin layers [28–30]. The flexibility, length, and packing characteristics of side-chain segments of these polymers influence the interfacial energy characteristics. It was shown that the surface energy of comb-like polymers decreased with an increase in the length of alkyl side chains [31,32]. The adsorption characteristics at different interfaces of comb-like polymers as controlled mainly by the copolymer composition have been well demonstrated in published reports [33]. Koh and Saunders [34] demonstrated that the thermally sensitive NIPAM segment in a comb-like polymer from poly(NIPAM-*co*-poly(ethylene glycol methacrylate) (PEGMA) provided thermally responsive O/W emulsion that switched between aggregated and gel structures. The temperature-triggered sticky microgel particle formation was shown to perform as a glue between emulsion droplets [35].

We have adopted a new approach to design amphiphilic polystyrene with a comb-like architecture by way of introduction of a surface-active side-chain monomer, namely sodium salt of octadecyl maleamic acid (ODMAS). ODMAS was shown to form hydrogel and promote a controlled heterophase aqueous polymerization reaction [36]. It is worth noting here that hydrogelator is used to synthesize potential materials [37]. In fact, Yang and co-workers demonstrated the application of ODMAS gel in the separation of *d* and *l* isomers of amino acids [38]. The polymer PS-*co*-ODMAS reported in this study is the first of its kind wherein the ODMAS segment that confers amphiphilicity forms an integral part of the polymer chain [15,20–22,24,25]. Poly(styrene-*co*-octadecyl maleamic acid salt) (PS-*co*-ODMAS) copolymers, OSEP1 and OSEP2, that vary in ODMAS content between 5 and 10 mol% were synthesized. The packing characteristics of the ODMAS side-chain segment on the polymer particle surface were derived from particle size measurements. We show here that the morphology and interracial adsorption characteristics of these polymers are significantly different. The latex OSEP1 and OSEP2 showed a tendency to undergo adsorption at the liquid/liquid interface. In this study, we address the issue of modification of surface energy and wetting characteristics of the two polymers, and the consequential effect in the emulsification properties. The results from adsorption and electron microscopy (EM) studies are rationalized. To the best of our knowledge, this is the first report of its kind that investigates the design and interfacial behavior of amphiphilic PS with a comb-like architecture. This report presents two important findings: the significant role of gel forming side-chain monomer on the morphology and surface energy of the latex, and the remarkable improvement in the emulsification property of latex the in presence of simple non-ionic surfactant additive. These findings have tremendous technological potential and are useful in the development of high viscous emulsion of functional materials such as drugs, lubricants, and dyes that are hydrophobic in nature. Furthermore, the correlation between latex characteristics and emulsification property contributes significantly to evolve high performing new particulate emulsifiers with novel features.

2. Materials and methods

N-Octadecyl maleamic acid (ODMA) was synthesized using the procedure reported elsewhere [36,39]. The gel phase structure of ODMA at a concentration of 5% was generated after conversion to sodium salt (ODMAS) at pH 10.5, as detailed in [40]. Styrene 98% pure was obtained from Aldrich. Potassium persulfate used as an initiator in the polymerization reaction, the surfactants, SDS (99%), CTAB (99%), and Triton X-100 (TX100) (99%) employed for modifying the surface properties of Ps-*co*-ODMAS copolymer particles and heptadecane (99%) in emulsion formation studies were all from S.D. Fine Chemicals Ltd., India. SDS (99%) was used in a control polymerization reaction as well.

2.1. Emulsion polymerization

To the 5% aqueous gel of ODMAS in a polymerization tube was added styrene. The mole fraction of ODMAS and styrene in the feed was varied between 0.95:0.05 and 0.90:0.10 m (m represents the mole fraction). Photopolymerization reactions of emulsions were performed on a Heber multilamp photoreactor Model HML-compact-LP-MP-812, 8 W medium-pressure UV lamp under inert atmosphere. The emulsion of monomer mixture was taken in the polymerization tube and irradiated with radiation of $\lambda = 365$ nm at 30 °C for a period of 6 h. About 0.1% initiator, $K_2S_2O_8$, was employed. Control emulsion polymerization reaction of styrene (PSSDS) was performed under the same conditions without ODMAS, and using SDS surfactant wherein the surfactant to monomer was chosen as 1:4. The polymer was isolated by a nonsolvent precipitation method using methanol as a precipitating solvent. The polymer was repeatedly washed with water and methanol to remove the unreacted monomers and physically adsorbed surfactant. The purified polymer was dried under vacuum until a constant weight was obtained.

2.2. Characterization of PS-co-ODMAS

^{1}H nuclear magnetic resonance (NMR) measurements in $CDCl_3$ solvent for the characterization of PS-*co*-ODMAS copolymers were performed on a JEOL ECA 500 (500 MHz) NMR spectrometer using tetramethylsilane as an internal standard. The copolymer composition was estimated using well-separated respective peaks of methyl and phenyl groups at $\delta = 0.9$ and $\delta = 6.3–7.2$ ppm. Molecular weight estimation of the polymers was performed on a JASCO gel-permeation chromatograph (GPC), MX-2080-31 fitted with PL gel 5-μm Mixed-C columns, 300 × 7.5 mm, in tetrahydrofuran with a flow rate at 1 mL min^{-1} at 30 °C using a refractive index (RI) detector. Differential scanning calorimetric (DSC) measurements and thermogravimetric analysis (TGA) on the polymers were performed on a TA calorimeter (DSC Q200) and TGA Q50, USA, under inert atmosphere with a heating rate of 10 °C/min.

2.3. Characterization of latexes

2.3.1. Particle size measurements

The particle size measurements were performed for the latexes on a Malvern particle size analyzer 1000HS/3000HS at a fixed scattering angle of 90°. The latex samples for analysis were dialyzed for more than a week with change of water to ensure complete removal of free surfactant (SDS) or free ODMAS if any. The samples were filtered using 0.45-μm filter paper before measurements. The value reported is the average of three measurements. The interfacial area of ODMAS (a) was calculated from N_p and D_w using the equation

$$\text{interfacial area} = N_p[4\pi(D_w/2)^2] \tag{1}$$

where D_w is the diameter of the particle and N_p is the number of particle. The latexes, OSEP1 and OSEP2, were chosen for detailed electron microscopic and adsorption studies. PSSDS latex was employed as the control in these investigations.

2.3.2. Transmission and scanning electron microscopic studies

Transmission electron microscopy (TEM) was performed on the latex with a Zeiss Libra 120 electron microscope operating at an