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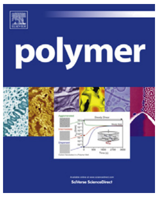

Tuning the aggregation and redispersion behavior of CO_2-switchable latexes by a combination of DMAEMA and PDMAEMA-*b*-PMMA as stabilizing moieties

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ABSTRACT

We have prepared CO_2-switchable poly(methyl methacrylate) and polystyrene latexes where the stabilizing CO_2-switchable moiety originated from either the monomer 2-dimethylaminoethyl methacrylate (DMAEMA) (copolymerized *in situ*) or previously synthesized poly(2-dimethylaminoethyl methacrylate)-*block*-poly(methyl methacrylate) (PDMAEMA-*b*-PMMA). The latexes can be aggregated by N_2 and heat, and redispersed through CO_2 bubbling and sonication. These two methods of incorporating the CO_2-responsive groups yield quite different switching behavior. Using PDMAEMA-*b*-PMMA as the only switchable compound produced latexes that are easily aggregated, however the redispersion step required relatively high energy input. In contrast when the stabilizing moieties originated from DMAEMA monomer copolymerized *in situ*, the latexes exhibit the opposite behavior; aggregation is difficult but redispersion is easier. By combining the use of both *in situ* polymerized DMAEMA monomer and PDMAEMA-*b*-PMMA, we were able to produce latexes with tunable aggregation and redispersion behavior.

1. Introduction

Emulsion polymerization is one of the most important industrial processes for the preparation of polymer latexes [1–3]. Latexes are used in many commercial products with a variety of applications such as coatings, rubber, textile, paints and also the biomedical and pharmaceutical fields [4–6]. Among the components used in emulsion polymerization, surfactants play a significant role. Surfactants provide electrostatic and/or steric repulsive forces on the surface of the dispersed particles and lead to stabilization of the immiscible phases. In many applications, the stabilization is only required during the polymerization process and a subsequent destabilization step is necessary for final application. Since water accounts for about half of an industrial latex's volume, the cost associated with transporting water from production site to application site is appreciable. Significant benefits, in terms of reduced cost and environmental impact, could be realized if latexes could be dewatered, shipped to their final destination, and then reconstituted by addition of water. “Switchable surfactants” may offer a solution. Surface activity of these kinds of surfactants can be reversibly altered by application of a trigger. Application of the trigger removes or reduces the repulsive forces between stabilized particles, causing aggregation of the dispersion. Earlier forms of switchable surfactants were triggered by altering pH (acid or base addition) [7,8], applying UV light [9], or adding redox reagents [10–14]. More recently, the use of CO_2 as a readily reversible trigger in switchable surfactants has been reported [15–22].

Many of the earlier switchable materials are not suitable for preparation of switchable polymer latexes because of cost and environmental effects. CO_2-triggered surfactants are promising because CO_2 is an inexpensive, benign and effective trigger for switchable compounds. They are a class of surfactants whose surface activity can be reversibly altered by the application of CO_2.

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Usually these surfactants are nitrogen based compounds including amidine [20–24], imidazoline [18,19], guanidine [15,25], and tertiary amines [17,18,20–24]. Monomers and initiators bearing such suitable functional groups can also yield switchable latexes [18,19,26]. The nitrogen in these functional groups reacts with dissolved CO_2 in the water phase and produces the corresponding bicarbonate salt of nitrogen in which the nitrogen is positively charged ("on" mode) [27]. Air (or any nonacidic gas such as Ar and N_2) and heat, by removing CO_2, can switch active surfactants to a surface inactive neutral state ("off" mode). In the absence of CO_2, the switchable surfactants are not able to stabilize emulsion particles and large aggregates are formed. In some cases, these aggregates can also be effectively redispersed if the surfactant is switched back "on" [18–23].

Long chain alkyl amidinium bicarbonates as well as long chain tertiary alkyl ammonium bicarbonates have been used effectively for stabilization of latex particles in the emulsion polymerization of MMA and styrene [23,24]. We also prepared a polystyrene latex by using only the bicarbonate salt of the initiator 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (VA-061), through surfactant free emulsion polymerization (SFEP) [19]. The bicarbonate salt of initiator (VA-061) can be switchable between the ionic and nonionic forms by the addition and removal of CO_2. Therefore the prepared latex can be aggregated and redispersed using CO_2 as a trigger. It has been shown that poly(dimethylaminoethyl methacrylate) (PDMAEMA) can also be CO_2 switchable [28]. By control of the protonation of the amine group in PDMAEMA via CO_2, the solubility of the polymer can be varied significantly, and the lower critical solution temperature (LCST) can be reversibly tuned. Also, copolymers and polymer crosslinked networks containing PDMAEMA have been shown to exhibit CO_2-responsive behavior. Pinaud et al., by taking the advantage of the switchability of 2-(diethyl)aminoethyl methacrylate (DEAEMA) as a switchable comonomer, prepared switchable polystyrene latexes with narrow size polydispersity [18]. Emulsion polymerization of MMA using well-defined PDMAEMA based block copolymer as a surfactant has been reported [22]. PDMAEMA was prepared in RAFT solution polymerization and used in emulsion polymerization of MMA under acidic conditions (HCl). When using HCl for preparation of the latex, aggregation of latexes required addition of caustic soda. Switchable latexes which contained the switchable comonomer (2-dimethyl-1-(4-vinylbenzyl)1-,4,5,6-tetrahydropyrimidinium bicarbonate) were also reported. In this study addition of caustic soda was required for aggregation since the initiator was the hydrochloride salt (rather than the bicarbonate salt) [20].

We have examined the role of the source of the tertiary amine stabilizing moieties in DMAEMA, and specifically whether they originate from (1): DMAEMA monomer that is polymerized *in situ* early in the reaction to provide stabilization, or; (2) added PDMAEMA in the form of diblock copolymers. We found there are indeed significant differences in both the aggregation and redispersion behavior of the latexes, depending on whether the tertiary amine moieties originate from monomer polymerized *in situ* versus added block copolymer. Using a greater fraction of DMAEMA results in difficult aggregation and facile redispersion while using diblock polymeric switchable surfactants typically give easier aggregation but more difficult redispersion. We hypothesized that it should be possible, by using a combination of switchable comonomer (DMAEMA) and its polymeric counterpart (PDMAEMA-*b*-PMMA), to tune the re-dispersion and aggregation rates of latex. We demonstrate here that that this concept can indeed be implemented, yielding latexes that are both readily aggregated as well as effectively redispersed, with aggregation and redispersion behavior tunable as required.

2. Experimental

2.1. Reagents

Carbon dioxide (CO_2, Praxair, Medical grade) and nitrogen (N_2,Praxair, 99.998%) were used as received. 2,2′-Azobis[2-(2-imidazolin-2-yl)propane] (VA-061), 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and 2,2′-azobis(2-methylbutyronitrile) (Vazo-67) $\geq$ 98.0% from DuPont Co. were used as initiators. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CTDPA) as a RAFT agent was supplied from Aldrich and used as received without further purification. 2-(Dimethyl)aminoethyl methacrylate (DMAEMA, 98%, Aldrich), styrene (St, 99%, Fischer) and methyl methacrylate (MMA, 99%, Aldrich) were used as monomers. Styrene and MMA contained monomethyl ether hydroquinone (MEHQ) and 4-*tert*-butylcatechol (TBC) inhibitors, respectively. Inhibitors were removed by passing through an aluminum oxide column (inhibitor removal column supplied from Aldrich). Deionized water (EMD Millipore Co.) was used in all experiments.

2.2. Characterization

A gel permeation chromatograph (GPC) from Waters was used for evaluation of molecular weight and molar mass dispersity (Đ) of PDMAEMA-*b*-PMMA. The system was equipped with three Styragel columns with separation limits between 400 and 1×10^6 g mol^{-1} and a differential refractive index detector. A calibration curve was obtained based on polystyrene (PS) standards from Polymer Standard Service. THF was used as a mobile phase at a flow rate of 0.3 mL min^{-1}. Polymeric samples after filtration through 0.2 μm pore-size membrane were injected to the column at a concentration of 5 mg mL^{-1}. Empower software was used for data analysis and data acquisition.

Since Mark-Houwink parameters for PDMAEMA were not found in the literature, Mark-Houwink parameters for poly(butyl methacrylate) (PBMA) were used ($K = 14.8 \times 10^{-5}$, $a = 0.664$, PS: $K = 11.4 \times 10^{-5}$, $a = 0.716$) [29]. ^{1}HNMR (nuclear magnetic resonance) measurements in deuterated chloroform ($CDCl_3$) were conducted out at room temperature using an automated Bruker DRX 300 spectrometer. Overall monomer conversion was determined gravimetrically. A 1–2 mL sample of latex was taken using a syringe, quenched in an ice/water bath and allowed to dry under a flow of air overnight followed by oven drying for 24 h at 80 °C.

Conductivity measurements were obtained using a Mettler Toledo conductivity meter (S230 Seven Compact). A known amount of switchable polymer (PDMAEMA) or monomer (DMAEMA) containing 0.5 mmol DMAEMA units (as either DMAEMA units in the surfactant or those copolymerized in the latex particle) was dissolved in a mixture of ethanol and water (10 mL of each). The final concentration of DMAEMA units was 25.0 mM CO_2 was bubbled through the solution using a needle at a flow rate of 90 mL min^{-1}, and the conductivity change over time was measured at room temperature (24 °C) until a constant value was obtained. Nitrogen was subsequently bubbled through the solution using a needle at a flow rate of 90 mL min^{-1}. This process was repeated for three cycles.

Zeta potentials were obtained using a Malvern Zetasizer Nano ZS. Each measurement was the average of five individual measurements. Samples for zeta potential measurement were prepared by diluting one drop of the latex into ~1 mL of water (water presaturated with carbon dioxide was used for the samples which were treated with CO_2). The measurements were taken using a quartz capillary cuvette. Latex particle sizes were determined using

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