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In situ charge neutralization-controlled particle coagulation and its effects on the particle size distribution in the one-step emulsion polymerization

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ABSTRACT

A novel approach to prepare sub-200 nm, narrowly dispersed polystyrene latex particles is proposed for the emulsion polymerization of a ca. 40 wt% solid-content solution. The presented method exploits the cationic comonomer methacryloxyethyltrimethyl ammonium chloride (MATMAC) or the initiator 2,2′-Azobis (2-methylpropionamidine) dihydrochloride (AIBA) to generate cationic oligomeric radicals shielded the negatively charged surfactant molecules adsorbed on the particles surface, further induced particle coagulation by *in situ* charge neutralization. By adjusting the types and amounts of the comonomer, the extent of the *in situ* charge neutralization is controlled. In consequence, the extent of the particle coagulation is controlled, resulting in the production of large-size latex particles. The particle coagulation induced by *in situ* charge neutralization occurs at the particle nucleation stage, which extends the times of particle completive growth and reversible coagulation, and therefore, narrowed the width of the particle size distribution of the ultimate latex particles. The resulting colloidal latexes containing 40 wt% solid content are very stable by presenting the absolute value of zeta potentials larger than 40 mV. This approach is likely to be used for large-scale industrial productions of narrowly dispersed polymer particles.

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1. Introduction

Polymer nanoparticles exhibiting a narrow particle size distribution are applied in many fields such as coatings, adhesives, pains, and plastic modifiers [1–3]. Generally, these polymer nanoparticles less than 1000 nm in average particle size can be synthesized by emulsion polymerization [1]. Typical emulsion polymerizations techniques are multistep reactions requiring long reaction time and employ semi-continuous monomer-starved [4–7], two-stage swelling [8], and dynamic swelling methods [9] to control the particle size distribution of the ultimate latex. In addition, several simple and one-step methods for emulsion polymerization have been proposed to produce narrowly dispersed polymer nanoparticles in recent investigations [10–13], but these methods are not applied in industry because they require a relative low solid-content (<10 wt%) system and unconventional and expensive reagents.

Particle coagulation technology can be considered as a method for preparing high solid content and narrowly dispersed nano-latexes and has been widely investigated in recent published reports [14–18]. Particle coagulation occurs in particle nucleation period, and also is a revisable process. Thus, the particle formed by particle aggregation have enough time to fuse and narrow particle size distribution (also called competitive growth), resulting in forming monodispersed latex particles. In detail, the process of particle coagulation consists of a particle collision followed by fusion [15]. The particle collision frequency of the different particle classes can be extracted from the Von Smoluchowski equation [16] but particle collision remains a complex dynamic process, during which several small particles can aggregate into a large one, and simultaneous disaggregation of the large particles can also occur. Behrens et al. and Ohshima et al. considered a set of coupled-nonlinear differential rate equations to describe this process and also established the early-stage aggregation kinetics [17,18]. However, particle nucleation together with coagulation disturbs this quantitative description. Indeed, the new particles might be formed by different nucleation mechanisms, especially during the particle nucleation period [19]. Thus, considering the particle collision during the particle nucleation period complicates the description of the process.

Particle coagulation occurs if the particle's kinetic energy is sufficiently high to overcome the potential energy barrier, which is the sum of the Van der Waals attraction energy and the electrostatic repulsion energy [16,20,21]. Therefore, particle coagulation is also a thermodynamic process. Particle fusion requires either a high kinetic energy of the particles or a low potential energy barrier. Carro et al. promoted particle coagulation by increasing the particle density and reaction temperature [22]. Dobrowolska et al. proposed another approach to promote particle coagulation by compressing the thickness of the electric double layer of particles via the addition of electrolytes that could increase the ionic strength [23]. Indeed, particle coagulation was induced by adding different electrolytes or co-solvents [24,25]. Controlling particle coagulation by the addition of electrolytes is very convenient but affects some end-product properties such as the minimum film forming temperature and time [26]. Therefore, developing alternatives for the controlled induction of particle coagulation without electrolytes and co-solvents has become a leading focus in this field of research.

A new approach based on the electrostatic stability of the latex particles was recently developed to induce particle coagulation [27–30]. Zhang et al. observed the particle nucleation of charge-stabilized dispersion polymers and indicated that particle coagulation could be controlled by varying the charge density of the particle's surface [31]. Chou et al. used mixed ionic/nonionic initiators systems to control the particle's electrostatic stability and prepared multi-scaled surfactant-free monodisperse latex by dispersion polymerization [32]. Fowler et al. utilized cationic switchable surfactants to control particle electrostatic stability of latex particles in the presence of CO_2 [33]. Shibuya et al. employed the amphoteric initiator 2,2′-azobis [N-(2-carboxyethyl)-2-methylpropionamidine] to adjust the electrostatic stability of latex particles by varying the pH value of a solution in a soap-free emulsion polymerization [34].

In a conventional emulsion-polymerization system, the electrostatic potential energy of the latex particles is attributed to the surfactant molecules adsorbed on the particle's surface and on the initiator's chain ends [35]. In principle, varying the type of differently charged surfactants and initiators or copolymerizing differently charged comonomers should allow the control of the electrostatic potential energy of the latex particles by *in situ* charge neutralization and subsequently the extent and duration of particle coagulation might be controlled. Particle coagulation induced by *in situ* charge neutralization can be advanced into the particle nucleation period, in which the particle coagulation is reversible because the colliding particles can desorb from the aggregated particles [36]. As a result, narrowly dispersed latex particles are obtained even though particle coagulation occurs [23,37,38]. In this study, we copolymerized styrene by conventional emulsion polymerization using methacryloxyethyltrimethyl ammonium chloride (MATMAC) and sodium styrene sulfonate (NaSS) as the cationic and anionic comonomer, respectively. The aim of the study is to discuss the role of *in situ* charge neutralization by determining the particle coagulation and particle size distribution of ultimate latexes. Furthermore, we propose a novel approach for the preparation of large-size, narrowly-dispersed, and high-solid content latexes induced *in situ* charge neutralization by using the cationic initiator 2,2′-azobis (2-methylpropionamidine) dihydrochloride (AIBA) replacing the anionic initiator by potassium persulfate (KPS).

2. Experimental section

2.1. Materials

The cationic initiator AIBA (98%), anionic initiator KPS (98.5%), surfactant sodium dodecyl sulfate (SDS, 99%), potassium carbonate (K_2CO_3, 99%), and anionic comonomer NaSS (90%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). and The cationic comonomer MATMAC (85%) was supplied by Shanghai Heng Yi Group Co., Ltd (Shanghai, China). Styrene (99%, Shanghai Chemical Reagent Co., Ltd., Shanghai, China) was distilled under −0.1 MPa to remove traces of inhibitors and stored in −5 °C prior to use. Distilled deionized (DDI) water was used for all experiments.

2.2. Synthesis of the polymer latex

All the polymerizations were conducted in a 500 mL four-neck round-bottom glass flask equipped with an anchor stirrer, a reflux condenser, a nitrogen pipe, and a sample connection. Firstly, SDS (1.5 g), K_2CO_3 (0.6 g), and the comonomer (NaSS or MATMAC) were introduced inside the flask at 65 °C then dissolved by adding DDI (130 mL). The monomer styrene (100 g)