



Preparation of copolymer particles by emulsion polymerization using a polymerizable amphiphilic macromonomer

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ABSTRACT

Monodisperse copolymer particles of styrene, *n*-butyl acrylate, and methacrylic acid were prepared by emulsion copolymerization using a polymerizable poly(ethylene glycol)-ethyl ether methacrylate (PEG-EEM) macromonomer. The good uniformity of the copolymer particles indicated that the aggregation of the unstable precursor particles during the particle nucleation period was uniform and no coagulation of the prepared copolymer particles suggested that the PEG-EEM macromonomer acted as an effective stabilizer in the replacement of surfactant in emulsion polymerization. The particle size and molecular weight of the copolymer particles increased with increasing PEG-EEM concentration up to 4 wt.%, and decreased at 6 wt.%, which was attributed to its solubility. The rate of polymerization increased with increasing reaction temperature due to increases in the rate of initiator decomposition, propagation rate, and diffusion rate of radicals and monomers. The size and molecular weight of the copolymer particles decreased with increasing temperature. The effects of the initiator concentration, monomer ratio, and concentration of chain transfer agent on the properties of the copolymer particles were also investigated.

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1. Introduction

The preparation of monodisperse polymer particles has attracted considerable academic and industrial attention due to their wide variety of applications such as instrument calibration standards, column packing materials for chromatography, electronic toners, microelectronics, and biotechnology [1–5]. Size control and narrow size distributions are of fundamental importance for most applications of polymer particles.

Monodisperse polymer particles are typically prepared by various heterogeneous polymerization procedures including emulsion, suspension, precipitation, and dispersion polymerization. Among these techniques, the emulsion polymerization process has several advantages [6]. The physical state of the colloidal system allows easy process control, and the latex product is often quite valuable. Emulsion polymerization, which has traditionally been the most important process for manufacturing polymer colloids, is the leading technology for producing monodisperse polymer particles [7]. However, the presence of surfactant is a disadvantage for certain applications such as coatings or electronic toners

due to migration problems. In electronic toners for laser printers, the presence of surfactants can make the tribo-charge more dependent on environmental changes in that the adhesive properties between the toner particles and substrate are poor at high relative humidity. The surfactants should be removed from the particles by washing. However, removal of the surfactant is very tedious and resource consuming. Therefore, an environmentally friendly and cost effective emulsion polymerization process that eliminates or at least minimizes the need for a surfactant is needed.

Soap-free emulsion polymerization has been used extensively to prepare polymer particles with functional groups on their surfaces for electronic toners and biomedical applications. Stabilization of polymer particles in soap-free emulsion polymerization depends on the adsorption of ionizable initiators or the hydrophilic comonomers containing ionic groups, such as carboxylic monomers [8]. However, the stabilizing effects of these species might be weak. Several mechanisms for particle nucleation and growth in soap-free emulsion polymerization have been proposed [9–11]. In a theory of coagulate nucleation of precursor particles [9], stable latex is formed from the coagulation and growth of unstable precursor particles formed by homogenous nucleation. The rate of particle formation is determined by the rate of homogeneous nucleation to form the primary precursors, the rate of coagulation of the precursor particles and the rate of propagation growth.

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Macromonomers have attracted considerable attention due to their amphiphilic nature, acting as a stabilizer in aqueous media. Macromonomers are a relatively new category of functionalized polymer or oligomer material with one or more polymerizable end groups. Therefore, the use of macromonomers provides an alternative route to stabilizing polymer particles in the replacement of surfactants in emulsion polymerization [12]. Macromonomers can act as both a stabilizer and a comonomer. Macromonomers should possess both hydrophobic and hydrophilic moieties in order to act as an emulsifier, which can form micelles in aqueous media. These micelles are generated by the aggregation of the macromonomers, and can serve as the polymerization loci. The macromonomers participate in polymerization by reacting with the monomers [13]. The copolymerization of macromonomers with monomers might produce grafted copolymers [14,15].

In this study, monodisperse copolymer particles of styrene, *n*-butyl acrylate, methacrylic acid (MAA), and macromonomers, such as poly(ethylene glycol)-ethyl ether methacrylate (PEG-EEM), were prepared by emulsion copolymerization. Styrene/butyl acrylate/MAA copolymer particles are commonly used in electronic toner formulations, and a relatively new macromonomer, PEG-EEM, has been used as an efficient polymerizable stabilizer. There are few reports on the preparation of monodisperse copolymer particles by semi-batch emulsion polymerization using a macromonomer. This study reports how the size and molecular weight of the resultant copolymer particles can be controlled via semi-batch emulsion polymerization at a fixed monomer feed rate, using various polymerization variables such as the PEG-EEM concentration, reaction temperature, and initiator concentration.

2. Materials and methods

2.1. Materials

Styrene (Sigma–Aldrich) was purified using an inhibitor-removal column (Aldrich) and stored at -5°C prior to use. Butyl acrylate (Aldrich) and methacrylic acid (Junsei) were used as monomer reagents without further purification. PEG-EEM (Aldrich) was used as a macromonomer. Isooctyl-3-mercaptopropionate (IOMP, Aldrich) was added to the monomer mixture as a chain transfer agent (CTA), and potassium persulfate (KPS, Sigma–Aldrich) was selected as a water-soluble initiator. Distilled-deionized (DDI) water was used in all experiments.

2.2. Polymerization procedure

Emulsion copolymerization was carried out in a 500-ml reactor at a constant stirring rate of 200 rpm in a nitrogen atmosphere. The reactor was initially charged with DDI water dissolving a macromonomer. DDI water was degassed by bubbling nitrogen gas at room temperature for 30 min prior to use. The reactor was then heated to the reaction temperature of 80°C , while being purged with nitrogen gas. An aqueous solution of the initiator was then added to the reactor. The monomer was added drop wise over a 2-h period. The overall monomer feed rate was 0.57 g/min for all polymerization. Polymerization begins with a small quantity of monomer with the rest being fed to the reactor over time [16]. Table 1 shows the methodology and polymerization conditions. The total solid content was 20%. During polymerization, aliquots of the sample were taken periodically from the reaction vessel for characterization.

2.3. Characterizations

The overall conversion was calculated gravimetrically. A Hitachi SEM (scanning electron microscopy) S-4700 was used to exam-

Table 1
Formulations for the soap-free emulsion polymerization

Code	Monomer (wt.%)			CTA ^a IOMP	Macromonomer ^a PEG-EEM	Initiator ^a KPS
	ST	BA	MAA			
TG40	70.1	27.8	2.1	1.5	4	2.1
TG50	75.0	22.9	2.1	1.5	4	2.1
TG60	80.0	17.9	2.1	1.5	4	2.1
TG70	84.5	13.4	2.1	1.5	4	2.1

^a wt.% relative to the monomer content.

ine the morphology of the polymer particles. The particle size and distribution were measured using a particle size analyzer (LS230[®], Beckman Coulter). The molecular weight was characterized by Viscotek Gel Permeation Chromatography (GPC) equipped with a 510 Differential Refractometer and a Viscotek T50 Differential Viscometer. A universal calibration curve was made using 10 PS standard samples (Polymer Laboratories) with molecular weights of 580–7,500,000 g/mol. The copolymer dissolved in THF was injected at a flow rate of 1.0 ml/min. The glass transition temperature (T_g) of the sample was measured using a Shimadzu differential scanning calorimeter (DSC-60). The sample was heated at a rate of $20^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere and quenched-cooled, and then reheated for a second run. The T_g was determined at the deflection point in the transition region from the second scan.

3. Results and discussion

3.1. Effect of polymerization temperature

Fig. 1 shows the polymerization conversion curves of the TG40 copolymer particles prepared by semi-batch emulsion polymerization at various temperatures. Table 1 shows the methodology for preparing the TG40 copolymer. The dependence of conversion on temperature was well observed from the figure. At 60°C , the conversion increased almost linearly up to the end of the polymerization, and the rate of conversion increased with increasing temperatures. The final conversion was >98% at all temperatures. The curves in Fig. 1 were produced by curve-fitting the experimen-

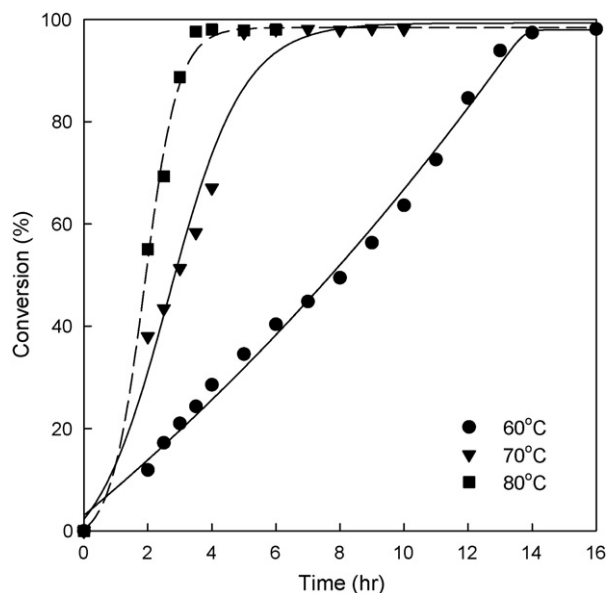


Fig. 1. Overall conversion of the TG40 copolymer particles prepared by emulsion polymerization at various temperatures.

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