Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

CrossMark

Preparation of polystyrene latex particles by miniemulsion polymerization using a predissolved fluorinated block copolymer as the sole co-stabilizer

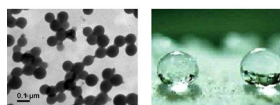Zhenqian Zhang[*], Xiang Ji, Pei Wang

Department of Materials Science and Engineering, Changzhou University, Changzhou 213164, People's Republic of China

HIGHLIGHTS

- The fluorinated block copolymer is prepared by ATRP.
- The copolymers are used as sole co-stabilizer in the miniemulsion polymerization.
- The fluorine content in copolymer has effect on the process of miniemulsion.
- The final latex films show the better surface hydrophobicity.
- The nucleation mechanism of miniemulsion polymerization is proposed.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The fluorinated block copolymer [P(St-b-DFM)] of styrene (St) and dodecafluoroheptyl methacrylate (DFM) was used as the sole co-stabilizer in St miniemulsion instead of the conventional co-stabilizers. The fluorinated block copolymer was prepared by atom transfer radical polymerization (ATRP). The fluorine content in P(St-b-DFM) was determined based on the relative number–average molecular weight of the macroinitiator and P(St-b-DFM). In St miniemulsion polymerization, the effects of the fluorine content in the block polymer on the size and number of the initial monomer droplets and latex particles were investigated. The ratio of the final number of latex particles to the initial number of monomer droplets was used to discuss the nucleation mechanism. The P(St-b-DFM) copolymers with 6% and 11% fluorine contents had a better effect on the stability of the monomer droplets, and monomer droplet nucleation almost dominated the process of St miniemulsion polymerization. The water contact angle on the surface of the polystyrene latex film demonstrated the surface hydrophobicity, and the surface tension was estimated according to Girifalco–Good–Fowkes–Young equation.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Miniemulsions are aqueous dispersions of relatively stable oil droplets having a droplet size in the range of 50–500 nm and consist of oil, water, a surfactant and a water-insoluble hydrophobe. The water-insoluble hydrophobe, called the co-stabilizer, is necessary to reduce the degradation of the monomer droplets from small droplets to large droplets (Ostwald ripening). Typical co-stabilizers normally have a low molecular weight, and examples include cetyl alcohol and hexadecane [1–3].

Recently, the use of polymers as co-stabilizers has been reported [1–6]. These water-insoluble hydrophobic polymers perform reasonably well and have the added advantage of being innocuous in the mixture [4,5]. The inclusion of a monomer–soluble polymer can slow the effects of Ostwald ripening. It has been found that polymer co-stabilizers can stabilize the droplets against diffusional

* Corresponding author. Tel.: +86 51986330096; fax: +86 51986330095.
 E-mail address: zhzhqian@hotmail.com (Z. Zhang).

degradation long enough to nucleate them into polymer particles [1–4]. Amalvy [6] applied the PVAc pre-polymer as a co-stabilizer in the miniemulsion polymerization of vinyl acetate and ultimately concluded that the particle size distribution of the coefficient d relations are as follows: $d_{(HD+PVAc)} > d_{HD} > d_{PVAc}$. Jia [5] used liquid polybutadiene as the sole co-stabilizer in styrene miniemulsion polymerizations. Fluorinated polymers, which are regarded as high-value-added materials, are potential candidates due to their outstanding properties. The small size and high electronegativity of the fluorinated atom confer strong C—F bond formation and a low polarizability. Such polymers show intermolecular interactions, which lead to low cohesive energy and therefore low surface energy. For the same reason, if the fluorinated block or graft copolymer is incorporated with other polymers, the surface of such a polymer blend will be enriched by the fluorinated segments to lower the surface energy, even if the concentration of the fluorinated block or graft copolymer in the blend system is low [7,8].

In the present study, the fluorinated block copolymer [P(St-b-DFM)] was prepared and used in place of the conventional co-stabilizer in St miniemulsion to improve the surface hydrophobicity of polystyrene (PS) latex film. P(St-b-DFM) was prepared by atom transfer radical polymerization (ATRP). Styrene (St) was the first monomer, and dodecafluoroheptyl methacrylate (DFM) was the second monomer. The influence of fluorine content in the P(St-b-DFM) on the size and number of the initial monomer droplets and latex particles was investigated. The form of the final latex particles was observed, and a mechanism of miniemulsion polymerization using a fluorinated block copolymer as the sole co-stabilizer was suggested. The effect of the fluorine content in the P(St-b-DFM) on the surface hydrophobicity of the PS latex film was discussed.

2. Experimental

2.1. Materials

St was supplied by Shanghai Lingfeng Chemical Reagent Co. Ltd., distilled under reduced pressure and stored in a refrigerator until use. Potassium persulfate (KPS), sodium dodecyl sulfate (SDS) (Shanghai Lingfeng Chemical Reagent Co. Ltd., China) were of analytical grade and used as received. Chemical-grade DFM was supplied by the Harbin Xeogia Fluorine-Silicon Chemical Co. Ltd., China. Analytical-grade methylene iodide, tertrahydrofuran (THF), pentamethyldiethylenetriamine (PMDETA), ethyl-2-bromoisobutyrate (EBiB), CuBr, cyclohexanone and methanol were supplied by No. 2 Shanghai Reagent Co. Ltd., China. Deionized water was used in the experiments.

2.2. Preparation of the fluorinated block copolymer as a co-stabilizer

A dry round-bottomed flask with a magnetic stir bar was charged with CuBr. The flask was sealed with a rubber septum, degassed and back-filled with nitrogen three times. Deoxygenated PMDETA, St and EBiB were introduced in turn using a syringe. The flask was then placed in an oil bath, heated at 110 °C for 5 h and then cooled to room temperature. The homopolymer (PS-Br) was precipitated in methanol/H$_2$O (1:1, volume ratio) after passing through an alumina column to remove the copper complexes and dried under vacuum at 60 °C for 24 h. The macroinitiator was successfully obtained. The reaction processes are shown in Fig. 1.

Block copolymerization was performed in the same manner as homopolymerization except that a macroinitiator was used. PS-Br and CuBr were added to a dry round-bottomed flask with a magnetic stir bar and then degassed and charged with nitrogen three times. Deoxygenated DFM and PMDETA were introduced. Finally,
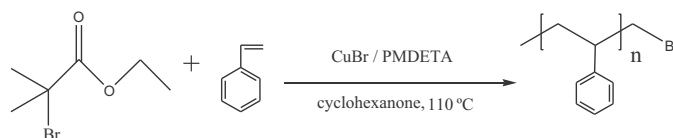

Fig. 1. Macroinitiator preparation (PS-Br).

the flask was placed in an oil bath and heated at 110 °C for 5 h. The block copolymer P(St-b-DFM) was isolated by precipitation with methanol after passing through an alumina column to remove the copper complexes. It was then dried under vacuum at 60 °C for 24 h. The reaction processes are shown in Fig. 2.

2.3. Miniemulsion polymerizations of styrene

SDS (0.144 g) was dissolved in deionized water (90 mL) for the aqueous phase, and P(St-b-DFM) (0.30 g) was dissolved in St (10 g) for the oil phase. For pre-emulsification, the oil and aqueous solutions were mixed with a magnetic stirrer for 10 min. The resultant emulsion was then homogenized with a homogeneous dispersion machine (Misonix Sonicator 3000) for 15 min. The homogenized mix was immediately transferred into a 250-mL four-necked flask equipped with a mechanical stirrer, thermometer, nitrogen inlet and reflux condenser. The reactor was purged with nitrogen for 30 min before being placed into the thermostat at the reaction temperature. The initiator (KPS) (0.025 g) was then charged into the reactor to start the polymerization. The St miniemulsion polymerization temperature was kept constant at 70 °C. The reaction was ended 180 min later after feeding KPS.

2.4. Characterization

Fourier transform infrared (FTIR) analysis was used to obtain information on the polymer composition. FTIR spectra were recorded on an Avatar 370 Spectrum instrument. The powder sample was mixed with KBr and pressed.

GPC analysis was carried out with a Waters 1515 instrument. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min, and calibration was performed with PS standards. Data acquisition was performed with Waters software. The ratio of the relative mass–average molecular weight and relative number–average molecular weight (M_w/M_n) was used to characterize the PDI.

The droplet sizes (Z-average size, D_z, and volume–average size, D_v) and distribution (intensity PSD) were measured by dynamic light scattering (DLS) with a Malvern Zetasizer Nano ZS instrument. Samples for the monomer droplet size measurements were prepared by diluting three drops of the homogenized mixture with approximately 25 g of St-saturated 0.16 wt% SDS solution. Approximately 2 mL of the diluted solution was placed in a quartz cuvette, and the droplet size was measured. The latex Z-average particle size and distribution (intensity PSD) were measured in a similar manner except that the dilution was performed with a 0.16 wt% SDS solution and a droplet of hydroquinone solution. The latex morphology was observed and imaged using transmission electron microscopy (TEM, JEM-1230 operated at 200 kV). The diluted sample solutions were applied to a 400-mesh carbon-coated copper grid and left to dry. From the TEM analyses, more than 1000 particles were counted for each sample. The average volume diameter $D_{v(TEM)}$ was calculated using the following equation:

$$D_{v(TEM)} = \left(\frac{\sum n_i D_i^3}{\sum n_i} \right)^{1/3} \tag{1}$$

where n_i is the number of polymer particles and D_i is the diameter of the polymer particles.