Chemical Engineering Journal 223 (2013) 8–17

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Fluorinated polyacrylate emulsifier-free emulsion mediated by poly(acrylic acid)-b-poly(hexafluorobutyl acrylate) trithiocarbonate via ab initio RAFT emulsion polymerization

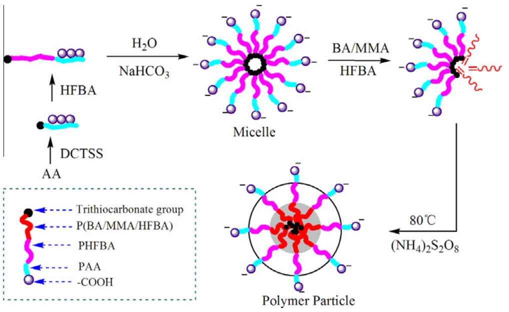
Jianhua Zhou [a,b,*], Lin Zhang [a], Jianzhong Ma [a,b]

[a] College of Resource and Environment, Shaanxi University of Science and Technology, Xi'an 710021, China
[b] Key Laboratory of Auxiliary Chemistry & Technology for Light Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an 710021, China

HIGHLIGHTS

- Fluorinated polyacrylate emulsion was synthesized via RAFT emulsion polymerization.
- The influence of PAA-b-PHFBA on emulsion polymerization was investigated.
- The film properties of the fluorinated polyacrylate were investigated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 November 2012
Received in revised form 24 February 2013
Accepted 27 February 2013
Available online 8 March 2013

Keywords:
Fluorinated polyacrylate emulsifier-free emulsion
Amphiphilic block copolymer
RAFT polymerization

ABSTRACT

Fluorinated polyacrylate emulsifier-free emulsion was synthesized via ab initio RAFT emulsion polymerization mediated by poly(acrylic acid)-b-poly(hexaflurobutyl acrylate) (PAA-b-PHFBA) trithiocarbonate macro-RAFT agent. The influence of the amount of PAA-b-PHFBA and hexafluorobutyl acrylate (HFBA) on emulsion polymerization and film properties was investigated. The monomer conversion increased, and latex particle size decreased as the amount of PAA-b-PHFBA increased from 2 wt% to 4 wt%, then the monomer conversion decreased slightly and particle size increased slightly. The latex particles presented spherical-like particles with diameters of 40–120 nm characterized by TEM. The results of contact angle and XPS revealed that the fluorine preferentially concentrated at the film surface during film formation process. The film–air interface of film was more hydrophobic than the film–glass interface. The water contact angle of the film increased initially as the amount of HFBA increased, then decreased slightly. The thermal stability increased with increasing the amount of HFBA. The film formed from the fluorinated polyacrylate latex with PAA-b-PHFBA as stabilizer showed higher thermal stability and hydrophobicity than that with reactive emulsifier.

1. Introduction

Fluorinated polymers have been a topic of substantial interest owing to their attractive properties such as low surface energy, high resistance to thermal, chemical and weather attack, and low dielectric constant [1–3]. Among numerous fluorinated polymers, fluorinated polyacrylate polymers with fluorine-containing groups have particularly useful characteristics. In particular, the pendant —CF$_3$ end groups can provide the material with extremely low surface energies, and the polyacrylate ensure the polymers to adhere well to various substrates [4]. Therefore, they have been widely used in surface coatings including paper, leather, textile, and walls of buildings [5]. Emulsion polymerization is one effective method

---

[*] Corresponding author at: College of Resource and Environment, Shaanxi University of Science and Technology, Xi'an 710021, China. Tel.: +86 029 86132559 609; fax: +86 029 86132559 603.

E-mail address: zhoujianh@21cn.com (J. Zhou).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.02.117

to obtain fluorinated polyacrylate. However, the residual emulsifier in materials will have negative effects on the properties of product and induce the environmental pollution [6].

In order to avoid the disadvantages of emulsion polymerization caused by emulsifier, the approaches to synthesize emulsifier-free emulsion have been explored. Attempts have been made to synthesize fluorinated polyacrylate emulsifier-free emulsion with ionic comonomers [7–9] and reactive emulsifiers [5,10,11]. However, the method of ionic comonomers cannot produce high solid content latexes. Reactive emulsifiers can connect covalently to the polymer, but it may get buried in the polymeric particles. When the reactivity of the polymerizable unit is too low, the unreacted emulsifiers in the final latex will migrate toward the film surface during the film formation process, resulting in the deleterious effects on the film properties [12]. The method to produce emulsifier-free emulsion with amphiphilic block copolymers has many advantages: easy to form micelle in water, better emulsion stability, narrow particle size distribution and no residual emulsifier migration during film formation process [13–16]. With the development of controlled/living radical polymerization (CLRP), the synthesis of amphiphilic block copolymers and their application in the emulsion polymerization has been widely studied [17–20].

Among the available controlled/living radical polymerization techniques, reversible addition-fragmentation chain transfer (RAFT) polymerization has advantages over other CLRP methods due to its compatibility with a wide range of monomers, functional groups and convenient experimental conditions [15,21,22]. However, RAFT polymerization in emulsion suffered severe colloidal instability. Most of the RAFT emulsion polymerization systems showed slow polymerization rate, poor control over molecular weight, broad molecular weight distribution, and phase separation into a RAFT-rich and a polymer rich phase [23–25]. A method developed by Ferguson et al. allowed these problems to be overcome and stable latexes to be obtained under RAFT control [26]. The process involved the formation of amphiphilic RAFT-caped block copolymers, which were then used as both stabilizer and control agent in emulsion polymerization. The final latex particles were formed from further polymerization of these amphiphilic diblocks. In this surfactant-free emulsion process the amphiphilic RAFT-capped diblocks were not merely stabilizers but grow further to become an inseparable part of the latex particles [16].

Synthesis of fluorine-containing amphiphilic block copolymers via RAFT polymerization has been reported. Mya et al. [27] synthesized poly(hexafluorobutyl methacrylate)-b-poly(propylene glycol acrylate) (PHFBMA-b-PPGA) via RAFT polymerization in the presence of cyano-2-propyldithiobenzoate RAFT agent. PHFBMA-b-PPGA can self-assemble to form micelles in aqueous solution. Tan et al. [28] reported the synthesis of a novel pH-responsive amphiphilic block copolymer poly(dimethylaminoethyl methacrylate)-block-poly (pentafluorostyrene) (PDMAEMA-b-PPFS) by RAFT polymerization. The critical micelle concentration (CMC) of PDMAEMA-b-PPFS depended on PPFS block lengths. The CMC of PDMAEMA$_{78}$-b-PPFS$_{82}$ was about 0.005 mg mL^{-1}. Xu and Liu [29,30] synthesized poly(methacrylic acid)-b-poly(dodecafluoroheptyl methacrylate) via RAFT polymerization in 2-butanone. Various morphologies of spheres, rods, and vesicles could be formed by changing the precipitant mixture contents. In addition, steady micelles in water with the diameter of 70–120 nm have been formed via RAFT emulsifier-free emulsion polymerization without any additional emulsifier. The fluorine-containing diblock copolymers were successfully synthesized by RAFT miniemulsion polymerization [31,32]. Until now, various fluorine-containing amphiphilic block copolymers have been synthesized via RAFT polymerization, and micellization behavior in aqueous solution was extensively studied. However, to the best of our knowledge, there is no report on the use of fluorine-containing amphiphilic block copolymer as a stabilizer in the synthesis of fluorinated polyacrylate emulsifier-free emulsion.

In this work, fluorinated polyacrylate emulsifier-free emulsion were synthesized by ab initio RAFT emulsion polymerization using poly(acrylic acid)-b-poly(hexaflurobutyl acrylate) (PAA-b-PHFBA) both as a stabilizer and a RAFT agent. Influences of the amount of PAA-b-PHFBA and fluorinated acrylate monomer on emulsion polymerization and film properties were studied. The resulting fluorinated polyacrylate was characterized by transmission electron microscopy (TEM), dynamic laser scattering (DLS), nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR), thermogravimetry (TG) analysis, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and contact angle (CA) analysis.

2. Experimental

2.1. Materials

Acrylic acid (AA) was distilled under reduced pressure prior to use. Hexafluorobutyl acrylate (HFBA), supplied by XEOGIA Fluorine–Silicon Chemical Company, was passed through alkaline alumina chromatographic column before use. Butyl acrylate (BA) and methyl methacrylate (MMA) were washed there times with 5 wt% sodium hydroxide (NaOH) aqueous solution to remove the phenolic inhibitor, followed by washing thoroughly with deionized water until the aqueous phase was neutral. After drying over anhydrous magnesium sulfate and filtering off the drying agent, the monomer was distilled under vacuum. The reactive emulsifier, ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy)(10) ether (DNS-86) (Fig. 1), was from Shuangjian Trade Company. 4,4′-Azobis (4-cyanopentanoic acid) (V-501) was supplied by Fluka Company. Ammonium persulfate (APS), 1,4-dioxane, sodium bicarbonate ($NaHCO_3$) were used as received. 2-{[(Dodecylsulfanyl)-carbonothioyl]sulfanyl} succinic acid (DCTSS) was synthesized and purified as described in Ref. [33].

2.2. Synthesis of the poly(acrylic acid)-b-poly(hexafluorobutyl acrylate) trithiocarbonate macro-RAFT agent

The poly(acrylic acid)-b-poly(hexafluorobutyl acrylate) (PAA-b-PHFBA) macro-RAFT agent was synthesized by a two-step solution polymerization. First, 0.18 g (4.50×10^{-4} mol) of DCTSS, 0.019 g (6.74×10^{-5} mol) of V-501, 0.97 g (1.35×10^{-2} mol) of acrylic acid, and 19.46 g of dioxane were mixed in a three-necked flask with reflux condenser. The mixture was deoxygenated with argon gas for 30 min, and then immersed in a heated water bath at 80 °C for 7 h. After the flask was cooled down to room temperature, 0.013 g (4.50×10^{-5} mol) of V-501, 1.60 g (6.76×10^{-3} mol) of hexafluorobutyl acrylate and 15.94 g of dioxane were added. The mixture was deoxygenated with argon gas for 30 min and reacted for further 7 h at 80 °C. Yellow powder was obtained after the precipitation of the mixture in hexane and dried at 50 °C under vacuum for 48 h.

2.3. Synthesis of fluorinated polyacrylate emulsifier-free emulsion

The recipes for fluorinated polyacrylate emulsifier-free emulsion were described in Table 1. For a typical reaction procedure

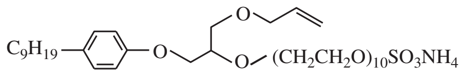


Fig. 1. Structure of DNS-86.