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Hydrophobic films of acrylic emulsion by incorporation of fluorine-based copolymer prepared through the RAFT emulsion copolymerization

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ABSTRACT

In this work, the hydrophobicity of traditional acrylic emulsion films was remarkably improved by introducing some fluorinated diblock copolymer emulsions. Reversible addition-fragmentation chain transfer (RAFT) was utilized to synthesize poly(methacrylic acid)-*b*-poly(2,2,2-trifluoroethyl methacrylate-*co*-2,2,3,4,4,4-hexafluorobutyl acrylate) (PMAA-*b*-P(TFEMA-*co*-HFBA)) amphiphilic block copolymer emulsion by using the PMAA homopolymer with dithiobenzoate end-groups as macro-RAFT agent. The hydrophobic block of P(TFEMA-*co*-HFBA) was designed with the various P(TFEMA-*co*-HFBA) block lengths and p_0 ($[TFEMA]_0/[HFBA]_0$). And the final conversion of mixed fluorinated monomers (TFEMA, HFBA) could reach about 70% when the value of p_0 was greater than 1/2. With the formation of solvophobic P(TFEMA-*co*-HFBA) block by propagating the fluorinated monomers on the PMAA chain, the PMAA-*b*-P(TFEMA-*co*-HFBA) block copolymer *in situ* self-assembled into core/shell particle with P (TFEMA-*co*-HFBA) and PMAA blocks as core and shell matrix, respectively. The number-average-particle-diameter of core/shell particles located in the range from 56 to 93 nm was discovered by the way of self-assembly nucleation. The particle size distribution (PSD) of all samples is close to the traditional acrylic emulsion system. The fluorinated block with low surface energy has good hydrophobicity, hence, the traditional acrylic emulsion film modified by the fluorinated diblock copolymer emulsions exhibited excellent hydrophobicity. The effects of various parameters such as the treatment temperature, the processing time, the fluorinated diblock copolymer emulsions ratios and the composition of fluorinated diblock copolymer emulsions on the hydrophobicity of fluorinated composite film were also investigated in this work. The water contact angles of the final fluorinated composite films with water are more than 100° and the fluorinated composite films have good hydrophobicity with low amounts fluoropolymer emulsions (5–20%).

1. Introduction

Fluorine-containing polymers have attracted widespread attention due to its desirable features, such as low surface energy, refractive index, dielectric constant, i.e. Refs. [1–4]. Fluorinated (meth) acrylate polymer as one kind of these special fluoropolymers with fluorinated side chains has particularly useful characteristics, fluorine-containing functional groups can provide the polymer film with extremely low surface energies and the polyacrylate main chain ensure the polymers excellent adhesion to various substrates [5]. Consequently, fluorinated (meth) acrylate polymer has been applied as textile finishing agents, adhesives, paints, surface modifiers, anti-fouling coatings and construction protection coatings [6]. However, most of fluoropolymers were gained through the solution polymerization [7], and it is difficult to synthesize fluoropolymer emulsions with high content of fluorinated monomer via classical emulsion polymerization technique because of the poor transport of these monomers to the micelles through water phase [8,9]. Although micro- [10] and mini- [11,12]

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emulsion polymerization techniques have been successfully introduced to promote the efficient incorporation of fluorinated component into polymer emulsions, it has to be noted that the fluorinated monomer content in these fluoropolymer emulsions is still quite limited due to the extremely low solubility of fluorinated monomer in water.

Recently, with the development of controlled radical polymerization (CRP) (nitroxide-mediated radical polymerization (NMP) [13,14], atom transfer radical polymerization (ATRP) [15] and reversible addition-fragmentation chain transfer polymerization (RAFT) [16,17]), various amphiphilic block copolymers with well-defined molecular architecture were synthesized, and amphiphilic block copolymers have shown a perfect application in many fields due to its unique amphiphilic structure. Koiry et al. [18] have reported the synthesis of polystyrene miniemulsion by using PPEGMA-*b*-PHFBA fluorinated amphiphilic block copolymers as surfactant agent conventional RAFT agent. Reversible addition-fragmentation chain transfer (RAFT) as one of the controlled radical polymerization provides an effective and versatile method to improve the solubility of fluorinated monomer in water [19]. Chakrabarty et al. [20] have reported the synthesis of PHFBA-*b*-PBA block copolymer via RAFT miniemulsion polymerization in water with sodium dodecyl sulfonate as emulsifier. But to the best of our knowledge, there are still seldom reports on the preparation of fluorinated acrylate amphiphilic block copolymer in emulsifier-free emulsion system. Recently, the well defined PMAA-*b*-PTFEMA amphiphilic diblock copolymer with high fluorinated monomer content was synthesized by RAFT emulsion polymerization in our previous work, and the PMAA-*b*-PTFEMA diblock copolymer with high fluorinated (meth) acrylate monomer ratio (M-F200) can reach the similar quantitative conversions up to 75% [21].

Generally, traditional acrylic emulsions are used in many applications such as emulsion paints, paper coatings, inks and adhesives [22,23]. As for the shortcomings of traditional acrylic emulsions, such as poor water resistance and stain resistance, which could be solved by introducing fluorine-containing functional group. An appropriate and efficient method for improving typical acrylic emulsion films surface hydrophobicity was the modification of the traditional acrylic emulsion by introducing high-fluorinated diblock copolymer emulsion. However, the relatively complicated preparation process and high market price of the RAFT agent limit the further industrial application of fluorinated diblock copolymer emulsion which was prepared by RAFT method. Therefore, much more attention should be paid to the hydrophobicity of traditional acrylic emulsion films which improved only with a small amount of fluorinated diblock copolymers, which method would highly save the dosage of RAFT agent and demand highly for the fluoropolymer emulsion performance. What is more, those composite emulsions combine some of the virtues of traditional acrylic resins and fluorinated acrylate copolymer, such as good chemical resistance, low water-absorptivity, attractive surface properties, and excellent adhesion properties.

The fluorine element proportion in the TFEMA monomer is only 34% and the fluorinated monomers with high content of fluorine element have better hydrophobicity [19]. In this work, higher-fluorine-containing monomer HFBA was introduced into the second block of the PMAA-*b*-PTFEMA diblock copolymer to improve the hydrophobicity of the fluorinated diblock copolymer film. Very few reports have focused on the preparation of block copolymer emulsion based on PHFBA in emulsifier-free system. When the polymerization of TFEMA was performed in pure water, the slight derivation was observed only as the monomer conversion higher than 70% [21]. Thus, considering the environmental protection, pure water was chosen as dispersion medium. The direct preparation of PHFBA segments in pure water is difficult because the fluorine element proportion of HFBA monomer is 48% and exhibits strong hydrophobicity. Thus, 2,2,2-trifluoroethyl methacrylate (TFEMA) not only acted as a comonomer, but also was used as the cosolvent to improve the solubility of 2,2,3,4,4,4-hexafluorobutyl acrylate (HFBA) monomer. In this contribution, more attention was paid to the performance improvement of the traditional acrylic emulsion films which were modified by fluorinated block copolymer emulsion, although most of the reports on RAFT agent mediated polymerization are concerning on the novel morphologies from the self-assembly of block copolymer. The preparation process of the fluorinated (meth) acrylate copolymers via the RAFT polymerization and the hydrophobicity variation of the fluorinated composite film modified by fluoropolymer emulsions were systematically investigated.

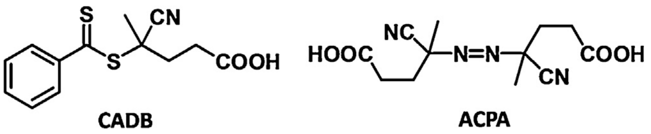
2. Experimental

2.1. Materials

Methacrylic acid (MAA, >99%), acrylic acid (AA), methyl methacrylate (MMA), butyl acrylate (BA), sodium persulfate (NaPS), sodium bicarbonate ($NaHCO_3$), and diacetone-acryloamide (DAAM) were purchased from Beijing Chemical Works and used as received. Sodium dodecyl sulfate (SDS, HLB = 13) and nonylphenol ethoxylate (NP-10) were obtained from Jiangsu Haian Petrochemical Plant and used as anion and a nonionic surfactant, respectively. 4,4′-azobis(4-cyanopentanoic acid) (ACPA, >98%, Admas-Beta, Scheme 1) and trimethylsilyldiazomethane (10% in hexane, ca. 0.6 mol/L, J&K Chemical) were directly used as received. The fluorinated acrylate monomers (2,2,2-trifluoroethyl methacrylate (TFEMA) and 2,2,3,4,4,4-hexafluorobutyl acrylate (HFBA)) were purchased from Haerbin Xuejia Fluorine Silicon Chemistry Company and purified by vacuum distillation prior to use. The RAFT agent of 4-cyanopentanoic acid dithiobenzoate (CADB, Scheme 1) was synthesized according to the literature [24]. The ^{1}H NMR spectra of the monomer conversion curve and the final GPC chromatograms of PMAA homopolymer have been displayed in our previous work [21]. indicating that the reaction conditions are suitable for the RAFT polymerization of MAA monomer with the reproducible performance. The actual polymerization degree (DP) of PMAA-CTA macro-RAFT agent used in this article was 98. Water used in this experiment was distilled followed by deionization, which was prepared in our laboratory.

2.2. Synthesis of PMAA-b-P(TFEMA-co-HFBA) diblock copolymer emulsions

The synthesis of PMAA-*b*-P(TFEMA-*co*-HFBA) amphiphilic block copolymer emulsions can be divided into two steps. The detailed experimental conditions and the characterization results of the synthesized PMAA-*b*-P(TFEMA-*co*-HFBA) block copolymers in the work are listed in Table 1. For the sake of convenience, the PMAA-*b*-P(TFEMA-*co*-HFBA) amphiphilic diblock copolymers with the various P(TFEMA-*co*-HFBA) block lengths and p_0 are designated hereafter as “M-TX-HY”, where M stands for PMAA block, T stands for PTFEMA block, X stands for the target DP of PTFEMA block, H stands for PHFBA block and Y stands for the target DP of PHFBA block, for example, M-T100-H50 means the PMAA-*b*-P(TFEMA-*co*-



Scheme 1. The chemical structures of CADB and ACPA.