Fluorinated poly(isobornyl methacrylate–co–butyl acrylate) core–shell latex nanoparticles: Synthesis, morphology and wettability of films

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ABSTRACT

A fluorinated acrylate monomer simultaneously containing one hydrophilic hydroxyl and one hydrophobic perfluoroalkyl group was synthesized, which was then utilized to copolymerize with isobornyl methacrylate and butyl acrylate to prepare core–shell-structured latex nanoparticles through two-step emulsion polymerization. In this synthesis process, no any organic solvents or fluorine-containing surfactants were added. The perfluoroalkyl moieties are in the shell layer and the fluorine contents in the whole system range from 0 to 12.83 wt%. A clear core–shell interface is observed by transmission electron microscopy. The dynamic light scatterings show that the average particle sizes are around 95 nm. After film-formation, the angle-resolved XPS demonstrates that the ratios of F/C and CF_3/CF_2 have a significant gradient growth from the inner bulk up to the film surface, indicating that the fluorinated groups have segregated to the topmost layer with the CF_3 termini oriented upward, which is consistent with the AFM images that some pointed bumps appear on the surface and the number increases with the fluorine content. As a consequence, the enriched perfluoroalkyl moieties, especially the CF_3 groups, result in that the film with small amount of fluorine in the polymer exhibits a very low surface tension and high water contact angle.

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1. Introduction

For fluorinated polymer coating materials, from the viewpoint of both cost-saving and self-cleanability, it is desirable that the expensive fluorine element can efficiently enrich on the surface to achieve excellent water/oil repellency property with only small amount of fluorinated groups in the polymer. Segregation of fluorine is principally driven by the difference in the surface tension between fluorinated group and non-fluorinated moieties in polymer backbone. However, the mutual entanglement of polymer chains and low segmental motion ability often seriously hinder the migration of fluorinated groups from the bulk to the surface so that the expected hydrophobic property can not be obtained. To enhance the fluorine segregation ability, in the past decade, numerous fluorinated polymers with various architectures were synthesized such as the polymers with perfluorinated group in the main chain or on the side chain as well as block, graft and comb-like copolymers [1–9]. In addition, it was observed that the thermal annealing can significantly improve the hydrophobic property of a fluorinated polymer coating, but this process is not suitable for

practical application considering the time consuming and the increase of energy cost [10,11]. For example, the annealing of the fluorinated layers on mica was conducted in an oven at 150 °C in nitrogen atmosphere for 24 h [10].

In recent years, latex nanoparticles constructed with a nonfluorinated polymer core surrounded by a thin layer of fluorinated polymer shell are receiving great attention [12–19]. The nanometer scale can endow the latex particles with excellent colloidal stability and good dispersion in aqueous medium. Compared to copolymers or blends of non-fluorinated and fluorinated polymers, the fluorinated moieties in the shell are advantageous for their enrichment on the surface during film-formation while the non-fluorinated chains in the core coalesce and remain in the bulk. Moreover, the core–shell latex particles are usually prepared in water, which can reduce the environmental concern to the largest extent, e.g., volatile organic compounds (VOC), in the synthesis process and the subsequent coating operation.

In spite of the above numerous merits, relative to nonfluorinated core–shell particles, the synthesis of nanoparticles with fluorinated polymer in the shell via conventional emulsion polymerization often meets some tough technique obstacles. The immiscibility between the fluorinated monomer and water medium due to their great difference in surface tension makes it difficult for the fluorinated monomer droplets to pass through the

continuous aqueous phase to polymerize on the pre-polymerized cores, leading to the low conversion rate of fluorinated monomer and the decrease of storage stability of latex. To overcome this issue, several attempts had been made in the previous studies. For example, Ha et al. added organic solvents in the system to reduce the surface tension of the aqueous medium [20]. Dreher employed fluorine-containing phosphoric acid bis(tridecafluorooctyl) ester ammonium as a surfactant to improve the affinity with fluorinated monomer, and thereby increase their transport ability in the polymerization system [21]. However, the addition of organic solvent or toxic and expensive fluorinated surfactant will inevitably give rise to cost increase and environmental issues.

With the above considerations in mind, the present work was undertaken to synthesize a fluorinated monomer, i.e., methyl-acryloyloxy-2-hydroxypropyl perfluorooctanoate (**FGOA**), which was then incorporated in the shell layer of nanoparticle composed of copolymers of butyl acrylate (BA) and isobornyl methacrylate (IBOMA) via a two-step emulsion polymerization technique. **FGOA** simultaneously contains one long-chain perfluoroalkyl and one hydroxyl group. The presence of hydrophilic hydroxyl can improve its solubility in water, and hence facilitate the transport of **FGOA** monomer in water medium and is advantageous for its polymerization on the surface of poly(IBOMA–BA) core. As a result, the addition of organic solvent or other fluorinated surfactants becomes unnecessary. IBOMA was selected because it has the density of 0.98 g/cm^3, very close to water. This characteristic is helpful for its uniform dispersion in the aqueous phase. The chemical structures, core–shell structure, morphology and size distribution of latex particles were examined by FTIR, ^{13}C NMR, DSC, TEM and dynamic light scattering methods. After film-formation, surface morphology, chemical composition and wettability for the film samples with different fluorine contents were investigated through AFM, angle-resolved XPS and contact angle measurements.

2. Experimental

2.1. Materials

Perflurooctanoic acid (PFOA) was purchased from J&K Chemical Co., Ltd. and used without further purification. Glycidyl methacrylate (GMA), n-butyl acrylate (BA) and isobornyl methacrylate (IBOMA) were from Guangzhou Yuanmao Chemical Corp. Tetrabutyl ammonium bromide (TBNB), ammonium persulfate (APS), Sodium Bisulfite (SHS), alkylphenol polyoxyethylene ether (OP-10) and dioxane were obtained from Shanghai Reagent Corp. and used as received.

2.2. Synthesis of methylacryloyloxy-2-hydroxypropyl perfluorooctanoate (*FGOA*)

A 250-mL three-necked round-bottom flask was equipped with a thermometer, a mechanical stirrer and a refluxing condenser. To this flask was charged 24 g (0.058 mol) of PFOA, 16 g (0.11 mol) of GMA, 0.12 g (0.37 mmol) of TBNB, and 30 mL dioxane. After reacting at 100 °C under stirring for 8 h, the mixture was washed successively with Na$_2$CO$_3$ aqueous solution and deionized water. The organic phase was dried over MgSO4. After filtration, the filtrate was distilled under reduced pressure to remove the excess GMA and solvent. The residue was further purified by distillation under reduced pressure to give colorless liquid having a boiling point of 68−70 °C at 9 mmHg (25.6 g, 81%). FTIR (cm^{-1}): 3472, 1786, 1723, 1623, 1244, 1208, 1150, 1013; ^{13}C NMR (CDCl$_3$, ppm): 167.5, 158.4, 135.9, 126.5, 105.7−119.0, 68.6, 67.4, 64.9, 18.4; HRMS (*m/z*): Calcd. for C$_{15}$H$_{11}$O$_5$F$_{15}$ 556.2399; Found 556.0363 [C$_{15}$H$_{11}$O$_5$F$_{15}$]$^+$.

2.3. Synthesis of core−shell latex particles

The core−shell latex particles were prepared in a similar procedure, so only the sample with fluorine content of 5.13 wt% is described here as an example. For the synthesis of core pre-emulsion, 0.71 g mixed emulsifier (OP-10: SDS = 2: 1) was dissolved in 27 mL water. Then, 14 g (63 mmol) of IBOMA and 6 g (47 mmol) of BA were added slowly, and the system was vigorously stirred for 30 min to obtain the core pre-emulsion. Into a 250-mL four-necked round-bottom flask equipped with a thermometer, a mechanical stirrer, a nitrogen inlet and a dropper was charged 0.23 g of OP-10, 0.11 g of SDS and 13 mL water. After stirring for 20 min, Under the nitrogen atmosphere, the system was heated to 60 °C, and the resultant cored pre-emulsion and the mixed radical initiator (0.052 g APS and 0.041 g SHS) dissolved in 10 mL water were added. The polymerization continued for 2 h to obtain the core-polymer emulsion.

The shell pre-emulsion was prepared by adding of 5.4 g (24 mmol) of IBOMA, 12.6 g (102 mmol) of BA and 4.2 g (7.55 mmol) of **FGOA** into the emulsifier aqueous solution (0.36 g OP-10 and 0.18 g SDS dissolved in 20 mL water) and subsequent vigorously stirring for 30 min. The resultant shell pre-emulsion and the initiator (0.069 g APS and 0.056 g SHS dissolved in 13 mL water) were added into the first-stage core-polymer emulsion at 60 °C. It was allowed to react at this temperature for about 2 h. After cooling, the PH value of system was adjusted to 8−9 using aqueous ammonia.

2.4. Film preparation

Latex film was obtained by directly casting the freshly prepared latex solution onto a slide glass, which was pre-cleaned by ultrasonic treatment in acetone at 50 °C for 1 h and rinsing with deionized water three times prior to use. The film was allowed to dry at room temperature and then was transferred to an oven and further dried for an additional 24 h.

2.5. Measurements

FTIR spectra were recorded on a Nicolet 20DXB FTIR spectrometer in the 400−4000 cm^{-1} region. All the samples were mixed with the KBr powder and then pressed into the flakes.

Nuclear magnetic resonance carbon spectra (^{13}C NMR) were recorded in deuterated chloroform (DCCl$_3$) on a Varian INOVA400 spectrometer with tetramethylsilane (TMS) as an internal reference.

DSC measurements were carried out on a NETZSCH DSC204 with indium metal as a standard. All samples (about 10 mg in weight) were heated from 40 to 250 °C at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. The glass transition temperatures (T_g) were read at the middle of the change in the heat capacity.

Dynamic light scatterings of latexes were performed on a Malvern Zetasizer Nano-ZS90 instrument at room temperature. The average sizes of the particles were calculated via the Stoke-Einstein equation.

Transmission electron micrographs (TEM) were conducted using a JEM-2000EX instrument. The latexes obtained were diluted in deionized water to a ratio of 1: 10000, and then coated on copper grids for TEM measurements.

Angle-resolved XPS measurements were performed in both survey and high resolution mode on a Thermo ESCALAB 250, with a Monochromatic Al Kα (hν = 1486.6 eV) X-ray light source of 150 W at 15 kV. Spectra were acquired at three different takeoff angles: 0°, 30° and 60°, which are defined as the angle between the sample surface normal and the optical axis of the photoelectron