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Synthesis and characterization of amphiphilic graft copolymers with hydrophilic poly(acrylic acid) backbone and hydrophobic poly(methyl methacrylate) side chains

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Abstract

A series of well-defined amphiphilic graft copolymers containing hydrophilic poly(acrylic acid) backbones and hydrophobic poly(methyl methacrylate) side chains were synthesized by successive atom transfer radical polymerization followed by the selective hydrolysis of poly(methoxymethyl acrylate) backbone. Grafting-from strategy was employed for the synthesis of graft copolymers with narrow molecular weight distributions. Hydrophobic side chains were connected with the backbone through stable C–C bonds instead of ester connections. The backbone can be easily hydrolyzed to poly(acrylic acid) with HCl without affecting the hydrophobic side chains. The amphiphilic graft copolymers can form stable micelles in water. The critical micelle concentration was determined by fluorescence spectroscopy. The micellar morphologies were found to be vesicles by transmission electron microscopy and changed to spheres with the addition of NaCl.

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Keywords: Graft copolymer; ATRP; Grafting-from

1. Introduction

The self-assembly behavior of amphiphilic copolymers in water has been extensively studied for decades [1–4]. Previous studies showed that experimental parameters, such as molecular weight, composition and architecture of the copolymer, solvent quality, concentration, and temperature, could affect the aggregation number, the size and the shape of the micelles [5–7]. So far, most of the investigations have been concerned with the micellization of linear block copolymers [2–4]. Graft copolymers may form a variety of micellar shapes due to their complicated and confined structure [8,9]. Due to the theoretical and experimental potential aspects, additional studies on amphiphilic graft copolymers are needed in order to elucidate the influence of the architecture and composition on the micellization.

The synthesis of well-defined graft copolymers is much more difficult compared with the synthesis of linear block copolymers, which restrained the studies of the self-assembly behavior of the more complex structured materials. Generally, three strategies, including grafting-through, grafting-onto and grafting-from, were used to synthesize the graft copolymers [10–14]. For the grafting-from strategy, the pendant initiation groups on the backbone can initiate the polymerization of the corresponding monomer to form side chains. Recently, well-defined graft copolymers with hydrophobic backbone and hydrophilic side chains were synthesized by the combination of atom transfer radical polymerization (ATRP) [15,16] and grafting-from techniques, and their self-assembly behaviors were preliminarily explored [10,17]. Unfortunately, there are only few reports about the synthesis of well-defined graft copolymers with hydrophilic backbone and hydrophobic side chains, as well as self-assembly behaviors in aqueous media [8,18–20].

This article describes the synthesis and characterization of amphiphilic graft copolymers with hydrophilic poly(acrylic

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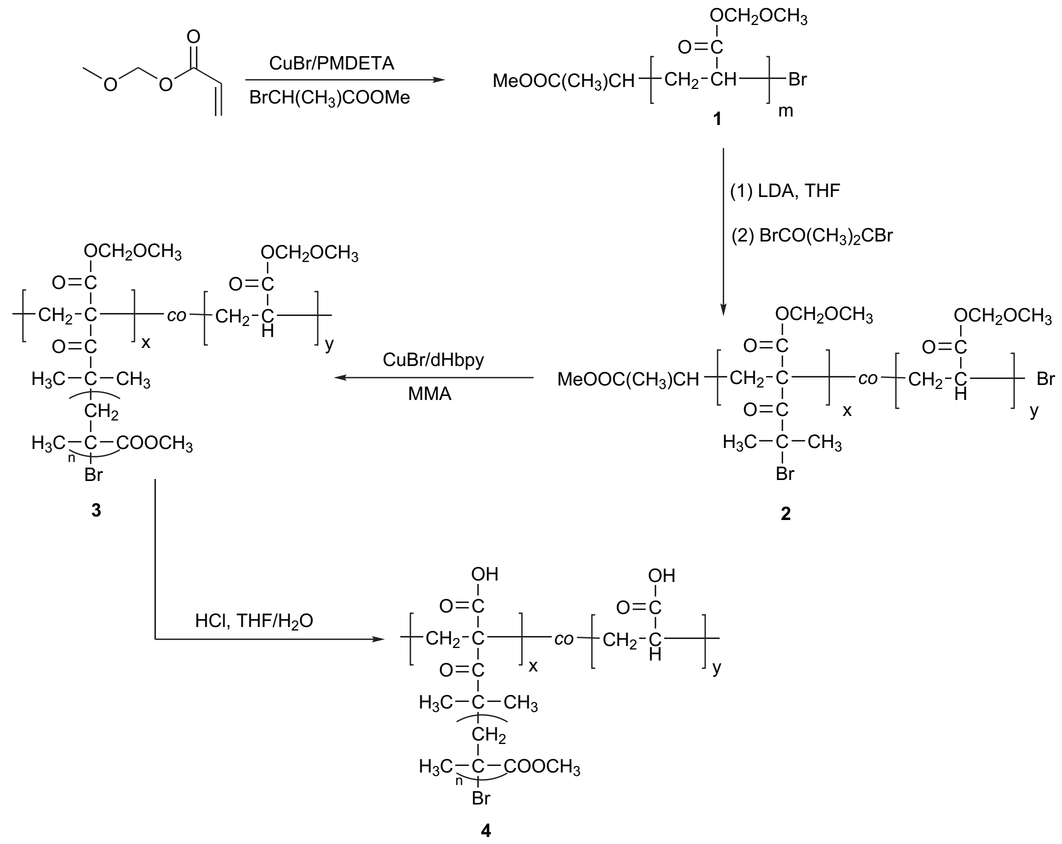

Scheme 1. Synthesis of PAA-*g*-PMMA amphiphilic graft copolymer.

acid) (PAA) backbone and hydrophobic poly(methyl methacrylate) (PMMA) side chains by ATRP and grafting-from techniques exhibiting narrow polydispersities (Scheme 1). This kind of amphiphilic graft copolymer can form vesicle micelles in aqueous media. The critical micelle concentration (cmc) of these graft copolymers in water was measured by fluorescence spectroscopy as well as the shapes and sizes of the micelles under different conditions were studied by transmission electron microscopy (TEM).

2. Experimental

2. 1. Materials

Methyl methacrylate (MMA, Aldrich, 99%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over $CaCl_2$ and distilled twice over CaH_2 under reduced pressure just before use. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH_3CO_2H at room temperature, followed by washing the solid with ethanol, diethyl ether and acetone prior to drying at 40 °C under vacuum for 1 day. Diisopropylamine (Aldrich, 99.5%) was dried over KOH for several days followed by distilling from CaH_2 under N_2 atmosphere. Tetrahydrofuran (THF) was dried over CaH_2 for several days and distilled from sodium and benzophenone under N_2 atmosphere prior to use. *N*,*N*,*N*′,*N*′,*N*″-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), methyl 2-bromopropionate (2-MBP, Acros, 99%), *n*-butyllithium (*n*-BuLi, Aldrich, 1.6 M in hexane) and α-bromoisobutyryl bromide (TCI, 98%) were used as received. Methoxymethyl acrylate (MOMA) and 4,4′-diheptyl-2,2′-bipyridine (dHbpy) were synthesized according to the previous literatures [19,21].

2.2. Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with 4 cm^{-1} resolution. All ^1H NMR and ^{13}C NMR measurements were performed on a Varian Mercury 300 spectrometer (300 MHz) in $CDCl_3$. TMS (^1H NMR) and $CDCl_3$ (^{13}C NMR) were used as internal standards. Bromine content was determined by the titration with $Hg(NO_3)_2$. Conversion of MMA was determined by gas chromatography (GC) using a HP 6890 system with an SE-54 column. Relative molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual absorbance detector (UV, $\lambda = 260$ nm) and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8 × 300 mm). GPC measurements were carried out at 35 °C using THF as eluent with a 1.0 mL/min flow rate. The system was calibrated with linear polystyrene standards. Steady-state fluorescent spectra were recorded on a Perkin Elmer LS55 spectrofluorometer with the bandwidth of 15 nm for excitation and 3 nm for emission, where λ_{ex}

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