Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 47 (2006) 6072–6080
polymer
www.elsevier.com/locate/polymer

Synthesis of amphiphilic graft copolymer with hydrophilic poly(acrylic acid) backbone and hydrophobic polystyrene side chains

Dan Peng, Xiaohuan Zhang, Xiaoyu Huang*

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, PR China

Received 9 April 2006; received in revised form 12 June 2006; accepted 18 June 2006
Available online 10 July 2006

Abstract

A series of well-defined amphiphilic graft copolymers consisting hydrophilic poly(acrylic acid) backbones and hydrophobic polystyrene side chains were synthesized by successive atom transfer radical polymerization (ATRP) followed by hydrolysis of poly(methoxymethyl acrylate) (PMOMA) backbone. Grafting-from strategy was employed for the synthesis of graft copolymers with narrow molecular weight distribution. Hydrophobic side chains were connected to the backbone through stable C–C bonds. The backbone can be easily hydrolyzed with HCl without affecting hydrophobic side chains. This family of amphiphilic graft copolymers can form stable micelles in water. The critical micelle concentration was determined by fluorescence spectroscopy. The micellar morphologies and sizes were studied using transmission electron microscopy (TEM) and dynamic light scattering (DLS). The sizes of micelles were dependent on ionic strength, pH value and preparation conditions.

Keywords: Amphiphilic graft copolymer; Poly(acrylic acid); Macroinitiator

---

1. Introduction

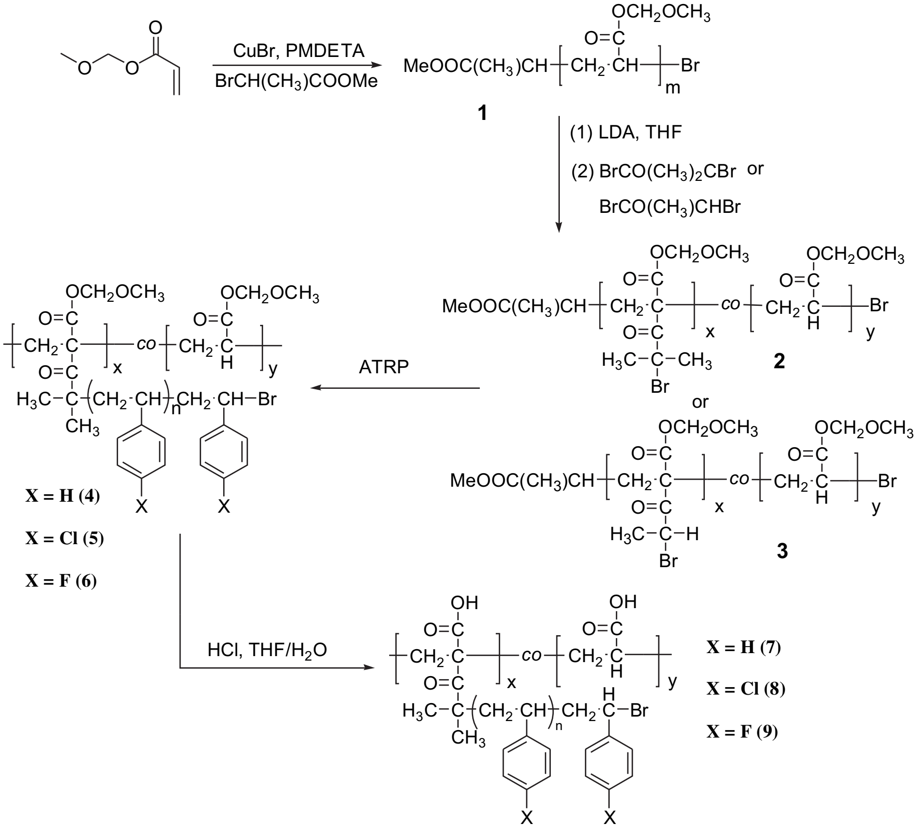
Intensive interests on self-assembly of amphiphilic copolymers in water have been risen during the past decades [1–6] due to its potential applications in drug delivery systems [7–9], cosmetics products, coatings and the synthesis of nano-materials [10,11], etc. Studies of self-assembly behaviors of *block* copolymers in water have showed that the critical micelle concentration (*cmc*), micelle radius (R_h), and micelle aggregation number (N_{agg}) as well as micelle shape are influenced by the pH value of the solution, ionic strength, preparation conditions, copolymer concentration, molecular weight of copolymer and compositions of copolymer [12–14], whereas few researches focused on the behaviors of amphiphilic graft copolymers in water [15]. Recently, it was revealed that the architecture of copolymer also played an important role in determining the properties of micelle [16–18]. Graft copolymer possesses additional complexity in solution assembly resulting from its complicated and confined structure. So we can get more information about the controlling of micellar morphologies and design of new nano-materials through the study of the self-assembly of graft copolymers.

The studies of the self-assembly of graft copolymers were restrained due to the difficulty in the synthesis of well-defined graft copolymers with controlled molecular weights and low polydispersities. Generally, three strategies, including grafting-through, grafting-onto and grafting-from, can be used to synthesize graft copolymers [19]. With the development of atom transfer radical polymerization (ATRP) [20,21], the grafting-from technique has been widely used. By this method, side chains can be formed via ATRP which was initiated by the pendant initiation groups on the backbone. Lately, some groups have synthesized well-defined graft copolymers with hydrophobic backbone and hydrophilic side chains by this

---

* Corresponding author. Tel.: +86 21 54925310; fax: +86 21 64166128.
E-mail address: xyhuang@mail.sioc.ac.cn (X. Huang).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.06.045



Scheme 1. Synthesis of amphiphilic graft copolymers.

way and their self-assembly behaviors have been explored [19,22]. However, there are only few reports about the synthesis of well-defined graft copolymers with hydrophilic backbone and hydrophobic side chains, as well as their self-assembly behaviors in aqueous solution [23,15].

In this paper, we report the synthesis of amphiphilic graft copolymers with hydrophilic poly(acrylic acid) backbone and hydrophobic polystyrene side chains (Scheme 1). The molecular weights of the backbone and the side chains were both controllable, and their polydispersities were kept low. Moreover, the self-assembly behaviors of these copolymers in water were preliminarily explored, the *cmc* was measured while the morphologies and sizes of the obtained micelles under different conditions were also studied with TEM and DLS.

2. Experimental

2.1. Materials

Styrene (St, Aldrich, 99%) was washed with 5% aqueous NaOH solution to remove inhibitor, and then with water, dried over $MgSO_4$ and distilled twice over CaH_2 under reduced pressure. *p*-Chloro-styrene (*p*-Cl-St, Aldrich, 99%) and *p*-fluoro-styrene (*p*-F-St, Aldrich, 99%) were distilled twice over CaH_2 under reduced pressure. 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. *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. Chloromethyl methyl ether was synthesized according to the previous literature [24].

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 analyses were performed on a Varian Mercury 300 spectrometer (300 MHz) in $CDCl_3$ and with TMS (^1H NMR) and $CDCl_3$ (^{13}C NMR) as internal standard. Bromine content was determined by titration with $Hg(NO_3)_2$. Relative molecular weights and molecular weight distributions were measured 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 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 polystyrene standards.