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ORIGINAL PAPER

Preparation and properties of fluorinated amphiphilic copolymers via iron-mediated AGET ATRP

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Abstract Fluorinated amphiphilic copolymers have attracted considerable attention recently due to their potential applications as well as intrinsic interest in the structures. In this paper, fluorinated amphiphilic copolymers of dodecafluoroheptyl methacrylate-poly[isobutyl methacrylate-*co*-(2-hydroxyethyl methacrylate)] [DFMA-P(IBMA-*co*-HEMA)] were prepared via activators generated by electron transfer atom transfer radical polymerization (AGET ATRP) using $FeCl_3 \cdot 6H_2O$ as the catalyst, vitamin C as the reducing agent, and commercially available organic acid, sulfosalicylic acid (SSA), as the ligand. To improve the amphipathy, copolymers with carboxyl groups were further obtained by esterification of hydroxyl groups in HEMA of fluorinated copolymers with maleic anhydride (MA) under mild conditions. The gel permeation chromatography data obtained verified the polymerization and showed the well controlling of Fe/SSA polymerization system. Fourier transform infrared spectroscopy and ^1H nuclear magnetic resonance methods confirmed the structures of the copolymers. The contact angle measurement indicated that the water contact angles decreased gradually with the increasing of MA content. Finally transmission electron microscopy measurement showed the self-assembly behavior of the polymers. The effects of water content and ions in the solvent on the self-assembly behavior were studied in detail. These results demonstrate that the fluorinated amphiphilic polymers obtained may have applications for drug delivery systems, encapsulation, and so on.

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Introduction

Since its discovery in 1995, atom transfer radical polymerization (ATRP) has become an efficient technique for synthesis of polymers with well-controlled molecular architecture (topology, composition, and functionality) [1]. Activator generated by electron transfer (AGET) ATRP is one of the improved techniques of ATRP, which developed to overcome the intrinsic limitations of the traditional ATRP system. Compared to ATRP, AGET ATRP shows the advantages of facile preparation, storage, and handling of catalysts [2]. It is becoming one of the most powerful, versatile, simple and inexpensive methods in living/controlled free radical polymerization [3]. (AGET) ATRP mediated by a transition-metal complex establishes a dynamic equilibrium between active and dormant species [4]. Polymerization was conducted using many metal complexes. Among them, iron-salt-based complex attracts particular attention in recent years owing to their low toxicity, low cost, and good biocompatibility [5]. For the transition-metal complexes, the ligands are very important. They can help dissolve the transition-metal complex in organic media and adjust the redox potential of the metal center for appropriate reactivity and dynamics for atom transfer [6]. According to published reports, nitrogen-based ligands, such as 2,2-bipyridine (Bpy) and phosphorus-based ligands [i.e., triphenylphosphine (PPh_3)] have a very wide range of applications [7, 8]. Unfortunately, Bpy and PPh_3 are usually toxic and harmful to human health [9]. Therefore, it is very desirable to use "green" ligands for iron-mediated AGET ATRP process.