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Study on synthesis of two-armed polymers containing a crown ether core and their self-assembly behaviors in selective solvents

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Abstract

A series of well-defined two-armed polymers containing a crown ether core, poly(stearyl methacrylate)-crown ether-poly(stearyl methacrylate) (PSMA-crown-PSMA), with different molecular weight were synthesized via atom transfer radical polymerization (ATRP). The resultant polymers were characterized by ^{1}H NMR and GPC. The self-assembly behaviors of this kind of polymer in selective solvents were studied by TEM, and it was found that polymers with different molecular weight can directly self-assemble into hollow spheres, solid spheres and a monolayer film with regular pores by varying molecular weight and water content. The possible molecular packing motels for their self-assembly behaviors were proposed.

Keywords: Self-assembly; Crown ether; Stearyl methacrylate; ATRP

1. Introduction

Over the past decades, supramolecular self-assembly of amphiphilic molecules in selective solvents is a topic of great current interest [1–3] because these self-assembled aggregates exhibit great values not only in theoretical studies but also in applications such as drug delivery, gene therapy and model systems of biomembranes [4–6]. Extensive studies have been performed on the preparation of polymeric aggregates, and it has been reported that various well-defined polymeric aggregates, such as spheres, vesicles, rods, large compound micelles (LCMs) and large compound vesicles (LCVs) and so on [7–9], can be directly formed in selective solvents by altering the parameters of the self-assembly system such as molecular weight of amphiphilic molecule [10], concentration [11], pH [12], aging time [13] and so on.

The compounds containing crown ether groups are especially interesting polymers which can form ordered structures because of the specific affinity between crown ether rings [14,15]. Recently, a wide range of two-armed polymers with a crown ether

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core have been synthesized, and the preparation of these honeycomb-like macroporous films by the self-assembly process has been extensively studied [16–18]. For example, Han et al. [17] prepared ordered macroporous films by spin coating tetrahydrofuran (THF) solutions of such two-armed polymer onto substrates. They [16] also studied the pore size and arrangement of the films by varying the solution concentration and the THF evaporation rate. In general, to the best of our knowledge, the studies mentioned above mainly focused on the film preparation by spin coating; however, little attention has been paid to the self-assembly of this kind of polymer in selective solvents. Moreover, the above studies were mainly performed on the synthesis and self-assembly of two-armed polymers which are amorphous polymers.

With these characteristics in mind, a two-armed polymer containing a crown ether core, PSMA-crown-PSMA, has been designed. Moreover, the resultant polymer is a brush-type crystalline polymer and possesses unique characteristics and has potential applications because SMA has a pendent long alkyl side chain which can form a crystalline domain [19].

In the present paper, we synthesize and characterize a novel brush-type two-armed polymer containing a crown ether core, PSMA-crown-PSMA, via ATRP in anisole solution and discover various morphologies of the self-assembled aggregates, such as hollow aggregates, solid spheres and microporous films, by varying molecular weight and water content, in contrast to block copolymers or random copolymers or functionally terminated homo polymers used before.

2. Experimental section

2.1. Materials

Stearyl methacrylate (SMA) was purchased from Tianjing Chemical Reagent Co. and treated by the literature method [20]. SMA was purified by dissolution in hexane and extraction three times with 5% aqueous NaOH. After drying the organic phase over magnesium sulfate, the solution was passed through neutral alumina and solvent was removed under reduced pressure. 2,2-Bipyridyl (bipy), an analytical reagent, was used as obtained from Shanghai No.1 Chemical Reagent Factory. Copper (I) chloride (CuCl, AR grade) was purified by stirring in acetic acid, washed with methanol, and then dried under reduced pressure. Dibenzo-18-crown-6 was used as received from Across. Bis[4′-(2-bromobutyryl)dibenzo-18-crown-6] (BBDC) was prepared by the literature method [17]. Other regents were all used as received.

2.2. Synthesis of PSMA-crown-PSMA by ATRP

In a typical ATRP polymerization, a Schlenk flask with a magenetic stir bar and a rubber septum was charged with CuCl (40.0 mg, 0.4 mmol), BBDC (132.0 mg, 0.2 mmol), bipy (124.8 mg, 0.8 mmol), SMA (3 ml, 7.6 mmol) and anisole (4 ml). The flask was degassed by three freeze-thaw cycles and then immersed in a thermostated oil bath at 90 °C. After several hours, the polymerization was stopped by cooling to room temperature and opening the flask to air. The crude product was dissolved in anhydrous THF, passed through a column of neutral alumina, and then precipitated in anhydrous ethanol. The sample was precipitated three times in anhydrous ethanol to remove SMA and anisole.

^{1}H NMR (400 MHz. $CDCl_3$): 0.88 (3H, in $CH_3(CH_2)_{15}$–), 0.86 and 0.90 (3H. in CH_3C–), 1.25 (30H, in –$(CH_2)_{15}$ CH_3), 1.60 (2H, in –$CH_2(CH_2)_{15}$ CH_3), 1.80 (2H, in –CH_2C), 3.93 (2H, in –OCH_2–), 4.04, 4.24 (16H, –OCH_2 CH_2O–). 6.87, 7.56 (6H, ArH).

2.3. Self-assembly of PSMA-crown-PSMA copolymer

In the present experiment, the effects of molecular weight and water content on the morphologies of PSMA-crown-PSMA aggregates were mainly discussed.

2.3.1. Molecular weight

The polymers with different molecular weight were first dissolved in THF to make a series of polymer solutions at designed concentrations, respectively. Subsequently, a given volume of deionized water was added to the polymer solution at a rate of 0.5 wt% per minute with stirring. As the addition of water progressed, the solubility of the polymer decreased gradually. The formation of the aggregates of PSMA-crown-PSMA, as indicated by the appearance of turbidity in the solution, typically occurred when water content reached ca. 10.0 wt%. The concentration of these polymers in the final solutions was 0.1 wt%.