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Novel organotin-containing diblock copolymer with tunable nanostructures: Synthesis, self-assembly and morphological change

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ABSTRACT

Interesting self-assembly behavior and morphological change of a novel organotin-containing diblock copolymer were firstly reported. The organotin-containing diblock copolymer, poly(methyl methacrylate)-*block*-poly(acetoxydibutyltin methacrylate) (PMMA-*b*-PADBTMA), was prepared via RAFT polymerization of ADBTMA with PMMA as the macroCTA and AIBN as the initiator in toluene. Both the FT-IR and TG analysis revealed an incorporation of both co-monomers in the resulted polymer backbone. The ratio of two segments was determined indirectly by TG analysis, gravimetric method and derivative process. All results from the different methods were well matched. And it was found that the morphology of the diblock copolymer could be changed easily from vesicles to nano-particle or cross-linked nano-composite under the ultrasonication or additional Ph_2SnCl_2, respectively. All the morphologies were analyzed by SEM, TEM and DLS. The self-assembly and the morphological change attributed to the strong coordination action between tin atoms and the carbonyl groups among PADBTMA segments.

1. Introduction

Organometallic compounds have always played a very important role in organic synthesis and material chemistry [1–5]. Tin is in the same group with carbon, which ensures that organotin compounds are more stable than most of other organometallic compounds. Hence, organotin compounds are one of the most extensively studied species [6–11]. Moreover, the self-assembly of organotin compounds has attracted more and more attention in view of their considerable structural diversity and topologies [12–15]. A multitude of structure types including monomers, dimers, tetramers, oligomeric ladders, and hexameric drums have been obtained [9,16,17]. On the other hand, block copolymers may microphase separate in bulk into well-defined nanoscopic morphologies simply by changing their molecular parameters [18,19]. In the past decade, the nanostructures, which were constructed by self-assembly of block copolymers [20–24], have been widely used in nanotechnologies in many different fields, such as their applications in nanofabrication [25–27], lithography [28,29], cell culturing [30,31], and drug delivery [32–34]. Lots of metallic polymers including organotin-containing polymers have been prepared and studied [35–44]. Chen's group has carried out lots of work following the strategy to synthesize various organic/inorganic nano-materials based on a reactive amphiphilic diblock copolymer bearing a gelable segment [45–51]. Hence, the introduction of the organotin complex into polymer chain could endow the resulting materials with diversely enthralling characters, which intrigued scientists in the past decades. However, to the best of our knowledge, previous reports mainly focused on the simple synthesis of organotin-containing polymers and hardly be involved in the morphology. Herein, we reported a facile method for preparation of a novel organotin-containing diblock copolymer with special nanostructure. A newly designed organotin compound, acetoxydibutyltin methacrylate (ADBTMA), was used as the monomer to prepare diblock copolymers with PMMA by RAFT polymerization [52]. Furthermore, the corresponding organotin-containing diblock copolymer was self-assembled into well-defined vesicles, which could be easily transformed into nano-spheres and cross-linked nano-composites under the ultrasonication or additional Ph_2SnCl_2, respectively. The mechanism of the self-assembly and the morphological change were also studied. It is the first report about the synthesis, characterization and morphological change of the organotin-containing diblock copolymer.

2. Experimental section

2.1. Materials

Methyl methacrylate (MMA) was purchased from Acros (99 wt%), purified by filtration through alumina (to remove inhibitors), stirred with CaH_2 overnight, and distilled prior to use. Azobis

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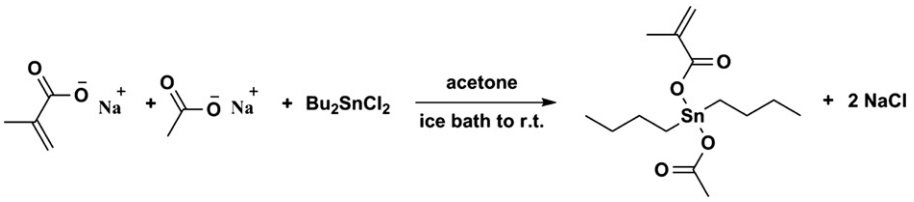


Scheme 1. Synthesis of acetoxydibutyltin methacrylate (ADBTMA).

(isobutyronitrile) (AIBN, from Regent Corp.) was recrystallized twice from methanol. Bu_2SnCl_2, Ph_2SnCl_2, sodium methacrylate, sodium acetate, and benzoyl chloride were purchased from Regent Corporation. All the solvents were purified prior to use.

2.2. Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded on a Brucker-600 or a Varian-400 NMR spectrometer using $CDCl_3$ as the solvent and tetramethyl silane (TMS) as the internal standard. Molecular weights and molecular weight distributions were measured using a Waters GPC (Waters 1515 liquid chromatograph connected with three Waters styragel GPC columns (HT2, HT3, HT4) and a Waters 2414 refractive index detector; eluent, THF; flow rate, 1 mL/min; temperature, 40 °C). The calibration was made with monodispersed polystyrenes as standards. Thermo-gravimetric analysis (TGA) was carried out with a NETZSCH TG 209 at heating rate of 10 °C/min under air atmosphere. The transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G220S-TWIN electron microscope operated at an accelerating voltage of 200 kV. The images were recorded by a Model 794 CCD camera (512*512) (Gatan Inc.). Solution samples were dropped onto carbon-coated copper grids for TEM observation. The scanning electron microscopy (SEM) was used to view surface morphologies of vesicles. To obtain SEM images, a drop of solution was spread on a glass and air dry. The sample was coated with platinum and viewed by a Hitachi S-3500N electron microscopy operated at 15 kV. The images were recorded by a digital camera. Fourier transform infrared (FT-IR) spectra were recorded using KBr disc on a Bruker EQUINOX 55. The elemental analysis was performed on the Elementar Vario EL instrument.

2.3. Synthesis procedure

2.3.1. Synthesis of the organotin monomer acetoxydibutyltin methacrylate (ADBTMA)

ADBTMA was prepared by a simple one-step methodology (Scheme 1). The mixture of 6.08 g (20 mmol) dibutyldichlorotin, 2.38 g (22 mmol) sodium methacrylate, 1.80 g (22 mmol) sodium acetate in dry acetone (100 mL) was stirred for overnight below 0 °C. And the resulting sodium chloride was removed by filtration. Evaporation of the filtrate under vacuum yielded the crude product. The pure product (5.70 g) was obtained by vacuum distillation with 75.6% yield. The attempt to get single crystal failed since it is a low melting point compound. ^1H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 5.44 (s, 1H), 1.94 (s, 3H), 1.81 (s, 3H), 1.53 (m, 8H), 1.25 (m, 4H), 0.76 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.90, 176.44, 135.71, 126.30, 26.13, 25.71, 24.56, 19.84, 17.93, 12.94; Anal. Calcd. for $C_{14}H_{26}O_4Sn$: C, 44.59; H, 6.95. Found: C, 44.76; H, 7.22.

2.3.2. Preparation of poly(methyl methacrylate)-block-poly (acetoxydibutyltin methacrylate) (PMMA-b-PADBTMA)

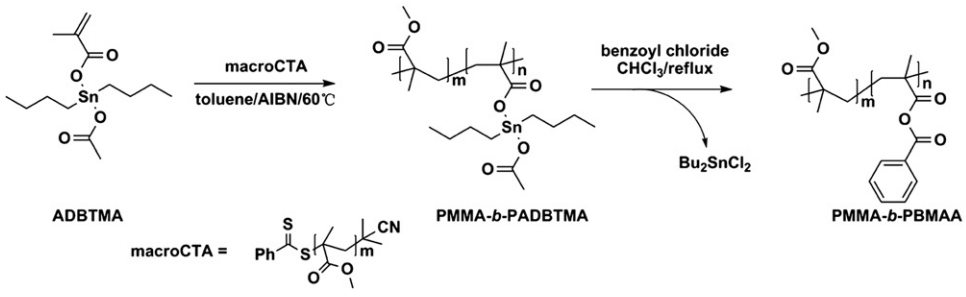
PMMA-*b*-PADBTMA was prepared by RAFT polymerization of ADBTMA with PMMA as macroCTA and AIBN as initiator in toluene (Scheme 2). It was carried out according to standard RAFT procedures described in the literature [52]. A typical procedure was as follows: A 50 mL Schlenk tube was charged with a solution of ADBTMA (2.017 g, 5.350 mmol), macroCTA (PMMA, D_{Pn} = 152, PDI = 1.14, synthesized according to standard RAFT procedure) (1.745 g, 0.11 mmol), and AIBN (0.004 g, 0.02 mmol) in toluene (15 mL). The contents were degassed by three "freeze-pump-thaw" cycles to remove oxygen, sealed by the vacuum line, and immersed into a preheated oil bath at 60 ± 1 °C. At the expected time, the tube was removed from the oil bath and cooled to room temperature by ice-water bath. It was diluted with THF, precipitated in methanol, filtered, washed with methanol, and then dried under vacuum to constant weight (2.576 g). Yield (gravimetrically): 41.2%.

2.3.3. Reaction of PMMA-b-PADBTMA with benzoyl chloride

Large excess of benzoyl chloride (2 mL) was dropped into gelatin of PMMA-*b*-PADBTMA (0.231 g) in $CHCl_3$ (8 mL) under N_2 atmosphere (Scheme 2). Clear solution was obtained after refluxing for 2–3 h under violent stirring. After evaporation of the solvent, the residue was precipitated in dry petroleum ether, filtered, washed with dry petroleum ether, and then dried under vacuum to constant weight. Poly(methyl methacrylate)-*block*-poly(benzoic methacrylic anhydride) was obtained as white powder (0.190 g).

2.3.4. Reaction of PMMA-b-PADBTMA with diphenyltin dichloride

Take Ph_2SnCl_2 as an example: under N_2 atmosphere, Ph_2SnCl_2 (0.024 g, 1 equiv. to organotin unit) was added in one portion into the gelatin of PMMA-*b*-PADBTMA (0.069 g) in $CHCl_3$ (3 mL). The



Scheme 2. Synthesis of diblock copolymer PMMA-*b*-PADBTMA mediated by RAFT polymerization and the reaction of PMMA-*b*-PADBTMA with benzoyl chloride.