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Dispersion of single-walled carbon nanotubes in an aqueous medium by using a cyclic copolymer

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ABSTRACT

A cyclic copolymer, poly(methoxy-PEG acrylate-*co*-3-(4-benzoylphenoxy) propyl acrylate), was successfully synthesized by Cu(0)-mediated controlled radical polymerization and Cu(I)-catalyzed azide–alkyne cycloaddition "click" chemistry. The self-assembly behaviours of the linear and cyclic copolymers were investigated. Subsequently, the linear and cyclic copolymers were used to disperse the single-walled carbon nanotubes (SWCNTs) in an aqueous medium. The results showed that cyclic copolymers could form uniformly stable, spherical morphologies by self-assembly more easily than their linear counterparts under the same conditions. Cyclic copolymers were also found to better disperse SWCNTs, thereby extending the applications of SWCNTs in an aqueous medium.

1. Introduction

The discovery of carbon nanotubes (CNTs) and CNT-based materials has attracted increasing attention because of their wide range of applications. To increase the use of CNTs, surfactants are highly desired because of their abilities to interact with CNTs through noncovalent interactions such as ionic bonds to improve the dispersion of CNTs [1,2]. The progress of dispersing CNTs by using surfactants has reached a new plateau in recent years because of its unique advantage. A remarkable achievement in this effort is dispersion by using the ionic surfactant sodium dodecylbenzene sulfonate (NaDDBS) reported by Yodh and colleagues [3]. When the concentration of the surfactant was above the critical micelle concentration (CMC), it was adsorbed onto the surface of the CNTs and self-organized into micelles. The mechanism of the surfactant-assisted aqueous dispersion of CNTs was also illustrated by a few other researchers [4–6]. Three most possible configurations were proposed: hemispherical micelles, cylindrical micelles, and randomly adsorbed molecules.

Because of the distinct structure of CNTs, π–π reaction was used to stabilize them [7]. For instance, a molecule with a π-conjugated backbone built from aromatic thiophene and dialkoxyphenylene units and substituted imidazolium groups was designed to obtain ultra-stable, single-walled carbon nanotube (SWCNT) dispersion in an aqueous medium [8]. The peptide aptamer IFRLSWGTYFS exhibited a high dispersion capability below the CMC. From the results of isothermal titration calorimetry and molecular dynamic simulations, it was observed that the effective binding capability of the peptide was because of the π–π interaction between the aromatic groups of the peptide aptamer and the side walls of SWCNTs [9]. Amphiphilic block copolymers were used to wrap and disperse CNTs in aqueous medium [6,10,11]. The wrapping and dispersion efficiencies were affected by the structure of the copolymers (chemical composition, molecular weight, and hydrophilic/hydrophobic balance). Aromatic groups such as benzene [12] or thiophene [13,14] were introduced into the amphiphilic block copolymers to disperse CNTs more effectively by the strong π–π interactions with CNTs.

The self-assembly behaviours of the cyclic polymers are different from those of the linear polymers [15,16]. Several studies compared the aggregation phenomenon between the linear and cyclic polymers [17–26] and found that the cyclic amphiphilic copolymers possessed their unique self-assembly behaviours and improved physical properties as well. Impressive micelles with a flower-like morphology were formed from amphiphilic block copolymers [18]. Previously, the facile synthesis and topological effects on the self-assembly and photoisomerization of polymers containing the azobenzene group [27,28] and on the self-assembly of amphiphilic macrocycles containing polymeric liquid crystal grafts in solution [29] were reported by our group. There are few publications reporting the interaction between the cyclic polymers and CNTs. Different methods to prepare cyclic polymers were proposed [30–34]. Herein, we synthesized a cyclic copolymer, poly(methoxy-PEG acrylate-*co*-3-(4-benzoylphenoxy) propyl acrylate) (poly(PEGA-*co*-BPPA)), containing a short PEG side chain and the benzophenone group through Cu(0)-mediated controlled radical polymerization [35] and Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) "click" chemistry [36,37]. The self-assembly of cyclic

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copolymers and its linear precursors was analysed systematically. The linear and cyclic copolymers were used to disperse SWCNTs in an aqueous medium. The benzophenone group tends to aggregate together and better interact with the SWCNTs through the π–π reactions, whereas the short PEG chains maintain the dispersion of SWCNTs more stable in the aqueous medium. The results showed that the cyclic copolymers self-assembled into uniformly stable, spherical structures in the aqueous medium and could disperse SWCNTs better than their linear precursors.

2. Experimental

2.1. Materials

Methoxy-PEG acrylate (PEGA; average *Mn* ~480) was purchased from Sigma-Aldrich. The inhibitors from PEGA were removed by passing it through a neutral alumina column. 4-Hydroxybenzophenone (>99% pure), Nile Red (>99.5% pure), and sodium azide (NaN_3; >99.5% pure) were purchased from Sigma-Aldrich. 3-Bromo-1-propanol, Alfa Aesar (98% pure), acryloyl chloride, triethylamine, and copper powder (Cu) were purchased from Energy Chemical. Tris(2-dimethylaminoethyl)amine (ME_6TREN) and *N*,*N*,*N*′,*N*″,*N*‴-pentamethyldiethylenetriamine (PMDETA) were purchased from J&K Scientific Ltd. Potassium carbonate, sodium sulfate, and all solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. Copper(I) bromide (CuBr, Adamas) was freshly purified by stirring in acetic acid overnight and then was washed with acetone and dried in vacuum. SWCNTs (PT25) were purchased from Nano-C.

2.2. Characterization

A recycling preparative SEC (Japan Analytical Industry Co., Ltd.) system equipped with differential refractive index detector was used to refine the crude copolymers. The dried crude copolymers were dissolved in tetrahydrofuran (THF) at a concentration of 200 mg/mL and filtered through a 0.45-μm PTFE syringe filter prior to injection. The preparative SEC flow rate was maintained at 6 mL/min, and THF was used as the eluent. The target fraction was collected manually and determined using the TOSOH HLC-8320 SEC equipped with refractive index and UV detectors as described above. The number-average molecular weight (*Mn*) and the molecular weight distribution (*Mw*/*Mn*) of the polymers were determined using the SEC (TOSOH HLC-8320), which was equipped with a refractive index detector (TOSOH), and using a TSKgel guard column SuperMP-N (4.6 × 20 mm) and two TSKgel Supermultipore HZ-N (4.6 × 150 mm, 3-μm bead size) with a measurable molecular weight ranging from 5×10^2 to 1.9×10^5 g/mol. THF was used as the eluent at a flow rate of 0.35 mL/min at 42 °C. The SEC samples were injected using a TOSOH plus autosampler and calibrated with PMMA standards purchased from TOSOH.

The ^1H NMR and ^{13}C NMR spectroscopies were recorded on a Bruker 300-MHz nuclear magnetic resonance instrument by using tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were obtained on a Bruker TENSOR-27 FT-IR spectrometer by mixing the polymers with KBr tablets. The UV–Vis spectra were recorded on a Shimadzu UV-3150 spectrophotometer (Shimadzu China, Shanghai, China). The hydrodynamic diameter (D_h) of spherical self-assembled morphologies were measured by dynamic light scattering (DLS) using Brookhaven's NanoBrook 90Plus PALS instrument at 25 °C at a scattering angle of 90°.

The morphologies of the copolymers, SWCNTs, and copolymers/SWCNTs were measured using a transmission electron microscope (TEM) (HITACHI HT7700) at a voltage of 120 kV. The samples were prepared by placing 10 μL of the self-assembled copolymer solution onto a carbon coated copper grid, and after 60 s, the superfluous solution was absorbed using a piece of filter paper. The same procedure was repeated three times, and the grid was left to dry overnight. The surface morphologies were measured by atomic force microscope (AFM) with a tapping mode (Veeco Instruments Inc., Nanoscope IV) and the self-assembled mixture solutions were diluted to 200 times and dropped onto a precleaned silicon wafer.

2.3. Synthesis of linear poly(PEGA-co-BPPA)

The specific procedure for the synthesis of the initiator propargyl 2-bromoisobutyrate (PBIB) and monomer 3-(4-benzoylphenoxy) propyl acrylate (BPPA) is shown in the supporting information. The linear poly(PEGA-*co*-BPPA) was prepared by following the typical procedure: PEGA (1.0 g, 2.08 mmol), BPPA (64.7 mg, 0.21 mmol), Cu (2.2 mg, 0.035 mmol), ME_6TREN (7.8 mg, 0.07 mmol), PBIB (14.2 mg, 0.069 mmol), and *N*,*N*′-dimethylformamide (DMF, 2 mL) were placed in a 5-mL flask and degassed by freeze-pump-thaw cycles for three times. The flask was filled with N_2 and transferred into a thermostat at 25 °C. After 2 h, the mixture was diluted with 2 mL of DMF and precipitated in a large amount of cold diethyl ether, and the copolymer was obtained by centrifugation. The product was washed using ethylenediaminetetraacetic acid (EDTA) disodium solution (DMSO) and extracted by dichloromethane. After removing the solvent and drying in a vacuum oven at 25 °C overnight, purified linear copolymer was obtained and refined by recycling preparative SEC (0.89 g, yield: 89%).

2.4. Synthesis of cyclic poly(PEGA-co-PBPPA)

To obtain cyclic poly(PEGA-*co*-PBPPA), the end group of linear poly(PEGA-*co*-BPPA) was modified to —N_3 group by sodium azide as follows: the linear copolymer poly(PEGA-*co*-BPPA) (0.89 g, 0.087 mmol) was dissolved in 20 mL of ultrapure water, and NaN_3 (283.6 mg, 4.35 mmol) was added. The solution was stirred overnight at 25 °C before extraction by dichloromethane and precipitation into cold diethyl ether, and the linear poly(PEGA-*co*-BPPA)-N_3 was obtained (0.73 g, yield: 82%). Subsequently, in a three-necked flask, 800 mL of anaerobic toluene was added, and PMDETA (260.4 mg, 1.5 mmol) and CuBr (140.6 mg, 1 mmol) were then added into the flask under Ar. The linear poly(PEGA-*co*-BPPA)-N_3 (100 mg, 0.01 mmol) dissolved in 20 mL of toluene was introduced through the syringe pump slowly (injection rate: 0.5 mL/h) for 40 h at 60 °C. After completion of this procedure, the mixture was stirred for another 48 h. Then, azide resin (100 mg) was added, and after 12 h, the mixture was cooled to room temperature and was purified using an EDTA-2Na column to remove the metal salt and the azide resin. After removing most solvents by evaporation, the residue was dissolved in saturated EDTA-2Na solution to allow the rest of the metal salt to precipitate. The final product was extracted by dichloromethane three times and dried by Na_2SO_4. The purified copolymer was obtained by precipitating in cold diethyl ether and dried in a vacuum oven overnight at 25 °C (0.059 g, yield: 59%).

2.5. Self-assembly of linear and cyclic copolymers

The self-assembly behaviours of linear poly(PEGA-*co*-BPPA) and cyclic poly(PEGA-*co*-BPPA) were investigated according to the previous studies [28,29,38]. The CMCs of the linear and cyclic copolymers were acquired on Nile Red fluorescence, and the data are presented in Fig. S9 (supporting information). A typical self-assembly solution was prepared by slowly adding H_2O into the DMF solution with a polymer concentration of 1.5 mg/mL. The polymer DMF solution was filtered through a PTFE filter with 0.22-μm pore size to remove any dusts to obtain the stock solution. Then, 1 mL of H_2O was added slowly at the rate of 0.1 mL/h through the syringe pump to the above solution while stirring (500 rpm), and the mixture was stirred overnight at room temperature. To obtain stable micelles, DMF was removed by dialyzing the solution against deionized water for 48 h. All these steps were required to be performed in dark.