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Metal ion induced-assembly of amylose in aqueous solution

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ABSTRACT

Cu^{2+}/amylose assemblies of various sizes were prepared through the Cu^{2+} ion induced-assembly of amylose. These assembly structures were characterized via transmission electronic microscopy (TEM), scanning electronic microscopy (SEM), dynamic light scattering (DLS), ^1H NMR analysis, fluorescence spectroscopy (FL) and UV–vis absorption spectroscopy (UV–vis). The results from these characterizations revealed the existence of a complexation effect and/or a bridging effect between the hydroxyl groups of amylose and Cu^{2+} ions, and that the formation of the hydrophobic domains promoted the formation of Cu^{2+}/amylose assemblies. The use of other metal ions to induce the formation of spherical, flower- and wire-like amylose assemblies was investigated as well. A preliminary investigation on the ability of amylose to capture various metal ions was also performed, and the results of this work demonstrated that amylose could bind quantitatively metal ions that were at low concentrations. This work provided an alternative strategy for the recovery of precious metals from metal ion-containing aqueous solutions and the reduction of water pollution.

1. Introduction

The field of polymer self-assembly holds great promise, and has attracted extensive interest in recent decades. Self-assembled polymers have been widely used as multi-functional polymeric materials fields for various applications, including drug release, catalysis, biomimetics, nano-devices, functional proteins, heavy metal absorbent materials, and for various other applications (Brown, Aksay, Saville, & Hecht, 2002; Moffitt & Eisenberg, 1997; Perez, Simeone, Saeki, Josephson, & Weissleder, 2003; Rosler, Vandermeulen, & Klok, 2001; Shen, Zhang, & Eisenberg, 1999; Sheparovych et al., 2006; Wang, Tang, Li, & Wang, 2009; Wen, Cao, Wang, Chen, & Luo, 2011; Xu, Ji, Chen, & Shen, 2005; Zhang & Eisenberg, 1996; Zhang et al., 2006). In a typical induced-assembly process, polymers tend to assemble and form fixed structures under certain external driving forces, such as changes to the pH (Shen et al., 1999), the presence of metal ions (Sheparovych et al., 2006; Zhang & Eisenberg, 1996) the use of templates (Brown et al., 2002), and various other external stimuli.

Research on metal ion-induced assembly began with the self-assembly of polypeptides and the development of supramolecular chemistry in the 1970s. The metal ion-induced assembly of polypeptide was initially investigated with the aim of designing multi-functional protein on demand. Since the 1990s, studies on metal ion-induced assembly have also been extended to block copolymers and proteins. Because they incorporated $-NH_2$ or $-COOH$ groups that could readily undergo complexation, these copolymers were capable of coordinating with metal ions, leading to the formation of polymeric assemblies with a great morphological diversity. There has been an abundance of literature describing the formation of polymer assemblies in the presence of metal ions. The metal-ion induced assembly of block copolymers was first reported by Zhang, Yu, and Eisenberg (1996). In their studies, the diblock copolymer poly(styrene-*b*-oxyethylene) assembled into rod-like micelles in block selective solvents. Meanwhile, the addition of Li^+ induced these structures to undergo a morphological transition to form flake-like assemblies. Similar phenomena were also observed among ionic and non-ionic copolymers. The inducing effect of the metal ions on the assembly of these copolymers was attributed to the binding or bridging interactions between the ions and the copolymers. Li, Gong, and Nakashima (2002) investigated

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the alkali ion induced-assembly behavior of poly(ethylene oxide-*b*-methacrylic acid) (PEO-*b*-PMA) by employing the PMA-metal ion complex as the core and hydrophobic PEO block as the corona.

Investigations on the metal ion induced-assembly of polymers have been extended from synthetic polymers to natural polymers in recent years. Starch is a renewable resource that is readily available and affordable. In addition, starch has a wide range of practical applications in various fields (Miles, Morris, Orford, & Ring, 1985). There are two types of starches, including linear and branched starch. The former is also named amylose, and consists of glucose residues that are connected via beta-1,4-glycosidic bonds in a linear screw-like structure. Meanwhile, branched starch consists of 24–30 glucose residues that are connected via alpha-1,4-glycosidic bonds in an end-to-end manner. Amylose is fully soluble in hot water due to the large number of hydroxyl groups contained in the glucose residues. According to recent reports, the hydroxyl groups of starch have been used by various researchers to construct amphiphilic polymers by introducing hydrophobic groups or hydrophobic polymer chains into the main chains, which facilitated assembly of the starch derivative in aqueous solutions (Akiyoshi, Maruichi, Kohara, & Kitamura, 2002; Besheer, Hause, Kressler, & Mader, 2007; Han, Borjihan, Bai, Chen, & Jing, 2008; Ju, Yan, & Zhang, 2012; Morimoto, Ogino, Narita, Kitamura, & Akiyoshi, 2007; Tan et al., 2009; Tan, Xu, Li, Sun, & Wang, 2010). For example, Mäder et al. reported the assembly behavior of hydroxyethyl starch, which had been modified with various organic acids. The polymer was initially dissolved in THF before water was added, which served as a good solvent for the hydroxyethyl starch backbone and as a poor solvent for the organic acid segments. Consequently, the polymer underwent self-assembly to yield vesicles (Besheer et al., 2007).

Although the assembly of starch through the introduction of hydrophobic groups and polymer chains has been widely investigated, the metal ions induced-assembly of amylose has never been reported so far. Herein, we describe the use of metal ions to induce the self-assembly of water-soluble amylose chains through a complexation effect or bridging effect to yield polymeric assemblies with various sizes and morphologies. In addition, we have preliminarily studied the ability of amylose to capture trace metal ions from aqueous solution. The research demonstrated that amylose could bind quantitatively with metal ions when the ions were at low concentrations.

Although there are a number of publications describing the removal of heavy metal ions from aqueous solution by utilizing xanthated, phosphorylated, or ammoniated starch (Dong et al., 2010; Guo, Sun, Li, Liu, & Ji, 2009; Xu, Wu, Chang, & Zhang, 2010) as well as starch that had been modified with copolymers (Chang, Hao, & Duan, 2008), the use of amylose to remove metal ion through the current strategy has never been reported. This report not only helps to provide an understanding of the induced-assembly mechanism of biomacromolecules, but also provides an alternative strategy for the recovery of precious metals from aqueous solutions and the remediation of water pollution.

2. Experimental

2.1. Materials and reagents

Amylose ($(C_6H_{10}O_5)_n$, was purified from potato starch (which was purchased from Tianjin Ruijinte Chemical Reagent Co. Ltd., China, >99%) in the following manner: the original starch sample was dissolved in dry DMSO at a concentration of 50 mg/mL before it was centrifuged at $2000 \times g$ for 5 min to remove any insoluble impurities. Ethanol was subsequently added to the supernatant to precipitate the amylose, which was dried under high vacuum for 72 h. The amylose was characterized via size exclusion chromatography (SEC), using narrowly dispersed polyethylene glycol samples as a calibration standards and water as a mobile phase. The SEC characterization revealed that the amylose samples possessed a M_w of 13,610 g/mol and a M_w/M_n of 4.55. $CuCl_2{\cdot}2H_2O$ (Tianjin Kemiou Chemical Reagent Co. Ltd., China, >97%), $FeCl_3{\cdot}6H_2O$ (Tianjin Fuchen Reagent Factory, China, >99%), $CdCl_2{\cdot}H_2O$ (Tianjin Fuchen Reagent Factory, China, >99%), $AgNO_3$ (Sinopharm Chemical Reagent Co. Ltd., China, ≥99.8%), and $AlCl_3$ (Tianjin Jinhuitaiya Chemical Reagent Co. Ltd., China, >99.8%) were used as received. All solvents were of analytical grade and used as received, unless indicated otherwise. Pyrene (Aladdin Reagent Co., 97%) was repeatedly crystallized with a solvent mixture consisting of petroleum ether and ethanol before usage. Doubly distilled water was prepared using a home-made water purification system.

2.2. Preparation of the amylose solutions

0.25 g of amylose (containing 0.0046 mol of hydroxyl groups as calculated by expression: $3 \times W_{amylose}/M_{glucose}$ here, W is the weight of amylose, and M is the molecular weight of glucose units of amylose) and 100 mL of distilled water were mixed together before this mixture was magnetically stirred and heated at $100 \pm 1\,^{\circ}C$ to yield a transparent solution, and then preserved at room temperature prior to use. The concentration of the amylose in this solution was 2.5 mg/mL, while the concentration of the hydroxyl groups ([—OH]) of the amylose was 0.046 M.

2.3. Preparation of the metal ion solution

4.3081 g of $CuCl_2$ was dissolved in doubly-distilled water in a 50 mL of volumetric flask, thus yielding an aqueous $CuCl_2$ solution with a concentration of 0.5054 M. $FeCl_3$, $CdCl_2$, $AgNO_3$, and $AlCl_3$ aqueous solutions with various predesigned concentrations were prepared in a similar manner.

2.4. Cu^{2+} induced-assembly of amylose

4.6 mL amylose solutions were transferred into six 10 mL vials. Subsequently, 0.013, 0.05, 0.1, 0.2, 0.4 or 1.6 mL of the $CuCl_2$ solutions were added into the different respective vials before the contents were stirred for 30 min at $70 \pm 1\,^{\circ}C$ to yield stable light blue solutions.

2.5. Characterization of the metal ion induced-assemblies

Transmission electron microscopy (TEM) was performed using a JEM-100 CXII-TEM system that was operated at 80 KeV. Samples were prepared by drying a droplet (10 μL, 1 mg/mL) of the solution on a copper grid that was coated with acetylcellulose membrane. The grid was finally dried overnight in a desiccator before TEM observation. The average size of the assemblies was evaluated from TEM images for more than 200 particles. Fluorescence spectra (FL) were measured using an F-4600 fluorescence spectrophotometer (Shimadzu) at room temperature. Pyrene was dissolved in acetone at a concentration of 6×10^{-7} M before 10 μL of above solution was added into the analysis samples. High purity nitrogen was bubbled to remove trace acetone and dissolved oxygen. 2.5 mL of each sample was placed in a quartz cell with a 1 cm path length to obtain fluorescence emission spectra. The fluorescence excitation wavelength was 334 nm, and the range of the emission wavelengths was 340–760 nm. The UV–vis absorption spectra were measured using a UV–vis–NIR spectrophotometer (UV-8000, Shimadzu). The size and size distribution of assemblies were determined by Dynamic Lighter Scattering (DLS) performed on a 90 plus system (Brookhaven Instruments Corporation, USA). Samples were filtered with a 0.45 μm filter membrane before DLS