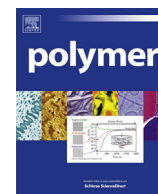




Contents lists available at ScienceDirect

Polymer

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# Hybrid polyion complex micelles from poly(vinylphosphonic acid)-based double hydrophilic block copolymers and divalent transition metal ions

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## ARTICLE INFO

### Article history:

Received 9 January 2015

Received in revised form

4 April 2015

Accepted 11 April 2015

Available online xxx

### Keywords:

Double hydrophilic block copolymers

Polyion complex micelle

Macromolecular design by interchange of xanthate (MADIX)

## ABSTRACT

Double-hydrophilic block copolymers (DHBC) containing neutral polyacrylamide and ionizable poly(vinylphosphonic acid) blocks were directly synthesized by quantitative chain extension of a polyacrylamide macroxanthate with vinylphosphonic acid. Formation of hybrid polyion complex (HPIC) micelles was investigated at low pH with divalent transition metal ions with an emphasis on the comparison with polyacrylate-based DHBC. The tendency to form HPIC micelles as a function of the polyvinylphosphonate block length was as follows  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+} < \text{Mn}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ ; it did not follow the charge to size ratio of cations or the Irving–Williams series, but was similar to the order obtained with phosphonate-bearing nucleotides and nucleic acids. The inclination to form HPIC micelles with asymmetric DHBC at low pH was stronger with polyvinylphosphonate-based than with polyacrylate-based polymers in accordance with the higher basicity of the phosphonate group. Moreover, it increased with the polyion block length.

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## 1. Introduction

Hybrid polyion complex (HPIC) micelles are organic–inorganic nanoassemblies which have attracted increasing interest related to their uses as reservoirs of inorganic ions and as nanoreactors for inorganic polycondensation reactions [1–7]. They are formed by complexation of multivalent metal ions by water-soluble polymers of complex architectures such as double hydrophilic block copolymers (DHBCs)—copolymers constituted of two water-soluble blocks of different chemical nature. DHBCs have many applications in aqueous media, including noble nanoparticle synthesis [1–5], drug delivery [8–12], colloid stabilization [13–17], growth of inorganic crystals such as  $\text{CaCO}_3$  [18–26],  $\text{BaSO}_4$  [5,27–30], and  $\text{ZnO}$  [31–33], synthesis of metal (hydr)oxide nanoparticles

[6,34,35], and preparation of mesoporous materials [36,37] using polyion complex micelles as reversible and potentially reusable polymer templates [38].

DHBCs are well-established as control agents for morphosyntheses and bioinspired mineralization processes [39]. For these applications, one block is chosen to interact with specific inorganic sites, while the other block promotes solubilization in water. DHBCs have been used to prepare highly stable hybrid colloids by mineralization of HPIC micelles in suspension [6,34,35]. Complexing (anionic)-stabilizing (neutral) DHBCs such as poly(acrylic acid)-*b*-polyacrylamide [40] allow polymer-coated metal hydroxide, oxide [41] or sulfide [42] nanoparticles to be prepared from HPIC micelle precursors: for example, stable Al, La, and Cu hydroxide nanoparticles of different shapes (plate-like, elongated, spherical) and controlled sizes. The particles exhibited a mineral core protected by a corona of water-soluble polymer chains at the surface. The mineral particle size could be tuned by varying the ratio of polymer to metal ions. Moreover, the minimum size of the mineralized nanoparticles was determined by the size of the precursor HPIC micelles.

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We have recently extended this preparation route to the case of layered double hydroxides (LDH) such as Mg–Al LDH [43], where we showed that the precursor HPIC micelles based on PAA-*b*-PAm DHBCs contained only Al ions while Mg ions were present as freely dissolved species. Mg ions were shown to be incapable of inducing micellization of the PAA-*b*-PAm polymers. It would be interesting to extend the preparation of LDH nanoparticles to other compositions including trivalent and divalent transition metal ions with catalytic or magnetic properties. For this reason, preparation of HPIC micelles of various trivalent and divalent metal ion compositions is an important challenge.

The preparation of well-defined HPICs requires access to well-defined DHBCs carrying a variety of complexing blocks. In particular, DHBCs comprising a polyphosphonate block offer new possibilities for complexation of different metal cations, as a result of the higher basicity of the phosphonate group compared to the carboxylate group.

Phosphonic acid-containing polymers are typically produced by free-radical polymerization of styrene [44], (meth)acrylate [45], (meth)acrylamide [46] or vinyl [47] derivatives bearing either a free phosphonic acid group or a phosphonic ester that is subsequently converted to the phosphonic acid via hydrolysis. Reversible deactivation radical polymerization (RDRP) technologies such as nitroxide mediated polymerization [48] and atom transfer radical polymerization [49] allow precisely controlled phosphonic ester-functional polymers to be synthesized. More recently, reversible addition fragmentation chain transfer polymerization (RAFT) [50] and macromolecular design by interchange of xanthates (MADIX) [50] have become the most versatile strategies for the preparation of phosphonated polymers of controlled molar mass and low dispersity [51–55].

Most importantly, RAFT/MADIX polymerizations allow the direct polymerization of monomers bearing unprotected phosphonic acid groups. A few years ago, we reported the first example of RDRP of a phosphonic acid-functional monomer, vinylphosphonic acid (VPA), which was successfully polymerized by aqueous MADIX polymerization with controlled  $M_n$  in the 1000–5000  $\text{g}\cdot\text{mol}^{-1}$  range [55]. This rendered possible the direct aqueous synthesis of poly(acrylic acid)-poly(vinylphosphonic acid) diblock copolymers.

In the following report we use a similar strategy to prepare neutral-anionic polyacrylamide-poly(vinylphosphonic acid) diblock copolymers (PAm-*b*-PVPA) from a polyacrylamide macroxanthate. The ability of the resulting copolymers to co-assemble into HPIC micelles is investigated with a selection of metal cations. We focus on the divalent transition metal ions  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , due to their wide range of applications. The performances of the PAm-*b*-PVPA copolymers are compared to their polyacrylamide-*b*-poly(acrylic acid) (PAm-*b*-PAA) counterparts.

## 2. Experimental

### 2.1. Materials

2,2'-Azobis(isobutyramidine) dihydrochloride (AIBA, 98%) and 4,4'-azobis(4-cyanovaleric acid) (ACP, 98%) were purchased from Acros. The *O*-ethyl-*S*-(1-methoxycarbonyl)ethyl dithiocarbonate (XA1) was prepared according to a procedure described elsewhere [56]. Vinylphosphonic acid (VPA, 90%) was supplied from BASF and used as received. Acrylic acid (AA, 99%, Aldrich) and acrylamide (Am, SNF, 50% in water stabilized with 100 ppm MEHQ) were used as received. Water, ethanol (VWR, 99.9%), and methanol (Aldrich,  $\geq 99.6\%$ ) were used without further purification.  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{Cl}_2) \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{Cl}_2) \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{Cl}_2) \cdot 6\text{H}_2\text{O}$  (Aldrich) and  $\text{Cu}(\text{Cl}_2)$  (Prolabo) were used as sources of metal ions. Deionized water

(Purelab, Elga, France) was always used for the preparation of the solutions.

### 2.2. Instrumentation

$^{31}\text{P}$  NMR spectra were recorded on a Bruker AMX 300 at 300 MHz in  $\text{D}_2\text{O}$ .

Size exclusion chromatography (SEC) was carried out using three Shodex columns ( $2 \times \text{SH 806 HQ}$  and  $\text{SH 802 HQ}$ ) and coupled with a differential refractometer (RI-101), a UV detector (Varian Prostar) set at 290 nm and a multi-angle laser light scattering (MALS) detector (Wyatt Dawn Heleos). The flow rate of eluent was  $1 \text{ ml min}^{-1}$  and the following eluent compositions were used (eluent was passed through a  $0.22 \mu\text{m}$  filter prior to use):

#### PAm-*b*-PVPA

Aqueous solution containing 0.1 M NaCl, 0.25 mM  $\text{NaH}_2\text{PO}_4$  and 0.25 mM  $\text{Na}_2\text{HPO}_4$ . The relevant values of  $\text{dn/dc}$  in this eluent are:  $0.099 \text{ ml g}^{-1}$  (PVPA,  $M_n \sim 750 \text{ g}\cdot\text{mol}^{-1}$ );  $0.105 \text{ ml g}^{-1}$  (PVPA,  $M_n \sim 2400 \text{ g}\cdot\text{mol}^{-1}$ ) and  $0.177 \text{ ml g}^{-1}$  (PAm) [57].

#### PAm-*b*-PAA

Aqueous solution containing 0.1 M  $\text{NaNO}_3$  and 200 ppm  $\text{NaN}_3$ . The relevant values of  $\text{dn/dc}$  in this eluent are:  $0.151 \text{ ml g}^{-1}$  (PAA) and  $0.185 \text{ ml g}^{-1}$  (PAm) [58]. The  $\text{dn/dc}$  of block copolymers were calculated from the average of the  $\text{dn/dc}$  of the constituent homopolymers, weighted according to their mass fraction. Samples were prepared at a concentration of  $0.5 \text{ mg ml}^{-1}$  and filtered through a  $0.45 \mu\text{m}$  filter prior to injection.

Dynamic light scattering (DLS) measurements were performed at  $25^\circ\text{C}$  using a Malvern Autosizer 4800 spectrogoniometer, with a 50 mW laser source operating at 532 nm. Scattered intensities ( $I$ ) of the DHBC solutions and of the complex mixture solutions were measured at a scattering angle of  $90^\circ$ , they were then corrected by the polymer weight concentration ( $C$ ) to yield  $I/C$  values. Intensity-averaged hydrodynamic diameters were determined at  $90^\circ$ .

### 2.3. Aqueous MADIX copolymerization of VPA or AA from PAm-XA1 macroxanthate

#### 2.3.1. Aqueous synthesis of PAm-XA1 macroxanthates

The synthesis of the macroxanthate  $\text{PAm}_{5000}\text{-XA1}$  was performed as follows: xanthate XA1 (4.77 g) was dissolved in 35.50 g of ethanol and degassed by bubbling argon for 30 min at ambient temperature while stirring. Separately, ACP (1 g) was dissolved in 10 g of distilled water and then added to the xanthate solution. The mixture was placed in a thermostated bath at  $70^\circ\text{C}$  and 220 g of 50% wt solution of Am dissolved in 90 g of distilled water were added dropwise to the xanthate/ACP solution at a rate of  $2 \text{ ml min}^{-1}$ . On completion of the addition, the reaction mixture was kept at  $70^\circ\text{C}$  for 2 h. Finally the ethanol was evaporated under vacuum. The Am conversion was higher than 99.9% (determined by  $^1\text{H}$  NMR), the  $M_{n,\text{MALS}}$  was  $5350 \text{ g}\cdot\text{mol}^{-1}$  ( $\text{dn/dc} = 0.177 \text{ ml g}^{-1}$ ) and the dry extract was 36% wt.

A similar procedure was followed for the synthesis of  $\text{PAm}_{10000}\text{-XA1}$ . The Am conversion was also higher than 99.9% (determined by  $^1\text{H}$  NMR), the  $M_{n,\text{MALS}}$  was  $11,470 \text{ g}\cdot\text{mol}^{-1}$  and the dry extract was 33% wt.

#### 2.3.2. General procedure for MADIX copolymerization of VPA from PAm-XA1

In a typical procedure,  $\text{PAm}_{5000}\text{-XA1}$  macroxanthate (58.80 g of the 36% wt aqueous solution), VPA monomer (6.70 g) and AIBA (0.40 g) were placed in a Schlenk flask. The solution was degassed by purging with argon for 30 min and heated to  $65^\circ\text{C}$  under stirring in a thermostated oil bath. The reaction was stopped after 8 h. The conversion of VPA was 36% (determined by  $^{31}\text{P}$  NMR).

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