



Synthesis and self-association in dilute aqueous solution of hydrophobically modified polycations and polyampholytes based on 4-vinylbenzyl chloride



Nikos D. Koromilas, Georgia Ch. Lainiotti, Evdokia K. Oikonomou¹, Georgios Bokias*, Joannis K. Kallitsis*

Department of Chemistry, University of Patras, 26504 Patras, Greece

ARTICLE INFO

Article history:

Received 20 December 2013

Received in revised form 6 February 2014

Accepted 10 February 2014

Available online 20 February 2014

Keywords:

Hydrophobically modified water-soluble polymers

Free radical copolymerization

Quaternization

Polyelectrolytes

Polyampholytes

Self-association

ABSTRACT

Linear copolymers, P(MMA-co-VBC) and P(SSNa-co-VBC), of 4-vinylbenzyl chloride (VBC) with hydrophobic (methyl methacrylate, MMA) or hydrophilic anionic (sodium styrene sulfonate, SSNa) monomers were prepared through free radical polymerization. The molar content of MMA or SSNa units ranges from 0% up to 90% (mol/mol). After polymerization, VBC was quaternized using short chain (triethylamine, TEAM) or long chain (*N,N*-dimethylhexadecylamine, HAM) amines. FTIR and ¹H NMR verified that the P(MMA-co-VBC) series were fully quaternized, leading to hydrophobic polycations P(MMA-co-VBCTEAM) or hydrophobic/hydrophobically modified polycations P(MMA-co-VBCHAM), while the P(SSNa-co-VBC) series were partially quaternized, leading to polyampholytes P(SSNa-co-VBCTEAM-co-VBC) and hydrophobically modified polyampholytes P(SSNa-co-VBCHAM-co-VBC). To overcome partial quaternization problems, hydrophobically modified polyampholytes P(SSNa-co-VBCHAM) were synthesized through direct polymerization of SSNa and vinylbenzyl dimethylhexadecylammonium chloride (VBCHAM). The solubility and self-association behavior of these copolymers in water were investigated through turbidimetry, Nile Red fluorescence probing, dynamic light scattering and ζ -potential measurements. It is found that phase separation and self-association are mostly affected by the copolymer's net charge and not the nature of the hydrophobic or charged unit. Moreover, the introduction of cationic amphiphilic units (VBCHAM) not only favors the self-association of the final hydrophobically modified polymers, forming aggregates in aqueous solution, but may also lead to polymers with antimicrobial activity.

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1. Introduction

The synthesis of novel copolymers containing functional groups has attracted great scientific and technological interest, which is continuously increasing in the last

two decades. An example of polymer functionality of particular importance is amphiphilicity, resulting in original interesting properties in water environments, related to intrinsic self-association phenomena [1–5]. This characteristic behavior makes such polymeric materials attractive for a large variety of potential applications like mineral separation, foodstuff, water treatment, detergency, cosmetics, enhanced oil recovery [6–9], as well as microreactors, microcapsules and drug delivery systems [10–13]. Moreover, they can be used as additives in aqueous fluids, due to their ability to control rheology and colloidal

* Corresponding authors. Tel.: +30 2610962952; fax: +30 2610997122.

E-mail addresses: nikoskoromil@upatras.gr (N.D. Koromilas), glainiotti@upatras.gr (G.Ch. Lainiotti), evi.oikonomou@espci.fr (E.K. Oikonomou), bokias@upatras.gr (G. Bokias), kallitsi@upatras.gr (J.K. Kallitsis).

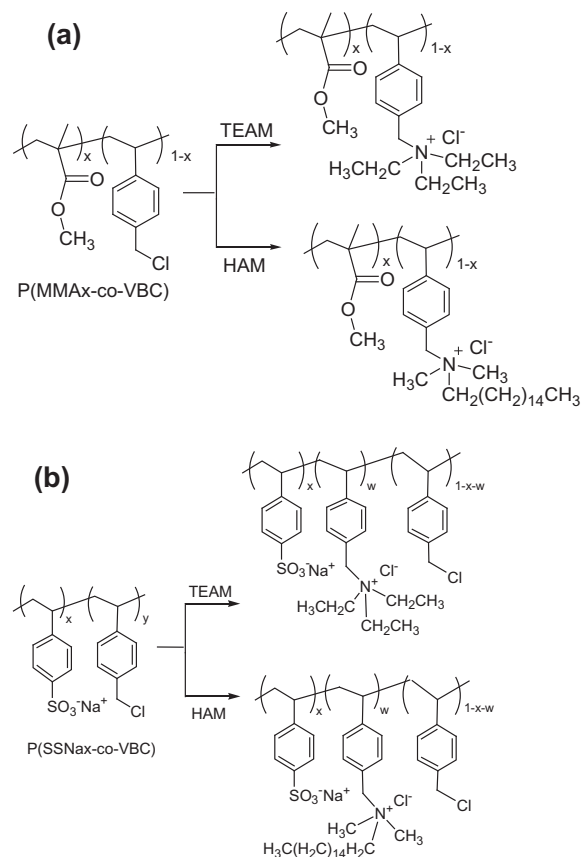
¹ Present address: Matière Molle et Chimie, ESPCI ParisTech-CNRS, UMR-7167, Paris, France.

stability of these fluids. Amphiphilic polymers can be divided in two categories: block and random polymers. The aggregation and self-association behavior of random copolymers is less clear than those of block copolymers, due to their complicated nature [14,15] and the fact that the characteristics of block copolymers are directly linked to the incompatibility between the blocks. On the other hand, amphiphilic random copolymers are usually more easily synthesized through, for instance, copolymerization of hydrophilic and hydrophobic units or post-modification of hydrophilic polymers with hydrophobic functionalities.

When the hydrophobic units contain not only simple water-insoluble monomers but also a long alkyl chain (typically, dodecyl- or octadecyl-chains), a comb-like architecture is obtained and the products are usually called hydrophobically modified water-soluble polymers (HMWSP) [16], since the backbone is typically a water-soluble polymer, like poly(sodium acrylate) [17–19], polyacrylamides [20–23] or natural derivatives [24–26]. While the hydrophobic alkyl-containing units are in most cases nonionic, HMWSP have also been developed based on charged (usually cationic) amphiphilic units and a nonionic or similarly charged backbone [27]. The combination of charged amphiphilic units (instead of hydrophobic alkyl-containing units) with hydrophobic or oppositely charged units (giving rise to hydrophobically modified polyampholytes) is rather rare. In fact, most reports dealing with hydrophobically modified polyampholytes usually refer to terpolymers of oppositely charged units and hydrophobic units [28–33].

Apart from HMWSP, we have also focused on the development of antimicrobial polymeric materials, with potential biocidal activity arising from the incorporation of ammonium type salts containing long alkyl chains. In fact, research on antimicrobial polymers has attracted considerable attention over the past years, due to their high efficacy in preventing and controlling the microbial infection, as compared to the monomeric biocidal species. Their use is of great importance in various fields, especially in medical devices, water purification, drugs, textiles, food packages, antifouling paints and fish nets [34–38]. A class of antimicrobial polymers is those containing quaternary ammonium groups bearing long alkyl chains. The mechanism of their action is well known for years and their antimicrobial activity has been tested against various microorganisms [39,40].

Depending on the way of the incorporation of these antimicrobial agents onto polymers, they can be classified in two categories: covalently attached or ionically bound. While previously [41–43] we focused on the second kind of attachment of the biocidal units, the first kind of attachment is our focus in the present work. Thus, initially, we adopted a post-polymerization quaternization methodology, as shown in Scheme 1. According to this procedure, copolymers (P(MMAx-co-VBC) and P(SSNax-co-VBC)) of 4-vinylbenzyl chloride (VBC) with methyl methacrylate (MMA) and sodium styrene sulfonate (SSNa), respectively, were first synthesized through free radical polymerization (FRP). The quaternization of VBC units with *N,N*-dimethylhexadecylamine (HAM) leads to potential antimicro-



Scheme 1. Reaction steps for the synthesis of the quaternized MMA-based and SSNa-based copolymers. The remaining VBC units in (b) could be partially hydrolyzed.

bial polymers with covalently attached biocidal units. For comparison reasons, quaternization of VBC units with a hydrophilic amine, namely triethylamine (TEAM), was also performed. The resulting products might also exhibit some antimicrobial activity, despite the short alkyl chain, as it has been reported in literature for poly[trialkyl(vinylbenzyl)ammonium chloride]s [44].

While this methodology was successful for the MMA-based products, leading to P(MMA_x-co-VBTEAM) and P(MMA_x-co-VBCHAM) copolymer series, we faced problems with the SSNa-based products, probably arising from the hydrolysis of chloromethyl group [45]. Hydrolysis of VBC, as reported in literature [46,47], occurs at high temperatures in the presence of water. The increased temperatures employed in our synthetic protocol, in combination with the use of hydrophilic and hygroscopic SSNa, suggest that hydrolysis is an important issue in these series of copolymers. Thus, as it will be shown in the next sections, terpolymers (P(SSNa_x-co-VBTEAM_y-co-VBC) and P(SSNa_x-co-VBCHAM-co-VBC)) are, in fact, obtained. To overcome this difficulty, for some of the desired products, we also employed a pre-polymerization quaternization methodology, as described in Scheme 2: after the successful quaternization of VBC with HAM, the free radical copolymerization of the resulting monomer vinylbenzyl

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