Chemical Engineering Journal 258 (2014) 386–393

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption of bisphenol-A by pH-responsive polymer grafted on porous polyethylene vinyl acetate disk: Effect of the side-chain length of hydrophobic component in polymer on adsorption

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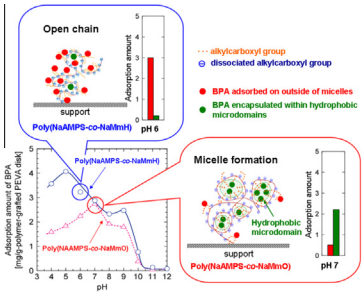
HIGHLIGHTS

- NaMmH and NaMmO were protonated at pH value lower than 7.
- Poly(NaAMPS-*co*-NaMmO) formed unimolecular micelles by the protonation of NaMmO.
- Micelle formation of poly(NaAMPS-*co*-NaMmH) was not observed at any pH.
- Poly(NaAMPS-*co*-NaMmO) encapsulated BPA stably within hydrophobic microdomains.
- The BPA adsorbed on poly(NaAMPS-*co*-NaMmH) easily desorbed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 June 2014
Received in revised form 22 July 2014
Accepted 23 July 2014
Available online 1 August 2014

Keywords:
pH-responsive unimolecular micelle
Peroxide plasma polymerization method
Porous polyethylene vinyl acetate
Adsorption
Bisphenol-A
Side-chain length

ABSTRACT

Random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) and sodium 6-methacrylamidohexanoate (NaMmH), [poly(NaAMPS-*co*-NaMmH)], and NaAMPS and 8-methacrylamidooctanoate (NaMmO), [poly(NaAMPS-*co*-NaMmO)], were grafted on the surface of a porous polyethylene vinyl acetate (PEVA) disk by peroxide plasma polymerization, respectively. By permeating the pH-adjusted bisphenol-A (BPA) solution through the disk, the adsorption behavior of BPA was examined. The pendant alkyl carboxyl groups in the hydrophobic components, i.e., NaMmH and NaMmO, were protonated at pH values lower than 7. The formation of polymer colloid composed of a single polymer chain, i.e., unimolecular micelle, by poly(NaAMPS-*co*-NaMmO) was observed according to the protonation of NaMmO. In contrast, polymer colloid formation by poly(NaAMPS-*co*-NaMmH) was not observed, even when NaMmH was protonated. The adsorption of BPA on the polymer-grafted PEVA disks increased abruptly at pH 10, although the protonation of NaMmH and NaMmO was not observed at this pH. Furthermore, the adsorption amount of BPA increased at pH 7, the pH at which the protonation of NaMmH and NaMmO occurred. In the case of poly(NaAMPS-*co*-NaMmO), BPA molecules were effectively and stably encapsulated in the hydrophobic microdomains in the micelles at pH values lower than 7. In contrast, in the case of poly(NaAMPS-*co*-NaMmH), BPA easily desorbed by permeation of an acidic solution through the disk.

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http://dx.doi.org/10.1016/j.cej.2014.07.100
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1. Introduction

Micelle composed of a single polymer chain such as hyperbranched polymer or dendrimer is referred to as a unimolecular micelle [1–10]. In addition, a few studies recently reported the formation of unimolecular micelles by linear random copolymers in response to solution pH [11–16]. These copolymers were composed of sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) as the hydrophilic component and a pH-sensitive hydrophobic component such as 8-acrylamidooctanoate (NaAmO) or sodium 11-acrylamidoundecanoate (NaAmU), i.e., poly(NaAMPS-*co*-NaAmO) or poly(NaAMPS-*co*-NaAmU) [14]. It was also reported that a random copolymer of NaAMPS and 12-methacrylamidododecanoate (NaMmD), i.e., poly(NaAMPS-*co*-NaMmD), exhibited pH-induced formation and disruption of unimolecular micelles [17,18]. Fig. 1 shows the structure of poly(NaAMPS-*co*-NaMmD).

The mechanism of the pH-induced formation and disruption of unimolecular micelles by these copolymers is as follows [13,17]: The formation of unimolecular micelles is induced by the protonation of the pendant alkyl carboxyl groups in the hydrophobic components, i.e., NaAmO, NaAmU, and NaMmD. Poly(NaAMPS-*co*-NaAmO), poly(NaAMPS-*co*-NaAmU), and poly(NaAMPS-*co*-NaMmD) form unimolecular micelles at pH ranges of 6–7, 7–8, and 9–10, respectively [14,17]. This implies that the pH at which the unimolecular micelles are formed can be controlled by the length of the hydrophobic components, i.e., the number of methylene groups in the pendant hydrophobic group.

Since the formation of unimolecular micelles by these copolymers is only dependent on the solution pH, there is no critical micelle concentration. Furthermore, the hydrophobic microdomains in the micelles stably encapsulate hydrophobic molecules via hydrophobic interactions. Based on these characteristics, we studied the adsorption behavior of bisphenol-A (BPA), a representative hydrophobic endocrine disruptor, using poly(NaAMPS-*co*-NaMmD) grafted onto polypropylene nonwoven fabrics by plasma-initiated polymerization [17]. The adsorption of BPA depended on the pH of the BPA solution, and was maximized at pH values around 9–10, which corresponded to the pH around which the protonation of NaMmD occurred. As expected, reversible adsorption and desorption of BPA via a pH swing was achieved. The adsorption of BPA resulted from the encapsulation of BPA within the hydrophobic microdomains in the micelles and the adsorption on the pendant hydrophobic MmD groups outside of the micelles by hydrophobic interactions, and the amount of BPA encapsulated within the hydrophobic microdomains increased by a gradual change in the pH of the BPA solution.

Furthermore, in order to gradually change the pH of the BPA solution and/or to facilitate continuous adsorption, we prepared a porous polyethylene vinyl acetate (PEVA) disk, the pore surface on which poly(NaAMPS-*co*-NaMmD) was grafted by plasma-initiated polymerization. The adsorption behaviors of BPA were examined by permeating the pH-adjusted BPA solution through this polymer-grafted PEVA disk, which was treated with an aqueous solution of NaOH (pH 13) [18]. Permeating a BPA solution with a pH of 10 resulted in an increase in the amount of BPA encapsulated within the hydrophobic microdomains. The amount that was encapsulated was maximized when the molar ratio of NaAMPS and NaMmD was 1:1, although the adsorption amount increased with increasing molar ratios of hydrophobic NaMmD.

Some adsorbents of hydrophobic materials such as activated carbon and sand have been reported [19–21]. The adsorption amount of hydrophobic materials by these adsorbents depends on the concentration of hydrophobic material, which make it difficult to adsorb the hydrophobic material at a lower concentration. Furthermore, the regeneration of these adsorbents requires complicated procedure and high cost. In contrast, it is expected that the adsorbent using pH-responsive unimolecular micelles proposed in our study adsorbs hydrophobic materials at a lower concentration. Furthermore, the adsorbent is easily regenerated by the pH swing.

However, pH 9–10, the pH at which the formation of unimolecular micelles by poly(NaAMPS-*co*-NaMmD) occurs, is too high for actual adsorption operations. The length of the hydrophobic pendant of hydrophobic component affects the pH of unimolecular micelle formation, as mentioned above. In this work, hydrophobic components with hydrophobic pendants of different lengths, i.e., sodium 6-methacrylamidohexanoate (NaMmH) and 8-methacrylamidooctanoate (NaMmO), were synthesized and the copolymers of these hydrophobic components and NaAMPS were grafted on the pore surface of PEVA by a manner similar to that described in our previous study, and the adsorption behavior of BPA was examined.

2. Experimental section

2.1. Synthesis of MmH and MmO

Fig. 2 shows the synthetic procedure utilized to fabricate MmH and MmO. MmH was synthesized from 6-aminohexanoic acid

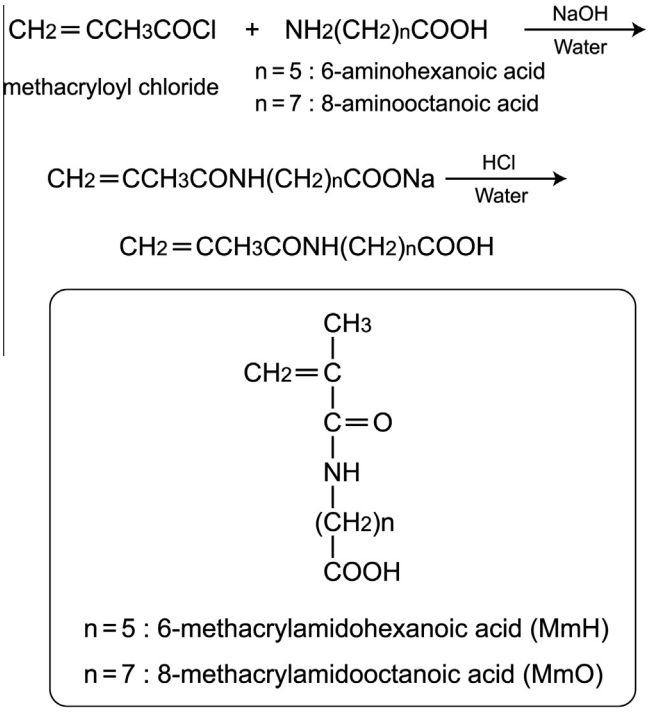

Fig. 2. Synthetic procedures for MmH and MmO.

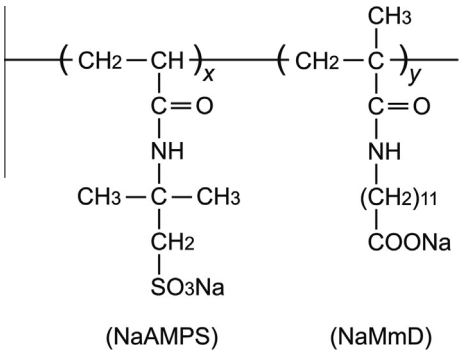

Fig. 1. Structure of poly(NaAMPS-*co*-NaMmD).

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