



Temperature and pH-responsive properties of poly(styrene-co-maleic anhydride)-grafting poly(oxypropylene)-amines

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ARTICLE INFO

Article history:

Received 26 February 2009

Accepted 27 March 2009

Available online 7 April 2009

Keywords:

Temperature-responsive

pH-responsive

Poly(styrene-co-maleic anhydride)

Poly(oxypropylene)-amine

ABSTRACT

A series of temperature- and pH-responsive copolymers were prepared by grafting poly(oxypropylene)-diamines (POP-amine) onto poly(styrene-co-maleic anhydride) (SMA) copolymers. Owing to the presence of poly(oxypropylene)-segments in the pendants and their expressive hydrogen bonding properties, the copolymers exhibited lower critical solution temperature (LCST) behavior in water with a range of 11–49 °C depending on the POP-segmental weight and the SMA backbone structure. Furthermore, the co-existence of –NH₂ termini in the pendants and amidoacids in the linking sites in the structures rendered the copolymers also responsive to environmental pH changes. Structural variations in the SMA backbones, particularly the ratio of styrene/maleic anhydride monomers, POP lengths, and amine functionalities largely influenced the copolymer aggregation in the medium with different pH or thermal conditions. The responsiveness was correlated to the surface morphologies observed by tapping/phase mode atomic force microscopy (TM-AFM) on Mica film surface and also fluorescent properties in aqueous solution.

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1. Introduction

Stimuli-responsive polymers are interesting materials because of their wide scope of industrial applications such as smart polymeric materials [1,2], drug delivery [3,4], membrane morphology control [5], biomaterial separation [6,7] and biosensing devices [8], etc. These polymers with a controllable conformation may respond to external stimuli such as changes in temperature [9,10], pH [11], salt concentration [12], light [13], etc. In the case of temperature-responsiveness, the behavior is often originated from the decreases of the hydrogen bonding force between water and polymer segments when elevating the medium temperature. At lower temperatures the polymers exhibit an intensive intermolecular hydrogen bonding with the water medium. Increasing the temperature of the polymer/water mixture promotes the hydrophobic interaction among the polymer chains, causing a coil-to-globule aggregation and consequently an increased opacity of the solution. On the other hand, pH-responsive copolymers generally consist of carboxylic acid or amine functionalities in the structures. The environmental pH influences dissociation and ionization of the acid or base functionalities. These changes in columbic charges can alter the hydrophilic interaction of the polymer chains and result a transformation of polymer aggregate conformations in water. In the literature, triblock poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) (POE-POP-POE) [14] copoly-

mers and poly(*N*-isopropylacrylamide) (PNiPAM) [15–17] are two classes of thermally responsive copolymers that have received a considerable attention. In these structures, both POE and amide functionalities are responsible for generating hydrogen bonding forces that respond to the temperature changes. For the pH-responsive polymers, examples are polyether-modified poly(-acrylic acid) [18,19], and poly[(2-diethylamino)ethyl methacrylate] [20,21], poly(4-vinylpyridine) [22]. The combination of temperature- and pH-responsive polymers may be applied in drug delivery and biomedical uses [23,24].

In this article, we reveal a new class of copolymers that are prepared from the reaction of SMA copolymers and poly(oxypropylene)-diamines and possess potentially both temperature- and pH-responsive properties. The copolymers are constructed in a comb-branched structure with a SMA backbone (styrene and maleic anhydride copolymers) and multiple poly(oxyalkylene)-amine pendants [25]. Specifically, the poly(oxypropylene) (POP) segments in the structures play a suitable role for the hydrogen bonding responsiveness. By judicious selections of the backbones with different styrene/maleic anhydride ratios and the poly(oxypropylene)-diamines (POP-amines) pendants in a M_w range of 200–2000 g/mol, the copolymers may be tailored to exhibit unique properties with both of temperature- and pH-responsiveness. In addition, the temperature-depending polymer morphologies [26,27] were observed by using atomic force microscopy (TM-AFM). The stimuli-responsive properties and aggregated conformations are structurally correlated to the functionalities of amine, carboxylic acid and POP segment in the SMA-derived copolymers.

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2. Experimental

2.1. Materials

Poly(styrene-co-maleic anhydride) copolymers with different styrene/maleic anhydride (ST/MA) molar ratios of 1/1 and 3/1 in the backbone (at 6000 M_w by GPC and names of SMA1000, SMA3000, respectively) were purchased from Aldrich Chemical Co. Poly(oxyalkylene)-diamines are commercially available polyether amines which have different poly(oxyethylene)- (POE) and poly(oxypropylene)- (POP) backbones in the structures, derived from the amination of polyols such as polyethylene glycols, polypropylene glycols and their mixed poly(oxyethylene-oxypropylene) [28,29]. The poly(oxypropylene)-diamines (POP-amines) with molecular weights of 230 and 400 M_w are hydrophilic and water-soluble diamines (POP230 and POP400, respectively), while the 2000 M_w POP2000 is a hydrophobic and water-insoluble diamine. All of these polyether amines were obtained from Aldrich Chemical Co. or Huntsman Chemical Co.

2.2. Instruments measurement

Gel permeation chromatography (GPC) was performed on a Waters apparatus (515 HPLC pump, 717 auto-sample, and 2410 refractive index detector). The Waters Stygel column set was used for analyzing the relative molecular weights under a 1.0 ml/min flow rate of tetrahydrofuran (THF), calibrated against the polystyrene standards. The coil-to-globule transition was accompanied with an increase in opacity of the comb-branched copolymer solutions, which was measured using a UV-visible spectrophotometer (Shimadze UV mini 1240) at 550 nm wavelengths at varying temperatures. The transmittance of the polymer solutions decreased as the temperature increased. The polymer solution concentration at 1 wt%, and the transmittance was recorded at 5 °C intervals. The lower critical solution temperature (LCST) of the comb-branched copolymers was defined as the temperature at which the transmittance was 50% at 550 nm.

Thermal analysis of the coil-to-globule transition was carried out using a differential scanning calorimeter (DSC, Perkin Elmer Pyris 6). The sample prepared in 10 wt% in aqueous solution and 7–9 mg on a sealed aluminum pan was generally used. A temperature range of 2–60 °C at a heating rate of 1 °C min⁻¹ with a nitrogen flow of 20 ml min⁻¹ was used. Tapping-mode atomic force microscopy (TM-AFM) was performed by a SPA-400HV with an SPI3800N controller (Seiko Instruments Industry Co., Ltd.) The cantilever used was fabricated from Si with a spring constant of 40 N/m and a resonance frequency of 320 kHz. TM-AFM is used to analyze the surface morphologies [30] of the prepared copolymers at different temperatures. The samples of copolymers for the TM-AFM observation are prepared at the concentrations of 1 wt% in de-ionized water, adjusted temperatures and spin-coated on a Mica substrate (3 × 3 cm²) at a spinning rate of 1000 rpm for 30 s. After spin-coating, the specimen was dried in a vacuum oven at r.t. for 3 h. The average particle size was estimated using a particle size analyzer (90 Plus Brookhaven Instrument Corp.) equipped with a 15 mW solid-state laser (675 nm). Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902A and operated at 80 kV. The samples were prepared in aqueous solution at 0.1 wt% and then dropped on a copper grid. The specimen was conditioned under a vacuum for 24 h to dryness.

2.3. Synthesis of the SMA-POP copolymers

In preparing the copolymers, it is crucial to dry the SMA and POP-amine starting materials at 120 °C in an oven under reduced pressure for 6 h before using. A twofold excess of POP-amines to

Table 1

Gel permeation chromatography and LCST of SMA-POP copolymers.

SMA-POP copolymers	GPC		LCST ^b (°C)
	M_w	(M_w/M_n)	
SMA1000	6000	1.8	N.F.
SMA3000	6000	2.0	N.F.
POP230	230	—	>60
POP400	400	—	>60
POP2000	2900	1.2	25
SMA3000/POP230	— ^a	— ^a	49
SMA3000/POP400	— ^a	— ^a	14
SMA3000/POP2000	13,800	1.2	11
SMA1000/POP2000	—	—	18

^a Not determined due to insolubility in THF; M_w (weight-averaged molecular-weight) determined by gel permeation chromatography using polystyrene as the standard; polydispersity (M_w/M_n).

^b LCST determined in 1 wt% aqueous solution at the temperatures showing a 50% transmittance at 550 nm wavelength; N.F. (not found).

SMA was employed to avoid the possible cross-linking side reaction between the SMA and diamines. An example of preparing POP2000-grafted SMA3000 is described below. To a three-necked and round-bottomed flask, equipped with a mechanical stirrer, POP2000 (97.6 g, 48.8 mmol) was charged and followed by the drop-wise addition of SMA3000 (10.0 g, 24.4 mmol of MA) in THF (50 mL). Under constant stirring, the solution temperature was maintained at 25 °C for 2–3 h. During the process, samples were taken periodically and monitored by using a FT-IR. It was monitored that the absorption peaks of anhydride functionality at 1780 cm⁻¹ (s) and 1850 cm⁻¹ (w) disappeared at the expense of the peaks at 1734 cm⁻¹ and 1690 cm⁻¹ for the carboxylic acid and amide, respectively. The characteristic absorption at 1100 cm⁻¹ of oxyalkylene was observed. The reaction products were extracted from the unreacted POP-amines several times by an ethanol/water mixture (1:2 by volume). The purified product was then analyzed by GPC analysis (Table 1) and an amine titration. The amine equivalents of these copolymers were estimated to be 560, 500, 2000 mequiv/g for SMA3000-POP230, SMA3000-POP400, and SMA3000-POP2000, respectively.

3. Results and discussion

3.1. Synthesis and characterization the SMA-POP polyamines

A series of comb-branched polyamines were prepared by grafting poly(oxypropylene)-diamines (POP-amines) onto the poly(styrene-co-maleic anhydride) (SMA) copolymers [31], as shown in Scheme 1. The synthesis involves the reaction of cyclic anhydride and primary amine (—NH₂) to generate amidoacid functionalities in the linking sites. The grafted POP-amines could vary the polymer solvating property in water, depending on the POP molecular weights ranging from 230 to 2000 g/mol. The uses of high molecular-weight and an excess equivalent amount of POP-amine at 2000 g/mol were required to prepare the low gelled products. The excess POP-amines were then removed by extraction with ethanol/water mixtures during the work-up process. The product consistency was confirmed by the analyses of FT-IR absorption and amine titration. The synthesis allows the preparation of a series of SMA-POP polyamines with varied styrene/anhydride ratios in the SMA backbone and the POP-amine molecular-weight. In addition, the copolymers are constituted with —NH₂ termini on the pendants and —COOH functionalities on the backbone. The combination of these organic functionalities rendered this class of copolymers with the dual nature of responsiveness for temperature and pH changes in the medium.

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