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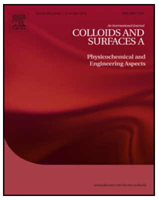

Electrospun thermo-responsive nanofibers of poly(hydroxyethylacrylate-*co*-coumaryl acrylate-*co*-ethylmethacrylate)

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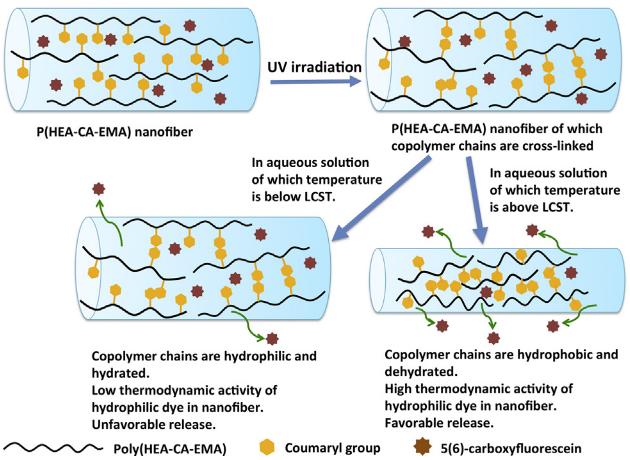
HIGHLIGHTS

- The copolymers of HEA/CA/EMA(P(HEA–CA–EMA)) exhibited LCST behavior in aqueous solution.
- P(HEA–CA–EMA) solutions could be spun into nanofibers when the concentration was 60–80%.
- The nanofibers were UV-treated to cross-link the constituent copolymer chains.
- The release of CF from the nanofibers was suppressed below LCST and promoted above LCST.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermo-responsive nanofibers were prepared by electrospinning poly(hydroxylethylacrylate-*co*-coumaryl acrylate-*co*-ethylmethacrylate) (P(HEA–CA–EMA)) dissolved in methanol. P(HEA–CA–EMA)s were prepared by free radical reaction using the reaction mixture of which HEA/CA/EMA molar ratio was 98:0:2, 96:2:2, 95:2.5:2.5, 94:3:3, and 92:4:4. P(HEA–CA–EMA) solutions (30% (w/v), in HEPES buffer (30 mM, pH 7.4)) became gel after they were subjected to UV irradiation (254 nm, 6 W) for 20 h. P(HEA–CA–EMA) exhibited lower critical solution temperature (LCST) behavior in aqueous solution and the LCST decreased from about 40 °C to below 20 °C, when the content of hydrophobic monomers (CA and EMA) increased from 0.7% to 5.5%. By an electrospinning process, P(HEA–CA–EMA) solutions in methanol were micronized into beads when the copolymer concentration was relatively low (e.g., 30%), and they were spun into nanofibers when the concentration was 60–80%. The nanofibers were subjected to UV irradiation to cross-link the constituent copolymer chains. The release of CF (a hydrophilic dye) from UV-treated P(HEA–CA–EMA) nanofibers was suppressed below LCST and promoted above LCST. As long as the temperature of release medium was higher than LCST, the release degree at a given temperature was higher when the nanofiber was composed of a copolymer exhibiting lower LCST. As LCST decreases, the dehydration degree and the hydrophobicity of the copolymers at a given temperature will increase thus the thermodynamic activity of the hydrophilic dye in the nanofiber will also increase, giving a rise to a higher release degree.

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1. Introduction

Polymer nanofiber has been finding its application in many fields, because it has unique property, such as large surface area to volume ratio and excellent mechanical property, owing to its nanoscale diameter (10–100 nm) [1–4]. Many methods including drawing, template synthesis, phase separation, self-assembly and electrospinning have been exploited to prepare polymer nanofiber. However, some of the methods have a limit for the fabrication of nanofiber. For example, polymer solution should be viscoelastic when drawing method is adopted. One-by-one continuous nanofiber could not be prepared by template synthesis. It takes a long time to fabricate nanofiber when phase separation and self-assembly are used. Electrospinning is claimed to circumvent the shortcomings other methods have, and to be one of potential methods to produce one-by-one continuous nanofiber in a large quantity [4–11]. Electrospinning system is composed of a voltage supplier, a capillary tube having a small orifice, and a metal collecting screen. When a high voltage is applied by the voltage supplier, polymer solution or polymer melt is electrically charged, and they are ejected as jet out of the orifice. While the jet travels from the orifice to the collector, the jet becomes dry fiber because the solvent is evaporated, and the fiber is deposited on the collector to form non-woven membrane. The polymer solution or melt is in contact with an electrode and the collector is connected to the opposite charged electrode or, in most cases, grounded. If electric field is applied to the liquid contained in the capillary tube, the surface of liquid is electrically charged. Thus, the electrode in the liquid will push the liquid out of the orifice by electrostatic repulsion and the opposite electrode connected to the collector attracts the liquid. As a result, the fluid surface takes a conical shape called Taylor cone. When the repulsion force is greater than the surface tension of the liquid, Taylor cone send out the charged jet of the liquid from its tip. While traveling from the tip of Taylor cone to collector, the charged jet is elongated to become thin and the solvent evaporates, leading to the formation of a dry charged polymer fiber. In case of polymer melt, the liquid jet becomes solid fiber upon cooling during the traveling to the collector [12–14]. Polymer fibers spun by electrospinning can be applied to protective clothing, electrets filter, optical sensor, drug delivery system, microelectronic wiring, wound healing, tissue engineering, hemostatic agent, conductive fiber, catalyst, anti-microbial agent, membrane, photovoltaic and conductive polymer, cosmetic, etc. [15–17].

In this study, thermo-responsive nanofibers were prepared by electrospinning poly(hydroxylethylacrylate-*co*-coumaryl acrylate-*co*-ethylmethacrylate) (P(HEA–CA–EMA)) dissolved in methanol. P(HEA–CA–EMA) was obtained by copolymerizing HEA with CA and EMA (hydrophobic monomers) by free radical reaction. The copolymer showed LCST behavior in an aqueous solution. The copolymer of HEA and hydrophobic monomers was reported to exhibit a lower critical solution temperature (LCST) in an aqueous solution [18–20]. The electrospun P(HEA–CA–EMA) nanofibers were subjected to UV irradiation to cross-link the copolymer chains of the nanofiber. Coumarin and its derivatives can be dimerized to form cyclobutane bridge under the irradiation of UV light [21,22]. P(HEA–CA–EMA) chains can be cross-linked by UV irradiation owing to its CA residues. In order to investigate the thermo-responsive release property of the UV-treated P(HEA–CA–EMA) nanofiber, 5(6)-carboxyfluorescein (CF, a hydrophilic dye) was loaded in the nanofiber. The release of the hydrophilic dye from the nanofiber in an aqueous phase would be unfavorable when the temperature of release medium is below LCST, possibly because below LCST, the P(HEA–CA–EMA) nanofiber is hydrophilic and hydrated, thus the thermodynamic activity of the hydrophilic dye in the hydrophilic nanofiber is relatively low. On the contrary, the release of the hydrophilic dye from the nanofiber would be favorable when the temperature of release medium is above LCST, possibly because above LCST, the P(HEA–CA–EMA) nanofiber is hydrophobic and dehydrated, thus the thermodynamic activity of the hydrophilic dye in the hydrophobic nanofiber is relatively high (Fig. 1). The LCST of the copolymer was controlled by adjusting the content of the hydrophobic monomers (CA and EMA), and the effect of LCST on the temperature-dependent release of CF from P(HEA–CA–EMA) nanofibers was extensively examined.

2. Materials and methods

2.1. Materials

Acryloyl chloride (M.W. 90.51) was purchased from TCI (Tokyo, Japan). 2-Hydroxyethyl acrylate (HEA, M.W. 116.12), 7-hydroxy coumarin (M.W. 162.14), ethyl methacrylate (EMA, M.W. 114.14), 5(6)-carboxyfluorescein (M.W. 376.32), ethanol (M.W. 46.07), sodium hydroxide (M.W. 40.00), and dimethylformamide (DMF) were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). α,α′-Azobisisobutyronitrile (AIBN, M.W. 164.21) was provided by Junsei Chemical Co. (Tokyo, Japan). *N*-(2-Hydroxyethyl)piperazine-*N*′-(2-ethanesulfonic acid) (HEPES) was obtained from USB corporation (OH, USA).

2.2. Preparation of P(HEA–CA–EMA)s

Coumaryl acrylate (CA) was prepared as one of the comonomers of P(HEA–CA–EMA) by a method described in a previous report [23,24]. 2 g of sodium hydroxide was put in 275 ml of absolute ethanol contained in a 500 ml-round bottom flask. Then, 8.1 g of 7-hydroxy coumarin was put in the mixture of sodium hydroxide and ethanol. The mixture was heated to 60 °C and stirred for 30 min. The mixture was cooled down to 4–6 °C by immersing the flask in an ice bath. While the flask being kept in the ice bath, 4.47 ml of acryloyl chloride was added dropwise to the mixture over 60 min, then the reaction mixture was stirred for 90 min. The reaction mixture was poured into 1 l of cold water (4 °C) to precipitate out CA, then the precipitate of CA was filtered using a filter paper (Whatman, No. 2). After washing with cold water, the precipitate was dried overnight in a vacuum oven thermostated at 40 °C. P(HEA–CA–EMA) was prepared by a free radical reaction [23,24]. 9.29 g of HEA, variable amounts of CA and variable amounts of EMA were dissolved in 80 ml of DMF contained in a 250 ml 3-neck round bottom flask so that the molar ratio of HEA/CA/EMA was 98:0:2, 96:2:2, 95:2.5:2.5, 94:3:3, and 92:4:4. Then, 70 mg of AIBN, an initiator, was added to the mixture solution. The reaction mixture was extensively degassed using nitrogen gas stream for 30 min, then it was heated to 75 °C and kept at the same temperature for 12 h. After cooled down to room temperature, P(HEA–CA–EMA) was precipitated out by pouring the reaction mixture into 2.5 l of diethyl ether. After filtration, the precipitate was purified by dissolving it in DMF and precipitating it out using diethyl ether. Purified P(HEA–CA–EMA) was dried overnight in a vacuum oven thermostated at 40 °C. The copolymer prepared using the reaction mixture whose HEA/CA/EMA molar ratio was 98:0:2, 96:2:2, 95:2.5:2.5, 94:3:3, and 92:4:4 was termed as P(HEA–CA–EMA) (98:0:2), P(HEA–CA–EMA) (96:2:2), P(HEA–CA–EMA) (95:2.5:2.5), P(HEA–CA–EMA) (94:3:3), and P(HEA–CA–EMA) (92:4:4), respectively. The schematic representation of the synthesis of CA and P(HEA–CA–EMA) is shown in Scheme 1.

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