

Preparation of thermally sensitive poly[N-isopropylacrylamide-co-(maleic acid)] hydrogel membrane by electrospinning using a green solvent

Amornrat Saithongdee, Puttaruksa Varanusupakul & Apichat Imyim

To cite this article: Amornrat Saithongdee, Puttaruksa Varanusupakul & Apichat Imyim (2014) Preparation of thermally sensitive poly[N-isopropylacrylamide-co-(maleic acid)] hydrogel membrane by electrospinning using a green solvent, Green Chemistry Letters and Reviews, 7:3, 220-227, DOI: [10.1080/17518253.2014.923519](https://doi.org/10.1080/17518253.2014.923519)

To link to this article: <https://doi.org/10.1080/17518253.2014.923519>



© 2014 The Author(s). Published by Taylor & Francis.



[View supplementary material](#)



Published online: 16 Jun 2014.



[Submit your article to this journal](#)



Article views: 642



[View related articles](#)



[View Crossmark data](#)



Citing articles: 1 [View citing articles](#)

RESEARCH LETTER

Preparation of thermally sensitive poly[*N*-isopropylacrylamide-*co*-(maleic acid)] hydrogel membrane by electrospinning using a green solvent

Amornrat Saithongdee^a, Puttaruksa Varanusupakul^b and Apichat Imyim^{b*}

^aProgram of Petrochemistry and Polymer Science, Chulalongkorn University, Bangkok, Thailand; ^bDepartment of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, Thailand

(Received 20 November 2013; final version received 8 May 2014)

Poly[*N*-isopropylacrylamide-*co*-(maleic acid)], poly(NIPA-*co*-MA), was synthesized by radical polymerization in an aqueous solution composing of 35% mol *N*-isopropylacrylamide/maleic acid. Poly(NIPA-*co*-MA) hydrogel nanofibrous membrane was fabricated by electrospinning using ethanol as solvent. The electrospun nanofibers were cross-linked using diethylene glycol as cross-linker, followed by a heat-induced esterification reaction at 145°C. The average diameter of electrospun fibers was 117 ± 33 nm. The hydrogel membrane exhibited a temperature sensitive property. Its minimum and maximum water absorption ratios were 4 ± 0 g g⁻¹ at 50°C and 17 ± 4 g g⁻¹ at 34°C, respectively. An equilibrium swelling state of the electrospun membrane was reached within 5 min.

Keywords: hydrogel; electrospinning; green solvent; nanofiber; poly(*N*-isopropylacrylamide)

Introduction

Hydrogel is a cross-linked polymer which is capable of absorbing much water to maintain within its structure which remains three-dimension polymer networks. Poly(*N*-isopropylacrylamide) or poly(NIPA) is the most popular temperature-responsive hydrogel. It has a lower critical solution temperature (LCST) in water around 31–34°C (1). It can be potentially applied for many applications such as chemical separation process (2, 3), sensors (4), drug delivery devices (5), and tissue engineering scaffold (6, 7). Recently, many researches on poly(NIPA) have been communicated and showed the innovation of smart hydrogel materials (8–11). The production of a good shape material is the important key for the most successful application of the smart hydrogels.

Electrospinning or electrostatic spinning is a simple technique but versatile to produce nanofibers with diameters ranging from sub-micrometers down to nanometers. The fibers intervene each other and cause non-woven fabric or membrane. It has very large surface-to-volume, length-to-diameter ratios, and porosity. In this regard, stimuli-responsive electrospun fiber fabrication and their applications especially in biomedical applications were recently reviewed (12). However, hydrogel nanofibrous membrane is impossible to be directly generated by electrospinning because it is cross-linked polymer network which is neither soluble nor meltable. Therefore, the cross-linking of

nanofibers has to be performed with special treatment techniques such as a heat-induced cross-linking (13, 14), a UV-visible radiation-induced cross-linking (15), and an *in-situ* photo-induced polymerization (16). The heat-induced cross-linking attracts more and more interests because it is an inexpensive and simple method. Esterification is a very common thermoreactive reaction and is widely used. It has been reported that carboxylic groups on a polymer backbone of copolymer acting as a cross-linking site can easily react with diol functionality. A cross-linking agent, such as diethylene glycol (DEG), can be mixed along with the copolymer during the electrospinning process. Afterward, the membrane is activated by heat in order to induce the esterification cross-linking reaction (17, 18).

As our knowledge, only few researches concerning the fabrication of nanofibrous membrane based on poly(acrylamide) copolymer via electrospinning have been reported. For example, Lui *et al.* have fabricated electrospun poly(acrylamide)/maleic acid (MA) nanofibers using 1:1(v/v) methanol/water solution (18). Poly(NIPA)-*co*-polystyrene nanofibers have been prepared by Song *et al.* using *N,N*-dimethylformamide (DMF) (19). The preparation of poly(*N*-isopropylacrylamide-*co*-acrylic acid) and poly(*N*-isopropylacrylamide-*co*-hydroxyethyl methacrylate) nanofibrous membrane using DMF has also been reported (20). In addition, electrospun poly(NIPA) fibers have been

*Corresponding author. Email: iapichat@chula.ac.th

fabricated using three types of solvents, i.e. water, acetone, and tetrahydrofuran (THF) (21). It was found that the continuous electrospinning was impossible using water and the diameters of the fibers electrospun via acetone and THF were fairly large (5–17 μm). Therefore, this research aimed to prepare poly[*N*-isopropylacrylamide-*co*-maleic acid] hydrogel membrane by electrospinning using ethanol as a greener solvent, followed by a heat-induced esterification cross-linking reaction with DEG as a cross-linker. Its water absorption behavior was investigated at different temperatures.

Results and discussion

Cross-linking of poly(*N*IPAA-*co*-MA) with DEG

Hydrogel or water-containing gels are polymeric materials characterized by both hydrophilicity and insolubility in water (22). From Table S1 (Supplemental data), as MA amount in feed increased from 35% to 50% mol/mol (keeping other parameters constant), films were insoluble in water and able to retain film form. Conversely, below 35% mol/mol MA in feed (keeping other parameters constant), films were readily soluble in water. As generally known, poly(NIPAA) is quickly soluble in water, but it becomes water-insoluble when there is three dimensional network form in the cross-link-poly(NIPAA) (23, 24). The principal purpose of the introduction of MA moieties into the backbone of poly(NIPAA) was to make the copolymer possessing cross-link sites with maintaining the properties of the poly(NIPAA) hydrogel. Consequently, 35% mol/mol MA in feed of copolymerization was selected for further experiments.

The effect of the solvent used in film casting was also investigated. As mentioned above, the cross-linked copolymer films prepared from 35% mol/mol MA in feed with DMF as a solvent were water-insoluble in any DEG concentrations; thus, the solvent used in film casting was changed to ethanol. The results of solubility test were also presented in Table S1 (Supplemental data). The property of the films prepared using ethanol was similar to those casted using DMF. It can be assumed that solvent works as only intimate connecting media between copolymer chains and the cross-linker. Thus, ethanol was selected for next experiments since it is commonly used organic solvent and has lower toxicity.

The weight loss represents the dissolution and diffusion of polymers that were not cross-linked in the material and indicates the uncompletion of cross-linking (25). The weight loss was calculated by $100(W_i - W_p)/W_i$ where W_i is the weight of the initial dried film (g) and W_p is the weight of the post-water treated

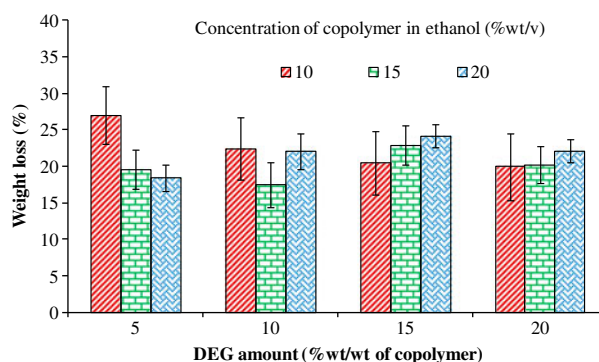


Figure 1. The weight loss of cross-linked poly(NIPAA-*co*-MA) film prepared from 35% mol/mol MA in feed solution with varying amounts of DEG and concentrations of copolymer in ethanol after water immersion at room temperature for 24 h.

and dried film (g). From Figure 1, changing the amount of cross-linking agent, DEG, from 5% to 20% wt/wt did not significantly affect the weight loss of cross-linked poly(NIPAA-*co*-MA) films. Thus, the minimum amount of DEG (5% wt/wt) was chosen. In addition, considering the effect of concentration of copolymer, the weight loss was not significantly different. Thus, the minimum concentration of copolymer was chosen for further experiments due to its low viscosity that is easy to obtain nanofibers by electrospinning (26).

Nuclear magnetic resonance (NMR) spectroscopy

The ^1H -NMR spectrum of synthesized poly(NIPAA-*co*-MA) was shown in Figure 2. The proton signals of NIPAA and MA units were found. For NIPAA units, ^1H -NMR signals of copolymer were observed at 1.40 ppm (broad, 2H) of CH_2 (backbone), 1.92 ppm (q, $J = 1.5$ Hz, 1H) of CH (backbone), 7.04–7.56 ppm (broad, 1H) of NH, 3.82 ppm (m, 1H) of CH (isopropyl), and 1.02 ppm (d, $J = 6.4$ Hz, 6H) of CH_3 (isopropyl). For MA units, ^1H -NMR signal of copolymer was observed at 2.48 ppm (t, $J = 2.0$ Hz, 2H) of CH (backbone). But the proton of carboxylic group could not be found at the chemical shifts from 0 ppm to 14 ppm since it was a de-shielding by the influence of electron-withdrawing effect that causes paramagnetic shift. Thus, the chemical shifts should be above 14 ppm which is agreed with ^1H -NMR spectra of poly[*N*-isopropylacrylamide-*co*-(maleic anhydride)] and poly[*N*-isopropylacrylamide-*co*-(maleic acid)]-graft-polyethyleneglycol that were reported by Kesim *et al.* (6). They reported that the proton of carboxylic group appeared at the chemical shift of 16.98 ppm.

Acid content

The composition of acid content in poly(NIPAA-*co*-MA) was determined by an acid-base titration of the

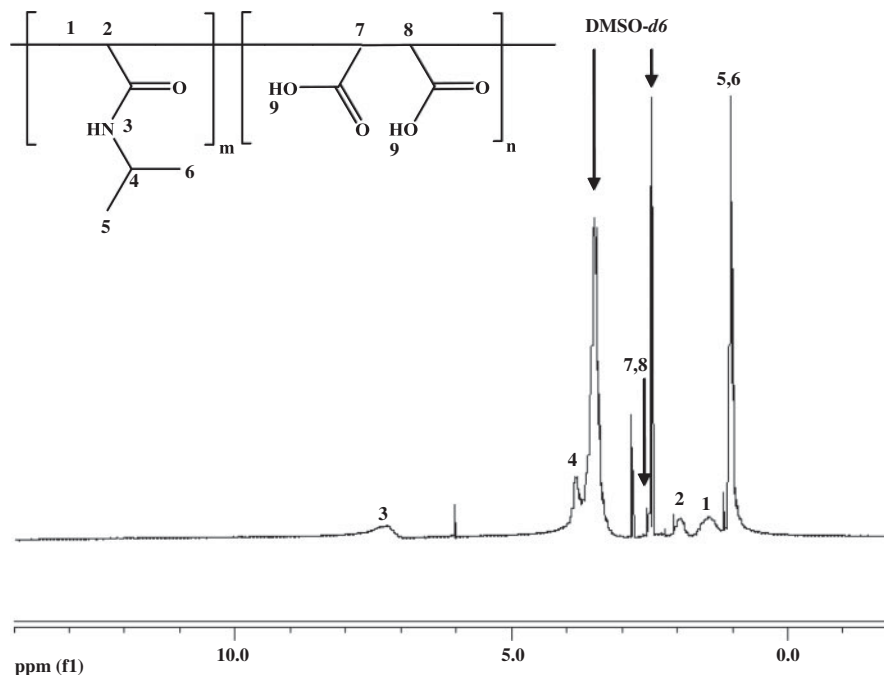


Figure 2. ^1H -NMR spectrum of poly(NIPA-co-MA).

carboxylic groups. The incorporation percentage of MA in poly(NIPA-co-MA) was $22.9 \pm 0.3\%$ ($n = 3$). The mole ratio of NIPA/MA in poly(NIPA-co-MA) was calculated by (mole NIPA)/(mole MA). The mole ratio of NIPA/MA in poly(NIPA-co-MA) was 2:1. In this work, MA comonomers were incorporated into the polymer chain and served as cross-linking sites for the cross-linking reaction with DEG. MA/DEG ratio (in eq/g_{copolymer}) could be calculated by MA composition in copolymer/DEG composition in copolymer. The MA/DEG ratio was defined as the ratio of MA to DEG equivalents in the cross-linked copolymer. This explains its cross-linking reaction. MA/DEG ratio was estimated as 1.5 times. This result suggested that copolymers had enough MA moieties as cross-link sites for the cross-linking reaction with DEG.

Electrospinning

Figures 3 and 4 show a series of scanning electron microscopy (SEM) images (with magnification of 3500 and 20,000, respectively) at different combinations of distance between the needle and the collection screen and electric potential on electrospinning of poly(NIPA-co-MA) containing 5% wt/wt DEG. The quantitative analysis of the results was summarized in Table S2 (Supplemental data). Normally, increasing electric potential will increase the levels of drawing stress of jet that will permit the fiber diameter to decrease (27). However, in this study, when the electric potential

changed from 15 kV to 30 kV, the average diameter of fibers increased. One possible reason was the evaporation of solvent which happened before drawing stress of jet by highly applied electric potential. Therefore, the diameter of the fibers did not decrease which agreed with the literature (28,29). When distances between the needle and the collection screen changed from 10 cm to 25 cm, the average diameter of fibers decreased because the longer distance means that there was a longer flight time for the solution to be stretched before it reached the collector. Further, the results showed that the node density decreased when electric potential increased. The increasing of the applied voltage raised to higher electrostatic repulsion forces which provided higher drawing stress in the jet between the needle and the collector that made density of nodes lower (30). Thus, the formation of nodes in the fibers had correlation to the spinning voltage. The high fiber-to-node ratio means the higher fiber density and suppresses the node (lower node density). The high fiber-to-node ratio was found at 25 cm 30 kV and 25 cm 25 kV with spindle like nodes on fibers. For the distance of 25 cm at 30 kV, it was found that the spinning produced severe static electricity and spark. Therefore, the optimal electric potential and distance between needle and collector screen were obtained at 25 kV and 25 cm, respectively.

Fourier transform infrared (FT-IR) spectroscopy

The IR spectrum poly(NIPA-co-MA) was shown in Figure 5(A). The absorption bands of NIPA and MA

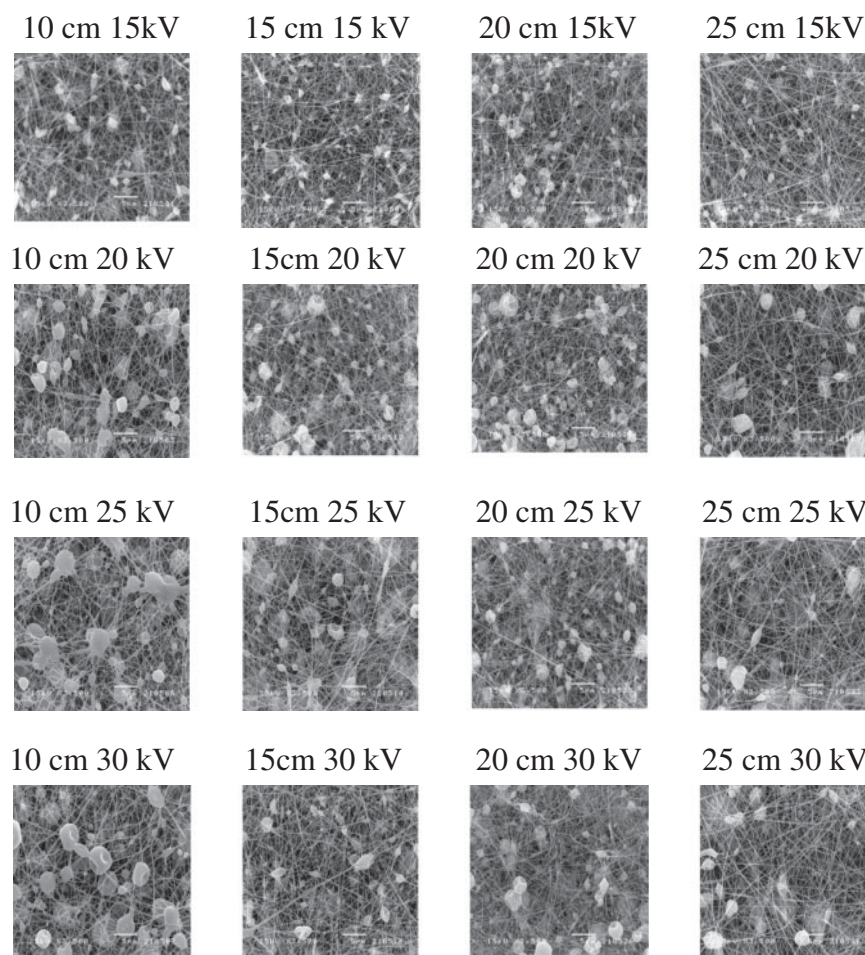


Figure 3. SEM images of electrospun poly(NIPA-co-MA) fibers containing DEG, original magnifications of 3500.

units were found. For NIPA units, the characteristic bands of copolymer were observed at 3301(m, broad) and 3075(w) cm^{-1} assigned to N–H stretching band of secondary amide, at 2976(s), 2929(w), and 2874(w) cm^{-1} assigned to C–H stretching band, at 1657(s) cm^{-1} assigned to C=O stretching of amide I band, at 1545(m-s) cm^{-1} assigned to N–H bending of amide II band, at 1461(s) cm^{-1} assigned to C–N stretching of amide III band, and at 1381(s) and 1271(m) cm^{-1} assigned to bands for CH_3 deformation in isopropyl group. For MA units, the characteristic bands of copolymer were observed at 3680–3200(s, broad) cm^{-1} assigned to O–H stretching band of carboxylic group and at 1778(w) and 1719(m) cm^{-1} assigned to C=O stretching band of carboxylic group. Therefore, FT-IR characterization was entirely clear to confirm the copolymerization of MA comonomer onto the NIPA polymer.

The IR spectrum of fibers was shown in Figure 5(B). The absorption bands of NIPA units and esterification of MA units with DEG were found. The new peaks appeared at 1872(w) and 1874(w) cm^{-1} assigned to

C=O stretching of ester group and at 1067(w, broad) and 1020(w) cm^{-1} assigned to C–O stretching of ester group. These are characteristic absorption peaks of cross-linked poly(NIPA-co-MA) membrane which exhibited significant difference with characteristic absorption of the synthesized copolymer. Therefore, it can be confirmed that successful esterification cross-link reaction of the membrane had taken place.

Water absorbing behavior in deferent temperatures

Temperature-responsive water absorption ratios of poly(NIPA-co-MA) hydrogel membrane were shown in Figure 6. The hydrogel fibers showed different temperature dependent swelling responses. When the temperatures raised from 34°C to 50°C, the water absorption ratio decreased from 17 g g^{-1} to 4 g g^{-1} . With increasing temperature, the hydrogen bonding weakens; it leads to a reduction in the structuring of water around the hydrophobic groups. As this water is released, the interactions between hydrophobic side groups of the polymer increase (31, 32). Moreover,

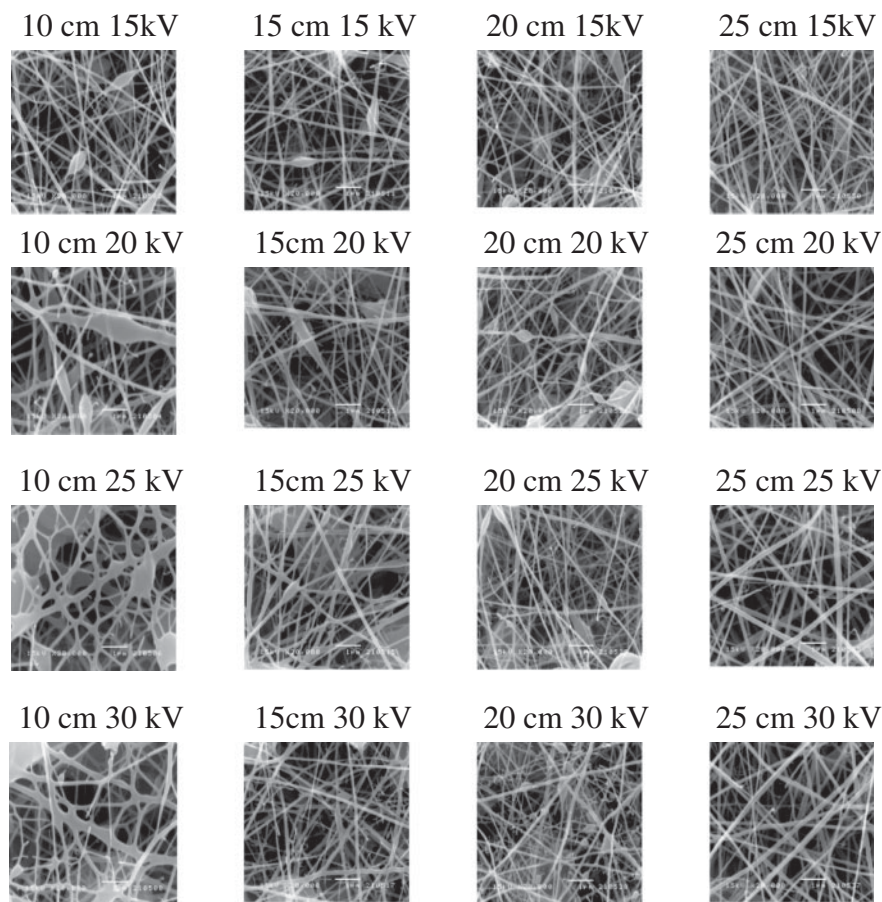


Figure 4. SEM images of electrospun poly(NIPA-co-MA) fibers containing DEG, original magnifications of 20,000.

at 34°C, the hydrogel membrane was translucent and swollen, while at 35°C and above, the hydrogel membrane became cloudy and shrunk. This observation indicates that the hydrogel exhibited LCST behaviors which look like the conventional poly(NIPA) hydrogel at LCST in the vicinity of 34°C (1). Moreover, when the temperature increased from 34°C to 50°C, the weight loss of the membrane decreased from 49% to 21%, while at below 34°C, the hydrogel membrane dissolved in water. When the hydrogel swelled up and was highly hydrated, it became hydrophilic state. It could not maintain fibrous morphology, on the other hand it might become distorted, exploded, and dispersed in water.

The swelling behavior of poly(NIPA-co-MA) hydrogel membranes was presented in Figure 7(A). It reached equilibrium in less than 5 min. On the contrary, the swelling rate of the cast film with the same polymer condition was much lower. As shown in Figure 7(B), it took more than 30 min for the gel to reach a swelling equilibrium. This indicated that the membrane has much more surface area than the cast film.

Experimental

Synthesis of poly(NIPA-co-MA)

Poly(NIPA-co-MA) was synthesized by free radical polymerization in aqueous solution. The method was adapted from Vaidya *et al.* (33). *N*-isopropylacrylamide (Aldrich) (0.13 g, 0.28 g, 0.49 g, 0.62 g, 0.75 g, and 1.1 g, corresponding to 10–50% mol/mol of the total monomer) was added to a two-necked round bottom flask containing 30 mL of Milli Q water and the mixture was stirred for 20 min. Then, nitrogen gas was purged in the solution for 1 h. Ammonium peroxodisulfate (Fluka) (0.12 g, 0.14 g, 0.16 g, 0.17 g, 0.19 g, and 0.22 g corresponding to 10% wt/wt of the total monomer) was added and followed by *N,N,N,N*-tetramethylethylenediamine (Aldrich; 300 μL dropwise). The polymerization proceeded at 37°C for 8 h under continuous nitrogen stream. The polymer was precipitated out of the solution by heating the solution at about 80°C for 20 min. The copolymer was separated and redissolved in Milli Q water, and then re-precipitated and washed several times with diethyl ether in order to remove any unreacted monomers and

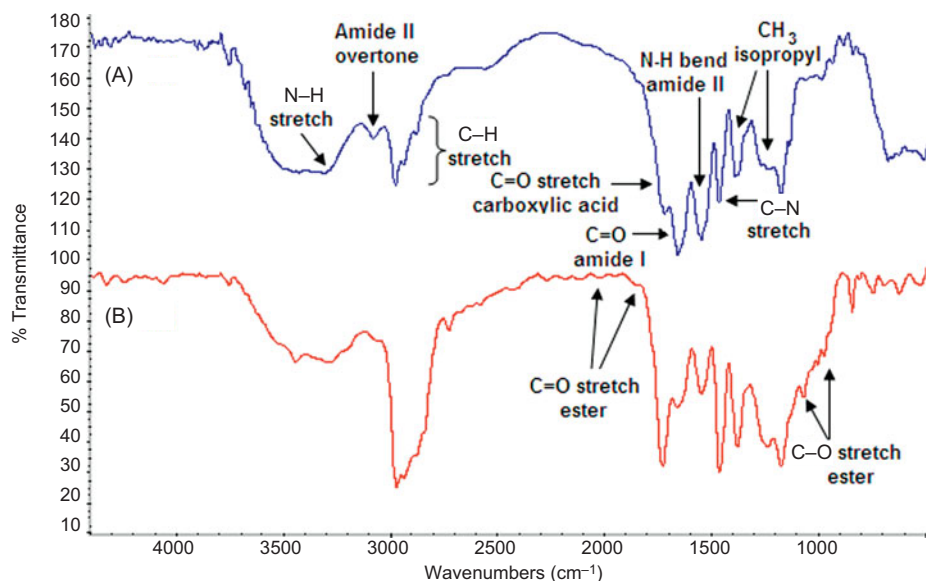


Figure 5. FT-IR spectra of poly(NIPA-co-MA) (A) and cross-linked poly(NIPA-co-MA) membrane (B).

impurities. The final product was dried in an oven at 80°C for 12 h and stored in a desiccator.

Investigation of monomer feed ratios of copolymer on cross-linking reaction

The mixture solutions were prepared by adding poly (NIPA-co-MA) (0.05 g) and either *N,N*-DMF or ethanol (EtOH; 500 μ L, 333 μ L, and 250 μ L corresponding to 10–20% wt/wt of copolymer) in a vial. The solid was completely dissolved after being vigorously shaken for 30 min. Then, DEG (2.23 μ L, 4.47 μ L, 6.71 μ L, and 8.94 μ L) was added into the solution and shaken again for 30 min. This homogeneous solution (30 μ L) was pipetted onto a glass slide and then manually casted into a thin film. The casted film on the glass slide was put in an oven at 145°C for 10 min to allow the cross-linking reaction to proceed completely and at 60°C for 12 h to remove residual solvent. The

film was peeled off and subject to a solubility test. The solubility characteristics of the film were determined by immersing the obtained films into distilled water at room temperature for 24 h.

Characterization of copolymer

FT-IR was used to identify the characteristic functional groups of the copolymer. Infrared spectra were recorded in the wavenumber range of 400–4000 cm^{-1} using the transmittance mode with four scans with the wavenumber resolution of $\pm 4 \text{ cm}^{-1}$ by KBr pellet technique.

NMR was used to confirm the structure of the copolymers. ^1H -NMR spectra were recorded in the chemical shift 0–14 ppm with repetitions of eight by using DMSO- d_6 as solvent.

Acid-base titration with standardized 0.1 M sodium hydroxide (NaOH) solution as titrant and phenolphthalein as indicator was used to determine

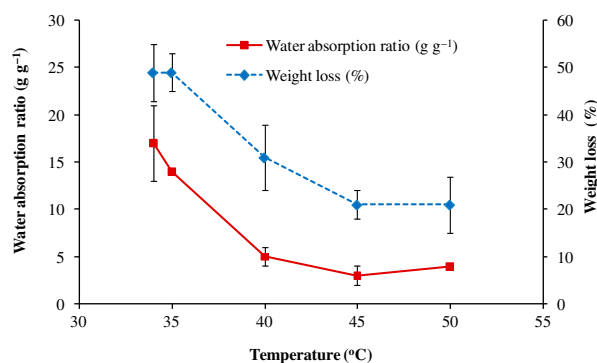


Figure 6. Temperature-responsive water absorption ratio and weight loss of poly(NIPA-co-MA) hydrogel membrane.

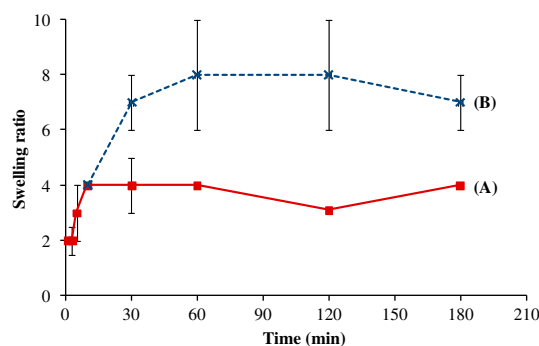


Figure 7. Swelling ratio of poly(NIPA-co-MA) hydrogel (A) electrospun membrane and (B) casted film (temperature = 50°C).

the composition of synthesized copolymers, thereby affording directly the mole fraction of MA-containing copolymer. Titrations of 10 mL of 1% (wt/v) copolymer were performed in triplicate. The determination of acid content was done by using different materials obtained from three batches of copolymerization.

Electrospinning and cross-linking of poly(NIPA-co-MA)

The electrospinning solution contained 10% (wt/v) of the poly(NIPA-co-MA) copolymer in ethanol and 5% (wt/wt) of DEG was loaded into a disposable syringe with a 0.80-mm diameter needle which was connected to a high-voltage supply being capable of generating an electric potential in the range of 15–30 kV. An aluminum foil was applied as a collector while the distances between the needle and the collection screen were 10–25 cm. The feeding rate was 1 mL h⁻¹. Such-obtained poly(NIPA-co-MA) nanofibrous membranes were put in an oven at 145°C for 10 min to complete the cross-linking reaction and then dried at 60°C for 12 h to remove residual solvent.

Characterization of electrospun copolymer hydrogel membrane

SEM was used to investigate the morphology of the electrospun copolymer hydrogel membrane. The magnification at 20,000 was used for the measurement of the diameter of the fibers and at 3500 for the measurement of the node fibers. The diameter of fibers was reported as the average values with standard deviation ($n = 30$) by a SemAfore software.

FT-IR was used to identify the characteristic functional groups of the electrospun copolymer hydrogel membrane. Infrared spectra were recorded by using the procedure previously.

Water absorption measurement was used to investigate the swelling characteristics at temperatures of water ranging from 10°C to 50°C. A membrane strip with a size of 2×2 cm² was weighed (W_i) and immersed in deionized water for 1 h. Then the membrane was taken out, the free water at the surface was removed by filter paper and brought to weigh (W_w). Later on, they were dried in an oven at 80°C until the weight of the dry membrane was constant and weigh (W_d). The water absorption ratio was calculated by $(W_w - W_d)/W_d$. The weight loss was calculated by $100(W_i - W_d)/W_i$.

Conclusions

The new copolymer poly[N-isopropylacrylamide-co-(maleic acid)] or poly(NIPA-co-MA) nanofiber

hydrogel membrane was successfully fabricated by electrospinning using DEG as a cross-linker and a subsequent heat-induced esterification cross-linking reaction using ethanol as a greener solvent instead of a more toxic solvent (DMF). The electrospun hydrogel membrane with regular, straight uniform diameter fibers, low node density, and uniform non-woven fabric structure was prepared through optimizing electrospinning parameter: the applied voltage at 25 kV and distance between the needle and the collection screen at 25 cm. The average diameter of electrospun fibers was 117 ± 33 nm. The electrospun hydrogel membrane behaved fast thermosensitive property and had a LCST in water in the vicinity of 34°C.

Supplemental data

The supplemental data for this article can be accessed at <http://dx.doi.org/10.1080/17518253.2014.923519>.

Acknowledgment

This study was carried out in the Environmental Analysis Research Unit (EARU) at Chulalongkorn University and financially supported by the Integrated Innovation Academic Center: IIAC Chulalongkorn University Centenary Academic Development Project (CU56-FW08).

References

- (1) Tasdelen, B.; Kayaman-Apohan, N.; Guven, O.; Baysal, B.M. *Radiat. Phys. Chem.* **2004**, *69*, 303–310.
- (2) Tokuyama, H.; Kanehara, A. *React. Funct. Polym.* **2007**, *67*, 136–143.
- (3) Tokuyama, H.; Iwama, T. *Langmuir*. **2007**, *23*, 13104–13108.
- (4) Cheng, X.; Canavan, H.E.; Stein, M.J.; Hull, J.R.; Kweskin, S.J.; Wagner, M.S.; Somorjai, G.A.; Castner, D.G.; Ratner, B.D. *Langmuir*. **2005**, *21*, 7833–7841.
- (5) Chung, H.J.; Park, T.G. *Adv. Drug. Deliver. Rev.* **2007**, *59*, 249–262.
- (6) Kesim, H.; Rzaev, Z.M.O.; Diner, S.; Piskin, E. *Polymer*. **2003**, *44*, 2897–2909.
- (7) Rzaev, Z.M.; Diner, S.; Piskin, E. *Prog. Polym. Sci.* **2007**, *32*, 534–595.
- (8) Zhang, X.Z.; Zhuo, R.X. *Eur. Polym. J.* **2000**, *36*, 2301–2303.
- (9) Liu, Q.; Zhang, P.; Qing, A.; Lan, Y.; Shi, J.; Lu, M. *Polymer*. **2006**, *47*, 6963–6969.
- (10) Chen, H.; Zhang, J.; Qian, Z.; Liu, F.; Chen, X.; Hu, Y.; Gu, Y. *Nanotechnology*. **2008**, *19*, 185707–185717.
- (11) Choi, Y.J.; Yamaguchi, T.; Nakao, S.I. *Ind. Eng. Chem. Res.* **2000**, *39*, 2491–2495.
- (12) Huang, C.; Soenen, S.J.; Rejman, J.; Lucas, B.; Braeckmans, K.; Demeester, J.; De Smedt, S.C. *Chem. Soc. Rev.* **2011**, *40*, 2417–2434.
- (13) Li, L.; Hsieh, Y.L. *Polymer*. **2005**, *46*, 5133–5139.
- (14) Jin, X.; Hsieh, Y.L. *Polymer*. **2005**, *46*, 5149–5160.

- (15) Lyoo, W.S.; Youk, J.H.; Lee, S.W.; Park, W.H. *Mater. Lett.* **2005**, *59*, 3558–3562.
- (16) Kim, S.H.; Kim, S.H.; Nair, S.; Moore, E. *Macromolecules*. **2005**, *38*, 3719–3723.
- (17) Tang, C.; Ye, S.; Liu, H. *Polymer*. **2007**, *48*, 4482–4491.
- (18) Liu, H.; Zhen, M.; Wu, R. *Macromol. Chem. Phys.* **2007**, *208*, 874–880.
- (19) Song, M.; Pan, C.; Li, J.; Zhang, R.; Wang, X.; Gu, Z. *Talanta*. **2008**, *75*, 1035–1040.
- (20) Wang, H.; Zheng, J.; Peng, M. J. *Appl. Polym. Sci.* **2010**, *115*, 2485–2492.
- (21) Rockwood, D.N.; Chase, D.B.; Akins, R.E.; Rabolt, J. F. *Polymer*. **2008**, *49*, 4025–4032.
- (22) Sperling, L.H. *Introduction to Physical Polymer Science*; Wiley: Hoboken, NJ, **2006**.
- (23) Xue, W.; Champ, S.; Huglin, M.B. *Polymer*. **2001**, *42*, 3665–3669.
- (24) Geever, L.M.; Devine, D.M.; Nugent, M.N.; Kennedy, J. E.; Lyons, J.G.; Higginbotham, C.L. *Eur. Polym. J.* **2006**, *42*, 69–80.
- (25) Chen, H.; Hsieh, Y.L. *J. Polym. Sci. Pol. Chem.* **2004**, *42*, 6331–6339.
- (26) Kameoka, J.; Orth, R.; Yang, Y.; Czaplewski, D.; Mathers, R.; Coates, G.W.; Craighead, H.G. *Nanotechnology*. **2003**, *14*, 1124–1129.
- (27) Deitzel, J.M.; Kleinmeyer, J.; Harris, D.; Tan, N. *Polymer*. **2001**, *42*, 261–272.
- (28) Uppatham, C.; Nithitanakul, M.; Supaphol, P. *Macromol. Chem. Phys.* **2004**, *205*, 2327–2338.
- (29) Meechaisue, C.; Dubin, R.; Supaphol, P.; Hoven, V.P.; Kohn, J.J. *Biomater. Sci. Polym. E.* **2006**, *17*, 1039–1056.
- (30) Lee, K.H.; Kim, H.Y.; Bang, H.J.; Jung, Y.H.; Lee, S. G. *Polymer*. **2003**, *44*, 4029–4034.
- (31) Krusic, M.K.; Filipovic, J. *Polymer*. **2006**, *47*, 148–155.
- (32) Erbil, C.; Kazancoglu, E.; Uyanik, N. *Eur. Polym. J.* **2004**, *40*, 1145–1154.
- (33) Vaidya, A.A.; Lele, B.S.; Kulkarni, M.G.; Mashelkar, R.A. *J. Biotechnol.* **2001**, *87*, 95–107.