

Shape Memory Properties of Electrospun Nafion Nanofibers

Fenghua Zhang, Zhichun Zhang, Yanju Liu¹, and Jinsong Leng*

Centre for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, China

¹*Department of Astronautical Science and Mechanics, Harbin Institute of Technology, Harbin 150001, China*

(Received June 7, 2013; Revised August 8, 2013; Accepted August 10, 2013)

Abstract: Nanoscaled non-woven fibers with shape memory effect are successfully fabricated via electrospinning method from Nafion solutions consisting of a little poly(ethylene oxide) (PEO). Scanning electron microscopy (SEM) investigation shows the electrospun nanofibers with average diameters in the range 170-410 nm. The electrospun nanofibers exhibit excellent shape memory properties. When deformed Nafion nanofibers are stimulated upon heat, the temporary shape responds rapidly, and then recovers to the permanent shape in less than one minute. The shape recovery ratios and shape fixity ratios of Nafion nanofibers with 0.3 wt%, 0.5 wt% and 0.7 wt% PEO are all above 90 %. In shape memory cycle, fibrous structure is stable after the stretching recovery. Shape memory Nafion nanofibers have various potential applications in smart structures and materials in the future.

Keywords: Shape memory property, Electrospinning, Polymer, Nanofibers, Nafion

Introduction

Shape memory polymers (SMPs) as a class of smart materials have attracted increasing interest in recent years [1,2]. They are able to be deformed in a predefined way from a temporary shape to a permanent shape upon exposure to an external stimulus such as heat [3], electricity [4], magnetism [5,6], light [7] and water [8]. Due to this property, SMPs are considered in a lot of fields involving medical materials [9], smart textiles [10], sensors and actuators [11], smart dry adhesives [12] and so on.

With the recent trend on miniaturizing smart materials and devices, it is a challenge to study micro/nano-sized polymeric fibers [13]. Electrospinning method is used to fabricate the shape memory fiber membranes. Due to the advantages of fibrous structure, shape memory fibers have garnered research interest. For instance, Jinlian Hu group has reported that shape memory polyurethane is electrospun into fibers, which shows an excellent shape memory effect [14,15]. Some degradable and biocompatible shape memory polymers are prepared by electrospinning method to be applied in biomedical fields [16-19].

Many researches on Nafion have appeared for many years. DuPont's Nafion[®] PFSA polymer with a polytetrafluoroethylene backbone and perfluoroether sulphonic acid side chains processes excellent properties of super-selective, chemical stability, thermal stability, acidity and electrical conductivity and mechanical properties [20]. In the past, Nafion nanofibers fabricated by means of electrospinning have enabled a variety of applications including fuel cell membranes [21], functional composite materials [22], sensors [23], catalysts [24] and ionic conducting nanofibers [25,26].

In this work, we aim to study and develop smart Nafion fibers with shape memory effect. Pure Nafion solutions

cannot be electrospinnable owing to the ionic interactions in solution, which result in low solution viscosities. Addition of PEO in Nafion can enhance the entanglements within the solution. The resulted fibers are made from smart polymer Nafion via functionalities integrated into non-woven structure. The novel morphing property can bring electrospun Nafion nanofiber membranes new functions. It is also assumed that the smart fibers may lead to novel fiber sensors, smart actuators and advanced biomedical devices (shape-changing scaffold, blood vessel support, sensors or actuators of biomedical devices, drug delivery systems).

Experimental

Materials

DuPont Nafion[®] PFSA polymer dispersions contain perfluorosulfonic acid/PTFE copolymer in the acid (H⁺) form, and are available in several polymer content and dispersant compositions. Nafion[®] PFSA polymer dispersion with polymer content 5.0 wt% was purchased from DuPont. The fundamental information of Nafion was shown in Table 1. Poly(ethyleneoxide) (PEO) (Mn=900,000 g/mol) as an electrospinning carrier was purchased from Changchun Jinghua Co., Ltd and used without further purification.

Preparation of the Electrospinning Solution

In this experiment, the Nafion/PEO solutions for electrospinning were obtained when the PEO was dissolved in 5.0 wt% Nafion solution at room temperature. For the investigation of the concentration influence, PEO concentrations were 0.3 wt%, 0.5 wt% and 0.7 wt%, respectively, which were prepared by magnetic stirring for 20 h to completely dissolve the polymer.

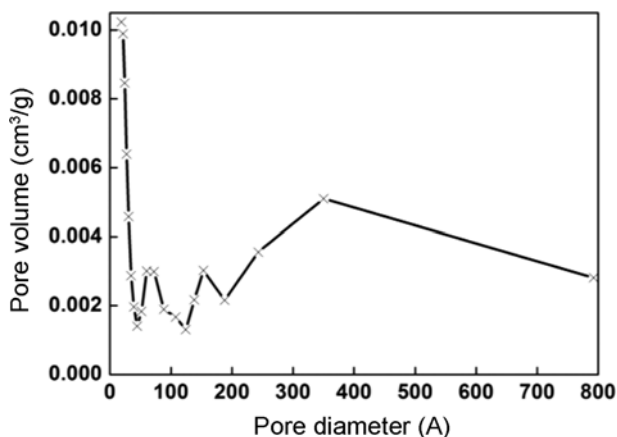
Electrospinning

The Nafion nanofibers were electrospun using a laboratory

*Corresponding author: lengjs@hit.edu.cn

Table 1. Nafion PFSA polymer dispersions by composition

Property	D-520
Polymer content (wt. %)	5.0 min 5.4 max
Water content (wt. %)	45±3
VOC content (wt. %)	50±3
1-Propanol	48±3
Ethanol	<4
Mixed ethers and other VOCs	<1
Specific gravity	0.92-0.94
Available acid capacity (meq/g, H ⁺ polymer basis)	>1.00
Total acid capacity (meq/g, H ⁺ polymer basis)	1.03-1.12
Viscosity (cP; at 25 °C and 40 sec ⁻¹ Shear Rate)	10-40

**Figure 1.** BJH desorption pore distribution.

electrospinning apparatus (Nanospider, Elmarco) which could provoke innumerable polymeric jets from a large liquid surface to obtain large area fibrous membranes. The uniform Nafion nanofibers (BET Surface Area=7.1011 m²/g) with PEO loadings of 0.3 wt%, 0.5 wt% and 0.7 wt% were fabricated by means of electrospinning. The applied high-voltage power between collector and electrode was 30 kV, the electrode-to-collector distance was 16 cm, and the electrode rotation rate was 0.9 rpm. Figure 1 shows the BJH desorption pore distribution results of Nafion nanofiber membranes.

Annealing

The Nafion nanofiber membranes were annealed at 130 °C for 120 min. In the step of annealing, intersecting nanofibers were welded to each other. All nanofiber membranes were annealed under air condition.

Characterization

An instrument of field emission environmental scanning electron microscopy (SEM, Quanta 200 FEG) was used to

observe the morphology and structure of fibers. The surface of sample was coated with gold for 10 min. The nanofiber diameter distributions in membranes were analyzed by Image J. 100 nanofibers were randomly selected from each of the micrographs for diameter measurements.

Nicolet AVATAR 360 Fourier Transform Infrared (FT-IR) spectroscopy was applied to analyze the interaction between different materials. The samples were conducted from 400 cm⁻¹ to 4 000 cm⁻¹ in a reflection mode at the room temperature.

The tangent delta was performed with a dynamic mechanical analyzer (DMA, Mettler Instruments) at a constant frequency of 1 Hz from 0 °C to 180 °C at heating rate of 3 °C/min.

The shape memory property tests were performed using an instrument in a fixed force controlled mode. The instrument contained three parts, such as temperature control chamber, infrared displacement sensor and computer software. The thickness of the electrospun membrane was 0.2 mm. The sample was cut into 23×3.5 mm and heated at a high temperature T_{high} (130 °C) for a period time. Then it was stretched under a tensile load (0.85 N) at T_{high} . The deformed sample was cooled down to lower temperature T_{low} (40 °C) where the deformation was fixed. The external force was removed at T_{low} , holding for a period of time under no stress condition. The deformation was recovered to the original shape when the sample was reheated to T_{high} . Shape fixing ratio (R_f) and shape recovery ratio (R_r) were used to characterize the shape memory effect in literatures [27,28]. The details of calculation were described in the part of results and discussion.

Results and Discussion

The Morphology of Nanofibers

The morphology and structure of Nafion fibers were characterized using SEM. As it can be observed, Figure 2(a), 2(b) and 2(c) present SEM images of Nafion nanofiber membranes with different PEO weight ratios, where the PEO concentration is 0.3 wt%, 0.5 wt% and 0.7 wt%, respectively. From SEM images, all of the membranes were of smooth and good quality with no-beads. The fibrous membranes had a porous structure. Changes in nanofiber morphology with PEO concentration were studied. Accordingly, histograms of the fiber diameter distribution are shown in Figure 2(d), 2(e) and 2(f), the mean diameter increases with increasing the PEO content. This is consistent with other researchers' result [29]. The nanofibers had a mean diameter ranging from appropriate 170 nm to 410 nm. The smallest mean fiber diameter (170 nm) for Nafion was obtained with a 0.3 wt% PEO in solution. It was a significant in carrier concentration. Electrospinnability was enhanced as the PEO concentration of electrospinning solution increased. The PEO content for electrospinning solution was critical. It also affected the shape memory properties of Nafion nanofiber membranes. The discussion will be shown in the following part.

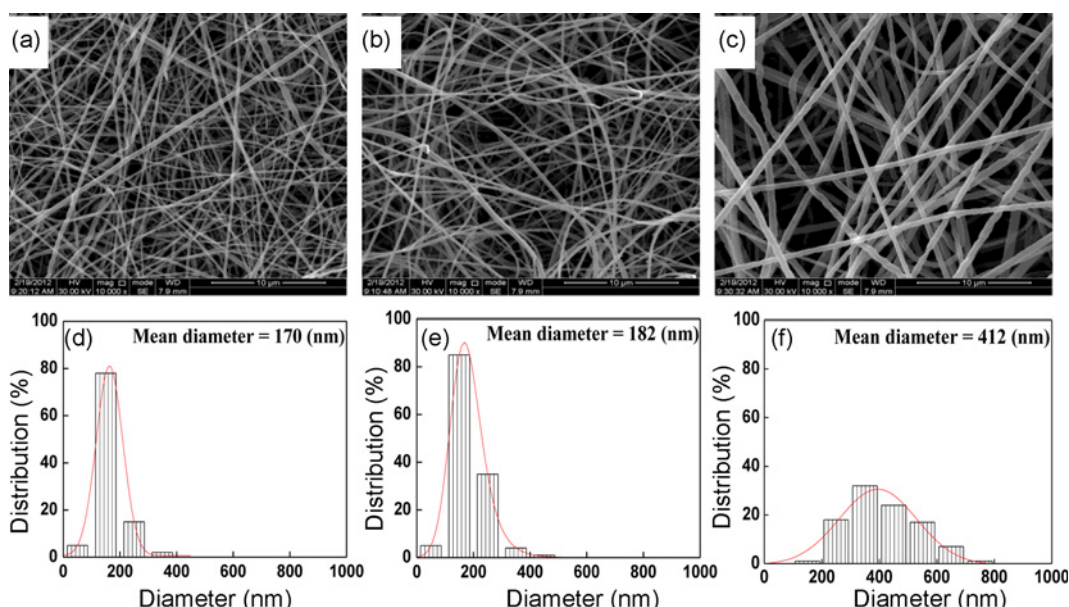


Figure 2. (a, b, c) were SEM of Nafion nanofibers with PEO concentrations: 0.3 wt%, 0.5 wt%, and 0.7 wt% at a magnification of 10,000 \times , and (d, e, f) were histograms of the nanofiber diameter distribution.

Fourier Transforms Infrared Spectroscopy

To find out the mechanism behind the interaction between the polymers, FTIR spectroscopy was used to study the interaction between Nafion and PEO. The results of FTIR spectra corresponding to a Nafion and a Nafion/PEO are shown in Figure 3. As it can be observed, at 528 cm^{-1} and 637 cm^{-1} , the absorption peaks belong to the stretching vibration of C-S and the bending vibration of $-\text{CF}_2-$; at 1060 cm^{-1} the peak belongs to $-\text{SO}_3\text{H}$ group; at 1155 cm^{-1} and 1236 cm^{-1} , the characteristic absorption peaks belong to $-\text{CF}_2-$; at 3508 cm^{-1} , the absorption peaks attributes to the stretching vibration of hydrogen bonds [30,31]. The results agreed with the work reported previously [32]. It explained that PEO in electrospun Nafion solution also increased the

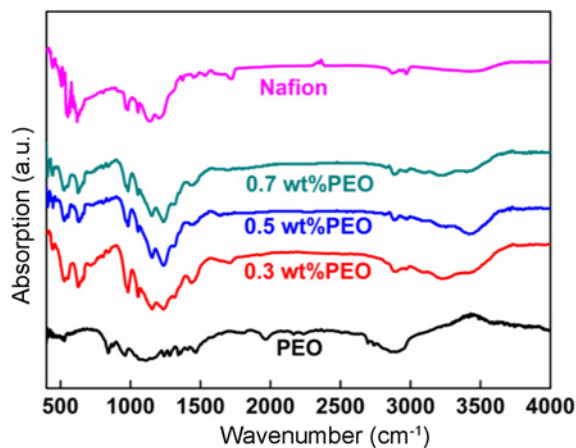


Figure 3. FTIR spectra of Nafion nanofibers with different contents of PEO.

electrospinnability. The reported literature demonstrated that hydrogen bonds between the sulfonic acid groups of Nafion and the lone-pair electrons of the ether oxygens in PEO may be formed [33]. It may contribute to shape memory properties of electrospun Nafion nanofibers.

Shape Memory Property

For Nafion nanofiber membranes, the structure change of fibers was observed after stretching and shape recovery tests. The tangent delta was performed with a dynamic mechanical analyzer (DMA) at a constant frequency of 1 Hz from 0 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$. From the Figure 4, the transition temperature that is 130 $^{\circ}\text{C}$ can be observed. SEM images Figure 5(a), (b) and (c) present the original annealed fibers,

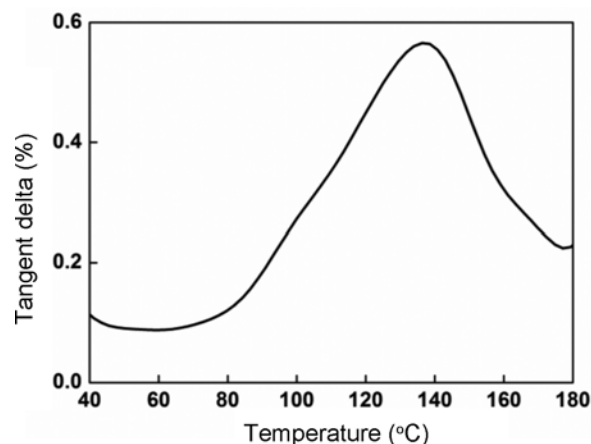


Figure 4. Tangent delta curve of electrospun Nafion nanofiber membranes.

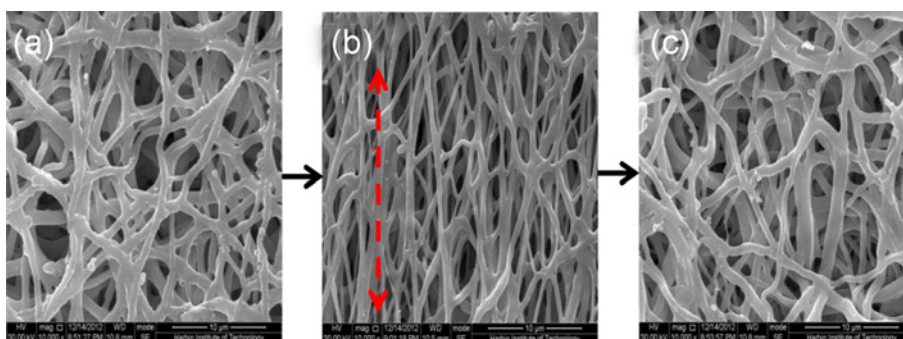


Figure 5. SEM images of Nafion nanofibers, (a) is the original fibers, (b) is the stretched fibers, and (c) is recovered fibers.

stretched fibers and recovered fibers, respectively, in the shape memory cycle of the stretching recovery. The results showed that after annealing at 130 °C for 120 min, intersecting fibers could be welded to each other during the annealing process and almost complete fusion of the nanostructure occurred with closure of most fiber voids. The fusion points between fibers made the Nafion nanofibers into network membranes. The SEM indicated that after cycle of shape memory test, the fibrous structure was stable. It has the same phenomenon with other research [34].

The nanotensile testing was conducted at room temperature, and the engineering stress-strain relationship for Nafion nanofiber membrane is plotted in Figure 6. Nafion nanofibers exhibit excellent dual shape memory property when deformed and recovered at 130 °C. The curves presented in Figure 7 clearly demonstrate the relationship between the stress, strain and temperature. Heating up at 130 °C leads to a motion of polymer chain segments, when cooling down the temperature from 130 °C to 40 °C, the stress level is kept at 0.85 MPa; it results in an increase of strain from $\epsilon_{A,load}$ to $\epsilon_{B,load}$. Ultimately, the stress level returns to zero and the strain $\epsilon_{A,rec}$ is obtained when the temperature is reheated to 130 °C. Shape memory polymers can memorize not only the strain, but also the thermomechanical history. For the dual-shape memory effect, Shape fixing ratio (R_f) and shape recovery ratio (R_r) were calculated using equations (1) and (2) [27].

$$R_r = \frac{\epsilon - \epsilon_{rec}}{\epsilon} \times 100\% \quad (1)$$

$$R_f = \frac{\epsilon}{\epsilon_{load}} \times 100\% \quad (2)$$

where ϵ_{load} was the maximum strain under load, ϵ was the fixed strain after cooling and load removal, and ϵ_{rec} was the strain after recovery.

Nafion nanofibers (annealed at 130 °C) were found to exhibit excellent shape memory performance when deformed and recovered above the transition temperature. The visual demonstration of shape memory effect was carried out using

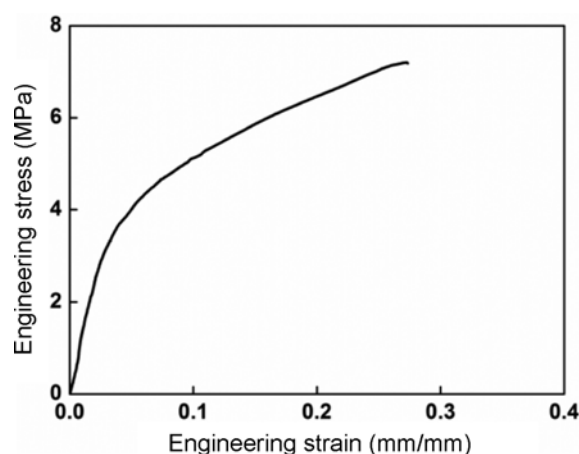


Figure 6. Engineering stress-strain responses for Nafion nanofiber membranes.

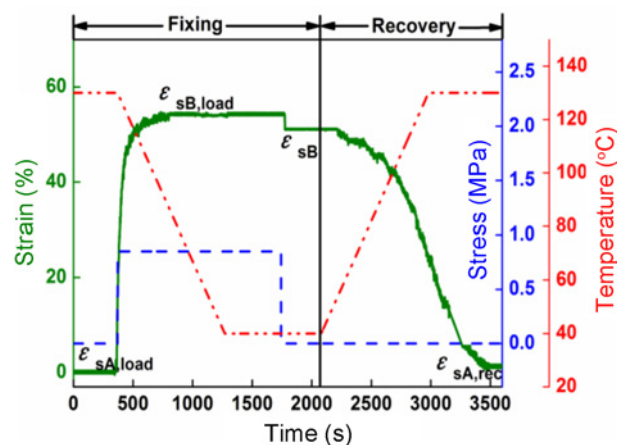


Figure 7. Shape memory cycle test.

oven heating. The shape memory effect for Nafion nanofiber is demonstrated in Figure 8. The permanent shape was rectangular strip. The permanent shape was deformed at 130 °C and fixed to yield the temporary shape 0 s. When Nafion nanofibers were put into the oven at 130 °C, the

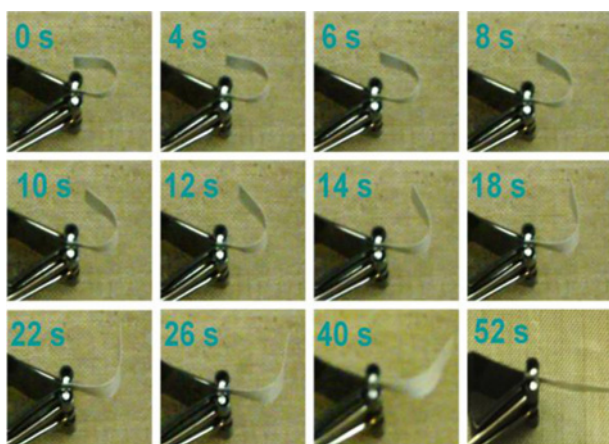


Figure 8. Shape recovery behavior.

Table 2. Shape memory effect of nafion nanofibers

Sample	R_f (%)	R_r (%)
Nafion nanofibers with 0.3 wt% PEO	88.68	94.35
Nafion nanofibers with 0.5 wt% PEO	89.24	93.79
Nafion nanofibers with 0.7 wt% PEO	91.94	92.82

temporary shape deformed rapidly, and then recovered to the permanent shape after 52 s. Nafion possessed a good shape fixation and shape recovery ratio above the shape memory transition to maintain shape fixing and recovery properties.

The results of shape fixity and shape recovery of the whole process are presented in Table 2. Nafion nanofibers showed an excellent shape memory behavior. It was seen that the shape recovery ratios and shape fixity ratios of Nafion nanofibers with 0.3 wt%, 0.5 wt% and 0.7 wt% PEO were all above 90 %. It was also seen that shape fixity decreased and shape recovery ratios increased with increasing PEO content. The above experimental results of clearly suggest that electrospun Nafion nanofibers show excellent shape memory performances in a series shape memory polymer system.

Conclusion

A novel smart material, morphing Nafion nanofiber which possesses shape memory effect, was successfully prepared by electrospinning method from Nafion solutions. Scanning electron microscopy was applied to investigate the morphology and structure of Nafion nanofibers. SEM images of the obtained nanofibers revealed surfaces with significant porosity. The smooth, no-bead fibers were observed. The solution concentrations were observed to influence fibers morphology and diameters. FTIR results showed that the characteristic peaks of Nafion. The visual demonstration gave a direct proof that the resulted nanofibers had good shape memory

properties, the shape recovery time was less than one minute and the shape recovery ratios and shape fixity ratios of Nafion nanofibers with different PEO concentrations were all above 90 %. The results showed that electrospun Nafion nanofibers possessed good morphing property and may be potential applied in many important fields.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant No.11225211, No.11272106).

References

1. C. Liu, H. Qin, and P. T. Mather, *J. Mater. Chem.*, **17**, 1543 (2007).
2. J. S. Leng, X. Lan, Y. J. Liu, and S. Y. Du, *Prog. Mater. Sci.*, **56**, 1077 (2011).
3. S. J. Chen, J. L. Hu, H. T. Zhuo, C. W. Yuen, and L. K. Chan, *Polymer*, **51**, 240 (2010).
4. J. S. Leng, X. Lan, Y. J. Liu, and S. Y. Du, *Smart Mater. Struct.*, **18**, 074003 (2009).
5. R. Mohr, K. Kratz, T. Weigel, M. Lucka-Gabor, M. Moneke, and A. Lendlein, *P. Natl. Acad. Sci. USA*, **103**, 3540 (2006).
6. X. J. Yu, S. B. Zhou, X. T. Zheng, T. Guo, Y. Xiao, and B. Song, *Nanotechnology*, **20**, 235702 (2009).
7. J. S. Leng, X. L. Wu, and Y. J. Liu, *J. Appl. Polym. Sci.*, **114**, 2455 (2009).
8. W. M. Huang, B. Yang, L. An, C. Li, and Y. S. Chan, *Appl. Phys. Lett.*, **86**, 114105 (2005).
9. A. Lendlein and R. Langer, *Science*, **96**, 1673 (2002).
10. F. L. Ji, Y. Zhou, J. L. Hu, Y. Liu, L. Y. Yeung, and G. D. Ye, *Smart Mater. Struct.*, **15**, 1547 (2006).
11. H. T. Zhuo, J. L. Hu, and S. J. Chen, *Mater. Lett.*, **62**, 2074 (2008).
12. T. Xie and X. Xiao, *Chem. Mater.*, **20**, 2866 (2008).
13. D. Cozzens, X. Y. Wei, and R. Faust, *J. Polym. Sci. Part B: Polym. Phys.*, **51**, 452 (2013).
14. H. T. Zhuo, J. L. Hu, and S. J. Chen, *J. Mater. Sci.*, **46**, 3464 (2011).
15. Q. H. Meng, J. L. Hu, L. Y. Yeung, and Y. Hu, *J. Appl. Polym. Sci.*, **111**, 1156 (2009).
16. H. Matsumoto, T. Ishiguro, Y. Konosu, M. Minagawa, A. Tanioka, K. Pichau, K. Kratz, and A. Lendlein, *Eur. Polym. J.*, **48**, 1866 (2012).
17. T. Gong, W. B. Li, H. M. Chen, L. Wang, S. J. Shao, and S. B. Zhou, *Acta Biomaterialia*, **8**, 1248 (2012).
18. C. Ruder, T. Sauter, T. Becker, K. Kratz, B. Hiebl, F. Jung, and A. Lendlein, *Clin. Hemorheol. Micro.*, **50**, 101 (2012).
19. J. S. Ahn, W. R. Yu, J. H. Youk, and H. Y. Ryu, *Smart Mater. Struct.*, **20**, 105024 (2011).
20. H. W. Carla, *J. Membrane Sci.*, **120**, 1 (1996).
21. G. Mostafa, S. Samaneh, I. Manal, Y. Zahira, R. Wan, and D. Wan, *J. Chem. Eng.*, **184**, 82 (2012).

22. W. L. Jang and Y. T. Yoo, *Sensor. Actuat. B-Chem.*, **159**, 103 (2011).
23. S. Lei, D. J. Chen, and Y. Q. Chen, *Nanotechnology*, **22**, 265504 (2011).
24. X. F. Chang, Y. Hu, and Z. L. Xu, *Mater. Lett.*, **65**, 1719 (2011).
25. A. Laforgue, L. Robitaille, A. Mokrini, and A. Aji, *Macromol. Mater. Eng.*, **292**, 1229 (2007).
26. B. Dong, L. Gwee, D. S. Cruz, K. I. Winey, and Y. A. Elabd, *Nano Lett.*, **10**, 3785 (2010).
27. T. Xie, *Nature*, **464**, 267 (2010).
28. J. Li, T. Liu, S. Xia, Y. Pan, Z. H. Zheng, X. B. Ding, and Y. X. Peng, *J. Mater. Chem.*, **21**, 12213 (2011).
29. J. Choi, K. M. Lee, R. Wycisk, P. N. Pintauro, and P. T. Mather, *J. Mater. Chem.*, **20**, 6282 (2010).
30. Q. Deng, C. A. Wilkie, R. B. Moore, and K. A. Mauritz, *Polymer*, **39**, 5961 (1998).
31. M. Ludvigsson, J. Lindgren, and J. Tegenfeldt, *Electrochim Acta*, **45**, 2267 (2000).
32. F. H. Zhang, Z. C. Zhang, Y. J. Liu, H. B. Lu, and J. S. Leng, *Smart Mater. Struct.*, **22**, 085020 (2013).
33. H. L. Chen, C. C. Ko, and T. L. Lin, *Langmuir*, **18**, 5619 (2002).
34. H. L. Chen, X. Y. Cao, J. N. Zhang, J. J. Zhang, Y. M. Ma, G. Q. Shi, Y. C. Ke, D. T. Tong, and L. Jiang, *J. Mater. Chem.*, **22**, 22387 (2012).