Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1084482

57 (2016) 16770–16778
August

The role of coagulation in the temperature-sensitive PVDF-g-PNIPAAm membrane properties

Zhan Li, Qian Wang, Xi Chen, Shuyi Lai, Xia Feng*, Yiping Zhao, Li Chen

State Key Laboratory of Hollow Fiber Membrane Materials and Membrane Processes, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China, Tel. +86 22 83955791; emails: lizhan0718@163.com (Z. Li), 290847036@qq.com (Q. Wang), Tel. +86 22 83955792; email: polychenxi@gmail.com (X. Chen), Tel. +86 22 83955791; email: 460921402@qq.com (S. Lai), Fax: +86 22 83955401; email: fengxia@tjpu.edu.cn (X. Feng), Tel. +86 22 83955791; email: yipingzhao@tjpu.edu.cn (Y. Zhao), Tel. +86 22 83955791; Fax: +86 22 83955055; email: tjpuchenlis@163.com (L. Chen)

Received 11 September 2014; Accepted 12 August 2015

ABSTRACT

An amphiphilic copolymer (PVDF-g-PNIPAAm) with poly (vinylidene fluoride) (PVDF) main chains and poly (N-isopropylacrylamide) (PNIPAAm) side chains was synthesized by free-radical polymerization, and flat sheet copolymer membranes were prepared via the phase inversion method with N,N-dimethylformamide (DMF) as the solvent and DMF/water as the coagulation bath. The influence of the coagulation bath composition on the structure and properties of PVDF-g-PNIPAAm membrane was studied. The structure and performance of membranes were characterized by X-ray photoelectron spectroscopy, scanning electron microscopy, contact angle test, and filtration experiment. The results showed that the coagulation bath composition could affect the resulting membrane properties including pore structure, hydrophilicity, permeability, and temperature sensitivity. The PVDF-g-PNIPAAm membrane prepared in 5 wt% DMF coagulation bath exhibited higher water flux and obvious temperature sensitivity.

Keywords: PVDF-g-PNIPAAm; Coagulation bath composition; Temperature-sensitive; Membranes

1. Introduction

Poly (vinylidene fluoride) (PVDF) membrane has been widely used in separation such as water treatment and bio-separation due to its outstanding properties, like chemical resistance, high temperature resistance, high mechanical strength, thermal stability, and radiation resistance [1–5]. In the last few decades, modification of PVDF membranes with functional materials has drawn much attention. The stimuli-responsive materials have been greatly focused on, because they can endow the membrane with stimuli-responsive property.

Nowadays, many kinds of stimuli-responsive PVDF membranes have been prepared and their properties can be triggered by external stimuli such as temperature [6–9], pH [10,11], ionic strength [12], electric field [13], or the addition of chemicals. As we all know, the environmental temperature is easy to manipulate, thus temperature-sensitive membranes have been extensively studied. Poly (N-isopropylacrylamide) (PNIPAAm) is a well-known temperature-sensitive

---

*Corresponding author.

polymer and exhibits a lower critical solution temperature (LCST) at about 32℃ in aqueous solutions [14]. Below the LCST, the PNIPAAm polymer chains have an extended random coil conformation in water. As the temperature is elevated over the LCST, the polymer chains dehydrate to form a compact structure [15,16]. The conformation transformation of PNIPAAm near the LCST influences the hydrophilicity and pore size of membrane. As a result, the membrane permeability changes with temperature. Temperature-sensitive membrane shows an attractive prospect in drug-controlled release [17], bio-separation [18], anti-pollution self-cleaning membrane [19], chemical separation [20], and other fields.

The temperature-sensitive behavior of PNIPAAm-based membrane is mentioned in our previous work [21], which can be tailored by not only the grafting density of PNIPAAm chains but also the initial pore size of membrane. For membranes with larger pores and shorter grafting PNIPAAm chains, the effective pore size decreases and water flux declines due to the stretched PNIPAAm chains at temperature below LCST. At temperature above LCST, when temperature increases, the effective pore size increases and water flux enhances due to the collapsed PNIPAAm chains.

In contrast, for membranes with smaller pores and longer PNIPAAm chains which is longer than pore size, the mouth of the pores is covered by stretched polymer brushes but the expanded PNIPAAm brush is highly hydrated leading to high permeability below the LCST; above the LCST, the collapsed PNIPAAm chains form an effective hydrophobic compact structure above the mouth of the pores, thereby including the low permeability [22]. From the above, the temperature-sensitive permeability could be controlled by membrane pore structure including the pore size and the PNIPAAm grafting chains on the pore surface. The pore structure is closely related to the conditions of membrane preparation. Especially, the effect of coagulation bath composition is the most obvious. Adding solvent into coagulation bath can effectively change the phase separation behavior and result in different membrane structures.

In this paper, the amphiphilic copolymer (PVDF-g-PNIPAAm) was synthesized by alkali treatment method, and the PVDF-g-PNIPAAm membranes were prepared by the phase inversion method in different coagulation baths. The influence of coagulation bath composition on membrane properties, especially temperature sensitivity, was investigated. In terms of application, the stimulus responsiveness of membrane is an important performance parameter and it not only refers to the response amplitude, but also the response speed. In previous studies about temperature-sensitive membranes, the response speed of membrane is rarely discussed [23,24]. Actually, the slow response speed would lead to incomplete and inefficient separation. In this paper, the response speed of PVDF-g-PNIPAAm membrane prepared in different coagulation baths was studied.

2. Experimental

2.1. Materials

PVDF powders were purchased from Solvay Company of Belgium and used as received; N-isopropylacrylamide (NIPAAm) was obtained from Tokyo Chemical Industry Co., Ltd of Japan, and purified by recrystallization from toluene and n-hexane; 2,2´-azobisisobutyronitrile (AIBN, 99%), used as an initiator, was supplied by Shanghai Shisihewei Chemical Co., Ltd of China and was recrystallized from ethanol; N,N-dimethylformamide was of chemically pure grade, supplied by Tianjin Reagent Co., Ltd of China; all other reagents were of analytical grade and used without further purification, supplied by Tianjin Kemiou Chemical Co., Ltd of China.

2.2. Synthesis of PVDF-g-PNIPAAm temperature-sensitive copolymer

The PVDF-g-PNIPAAm copolymer was synthesized by the method described in previous publication [25]. The alkali treatment was manipulated as follows: PVDF powders were immersed in a 2.5 mol/L KOH solution containing 0.05 wt% ethanol, and then the suspension was stirred for 10 min at 60℃. After the suspension cooled, the precipitate was collected by filtration and washed three times with distilled water to remove the alkali solution and ethanol. The alkali-treated PVDF powder was dissolved in N,N-dimethylformamide (DMF) at 60℃. Subsequently, NIPAAm and AIBN were added to the reaction system in order to prompt graft polymerization. The solution was saturated with nitrogen for 30 min. The polymerization was allowed to proceed at 60℃ for 10 h with continuous stirring. The product was precipitated by methanol and collected by filtration. To remove the residue of NIPAAm monomers and PNIPAAm homopolymers, the raw product was washed with amounts of distilled water several times. The resulting PVDF-g-PNIPAAm copolymer was dried fully in a vacuum oven at 40℃ before further characterization and membrane preparation. Fig. 1 depicts the reaction equation of the alkali treatment process and polymerization reaction.

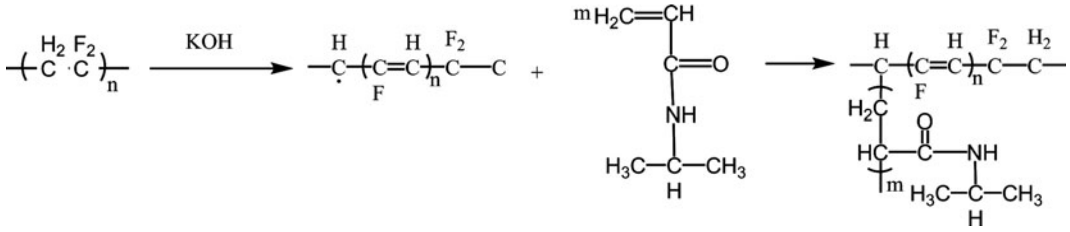

Fig. 1. The reaction equation of the PVDF-g-PNIPAAm copolymer.

2.3. Preparation of PVDF-g-PNIPAAm membrane

PVDF-g-PNIPAAm membrane was prepared via the conventional phase inversion method [26]. In a representative procedure, a casting solution was prepared by fully dissolving the PVDF-g-PNIPAAm copolymer in DMF with the concentration of 15 wt%. The solution was stirred for 2 h at 60℃ and then left for 6 h to allow complete release of air bubbles. After cooling to room temperature, the copolymer solution was cast on a glass plate by a casting knife with the thickness of 0.2 mm, and then immersed into 0, 5, 10, and 30 wt% DMF aqueous solution at 25℃ to induce the formation of membranes. The resulting PVDF-g-PNIPAAm membranes coagulated in 0, 5, 10, and 30 wt% DMF aqueous solution were assigned as M0, M5, M10, and M30, respectively. The formed membranes were soaked in distilled water for further characterizations.

2.4. Characterization of PVDF-g-PNIPAAm copolymer and membrane

The ^{1}H-NMR spectra of PVDF-g-PNIPAAm copolymer in DMSO was recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for protons. The PVDF-g-PNIPAAm copolymer has been characterized in our previous work [21,23,25].

The mole fraction of NIPAAm in the PVDF-g-PNIPAAm copolymer, abbreviated as M_c, is defined as follows: M_c = mole number of NIPAAm in PVDF-g-PNIPAAm/(mole number of NIPAAm in PVDF-g-PNIPAAm + mole number of CH_2-CF_2 repeating units in PVDF-g-PNIPAAm). According to the ^{1}H-NMR spectra of PVDF-g-PNIPAAm copolymer, the mole fraction of NIPAAm in the copolymer is 16.7%.

The cross-section and surface morphology of the membranes were inspected by scanning electron microscopy (SEM, s-4800, Hitachi, Tokyo, Japan). The membranes were fractured in liquid nitrogen to obtain a tidy cross-section, and then sputtered with gold for 3 min before observation.

The surface chemical composition of PVDF-g-PNIPAAm membrane was analyzed by GENESIS 60S (EDAX, USA) X-ray photoelectron spectroscopy (XPS) on Thermo Fisher Advantage spectrometer with a monochromatized Al Kα X-ray source (1,486.6 eV photons) at pass energy of 50 eV. All binding energies (BE) were referenced to the C1s hydrocarbon peak at 284.8 eV from adventitious carbon.

The surface hydrophilicity of PVDF-g-PNIPAAm membrane was determined using contact angle (CA, JYSP-180, JINSHENXIN, Testing Machine Co., Ltd of China) drop method. As a function of time, the CA of surface was measured. The membranes were attached on the glass slide, and then, the values of CA were determined. All the tests were performed at 25℃.

The water flux through the membrane was measured using a homemade filtration apparatus. The membrane was pressurized with pure water under a pressure of 0.1 MPa for 2 h before test to get a steady flux. The water flux was recorded under 0.1 MPa at 20 and 40℃. Further, to test the response speed of the membrane, the water flux was recorded at short intervals when a temperature of 40℃ was reached and this process continued until the flux remained constant.

The flux (J, L/m^2 h) was obtained by the following Eq. (1):

$$J = \frac{V}{At} \tag{1}$$

where J is the flux (L/m^2 h), V is the volume of water flowed through the membrane (L), t is the permeation time (h), and A is the effective area of membrane surface (m^2).

3. Results and discussions

3.1. Membrane morphology

Fig. 2 shows the cross-section and surface morphology of PVDF-g-PNIPAAm membranes prepared in different coagulation baths. Fig. 2((a)–(d)) depicts the

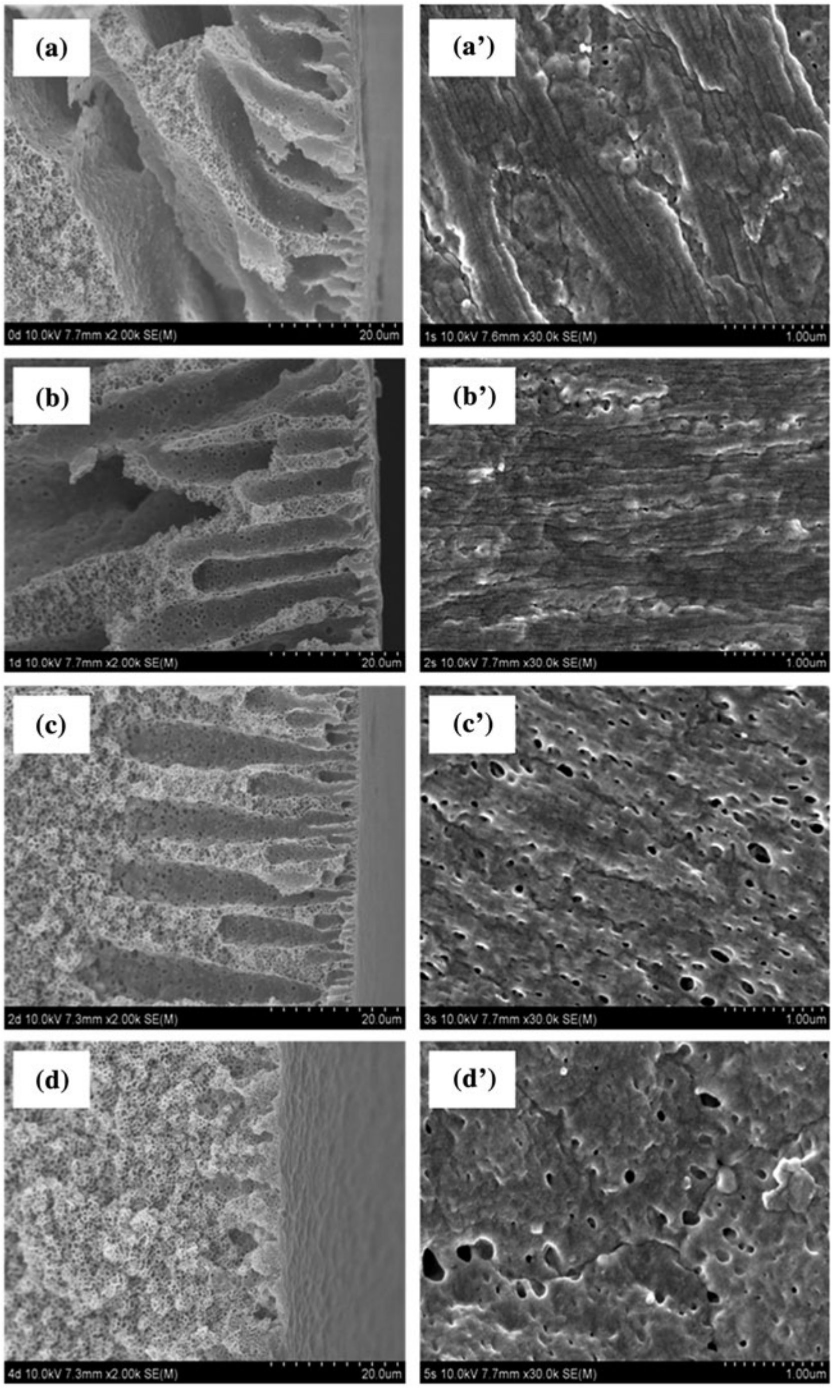

Fig. 2. SEM images of PVDF-g-PNIPAAm membranes prepared in different coagulation baths with various DMF concentrations: (a) cross-sectional morphology of M0 and (a′) surface morphology of M0; (b) cross-sectional morphology of M5 and (b′) surface morphology of M5; (c) cross-sectional morphology of M10 and (c′) surface morphology of M10; (d) cross-sectional morphology of M30 and (d′) surface morphology of M30.

cross-section morphologies of PVDF-g-PNIPAAm membranes, as observed by SEM. It can be seen that when prepared in harsh coagulation bath (for M0), the membrane has an asymmetric structure consisting of a thin dense skin and a thick porous support which comprised mainly finger-like macrovoids extending almost to the bottom surface. This kind of membrane structure is derived largely from instantaneous liquid–liquid demixing. When the DMF concentration in the coagulation bath is less than 10 wt% (for M5 and M10), the finger-like macrovoids still dominate the cross-section of membrane, but the macrovoids are less prevalent, and the size of the macrovoids is significantly smaller than that of M0. This indicates that instantaneous liquid–liquid demixing still dominates the precipitation process though the double diffusion rate between solvent (DMF) and non-solvent (H_2O) is reduced in a certain degree. When DMF concentration in coagulation bath is 30 wt% (for M30), it can be observed that the finger-like macrovoids have completely disappeared and the cross-section of the membrane demonstrated almost sponge-like structure. This kind of membrane structure is derived largely from delayed liquid–liquid demixing. Adding DMF to the coagulation bath decreases the diffusion rate of solvent and non-solvent, which makes the membrane formation speed slow down. When the DMF concentration in the coagulation bath is raised to 30 wt% (for M30), the membrane formation speed decreases remarkably, and the demixing type during membrane formation is dominated by delayed liquid–liquid demixing. Then the membrane presents a uniform sponge-like structure.

The surface SEM images of M0, M5, M10, and M30 are shown in Fig. 2((a′)–(d′)). It is observed that, in general, when the coagulation bath consists of pure water or 5 wt% DMF, the membrane surface structure is relatively dense. This happens because coagulation ability is so strong that polymer solidifies quickly. In this case, the polymer concentration is very high on the interface between casting solutions and coagulation. Such a high polymer concentration brings rapidly the polymer-rich region into a vitrification and generates the stiff and dense skin layer. When DMF concentration in coagulation bath further increases (for M10 and M30), the number of the pores on the membrane surface increases. In this case, the polymer concentration on the interface between casting solution and coagulation is very low and the delay phase separation is easy to occur. When the membrane solidifies, the polymer concentration at the interface is low due to the high solvent content in the coagulation bath, resulting in the porous surface.

3.2. Surface analysis of the PVDF-g-PNIPAAm membrane by XPS

The surface compositions of the copolymer membranes prepared in different coagulation baths are studied by XPS. Fig. 3 shows the wide-scan spectra for M0, M5, M10, and M30, respectively. BE at 687.3 and 285.7 eV, associated with F1s and C1s signals, are shown in all samples. Besides, signals from O1s and N1s occur at BE of about 532.3 and 398.5 eV, which is from the grafted PNIPAAm.

The XPS results present the element percentage of N and F on the membrane surface. The surface NIPAAm mole fraction of PVDF-g-PNIPAAm membrane, which is abbreviated as Ms, is readily calculated according to the Eq. (2):

$$Ms = \frac{[N]}{[N] + 0.5[F]} \times 100\% \tag{2}$$

where $[N]$ and $[F]$ are the percentages of N and F, respectively; coefficient 0.5 represents that each repeating unit of the PVDF has two F atoms.

The NIPAAm mole fraction of PVDF-g-PNIPAAm membrane prepared in various DMF concentration coagulants are shown in Table 1.

According to previous work [23], we can see the Mc of PVDF-g-PNIPAAm copolymer is 16.7%. Comparing the Ms (determined by XPS) of PVDF-g-PNIPAAm membrane with the Mc of the corresponding PVDF-g-PNIPAAm copolymer, it can be found that the former is much higher than the latter. This phenomenon is due to the enrichment of the PNIPAAm polymer at the outermost surface during membrane formation process in the aqueous medium. The copolymer possesses an amphiphilic structure with hydrophobic PVDF chains and hydrophilic PNIPAAm chains below its LCST. When pure water is used as the coagulation bath, the stronger affinity between PVDF-g-PNIPAAm and coagulation bath facilitates the higher Ms because the driving force for PNIPAAm moving to the coagulation. Therefore, the PNIPAAm content on the membrane surface is higher than that in the bulk copolymer.

Though the NIPAAm content on membrane surface is higher than that in the bulk copolymer, it is found that initially, the Ms of PVDF-g-PNIPAAm membrane decreases as DMF concentration in coagulation bath raises, but then increases when the DMF concentration is 30 wt%. This result can be explained by considering the affinity between PVDF-g-PNIPAAm and coagulation bath and the membrane solidified time. Nosaka [27] has investigated the swelling degree of PNIPAAm gel in DMF aqueous solution and found that with the DMF concentration in water increased, the swelling degree of PNIPAAm gels declined and the affinity between PNIPAAm and DMF aqueous solution decreased. In the membrane formation process of M0, M5, and M10, the affinity between PVDF-g-PNIPAAm and coagulation bath decreases in sequence, so the Ms decreases following the sequence of M10 < M5 < M0. But for M30, though the affinity between PVDF-g-PNIPAAm and

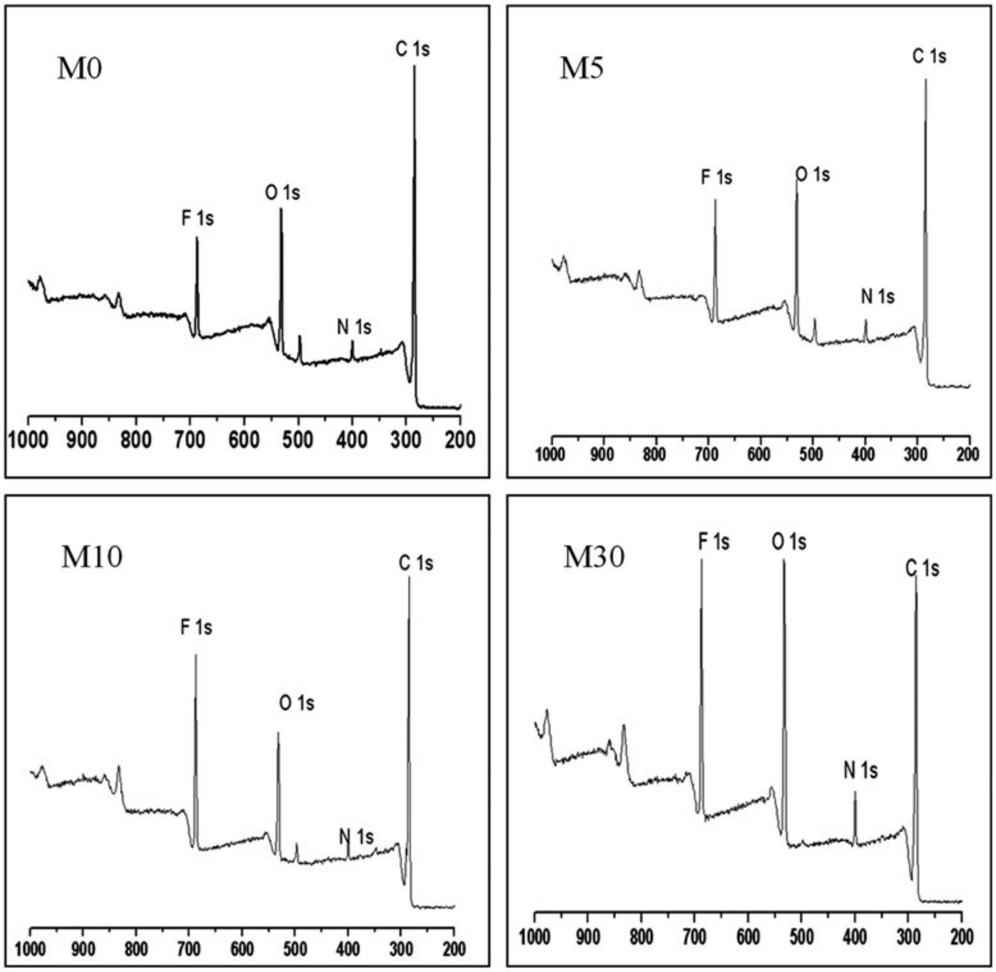

Fig. 3. XPS wide-scan spectra of PVDF-g-PNIPAAm membrane prepared in various DMF concentration coagulants.

Table 1
Element percentages and NIPAAm mole fraction for the PVDF-g-PNIPAAm membrane surfaces analyzed by XPS

Membrane ID	C1s (%)	O1s (%)	F1s (%)	N1s (%)	NIPAAm mole fraction (%)
M0	74.00	13.42	6.62	2.80	45.8
M5	70.06	14.60	8.22	3.25	44.2
M10	71.62	11.76	11.19	2.56	31.3
M30	64.61	18.49	11.22	4.56	44.4

coagulation bath is the weakest, the *Ms* is not the lowest among the membranes. It has been observed in our experiments that the membrane formation time of M30 is much longer than that of other membranes, and the longer membrane solidified time facilitates the higher *Ms*, because there is enough time for PNIPAAm chain changing its conformation and moving to the interface.

3.3. Membrane hydrophilicity analysis

Water contact angle is often used to evaluate the hydrophilicity of membranes. Generally, low water contact angle means high surface hydrophilic property [28]. The hydrophilicity of the PVDF-g-PNIPAAm membrane evaluated by water contact angle measurement is displayed in Table 2.

Among all the membranes, M0 has the lowest contact angle which is 54.2˚. With the increase of solvent in coagulation bath, the water contact angles for the PVDF-g-PNIPAAm membranes exhibit an increasing tendency except for M30 whose contact angle is not the maximum value.

This phenomenon can be analyzed from the following perspectives: firstly, compared to PVDF, PNIPAAm is hydrophilic. So the membrane hydrophilicity increases with the increase in NIPAAm content on membrane surface. According to the XPS results, the NIPAAm content of PVDF-g-PNIPAAm membrane surface decreased with the increase in solvent in coagulation bath, therefore, the hydrophilicity of M0, M5, and M10 decreases successively and the contact angle increases. On the other hand, the contact angle of M30 is 68.5˚ although the surface NIPAAm content of M30 is close to that of M5. As known to us, the contact angle also has a relationship with the morphology of the membrane surface. As the DMF concentration in coagulation bath increases, membrane structure changes from finger-like macrovoids to sponge-like structure and the porous surface. The porous surface leads to the water drop absorbed rapidly. So the contact angle of M30 is less than that of M5.

3.4. Permeability of PVDF-g-PNIPAAm membrane

Water flux was measured at 20 and 40˚C to investigate the permeability and temperature-sensitivity of the PVDF-g-PNIPAAm membrane. The results are shown in Fig. 4. It can be seen that the permeability of PVDF-g-PNIPAAm membrane is greatly influenced by the composition of coagulation bath. The flux of the PVDF-g-PNIPAAm membranes decreases with the DMF concentration in coagulation bath. The flux of M0 is the highest among the four membranes and could reach to 79 L/m^2 h. Compared to M0, the flux of M30 is the lowest, and the value is 21 L/m^2 h. The permeability of membrane depends on the hydrophilicity of membrane surface and membrane pore structure. As is known to all, stronger hydrophilicity of membrane surfaces and bigger membrane pore structures result in the higher flux. For M0, the finger-like macrovoids and higher NIPAAm content on the membrane surface, lead to the high flux value. However, for M30, the cross-section structure changes from finger-like macrovoids to sponge-like structure completely, so the flux is low.

Table 2
Contact angles of the PVDF-g-PNIPAAm membrane prepared in various DMF concentration coagulants

Membrane ID	M0	M5	M10	M30
Contact Angle (˚)	54.2	57.7	73.2	68.5

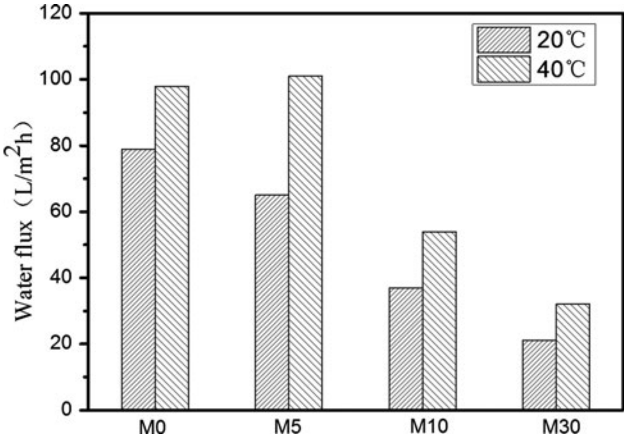

Fig. 4. Influence of coagulation bath composition on the water fluxes of PVDF-g-PNIPAAm membranes manipulated at different temperatures.

As shown in Fig. 4, when temperature increases from 20 to 40˚C, the flux of all the PVDF-g-PNIPAAm membranes increases in some degree. This is due to the fact that the viscosity decreases with water at higher temperature.

Fig. 5 shows the water flux changes of PVDF-g-PNIPAAm membranes at 40˚C for 90 min. When temperature is 40˚C, the flux of all the PVDF-g-PNIPAAm membranes prepared in different coagulation baths decreases with the extension of time. The reason for this phenomenon maybe that the hydrophobic groups of PNIPAAm are easy to arrange on the surface of the

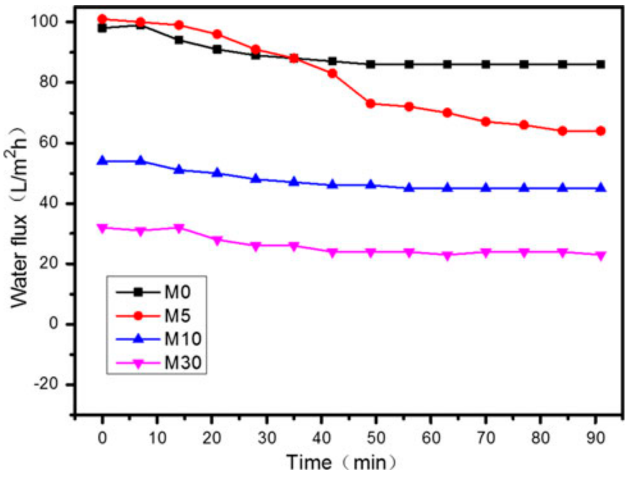

Fig. 5. Water flux variation of PVDF-g-PNIPAAm membranes prepared in different coagulation baths at 40˚C.

copolymer membrane at 40℃, and the hydrophilicity of membranes. Consequently, the water flux of the membranes reduces with the extension of time.

Fig. 5 presents a distinct variation of water flux when the DMF concentration of coagulation bath is 5 wt%. The response speed and amplitude are the biggest. That is to say, the temperature sensitivity of PVDF-g-PNIPAAm membrane is so obvious in this condition. From the results, we can see that the permeability and the temperature sensitivity of PVDF-g-PNIPAAm membrane are greatly affected by the membrane structure and could be regulated by simply varying the coagulation bath composition. As stated in introduction of this paper, the temperature sensitivity of membrane based on PNIPAAm closely correlates with the PNIPAAm content, length on the membrane surface, and the pore structure, this cannot be described by a simple linear relationship. The interaction between pore structure and PNIPAAm content and length, and the temperature-sensitive performance of PVDF-g-PNIPAAm membrane prepared in 5 wt% DMF coagulation bath, will be studied in our next work.

4. Conclusion

PNIPAAm grafted PVDF copolymer was successfully synthesized by alkali treatment method. The PVDF-g-PNIPAAm membranes were prepared by the immersion–precipitation method in different coagulation baths. The membrane structure and the temperature-sensitive behavior were studied with different concentrations of DMF aqueous solution as coagulation bath. When water is used as the coagulation bath, instantaneous liquid–liquid demixing dominates the demixing process and results in finger-like macrovoids. When 5, 10, and 30 wt% DMF aqueous solution are used as the coagulation bath, the liquid–liquid demixing was delayed and the pore structure changes from finger-like macrovoids to uniform sponge-like structures, the PNIPAAm content on the membrane surface decreases and then increases with the increase in DMF concentration in coagulation bath.

The PVDF-g-PNIPAAm membrane prepared in different coagulation baths shows typical temperature-sensitive behavior, that is, a sharp change appears at 40℃ and the water flux decreases accordingly with the increase in the DMF concentration. In addition, when the DMF concentration of the coagulation bath is 5 wt%, the membrane obtained in this condition exhibited obviously temperature-sensitive performance, that is, the flux of M5 shows the biggest response speed and amplitude.

References

[1] K.H. Oshima, T.T. Evans-Strickfaden, A.K. Highsmith, E.W. Ades, The use of a microporous polyvinylidene fluoride (PVDF) membrane filter to separate contaminating viral particles from biologically important proteins, Biologicals 24 (1996) 137–145.

[2] X. Tan, S.P. Tan, W.K. Teo, K.J. Li, Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water, J. Membr. Sci. 271 (2006) 59–68.

[3] A. Bottino, G. Capannelli, A. Comite, Novel porous poly (vinylidene fluoride) membranes for membrane distillation, Desalination 183 (2005) 375–382.

[4] D. Wang, W.K. Teo, K. Li, Selective removal of trace H_2S from gas streams containing CO_2 using hollow fiber membrane modules/contactors, Sep. Purif. Technol. 35 (2004) 125–131.

[5] F. Liu, C.H. Du, B.K. Zhu, Y.Y. Xu, Surface immobilization of polymer brushes onto porous poly(vinylidene fluoride) membrane by electron beam to improve the hydrophilicity and fouling resistance, Polymer 48 (2007) 2910–2918.

[6] L.Y. Chu, S.H. Park, T. Yamaguchi, S.I. Nakao, Preparation of thermo-responsive core-shell microcapsules with a porous membrane and poly(N-isopropylacrylamide) gates, J. Membr. Sci. 192 (2001) 27–39.

[7] Y. Li, L.Y. Chu, J.H. Zhu, H.D. Wang, S.L. Xia, W.M. Chen, Thermoresponsive gating characteristics of poly (N-isopropylacrylamide)-grafted porous poly (vinylidene fluoride) membranes, Ind. Eng. Chem. Res. 43 (2004) 2643–2649.

[8] L.Y. Chu, Y. Li, J.H. Zhu, W.M. Chen, Negatively thermoresponsive membranes with functional gates driven by zippe-type hydrogen-bonding interactions, Angew. Chem. Int. Ed. 44 (2005) 2124–2127.

[9] K. Zhang, X.Y. Wu, Temperature and pH-responsive polymeric composite membranes for controlled delivery of proteins and peptides, Biomaterials 25 (2004) 5281–5291.

[10] J.B. Qu, L.Y. Chu, M. Yang, R. Xie, L. Hu, W.M. Chen, A pH-responsive gating membrane system with pumping effects for improved controlled release, Adv. Funct. Mater. 16 (2006) 1865–1872.

[11] T. Peng, Y.L. Cheng, pH-responsive permeability of PE-*g*-PMAA membranes, J. Appl. Polym. Sci. 76 (2000) 778–786.

[12] A.M. Mika, R.F. Childs, J.M. Dickson, B.E. McCarry, D.R. Gagnon, A new class of polyelectrolyte-filled microfiltration membranes with environmentally controlled porosity, J. Membr. Sci. 108 (1995) 37–56.

[13] Y. Ly, Y.L. Cheng, Electrically-modulated variable permeability liquid crystalline polymeric membrane, J. Membr. Sci. 77 (1993) 99–112.

[14] Y. Hirokawa, T. Tanaka, Volume phase transition in a nonionic gel, J. Chem. Phys. 81 (1984) 6379–6380.

[15] J. Zhang, L.Y. Chu, C.J. Cheng, D.F. Mi, M.Y. Zhou, X.J. Ju, Graft-type poly (N-isopropylacrylamide-co-acrylic acid) microgels exhibiting rapid thermo- and pH-responsive properties, Polymer 49 (2008) 2595–2603.

[16] J.G. Cheng, L. Wang, J. Huo, H.J. Yu, Q. Yang, L.B. Deng, Study on synthesis of poly(N-isopropylacrylamide) grafted carbon black and temperature-dependence conductivity of grafted carbon black/epoxy

composites, J. Polym. Sci., Part B: Polym. Phys. 46 (2008) 1529–1535.

[17] T. Ta, A.J. Convertine, C.R. Reyes, P.S. Stayton, T.M. Porter, Thermosensitive liposomes modified with poly (N-isopropylacrylamide-co-propylacrylic acid) copolymers for triggered release of doxorubicin, Biomacromolecules 11 (2010) 1915–1920.

[18] S. Rattan, T. Sehgal, Stimuli-responsive polymeric membranes through graft copolymerization of N-isopropylacrylamide onto polycarbonate track etched membranes for biomedical applications, Procedia Chem. 4 (2012) 194–201.

[19] D. Wandera, S.R. Wickramasinghe, S.M. Husson, Modification and characterization of ultrafiltration membranes for treatment of produced water, J. Membr. Sci. 373 (2011) 78–188.

[20] A.L. Golden, C.F. Battrell, S. Pennell, A.S. Hoffman, J.J. J. Lai, P.S. Stayton, Simple fluidic system for purifying and concentrating diagnostic biomarkers using stimuli-responsive antibody conjugates and membranes, Bioconjugate Chem. 21 (2010) 1820–1826.

[21] Y.F. Guo, X. Feng, L. Chen, Y.P. Zhao, J. Bai, Influence of the coagulation-bath temperature on the phase-separation process of poly (vinylidene fluoride)-graft-poly (N-isopropylacrylamide) solutions and membrane structures, J. Appl. Polym. Sci. 116 (2010) 1005–1009.

[22] H. Alem, A.S. Duwez, P. Lussis, P. Lipnik, A.M. Jonas, S. Demoustier-Champagne, Microstructure and thermo-responsive behavior of poly (N-isopropylacrylamide) brushes grafted in nanopores of track-etched membranes, J. Membr. Sci. 308 (2008) 75–86.

[23] X. Feng, Y.F. Guo, X. Chen, Y.P. Zhao, J.X. Li, X.L. He, L. Chen, Membrane formation process and mechanism of PVDF-g-PNIPAAm thermo-sensitive membrane, Desalination 290 (2012) 89–98.

[24] X. Feng, Y.F. Guo, Y.P. Zhao, J.X. Li, X. Chen, X.L. He, L. Chen, Influence of coagulant temperature on the membrane formation process and properties of PVDF-g-PNIPAAm temperature-sensitive membranes, Chem. J. Chin. U. 32 (2011) 1424–1430.

[25] L. Chen, E.L. Lu, W.Y. Wang, X. Feng, Y.P. Zhao, Synthesis and characterization of temperature-sensitive poly (vinylidene fluoride) membrane materials, Chin. J. Funct. Mater. 38 (2007) 1990–1992.

[26] F. Schacher, T. Rudolph, F. Wieberger, M. Ulbricht, A.H. Müller, Double stimuli-responsive ultrafiltration membranes from polystyrene-block-poly (N,N-dimethylaminoethyl methacrylate) diblock copolymers, ACS Appl. Mater. Interfaces 1 (2009) 1492–1503.

[27] S. Nosaka, T. Ishida, K. Urayama, T. Takigawa, Steady flow properties of a mixed solvent through a poly (N-isopropylacrylamide) gel, J. Membr. Sci. 305 (2007) 325–331.

[28] Y.L. Su, C. Mu, C. Li, Z. Jiang, Antifouling property of a weak polyelectrolyte membrane based on poly (acrylonitrile) during protein ultrafiltration, Ind. Eng. Chem. Res. 48 (2009) 3136–3141.