



# Thermoresponsive Microfiltration Membranes Prepared by Atom Transfer Radical Polymerization Directly from Poly(vinylidene fluoride)

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## ABSTRACT

The smart polymers are of particular interest due to their quick response to external environmental chemical and/or physical stimuli, such as temperature, pH, ionic strength, electric field, and photo-irradiation. These polymers may be used in many fields, such as protein adsorption, immobilization and separation, stimuli-responsive controlled releases and biotechnology. In the present work, a graft copolymer of poly(vinylidene fluoride) with poly(*N*-isopropylacrylamide) (PVDF-*g*-P(NIPAAm)) was synthesized by atom transfer radical polymerization (ATRP) directly using poly(vinylidene fluoride) (PVDF) as a macroinitiator. The copolymer can be readily cast into temperature-sensitive microfiltration membranes by the phase inversion technique. The effect of molar feed ratio of NIPAAm/PVDF on the properties of the copolymers was studied. The bulk and surface compositions of the membranes were obtained by elemental analysis and X-ray photoelectron spectroscopy (XPS), respectively. XPS results of the copolymer membranes obtained by phase inversion technique revealed a substantial surface enrichment of the grafted P(NIPAAm). The thermal stability of the copolymers was investigated by thermogravimetric analysis (TGA). The permeability of water through the pristine PVDF membrane exhibited the almost temperature-independent flux behaviour. However, the rate of water flux through the PVDF-*g*-P(NIPAAm) membrane increased with the increase in permeate temperature from 20°C (below the LCST) to 50°C (above the LCST), with the most drastic increase being observed at the permeate temperature of about 32°C. The temperature-dependent permeation rate may result from the change in conformation of the P(NIPAAm) chains in the PVDF-*g*-P(NIPAAm) membrane. The thermoresponsive membranes obtained via the present approach may be applied to the biomedical and biotechnology fields.

### Key Words:

atom transfer radical polymerization;  
poly(vinylidene fluoride);  
poly(*N*-isopropylacrylamide);  
thermoresponsive membrane;  
microfiltration.

## INTRODUCTION

The smart polymers are of particular interest due to their excellent mechanical strength and quick response to external stimuli, such as temperature, pH, ionic strength, glucose concentration, electric field, and photo-irradiation [1-4], which can be used in the fields of controlled drug delivery, bioseparation, chemical separation, water

treatment, chemical sensors, tissue engineering, etc. [5]. The fabrication of these smart membranes is of both scientific and technological interest. For instance, poly(*N*-isopropylacrylamide) (P(NIPAAm)) is the most widely studied thermo-sensitive polymer [6,7]. It exhibits a lower critical solution temperature (LCST) at around 32°C

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in aqueous solution. Below this temperature, it adopts an extended random coil conformation. As the temperature is increased, the hydrogen bonds weaken with the concomitant release of water of hydration. The hydrophobic interaction tends to overcome the hydrophilic interaction, leading to a coil-to-globule transition and finally to phase separation [8].

Poly(vinylidene fluoride) (PVDF) has outstanding physical and chemical resistance and wide industrial and biomedical applications [9,10]. Therefore, PVDF grafted with P(NIPAAm) has become one of the most attractive research targets as smart copolymers for membrane materials. The modification of polymers via molecular design is one of the most versatile approaches. Yang et al. reported that P(NIPAAm)-grafted PVDF membranes were prepared by plasma-graft pore-filling polymerization [11]. Recent advances in atom transfer radical polymerization (ATRP) have provided opportunities for synthesizing polymers with well-defined macromolecular architectures [12-16]. ATRP facilitates the control over the molecular weight, macromolecular architecture, and specific functionality. Moreover, polymers prepared by ATRP have a living and dormant end functionality that can re-activate further polymerization. The halogen atoms serve as initiation sites for the polymerization of side chains by ATRP. The direct preparation of amphiphilic graft copolymers having PVDF backbones by ATRP of hydrophilic side chains initiated at the secondary halogenated sites of PVDF has been reported by Hester et al. [17].

In the present study, PVDF-*g*-P(NIPAAm) copolymers were synthesized by ATRP directly using PVDF as a macroinitiator. The effect of molar feed ratio of NIPAAm/PVDF on the properties of the copolymers was studied. Elemental analysis, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were used to characterize the PVDF-*g*-P(NIPAAm) copolymers. The membranes cast subsequently from the PVDF-*g*-P(NIPAAm) copolymers exhibited strong and reversible temperature-dependent flux properties for pure water. The grafted side chains of PNIPAAm impart stimuli-responsive properties into the resulting membranes. The thermoresponsive membranes obtained via the present approach may be applied to

the biotechnology fields.

## EXPERIMENTAL

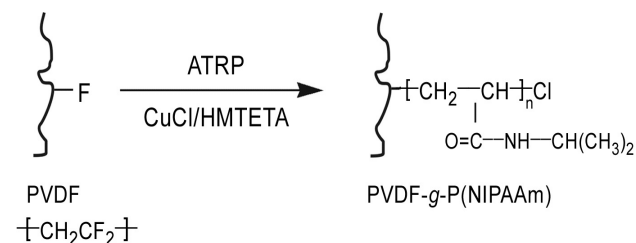
### Materials

PVDF (molecular weight = 441,000; polydispersity index = 1.24) and *N*-isopropylacrylamide (NIPAAm) were obtained from Aldrich Chemical Co. 1,1,4,7,10,10,-Hexamethyltriethylene-tetramine (HMTETA), *N*-methyl-2-pyrrolidone (NMP) and copper(I) chloride (CuCl) were purchased from Aldrich Chemical Co. The solvents were analytical grades and used without further purification unless otherwise mentioned.

### ATRP of NIPAAm with PVDF

The reactions involved are illustrated schematically in Figure 1. Two grams PVDF was dissolved in 30 mL NMP in a three-necked round bottom flask equipped with a thermometer, a condenser, and a gas line, then NIPAAm, CuCl, and HMTETA were added. The polymerization was allowed to proceed at 60°C for 10 h, under a nitrogen atmosphere [18]. The copolymer was then precipitated in excess water. After exhaustive extraction in copious amounts of doubly distilled water, the copolymer sample was dried by pumping under reduced pressure.

PVDF and PVDF-*g*-P(NIPAAm) membranes were prepared by phase inversion [19] from NMP solutions containing 10 wt% polymer or the copolymer. The polymer blend solution was cast onto a glass plate, which was subsequently immersed in a bath of doubly distilled water. The temperature of the water in the casting bath was at 25°C. Each membrane was left in water for about 20 min after separation from the glass plate. The membrane was washed



**Figure 1.** Schematic diagram illustrating the direct process of ATRP from PVDF.

thoroughly with copious amounts of doubly distilled water for 2 h under vigorous stirring. The purified membranes were dried under reduced pressure for subsequent characterization.

### Characterization

The copolymers were characterized by X-ray photoelectron spectroscopy (XPS). XPS was performed on a Kratos AXIS HSi spectrometer with a monochromatized Al K $\alpha$  X-ray source (1486.6 eV photons). The pressure in the analysis chamber was kept at 10<sup>-8</sup> Torr or lower during each measurement. Surface elemental stoichiometries were determined from the ratios of the sensitivity factors-corrected spectral area and were reliable to within  $\pm 5\%$ . The bulk C, H, and N contents were determined on a Perkin-Elmer 2400 elemental analyzer. The F content was determined, on the other hand, by the Schoeniger combustion method [20]. TGA was carried out on a TA Instruments 2100 thermogravimetric analyzer at a heating rate of 20°C/min under a dynamic dry N<sub>2</sub> flow of 100 cm<sup>3</sup>/min. Pure water was used to study the dependence of permeation rate on temperature. Flux experiments were carried out under 5.9 kPa pressure, using a stirred micro-filtration cell. The micro-filtration cell containing the fluid was kept in a thermostated water bath for at least 20 min prior to the flux experiment.

## RESULTS AND DISCUSSION

### Characterization of the PVDF-*g*-P(NIPAAm) Copolymers

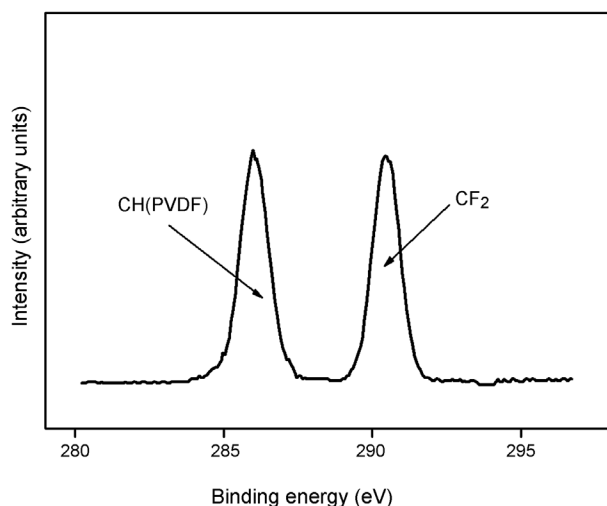
The molar feed ratios of [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-] for the preparation of the PVDF-*g*-P(NIPAAm)

copolymers ranged from 1.21 to 2.67 in the present study. The bulk graft concentration of the copolymers can be derived from the carbon to fluorine ratio, determined by the elemental analysis. The graft concentration in terms of the number of NIPAAm repeat units per PVDF repeat unit, the ([NIPAAm-]/[-CH<sub>2</sub>CF<sub>2</sub>-])<sub>bulk</sub> molar ratio, can be obtained readily from the ([C]/[F])<sub>bulk</sub> molar ratio by taking into account the carbon stoichiometries of the graft and the main chains, and the carbon to fluorine ratio of the PVDF main chain. As it is shown in Table 1, the results of elemental analysis suggest that the bulk graft concentration increases with the increase in NIPAAm monomer concentration used for ATRP.

The surface chemical compositions of the PVDF-*g*-P(NIPAAm) temperature-sensitive membranes were studied by XPS. Figures 2-4 show the C 1s core-level spectra of the membranes prepared from the pristine PVDF, PVDF-*g*-P(NIPAAm)1 and PVDF-*g*-P(NIPAAm)3 copolymers. The C 1s core-level spectrum of the pristine PVDF membrane can be curve-fitted with two peak components, with binding energies (BEs) at 285.8 eV for the CH<sub>2</sub> species and at 290.5 eV for the CF<sub>2</sub> species [21]. The ratio for the two peak components is about 1.03 and in good agreement with the chemical stoichiometry of PVDF. The C1s core-level spectra of the PVDF-*g*-P(NIPAAm) membranes are curve-fitted with the following five chemical species. The two peak components with BEs at 285.8 eV for the CH<sub>2</sub> species and at 290.5 eV for the CF<sub>2</sub> species can be assigned to the PVDF main chains. The component with BE at 287.4 eV is assigned to the N-C=O species of the grafted NIPAAm polymer chains [22]. The component with the BE at 284.6 eV is attributed to the CH<sub>2</sub> species of the grafted NIPAAm polymer chain.

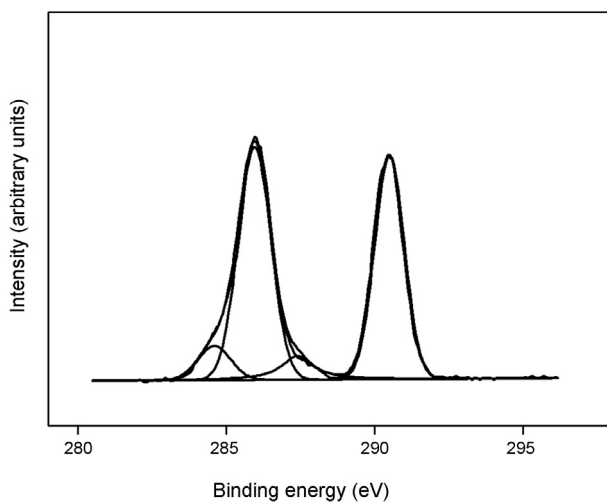
**Table 1.** Dependence of graft concentration and the average pore-size of the PVDF-*g*-P(NIPAAm) membranes on [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-] molar feed ratio.

Sample	Molar feed ratio [NIPAAm]/[-CH <sub>2</sub> CF <sub>2</sub> -]	([C]/[F]) <sub>bulk</sub>	([NIPAAm-]/ [-CH <sub>2</sub> CF <sub>2</sub> -]) <sub>bulk</sub>	([C]/[F]) <sub>surface</sub>	([NIPAAm-]/ [-CH <sub>2</sub> CF <sub>2</sub> -]) <sub>surface</sub>	Average pore size (μm)
PVDF- <i>g</i> -P(NIPAAm)1	1.21	1.08	0.03	1.21	0.07	1.60
PVDF- <i>g</i> -P(NIPAAm)2	1.65	1.22	0.07	1.81	0.27	1.57
PVDF- <i>g</i> -P(NIPAAm)3	2.13	1.33	0.11	1.98	0.33	1.53
PVDF- <i>g</i> -P(NIPAAm)4	2.67	1.47	0.16	2.46	0.49	1.51

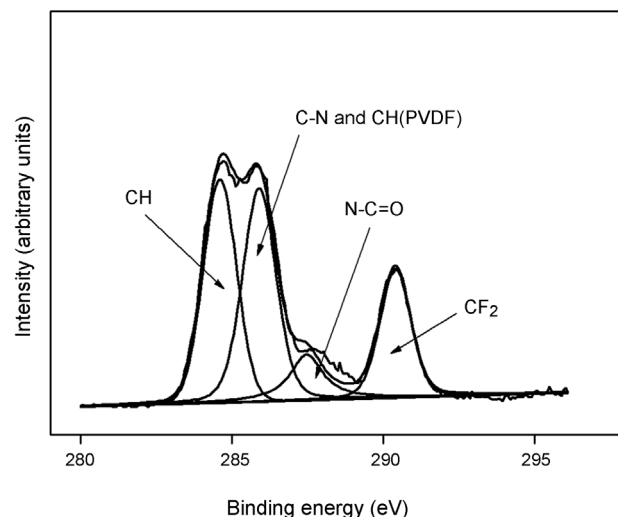


**Figure 2.** XPS C 1s core-level spectra of the pristine PVDF.

Because the CN (NIPAAm) and CH<sub>2</sub> (PVDF) peak components have similar BEs, they are combined and shown as a single peak component at the BE at 285.8 eV [22]. The steady increase in the N-C=O peak component intensity and the steady decrease in the CF<sub>2</sub> peak component intensity in Figures 3 and 4 indicate the increase in surface graft concentration with the molar feed ratio [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-]. A strong N 1s signal (BE at 399 eV) [23] in the XPS spectrum of the PVDF-*g*-P(NIPAAm)**3** copolymer (Figure 5) also suggests that NIPAAm has been successfully grafted on the PVDF chain via direct ATRP. The XPS results show the dependence of the

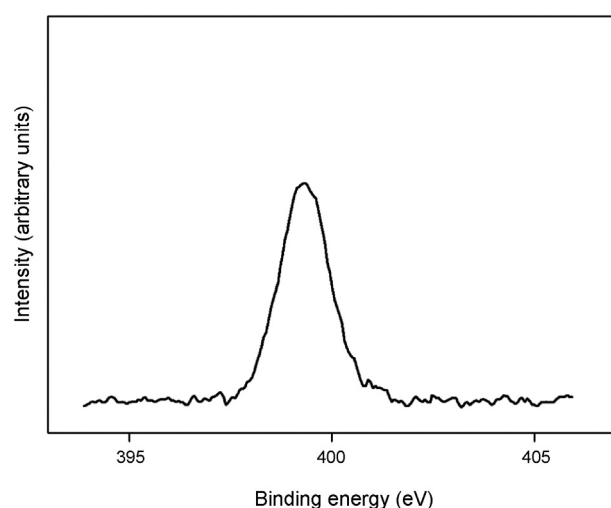


**Figure 3.** XPS C 1s core-level spectra of PVDF-*g*-P(NIPAAm)**1**.

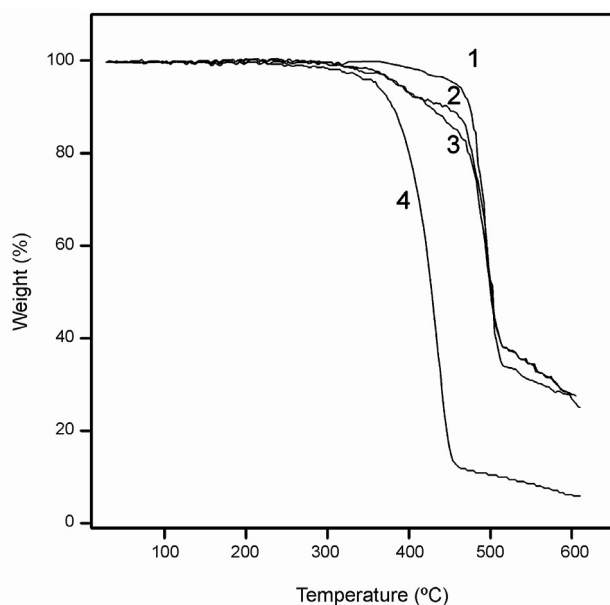


**Figure 4.** XPS C 1s core-level spectra of PVDF-*g*-P(NIPAAm)**3**.

surface graft concentration in the PVDF-*g*-P(NIPAAm) membranes on the molar feed ratio [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-]. Comparing the surface [C]/[F] ratio (determined by XPS) with the bulk [C]/[F] ratio (determined by elemental analysis) of the corresponding PVDF-*g*-P(NIPAAm) copolymer (Table 1), the former is much higher than the latter. This phenomenon is consistent with the enrichment of P(NIPAAm) at the outermost surface during the process of membrane formation by the phase-inversion technique in water. The surface enrichment of the grafted NIPAAm segments could be ascribed to



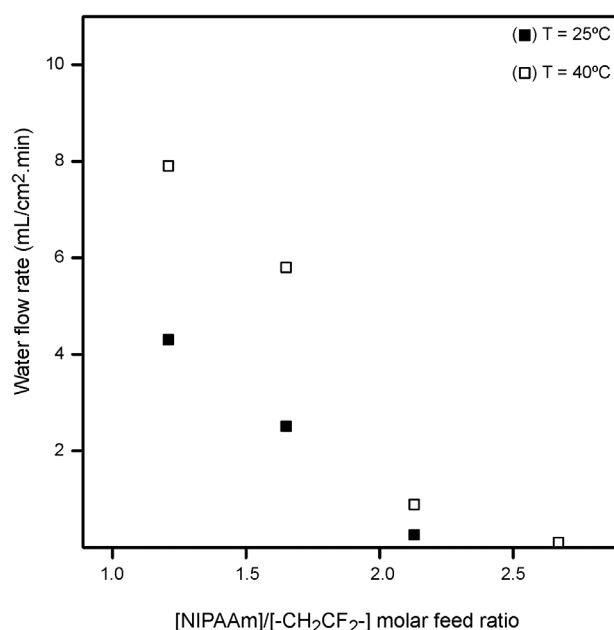
**Figure 5.** XPS N 1s core-level spectra of PVDF-*g*-P(NIPAAm)**3**.



**Figure 6.** TGA curves of (1) the pristine PVDF, (2) PVDF-*g*-P(NIPAAm)**2**, (3) PVDF-*g*-P(NIPAAm)**3**, and (4) the P(NIPAAm) homopolymer.

the lack of complete miscibility between the crystalline phase of PVDF and P(NIPAAm) and the strong interaction of P(NIPAAm) with the aqueous environment. On the other hand, the average pore size of the PVDF-*g*-P(NIPAAm) membranes decreases from about 1.60  $\mu\text{m}$  to about 1.51  $\mu\text{m}$  with the [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-] molar feed ratio from about 1.21 to about 2.67.

Figure 6 shows respective TGA curves of the pristine PVDF, PVDF-*g*-P(NIPAAm)**2**, PVDF-*g*-P(NIPAAm)**3**, and the P(NIPAAm) homopolymer. For the pristine PVDF membrane (curve 1), it is stable up to about 400°C and suffers a weight loss of less than 5% at 430°C. For the PNIPAAm homopolymer (curve 4), an initial minor weight loss at around 150°C and the main weight loss commences at about 350°C, which is in accordance with the result reported by Kim et al. [24]. The PVDF-*g*-P(NIPAAm) membranes show intermediate weight loss behaviour (curves 2 and 3) in comparison to that of the pristine PVDF membrane (curve 1) and that of the PNIPAAm (curve 4). A distinct two-step degradation process is observed for the grafted membrane samples. The first major weight loss occurs at about 350°C, corresponding to the decomposition of the P(NIPAAm) component. The second major weight

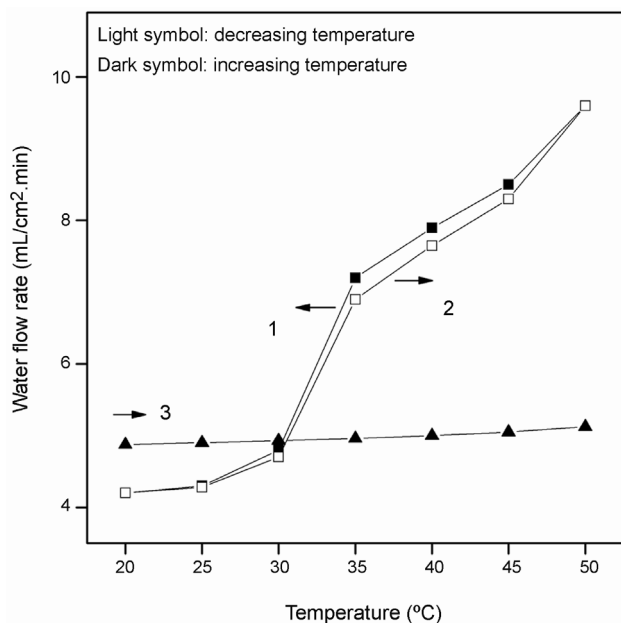


**Figure 7.** Effect of [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-] molar feed ratio on the water flux through PVDF-*g*-P(NIPAAm) membranes.

loss commences at about 450°C, corresponding to the decomposition of the PVDF main chains.

### Thermoresponsive Behaviour of PVDF-*g*-P(NIPAAm) Membrane

Figure 7 shows the effect of [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-] molar feed ratio on the water flux through PVDF-*g*-P(NIPAAm) membranes. The water fluxes decrease at both 25°C and 40°C with the increase in [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-] molar feed ratio. It can be ascribed to the increase in the length and density of the grafted P(NIPAAm) chains with increasing [NIPAAm]/[-CH<sub>2</sub>CF<sub>2</sub>-] molar feed ratio, as shown in Table 1. On the other hand, the water flux at 40°C is always larger than that at 25°C because of the swelling/shrinking property of the grafted P(NIPAAm) chains. At 25°C below the LCST (about 32°C) of the P(NIPAAm) homopolymer, the P(NIPAAm) chains are solvated and extended into the pores to reduce the flux of pure water. However, at 40°C above the LCST, the grafted P(NIPAAm) chains shrink and results in an opening of the pores of the membrane and hence the observed increase in the flux of pure water. The phenomena are consistent with those of P(NIPAAm)-grafted PVDF membranes by plasma-graft pore-filling polymerization [11].



**Figure 8.** Temperature-dependent water permeability through the PVDF-*g*-P(NIPAAm)1 membrane and the pristine PVDF membrane. Curves 1 and 2 are the water fluxes through the PVDF-*g*-P(NIPAAm)1 membrane when subjected to temperature cycling. Curve 3 is the flux through the pristine PVDF membrane.

The temperature-dependent fluxes of water through the PVDF and PVDF-*g*-P(NIPAAm)1 membranes are shown in Figure 8. The permeability of water through the pristine PVDF membrane exhibits almost temperature-independent flux behaviour (curve 3). In contrast to the pristine PVDF, the rate of water flux through the PVDF-*g*-P(NIPAAm)1 membrane increases with the increase in permeate temperature from 20°C to 50°C, with the most drastic increase being observed at the permeate temperature of about 32°C (curve 1). The temperature-dependent permeation rate probably has also resulted from the change in conformation of the P(NIPAAm) chains in the PVDF-*g*-P(NIPAAm) membrane. When the permeate temperature is below the LCST, the grafted P(NIPAAm) chains on the pore surfaces are in the swollen state. The grafted NIPAAm chains are also enriched on the surface of the membrane during the phase inversion process. As a result, the water flux is lower. In contrast, when the permeate temperature is above the LCST, the grafted P(NIPAAm) chains on the pore surfaces are in the shrunken state and

associate hydrophobically on the membrane and pore surfaces. Therefore the pore size increases and results in a larger water flux.

The reversible decrease in the permeation rate can be observed when the permeate temperature is decreased, as shown in curve 2. This indicates that the temperature-dependent changes in permeation rate for water at temperatures between 20°C and 50°C are completely reversible. This result suggests that both the extent of interaction with the aqueous environment and the conformation of the graft P(NIPAAm) chains vary reversibly with the permeate temperature to control the effective pore size of the membrane. The grafted P(NIPAAm) chains can act as temperature sensors and as valves to regulate the filtration rate of the membrane for water.

## CONCLUSION

The PVDF-*g*-P(NIPAAm) copolymer was synthesized through ATRP with NIPAAm using PVDF as a macroinitiator. The copolymer membranes obtained by phase inversion technique show enrichment of the grafted P(NIPAAm) segments in the surface region. The membranes exhibit a strong and reversible temperature-dependent permeability to water. The thermoresponsive membranes, obtained via the present approach, may be applied to the biomedical fields.

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## REFERENCES

1. Kulikovska O, Goldenberg LM, Kulikovskiy L, Stumpe J, Smart ionic sol-gel-based azobenzene materials for optical generation of microstructures,

- Chem Mater*, **20**, 3528-3534, 2008.
- Lomas H, Canton I, MacNeil S, Du J, Armes SP, Ryan AJ, Lewis AL, Battaglia G, Biomimetic pH sensitive polymersomes for efficient DNA encapsulation and delivery, *Adv Mater*, **19**, 4238-4241, 2007.
  - Kaith BS, Kumar K, Preparation of psyllium mucilage and acrylic acid based hydrogels and their application in selective absorption of water from different oil/water emulsions, *Iran Polym J*, **16**, 529-538, 2007.
  - Boddohi S, Killingsworth CE, Kipper MJ, Polyelectrolyte multilayer assembly as a function of pH and ionic strength using the polysaccharides chitosan and heparin, *Biomacromolecules*, **9**, 2021-2028, 2008.
  - Chu LY, Park SH, Yamaguchi T, Nakao SI, Preparation of thermo-responsive core-shell microcapsules with a porous membrane and poly(*N*-isopropylacrylamide) gates, *J Membr Sci*, **19**, 227-239, 2001.
  - Ebara M, Aoyagi T, Sakai K, Okano T, Introducing reactive carboxyl side chains retains phase transition temperature sensitivity in *N*-isopropylacrylamide copolymer gels, *Macromolecules*, **33**, 8312-8316, 2000.
  - Ishida N, Biggs S, Salt-induced structural behavior for poly(*N*-isopropylacrylamide) grafted onto solid surface observed directly by AFM and QCM-D, *Macromolecules*, **40**, 9045-9052, 2007.
  - Harada A, Johnin K, Kawamura A, Kono K, Preparation of temperature-responsive polymer gels physically immobilizing core-shell type bioconjugates, *J Polym Sci Part A Polym Chem*, **45**, 5942-5948, 2007.
  - Souzy R, Ameduri B, Boutevin B, Synthesis and (co)polymerization of monofluoro, difluoro, trifluorostyrene and ((trifluorovinyl)oxy)benzene, *Prog Polym Sci*, **29**, 75-106, 2004.
  - Dargahi J, Najarian S, Analysis of a membrane-type polymeric-based tactile sensor for biomedical and medical robotic applications, *Sensors Mater*, **16**, 25-41, 2004.
  - Yang M, Chu LY, Li Y, Zhao XJ, Song H, Chen WM, Thermo-responsive gating characteristics of poly(*N*-isopropylacrylamide)-grafted membranes, *Chem Eng Technol*, **29**, 631-636, 2006.
  - Coad BR, Kizhakkedathu JN, Haynes CA, Brooks DE, Synthesis of novel size exclusion chromatography support by surface initiated aqueous atom transfer radical polymerization, *Langmuir*, **23**, 11797-11803, 2007.
  - Semsarzadeh MA, Daronkola MRR, <sup>1</sup>H NMR studies of the molecular structure of PVAc-*b*-(MA-*co*-MMA) block terpolymer in atom transfer radical copolymerization reaction, *Iran Polym J*, **16**, 47-56, 2007.
  - Samadi A, Husson SM, Liu Y, Luzinov I, Kilbey SM, Low-temperature growth of thick polystyrene brushes via ATRP, *Macromol Rapid Comm*, **26**, 1829-1834, 2005.
  - Yamamoto S, Pietrasik J, Matyjaszewski K, ATRP synthesis of thermally responsive molecular brushes from oligo(ethylene oxide) methacrylates, *Macromolecules*, **40**, 9348-9353, 2007.
  - Mohajery S, Entezami AA, Structural characteristics and thermal properties of poly(methyl methacrylate) and atactic polystyrene grafted onto metallocene based ethylene-allylbenzene copolymer, *Iran Polym J*, **16**, 345-355, 2007.
  - Hester JF, Banerjee P, Won YY, Akthakul A, Acar MH, Mayes AM, ATRP of amphiphilic graft copolymers based on PVDF and their use as membrane additives, *Macromolecules*, **35**, 7652-7661, 2002.
  - Xu FJ, Zhong SP, Yung LYL, Tong YW, Kang E, Neoh K, Thermoresponsive comb-shaped copolymer-Si(1 0 0) hybrids for accelerated temperature-dependent cell detachment, *Biomaterials*, **27**, 1236-1245, 2006.
  - Ying L, Zhai G, Winata AY, Kang ET, Neoh KG, pH effect of coagulation bath on the characteristics of poly(acrylic acid)-grafted and poly(4-vinylpyridine)-grafted poly(vinylidene fluoride) microfiltration membranes, *J Colloid Interf Sci*, **265**, 396-403, 2003.
  - Walton HF, *Principles and Methods of Chemical Analysis*, 2nd ed, Prentice-Hall, Englewood Cliffs, New Jersey, 1964.
  - Beamson G, Briggs D, *High Resolution XPS of Organic Polymers: The Sienta ESCA Database*, John Wiley, New York, 1992.
  - Pan YV, Wesley RA, Luginbuhl R, Denton DD, Ratner BD, Plasma polymerized *N*-isopropyl-

- acrylamide: synthesis and characterization of a smart thermally responsive coating, *Biomacromolecules*, **2**, 32-36, 2001.
23. Moulder JF, Stickle WF, Sobol PE, Bomben KD, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, 1992.
  24. Kim SY, Cho SM, Lee YM, Kim SJ, Thermo- and pH-responsive behaviors of graft copolymer and blend based on chitosan and *N*-isopropylacrylamide, *J Appl Polym Sci*, **78**, 1381-1391, 2000.