

# "Smart" Membrane Materials: Preparation and Characterization of PVDF-g-PNIPAAm Graft Copolymer

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**ABSTRACT:** In this research, a smart membrane material of graft copolymer of poly(vinylidene fluoride) with poly(*N*-isopropylacrylamide) (PVDF-g-PNIPAAm) was synthesized by atom transfer radical polymerization (ATRP) using poly(vinylidene fluoride) (PVDF) as a macroinitiator and direct initiation of the secondary fluorinated site PVDF facilitates grafting the *N*-isopropylacrylamide comonomer. The copolymers were characterized by Fourier transform infrared (FTIR), <sup>1</sup>H NMR, gel permeation chromatography (GPC), and X-ray photoelectron spectroscopy (XPS). The temperature-sensitive membrane was prepared from the PVDF-g-PNIPAAm graft copolymers by the

phase inversion method. The effects of temperature on the flux of pure water of membrane was investigated. The results showed that alkyl fluorides were successfully applied as ATRP initiators in the synthetic condition and the flux of pure water through the PVDF-g-PNIPAAm membrane depended on the temperature change. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1482–1486, 2007

**Key words:** poly(vinylidene fluoride); poly(*N*-isopropylacrylamide); atom transfer radical polymerization; membrane

## INTRODUCTION

The ability of "smart": polymers to respond to small changes in environmental conditions can be used in the production of permeability-controlled membranes. "Smart" or "intelligent" polymers are nicknames of the water soluble polymers and hydrogels. They are able to drastically change some of their properties (volume of macromolecules) in water solution even at small changes in environmental conditions (temperature, pH, magnetic field strength, etc.). Among the smart polymers, the greatest number of articles have been devoted to poly-*N*-isopropylacrylamide (PNIPAAm), a temperature-sensitive polymer. This polymer has a lower critical solution temperature (LCST) of about 32°C in water.

Poly(vinylidene fluoride) (PVDF) has outstanding resistance to weathering and chemical and melt processes, and wide practical use (coating materials, electrical/electronic component, chemical processing components such as piping, tank linings, filtration, etc.). Therefore, PVDF-g-PNIPAAm copolymers have become one of the most attractive research targets as "smart" membrane

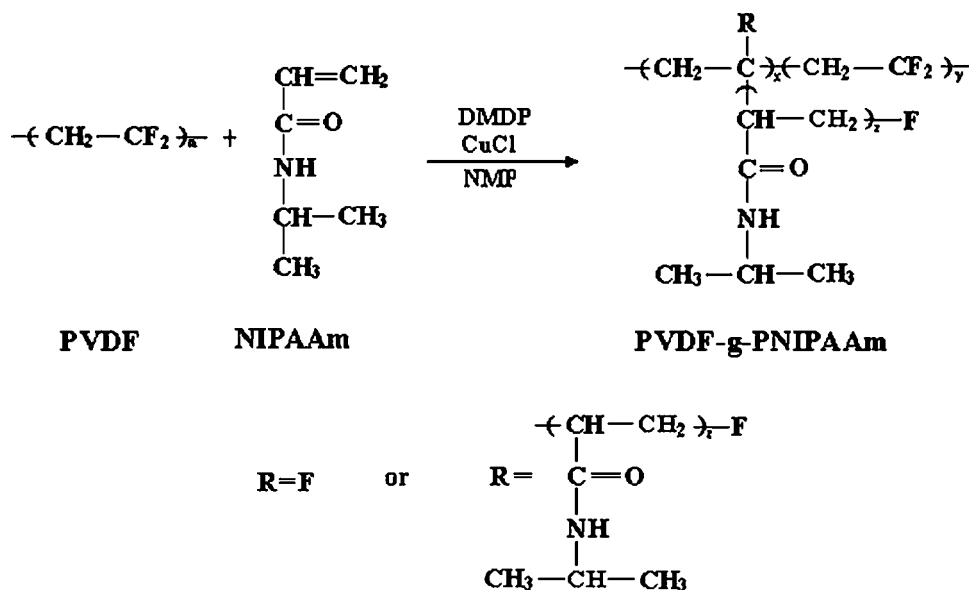
materials. Various synthetic approaches for the preparation of PVDF-g-PNIPAAm copolymers from PVDF have been reported in the membrane field, such as thermally induced graft<sup>1–3</sup> and plasma treatment.<sup>4</sup>

Atom transfer radical polymerization (ATRP)<sup>5,6</sup> has provided new and effective ways to prepare graft copolymers. It is based on the combination of an organic halide initiator (RX) with a megal/ligand catalytic system that is able to promote fast initiation compared to propagation and the reversibly activate halogenated chain ends (RnX) during polymerization.<sup>7–13</sup> ATRP has recently been used to prepare graft copolymers from polymeric macroinitiators, polymer chains with regularly spaced, pendant chemical groups containing radically transferable halogen atoms.<sup>14–17</sup> The halogen atoms serve as initiation sites for the polymerization of sidechains by ATRP. For example, Beer et al. and Gu et al.<sup>15,16</sup> polymerized 2-(2-bromopropionyloxy)ethyl acrylate free radically to obtain a macroinitiator with a pendant bromine atom on every repeat unit. The pendant bromine atoms were then used as initiation points for the ATRP of styrene and butyl acrylate sidechains. Similarly, styrene and various methyl (meth)acrylate sidechains have been grafted onto a poly(vinyl chloride)-*co*-(vinyl chloroacetate) macroinitiator, using the chloroacetate groups as initiation sites for ATRP of the monomers. In these studies, no evidence of homopolymerization was observed, and the achievable grafting density was high due to the controlled nature of ATRP. A number of high-volume commercial polymers, including PVC, PVDF, and chlorinated polyolefins,

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Scheme 1 Synthesis of PVDF-g-PNIPAAm graft copolymer.

comprise repeat units with secondary halogen atoms pendant. In principle, these polymers might be utilized as ATRP macroinitiators for the preparation of functionalized derivatives. However, it has been reported<sup>17</sup> that the secondary chlorine atoms of PVC are too strongly bonded to serve as ATRP initiation sites.

PVDF has a similar structure as PVC and the C—F binding energy is more stronger than C—Cl; therefore, there are some graft copolymers of PVDF that have been prepared using iodine,<sup>18</sup> bromine,<sup>19</sup> or chlorine<sup>20</sup> terminated PVDF as ATRP initiator. In recent studies PVDF copolymers were reported that were synthesized using secondary fluorine as ATRP initiator and the copolymer only focused on PVDF-g-POEM and PVDF-g-PMMA.<sup>21</sup> But to our knowledge there are no reports that focused on PVDF-g-PNIPAAm graft copolymer polymerized by ATRP. In this article we demonstrate the first example of using PVDF as macroinitiator to polymerize temperature-sensitive PVDF-g-PNIPAAm copolymer as "smart" membrane materials by ATRP (Scheme 1). The effects of temperature on the flux of pure water through membrane prepared from the PVDF-g-PNIPAAm graft copolymer was also investigated.

## EXPERIMENTAL

### Materials

PVDF and 4,4'-dimethyl-2,2'-dipyridyl (DMDP) were purchased from Aldrich Chemical (Milwaukee, WI); N-isopropylacryamide (NIPAAm, Kohjin, Japan); Copper(I) chloride (CuCl), N,N-dimethylformamide (DMF), 1-methyl-2-pyrrolidinoe (NMP), petroleum ether, and methanol were purchased from Shanghai Chemical Reagents (China).

### Synthesis of graft copolymers PVDF-g-PNIPAAm

PVDF and NIPAAm were dissolved in NMP in a conical flask at 50°C, then CuCl and DMDP were added. Nitrogen gas was bubbled through the reaction mixture for 15 min under stirring. The reaction vessel was then placed in an oil bath preheated to 90°C and the reaction was allowed to proceed for 25 h under constant agitation and the protection of nitrogen. At timed intervals, samples were withdrawn from the flask using degassed syringes to determine molecular weight. The graft copolymer was precipitated into a mixture of 1 part methanol and 1–2 parts petroleum ether. Precipitated PVDF-g-PNIPAAm was dried, then the graft copolymer was purified by thrice redissolving in NMP and reprecipitating in methanol/

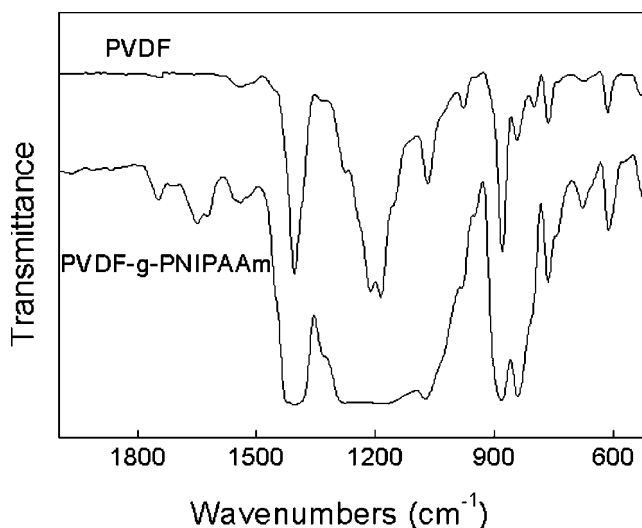


Figure 1 FTIR spectra of PVDF and PVDF-g-PNIPAAm.

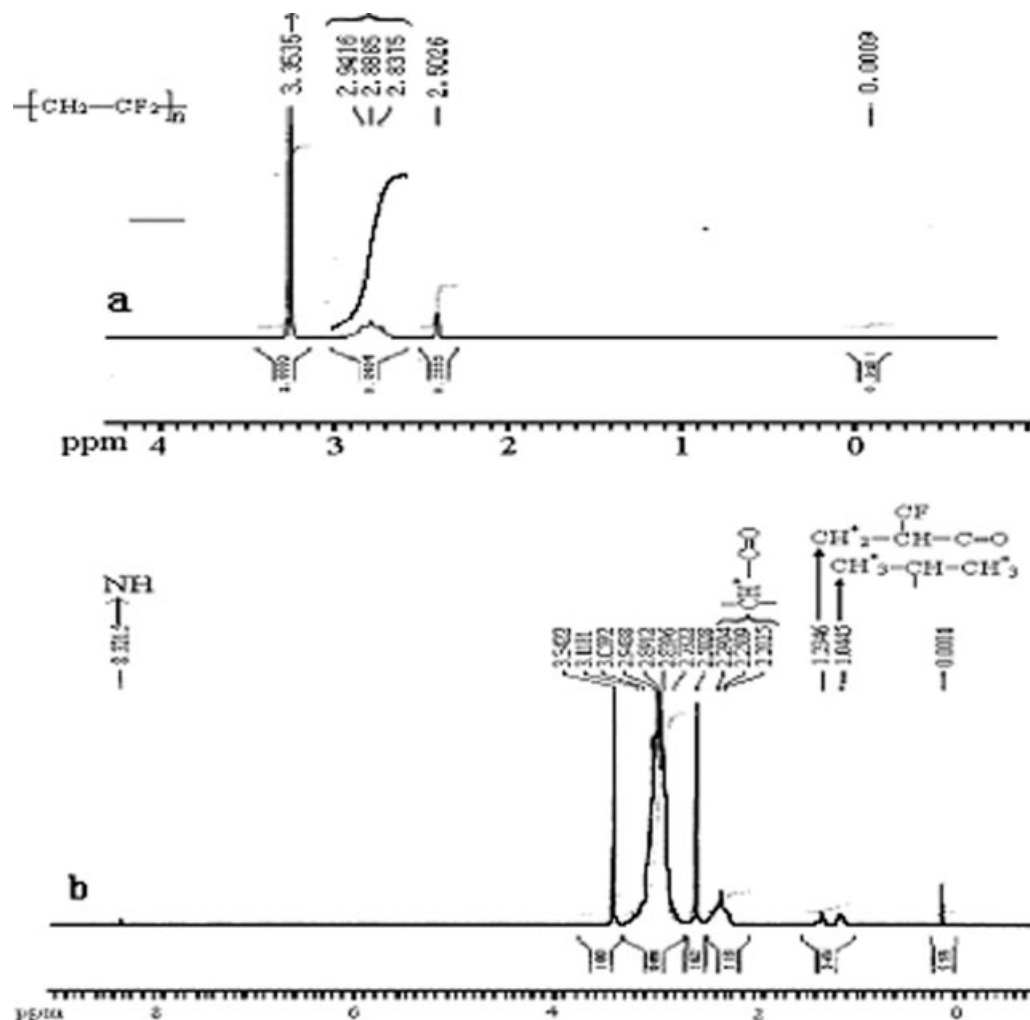


Figure 2  $^1\text{H}$  NMR spectra for (a) PVDF, (b) PVDF-g-PNIPAAm.

petroleum. Finally, the polymer was dried under vacuum overnight at room temperature.

### Characterization of graft copolymers

Molecular weights and molecular weight distributions of PVDF and PVDF-g-PNIPAAm were measured by gel permeation chromatography (GPC) on a system equipped with a Waters (Milford, MA) 515 pump, three columns (Styragel HR1, Styragel HR3, and Styragel HT4), and a 2410 differential refractometer detector. The eluant was DMF and the flow rate was 1 mL/min. Monodisperse polystyrene was used as the standard to generate the calibration curve.  $^1\text{H}$  NMR was performed on PVDF and its graft copolymer in deuterated DMSO using a Bruker (Billerica, MA) DPX 400 spectrometer. The PVDF and PVDF-g-PNIPAAm were powdered and ground with KBr. The Fourier transform infrared (FTIR) spectra were recorded on a Bruker model Tensor 37 spectrophotometer. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from

VG Scientific (Waltham, MA) using 300W  $\text{AlK}\alpha$  radiation. The base pressure was about  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.

### Preparation of membranes

PVDF or PVDF-g-PNIPAAm membrane was prepared by phase inversion from a DMF solution containing 15 wt % polymer or copolymer. The polymer or copolymer solution was cast onto a glass plate, which was then immersed in a bath of doubly distilled water (nonsolvent) after the polymer solution had been subjected to a brief period of evaporation in air. Each membrane was left in water for about 20 min after separation from the glass plate.

### Measurements of the temperature-dependent flux through the membranes

Pure water was used to study the dependence of permeation rate on temperature. Flux experiments through the membranes were carried out under a pressure of

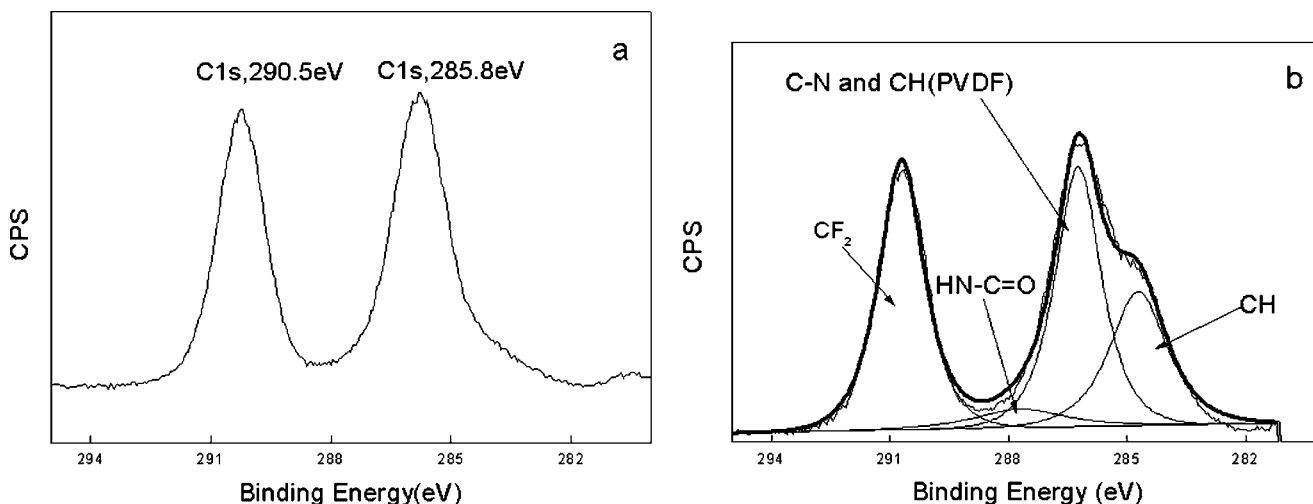


Figure 3 XPS spectra of (a) PVDF, (b) PVDF-g-PNIPAAm.

0.03 kg/cm<sup>2</sup>. During the measurement the cell and permeating solution were kept in a thermostat water bath, allowing the exact control of temperature. Flux (J/L/m<sup>2</sup>h) was calculated as:  $J = V/(At)$ , where V is the volume of liquid (L), A is effective area of membrane, and t is time (h).

## RESULTS AND DISCUSSION

### Characterization of the PVDF-g-PNIPAAm graft copolymers

ATRP polymerization of PNIPAAm was carried out using PVDF as macroinitiator. Figure 1 shows the FTIR spectra of the pristine PVDF and PVDF-g-PNIPAAm. By comparison with the PVDF curve, the absorption band at 1655 cm<sup>-1</sup> in curve b was attributed to the stretching vibrations of CONH groups in NIPAAm.

The <sup>1</sup>H NMR spectra for PVDF and PVDF-g-PNIPAAm are shown in Figure 2. The PVDF spectrum exhibits two well-known peaks due to head-to-tail (ht) and head-to-head (hh) bonding arrangements.<sup>8</sup> Grafting of PNIPAAm to PVDF resulted in the appearance of peaks in the region of 8–8.3 ppm, 2.7–3.1 ppm, and 2.2–2.3 ppm due to the proton of the amide group (NH\*), the methyl proton of the isopropyl group ((CH<sup>\*</sup>)<sub>2</sub>CH), and the proton of the CH\*(CO) group in PNIPAAm, respectively. The mole fraction of PNIPAAm in the copolymer was then calculated as 27.3% based on the intensities of resonances PVDF(ht), PVDF(hh), the CH\*(CO) group, ((CH<sup>\*</sup>)<sub>2</sub>CH) group, and the NH\* group.

The composition of PVDF and PVDF-g-PNIPAAm graft copolymer was studied by XPS as shown in Figure 3. In the case of PVDF, the C1s spectrum can be curve-fitted with two peak components, with binding energies (Bes) at 285.8 eV for CH<sub>2</sub> species and at 290.5 eV for the CF<sub>2</sub> species. The molar ratio of [C]/[F] of PVDF in this research is 1.24, which was calculated from the ratio for the two peaks components of XPS. On

the other hand, the C1s spectra of the PVDF-g-PNIPAAm copolymer was curve-fitted with five chemical species using the following approaches. The peak components of about equal intensities (with BE at 285.8 eV for 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 HNC=O species of the grafted NIPAAm polymer chains. The component with BE at 284.6 eV is attributed to the hydrocarbon backbone of the grafted NIPAAm polymer chain. Finally, the remaining area of the peak component with BE at about 285.8 eV is assigned to CN species. As the CN and CH<sub>2</sub>(PVDF) peak components have the same BE, they are combined and shown as a single peak component in Figure 3. In addition, the mole fraction of PNIPAAm in the graft copolymer was determined as 26.7% from the XPS-derived [C]/[F] ratio, which is in good agreement with the results of <sup>1</sup>H NMR.

GPC traces for PVDF and PVDF-g-PNIPAAm are shown in Figure 4. As can be seen, the initial negative

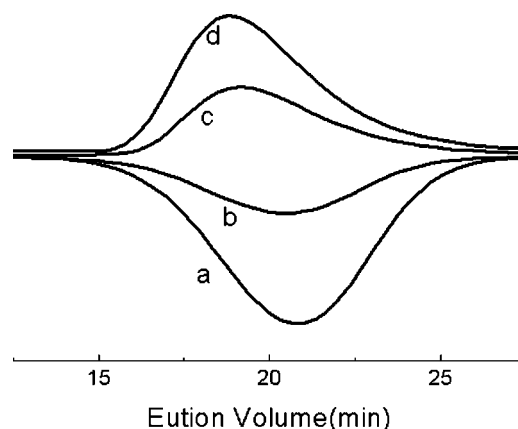


Figure 4 GPC traces of (a) PVDF, (b) PVDF-g-PNIPAAm proceed for 9 h, (c) PVDF-g-PNIPAAm proceed for 18 h, (d) PVDF-g-PNIPAAm proceed for 25 h.

**TABLE I**  
Properties of Base Polymer and Graft Copolymers

Number	Polymer	Time (h)	$M_n$	$M_w/M_n$
1	PVDF		107000	2.10
2	PVDF- <i>g</i> -PNIPAAm	9	126178	2.01
3	PVDF- <i>g</i> -PNIPAAm	18	159403	1.73
4	PVDF- <i>g</i> -PNIPAAm	25	170732	1.64

PVDF = 10 g [NIPAAm] = 0.47 mol, [CuCl] = 0.0004 mol, [DMDP] = 0.000125 mol.

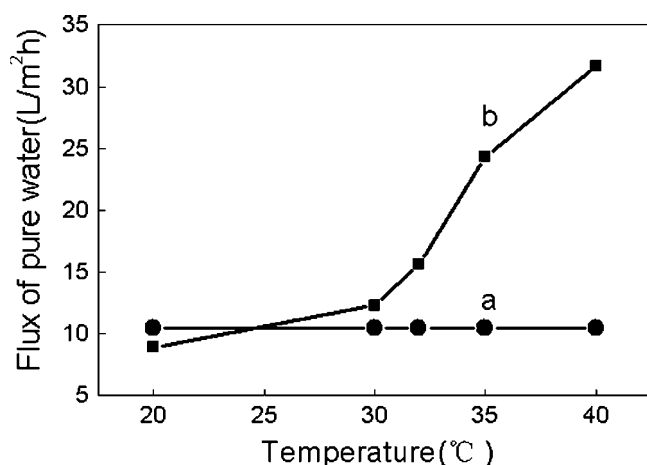
Reaction temperature 90°C.

refractive index signal (relative to solvent) of the PVDF macroinitiator changed to positive and shifted to the higher molecular weights. The polydispersity of each polymer obtained directly from the GPC trace are shown in Table I. The grafting of PNIPAAm to PVDF resulted in distributions shifted up significantly in molecular weight relative to the PVDF homopolymer.

The combined FTIR, GPC,  $^1\text{H}$  NMR, and XPS results indicate unambiguously that PNIPAAm was grafted to the PVDF base polymer, apparently by ATRP initiation at the secondary fluorinated site, which provides an example of an alternative method for a polymerization route of PVDF-*g*-PNIPAAm.

#### Temperature-sensitive behavior of PVDF-*g*-PNIPAAm membrane

The effect of temperature on the flux of pure water through pristine PVDF membrane and PVDF-*g*-PNIPAAm membrane is shown in Figure 5. The pristine PVDF membrane exhibited almost constant values of the flux of pure water and did not show temperature-sensitive behavior. In contrast to pristine PVDF, PVDF-*g*-PNIPAAm membrane showed that the flux of pure water changed with temperature. At temperatures below the LCST of the NIPAAm polymer, the NIPAAm polymer sidechains are solvated. However, they cannot



**Figure 5** Effect of temperature on the flux of pure water (a) pristine PVDF, (b) PVDF-*g*-PNIPAAm.

dissolve into the solution phase, since the NIPAAm chain-ends are covalently tethered to the PVDF backbone. Thus, the grafted NIPAAm chains extend into the pores and reduce the flux of pure water. On the other hand, at temperatures above the LCST the grafted NIPAAm polymer chains shrink and associate hydrophobically on the membrane and pore surfaces, resulting in an opening of the pores of the membrane and hence the observed increase in the flux of pure water.

#### CONCLUSION

This is the first example that offers an effective and relevant alternative to conventional free radical routes for the preparation of PVDF-*g*-PNIPAAm graft copolymer as "smart" membrane materials. In this research, PVDF-*g*-PNIPAAm graft copolymer was synthesized by ATRP initiation of the secondary fluorinated site PVDF facilitates grafting the *N*-isopropylacrylamide comonomer. PVDF-*g*-PNIPAAm graft copolymers were characterized by FTIR,  $^1\text{H}$  NMR, GPC, and XPS and the results showed that PVDF was successfully applied as ATRP macroinitiator in the synthetic condition. In addition, the "smart" membrane prepared from the PVDF-*g*-PNIPAAm graft copolymer by the phase inversion technique in water showed the flux of pure water through the PVDF-*g*-PNIPAAm membrane depended on the temperature changes.

#### References

- Ying, L.; Kang, E. T.; Neoh, K. G. *J Membr Sci* 2003, 224, 93.
- Ying, L.; Kang, E. T.; Neoh, K. G.; Kato, K.; Iwata, H. *Macromol Mater Eng* 2003, 288, 11.
- Ying, L.; Kang, E. T.; Neoh, K. G. *Langmuir*, 2002, 18, 6416.
- Iwata, H.; Dodate, M.; Uyama, Y.; Amemiya, H.; Ikada, Y. *J Membr Sci* 1991, 55, 119.
- Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 114, 5614.
- Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
- Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
- Percec, V.; Barboiu, B. *Macromolecules* 1995, 28, 7970.
- Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* 1996, 29, 8576.
- Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1998, 31, 6756.
- Kamigaito, M.; Watanabe, Y.; Ando, T.; Sawamoto, M. *J Am Chem Soc* 2002, 124, 9994.
- Matyjaszewski, K.; Wei, M.; Xia, J. *Macromolecules* 1997, 30, 8161.
- Moineau, G.; Granel, C.; Dubois, P.; Jerome, R. *Macromolecules* 1998, 31, 542.
- Wang, X. S.; Luo, N. *Polymer* 1999, 40, 4515.
- Beer, K. L.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* 1998, 31, 9413.
- Gu, L.; Zhu, S.; Hrymak, A. N. *J Polym Sci B Polym Phys* 1998, 36, 705.
- Paik, H. J.; Gaynor, S. G.; Matyjaszewski, K. *Macromol Rapid Commun* 1998, 19, 47.
- Jol, S. M.; Lee, W. S.; Ahn, B. S.; Park, K. Y.; Kim, K. A.; Rhee Paeng, I. S. *Polymer Bull* 2000, 44, 1.
- Zhang, Z.; Ying, S.; Shi, Z. *Polymer* 1999, 40, 1341.
- Destarac, M.; Matyjaszewski, K.; Silverman, E. *Macromolecules* 2000, 33, 4613.
- Hester, J. F.; Banerjee, P.; Won, Y. Y. *Macromolecules* 2002, 35, 7652.