

Influence of the Coagulation-Bath Temperature on the Phase-Separation Process of Poly(vinylidene Fluoride)-*graft*-Poly(*N*-isopropylacrylamide) Solutions and Membrane Structures

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ABSTRACT: A poly(vinylidene fluoride)-*graft*-poly(*N*-isopropylacrylamide) (PVDF-*g*-PNIPAAm) copolymer was synthesized, and flat-sheet membranes were prepared via the phase-inversion method with *N,N*-dimethylformamide (DMF) as the solvent and water as the coagulation bath. The effects of the coagulation-bath temperature on poly(vinylidene fluoride) (PVDF)/DMF/water and PVDF-*g*-PNIPAAm/DMF/water ternary systems were studied with phase diagrams. The results showed that the phase-separation process could be due to the hydrophilicity/hydrophobicity of poly(*N*-isopropylacrylamide) at low temperatures, and the phase-separation process was attributed to crystallization at high temperatures. The structures and properties of

the membranes prepared at different coagulation-bath temperatures were researched with scanning electron microscopy, porosity measurements, and flux measurements of pure water. The PVDF-*g*-PNIPAAm membranes, prepared at different temperatures, formed fingerlike pores and showed higher water flux and porosity than PVDF membranes. In particular, a membrane prepared at 30°C had the largest fingerlike pores and greatest porosity. The water flux of a membrane prepared in a 25°C coagulation bath showed a sharp increase with the temperature increasing to about 30°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1005–1009, 2010

Key words: phase separation; phase diagrams; membranes

INTRODUCTION

Intelligent membranes that can respond predictably to changes in the pH, temperature, electric field, or ionic strength have been the focus of research in the field of membranes for the last few decades. *N*-Isopropylacrylamide (NIPAAm) is a typical monomer for temperature-sensitive polymers with a lower critical solution temperature around 32°C. It has been widely applied for preparing temperature-sensitive porous membranes. In recent years, the temperature-sensitive poly(vinylidene fluoride)-*graft*-poly(*N*-iso-

propylacrylamide) (PVDF-*g*-PNIPAAm) separation membrane, which has temperature-sensitive performance while retaining the desirable properties of the matrix, has been extensively studied.^{1–3} However, most of these studies have focused on the preparation, morphology, chemical structure, and temperature-sensitive performance of the flux and rejection of the membrane; little attention has been paid to the membrane-formation mechanism and the process of phase separation. In fact, the phase-separation process influences the morphology and characteristics of the membrane greatly. Through the careful regulation of the immersion–precipitation parameters, such as the dope and bath compositions, precipitation temperature, and additives, a wide variety of morphologies and properties can be obtained.⁴

A ternary phase diagram is very useful in the description of the thermodynamic properties of a three-component polymer/solvent/nonsolvent system, which is usually used to make asymmetric membranes by immersion precipitation;⁵ different ternary systems result in different membranes with different structures.^{4,6,7} Using *N,N*-dimethylformamide (DMF) as the solvent, Cheng and coworkers^{8,9} investigated the membrane-forming phase behavior of water/DMF/poly(vinylidene fluoride) (PVDF)

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and 1-octanol/DMF/PVDF systems. They found that liquid–liquid demixing took place earlier than crystallization, and asymmetric cellular morphologies were produced at elevated temperatures. If water was added to the dope to form an incipient dope or if the coagulation bath contained a high concentration of DMF, a uniform particulate structure dominated by the crystallization mechanism of the membrane was obtained.

In this research, ternary phase diagrams of water/DMF/PVDF and water/DMF/PVDF-*g*-PNIPAAm systems were determined by the cloud-point method, and the effect of temperature on the phase diagrams was studied. Correspondingly, the effects of the coagulation-bath temperature on the membrane morphology, structure, and filter performance were also investigated.

EXPERIMENTAL

Materials

PVDF (Solef 1010) was purchased from Solvay Co., Ltd. (Brussels, Belgium); NIPAAm (95%) was obtained from Kohjin Co., Ltd. (Tokyo, Japan), and was used after further purification. 2,2'-Azobisisobutyronitrile (99%), used as an initiator, was supplied by Shanghai Shisihewei Chemical Co., Ltd. (Shanghai, China), and was recrystallized from ethanol before use; all other reagents (Tianjin Kemiou Chemical Co., Ltd., Tianjin, China) were analytical-grade and were used without further purification.

Synthesis of the PVDF-*g*-PNIPAAm graft copolymers

Before graft polymerization, the PVDF powder was treated with potassium hydroxide (KOH). In brief, PVDF was immersed in a 10 wt % KOH solution containing 0.05 wt % ethanol, and then the solution was stirred for 10 min at 60°C. After the solution cooled, the precipitate was collected by filtration and then washed four times with distilled water to remove the alkali solution.

The alkaline-treated PVDF powder was dissolved in DMF at 60°C with a concentration of 15 wt %, and then NIPAAm and 2,2'-azobisisobutyronitrile were added to the system under an N₂ atmosphere with continuous stirring. The reaction was allowed to proceed for 10 h under constant agitation at 60°C. The graft copolymer was precipitated by methanol and collected by filtration. To remove the residue of the NIPAAm monomer, the graft copolymer was washed with a mass of distilled water several times and then was dried *in vacuo*.¹⁰

The PVDF, alkaline-treated PVDF, and PVDF-*g*-PNIPAAm powder were ground with KBr. The Fou-

rier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 37 spectrophotometer.

Phase diagrams of the polymer/DMF/water systems

The phase diagram at a certain temperature was determined with the widely used cloud-point method. Briefly, a specific amount of the polymer was dissolved in DMF at 60°C and sealed in a glass bottle with a Teflon-lined cap. Some known quantity of water was added to this solution, and local precipitation was observed. Then, the mixture was further blended at 60°C until a clear, homogeneous solution was obtained again. It was then put in a thermostatically controlled bath maintained at a certain temperature over a period of 3 h. The gelation points were identified as the compositions at which homogeneous solutions began to gel in a series of samples with different water/solvent ratios.⁴

Preparation and characterization of the membranes

PVDF and PVDF-*g*-PNIPAAm membranes were prepared by phase inversion from a DMF solution with a 15 wt % concentration of the polymer or copolymer. The solution of PVDF or PVDF-*g*-PNIPAAm was cast onto a glass plate and subsequently immersed in a coagulation bath. Distilled water at 25, 30, and 40°C was used as the coagulation bath. Each membrane separated from the glass plate by itself after immersion in water for about 1 min. The formed membranes were soaked in distilled water for further characterization.

Scanning electron microscopy (SEM; model 200 scanning electron microscope, Quanta) was used to characterize the surface and cross-section morphologies of the membranes after the samples were freeze-dried and sputtered with gold films.

The porosity was measured by the immersion of each membrane into pure water for 1 day, after which the membrane surface was dried with filter paper. The membrane was weighed before and after freeze drying. The porosity was calculated with the following equation:

$$V_r = [(m_1 - m_2)/\rho_{\text{water}}]/V \times 100\% \quad (1)$$

where V_r is the porosity; ρ_{water} is the density of water (g/mL); m_1 and m_2 are the weights of the membrane in the wet and dry states, respectively (g); and V is the volume of the membrane (cm³).

Measurements of the temperature-dependent flux through the membranes

Pure water was used to study the dependence of the permeation rate on temperature. Flux experiments

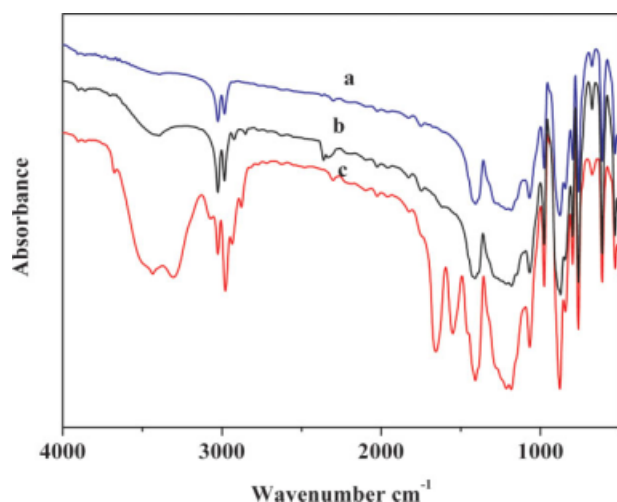


Figure 1 FTIR spectra of the polymers: (a) PVDF, (b) alkaline-treated PVDF, and (c) PVDF-g-PNIPAAm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

were carried out under a pressure of 0.1 MPa. During the measurements, the cell and permeating solution were kept in a thermostat water bath, which allowed exact control of the temperature.¹¹ The flux was calculated as follows:

$$J = V/(At) \quad (2)$$

where J is the flux ($L/m^2 h$), V is the volume of the liquid (L), A is the effective area of the membrane (m^2), and t is the time (h).

RESULTS AND DISCUSSION

FTIR analysis

Figure 1 shows FTIR spectra of the PVDF, alkaline-treated PVDF, and PVDF-g-PNIPAAm copolymer. In comparison with Figure 1(a), the weak absorbance at 1680 cm^{-1} and strong absorbance at 2250 cm^{-1} in

Figure 1(b) indicate the formation of C=C double bonds and C≡C triple bonds. Figure 1(c) presents two main differences with respect to Figure 1(b). The C≡C stretch bands around 2250 cm^{-1} are weak, and this suggests NIPAAm grafting on the alkaline-treated PVDF powder. Meanwhile, the absorption at 1655 cm^{-1} was attributed to the stretching vibrations of C=O groups in NIPAAm; the 1150-cm^{-1} vibration and 1380-cm^{-1} framework vibration were assigned to the isopropyl $[CH(CH_3)_2]$ in NIPAAm, and this indicated that NIPAAm had been grafted to the alkaline-treated PVDF.

Phase diagrams of the polymer/DMF/water systems

Ternary phase diagrams of the PVDF/DMF/water and PVDF-g-PNIPAAm/DMF/water systems at different temperatures are shown in Figure 2. The data points on the gelation line represent the measured compositions at which gelation was observed at different temperatures. Figure 2(a) indicates that the gelation line moved to the water–PVDF axis when the temperature rose from 25 to 40°C . A contrary result was observed for the PVDF-g-PNIPAAm/DMF/water system [Fig. 2(b)]. For the PVDF/DMF/water ternary system, precipitation occurred only by the nucleation and growth of polymer crystallites. Liquid–liquid demixing initiated phase separation, and crystallization of the polymer-rich phase followed at a lower temperature. Also, liquid–liquid demixing dominated phase separation instead of crystallization at higher temperatures.¹² However, in the PVDF-g-PNIPAAm/DMF/water system, the process of phase separation could be attributed to the crystallization and conversion of the hydrophilicity/hydrophobicity of poly(*N*-isopropylacrylamide) (PNIPAAm). This means that the chains of PNIPAAm spread at 25°C and showed hydrophilicity. As the temperature increased to 30°C , the chains of PNIPAAm contracted and showed hydrophobicity.

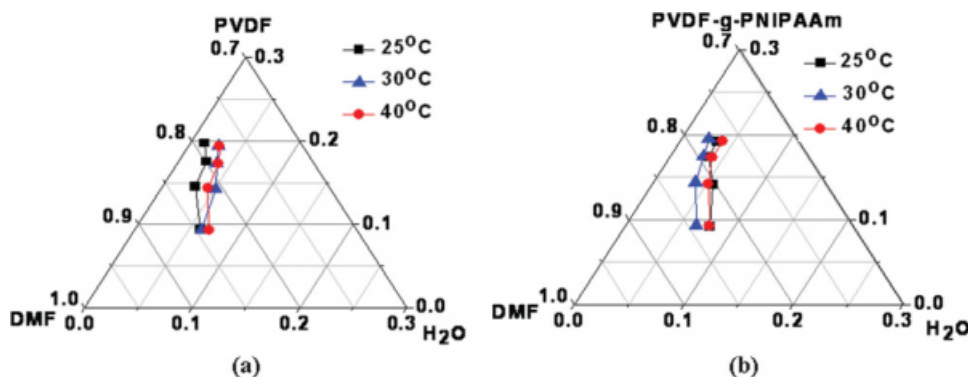


Figure 2 Phase diagrams of (a) the PVDF/DMF/water system and (b) the PVDF-g-PNIPAAm/DMF/water system at different gelation-line temperatures: (■) 25, (▲) 30, and (●) 40°C . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

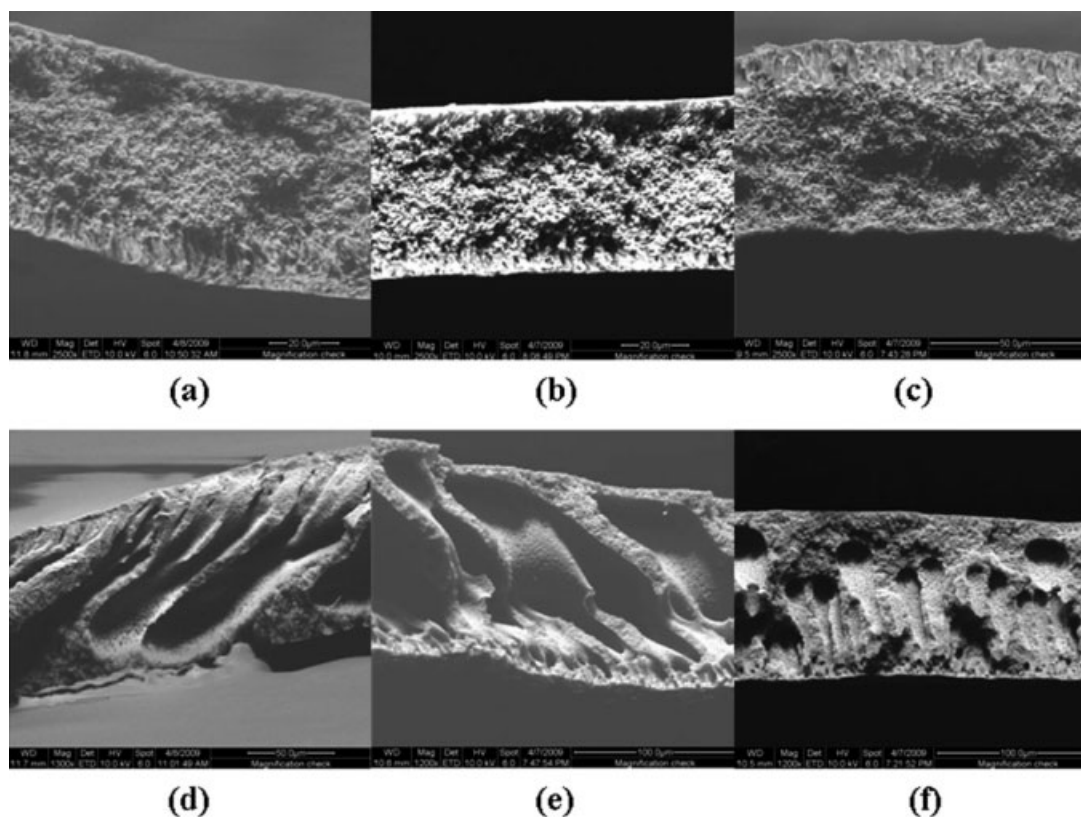


Figure 3 SEM micrographs of membranes prepared at different coagulation-bath temperatures: (a) PVDF membrane at 25°C, (b) PVDF membrane at 30°C, (c) PVDF membrane at 40°C, (d) PVDF-g-PNIPAAm membrane at 25°C, (e) PVDF-g-PNIPAAm membrane at 30°C, and (f) PVDF-g-PNIPAAm membrane at 40°C.

Consequently, it is reasonable to deduce that the hydrophilicity/hydrophobicity of PNIPAAm played a leading role in the phase-separation process when the temperature was below 30°C. However, when the temperature rose to 40°C, phase separation was induced by crystallization of the PVDF-g-PNIPAAm polymers.

Structures of the PVDF and PVDF-g-PNIPAAm membranes

During the membrane-formation process, all membranes precipitated rapidly about 1 min after the dope was immersed into the nonsolvent. In general, unlike ordinary water-precipitated membranes whose asymmetric morphologies were dominated by fingerlike macrovoid pores,¹³ the PVDF membranes at each temperature had spongelike pores and very uniform cross sections, as illustrated in Figure 3. Also, the PVDF-g-PNIPAAm membranes prepared at different temperatures showed fingerlike pores. That was why the porosity of the PVDF membrane was less than that of the PVDF-g-PNIPAAm membrane (Table I). PVDF is a semicrystalline polymer; the gelation initiated by the formation of microcrystallites occurred before liquid-liquid demixing.

These microcrystallites could connect various polymeric chains together to form a three-dimensional fibroform network.¹⁴ To PVDF-g-PNIPAAm, at low temperatures (e.g., 25°C), the grafted PNIPAAm showed hydrophilicity; this was propitious for the exchange between the solvent and nonsolvent, and hence fingerlike pores, based on it, were then formed. At 30°C, the grafted PNIPAAm chains exhibited hydrophobicity and curliness, which availed the formation of large top-layer pores; therefore, the exchange between the solvent and nonsolvent occurred easily, and larger fingerlike pores were formed [Fig. 3(e)]. This is evidenced by the higher porosity shown in Table I. When the temperature was raised to 40°C, the exchange of the solvent and nonsolvent was expedited, and a thin, dense

TABLE I
Porosities of the Membranes Prepared at Different Coagulation-Bath Temperatures

Coagulation-bath temperature (°C)	Porosity (%)	
	PVDF	PVDF-g-PNIPAAm
25	64.25	76.77
30	60.91	79.1
40	60.65	68.72

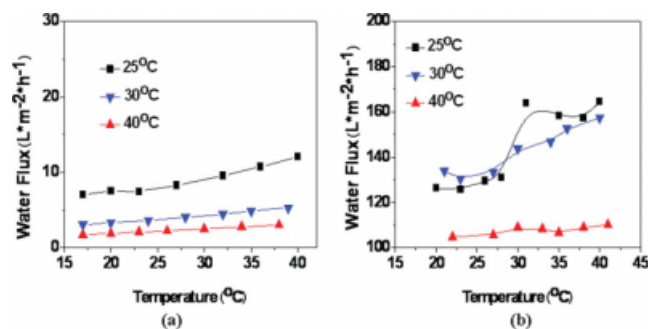


Figure 4 Water flux of (a) PVDF and (b) PVDF-g-PNIPAAm membranes at different coagulation-bath temperatures: (■) 25, (▼) 30, and (▲) 40°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

skin was soon formed that hindered the exchange; therefore, smaller fingerlike pores and less porosity were obtained [Fig. 3(f) and Table I].

Temperature-dependent flux of the PVDF-g-PNIPAAm membranes

The influence of temperature on the flux of pure water through membranes of pristine PVDF and PVDF-g-PNIPAAm is shown in Figure 4. This evidently suggests that with the temperature of pure water increasing, the flux of the PVDF membranes increased accordingly, as shown in Figure 4(a). Compared to the pristine PVDF membranes, the PVDF-g-PNIPAAm membranes showed higher flux of pure water at every tested temperature, and this could be attributed to the hydrophobicity of the grafting of PNIPAAm. Moreover, the PVDF-g-PNIPAAm membrane prepared in the 25°C coagulation bath showed a sharp increase when the pure water was heated to about 30°C. Among the PVDF-g-PNIPAAm membranes prepared in coagulation baths of three different temperatures, the membranes prepared at 30°C showed the highest initial flux, and the flux had no outstanding increase when the temperature was raised. The membranes prepared at 40°C showed the lowest water flux, and there was no sharp change with the increase in the temperature. As described in the literature,¹¹ the hydrophilic groups of PNIPAAm were easy to arrange on the surface of the PVDF-g-PNIPAAm membrane in the coagulation bath at 25°C. When the temperature of pure water was under 30°C, the chains of PNIPAAm were spread, and this led to the shrinkage of pores on the surface of the membrane; therefore, the flux became lower. When the temperature of pure water rose

above 30°C, the chains shrank promptly, and this resulted in a sharp increase in the flux. However, when the temperature of the coagulation bath was above 30°C, the hydrophobic groups of PNIPAAm were easy to arrange on the surface of the copolymer membrane, so the movement of the chains of PNIPAAm was hindered. Consequently, the pure water flux of the membranes prepared at 30 and 40°C had no temperature-responsive properties.

CONCLUSIONS

The PVDF and PVDF-g-PNIPAAm membranes were prepared by the immersion-precipitation method at different coagulation-bath temperatures. An attempt was made to correlate the membrane structure with the membrane-formation process for the PVDF/DMF/water and PVDF-g-PNIPAAm/DMF/water systems.

Phase diagrams of the PVDF/DMF/water and PVDF-g-PNIPAAm/DMF/water ternary systems were obtained. For the PVDF-g-PNIPAAm/DMF/water system, the process of phase separation could be attributed to crystallization and conversion of the hydrophilicity/hydrophobicity of PNIPAAm.

The PVDF-g-PNIPAAm membrane prepared in a 25°C coagulation bath showed typical temperature-sensitive behavior; that is, with an increase in the temperature, the water flux increased accordingly, and a sharp change appeared at 30°C.

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