

Poly(vinylidene fluoride) Membrane with Piezoelectric β -Form Prepared by Immersion Precipitation from Mixed Solvents Containing an Ionic Liquid

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) membranes with exclusive β -form have been directly obtained by immersion precipitation from the mixed solvents containing an ionic liquid (IL). In contrast, without the IL only the α -form is generated. The ion–dipole interactions between the IL and PVDF chains should account for the formation of the β -form with TTTT conformation. In addition, the presence of the IL accelerates the crystallization and gelation of PVDF, responsible for the particulate morphology and high water flux in the membranes. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40505.

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INTRODUCTION

The morphology of poly(vinylidene fluoride) (PVDF) membranes prepared by immersion precipitation is determined by the competition between liquid–liquid demixing and crystallization.^{1–4} Sponge- or finger-like structure is a common observation in the membranes where preferential liquid–liquid demixing occurs. If crystallization dominates the precipitation process, particulate morphology with interlinked crystalline particles can be generated. However, in most conditions crystallization lags behind liquid–liquid demixing, and thus, it is not easy to obtain membranes with particulate morphology. Until now, it has been reported that crystallization can be enhanced in advance of liquid–liquid demixing by (1) lowering precipitation temperatures, (2) reducing the harshness of precipitation bath, (3) adopting mixed solvents, and so on.^{2,5–9}

Polymorphism control is another issue as regarding the preparation of PVDF membranes. PVDF has three main crystal forms, namely, α , β , and γ , respectively. The α -form is nonpolar, whereas β - and γ -forms are polar and electrically active.^{10–15} Of them, the β -form is most attractive because of its superior piezoelectric properties. Immersion precipitation usually produces nonpolar α -form in the PVDF membranes; and the generation of piezoelectric β -form is occasional.^{16,17} By intense electrical poling of PVDF membranes nonpolar α -form was transformed to piezoelectric β -form. The piezoelectrically active PVDF membranes greatly reduced fouling during filtration processes, and thus, improved separation efficiency.¹⁸ However, electrical

poling under intense electric field had the risk of electrical breakdown of porous PVDF membranes. And, transformation of nonpolar α -form was not complete; the α -form coexisted with the β -form in the poled membranes.

In this article, PVDF membranes with exclusive piezoelectric β -form were directly prepared by immersion precipitation from mixed solvents containing an ionic liquid (IL). Moreover, the preferential crystallization of PVDF, which became significant at low coagulation temperatures and high IL loadings, was responsible for the particulate morphology, and thus, high water flux in the membranes.

EXPERIMENTAL

Materials

The PVDF (trade name FR907), provided by Shanghai 3F New Materials Co. China, had a melt flow index of 8 g / 10 min (230°C, 2.16 kg). The IL, 1-butyl-3-methylimidazolium tetrafluoroborate BF₄, was obtained from Lanzhou institute of Chemical Physics, China, and used as received. The purity of the IL was better than 99%, as provided by the supplier. Dimethylformamide (DMF, purity > 99.5%, water content < 0.1%) and ethanol (purity > 99.7%, water content < 0.3%) were analytical reagents and used without further purification.

Membrane Preparation

PVDF pellets were first dissolved in DMF at 95°C under stirring to form a homogenous solution, followed by the addition of the IL. The concentration of PVDF in the solution was fixed at 18%

(w/v), and the IL loading in the mixed solvents was 0–30% (v/v). After air bubbles were removed completely, the solution was uniformly spread on a glass plate at 90°C and the resulted thickness of liquid membranes was about 200 μm (controlled by a spacer). After then, the glass plate was immediately immersed into a coagulation bath of deionized water. The temperature of coagulation bath was controlled at 0 and 80°C, respectively. The solidified membranes were soaked in a large amount of deionized water and ethanol for 24 h, respectively, to remove residual DMF and the IL. Thereafter, the membranes were kept in fresh ethanol to prevent possible shrinkage before characterizations.

Characterizations

Morphology was probed by a Hitachi SU1510 scanning electron microscope (SEM) at an acceleration voltage of 20 kV. Membranes, dried naturally at room temperature, were first fractured in liquid nitrogen, and then the fractured surfaces were sputtered by a thin gold layer.

The crystalline phase was determined by an X-ray diffractometer equipped with an X-ray generator and a goniometer at room temperature. The wavelength of the monochromated X-ray was 0.154 nm.

Fourier-transform infrared spectroscopy (FTIR) measurements were conducted on a Thermo Nicolet FTIR spectrometer equipped with an attenuated total reflection accessory at room temperature. Spectra were collected with a resolution of 4 cm^{-1} and a total of 32 scans were added.

A small angle light scattering (SALS) setup was used to probe crystal morphology of PVDF gels at room temperature. The wavelength of laser was 532 nm and Hv geometry was adopted.

Water flux was measured with a stainless cell (effective area 23.75 cm^2) at 0.6 MPa pressure and constant feed. After running for 5–10 min the pressure achieved stable and water was collected. Three samples were measured and their average result was reported.

RESULTS AND DISCUSSION

Gelation and Crystallization of PVDF in the Mixed Solvents

PVDF solution with only DMF as the solvent behaves liquid-like at room temperature, as shown by optical photographs in

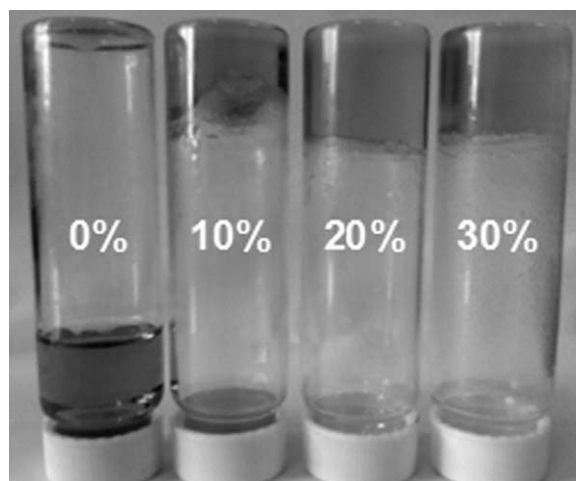


Figure 1. Optical photographs of PVDF solution with the indicated IL loading in the mixed solvents after being kept at room temperature.

Figure 1. In contrast, gelation is observed in the PVDF solution containing the IL. It becomes significant with increasing the IL loading in the mixed solvents, deduced from the flow ability of gels as well as the gelation time. The gelation time, determined by tilting the vials, was about 48, 6, and 1 h for PVDF solution with 10%, 20%, and 30% IL loading, respectively. One may argue that gelation could arise from the increase in the ratio of PVDF to DMF in the solutions with incorporation of the IL. As a matter of fact, no gelation is observed in a PVDF/DMF solution with a high concentration of 25.7% (w/v), that is, 18%/0.7.

Conversely, gelation in the mixed solvents correlates with the crystallization of PVDF, as demonstrated by the typical SALS patterns in Figure 2. Of note, samples for SALS measurements were taken from the vials shown in Figure 1 and then sandwiched between two glass coverslips. No scattering from crystals is observed in the PVDF solution with only DMF as the solvent because PVDF remains dissolution in DMF. In contrast, significant scattering from crystals is exhibited by the gels produced from PVDF solution with 30% IL loading in the mixed solvents. The crystals help the construction of three-dimensional molecular network where the solvents are trapped in, responsible for the appearance of gelation. It, in turn, suggests that the presence

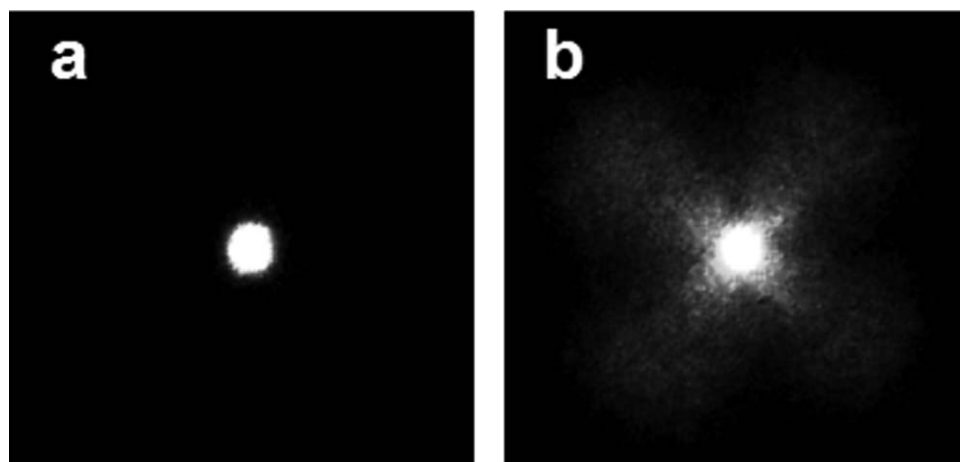


Figure 2. Typical SALS patterns of PVDF solution with (a) 0% and (b) 30% IL loading in the mixed solvents after being kept at room temperature.

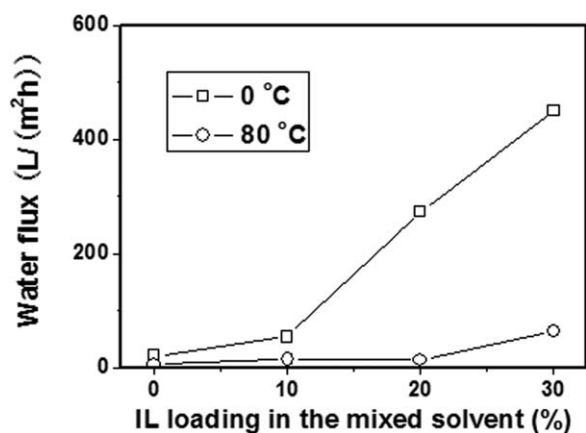


Figure 3. Evolution of water flux with respect to the IL loadings in the mixed solvents and coagulation temperatures.

of the IL promotes the crystallization of PVDF in the solution, which could alter the microstructure and performance of membranes prepared by immersion precipitation where liquid–liquid demixing is competed with crystallization.

Water Flux and Morphology of Membranes

As shown in Figure 3, incorporation of the IL in the mixed solvents largely enhances the water flux of membranes prepared by immersion precipitation especially at 0 °C. The more the IL loading in the mixed solvents, the higher water flux is exhibited. For instance, water flux is enhanced by about 22 times in the membranes prepared at 0 °C from the mixed solvents with 30% IL loading, as compared to that of membranes prepared from DMF only. Conversely, at a high coagulation temperature, that is, 80 °C, effect of the IL on the water flux is less remarkable; and only a slight increase in the water flux is observed in the membranes prepared from the mixed solvents containing 30% IL. The change of water flux with the IL loadings and coagulation temperatures should be related to the competition between liquid–liquid demixing and crystallization during immersion precipitation. In other words, the enhanced crystallization of

PVDF in the solution containing the IL could dominate the precipitation process at 0 °C, and thus, contribute to high water flux. In contrast, at 80 °C liquid–liquid demixing could be preferential even in the presence of the IL because crystallization of PVDF could be retarded at high temperatures.

To confirm this, morphological observations on the cross-section of membranes were conducted; and corresponding SEM pictures are given in Figure 4. The morphology of membranes prepared at 0 °C changes significantly with respect to the IL loading in the mixed solvents. Finger- and sponge-like structures in the top and bottom part of membranes, respectively, are observed in the membranes without and with 10% IL loading [Figure 4(a,b)]. This typical morphology corresponds to preferential liquid–liquid demixing as well as slow solvent–non-solvent interdiffusion in the precipitation process.¹ While 20% and 30% IL are incorporated, particulate morphology, induced by preferential crystallization of PVDF,² is generated in the bottom part of membranes [Figure 5(c,d)]. Conversely, the membranes prepared at 80 °C show sponge-like structure along the whole cross-section, irrespective of the IL loadings [Figure 4(a'–d')]. It arises from preferential liquid–liquid demixing and fast solvent–non-solvent interdiffusion at high coagulation temperatures. The above results clearly demonstrate that incorporation of the IL in the PVDF solution favors particulate morphology and high water flux of membranes prepared at low coagulation temperatures because crystallization of PVDF is enhanced over liquid–liquid demixing during the precipitation process.

Formation of Piezoelectric β -Form

As depicted by the X-ray diffraction (XRD) profiles in Figure 5, PVDF membranes, prepared at either 0 or 80 °C from DMF only, have characteristic diffractions of α -form at 2θ of around 18.4, 20, and 26.6°. While the mixed solvents containing the IL are used, the characteristic diffractions of α -form disappear completely, replaced by a diffraction at 2θ of about 20.4°. This diffraction is assigned to β - or γ -form of PVDF. It means that the presence of IL promotes the formation of β - or γ -form in the membranes, and it is almost independent of the IL loadings

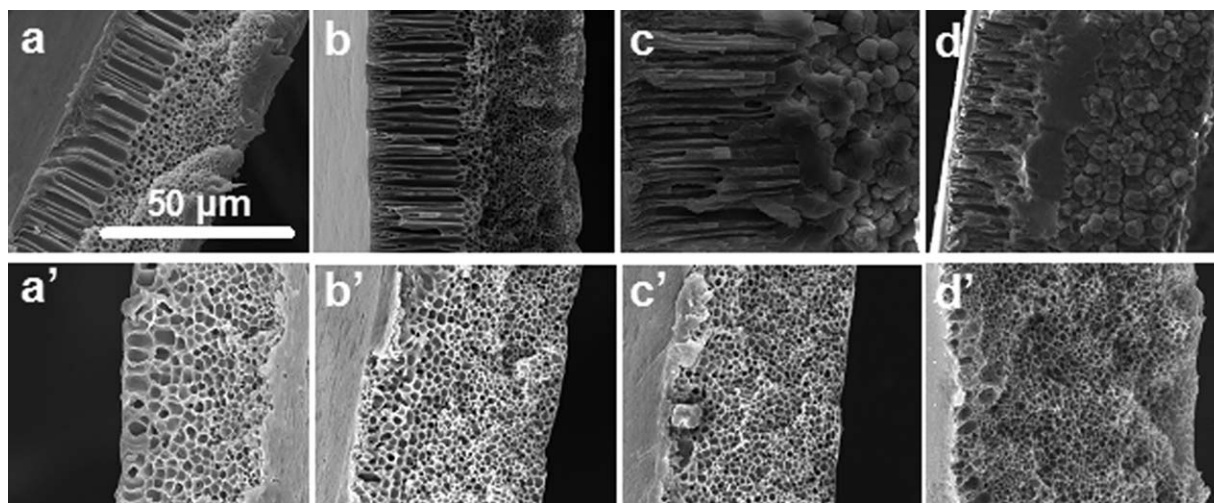


Figure 4. SEM micrographs of the cross-section of PVDF membranes prepared from the mixed solvents with various IL loadings at (a–d) 0 and (a'–d') 80 °C, respectively: (a, a') 0%, (b, b') 10%, (c, c') 20%, (d, d') 30%.

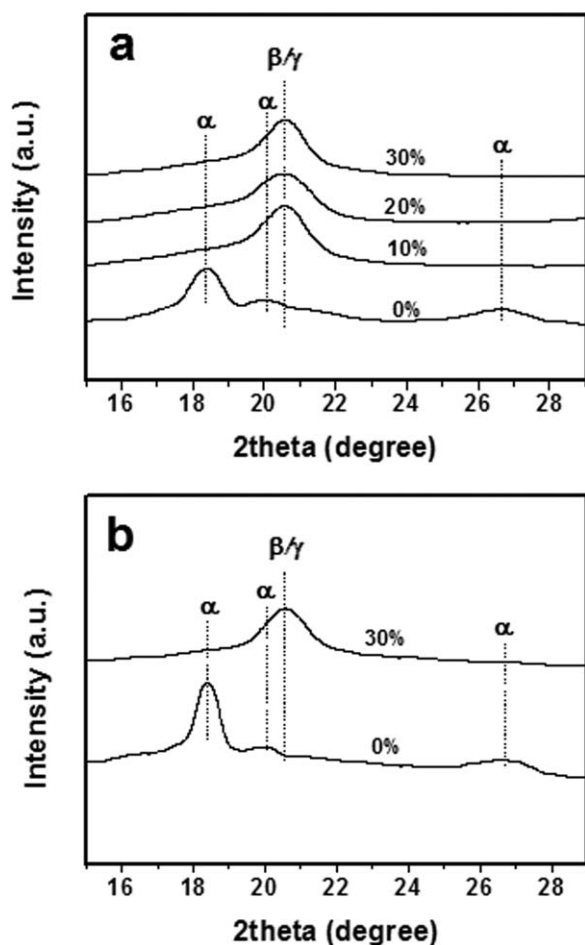


Figure 5. XRD profiles of PVDF membranes prepared at (a) 0 and (b) 80°C from the mixed solvents with the indicated IL loadings.

and coagulation temperatures. The crystallinity, deduced from the XRD profiles, is higher in the membranes prepared from the mixed solutions containing the IL than that in the membranes prepared from DMF only at each coagulation temperature. It further indicates that the presence of the IL favors the crystallization of PVDF during immersion precipitation.

Due to their similar diffractions, it is difficult to distinguish β - and γ -form from the XRD profiles. Rather, FTIR is very powerful to disclose the crystal structure of PVDF; and α -, β - and γ -forms have distinct absorption bands in the FTIR spectra.^{19–21} As demonstrated by Figure 6, the absorption bands at 764 and 796 cm^{-1} are assigned to the α -form, and those at 840 and 1274 cm^{-1} are contributed by the β -form. The γ -form has a typical absorption band at 1234 cm^{-1} . Exclusive β -form, in the absence of α - and γ -forms, is observed in the membranes prepared at 0°C from the mixed solvents containing the IL. As a comparison, only α -form is present in the membranes precipitated from DMF only. Similar results are also observed in the membranes prepared at 80°C; and the only difference is that a little γ -form is coexisted with remarkable β -form.

ILs, composed of cations and anions, have strong Coulombic interactions with polymers.²² Therefore, it is expected that ion-dipole interactions between the IL and polar PVDF chains in

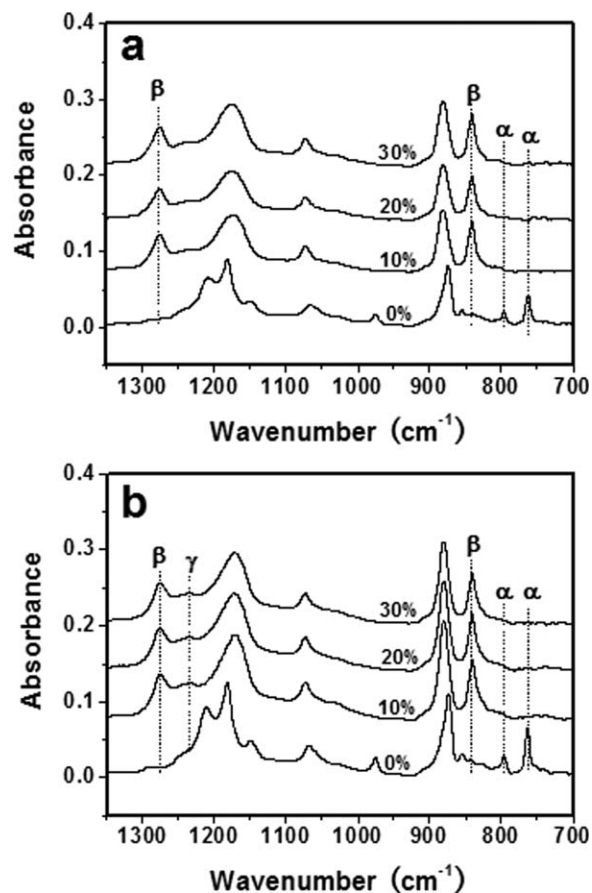


Figure 6. FTIR spectra of PVDF membranes prepared at (a) 0 and (b) 80°C from the mixed solvents with the indicated IL loadings. For clarification, vertical shift was done for the spectra.

the solution promotes TTTT conformation, that is, a prerequisite for the formation of the β -form. Similar argument was proposed to explain the formation of the β -form in the melt crystallization of PVDF-containing inorganic fillers and in the solution crystallization of PVDF from polar solvents.^{23–25} On the contrary, without the IL TGTC' conformation prevails, and thus, the α -form is produced. The little amount of the γ -form with TTTGTTT' conformation in the membranes prepared at 80°C could arise from the conformational rearrangement or incorporation of gauche isomers into TTTT conformation at high temperatures.²⁶

CONCLUSIONS

The addition of the IL in DMF favors the crystallization of PVDF in advance of liquid–liquid demixing, which becomes significant at low coagulation temperatures and high IL loadings. As a result, particulate morphology and high water flux are achieved in the membranes. What is more, the presence of the IL promotes the crystallization of PVDF into exclusive β -form without any trace of α - and γ -forms at low coagulation temperatures, irrespective of the IL loadings. It should arise from the generation of TTTT conformation in the mixed solvents due to ion–dipole interactions between the IL and polar PVDF chains. The piezoelectric β -form could improve the antifouling and

separation efficiency of PVDF membranes during filtration process.

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