Morphological Study of Poly(vinylidene fluoride) Asymmetric Membranes: Effects of the Solvent, Additive, and Dope Temperature

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ABSTRACT: Asymmetric poly(vinylidene fluoride) (PVDF) membranes were cast with commercial-grade Kynar K760 polymer pellets and four different solvent systems: *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide, 1-methyl-2-pyrrolidone, and triethyl phosphate. With a focus on the PVDF/DMAc system, the effects of various additives (i.e., ethanol, glycerol, lithium chloride, lithium perchlorate, and water) on the resulting membrane morphology were investigated. The membrane morphology was examined with scanning electron microscopy. The effect of the dope solution temperature on the membrane morphology was also studied for the various additives used. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1782–1789, 2004

Key words: membranes; morphology

INTRODUCTION

The emergence of poly(vinylidene fluoride) (PVDF) as a popular membrane material can be attributed to its excellent chemical and thermal resistance,[1,2] especially in applications involving alkaline or acidic wastewater treatment. In brief, different applications require different membrane properties, which are related to the membrane structure. Semicrystalline polymers, such as PVDF, have been reported to exhibit more complicated phase-separation behavior than amorphous polymers.[3] Knowledge of a polymer's crystallinity and its resulting membrane morphology is important as a basis of understanding its membrane permeability and selectivity, as well as its various chemical and mechanical properties.[4] The selection of the solvent and the additive is among the many factors that have a strong impact on the final membrane morphology. With the proper selection, we can anticipate a desired membrane structure and, therefore, satisfactory membrane separation performance. Apart from that, the temperatures of the polymer solution and coagulation bath are also frequently considered, as well as the composition of the coagulation bat.[5]

Much research into PVDF membranes has been conducted, mostly with the goal of finding a correlation between the membrane morphology and performance and the various preparation parameters, such as the dope compositions, additives, coagulation medium, quenching bath temperature, and evaporation time.[4–21] In most cases, it is interesting to obtain membranes with good permeability and high mechanical strength, that is, properties commonly related to the membrane morphology.

In brief, additives used in the fabrication of PVDF membranes can be broadly categorized into (1) polymeric additives such as poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG), (2) weak nonsolvents such as glycerol, (3) weak cosolvents such as ethanol and acetone, and (4) low-molecular-weight inorganic salts such as lithium chloride (LiCl) and lithium perchlorate ($LiClO_4$). The effects of these additives on the resulting PVDF membrane morphology have been reported in various publications.[14–21] The roles of different additives nevertheless vary in different polymer/solvent systems.

The addition of PVP and PEG has been reported to favor macrovoid formation in the fabrication of PVDF membranes.[15–17] The solution viscosity increases with the addition of either PVP or PEG, which increases with an increase in the additive molecular mass. The increase in the solution viscosity reduces the miscibility of a casting solution with a nonsolvent and, therefore, hinders the phase-separation kinetics but greatly enhances the thermodynamics for phase separation. Even so, Deshmukh and Li[15] showed that the controlling mechanism for the formation of the PVDF hollow fiber was dominated by the kinetic parameter in a

PVDF/*N,N*-dimethylacetamide (DMAc) system. A dramatic increase in the dope solution viscosity with the addition of LiCl was reported to be the result of the formation of a complex between DMAc and LiCl, as well as macromolecular fluctuating networks between Li$^+$ and the electron-donor group of PVDF.[18] Also, the addition of LiCl has been reported to enhance the membrane permeation performance, but with a reduction in its mechanical strength.[18,19] Wang et al.,[20] however, managed to retain the membrane mechanical strength by cointroducing 1-propanol. Because of its good water affinity, the presence of LiCl tends to encourage water inflow and enhance the coagulation rate and, therefore, produce membranes with good interconnectivity. For an additive with a weak nonsolvent nature such as glycerol, its presence in the dope solution brings the initial composition of the casting solution closer to the binodal.[21]

In this study, we first compare the morphology of PVDF membranes cast with four different solvents that have been reported to be good solvent for PVDF: DMAc, *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP), and triethyl phosphate (TEP). Using the PVDF/DMAc system, we compare the effects of different additives (ethanol, glycerol, LiCl, LiClO$_4$, and water) on the resulting membrane morphology at different dope temperatures.

EXPERIMENTAL

Materials

Kynar K760 PVDF polymer pellets were purchased from Elf Autochem (Philadelphia, PA) and were predried at 50°C before use. DMAc (>99.9%, high-performance liquid chromatography grade), NMP (>99.9%, spectrophotometric grade), DMF (99.8%, ACS reagent grade), and TEP (99%, gas-chromatography grade) were used as solvents. Ethanol (reagent grade), glycerol (Formula weight [F_w] = 92.09, 99%), LiCl (>99.9%, ACS reagent grade), LiClO$_4$ (>99.9%, ACS reagent grade), and water were used as additives. PVP (>99.9%, weight-average molecular weight = 10,000 or 90,000) was used as a pore former. All chemicals were purchased from Sigma-Aldrich (Dorset, UK) and were used as received. In all cases, tap water was used as the coagulation bath medium.

Membrane casting and characterization

Desired amounts of PVDF polymer pellets were weighed and poured into preweighed solvents contained in Duran poly(tetrafluoroethylene)-lined bottles. After each mixture was subjected to vigorous shaking to ensure thorough wetting of the polymer pellets, a desired quantity of an additive (when applicable) was added. The mixture was kept in a 60°C isothermal water bath and was subjected to intermittent mechanical rotating to assist with its dissolution. Once fully dissolved, the mixture was allowed to return to room temperature before use. The polymer dope solution was cast as a thin film onto a glass plate at either 20 or 50°C and 60 ± 5% relative humidity with a 200-μm gap casting knife and was immersed into a water bath at either 20 or 50°C after approximately 10 s of evaporation time. The flat-sheet membranes formed were kept in a fresh water bath for 3 days before characterization to ensure the complete removal of the residual solvent.

The cross-sectional structures of the flat-sheet membranes were examined with scanning electron microscopy (SEM; JEOL JSM-T330 and JSM-T6310; Tokyo, Japan). The flux measurements were carried out with a laboratory-scale test unit. With an active membrane area of about 5 cm^2, the water permeation flux was measured with distilled water at room temperature (19–20°C) and at a constant working pressure of 1 bar, by which a stable flux was obtained after an hour of operation.

RESULTS AND DISCUSSIONS

Effects of the different solvents on the membrane morphology

In the preparation of polymer membranes via a phase-inversion process, it is crucial that the polymer solution remains in a uniform and stable state. Although one or more solvents may be suitable for a particular polymer, another key thing to consider is that the solvent and nonsolvent must be completely miscible with each other. Here, with water as the coagulation medium, four solvents (DMAc, DMF, NMP, and TEP) with different solvent powers to PVDF were used to study the morphology of PVDF flat-sheet membranes prepared by an immersion–precipitation method. The SEM photographs of these membranes are shown in Figure 1.

Figure 1 shows that, with TEP as the solvent (the poorest solvent of the four used), the membrane exhibited a symmetry sponge structure through the whole thickness, with no cavities at all. Because of its weak solvent power, the minority presence of the nonsolvent was sufficient to induce the phase inversion of the polymer solution; therefore, liquid–liquid phase separation occurred at an early stage, and macrovoids could not develop. Another reason might be the weaker mutual affinity between TEP and water in comparison with NMP, DMF, and DMAc; this would favor the formation of a sponge membrane structure. In the case of NMP, irregular macrovoids were observed beneath the skin layer. This structure indicated the formation of a skin layer at an early stage; this left insufficient time for the further exchange of the solvent and nonsolvent. With further outflow of the solvent prevented by the skin layer, macrovoids formed beneath the skin layer; there, the solvent existed, and
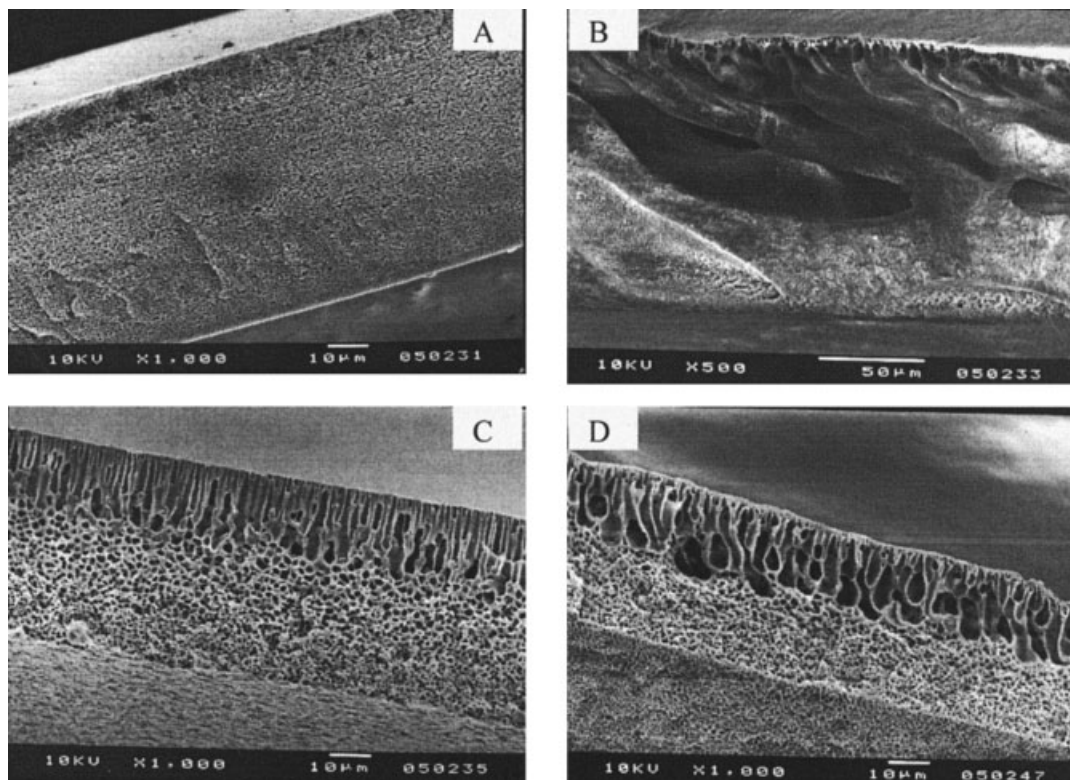
Figure 1 SEM pictures of the cross sections of membranes cast from polymer dope containing 15% PVDF and different solvents: (A) TEP, (B) NMP, (C) DMF, and (D) DMAc.
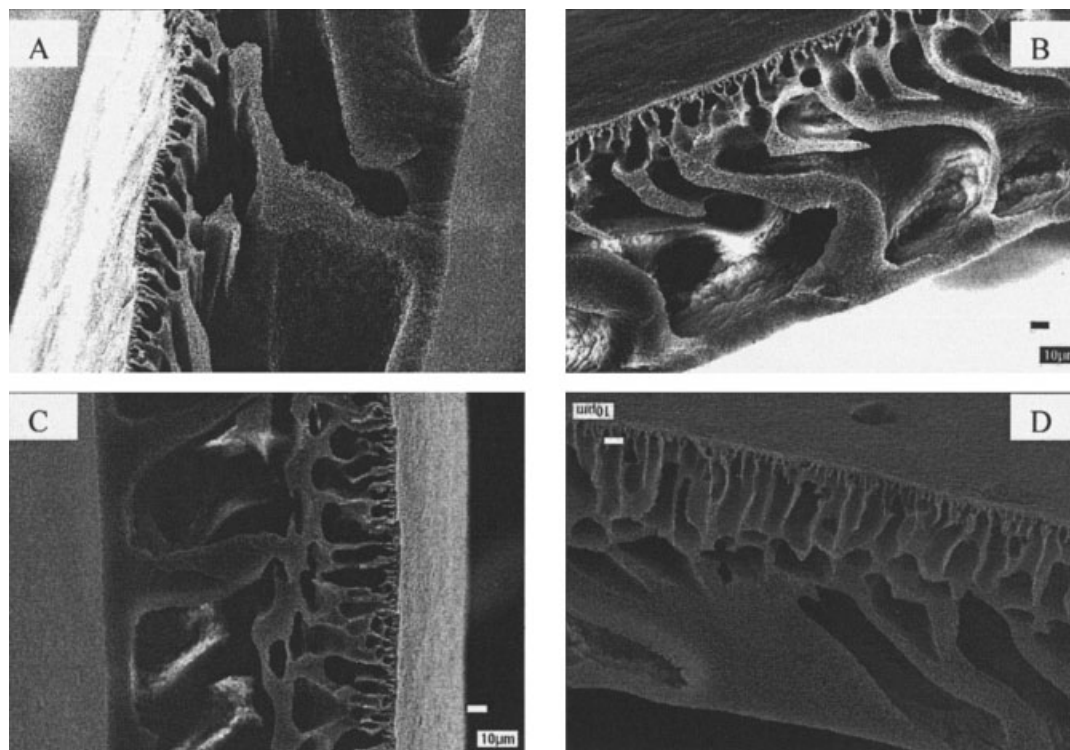

Figure 2 SEM pictures of cross sections of membranes cast from polymer dope containing 15% PVDF, 10% PVP (K10) as a pore former, and different amounts of water as a nonsolvent additive: (A) 0, (B) 2, (C) 3.7, and (D) 4.6%.
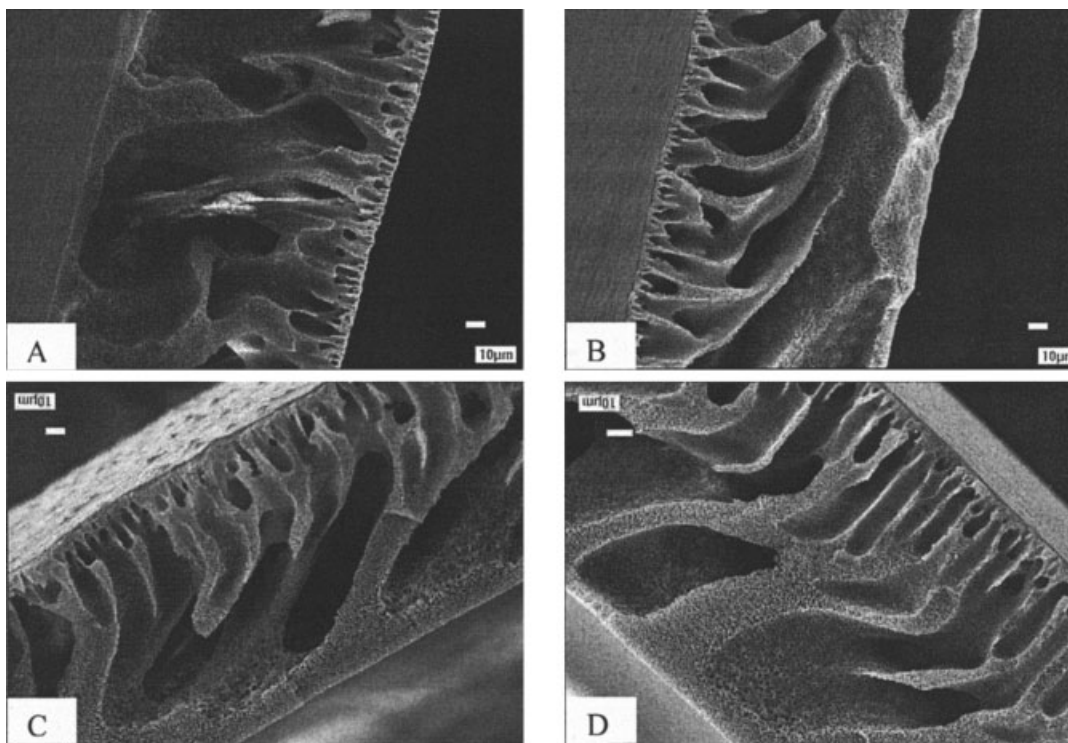
Figure 3 SEM pictures of cross sections of membranes cast from polymer dope containing 15% PVDF, 4% PVP (90 K) as a pore former, and different amounts of water as a nonsolvent additive: (A) 0, (B) 2, (C) 3.6, and (D) 5.5%.

the nonsolvent continued to enter. Another possible reason may be the high hydrophobic property of the PVDF material, which repelled water. As a result, there was not enough water in the substrate phase to induce phase inversion, and macrovoids developed. Flat-sheet membranes cast with DMF and DMAc as solvents exhibited similar shorter fingerlike structures with sponge substrates. These two typical structures indicated a slow exchange rate between the solvent and nonsolvent in the immersion–precipitation processes.

In this study, all membranes were cast with the same casting knife, that is, with a gap of 200 μm. However, the resulting membrane thickness followed the trend of NMP > TEP > DMF, DMAc. A membrane with a thickness of about 130 μm, obtained with NMP as a solvent, was the thickest of the four. In this case, membrane shrinkage caused by the outflow of the solvent from the original casting solution was very small because of the formation of a membrane skin at an early stage; this indicated a fast phase-inversion process. A membrane cast with TEP as a solvent was approximately 60–70 μm thick, and the thicknesses of the other two membranes cast with DMF and DMAc as solvents were about 50 μm. More shrinkage was caused by a greater lost of the solvent before phase inversion was completed. To understand the phase-inversion behavior of the PVDF polymer solution, we need a detailed investigation into its kinetics. Because PVDF is a hydrophobic material, the entrance of water

into a PVDF casting solution is relatively slow in immersion–precipitation processes. According to common sense, a greater amount of the nonsolvent is needed to induce phase inversion when a stronger solvent is used. Introducing a nonsolvent into the casting solution could accelerate this phase-inversion process. In our preliminary investigation,[22] of the four solvents, DMAc demonstrated the strongest solvent power to PVDF. Therefore, DMAc was used in our further investigation on the effects of additives and other parameters on the membrane morphology, as discussed in the following sections.

Effects of the additives on the membrane morphology

Nonsolvent additive (water)

In this section, we focus on the effect of the amount of water on the membrane morphology and the mem-

TABLE I
Water Flux of Membranes Cast from Polymer Dope Containing 15% PVDF, 10% PVP (K10), and Different Amounts of Water

	Flux (L/m² h bar)
Membrane A: 0% water	low
Membrane B: 2% water	116
Membrane C: 3.7% water	980
Membrane D: 4.6% water	1640

TABLE II
Water Flux of Membranes Cast from Polymer Dope
Containing 15% PVDF, 4% PVP (K90),
and Different amounts of Water

	Flux (L/m^2 h bar)
Membrane A: 0% water	145
Membrane B: 2% water	380
Membrane C: 3% water	417

brane performance in terms of the pure water flux. PVP (K10) or PVP (K90) was used to form pores and to increase the solution viscosity. The cross-sectional structures of these membranes are shown in Figures 2 and 3, and the water permeation flux was measured and is listed in Tables I and II.

The amount of water added to the casting solutions was gradually increased, and the corresponding membranes are shown in Figures 2 and 3. As more water was added, the macrovoids became smaller and appeared to be more regular. The membrane permeation flux also increased as more water was added, as shown in Tables I and II. The flux of the membrane cast with PVP (K10) as an additive was much higher than the flux of the membrane cast with PVP (K90) as an additive.

Other additives

Other additives (LiClO$_4$, glycerol, and ethanol) were investigated briefly for their effects on the resulting membrane morphology. With ethanol as an additive, the resulting membranes exhibited symmetric structures composed of uniform nodules, as shown in Figure 4(A). This phenomenon could be attributed to the occurrence of gelation induced by crystallization before liquid–liquid demixing. A similar phenomenon was also observed by Cheng et al.[23] for 1-octanol/ DMF/PVDF and water/DMF/PVDF with a soft coagulation bath, which could suppress the liquid–liquid demixing.

With the presence of 2% LiClO$_4$ as an additive in the polymer solution, the gelation of the polymer solution took place easily. As illustrated in Figure 4(B), the membrane had a very irregular structure, and this indicated the strong effect of the Li salt on the polymer solution. Figure 4(C,D) shows the membrane structure when glycerol was used as an additive. No distinctive structure was observed with the addition of a small amount of glycerol to the casting solution. However, the membrane structure became more regular with fingerlike macrovoids, supported by a more porous substrate, when 22.5% glycerol was present in the casting solution. The addition of glycerol is, therefore, believed to have suppressed the polymer interaction and favored liquid–liquid demixing.

Effects of the temperature on the membrane morphology

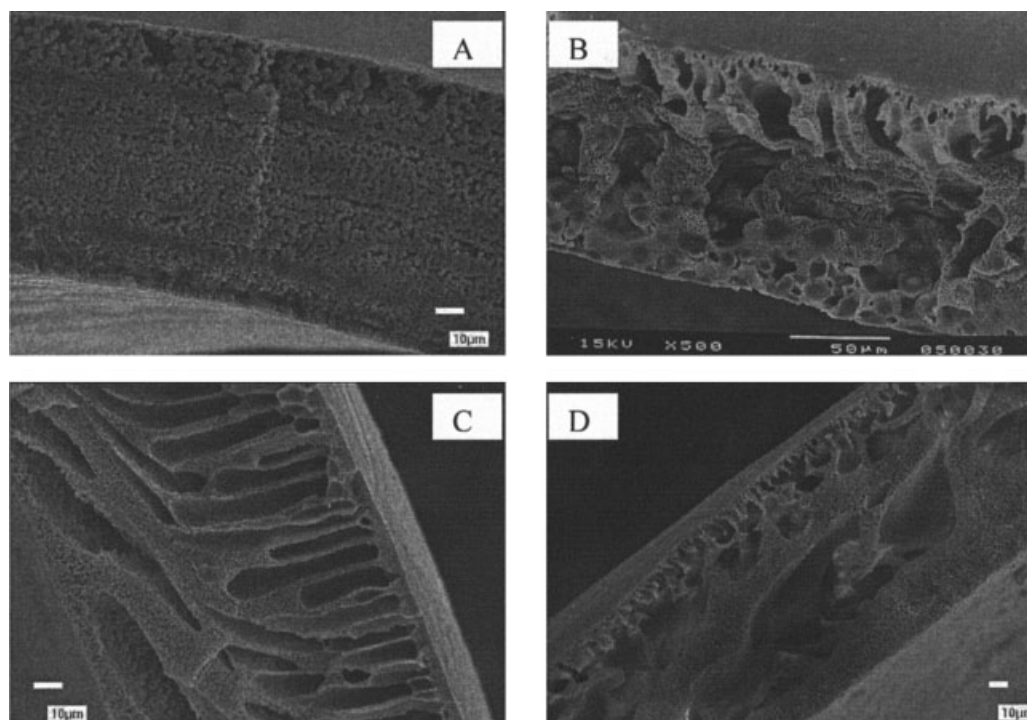Wang et al.[20] reported that an increase in the coagulation bath temperature had little influence on the

Figure 4 SEM pictures of cross sections of membranes cast from (A) 15% PVDF and 35% EtOH (with DMAc as the balance), (B) 20% PVDF and 2% LiClO$_4$ (with DMAc as the balance), (C) 16% PVDF and 22.5% glycerol (with DMAc as the balance), and (D) 15.4% PVDF and 7.7% glycerol (with DMAc as the balance).
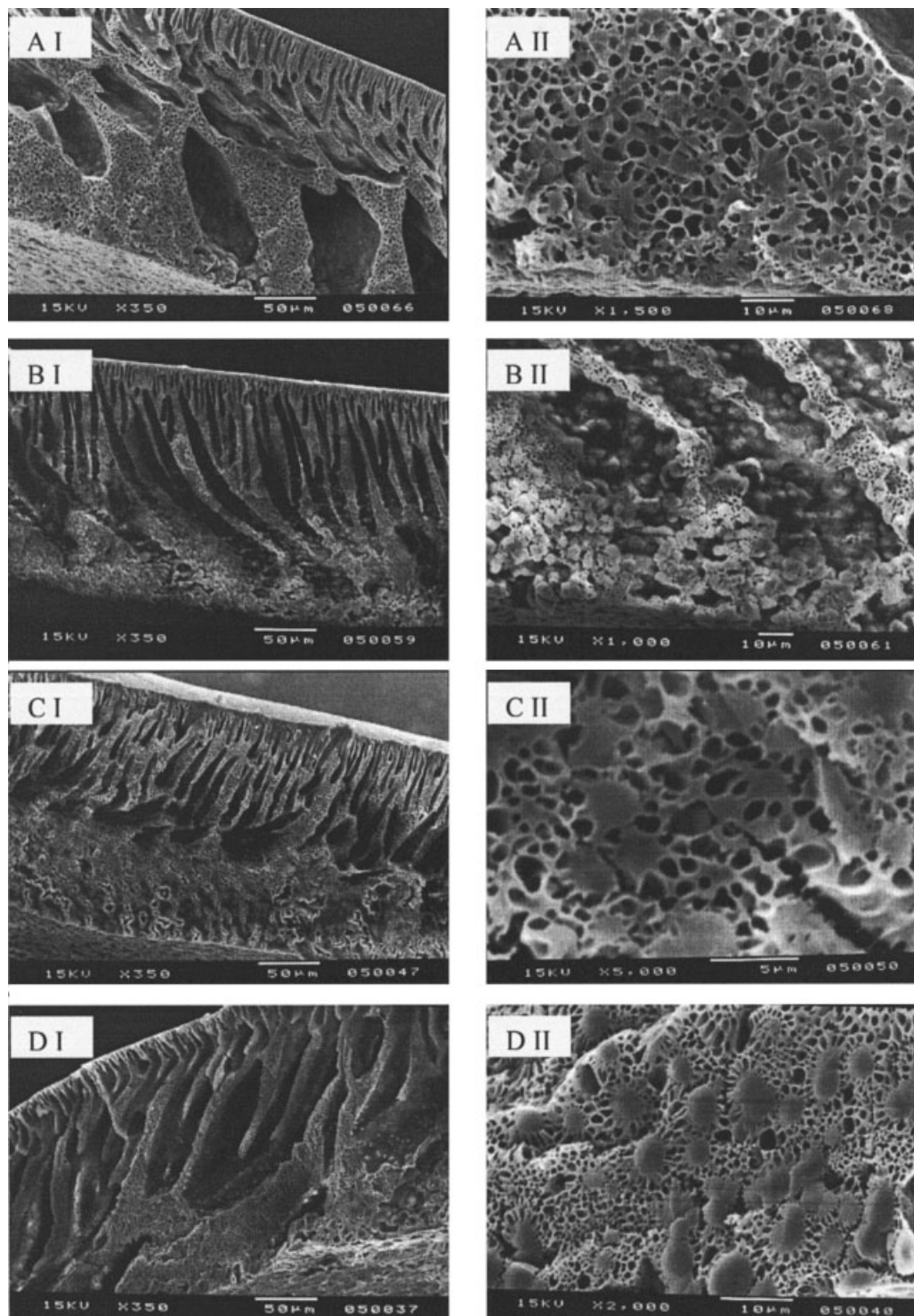
Figure 5 SEM pictures of (I) the cross sections and (II) the substrates of membranes cast at 20°C for both dope solutions and coagulation baths: (A) 20% PVDF, 2.8% glycerol, and 1.95% ethanol (with DMAc as the balance), (B) 20% PVDF, 2.93% glycerol, and 2.18% LiCl (with DMAc as the balance), (C) 20% PVDF and 2.25% LiCl (with DMAc as the balance), and (D) 20% PVDF and 3.1% LiClO$_4$ (with DMAc as the balance).

PVDF membrane coagulation rate because of the slow interaction between water and PVDF. In this study, an obvious structural change was noted when both the dope solution and coagulation bath temperatures were increased, especially in the presence of additives.

It is believed that at higher dope and coagulation bath temperatures, the kinetics of the solvent outflux and water influx were enhanced.[8] At a higher temperature, crystallization could be suppressed, and liquid–liquid demixing could take place before crystallization. A
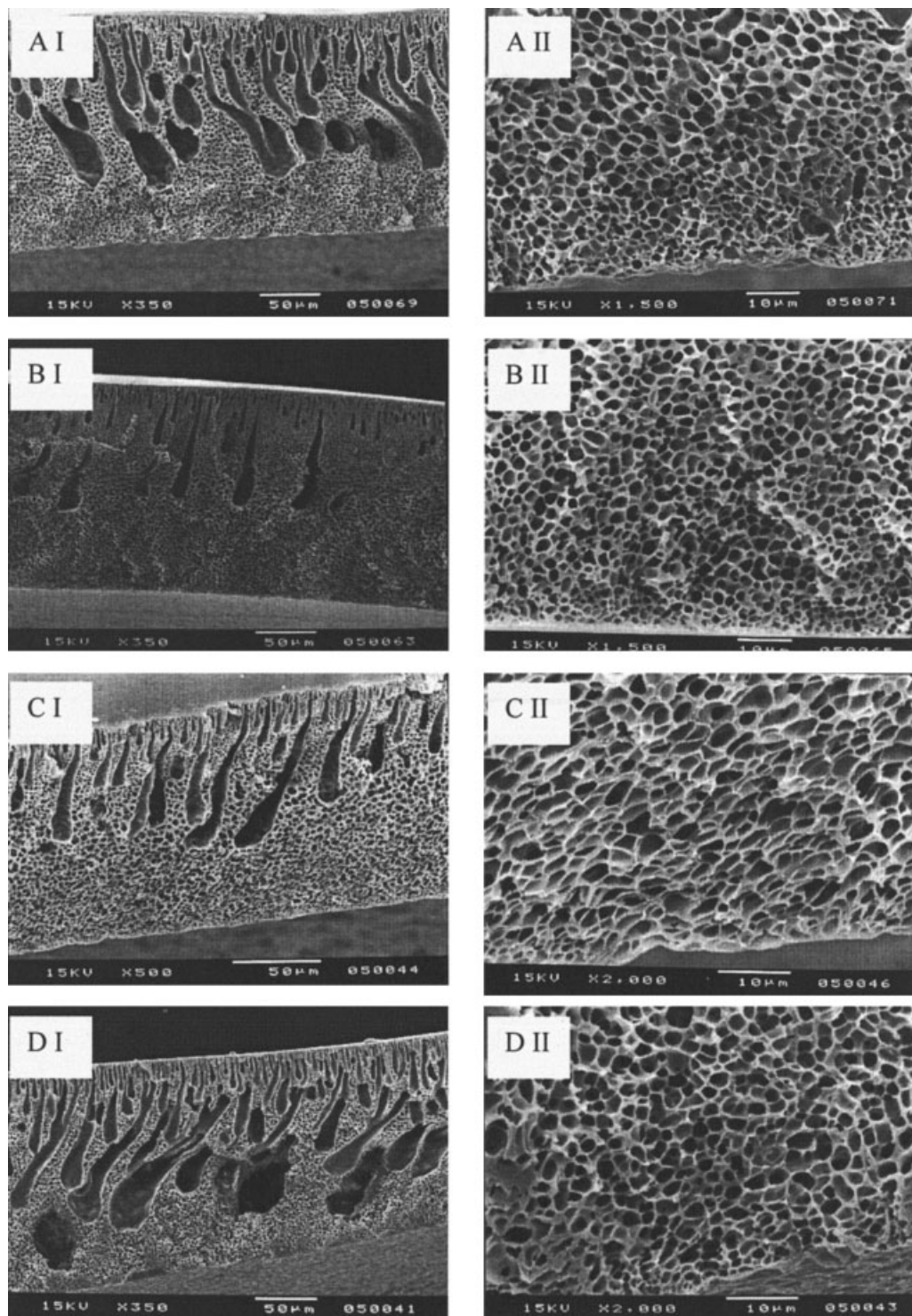
Figure 6 SEM pictures of (I) the cross sections and (II) the substrates of membranes cast at 50°C for both dope solutions and coagulation baths: (A) 20% PVDF, 2.8% glycerol, and 1.95% ethanol (with DMAc as the balance), (B) 20% PVDF, 2.93% glycerol, and 2.18% LiCl (with DMAc as the balance), (C) 20% PVDF and 2.25% LiCl (with DMAc as the balance), and (D) 20% PVDF and 3.1% LiClO$_4$ (with DMAc as the balance).

similar conclusion was drawn by Cheng[24] in their study on the effect of temperature on the formation of PVDF membranes by 1-octanol/DMF/PVDF and water/DMF/PVDF systems. Figure 5 shows the morphology of the membranes cast and coagulated at 20°C. Figure 5(AI–DI) shows irregular fingerlike cross-sectional structures with macrovoids. With reference to the substrate structures shown in Figure 5(AII–DII), some isolated islands of a dense polymer phase could be clearly seen. Approximately 3–5-μm particles could

be seen trapped in the membrane matrix, as shown in Figure 5(BII). This could be due to the precipitation of highly localized concentrated PVDF as a result of crystallization. The structure of these crystallization-associated precipitation behaviors was not observed when the membranes were cast and coagulated at 50°C, as shown in Figure 6. In this case, an elevated temperature favored liquid–liquid demixing and so resulted in membranes with a cellular morphology in the substrate and a regular fingerlike structure beneath the skin layer. This could be explained by the observation made in the experiments of the cloud-point measurements.[22] For a high-concentration polymer solution, with the presence of an additive, the phase-separation point was marked by the formation of a transparent gel at a lower temperature of 25°C. At a higher temperature, its phase-separation point was marked by the solution becoming turbid. At a lower temperature, gelation induced by crystallization occurred first in the membrane formation processes, and the crystal could grow because of slow liquid–liquid demixing. At a higher temperature, a different phenomenon was observed, as an elevated temperature suppressed gelation but favored liquid–liquid demixing; therefore, the end point was marked by the solution becoming turbid.

CONCLUSIONS

The morphology of PVDF membranes with different solvent systems, including NMP, DMF, DMAc, and TEP, and some additives, such as ethanol, glycerol, and $LiClO_4$, was investigated with SEM. The effect of the temperature on the membrane formation was also discussed. Experimental results revealed the distinctive influences of various solvents on the resulting membrane structure, indicating the importance of the solvent. The use of water as a nonsolvent additive could improve the membrane permeability; that is, a flux increment to 1640 L/m^2 h bar was noted with the addition of 4.6% water to a casting solution. The phase behavior of PVDF polymer solutions in the membrane formation process changed greatly in the presence of additives. Glycerol suppressed gelation induced by crystallization, whereas Li salt enhanced the gelation behavior. The temperature was found to be an interesting parameter affecting the PVDF polymer solution system; an elevated temperature in both the polymer dope and coagulant suppressed crystallization, and liquid–liquid demixing could occur before gelation with an increased temperature.

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