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Preparation of PVDF Membranes via TIPS Method: The Effect of Mixed Diluents on Membrane Structure and Mechanical Property

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PVDF membranes were prepared via thermally induced phase separation method (TIPS). Two series of mixed solvents were used as diluents, and they were composed of γ-butyrolactone(γ-BA)/cyclohexanone(CO) or cyclohexanone(CO)/dibutylphthalate(DBP), respectively. In this paper, all the membrane formation processes only went through the solid-liquid phase separation. The polymer melting/crystallization temperature in different mixed diluent was determined using differential scanning calorimeter (DSC). The effect of mixed diluents on crystal phase of membrane, crystallinity of membrane and membrane cross-section morphology was investigated using wide angle X-ray diffractometer (WAXD) and FT-IR spectrometer. The obtained membrane exhibited two kinds of cross-section morphology, including spherulite-like crystallite and sheaf-like crystallite. The membrane with a plenty of sheaf-like crystallites had good tensile strength and permeation flux for pure water.

Keywords: poly(vinylidene fluoride) membrane; thermally induced phase separation; membrane morphology; polymer crystallization

1 Introduction

PVDF is a perfect membrane material due to its excellent solvent resistance, acid and alkali resistance, oxide resistance and ultraviolet radiation resistance. Most of PVDF membranes were prepared via non-solvent induced phase separation method (NIPS). These membranes usually have a macrovoid structure or finger-like structure in their cross-section and show unsatisfactory strength. They were easy to rupture in the practical application, especially in the membrane bioreactor (MBR) application.

The thermally induced phase separation process is one of the most useful techniques to prepare the porous membranes. In the membrane preparation via TIPS, a polymer is dissolved in a diluent at high temperature and then the homogenous polymer solution is cooled to induce the phase separation. The membrane forms gradually as the polymer is solidified by crystallization or glass transition. Then, the membrane is immersed into an extractant to remove the diluent. The TIPS process is a temperature-driven process, and it has a different membrane formation mechanism in comparison with NIPS. Thus, it is hopeful to obtain a different membrane cross-section structure by the TIPS method and thereby to improve the membrane strength. In addition, the TIPS method has several well-documented advantages including: [1] greater flexibility and easier control than conventional casting process; [2] a very low tendency for defect formation; and [3] very high overall porosity and effective control of the final pore size.

Currently, the literature on the PVDF microporous membrane via the TIPS method is rare (1–5). And this literature only makes some brief description rather than a detailed and systemic study.

The diluent plays an important role in the TIPS process. It determines the polymer crystallization process and the resulting membrane cross-section morphology, and thereby affects the membrane properties, such as pore size, permeability, strength etc. Lloyd et al. investigated the effects of all kinds of diluents on PP membrane formation in detail. They found that only the solid-liquid phase separation (that is, the polymer crystallization) occurred in the membrane formation process when aliphatic saturated hydrocarbon or aliphatic saturated acid were used as diluents (6–9). And, with the increase of freezing point of diluent, the membrane cross-section morphology changed from the spheric structure to the net-like structure. They also found that the liquid-liquid phase separation occurred before the solid-liquid phase separation at low polymer concentration when

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n,n-bis(2-hydroxyethyl) tallowamine (TA) or diphenyl ether (DPE) were used as diluents (6, 10–14). Furthermore, the membrane cross-section took on the porous structure. Lee et al. prepared the PP membranes using dialkyl phthalate with a different number of carbon atoms in the alkyl chain as diluents (15). With the increase of number of carbon atoms, the affinity between diluent and PP strengthened and the liquid-liquid phase temperature reduced. When the number of carbon atoms was more than eight, the membrane formation process only went through the solid-liquid phase separation and resulted in the obvious spherulite-like structure. Yang et al. used camphene as diluent to prepare a series of PP tubular membranes with different morphology (16). The membrane formed at high quenching temperature contained spheric crystallites, and had low strength and high permeation flux. However, the membrane formed at the low quenching temperature contained the interconnected spheric crystallites and exhibited higher strength and lower permeability.

In addition, PVDF can form three kinds of crystal phases, including α-crystal phase, β-crystal phase and γ-crystal phase (17). The α-crystal phase is non-polar, whereas β-crystal phase has a strong polarity, and the polarity of γ-crystal phase is in the middle. Thus, the PVDF membrane with a different crystal phase could have a different adsorption property for protein and fouling resistance. Thus, the crystal phase of PVDF membrane was worthy of being studied.

We always used four single-diluents to study the effects of diluent, cooling rate, polymer concentration on the polymer crystallization rate and membrane cross-section morphology (18). In this paper, we selected three different diluents and mixed them with each other to investigate the effect of mixed diluent on the crystal phase of membrane, crystallinity of the membrane and membrane cross-section morphology. In addition, a good membrane was obtained when cyclohexanone was used as a diluent. This membrane contained an abundance of sheaf-like crystallites in the cross-section and exhibited the permeation flux of about 400 kg/m^2.h for pure water.

2 Experimental

2.1 Materials

PVDF (weight-averaged molecular weight of 170,000) was purchased from SOLEF International Ltd of Belgium. Three organic solvents were used as diluents, including γ-butyrolactone (γ-BA), cyclohexanone (CO) and dibutyl phthalate (DBP). They have different polarity, viscosity and molar volume, etc., and these properties are listed in Table 1. Ethanol was used as extractant. All chemicals were commercial and analytical grade, and were used without further purification.

2.2 DSC Measurement

A DSC(Seiko DSC6200, Japan) was used to determine the polymer dynamic melting/crystallization temperature. The detailed measure method was same as the literature reported by Lloyd (1): Samples were prepared by weighting the polymer and the mixed diluent into a sample pan (the mixed diluent was prepared prior to weight; the pan can be sealed and tolerate the pressure of 0.3 MPa, and the sample weight had no significant change after measure; this result indicated that no diluent was nearly lost in the DSC experiment). The weight of each component was known to an accuracy of 0.1 mg. The pan was sealed and heated to at least 40°C above the melting point of PVDF-diluent mixtures. After waiting 5 min to ensure complete melting and equilibration, the sample was cooled at the cooling rate of 10°C/min. The polymer crystallization temperature (T_c) was taken as the peak temperature on the resulting exotherm. And then the sample was heated again at the heating rate of 20°C/min. The polymer melting temperature (T_m) was taken as the peak temperature on the endothermic curve.

2.3 Membrane Preparation

PVDF and mixed diluent were added into a glass vessel with a sealed stopper, and then the mixed system was heated to a certain high temperature (that is, membrane preparation temperature) with nitrogen protection until the polymer was dissolved completely in the diluent. The resulting homogenous solution was molded rapidly between two glass plates in an oven (the oven had the same temperature as the membrane preparation temperature). The glass plates with the polymer solution were then cooled by putting them immediately into ambient air of 15°C. As the polymer crystallized gradually, the membrane formed and was then removed from the glass plate. Afterward, the membrane was immersed into ethanol to remove the diluent. The final membrane was

Table 1. The properties of diluents (19)

Diluents	Boiling point (°C)	Dipole moment (10^{-30}C m)	Viscosity (mPa · s)	Molar volume (cm^3/mol)	Surface tensile (mN/m)
γ-BA	204	13.74	1.7 (25°C)	76.5	43.2[a]
CO	155	10.0	2.2 (25°C)	103.6	34.5
DBP	338	8.0	9.72 (37.8°C)	265.6	33.4

[a] Measured.

dried in the air. Table 2 lists the membrane formulations and membrane preparation temperatures. When the CO/DBP ratio was 2 : 2, the membrane preparation temperature was 135°C, which was close to the boiling point of CO (155°C, as shown in Table 1). However, since DBP and CO has a strong interaction and DBP has the boiling point of 338°C, the evaporation of CO was limited by DBP. Thus, the evaporation of CO in the membrane preparation process was small. We measured the weight loss of all the systems in the membrane preparation process, and found that the maximum weight loss among all the systems was 2.2 wt%, which was similar as the literature (11).

2.4 Membrane Characterization

The crystallinity of membrane was calculated using the following equation:

$$X_c\% = (\Delta H_u/105) \times 100\%$$

where X_c means the crystallinity of the membrane sample, ΔH_u represents the fusion enthalpy of membrane sample (the fusion enthalpy was determined from the endothermic peak area of DSC melting curve of membrane sample), and the fusion enthalpy of PVDF with 100% crystallinity was considered to be 105 mJ/mg (20).

The crystal phase of membranes was determined using a wide angle X-ray diffraction (WAXD) method and FT-IR spectrometer. 1 cm^2 square samples were cut for WAXD measurements. The measurements were taken using an X-ray diffractometer (Model, D/max-RB, Japan) with Cu Kα ($\lambda = 0.154$ nm), and the scanning step was of 4°/min. In addition, 1 cm × 4 cm samples for FT-IR spectrometer were cut and then clamped on the sample-stage. The measurements were taken using a FT-IR spectrometer (Nicolet-560, USA).

The membrane sample was fractured in liquid nitrogen and mounted vertically on a sample holder. The cross-section of sample was coated with gold-palladium. A scanning electron microscope (SEM) (JEOL JSM-6301F, Japan) with an accelerating voltage of 5 KV was used to examine the membrane cross-section morphology.

The tensile strength of membrane was measured at the tensile rate of 10 mm/min and room temperature using the material testing machine (GT-TS-2000, GOTECH Co.).

Table 2. The membrane formulations and their serial numbers[a]

Membrane no.	Membrane formulation	Membrane preparation temperature
1#	γ-BA	90°C
2#	γ-BA/CO = 2 : 2	100°C
3#	γ-BA/CO = 1 : 3	100°C
4#	CO	105°C
5#	CO/DBP = 3 : 1	125°C
6#	CO/DBP = 2 : 2	135°C
7#	DBP	180°C

[a] All the membrane formulations contained the polymer concentration of 25 wt.%, and all the membranes were cooled at the ambient air of 15°C.

3 Results and Discussions

3.1 The Effect of Diluent on Polymer Melting/Crystallization Temperature

We mixed γ-BA and CO, CO and DBP into two series of mixed diluents and measured the polymer melting/crystallization temperature in different mixed diluent. The results are listed in Table 3. When γ-BA/CO was used as diluent, the polymer melting/crystallization temperature increased with the increase of CO content. PVDF had a better affinity for the polar solvent due to its strong polarity. Compared with CO, γ-BA has the higher dipole moment and thereby exhibits the stronger polarity, as shown in Table 1. Therefore, it has the stronger interaction with PVDF. The strong interaction promoted the melting of PVDF and prevented the crystallization of PVDF. As a result, PVDF exhibited the lower polymer melting/crystallization temperature in γ-BA. Similarly, when CO/DBP was used as diluent, the polymer melting/crystallization temperature increased with the increase of DBP content.

In addition, no significant liquid-liquid phase separation was observed in the cooling process of all the systems. This result indicated that the membrane formation process only went through the solid-liquid phase separation. Thus, the resulting membrane morphology was controlled completely by the polymer crystallization.

3.2 The Effect of Diluent on the Crystal Phase and Crystallinity of Membrane

Different PVDF crystal phases have different polarity, which would affect the absorption of the PVDF membrane for protein and thereby affect the membrane fouling-resistance. Thus, the membrane crystal phase was worthy of being

Table 3. The polymer melting/crystallization temperatures in different mixed diluents[a]

Ratio of mixed diluent	Polymer melting temperature (°C)	Polymer crystallization temperature (°C)
γ-BA	64.5	14.1
γ-BA/CO = 2 : 2	76.5	15.4
γ-BA/CO = 1 : 3	78.8	20.1
CO	80.2	29.8
CO/DBP = 3 : 1	107.2	64.7
CO/DBP = 2 : 2	120.8	80.5
DBP	152.2	107.4

[a] All the systems contained the polymer concentration of 25 wt.%.

studied. In the experiment, it was found that the crystal phase of membranes exhibited a regular change with the change of a mixed diluent ratio. Figure 1(a) shows the DSC melting curves of membranes from the γ-BA/CO mixed diluents. When γ-BA was used as diluent, the melting curve showed only one wide temperature peak at about 168°C. With the increase of CO content, the temperature peak appeared at about 150°C and strengthened gradually. This phenomenon suggested that a new crystal phase formed with the addition of CO.

To prove this, we further determined the WXRD spectra of these membranes, as shown in Figure 2(a). Weinhold et al. reported the d space and 2θ of γ-crystal in detail (17), and the d space and 2θ of α-crystal and β-crystal can be found from the XRD criterion spectrum card. According to the literature, we could determine the relationship between an X-ray diffraction peak and the corresponding crystallographic plane(hkl) of a given crystal phase, and the results are listed in Table 4. As shown in Figure 2(a) and Table 4, 1# WXRD spectrum exhibits four peaks (a, b, c, d). These peaks are characteristic peaks of the γ-crystal phase. With the increase of CO content, several new peaks appeared (a, b, d, e of 4# WXRD spectrum). These peaks are characteristic peaks of the α-crystal phase.

Furthermore, we used a FT-IR spectrometer to validate the above conclusion further. According to the literature (21), 1# IR spectrum in Figure 3 shows the characteristic peaks of γ-crystal phase at $1234\ \mathrm{cm}^{-1}$, $834\ \mathrm{cm}^{-1}$, $510\ \mathrm{cm}-1$, $485\ \mathrm{cm}^{-1}$ and $430\ \mathrm{cm}^{-1}$. However, 4# IR spectrum showed some new peaks at $1423\ \mathrm{cm}^{-1}$, $1384\ \mathrm{cm}^{-1}$, $1293\ \mathrm{cm}^{-1}$, $1211\ \mathrm{cm}^{-1}$, $1150\ \mathrm{cm}^{-1}$, $975\ \mathrm{cm}^{-1}$, $853\ \mathrm{cm}^{-1}$, $796\ \mathrm{cm}^{-1}$, $763\ \mathrm{cm}^{-1}$, $615\ \mathrm{cm}^{-1}$, $533\ \mathrm{cm}^{-1}$ and $489\ \mathrm{cm}^{-1}$, which represented α-crystal phase. Thus, it can be concluded from all the above results that the DSC melting peaks at about 150°C and 168°C (in Figure 1(a,b)) represent α-crystal phase and γ-crystal phase, respectively. (In general, the melting temperature of γ-crystal is higher than that of α-crystal, which was ever reported by Prest et al. (22)). Thus, the addition of CO helped for the formation of α-crystal phase. In addition, 1# IR spectrum in Figure 3 exhibits two weak peaks at $763\ \mathrm{cm}^{-1}$ and $615\ \mathrm{cm}^{-1}$, which

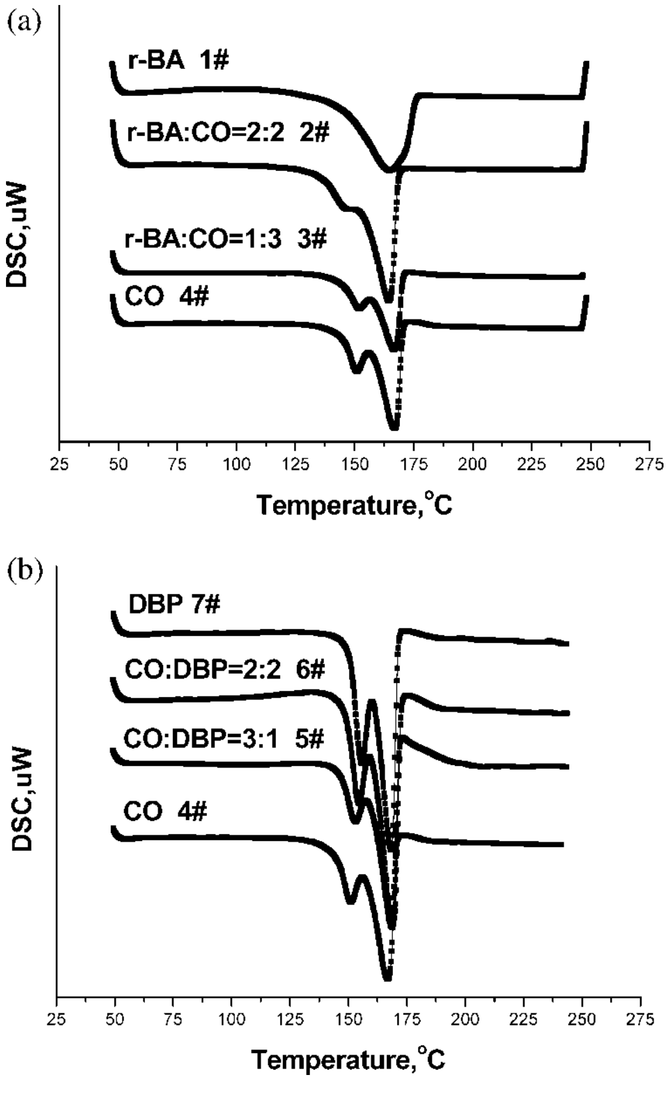

Fig. 1. DSC melting curves of PVDF membranes.

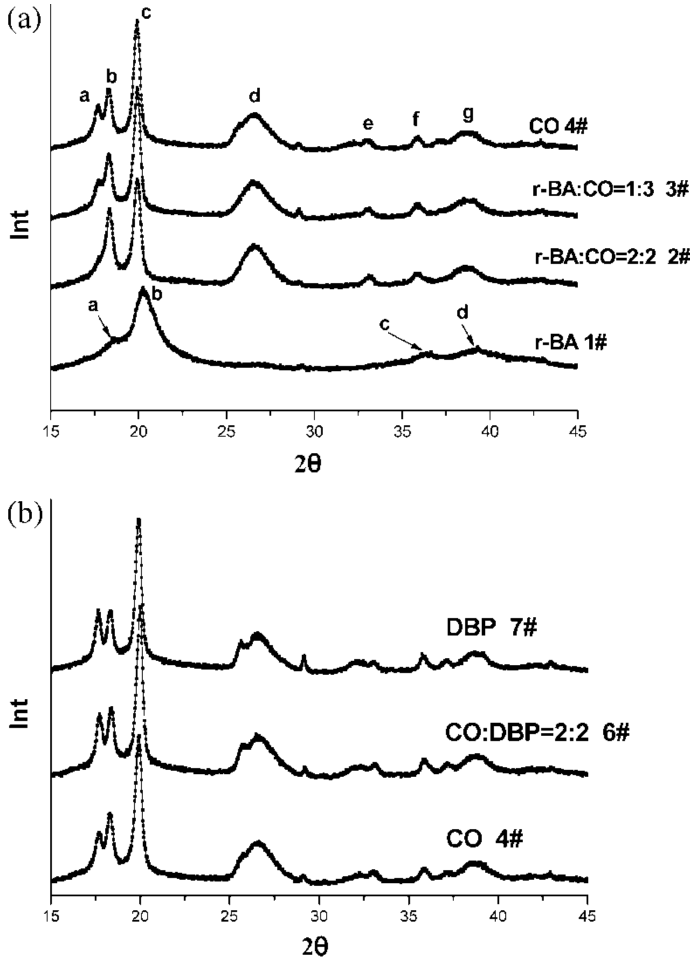

Fig. 2. The WXRD spectra of PVDF membranes.

Table 4. The relationship between an X-ray diffraction peak and the corresponding crystallographic plane(hkl) of a given crystal phase

WXRD spectrum no.		The crystal phase (hkl)
1# (Fig. 2a)	a	γ(020)
	b	γ(110)
	c	γ(200)
	d	γ(004), γ(041), γ(201), γ(132)
4# (Fig. 2a)	a	α(100)
	b	γ(020), α(020)
	c	γ(110), α(110)
	d	α(120), α(021)
	e	α(121), α(130)
	f	α(200), γ(200)
	g	α(131), γ(004), γ(041), γ(201), γ(132)

suggests that 1# membrane might contain a little of α-crystal phase.

Similarly, Figure 1(b) and Figure 2(b) exhibits the DSC melting curves and X-ray diffraction spectra of membranes from CO/DBP mixed diluents. It can be seen that the addition of DBP promoted the formation of α-crystal phase further.

As shown in Figure 1(a, b), compared with α-crystal phase, γ-crystal phase occupies a dominant proportion in all the membranes. In general, γ-crystal phase may form in the following conditions: high-crystallization from the melt at atmospheric pressure; or crystallization from certain organic solvents, such as dimethyl sulfoxide, dimethylacetamide (DMA), and dimethylformamide solutions (17). However, the membrane formation process in this paper doesn't agree with the former condition. Thus, the solvent is considered to be a possible factor for the crystal phase change, and we would investigate this further in our work.

Table 5 lists the membrane crystallinity. The crystallinity didn't show a regular change with the increase of CO content when γ-BA/CO as diluent. However, when CO/DBP as diluent, the crystallinity decreased and then increased with the increase of DBP content, which might be attributed to two factors. On the one hand, DBP has a high viscosity and a large molar volume (as shown in Table 1), which would limit the regular folding of polymer molecules in the crystallization process. This factor was unfavorable for the increase of crystallinity. On the other hand, the addition of DBP raised the polymer crystallization temperature, and thereby the polymer molecules had higher activity at the moment of crystallization. This factor promoted the regular folding of polymer molecules and helped for the increase of crystallinity. The competition of two factors might lead to the observed crystallinity changes.

3.3 *The Effect of Diluent on Membrane Cross-Section Morphology*

Figure 4 shows the cross-section morphologies of membranes from the γ-BA/CO mixed diluents. With the increase of CO content, the membrane cross-section changed from the spherulite-like crystallites to the sheaf-like crystallites, and the crystallite size diminished and the crystallite number increased dramatically. The membrane with abundant sheaf-like crystallites had better connectivity and smaller pore

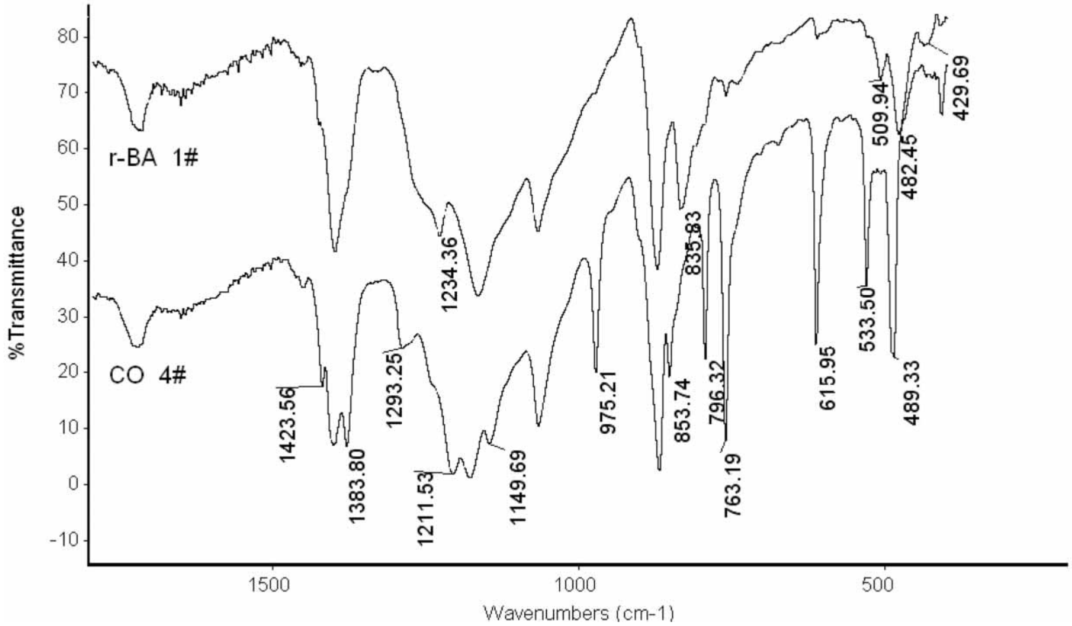

Figure 3. FT-IR spectra of PVDF membranes from γ-BA/CO systems.

Table 5. The crystallinity of membranes from different mixed diluents

Ratios of γ-BA/CO	Membrane crystallinity (%)	Ratios of CO/DBP	Membrane crystallinity (%)
γ-BA	59.8	CO	61
γ-BA/CO = 2 : 2	64.1	CO/DBP = 3 : 1	55.6
γ-BA/CO = 1 : 3	57.6	CO/DBP = 2 : 2	49.1
CO	61	DBP	53.7

size. These results indicate that the addition of CO helped the primary nucleation, and we have yet to find the reason. However, in the research, we found that a diluent with low surface tension and low viscosity always led to an abundance of sheaf-like crystallites. Thus, we suspected that this phenomenon might be relative to the low surface tension of CO.

Figure 5 shows the cross-section morphologies of membranes from the CO/DBP mixed diluents. When a small quantity of DBP was added into the polymer solution (CO/DBP = 3 : 1), the membrane cross-section changed from the sheaf-like crystallite to the spherulite-like crystallite, and the crystallite number decreased significantly. However, as the DBP content increased further, the spherulite-like crystallites became more numerous and smaller, and the crystallite shape increasingly deviated from the sphericity.

In the solid-liquid phase separation process of TIPS, as the temperature of the polymer solution decreases, the polymer

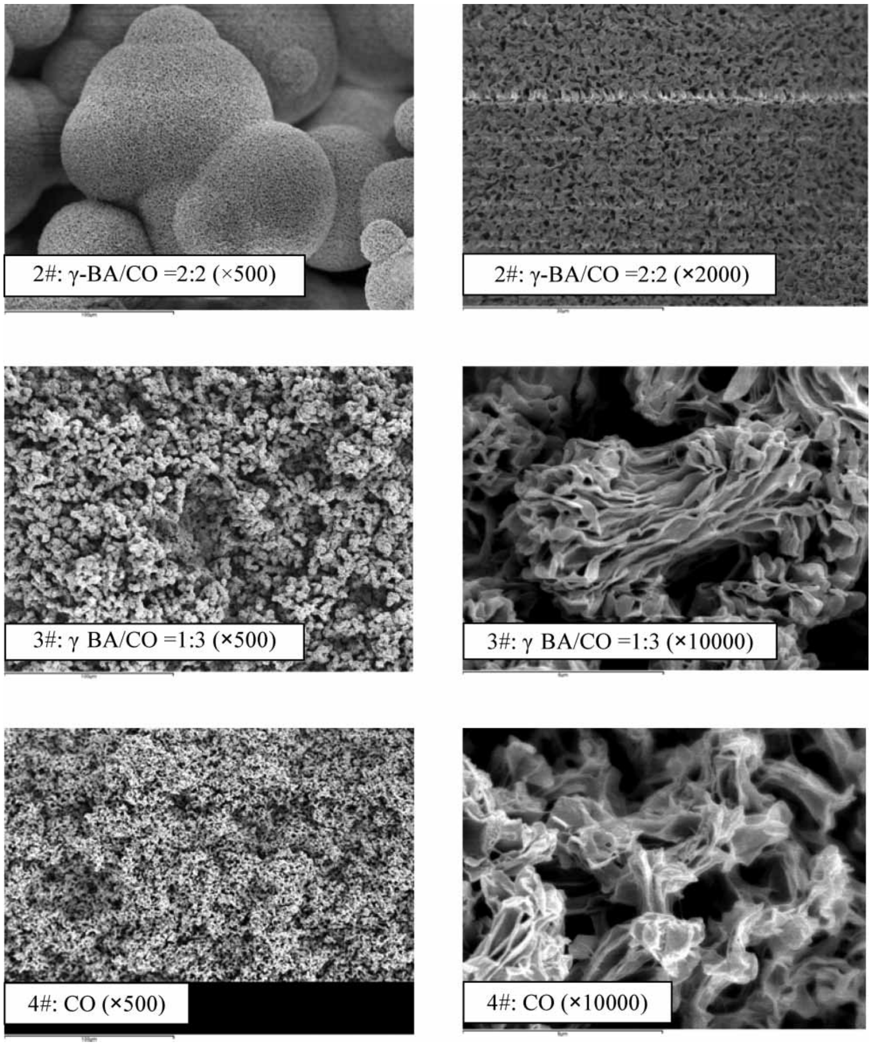

Fig. 4. The cross-section morphologies of membranes from the γ-BA/CO mixed diluents.

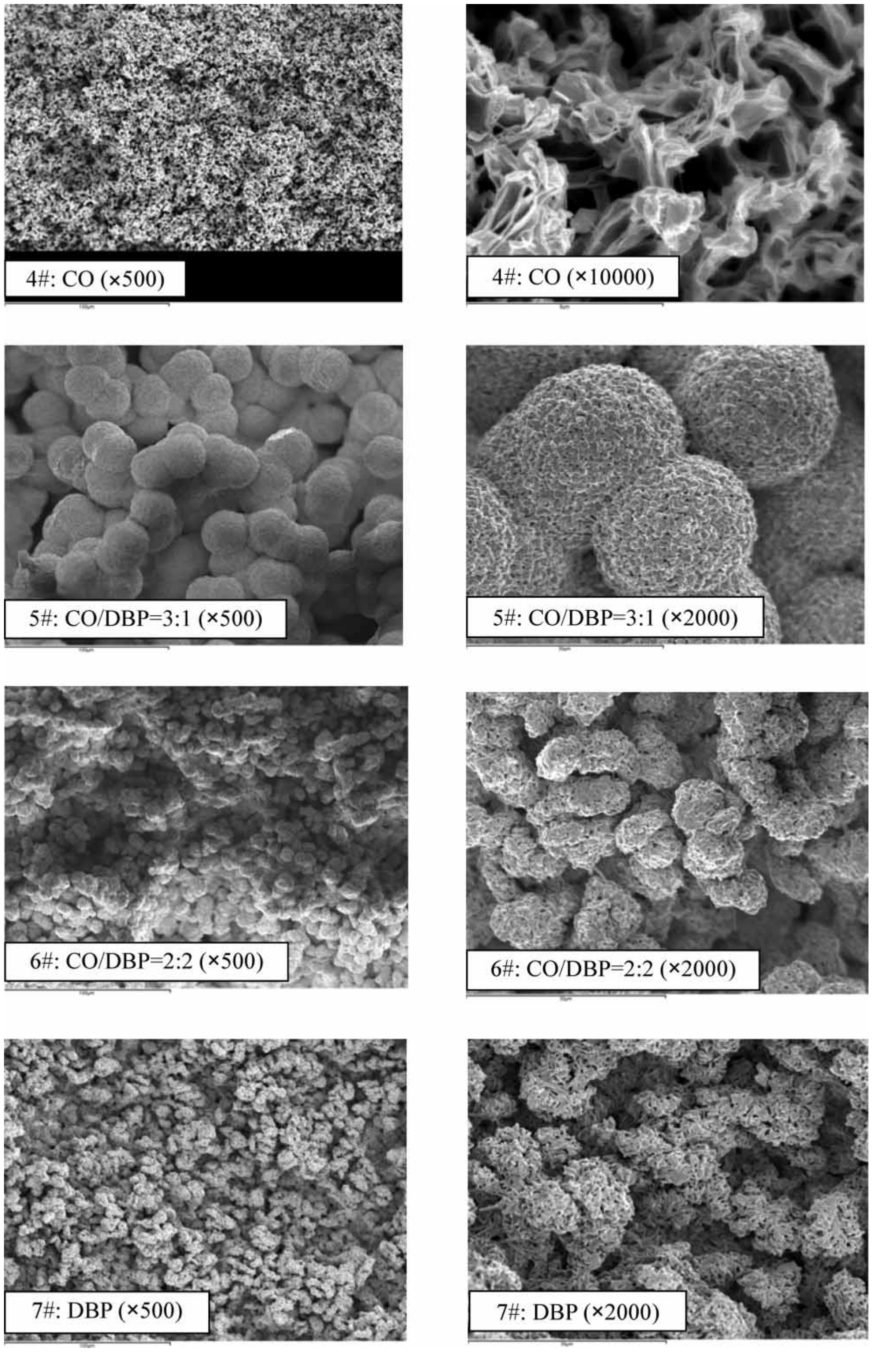

Fig. 5. The cross-section morphologies of membranes from the CO/DBP mixed diluents.

chains tend to aggregate each other. If there are a sufficient number of molecular segments being accumulated together to form a stable aggregation, primary nuclei will form at first, and then the other polymer chains will move to the nuclei by diffusion and further transport across the liquid-nucleus interface to crystallize on the surface of the nucleus. The nuclei would increase continuously (23). Thus, it can be seen that the primary nucleation occurred mainly at the beginning of crystallization.

The addition of DBP led to two results. It enhanced the polymer crystallization temperature and the mixed diluent viscosity. And we also found that the effect of DBP on the mixed diluent viscosity was significant within a low temperature range, and was slightly within a high temperature range. When a small quantity of DBP was added, the polymer crystallization temperature increased from 29.8°C to 64.7°C. Within the temperature range of 29.8–64.7°C, DBP enhanced the mixed diluent viscosity significantly. The viscosity increase limited the primary nucleation. As a result, the abundant sheaf-like crystallites in Figure 5 (4#) changed into the limited spheric crystallites in Figure 5 (5#). As the DBP content increased further, the polymer crystallization temperature increased from 64.7°C to 107.4°C. Within the temperature range of 64.7°C–107.4°C, the viscosity increase of mixed diluent led by the DBP increase was slight. The increase of primary nuclei was ascribed mainly to the enhancement of polymer crystallization temperature. The polymer solution containing more DBP had the higher crystallization temperature and thereby should have a higher supersaturation degree in the fixed cooling environment. The higher supersaturation degree promoted the primary nucleation. Thus, as the DBP content increased further, the number of spherulite-like crystallites increased, as shown in Figure 5 (5#, 6#, 7#).

Furthermore, as PVDF crystallizes into lamellae and then crystallites, the diluent was rejected to the inter-lamellae and inter-crystallite regions. It was also continuously pushed ahead by the growing crystallites. Finally, most of the rejected diluent accumulated in the inter-crystallite regions, and the other diluent remained between the lamellae. Consequently, the accumulated diluent caused disruption of the lamellae formed at the latter stage of crystallization and formed the outer regions of the crystallite structure (23). With the increase of DBP content, the fluidity of mixed diluent became weaker at the latter stage of crystallization. The mixed diluent which accumulated in the inter-crystallite regions prevented the crystallites from growing equally toward the radiant direction. Thus, the shape of final crystallites deviated from the sphericity gradually with the increase of DBP content.

3.4 The Tensile Strength of PVDF Membrane

Table 6 lists the tensile strength of membranes obtained from different mixed diluents. It was found that the tensile strength had a close correlation with the membrane cross-section morphology. The membranes containing the spherulite-like crystallites always had weak strength. With the increase of crystallite number, the tensile strength of membrane increased gradually. When CO was used as diluent, the membrane possessed ample sheaf-like crystallites and exhibited the highest tensile strength, 2.08 MPa. This membrane also showed a good permeation flux of about 400 kg/m^2.h for pure water at 0.1 MPa.

Table 6. The tensile strength of PVDF membranes

Ratios of mixed diluent	Tensile strength (MPa)
γ-BA/CO = 2 : 2	0.22
γ-BA/CO = 1 : 3	1.78
CO	2.08
CO/DBP = 3 : 1	0.40
CO/DBP = 2 : 2	0.55
DBP	0.55

4 Conclusions

PVDF membranes were prepared successfully with γ-BA/CO and CO/DBP as diluents via a thermally induced phase separation method. When γ-BA/CO mixture was used as diluent, the polymer melting/crystallization temperature increased with the increase of CO content. Similarly, when CO/DBP mixture was used as diluent, the polymer melting/crystallization temperature increased further with the increase of DBP content. It was found that CO and DBP promoted the formation of α-crystal phase of PVDF, whereas γ-BA led to the formation of γ-crystal phase. Two kinds of membrane cross-section morphologies were obtained, including the spherulite-like crystallite and sheaf-like crystallite. The membrane tensile strength increased with the increase of crystallite number in the membrane cross-section. When CO was used as a diluent, the membrane had plenty of sheaf-like crystallites in the cross-section and exhibited good tensile strength and permeability for pure water.

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