Preparation of Microporous PVDF Membrane via Tips Method Using Binary Diluent of DPK and PG

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ABSTRACT: Microporous polyvinylidene fluoride (PVDF) membrane was prepared via thermally induced phase separation (TIPS) method using a binary diluent of diphenyl ketone (DPK) and 1,2-propylene glycol (PG). The phase diagram for the PVDF/binary diluent of DPK and PG system was measured in the range of the PG/DPK mass ratio changing from 0 to 2/3. Then the effects of the PG/DPK mass ratio and the PVDF concentration on membrane cross-section structures and tensile strength were also investigated. The results showed that the addition of PG brought about a shift of the cloud point curve to a higher temperature and the extension of the liquid–liquid phase separation region to a higher polymer concentration. Therefore a bicontinuous cross-section structure was obtained when the PG/DPK mass ratio was 3/7 and the polymer concentration was 30 wt %. As an increase of the PG/DPK mass ratio, the tensile strength increased gradually at a fixed PVDF concentration. Moreover, for the same PG/DPK mass ratio, the cross-section microstructure changed from a bicontinuous or a cellular structure to a spherulitic structure, and the tensile strength increased drastically as the polymer concentration increased from 20 to 50 wt %. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3518–3523, 2010

Key words: polyvinylidene fluoride; thermally induced phase separation; membrane; binary diluent; 1,2-propylene glycol

INTRODUCTION

Since the thermally induced phase separation (TIPS) method was introduced by Castro in the late 1970s and early 1980s,[1] using this method to prepare polyvinylidene fluoride (PVDF) membranes has aroused more and more attention.[2,3] Such membranes were mainly prepared from binary systems of PVDF in different diluents namely cyclohexanone (CO),[4] propylene carbonate (PC),[4] γ-butyrolactone (γ-BL),[4] carbitol acetate (AC),[4] dibutyl phthalate (DBP),[5,6] dimethyl phthalate (DMP),[7,8] glyceryl triacetate (GTA),[9–11] sulfolane.[12] But these systems mostly underwent the solid–liquid (S–L) phase separation when the temperature decreasing and the resulting membranes presented spherulitic morphologies.

Besides single diluents, diluents mixtures such as DBP/DEHP[13] and DBP/DOP[14,15] have also been used to prepare PVDF membranes. However, still closer spherulitic morphologies were obtained in these works,

A lot of efforts have been done in preparing PVDF membrane with good mechanical strength and a high porosity via the TIPS method by our group. In the preceding work,[2] diphenyl ketone (DPK) was used as the diluent to prepare the microporous PVDF membrane. The liquid–liquid (L–L) phase separation phenomenon was found in this system and a bicontinuous structure was obtained when the PVDF concentration was less than 30 wt %. As one of the subsequent work,[3] diphenyl carbonate (DPC) with a litter lower compatibility with PVDF than DPK was chosen as the diluent basing on the design of the molecular structure to prepare the PVDF membrane. In that manuscript, a wider L–L phase separation region of approximately 56 wt % was obtained, and the resulting membrane presented a bicontinuous structure and high tensile strength when the PVDF concentration was 30 wt %.

As stated previously, it's really hard to find a proper single diluent for PVDF to obtain a bicontinuous structure at a higher PVDF concentration via the TIPS method. Herein basing on our previous work, the L–L phase separation region was extended

to a higher polymer concentration by a method of adding a nonsolvent of PVDF into the PVDF/DPK system. In this work, 1,2-propylene glycol (PG) was used as the nonsolvent and a binary diluent mixing with DPK and PG was used to prepare the PVDF membrane via the TIPS method to get a bicontinuous structure at a higher polymer concentration. The phase diagram for the PVDF/binary diluent system was measured in the range of the PG/DPK mass ratio changing from 0 to 2/3. In addition, the effects of the PG/DPK mass ratio and the PVDF concentration on the membrane structure and tensile strength were also investigated.

EXPERIMENTAL

Materials and membrane preparation

Polyvinylidene fluoride (PVDF, M_w = 370,000, M_w/M_n = 2.5, Kynar®) was supplied by Arkema corporation. Diphenyl ketone (DPK, M_w = 182.21) and 1,2-propylene glycol (PG, M_w = 76.10) were chosen as the binary diluent. DPK was from Dalian Xueyuan Specialty Chemical Ltd. and PG was from Beijing Modern Eastern Fine Chemical. All chemicals were analytical graded and used without further purification.

In this research, 20 samples with different PVDF concentrations and BD compositions (in this manuscript, the binary diluent is called BD for short) were prepared and they were given in Table I. Five PG/DPK mass ratios: 0 (I), 1/9 (II), 1/4 (III), 3/7 (IV), 2/3 (V) and four PVDF concentrations: 20 wt % (A), 30 wt % (B), 40 wt % (C), 50 wt % (D) were adopted to study the effects of the PG addition and the PVDF concentration on the membrane structure formation and the tensile strength.

Appropriate amounts of PVDF, DPK, and PG were weighted into an ampoule and protected by argon atmosphere. The ampoule was sealed and then put into an oven at 200°C for 48 h to yield a homogeneous solution. The solution was coated on the inner surface of the sealed ampoules. Then the ampoules were scraped and quenched into an ice water bath to induce phase separation and polymer solidification, as a result the membrane precursors were obtained. The diluents remained in the membrane precursors were extracted with ethanol and PVDF membrane samples were obtained after the volatilization of ethanol.

Phase diagram

To get PVDF/BD mixture samples, At 200°C the homogeneous PVDF/BD solution obtained by the way depicted above was scraped and quenched into liquid nitrogen. Cloud points of these PVDF/BD mixture samples visually by the appearance of turbidity

TABLE I
The Compositions of the Samples and Their Tensile Strength

No.	PVDF (wt %)	BD (PG/DPK) (wt %)	Tensile strength (MPa)
A-I	20	80 (0/80)	0.65
A-II		80 (8/72)	1.19
A-III		80 (16/64)	1.88
A-IV		80 (24/56)	1.92
A-V		80 (32/48)	1.99
B-I	30	70 (0/70)	2.13
B-II		70 (7/63)	2.19
B-III		70 (14/56)	2.60
B-IV		70 (21/49)	3.85
B-V		70 (28/42)	4.16
C-I	40	60 (0/60)	5.08
C-II		60 (6 /54)	5.57
C-III		60 (12/48)	6.00
C-IV		60 (18/42)	6.64
C-V		60 (24/36)	7.01
D-I	50	50 (0/50)	–
D-II		50 (5/45)	–
D-III		50 (10/40)	–
D-IV		50 (15/35)	–
D-V		50 (20/30)	–

The tensile strength of the membranes is mostly nearly 10 MPa and so has not been tested exactly when the PVDF concentration is 50 wt %.

under an optical microscopy (Olympus BX51). The small pieces of the samples were placed between a pair of microscope cover slips. A hot stage (Linkam THMS600) was adopted to hold the temperature of the samples at 200°C for 5 min then cool to 50°C at a rate of 10°C/min.

The dynamic crystallization temperatures were measured by a differential scanning calorimetry (DSC) (TA Q200). The PVDF/BD samples in an aluminum pan were kept at 200°C for 5 min and cooled to 50°C at a rate of 10°C/min. The onset of the exothermic peak in the cooling was taken as the dynamic crystallization temperature of the sample.

Microstructure and tensile strength

The cross-section structures and the surface morphologies of the membranes were examined by a scanning electron microscope (SEM) (JEOL JSM7401) with the accelerating voltage set to 1.0 kV. The PVDF membranes were fractured in liquid nitrogen and coated with platinum for the SEM cross-section structure observation.

The tensile strength of the PVDF membranes was measured by a universal testing machine (Shimadzu AGS-J 20N) equipped with a 5-kg load cell. Before the test, the membranes were cut into a 50×10 mm^2 strip. The stretch speed was 2 mm/min.
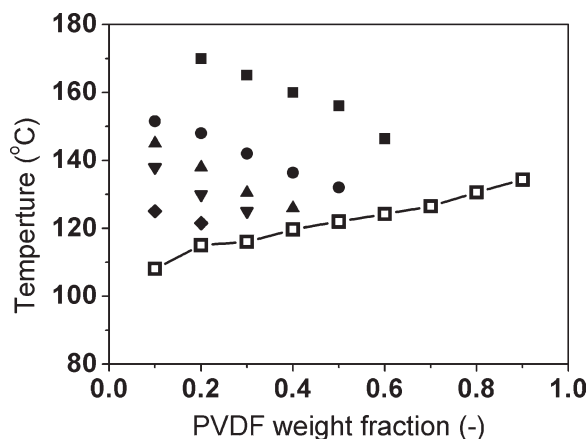
Figure 1 Phase diagram for the PVDF/BD system. Solid symbols present cloud points: ■●▲▼◆ represent the PG/DPK mass ratio are 2/3, 3/7, 1/4, 1/9, 0, respectively; Hollow symbols □ show the crystallization temperatures. As the difference in the crystallization temperatures were not more than 5% when the PG/DPK mass ratio changing from 0/10 to 2/3 at a fixed PVDF concentration. The temperatures here were averaged temperatures in the five PG/DPK mass ratios at a fixed PVDF concentration.

RESULTS AND DISCUSSION

L-L phase separation

It is the key problem that the polymer/diluent solution can undergo the L–L phase separation to obtain a bicontinuous structure at a higher polymer concentration when quenching. Therefore it is necessary to extend the L–L phase separation region of the PVDF/DPK system to a higher polymer concentration.

The phase diagram for the PVDF/BD system is shown in Figure 1, which represents the UCST type L–L phase behavior. At a fixed PVDF concentration, the cloud points shift to a higher temperature and the L–L phase separation region is extended with an increase of the PG/DPK mass ratio. However, the experiment results present that crystallization temperatures are not influenced much by the addition of PG. The differences in the crystallization temperatures are not more than 5% as the PG/DPK mass ratio changing from 0 to 2/3 at a fixed PVDF concentration. Therefore the crystallization temperatures shown here are obtained by averaging the five crystallization temperatures of the five PG/DPK mass ratios. Therefore the polymer concentration on the monotectic point[14] (the intersection of the binodal curve and the dynamic crystallization temperature curve) increases from almost 20 wt % to nearly 70 wt % gradually.

The changes in the cloud points accompanying with an extended L–L phase separation region can be explained by the compatibility between polymer and diluent. PG is a common chemical material and cannot solve PVDF at any temperatures. Therefore

the compatibility between PVDF and BD becomes worse as the PG/DPK mass ratio increases, which results in an increase of the cloud point temperature. Moreover, the crystallization temperature was less influenced by the addition of PG. As a result the L–L phase separation region can be extended to a higher polymer concentration accompanying an increase of the polymer concentration on the monotectic point, which are consistent with the other literatures.[8,16]

Microstructure and morphology

Figures 2 and 3 show the cross-section structures and surface morphologies of the 20 samples shows in the table I separately. As shown in Figure 2, when the PVDF concentration is 20 wt % (A) or 30 wt % (B), as the PG/DPK mass ratio changing from 0 (I) to 2/3 (V), the spherulitic morphology is unclear and disappears gradually, then replaced by a bicontinuous structure. This is because that the TIPS process changes from an S–L phase separation process to an L–L phase separation process.

When the PVDF concentration is 40 wt % (C) or 50 wt % (D), as the PG/DPK mass ratio changing from 0 (I) to 2/3 (V), the cross-section structure changes from a spherulitic morphology to a cellular structure. The cellular structure as the PG/DPK mass ratio is 3/7 (IV) or 2/3 (V) can be explained by the phase diagram shown in Figure 1. As the temperature is decreasing from 200°C, the L–L phase separation occurs and the membrane with a cellular structure would be obtained.

When the PG/DPK mass ratio changes over from 0 (I) to 1/4 (III), the diameter of sphere increases gradually as the PVDF concentration is 40 wt % (C) or 50 wt % (D), which dues to that adding PG decreases the interaction of the system, resulting in fewer number of spherulites and giving them more time and space to grow.

In another view, Figure 2 also shows the effect of the PVDF concentration on the cross-section structure of the membrane at a fixed PG fraction. For the PG/DPK mass ratio is 2/3 (V) or 3/7 (IV), the structure changes from a bicontinuous structure to a cellular structure with an increase of the PVDF concentration. As the PG/DPK mass ratio changes to 1/4 (III), 1/9 (II) and 0 (I), the membrane presents a cellular structure at the polymer concentration of 20 wt % (A), and then changes to a spherulitic morphology. These results are also in accordance with the phase diagram shown in Figure 1.

Tensile strength

Table I also shows the tensile strength of the membranes of these samples. With an increase of the
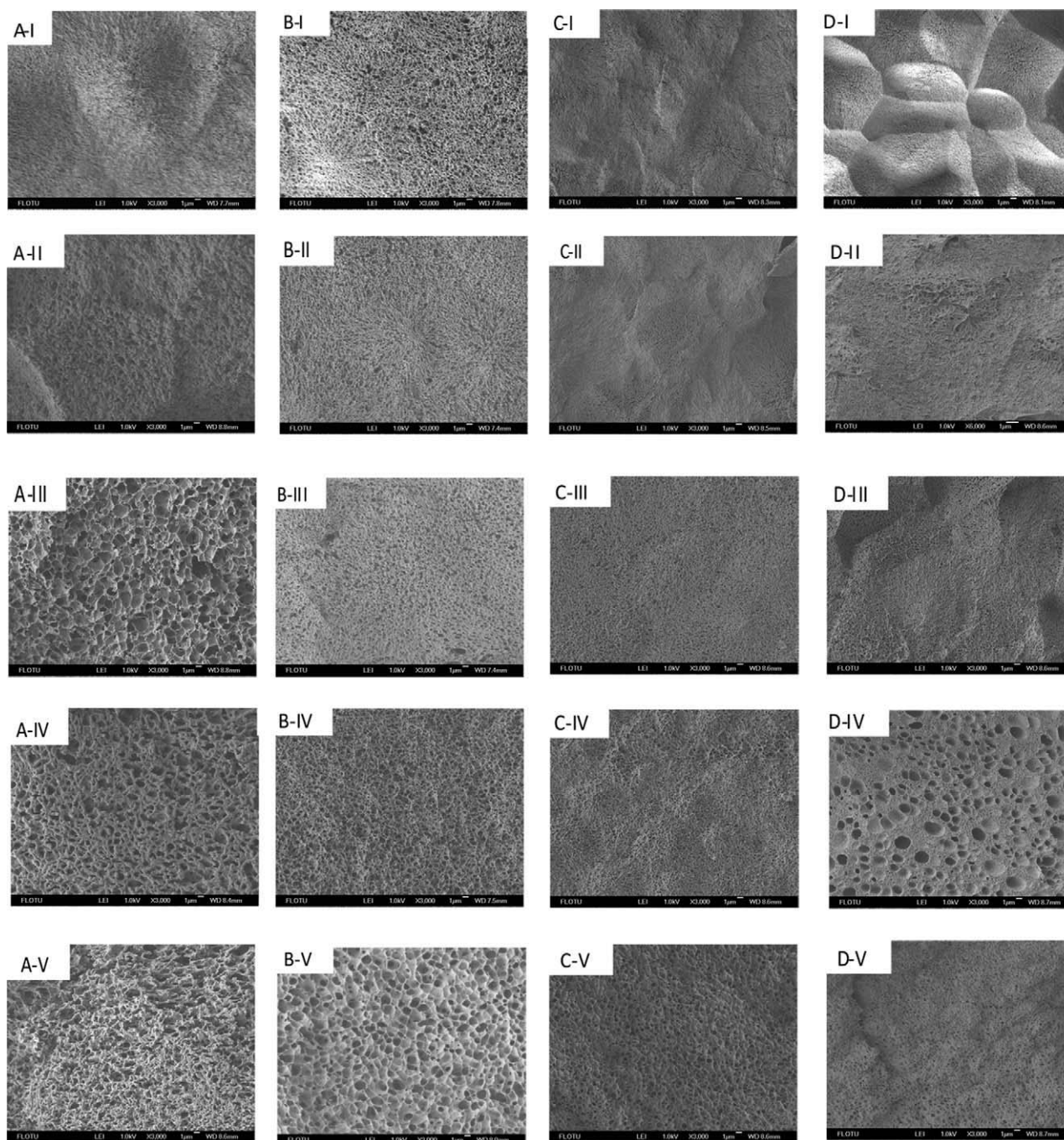
Figure 2 SEM images of the cross-section structures of the PVDF membranes of the PVDF/BD systems. The PVDF concentrations of A, B, C, D are 20, 30, 40, 50 wt %, meanwhile, PG/DPK the mass ratios are 0(I), 1/9(II), 1/4(III), 3/7(IV), 2/3(V), respectively.

PVDF concentration from 20 to 40 wt %, the strength average value increases from 0.65 MPa to 7.01 MPa. In addition, at a fixed PVDF concentration, the strength of the membranes increases gradually as the DPK/PG mass ratio increasing from 0 to 2/3. This behavior can be attributed to the change of the membrane cross-section structure induced by the addition of the non-solvent PG. The tensile strength of the membrane, which presents bicontinuous or cellular behaves much higher than that presents spherulitic for the same polymer concentration. Therefore it is apparent that adding PG can improve the structures of the PVDF/DPK membranes and then increases the tensile strength. The membrane prepared by quenching PVDF/BD(PG/DPK):30/70(3/7) mixture solution to 0°C has the tensile strength of 3.85 MPa, which implies that this system owns a potential to industrialize.
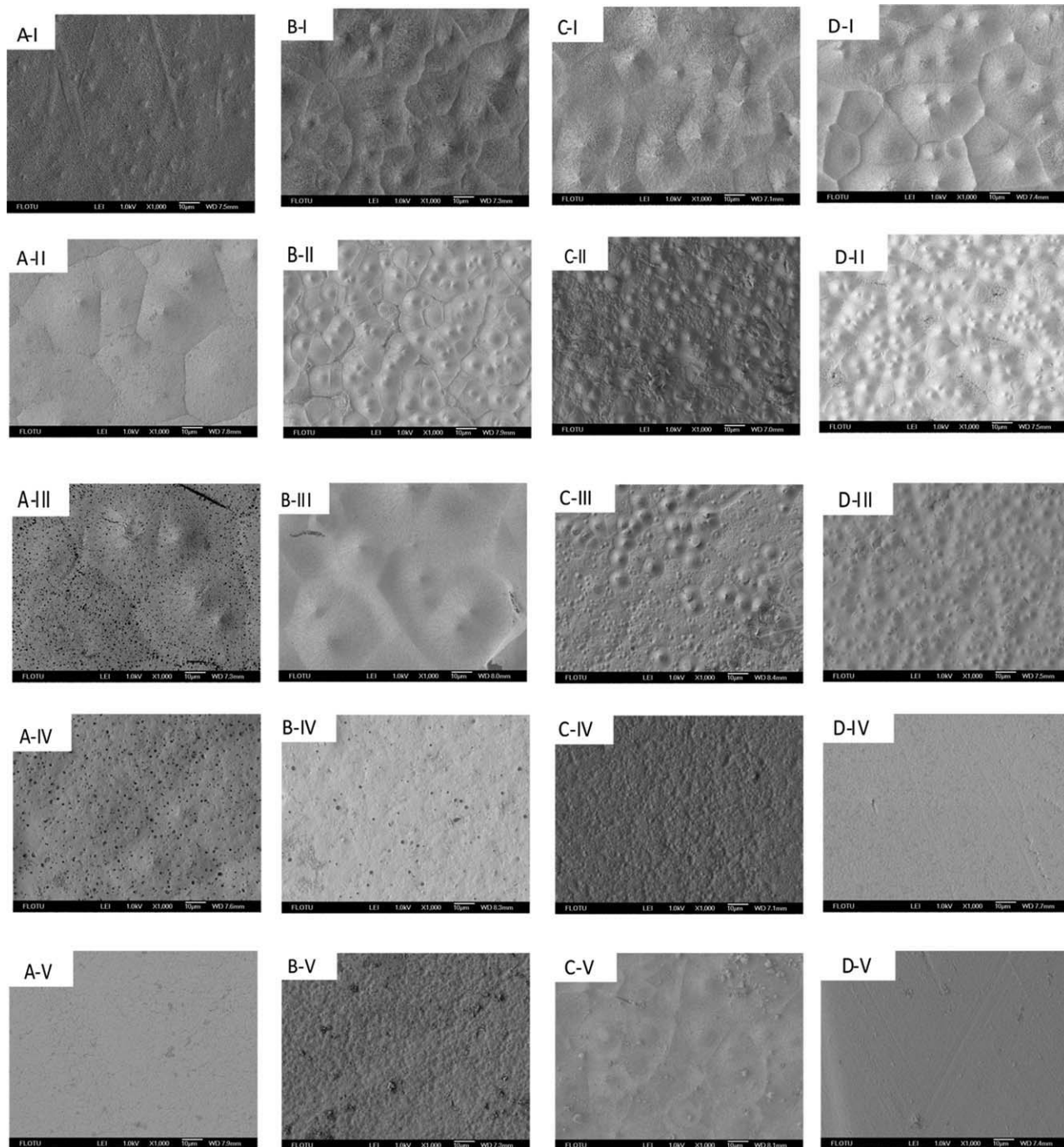
Figure 3 SEM images of the surface morphologies of the PVDF membranes of the PVDF/BD systems. The PVDF concentrations of A, B, C, D are 20, 30, 40, 50 wt %, meanwhile, PG/DPK the mass ratios are 0(I), 1/9(II), 1/4(III), 3/7(IV), 2/3(V), respectively.

CONCLUSIONS

Microporous PVDF membranes were prepared via the TIPS method using a binary diluent of DPK and PG. The results were compared with those of membranes prepared without PG. It was found that adding PG to the PVDF/DPK system could extend the L–L phase separation region to a higher polymer concentration. Therefore a bicontinuous cross-section structure and good mechanical strength can be obtained simultaneously for the membrane when the PVDF concentration is 30 wt % and the PG/DPK mass ratio is 3/7. The PG/DPK mass ratio and the polymer concentration were both chosen to control the mechanism of the phase separation, and so kinds of pore cross-section structures and surface morphologies will be obtained, including bicontinuous, cellular, and compact spherulitic structures or morphologies.

In addition, at a fixed PVDF concentration, the tensile strength of the membrane increases gradually as the PG/DPK mass ratio increasing from 0 to 2/3. In summary, this research can serve some clues for preparing PVDF membranes with good porosity and strength.

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