Formation of a Bicontinuous Structure Membrane of Polyvinylidene Fluoride in Diphenyl Ketone Diluent Via Thermally Induced Phase Separation

J. Yang,[1,2] D. W. Li,[2] Y. K. Lin,[2] X. L. Wang,[2] F. Tian,[1] Z. Wang[1]

[1]Tianjin Institute of Medical Equipment, Tianjin 300161, People's Republic of China
[2]Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

ABSTRACT: The polyvinylidene fluoride (PVDF)-diphenyl ketone (DPK) mixture was studied as a new system to prepare PVDF membranes via thermally induced phase separation (TIPS). The phenomena of liquid–liquid phase separation was found in this mixture when the temperature of mixture was decreasing and the PVDF concentration was less than 30 wt %. Using DPK as diluent, PVDF membrane with bicontinuous structure was obtained without necessity to add a nonsolvent or a stretching process further. The phase diagram of PVDF-DPK system was also constructed to help investigate the effect of PVDF concentration and coarsening temperature on morphology of resulting membrane.

The experiments showed that high coarsening temperatures and low PVDF concentrations resulted in the formation of the large pore size membrane. The strength of the wet membrane was decreasing with decreasing PVDF concentration. On condition that the PVDF concentration was larger than 30 wt %, thermally induced solid–liquid separation occurred and bicontinuous structure disappeared. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 341–347, 2008

Key words: membranes; thermally induced phase separation; bicontinuous structure; polyvinylidene fluoride; diphenyl ketone

INTRODUCTION

Thermally induced phase separation (TIPS) method is a promising technology for membrane formation.[1–6] By the TIPS method, a wide range of amorphous or semicrystalline polymers have been prepared into membranes, including the polymers that could not be formed into membranes via the nonsolvent-induced phase separation techniques for their poor solubility. In TIPS process, a suitable diluent is one of the important factors for better mechanism understanding and structure control of membrane formation. For example, when diphenyl ether or methyl salicylate (MS) was used as the diluent, the polypropylene (PP) membrane with a bicontinuous structure was obtained in the mechanism of thermally induced liquid–liquid phase separation.[7–9] Besides the bicontinuous structure, membranes characterized as particles connected by tie fibrils, leafy, leafy spherulitic, and fuzzy spheres structure were prepared in PP-mineral oil, polyethylene-mineral oil and PVDF-dibutyl phthalate (DBP) mixture by thermally induced solid–liquid phase separation.[7] Moreover, in PP-MS, Griltex nylon-ethanol and PE-isoamyl acetate mixtures, the microparticle could also be prepared in the region of nucleation and growth of polymer rich phase where the polymer concentration was less than the critical concentration.[10–13]

Polyvinylidene fluoride (PVDF) has high chemical resistance to strong acid, alkali, oxidant, halogen, heat, and r-radiation.[14,15] Therefore, PVDF membranes prepared by nonsolvent-induced phase separation are proved useful in many fields.[16–22] In the past 30 years, to prepare PVDF membrane via TIPS has received many interests. Cyclohexanone, butyrolactone, propylene carbonate, and carbitol acetate[23] were selected as the diluent respectively, to produce PVDF membranes by TIPS. The result showed that the fuzzy spheres structure would be formed in PVDF-cyclohexanone, PVDF-butyrolactone, and PVDF-propylene carbonate mixtures. Under the condition of rapid cooling the PVDF-carbitol acetate mixture, PVDF membranes presented the leaf-like structure at surface layer. With DBP as the substitute diluent,[7] PVDF-DBP mixture underwent solid–liquid phase separation and got the fuzzy spheres structure at the PVDF concentrations studied. In general,

PVDF-diluent binary mixture was seldom reported to undergo the liquid–liquid phase separation.

The aim of the present study is to find a suitable diluent which could undergo the liquid–liquid phase separation with PVDF when the temperature of PVDF-diluent solution is decreasing. Because diphenyl ketone (DPK, benzophenone) is capable to dissolve PVDF and form PVDF-DPK homogeneous solution, it is selected as a novel diluent for the PVDF membrane preparation by TIPS. The phase separation mechanism of PVDF-DPK mixture induced by TIPS is investigated. How the coarsening temperature and concentration affect the morphology of PVDF membrane is included within the scope of study. It is found that the liquid–liquid phase separation takes place in PVDF-DPK mixture with the temperature decreasing. With the help of PVDF-DPK phase diagram, the bicontinous microstructure was achieved in PVDF membrane.

EXPERIMENTAL

Materials

KYNAR polyvinylidene fluoride (PVDF, $M_w = 370,000$, $M_n/M_w = 2.5$) was supplied by CMDIC XIAMEN (China). Diphenyl ketone (DPK, benzophenone) was of analytical grade and used as the diluent without further purification.

Measurements of cloud points, equilibrium melting temperatures, and dynamic crystallization temperature

Appropriate amounts of PVDF and DPK were weighted into a 20-mL standard ampoule and protected by argon atmosphere. The ampoule was sealed to avoid evaporation of DPK before it was put into an oven at 200°C to make PVDF dissolve in DPK. To get homogenous solution, the ampoule was shook several times at 200°C by a vortex shaker. After 48 h, the ampoule was moved out of the oven and quenched in liquid nitrogen to get a PVDF-DPK mixture sample.

Cloud points of PVDF-DPK samples were determined visually by the appearance of turbidity under an optical microscope (Olympus BX51). The small pieces of sample were placed between a pair of microscope cover slips. To prevent DPK loss by evaporation, Teflon film of 200 μm thickness with a circle opening was inserted between the cover slips.[24] A hot stage (Linkam THMS 600) was adopted to hold the temperature of samples at 200°C for 5 min then cool to 50°C at the controlled rate of 2°C/min.

The equilibrium melting temperatures of PVDF-DPK samples were measured with a differential scanning calorimetry (DSC, TA Q100) using the Hoffman-Week's approach. About $3 \sim 6$ mg PVDF-DPK sample in an aluminum pan was kept at 200°C for 10 min and then quenched to a crystallization temperature. The pan with the sealed sample was kept in DSC cell at the crystallization temperature until the crystallization peak ceased to appear. Then the melting temperature of the sample was analyzed by heating at the rate of 10°C/min. Crystallization temperatures extrapolate linearly to intersect the straight line where crystallization temperature was equal to melting temperature. The point of intersection leads to equilibrium melting temperature in principle.[25]

The dynamic crystallization temperatures were obtained with the DSC by cooling samples from 200 to 50°C at the rate of 10.0°C/min. The onset of the exothermic peak during cooling was taken as the dynamic crystallization temperature of the sample.

Membrane preparation and SEM observation

At 200°C the homogeneous PVDF-DPK solution obtained by the way depicted above was coated on the inner surface of the sealed ampoules. Then two kinds of cooling procedures were adopted to induce phase separation of homogeneous PVDF-DPK solution. In procedure I, the homogeneous PVDF-DPK solution was quenched from 200 to 120°C and held at 120°C for 5 min, then quenched into ice-water of 0°C. During procedure II, the homogeneous PVDF-DPK solution was quenched into ice-water directly from 200 to 0°C. At the temperature of 0°C, the PVDF-DPK solution was solidified completely to be a membrane precursor on the inner surface of the ampoule. The DPK in the membrane precursor was extracted with ethanol and PVDF membrane sample was obtained after volatilization of ethanol. The thickness of membrane samples was about $200 \sim 300$ μm.

PVDF membrane samples were fractured in liquid nitrogen. The cross section and the surface of the membrane samples were sputtered with platinum in vacuum. A scanning electron microscope (SEM, JSM7401) was adopted to observe the morphology of membranes with an accelerating voltage of 1 kV.

Measurements of pore size and tensile strength

The pore size of PVDF membranes was measured by a porometer (Coulter porometer II). PVDF membranes were cut into 25 mm in diameter. About 75 wt % alcohol was used as the wetting agent. The maximum pore size and mean flow pore size were recorded. The maximum pore size corresponds to the pressure required to form a bubble. The mean flow pore size is the micron size where 50% of the
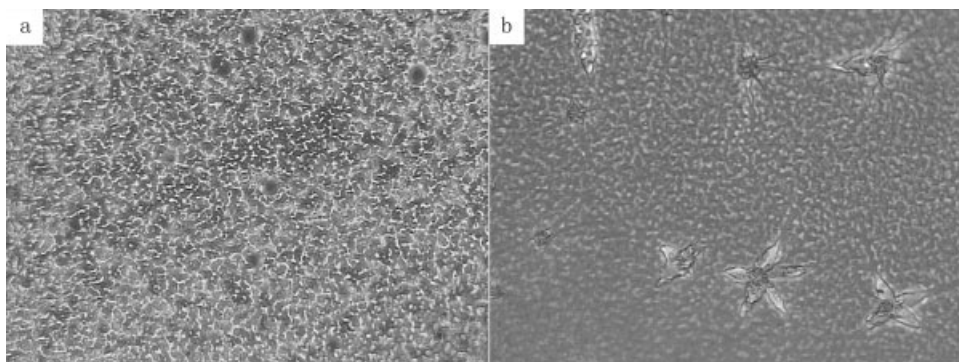
Figure 1 Optical micrographs of liquid–liquid phase separation. The PVDF (10 wt %)-DPK mixture is hold at 150°C for 10 min (a) and for 60 min (b).

flow is higher and 50% of the flow is lower. The standard deviation was calculated for five determinations on each sample.

Tensile strength of the wet flat membrane was measured by an instron (INSTRON 5865). The membranes with 200 μm thickness were cut into the 50 × 10 mm² strips. The stretch speed was 2 mm/min.

RESULTS AND DISCUSSION

Phase diagram

The function of phase diagram is the phase behavior exhibition of polymer-diluent mixture. In previous research about PVDF-DBP,[7] only equilibrium T_m curve, dynamic crystallization curves and no cloud point curve in phase diagram suggest that thermally induced solid–liquid phase separation should be in dominant position. However, in present experiment of PVDF-DPK mixture, with the temperature decreasing, PVDF-DPK solution undergoes the liquid–liquid phase separation, which could be observed

under the microscope [Fig. 1(a)] in the temperature range of 110 ~ 150°C when PVDF concentration is less than 30 wt %. So the cloud points curve is drawn in phase diagram of PVDF-DPK [Fig. 2(a)]. The dynamic crystallization curve determined by DSC intersects the cloud point curve at the point of 110°C and 30 wt % PVDF concentration. In the region encircled by the cloud points curve and the dynamic crystallization curve, liquid–liquid phase separation is likely to occur with the temperatures between 110°C and 150°C and PVDF concentration less 30 wt %. If the temperature of 10 wt % or 20 wt % PVDF-DPK mixtures were held in liquid–liquid region for a long time, the PVDF lamellar crystal would formed in course of liquid–liquid phase separation [Fig. 1(b)]. This phenomenon is explained by the equilibrium melting temperature (T_m) curve of PVDF-DPK mixtures obtained by Hoffmann-Week's plot [Fig. 2(b)]. In Figure 2(a), the equilibrium T_m curve lies above the cloud point curve, which proves that in the course of liquid–liquid phase separation, local PVDF concentration of rich phase must have
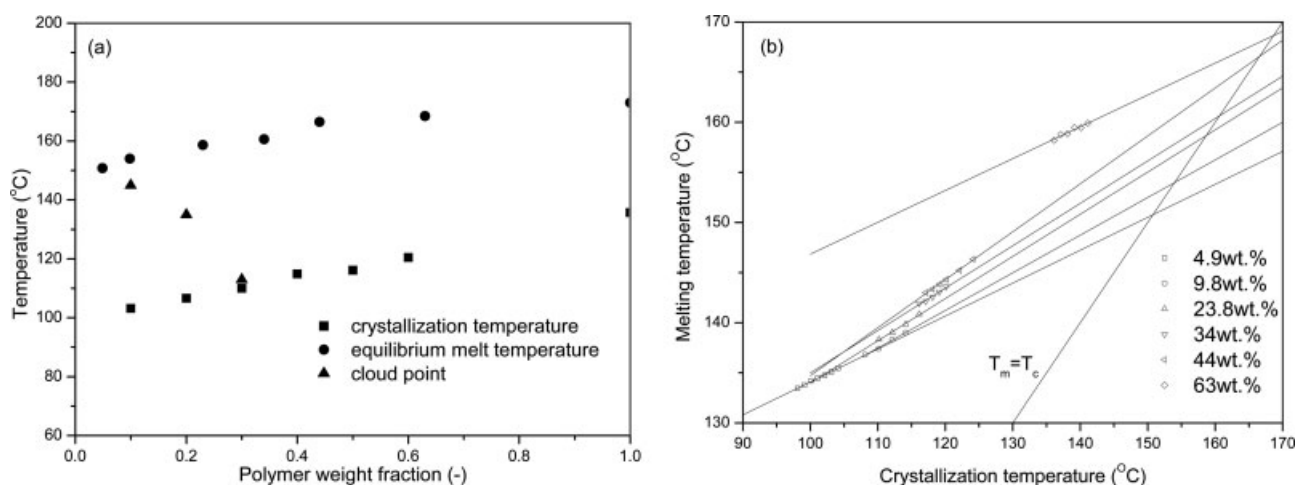
Figure 2 (a) Phase diagram of PVDF-DPK mixture; (b) Hoffmann-Week's plot of PVDF-DPK mixture.
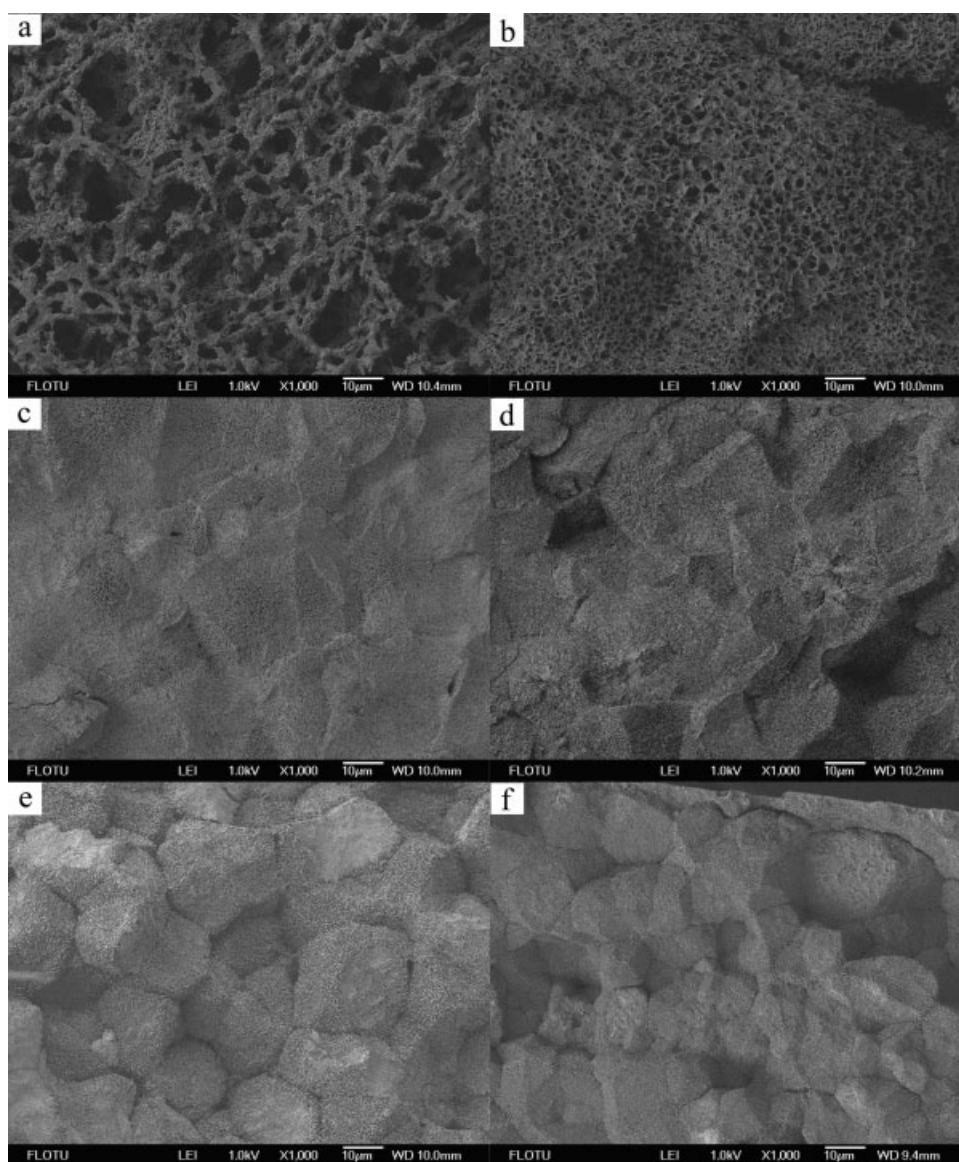
Figure 3 Cross section morphology of PVDF membranes prepared by procedure I. The PVDF concentrations of (a)-(f) are 10 wt %, 20 wt %, 30 wt %, 40 wt %, 50 wt %, and 60 wt %, respectively.

been greater than that of monotectic point to result in lamellar crystal formation provided enough time.

Morphology of PVDF membrane

Since the suitable diluent was not found in the previous research and the microstructure of PVDF membranes always presented the fuzzy sphere, to mix a nonsolvent of PVDF or inorganic particles with the diluent has to be an optional technique to adjust structure of PVDF membrane, such as dioctyladipate[26] or diethylene glycol[27] in glycerin triacetate, hydrophobic silica[28] or $CaCO_3$[29] in DBP. Sometimes, the mixture technique still requires the stretching process to aid.[27,30] But in PVDF-DPK mixture, liquid–liquid phase separation mechanism leads to form polymer-rich phase and polymer-lean phase. As a result, the PVDF membrane with the biocontinuous structure is obtained by liquid–liquid phase separation.

PVDF concentrations and coarsening temperatures affect the morphology of the PVDF membrane significantly. The phase diagram of PVDF-DPK mixture indicates that the concentration of monotectic point is about 30 wt %. When the concentration of PVDF is less than 30 wt %, the PVDF-DPK mixtures undergo thermally induced liquid–liquid phase separation. Once the concentration of PVDF is above 30 wt %, thermally induced solid–liquid phase separation occurs in PVDF-DPK mixtures. Figure 3 shows the change of microstructure of PVDF membrane with the increasing of PVDF concentration. In Figure 3(a,b), the morphology of PVDF membranes presents
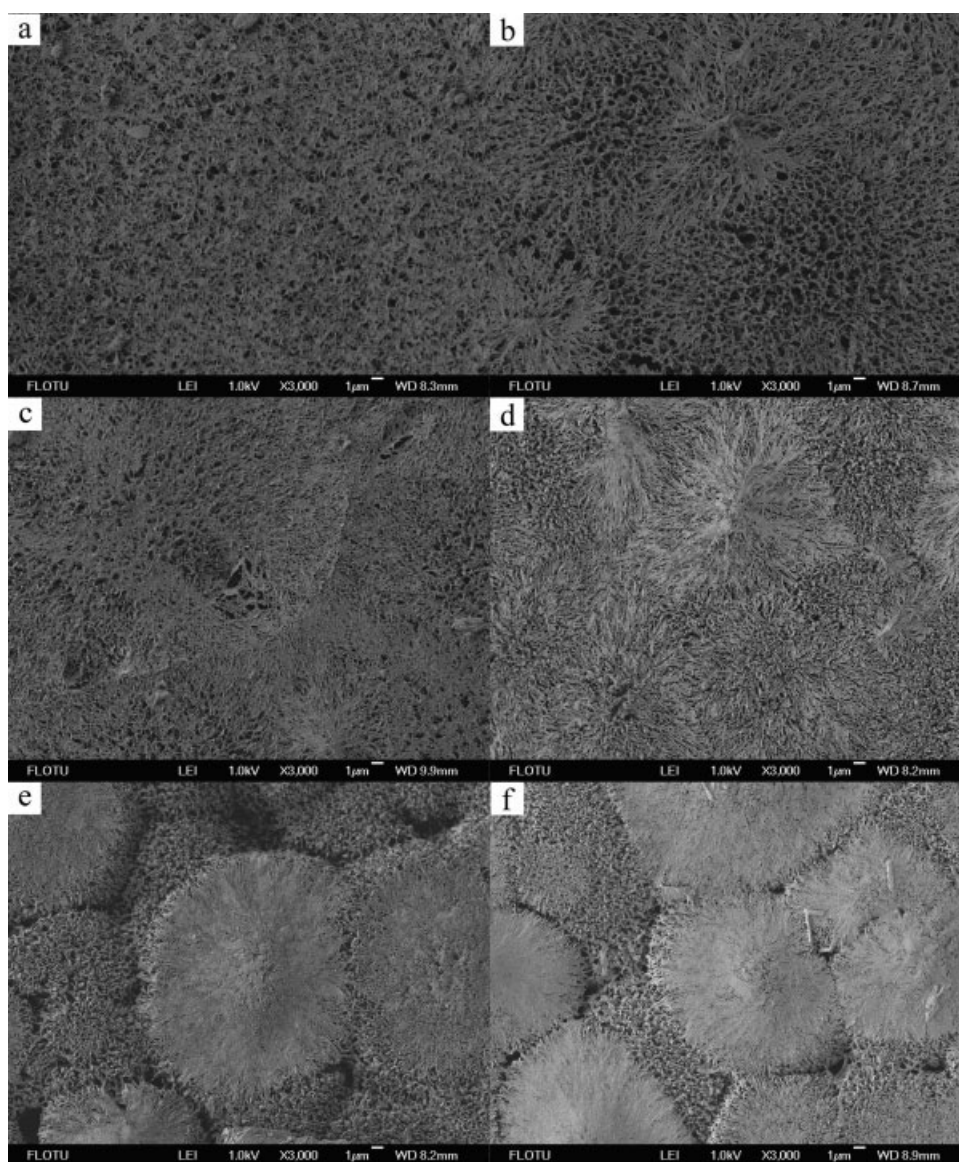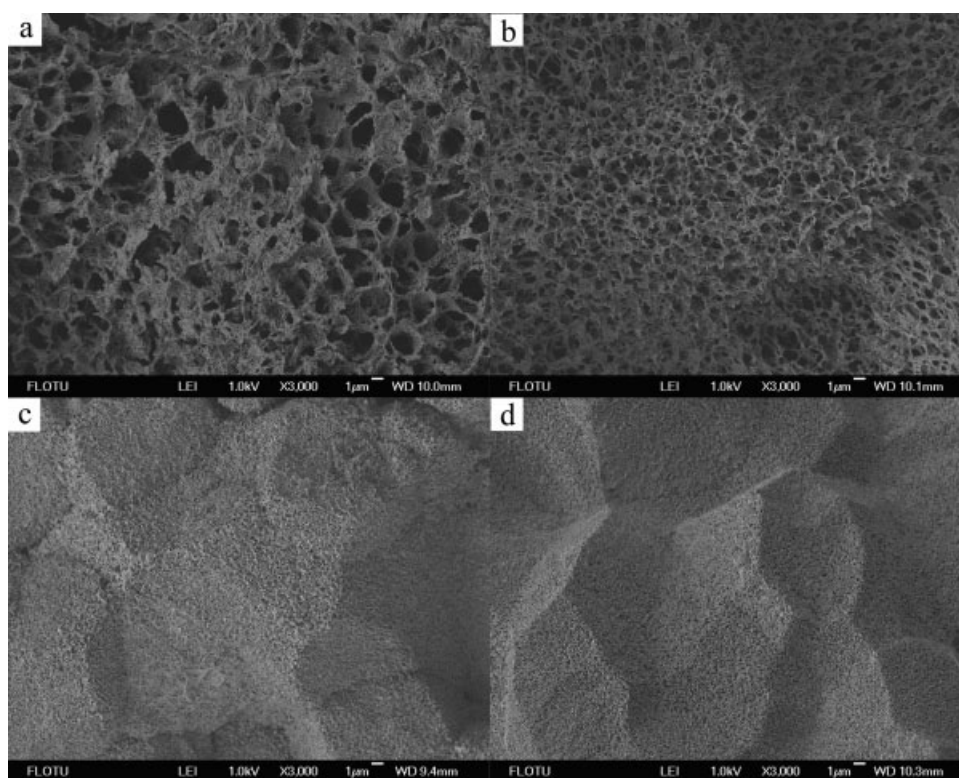
Figure 4 Surface morphology of PVDF membranes prepared by procedure I. The PVDF concentrations of (a)-(f) are 10 wt %, 20 wt %, 30 wt %, 40 wt %, 50 wt %, and 60 wt %, respectively.

the bicontinuous structure. When PVDF concentration is 30 wt %, the bicontinuous structure turns to be ambiguous [Fig. 3(c)]. And there is a clear evidence of pore size significant decreasing. In Figure 3(d) ~ 3(f), PVDF molecules crystallized from PVDF-DPK solution to form compacted spherulites. This change is consistent with the indication of phase diagram.

Figure 4 presents the surface morphology of PVDF membrane. No matter on the surface or in the inner, the effect of PVDF concentration on membrane structure is consistent. With the increasing of PVDF concentration, the pore size of the membrane is decreasing, and up to 30 wt % PVDF concentration, the crystallization becomes apparent. Compare Figures 4 and 3. If the PVDF concentration is less than 30 wt %, the surface pores are much smaller than the inner ones,

which should be account for by the evaporation of DPK and temperature gradient. Once the PVDF concentration is greater than 30 wt %, solid–liquid phase separation is in the ascendant, and the effect of the evaporation of DPK and the temperature gradient on the membrane structure turns weak.

Figure 5 shows the effect of coarsening temperature on the morphology of PVDF membranes. Compare Figure 5(a) with Figure 5(b), the pore size of the membrane prepared by procedure I is significantly larger than that prepared by procedure II. The reason is that if the temperature of PVDF (20 wt %)-DPK mixture is held at 120°C for 5 min, PVDF lean phase and PVDF rich phase have more time to grow separately to form large pores. If the temperature quenched to 0°C directly, the mixture must have
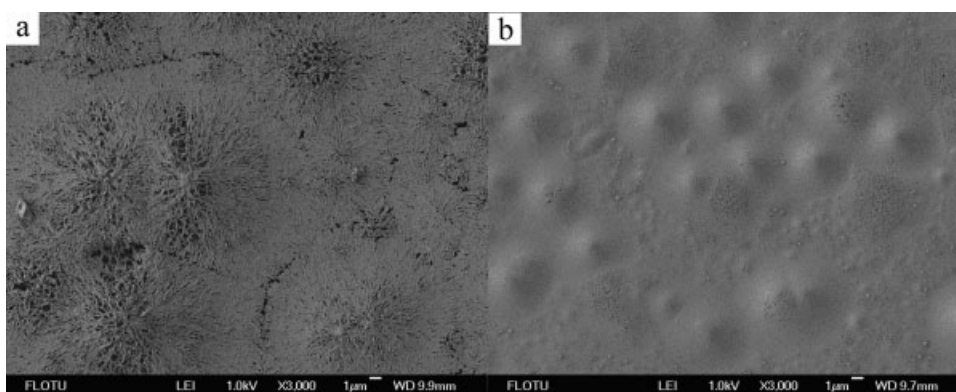
Figure 5 Morphology of PVDF membranes. (a) 20 wt % PVDF, procedure I; (b) 20 wt % PVDF, procedure II; (c) 60 wt % PVDF, procedure I; (d) 60 wt % PVDF, procedure II.

crossed the region of liquid–liquid phase separation rapidly and arrived in the region of crystallization. As the result of growing time shortage, small pores are the majority. In Figure 5(c,d), the pore size is approximate because only solid–liquid phase separation happens in the PVDF-DPK mixture in which PVDF concentration is 60 wt %, which is much larger than the concentration of monotectic point. However, once quenched to 0°C directly, the mixture has deeper supercooling degree to induce large numbers of crystal nucleus formation. The large numbers of spherulites grow and extrude to appear more obvious edges in Figure 5(d).

Figure 6 is the surface morphology of PVDF membranes prepared by procedure II. Though the liquid–liquid phase separation occurs possibly in 20 wt % PVDF-DPK mixture, no bicontinuous structure but a skin could be found in the membrane because of too rapid cooling.

Pore size and tensile strength

Table I shows the maximum pore size, mean flow pore size of wet membranes prepared by procedure II is decreased with the PVDF concentration increasing, as the change of pore sizes with PVDF concen-

Figure 6 Surface morphology of the PVDF membranes prepared by procedure II. The PVDF concentrations of (a) and (b) are 20 wt % and 60 wt %, respectively.

TABLE I
The Pore Size and the Tensile Strength of PVDF Membranes

PVDF concentration	Mean flow pore size (μm)	Maximum pore size (μm)	Tensile strength (MPa)
10 wt %	0.538 ± 0.097	0.605 ± 0.017	0.32
20 wt %	0.143 ± 0.014	0.233 ± 0.043	0.48
30 wt %	0.089 ± 0.003	0.146 ± 0.034	1.60

trations in Figures 3 and 4. However, the pore size measured by bubble point method is much smaller than inner pore size measured by SEM (Fig. 3) and is approximate to the surface one (Fig. 4). It proves that the surface pore size must have been important to future application of PVDF membranes prepared by TIPS. Table I also shows that the strength of wet PVDF-DKP membranes rises with the increasing PVDF concentration. The membrane prepared by quenching 30 wt % PVDF-DPK mixture to 0°C has 1.6 MPa tensile strength and about 0.1 μm effective pore size.

CONCLUSIONS

Thermally induced liquid–liquid phase separation is found in the PVDF-DKP binary mixture. In the phase diagram of the PVDF-DKP mixture, the equilibrium melting point curve is above the cloud point curve, and the monotectic point of the mixture lies at about 30 wt % PVDF concentration and 110°C. The PVDF membrane with biocontinuous structure via TIPS could be prepared by the control of coarsening temperature and PVDF concentration without necessity to add the nonsolvent or stretching process. On condition that PVDF concentration is less than 30 wt %, high coarsening temperature and low PVDF concentration result in the large pore size of PVDF membrane. In case that PVDF concentration is larger than 30 wt %, the bicontinuous structure disappears because thermally induced solid–liquid separation occurs.

References

1. Kim, J. J.; Hwang, J. R.; Kim, U. Y.; Kim, S. S. J Membr Sci 1995, 108, 25.
2. Kim, S. S.; Lloyd, D. R. J Membr Sci 1991, 64, 13.
3. Lloyd, D. R.; Kim, S. S.; Kinzer, K. E. J Membr Sci 1991, 64, 1.
4. Matsuyama, H.; Berghmans, S.; Lloyd, D. R. J Membr Sci 1998, 142, 213.
5. Matsuyama, H.; Okafuji, H.; Maki, T.; Teramoto, M.; Kubota, N. J Membr Sci 2003, 223, 119.
6. Matsuyama, H.; Yuasa, M.; Kitamura, Y.; Teramoto, M.; Lloyd, D. R. J Membr Sci 2000, 179, 91.
7. Lloyd, D. R.; Kinzer K. E.; Tseng, H. S. J Membr Sci 1990, 52, 239.
8. Castro, A. J. U.S. Pat. 4,247,498 (1981).
9. Matsuyama, H.; Teramoto, M.; Kudari S.; Kitamura, Y. J Appl Polym Sci 2001, 82, 169.
10. Matsuyama, H.; Teramoto, M.; Kuwana M.; Kitamura, Y. Polymer 2000, 41, 8673.
11. Schaaf, P.; Lotz, B.; Wittmann, J. C. Polymer 1987, 28, 193.
12. Hou, W. H.; Lloyd, T. B. J Appl Polym Sci 1992, 45, 1783.
13. Hou, W. H.; Lobuglio, T. M. J Appl Polym Sci 1994, 54, 1363.
14. Zeman, L. J.; Zydney, A. L. Microfiltration and Ultrafiltration Principles and Applications; Marcel Dekker: New York, 1996.
15. Brandrup, J.; Immergut, E. H.; Grulke, E. A. Polymer Handbook, 4th ed; Wiley: New York, 1999.
16. Cheng, L. P.; Young, T. H.; Fang, L.; Gau, J. J. Polymer 1999, 40, 2395.
17. Curcio, E.; Fontananova, E.; Di Profio, G.; Drioli, E. J Phys Chem B 2006, 110, 12438.
18. Khayet, M.; Feng, C. Y.; Khulbe, K. C.; Matsuura, T. Polymer 2002, 43, 3879.
19. Banat, F. A.; Simandl, J. J Membr Sci 1999, 163, 333.
20. Jarvinen, K.; Akerman, S.; Svarfvar, B.; Tarvainen, T.; Viinikka, P.; Paronen, P. Pharm Res 1998, 15, 802.
21. Lee, N. H.; Frank, C. W. Polymer 2002, 43, 6255.
22. Madaeni, S. S.; Yeganeh, M. K. J Porous Mater 2003, 10, 131.
23. Hiatt, W. C.; Vitzhum, G. H.; Wagener, K. B.; Gerlach, K.; Josefiak, C. ACS Symp Ser 1985, 269, 229.
24. McGuire, K. S.; Laxminarayan, A.; Lloyd, D. R. Polymer 1995, 36, 4951.
25. Hoffman, J. D.; Weeks, J. J. J Res NBS A 1962, 66, 13.
26. Josefiak, C.; Wechs, F. U. S. Pat. 4,666,607 (1987).
27. Beck, T. W.; Lee, M. B.; Grant, R. D. U.S. Pat. 5,489,406 (1996).
28. Doi, Y.; Matsumura, H. U. S. Pat. 5,022,990 (1991).
29. Li, X. F.; Lu, X. L. J Appl Polym Sci 2006, 101, 2944.
30. Smith, S. D.; Shipman, G. H.; Floyd, R. M.; Freemyer, H. T.; Hamrock, S. J.; Yandrasits, M. A.; Walton, D. G. S. World. Pat. WO 2005/035641 A1 (2005).