

# Preparation of Porous PVdF Membrane via Thermally Induced Phase Separation Using Sulfolane

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**ABSTRACT:** Sulfolane was acted as a kind of diluent to prepared PVdF porous membranes via TIPS process. Its impact on structure and morphology was studied. Phase diagram for this system was determined by different scanning calorimetry (DSC). Not any structure in the region higher than the dynamic crystallization temperature can be found and the temperature at which particle formation was observed by the optical microscope was approximately in agreement with the dynamic crystallization temperature, which revealed that only S-L phase separation happened for PVdF/sulfolane system during TIPS process. It was found that the heat of crystallization increased with the increase of polymer content. The increase of the cooling rate will increase the crystallization rate. SEM, which

showed that membranes had symmetrical structure and pores formed between PVdF crystallization, revealed that PVdF will present different crystallization morphology as the cooling rate changed. With the cooling rate decrease, both the size of particles and the channel size of open pores between particles became larger, but more uneven. As the cooling rate increased, the size of particles decreased and pore became well interconnected and uniform, which were confirmed by the measurement of average pore size and pore size distribution. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 272–280, 2008

**Key words:** structure; morphology; membranes; phase separation; crystallization

## INTRODUCTION

Poly (vinylidene fluoride) (PVdF), a semicrystalline polymer material, is one of the most useful membrane materials because of its good chemical resistance, thermal stability, and antifouling. PVdF membranes have been widely used in chemical industry, waste water disposal, and gas filtration, etc.

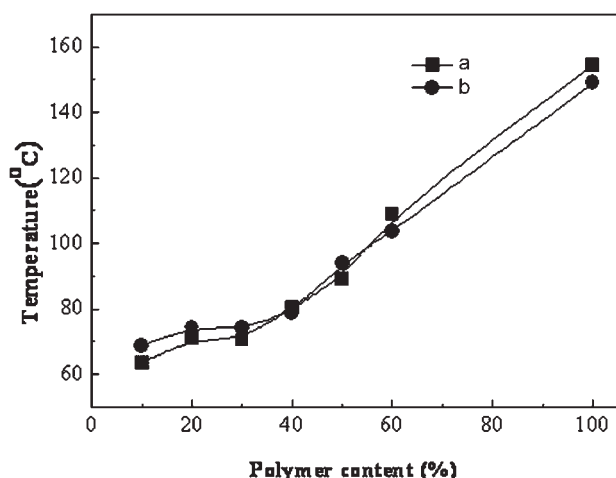
There are two kinds of applicable ways to prepare porous membranes. One is immersion precipitation, which is the main method.<sup>1</sup> That is, the solution is cast onto a support or extruded from a nozzle and then immersed in a nonsolvent. Phase separation occurs as a result of the exchange of a solvent and a nonsolvent. Although this method can produce different membranes with spherulitic, spongy, and cellular structures,<sup>2</sup> it usually produces an asymmetric membrane structure with the skin layer near the surface contacted with a nonsolvent. What's more, finger-like cavities were often formed inevitably by this method,<sup>3</sup> which makes the membrane fragile. The other method is thermally induced phase separation (TIPS) process.<sup>4–8</sup> In this process, a polymer is dissolved in a diluent at high temperature and then the solution is cooled to induce phase separation. Com-

pared with immersion precipitation, TIPS has many advantages. Such as fewer factors of controlling membrane structure, obtaining not only cellular, dendritic, and net structure, but also symmetrical structure in laboratory preparation. What's more, the pore size distribution is narrow. Besides traditional liquid separation, these structural characters made it suitable for separators of lithium ion batteries. TIPS can be classified into two processes: Solid-liquid (S-L) phase separation and liquid-liquid (L-L) phase separation.<sup>9</sup> L-L phase separation occurs as the cooling temperature reaches the binodal line. Two mechanisms should be considered for L-L phase separation: spinodal decomposition (SD) and nucleation growth (NG)<sup>10</sup>; the NG mechanism occurs in a metastable region between the spinodal line and the binodal line in the phase diagram and SD occurs in an unstable region under spinodal lines. Therefore, different morphology and structure of membrane will be formed by SD or NG mechanisms. S-L phase separation occurs when the cooling temperature reaches the crystallization temperature of the polymer, then the polymer starts to crystallize and the polymer/diluent structure is fixed. Finally, the diluent is removed by extraction and the porous membrane is obtained. Microporous membranes of various polymers such as PE, PP, PS have been prepared successfully by TIPS process. But few researches have focused on PVdF.<sup>5,11,12</sup> Recent research on

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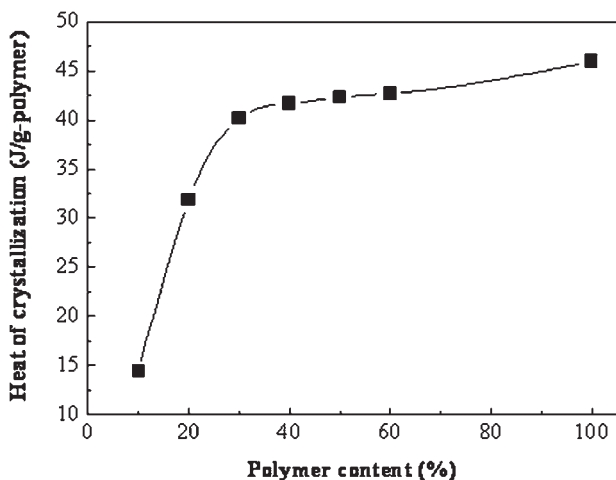
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**Figure 1** Phase diagram in PVdF/sulfolane system. (a) Temperature at which particle was observed by an optical microscope; (b) dynamic crystallization temperature by DSC.

PVdF is mainly focused on the selection of diluents, such as dibutyl-phthalate (DBP),<sup>5</sup> cyclohexanone, crylic acid,  $\gamma$ -butyrolactone<sup>11</sup>; dioctyl-sebacate (DOS), dioctyl-phthalate (DOP), and dimethyl-phthalate.<sup>12</sup> However, spherulitic microstructures with irregular pores were observed. How to control the irregular membrane porous structure remains to be the key problem for PVdF membranes via TIPS.

Because of its high boiling point (285°C), high melting point (27°C), good chemical stability, and relatively good compatibility with many kinds of polymers at higher temperature, sulfolane can be considered as diluent for PVdF. However, no such study has so far been carried out to analyze its influence on membrane morphology and structure. In this work, PVdF/sulfolane system was the first pre-



**Figure 2** Relationship between polymer content and heat of crystallization. Cooling rate: 10°C/min.

sented here and effects of sulfolane on membrane structure and morphology were studied.

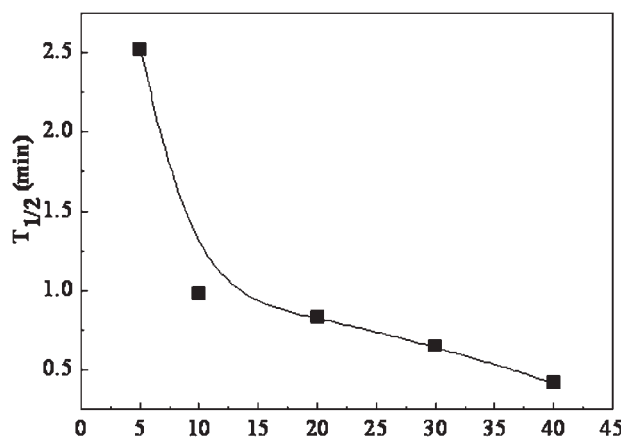
## EXPERIMENTAL

### Materials

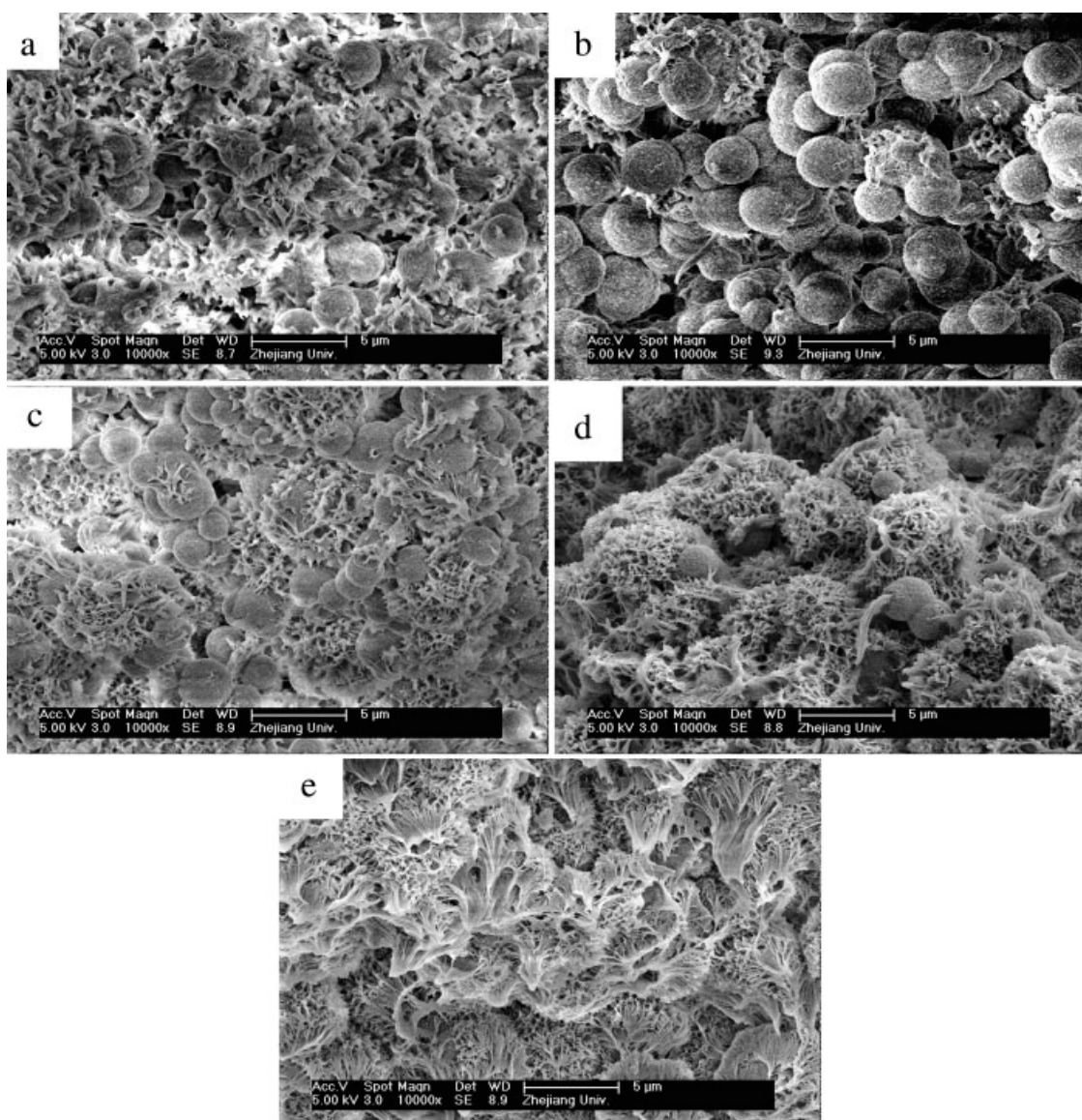
The polymer is commercial PVdF ( $M_n = 59,000$ ,  $M_w/M_n = 2.88$ ), kindly offered by Solvay Silexis, Belgium chemical pure grade sulfolane was used as diluent without further purification, and it was purchased from Siopharm Chemical Reagent, P R China.

### Membrane preparation

Appropriate amounts of polymer and the diluent were weighed into a test tube, which was purged with nitrogen and sealed to prevent oxidation during melt blending. The test tube was heated in an oil bath for hours at 160°C with strong stir to form homogeneous solution, then quenched in liquid nitrogen to solidify sample, and broken open to yield a solid polymer/diluent sample, the solid sample was chopped in small pieces and placed between a pair of stainless steel cover slips. A polyimide film of 75  $\mu\text{m}$  thickness with a circle opening in the center was inserted between the cover slips to control the thickness of membrane and vacuum silicone grease was applied to the edges of the bottom cover slips to prevent diluent loss by evaporation. After the cover slips containing the sample were heated on a hot stage at 160°C for 5 minutes, they were taken out to quench in the water bath at different temperatures or in liquid nitrogen for 10 minutes to ensure complete TIPS. Finally, sulfolane was extracted with water for 72 hours, and then 24 hours ethanol extraction was used to remove residue water and sulfolane. Finally ethanol was evaporated in air.



**Figure 3** Relationship between  $t_{1/2}$  and cooling rate.



**Figure 4** SEM photomicrographs of cross section of membranes in PVdf/sulfolane system. Cooling condition: in 30°C water bath. (a) 10 wt % PVdF; (b) 20 wt % PVdF; (c) 30 wt % PVdF; (d) 40 wt % PVdF; (e) 50 wt % PVdF.

### Phase diagram and thermal analysis

An optical microscope (Nikon eclipse E600 POL) was used to determine the temperature at which particle structures started to form. Samples with various polymer concentrations were sealed between two microcover slips and placed on the hot stage (Linkam THMS600), which was placed on the platform of the optical microscope. The sample was heated from ambient temperature to 160°C at 50°C/min, kept 1 minute and cooled at 10°C/min to 40°C. The temperature at which the particle structure started to form was recorded.

Different scanning calorimetry (DSC, Perkin-Elmer DSC-7) was used to determine the dynamic crystallization temperature. The samples were sealed in an aluminum DSC pan, held at 160°C for 5 minutes to

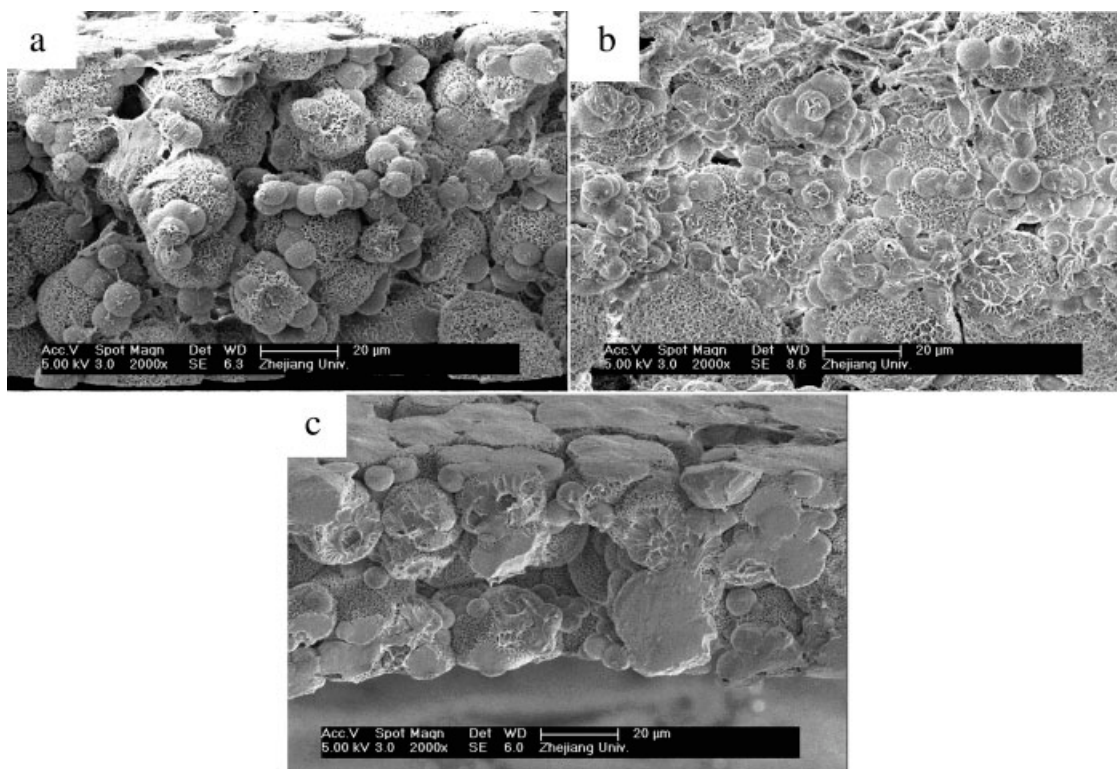
eliminate the influence of thermal history, and then cooled to room temperature at 10°C/min. The onset of the exothermic peak during the cooling was taken as the dynamic crystallization temperature.

### Measurement of half-time ( $t_{1/2}$ ) and the heat of crystallization

The heat of crystallization was determined from the exothermic peak area during cooling and  $t_{1/2}$  is determined by the half time between crystallization onset time and crystallization ending time.

### SEM observation

The membranes were fractured in liquid nitrogen and then sputtered with gold to observe the mor-



**Figure 5** SEM photomicrographs of cross section of membranes in PVdF/sulfolane system. Cooling condition: in 70°C water bath. (a) 30 wt % PVdF; (b) 40 wt % PVdF; (c) 50 wt % PVdF.

phology of the cross section by scanning electron microscopy (SEM, SIRion).

#### Porosity, average pore size, and pore size distribution measurement

Porosity, average pore size and pore size distribution were measured on a mercury porosimetry (Auto Pore IV9500), the extent of pressure is from 0.5 to 60,000  $\psi$ .

## RESULTS AND DISCUSSIONS

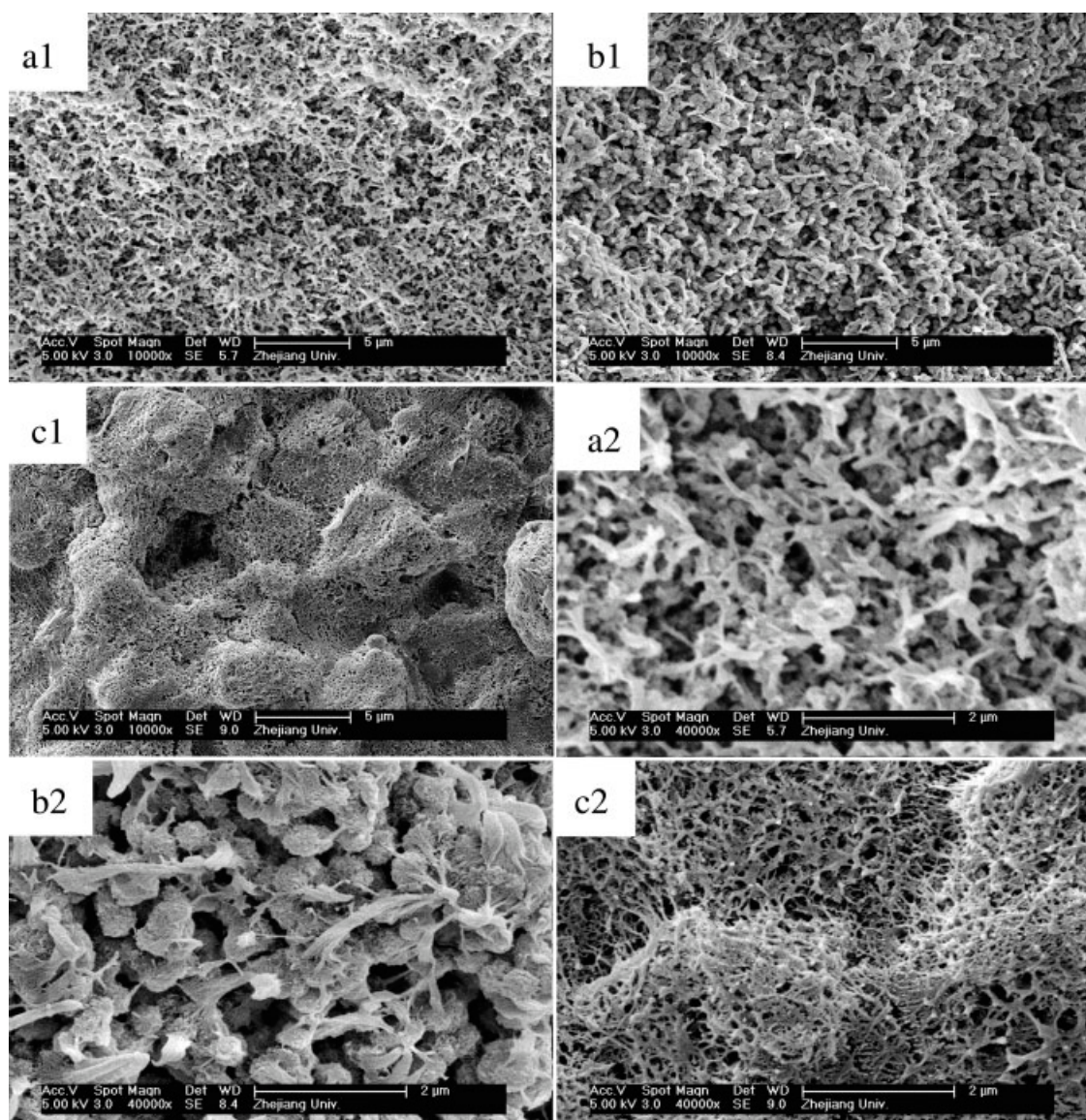
The phase diagram of PVdF/sulfolane system was shown in Figure 1. Observation by the optical microscope was used to determine the binodal line<sup>6</sup> and measurement by DSC was used to determine the crystallization curve. In this system, the temperature at which particle formation was observed by the optical microscope was approximately in agreement with the dynamic crystallization temperature, and we could not observe any structure with the microscope in the region higher than the dynamic crystallization temperature. So, this system should undergo S-L phase separation due to polymer crystallization.

Figure 2 shows the influence of polymer content on the heat of crystallization. In general, the heat of crystallization decreases with increasing polymer

content.<sup>13</sup> The reason is that high polymer content increases viscosity of polymer solution and in turn decreases the polymer mobility, thus leading to lower crystallinity. In this work, however, we come to the conclusion that the heat of crystallization increased with the increase of polymer concentration. The increasing of the heats of crystallization means the increase of crystallinity. Hideto et al.<sup>14</sup> had given explanation for this: with the polymer content increase, it is a chance of contact in polymer molecules becoming higher that leads to high crystallinity. But, further study is needed to clarify the mechanism.

Figure 3 reflects the influence of cooling rates on  $t_{1/2}$ .  $t_{1/2}$  presents the overall crystallization rate. That is, the shorter  $t_{1/2}$  is, the faster the overall crystallization rate. It can be seen that with the cooling rate increase,  $t_{1/2}$  reduced. The explanation is that, two factors, namely, nucleation and growth rate of crystallization control the overall crystallization rate. Increasing the cooling rate can raise the nucleation density and increase nucleation rate, but reduce growth rate. In general,<sup>15</sup> the increase of nucleation rate is faster than the decrease of growth rate as cooling rate increases. Thus the cooling rate increase will result in increasing overall crystallization rate.

Figure 4 is SEM photomicrographs of crosssections of PVdF porous membranes prepared by cooling in



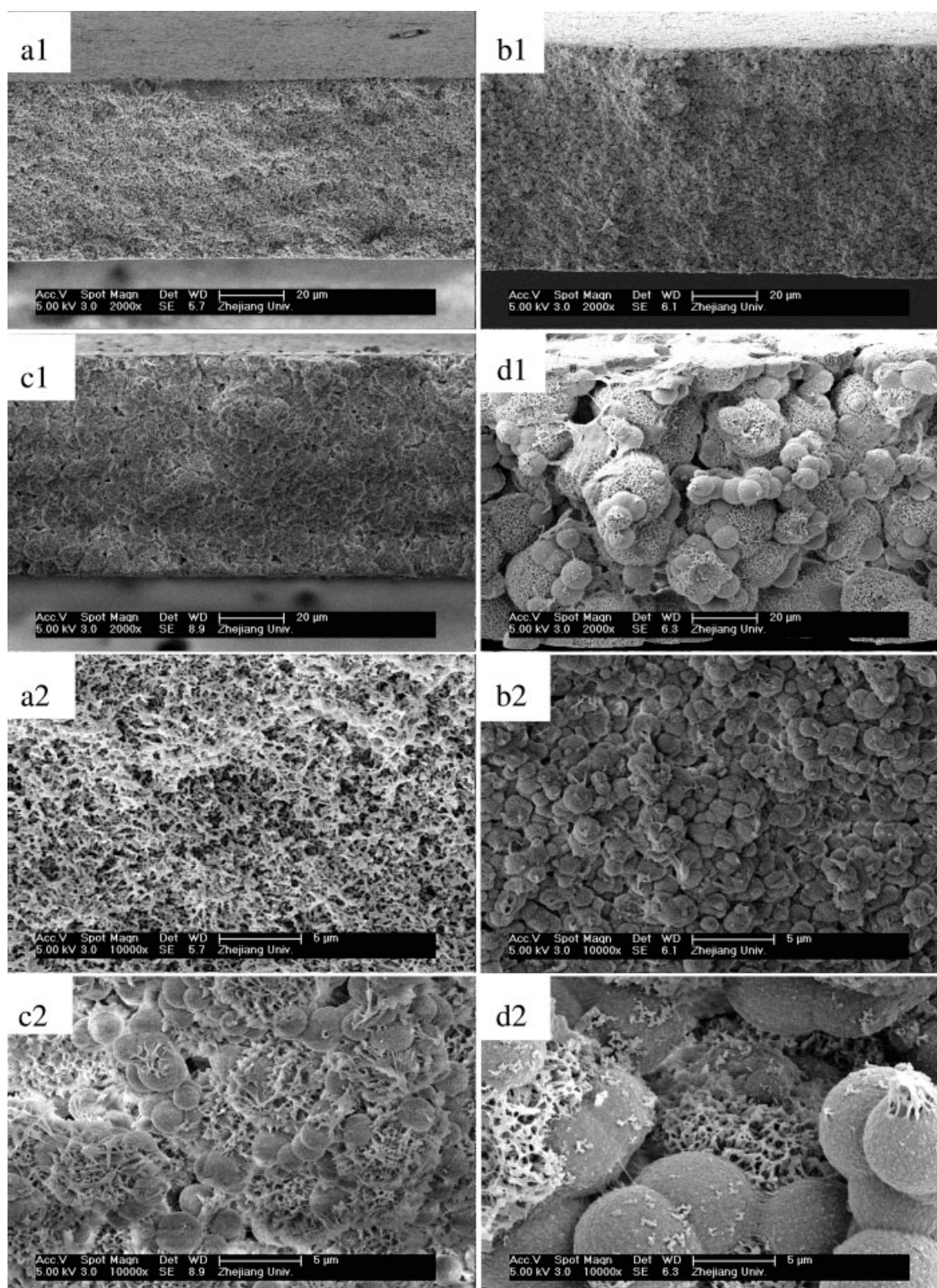
**Figure 6** SEM photomicrographs of cross section of membranes in PVdF/sulfolane system. Cooling condition: in liquid nitrogen. (a1) 30 wt % PVdF; (b1) 40 wt % PVdF; (c1) 50 wt % PVdF; (a2) 30 wt % PVdF; (b2) 40 wt % PVdF; (c2) 50 wt % PVdF. (a1–c1) magnifying 10,000; (a2–c2) magnifying 40,000.

30°C water bath as the polymer content was changed. It was found that blocks of spherulitic particles and nonspherulitic structure coexisted and pores were formed between crystallization as polymer content is between 10 and 40%. When polymer content reaches 50%, only irregular particles were observed. All these structures of membrane presented different crystallization morphology of PVdF, which further proved that S–L phase separation happened during TIPS process for PVdF/sulfolane system.

Another phenomenon from Figure 4 is that spherulitic particle is becoming more and more irregular with polymer content increase, especially 50% of PVdF content. This may be ascribed to the influence of viscosity. High polymer content will lead to

higher viscosity, which in turn prevent PVdF from crystallizing during TIPS process.

Figure 5 shows SEM photomicrographs of cross-section of membranes prepared in 70°C water bath. These membranes were prepared at a higher temperature than those shown in Figure 4. Spherulitic particles both with and without surface pores were observed. The size of spherulitic particles with surface pores is bigger than those shown in Figure 4. It is because higher cooling temperature is in favor of the growth of spherulitic crystallization but is disadvantage for the formation of nucleation.<sup>16</sup> So nucleation rate cooling in 70°C water bath is slower than that in 30°C water bath while growth rate is faster. However, the size of spherulitic particle of 50%



**Figure 7** Influence of cooling condition on membrane structure in PVdF/sulfolane system (cross section, polymer content: 30%). (a1, a2) in liquid nitrogen; (b1, b2) in 0°C ice water bath; (c1, c2) in 30°C water bath; (d1, d2) in 70°C water bath. (a1–d1) magnifying 2000; (a2–d2) magnifying 10,000.

didn't seem bigger than that of 40%. This may be that increasing polymer content decreased the free volume and limited the growth of nucleation.

Figure 6 is SEM photomicrographs of cross section of membrane cooled in liquid nitrogen, which means much faster cooling rate than those of Figures

**TABLE I**  
Porosity and Average Pore Size for PVdF/Sulfolane System

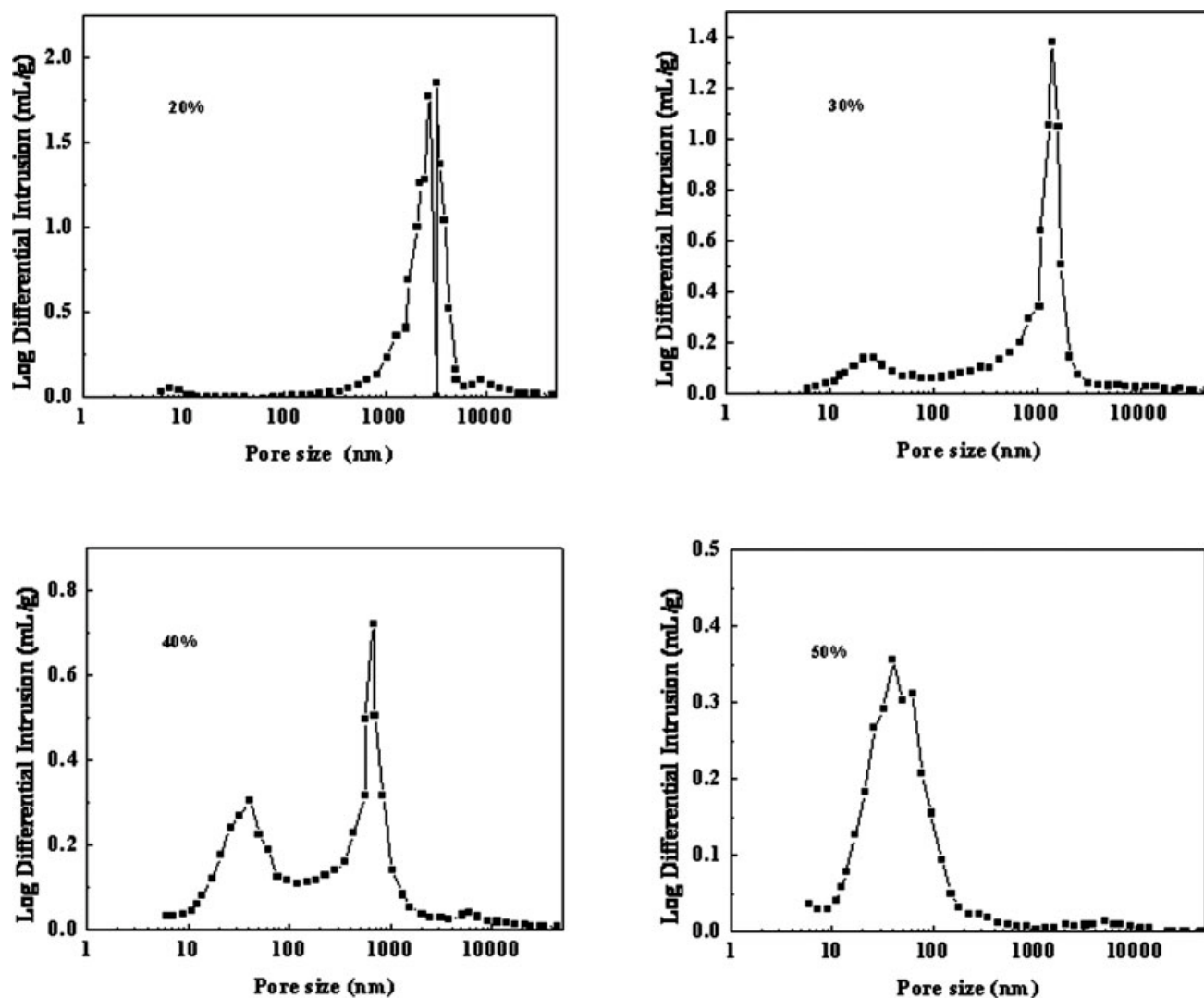
Polymer content (%)	Cooling condition	Porosity (%)	Average pore size ( $\mu\text{m}$ )
20	in 30°C water bath	68.61	0.821
30	in 30°C water bath	60.82	0.126
40	in 30°C water bath	59.26	0.102
50	in 30°C water bath	45.99	0.077
30	in 70°C water bath	61.67	0.134
30	in 0°C water bath	60.53	0.119
30	in liquid nitrogen	60.14	0.070

4 and 5. In all cases, interconnected structures were obtained. This is because the cooling rate is so quick that phase separation finished before PVdF crystallizes into more perfect form and sulfolane has enough time to assemble into bigger domain and thus sulfolane was entrapped within the crystallization of PVdF, after sulfolane was extracted, interconnected

pore structure was obtained. At higher magnification (see a2, b2, c2), it was found that the interconnected pores were very small and even.

Meguire et al.<sup>17</sup> reported that at a high cooling rate, the size of crystalline particles decreased with polymer concentration increase, because nucleation rate increases faster than that of crystallization growth. But the result in this work shows an opposite tendency, that is, the size of crystalline particles increased with polymer concentration increasing at a high cooling rate. This maybe ascribed to the quick crystallization of diluent and thus limited PVdF from nucleation.

The effect of the cooling rate on the membrane structure is shown in Figure 7. Seen from the whole crosssection, membranes have symmetrical structure. Higher cooling temperature means slower cooling rate. The faster the cooling rate, the smaller and more even particle size became. This is because low cooling temperature is in favor of nucleation but dis-



**Figure 8** The influence of polymer content on pore size distribution (cooling condition: in 70°C water bath).

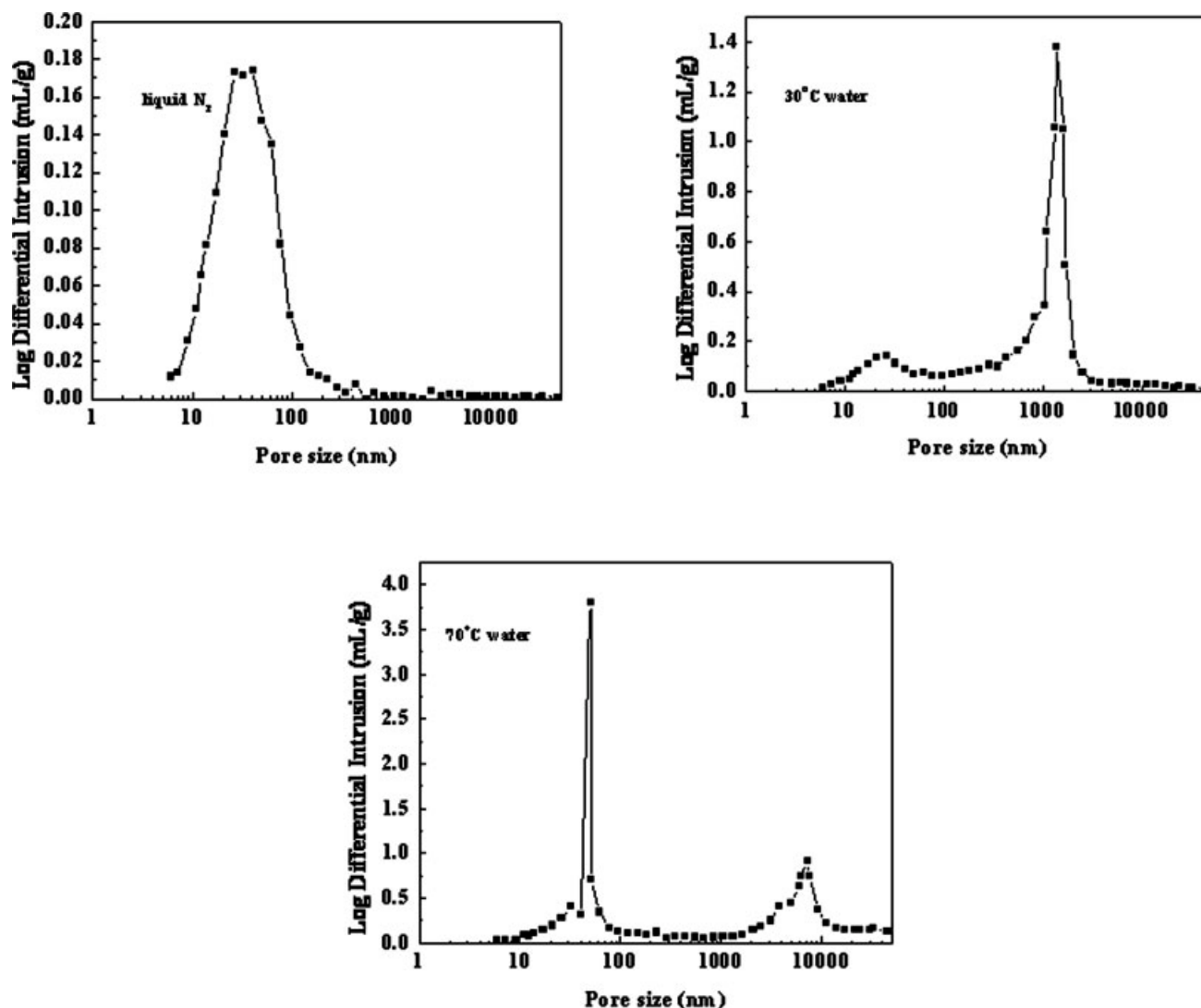


Figure 9 The influence of cooling condition on pore size distribution (polymer content: 30 wt %).

advantage of the growth of crystalline particle.<sup>6</sup> Small and even particle size means that the interconnection and uniformity of pore are good. On the contrary, as the cooling rate became slower, membranes were composed of larger spherulitic particles and the channel size of open pores between the particles was large, but more uneven. This is because slower cooling rate means both PVdF having enough time to crystalline into bigger blocks and sulfolane having enough time to assemble into bigger domain, which will convert into the pores or channel via extraction operation.<sup>6</sup> It is evitable that the strength of membrane is poor.

The values of porosity and average pore size were listed in Table I. At the same cooling temperature, with polymer content increase, both porosity and average pore size decreased. However, for the same polymer content, with the cooling rate decrease, average pore size increased but porosity was approxi-

mately the same, Hideto et al.<sup>14</sup> had reported similar experimental results.

Figures 8 and 9 were pore size distribution of membranes prepared at different cooling rate. It can be seen that pore size distribution became narrow with increasing polymer content or cooling rate, the results further confirmed that pore size became more even at faster cooling rate or higher polymer content.

## CONCLUSIONS

PVdF porous membranes were prepared by TIPS process with a new kind of diluent—sulfolane. Phase diagram for this system was determined. The dynamic crystallization temperature measured by DSC was approximately in agreement with the temperature of particle formation measured by the optical microscope. This meant that the S-L phase separa-



ration happened during TIPS process. The heat of crystallization increased with the increase of polymer content.  $t_{1/2}$  revealed that with cooling rate increase, the overall crystallization rate increased.

SEM photomicrographs of crosssection of membranes showed that different crystallization morphology of PVdF, such as spherulitic and nonspherulitic structure will be produced as the cooling rate changed. The values of average pore size and pore size distribution revealed that with the cooling rate decrease, the size of spherulitic particles, and the channel size of open pores between particles became larger, which means the wider pore size distribution and poor mechanical strength of porous membrane.

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