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Effect of Diluent Mixture on Porous Structure of Polyphenylene Sulfide via Thermally Induced Phase Separation

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Polyphenylene sulfide (PPS) microporous membranes were prepared via the thermally induced phase separation process using diluent mixtures of diphenyl ether (DPE) and diphenyl ketone (DPK). The effects of DPE ratio to DPK in the diluent mixture on the microstructure were investigated. The results showed that the pore morphology of the membranes prepared from the diluent mixture was different from those of fabricated from pure diluents. Moreover, the pore structures of the membranes were changed along with the variation of the diluent composition.

Keywords: Diluent mixtures, thermally induced phase separation, polyphenylene sulfide

1 Introduction

Thermally induced phase separation (TIPS) process is a well known method for obtaining membrane with controlled morphology which was first introduced by Castro in the 1980s. The TIPS method has gained much interest because of its excellent advantages, such as (1) greater flexibility and ease of control than conventional casting process, (2) a very low tendency for defect formation, and (3) morphology characterized by very high overall porosity and effect control of the final pore size. In the TIPS process, homogeneous solution needs to be formed by the dissolution of a polymer in a diluent at high temperature, and phase separation is induced by the cooling of the polymer solution. The final morphology of the membrane in TIPS process depends on the kinetics, as well as the thermodynamics of the phase separations. The effects of the diluents on the structure of TIPS membranes were investigated for

solid-liquid phase separation systems in terms of the diluent mobility and crystallization temperature. In the 1990s, Lloyd et al. (1–7) systematically studied the phase separation mechanism, effecting factors of TIPS method about PP, PE and PVDF. H. Matsuyama's research group (8–16) further investigated the membrane formation of TIPS method about effecting factors and the control of porous structure in different systems. Recently, the work teams in Korea performed many researches on biodegradable membrane as drug delivery carrier and tissue engineering scaffolds. The research for special property of membrane by TIPS method is the recent important direction, and the research included the fluorinated polymers (17, 18), PEEK (19, 20), and polyoxymethylene (21).

PPS is a kind of semi-crystalline polymer and it has high melting temperature (265.6°C), high glass transition temperature (103.9°C) and is insoluble in most common solvents under 200°C. Therefore, polymer PPS has the excellent solvent resist and thermal resist. We have done some researches about PPS membrane, which relate to the possibility of preparation of PPS membrane via TIPS method and the effects of the polymer blending. (22–24).

In this paper, the polyphenylene sulfide (PPS) membranes were prepared via TIPS method by using diluent mixtures (DPE and DPK). The cloudy temperatures for PPS/DPE/DPK blends were determined. The effects of diluents mixture on the microstructure of polyphenylene sulfide PPS membranes were investigated in detail.

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2 Experimental

2.1 Materials

Polyphenylene sulfide (PPS) is commercial product of Chengdu Letian Plastic Co. (Chengdu City, Sichuan Province. $M_n = 94000$, T_m is 265.6°C and T_g is 103.9°C). Both diphenyl ether (C.P., T_m is 27°C , T_b is 159°C) and diphenyl ketone (A.R., T_m is 48.5°C , T_b is 305.5°C) are commercial products of Beijing Chemical Factory.

2.2 Membrane Preparation

The steps of preparing porous polymer samples are stated below. First some polymer (PPS), diluent (diphenyl ether and diphenyl ketone) with certain weight ratio were put in a test tube and mixed. After the test tube was full of nitrogen, it was sealed with stopper. The test tube was then put in an electric heating apparatus and heated to $20\sim 30^\circ\text{C}$ above the cloudy point of solution for 30 min, until PPS was completely dissolved in the diluents. Finally, the test tube was put into cooling medium. The diluents in the samples were extracted by acetone and dried in vacuum oven at 80°C for 12 h. The samples were then obtained before characterization tests.

2.3 The Measurement of Cloudy Point Temperature

The cloudy point (L-L phase separation) was observed by optical microscopy (Olympus BH2) as in the steps below. The mixture sample was sealed in two slides, and then was heating on a hot stage to be homogeneous solution. When the solution was slowly cooling down to the cloudy point, at which phase separation occurs, the transparent solution turned to be turbid.

2.4 Scanning Electron Microscopy (SEM) Observation

For the cross section observation, the microporous membrane was freeze-fractured in liquid nitrogen and then sputtered with Au/Pd *in vacuo*. A scanning electron microscope (SEM; Hitachi Co., Tokyo, Japan, S-4300) with an accelerating voltage of 30 kV was used to observe the porous structure.

2.5 Membrane Porosity Measurement

The sample porosity, A_k , is defined as the volume of the pores divided by the total volume of the porous membrane. The dry sample was soaked in the pure alcohol for 10 h, then the sample was taken out, the alcohol on the surface of the sample was softly wiped up by filter paper. Finally, the sample was weighed quickly. The formula of the membrane porosity is the following:

$$A_k = \frac{(W_0 - W)\bar{\rho}}{\bar{\rho}W_0 + (\rho - \bar{\rho})W} \times 100\%$$

Table 1. Cloudy point temperatures for different diluent mixture

Polymer concentration	20 wt%	30 wt%	40 wt%
DPK:DPE = 10:0	227	225	221
DPK:DPE = 8:2	198	196	203
DPK:DPE = 5:5	191	194	200
DPK:DPE = 2:8	196	197	204
DPK:DPE = 0:10	203	207	205

W is the total weight of the dry sample, W_0 is the weight of the wet sample, $\bar{\rho}$ is the polymer density, ρ is the absolute alcohol density.

3 Results and Discussion

3.1 Analysis of the Cloudy Point Temperature

The cloudy point temperatures were used to draw binodal curve, which was one of important part of the phase diagram of polymer/diluent system. In the Liquid-Liquid (L-L) phase separation, the binodal curve affected not only the mechanism of phase separation but also the coarsening process (1–16). The mechanism of phase separation mainly affects the pore structure type, and the coarsening process mostly influences the branch thickness and pore size, which were both very important for membrane preparation via TIPS method. The coarsening time is direct proportion with the L-L phase separation time.

The cloudy point temperatures of polymer/diluent mixture system with different polymer concentration and different ratio are shown in Table 1. It can be found that the cloudy point of PPS/DPK/DPE mixture blend first shifted to lower temperature with the increasing of DPE content, went through a minimum centered at about 50%, and then increased.

The decreasing of the cloudy point temperature meant the declining of binodal curve, which also meant the reduction of L-L phase separation and coarsening time. The pore size and branch thickness was influenced by the coarsening time of polymer-rich phase or polymer-lean phase. Therefore, it could be deduced that the diluent mixture would affect the final pore structure, pore size and branch thickness of the membranes.

3.2 20 wt% PPS/80 wt% Mixed Diluents System

The effect of single diluent DPE or DPK on cross-sectional structures of the PPS membrane is shown in Figure 1. The polymer concentration is 20 wt% and the system is cooled in air, as seen in Figure 1, the branch-like structure is both obtained in the above two systems and the corresponding parameters, such as the pore size, branch thickness and porosity, is summarized in Table 2. The branch-like pore structures in Figure 1 a and b are due to spinodal decomposition of the L-L phase separation. Following the L-L phase

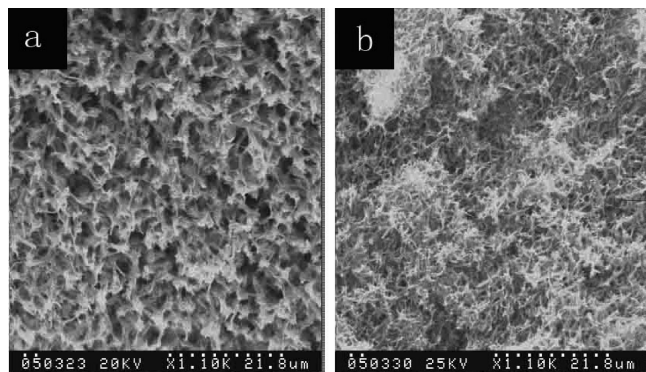


Fig. 1. Porous structures of PPS/single diluent system (polymer concentration 20 wt%). (a) diphenyl ether, (b) diphenyl ketone.

separation, the poly-rich phase solidifies to be a branch-like structure. Because the coarsening process of polymer-rich phase plays leading role in this system, the coarsening time has more important effect on the branch thickness, and has less effect on the pore size and porosity. Therefore, the middle pore size and thinnest branch thickness are obtained (Table 2). At the same time, the porosity with different ratio of mixed diluents is high and similar, this express the similar efficiency of separation.

Figure 2 shows the SEM images of PPS/DPE/DPK systems with the polymer concentration is 20 wt%. It can be seen that all the images are branch-like structures. However, the branch length and thickness of membranes in Figure 2 are larger than those in Figure 1. The reason lies in the declining of the coarsening time in the process of the membrane formation when the diluent mixture was used in the

Table 2. The structure parameters of PPS/ diluent mixture system (polymer concentration is 20 wt%)

DPE:DPK	8:2	5:5	2:8
Pore thickness (μm)	0.90	0.43	0.92
Pore size (μm)	0.40	1.00	2.00
Porosity	73.8	75.6	76.0

system. From the data in Table 1, the cloudy point temperature of diluent mixtures is lower than that of single diluent and the lower cloudy point temperature brings the shorter coarsening time. Although the branch thickness should be decided by coarsening time, when the ratio of DPE: DPK is 5:5, the cloudy point temperature is the lowest in different systems (Table 1), the thinnest branch thickness is caused by the less coarsening time (Fig. 2b, 2e).

3.3 30 wt% PPS/70 wt% Diluent Mixture System

Figure 3 shows the SEM images of PPS/DPE and PPS/DPK systems with the concentration of PPS is 30 wt%, the branch-like structure (Fig. 3a) is obtained in PPS/DPE system due to spinodal decomposition of the L-L phase separation, and the spherical structure (Fig. 3b) appears in the PPS/DPK system due to nucleation-growth of the polymer-rich phase in the L-L phase separation process and the crystallization of the polymer in the polymer-rich phase.

When the polymer concentration is 30 wt%, the different pore structures are obtained with different diluent mixture ratio (Fig. 4). The phase separation mechanisms are different in different PPS/diluents system because of the

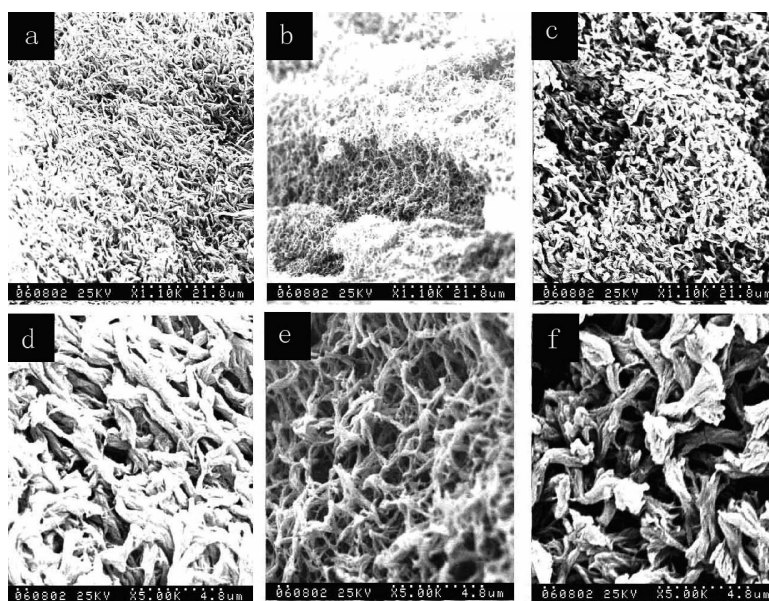


Fig. 2. Porous structures of PPS/diluent mixture system with different ratios. DPE : DPK (a) 8:2, (b) 5:5, (c) 2:8, (low power), (d) 8:2, (e) 5:5, (f) 2:8, (high power).

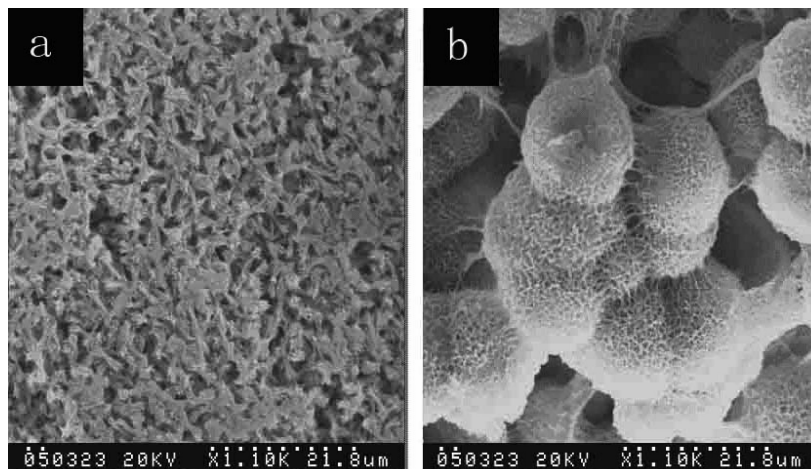


Fig. 3. Porous structures of PPS/single diluent system (polymer concentration 30 wt%) (a) diphenyl ether, (b) diphenyl ketone.

interaction between the polymer and diluent mixture. When the ratio of DPE:DPK is 2:8, the branch-like structure is got due to spinodal decomposition (Fig. 4a, 4d). When the ratio of DPE:DPK is 5:5 and 8:2, the spherical structure can be obtained due to nucleation-growth (Fig. 4b, 4e, 4c, 4f). Therefore, with the change of proportion of mixed diluents, the different pore structures can be obtained.

From Figures 3 and 4, we can find the change of pore structure and size is gradually. The spherical pore size is affected by the coarsening time. The spherical pore structures are gradually changed (Fig. 3b, Fig. 4b, 4c). It is obvious that the spherical size and pore size decreased with the reduction of DPK. That is, the decrease of cloudy point

temperature caused the decreasing of coarsening time in polymer-rich phase, so the size of spherical decreased.

3.4 40 wt% PPS/60 wt% Diluent Mixture System

Figure 5 shows the SEM images of PPS/DPE and PPS/DPK systems when the concentration of PPS is 40 wt%, the branch-like structure (Fig. 4a) is obtained in PPS/DPE system due to spinodal decomposition of the L-L phase separation, and the spherical structure (Fig. 4b) is obtained in the PPS/DPK system because of the nucleation-growth of the polymer-rich phase in the L-L phase

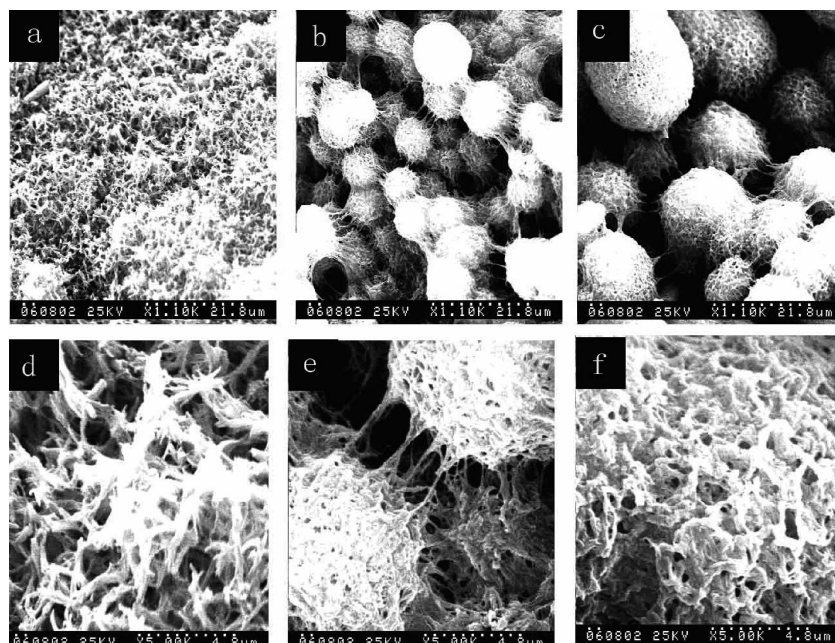


Fig. 4. Porous structures of PPS/ diluent mixture system with different ratios (polymer concentration:30 wt% DPE:DPK = (a) 8:2, (b) 5:5, (c) 2:8, (low power) (d) 8:2, (e) 5:5, (f) 2:8, (high power).

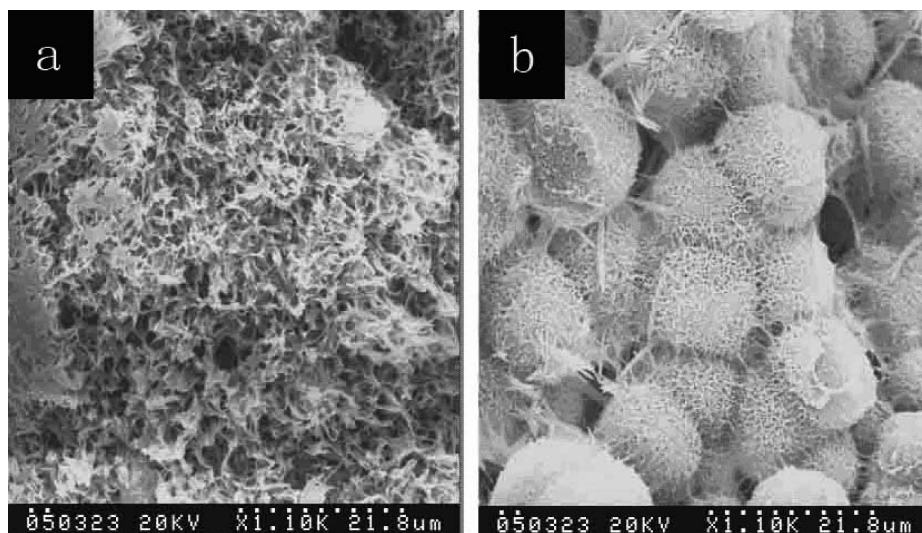


Fig. 5. Porous structures of PPS/single diluent system (polymer concentration: 40 wt%). (a) diphenyl ether, (b) diphenyl ketone.

separation process and the crystallization of the polymer in the polymer-rich phase.

When the proportion of diluents is changed, with the polymer concentration of 40 wt%, the SEM images are all branch-like structures (Fig. 5). With the change of proportion of diluent mixture, the mechanism of phase separation is changed because of the interaction between the polymer and diluents. When the polymer concentration is 40%, the branch-like structure can be obtained at different ratio of diluents. The difference lies in the branch thickness and pore size, which is

mainly caused by the coarsening time and polymer concentration. According to the cloudy point temperatures (Table 1), when DPE: DPK is 5:5, the coarsening time of polymer-rich phase is the shortest in these systems because the cloudy point temperature is the lowest. It can be seen that the pore size and branch thickness are determined by the coarsening time and polymer concentration. Therefore, the middle pore size and thinnest branch thickness are obtained (Table 3, Fig. 6a, 6e). When DPE: DPK is 5:5 at different polymer concentrations, comparing the SEM images at polymer concentration of 20% with 40%

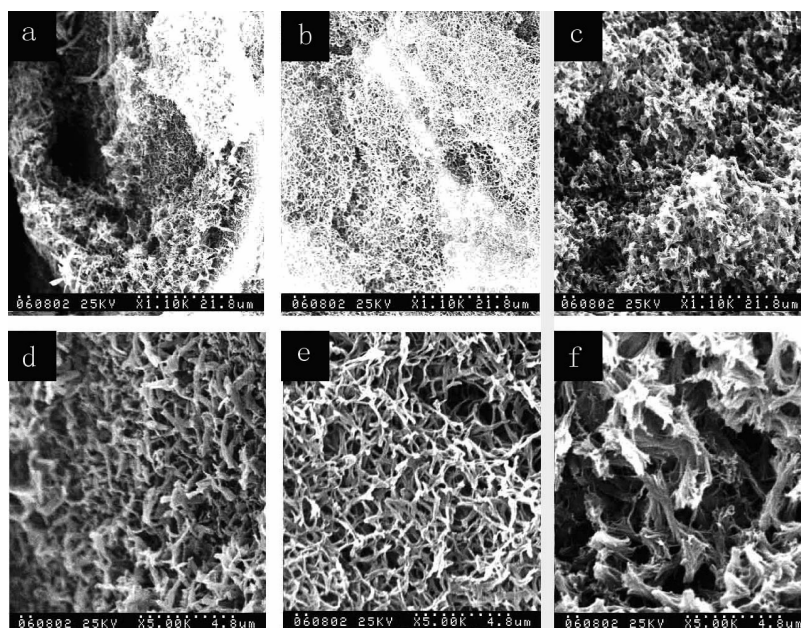


Fig. 6. Porous structures of PPS/diluent mixture system with different ratios: (polymer concentration: 40 wt%) DPE : DPK = (a) 8:2, (b) 5:5, (c) 2:8 (low power), (d) 8:2, (e) 5:5, (f) 2:8 (high power).

Table 3. The structure parameters of PPS/diluent mixture system (polymer concentration is 40 wt%)

DPE:DPK	8:2	5:5	2:8
Pore thickness (μm)	0.38	0.24	0.56
Pore size (μm)	0.85	1.20	2.50
Porosity	74.2	75.5	78.1

(Fig. 2b, e, Fig. 6b, e), the higher cloudy point temperature has the thinnest branch because the higher polymer concentration restrains the coarsening process. At the same time, the similar porosity shows the similar efficiency of separation (Table 3).

4 Conclusions

The diluent mixture can effectively change the cloudy point temperature (binodal curve), and change the mechanism of phase separation and coarsening process, which cause the change of the pore structure, pore size and branch thickness.

The coarsening process can be separate into polymer-rich phase and polymer-lean phase. When the polymer crystallizes firstly, the coarsening process of polymer-rich phase plays a leading role, or else, the polymer-lean phase is dominant. In this paper, the coarsening process of polymer-rich phase plays leading role. Therefore, the pore size and branch thickness are determined by the coarsening time and polymer concentration.

In this paper, it can be seen that the coarsening time has more important effect on the branch thickness, and has less effect on the pore size and porosity.

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