

Effects of Nucleating Agents on the Porous Structure of Polyphenylene Sulfide Via Thermally Induced Phase Separation

Xuntong Han,¹ Huaiyu Ding,² Lihua Wang,² Changfa Xiao¹

¹Tianjin Municipal Key Laboratory of Fiber Modification and Functional Fiber, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China

²Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 13 April 2007; accepted 31 August 2007

DOI 10.1002/app.27255

Published online 9 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The different molecular weight Polyethylene glycol (PEG) was chosen to be the nucleating agent to investigate the effects of nucleating agents on the porous structure of polyphenylene sulfide (PPS) via thermally induced phase separation (TIPS). The pore structures were changed with the addition of PEG, due to the different mechanism on pattern formation. Moreover, some effecting factors, such as the molecular weight and concentration of

PEG, were used to control the pore structure and size. With addition of nucleating agent, it can be estimated that the pore size (radius) should be about 0.5 ~ 0.05 μm and the porosity should be above 70%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2475–2479, 2008

Key words: thermally induced phase separation; PPS; nucleating agent

INTRODUCTION

Since TIPS method first was used by Castro in 1980s,¹ this method has gained much interest. In 1990s, Lloyd et al.^{2–8} systematically studied the phase separation mechanism, effecting factors of TIPS method about PP, PE, and PVDF. H. Matsuyama's research group^{9–17} further investigated the formation of porous structure 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 polymer membrane as drug delivery carrier and tissue engineering scaffolds.^{18–20} The research for special property of porous structure by TIPS method is the recent important direction. For the solvent-resist and thermal-resist porous structures, the polymer materials that included the fluorinated polymers,^{21,22} PEEK,^{23,24} polyoxymethylene,²⁵ etc. had been investigated.

Polyphenylene sulfide (PPS) is a kind of semicrystalline polymer that has high melting temperature (265.6°C) and high glass transition temperature (103.9°C). PPS is insoluble in most common solvents under 200°C, so it is regarded as the high performable polymer material that has excellent solvent and thermal resist. We have done some researches about PPS porous structure prepared by TIPS method, which

relate to the possibility of preparation of PPS porous structure, the selection of diluents, and then polymer blending etc.^{26,27} There are many different effecting factors on pattern formation, such as selection of diluents, polymer concentration, cooling rate, etc.

The nucleating agents also play one of the important role in preparation of porous structure sample via TIPS.^{28,29} In this article, The different molecular weight Polyethylene glycol (PEG) was chose to be as the nucleating agents. The mechanism on pattern formation was investigated. Moreover, some effecting factors to control the pore structure and size, such as the molecular weight and concentration of PEG, were also tested.

EXPERIMENTAL

Materials

PPS is commercial product of Chengdu Letian Plastic Co. (Cheng Du city, $M_n = 94,000$ Dalton, T_m is 265.6°C and T_g is 103.9°C, density of PPS is 1.44 g/cm³). Diphenyl ketone (A.R, T_m is 48.5°C, T_b is 305.5°C), ethanol and nucleating agents, such as PEG 800, PEG 1000, and PEG 4000, are of reagent grade from of Beijing Chemical Factory.

Porous sample preparation

The steps prepared for porous polymer samples are stated below. First some polymer (PPS), diluent (diphenyl ketone) and nucleating agents with special

Correspondence to: L. Wang (wanglh@iccas.ac.cn).

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 ~ 30°C above the cloud point temperature of solution for 30 min, and then mixed by stirrer, until PPS was completely dissolved in the diluent. Finally, the test tube was put into cooling medium. The diluent in the samples was extracted by acetone and dried in vacuum drying oven at 80°C for 12 h. The samples were then obtained.

Scanning electron microscopy observation

The porous samples were fractured in liquid nitrogen and mounted vertically on sample holders. The surfaces of the samples were sputtered with Au/Pd *in vacua*. A scanning electron microscope (SEM; Hitachi, Tokyo, Japan, S-4300) with an accelerating voltage of 30 kV was used to observe the porous structure.

Porous sample porosity

The porosity, A_k , is defined as the volume of the pores divided by the total volume of the porous sample. The dry porous 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. For a sample, the porosity was tested for five times. The data were the average of those results. The formula of the porous sample porosity is the following:

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

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

RESULTS AND DISCUSSION

Effect of PEG on the formation of porous sample

When the PPS concentration is beyond 30 wt % in PPS/diphenyl ketone system, the PPS porous sample will be the spherical structure.²⁶ The spherical structures in Figure 1(a,c) are the typical structure of nucleation growth mechanism of L-L phase separation. The character of spherical structure has worse pore structure and nonuniform pore sizes. When the PPS sample is prepared with 2 wt % PEG and cooled in 20°C air, the compact branch-like structures can be got in Figure 1(b,d). The addition of a nucleating agent for TIPS at 20°C, generates a porous structure with significantly smaller pores. In previ-

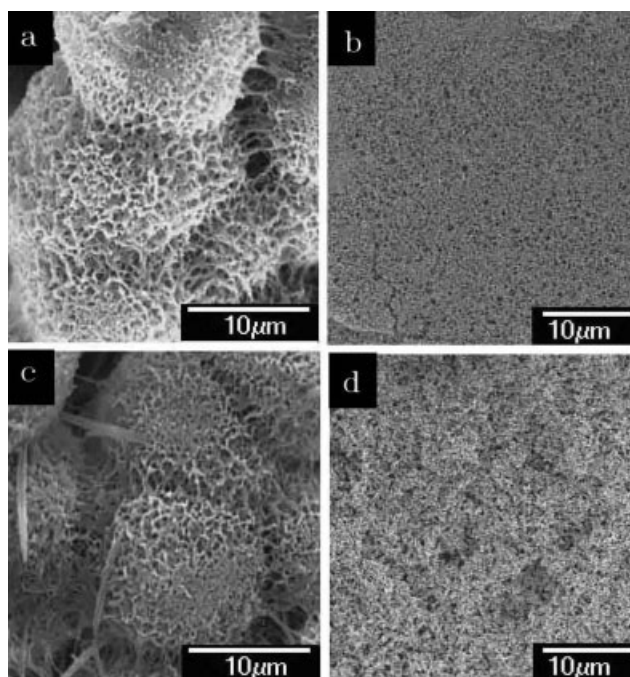


Figure 1 The SEM images of PPS membrane under different condition (cooled in 20°C air, PEG is 2 wt %) PPS is 30 wt %: (a) without PEGs, (b) PEG 4000 PPS is 40 wt %: (c) without PEGs, (d) PEG 4000.

ous literature, heterogeneous nucleation is defined by Binsbergen²⁴ as nucleation due to the presence of a second phase and occurring at the interface between this second phase and the parent phase. The surface of the foreign phase is made unstable by the crystalline phase, and hence facilitates nucleation. The addition of a nucleating agent increases the nucleation density²⁴ and thereby decreases final spherulitic size. So the pore size decreases by this reason [Fig. 1(b,d)]. For the change of phase separation mechanism, the addition of PEG may change the surface energy of spherulites and make the phase separation proceed faster, giving both smaller spherulites and probably the different phase separation mechanism.

According to the analysis of experimental results (Fig. 1), in the process of phase separation, the nucleating agent can change the nucleation density, so the pore density increases and the pore size decreases. Moreover, the nucleating agent also can result in the change of phase separation mechanism and the pore structure changes from spherulites to branch like.

Effect of molecular weight of PEG

PEG 800/PEG 1000 and PEG 4000 were respectively added to the PPS/diphenyl ketone system to investigate the effect of molecular weight of PEG.

Figure 2(a-h) are the SEM images with different molecular weight PEGs at the PPS concentration of

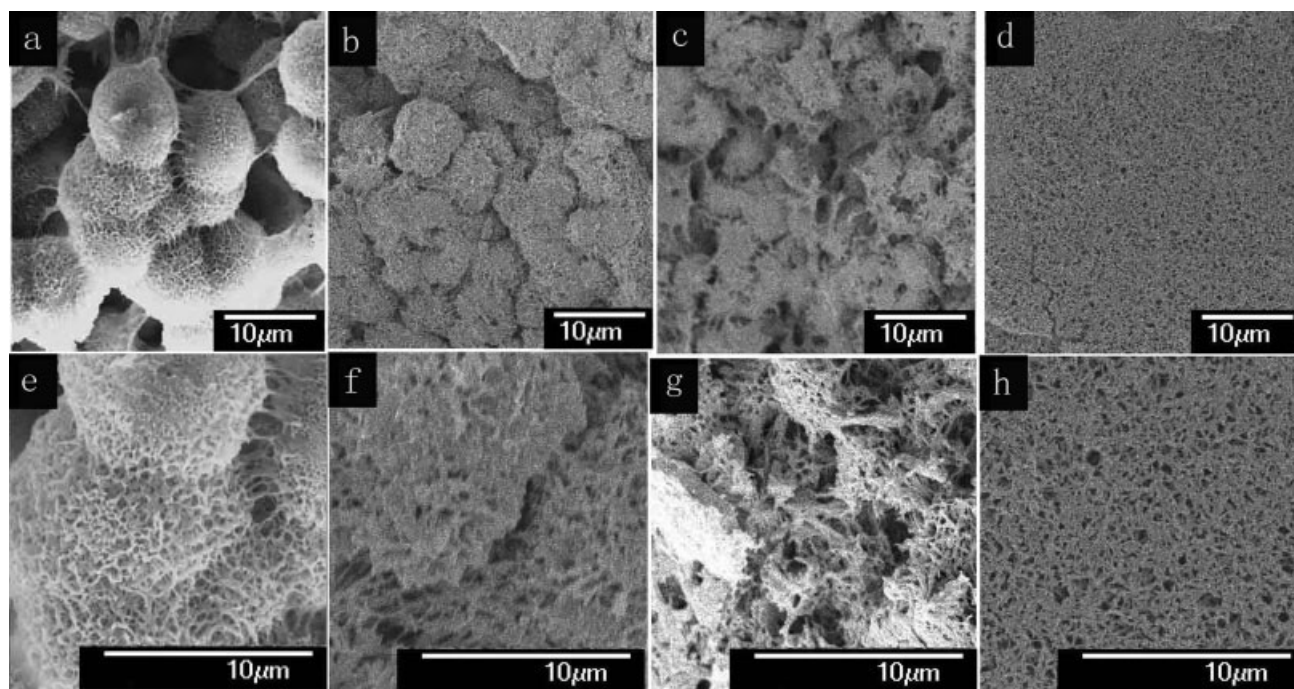


Figure 2 The SEM images with different molecular weight PEG (PPS is 30 wt %, cooled in 20°C air, PEG is 2 wt %) (a) without PEG; (b) PEG 800; (c) PEG 1000; (d) PEG 4000 (low power); (e) without PEG; (f) PEG 800; (g) PEG 1000; (h) PEG 4000 (high power).

30 wt %. Without the nucleating agent PEG, the pore structure is spherical and the pore size is micron. With the increase of PEG of molecular weight, the pore structure is changing from spherical [Fig. 2(a-c)]

to branch-like (Fig. 2d) and the pore size is about 0.5 μm [Fig. 2(e-h)]. The pore structure is determined by the mechanism of phase separation, but the mechanism affected by the nucleating agent

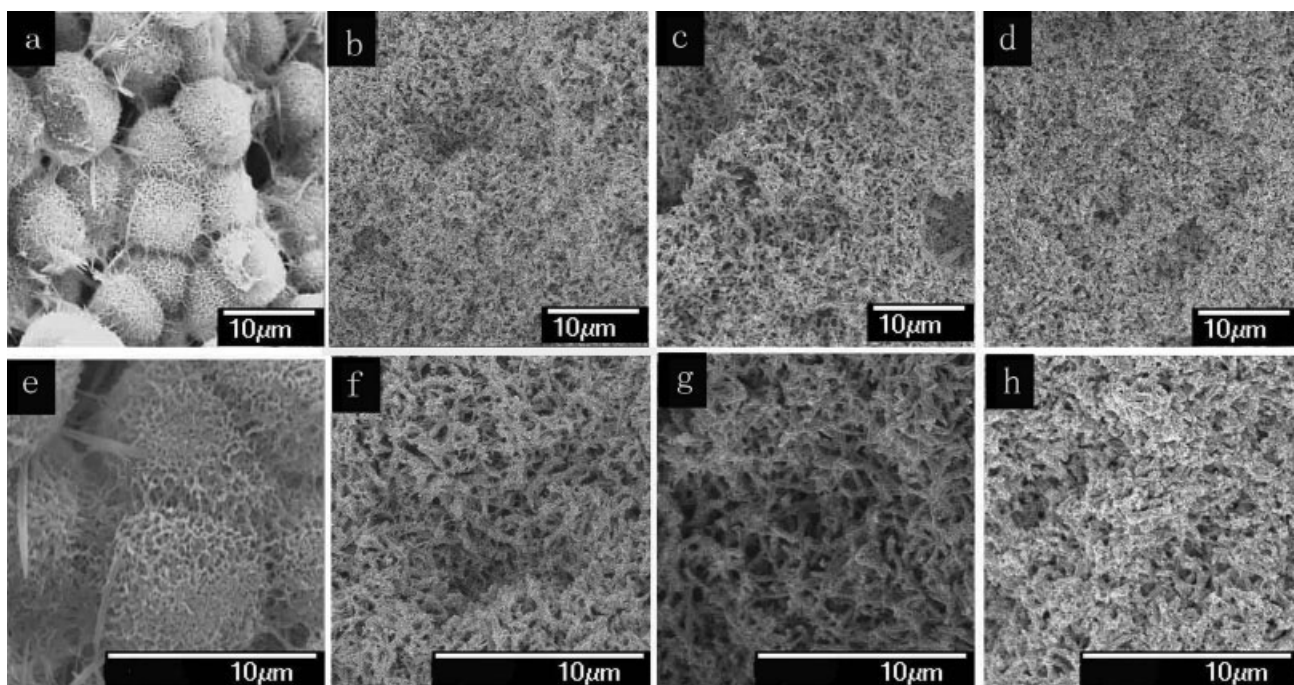


Figure 3 The SEM images with different molecular weight PEG (PPS is 40 wt %, cooled in 20°C air, PEG is 2 wt %) (a) without PEG; (b) PEG 800; (c) PEG 1000; (d) PEG 4000 (low power); (e) without PEG; (f) PEG 800; (g) PEG 1000; (h) PEG 4000 (high power).

TABLE I
The Porosities of PPS at Different Conditions (PEG is 2 wt %)

	Without PEG	PEG 800	PEG 1000	PEG 4000
Porosity (PPS is 30 wt %)	83.8%	76.1%	79.0%	80.2%
Porosity (PPS is 40 wt %)	78.4%	77.2%	79.5%	80.0%

because the nucleating agents mainly change the surface energy of spherulites. However, the pore size in Figure 2 change little. Figure 3(a–h) are the SEM images with different molecular weight PEG at the PPS concentration of 40 wt %. Just like Figure 2(a–h), the same branch-like structures can be obtained. However, the range of pore size (radius) is clearly changed from 0.05 to 0.5 μm in Figure 3. The nucleating agents increased the number of nuclei, and then increased the number of pore, which led to the decrease of the pore size.

In Figures 2 and 3, keeping the weight of PEG constant, the pore structure and size is different as polymer concentration varies. It may be caused by the different weight ratio of PEG/PPS because the 2 wt % PEG in the paper is weight ratio of PEG/solution. For the porosities at different condition (Table I), the similar porosities can be obtained with the addition of PEG. The reasons of similar porosities may be rejection of diluent when polymer is solidified or the porosity is varied by exchange of diluent and extractor in the extraction process.

The best nucleating agent is PEG 4000 among these agents because the branch-like pore and higher porosities can be got.

Effect of weight percent of PEG

Figure 4 is the SEM images with the different PEG 4000 concentration. The three PEG concentrations are set to 0.5 wt %, 2.0 wt %, and 8 wt %. From Figure 4, when the PEG concentrations is 0.5 wt % and 2.0 wt % the branch-like structures and the small size pores are obtained [Fig. 4(a,b,d,4)], due to the change of surface energy and the increase of nucleation density with addition of PEG. When PEG concentration is 8 wt %, the broken pore structure [Fig. 4(c,f)] are formed. It may be caused by the lower melting points and the excellent fluidity of PEG. When the solution was cooled at high temperature, L-L phase separation and polymer crystallization both happened. At the process of coarsening, PEG gathered together and formed the large cavity because of its lower viscosity and excellent fluidity, so the gather of PEG destroyed the pore structures. The porosities of different PEG concentration also have the same results (Table II). When PEG 4000 is 2 wt %, the porosity is about 80.2%. When PEG 4000 is 8 wt %, the porosity is 81.3% because it is formed by the gather of PEG [Fig. 4(c)].

Although too high concentration of PEG would destroy the pore structures because of the gather of

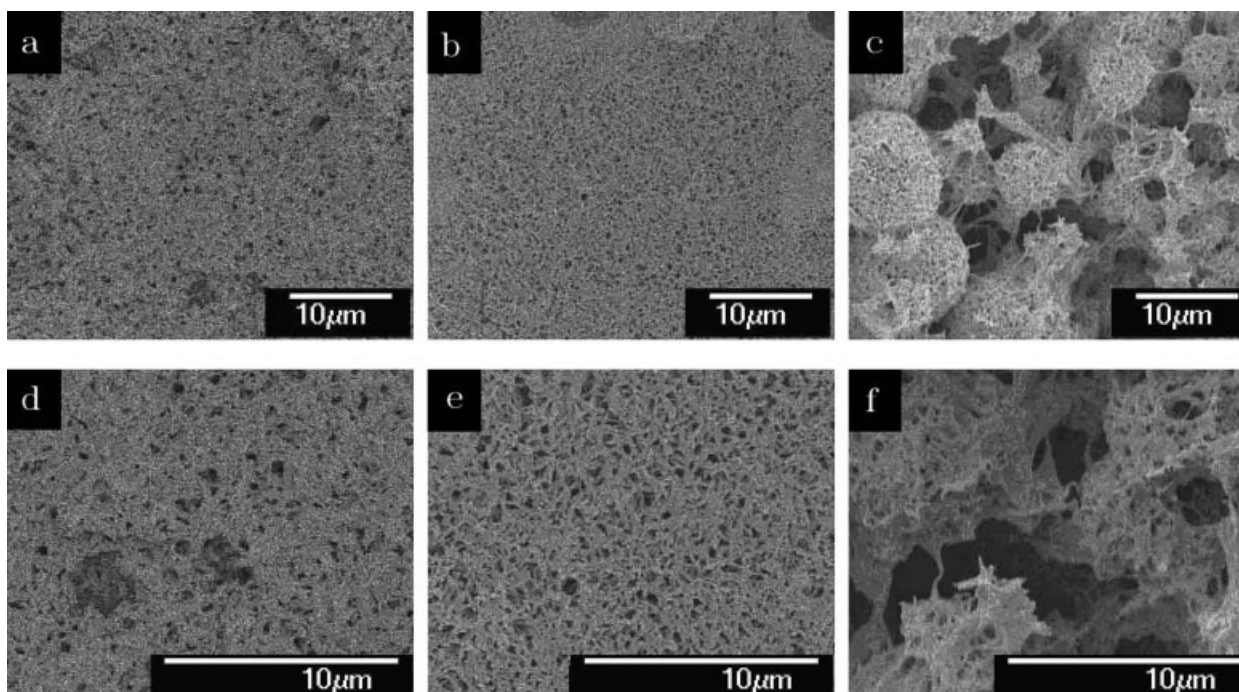


Figure 4 The SEM image with the different PEG concentration (PPS is 30 wt %, cooled in 20°C air) (a) 0.5 wt %, (b) 2.0 wt %, (c) 8 wt % (low power), (d) 0.5 wt %, (e) 2.0 wt %, (f) 8 wt % (high power).

TABLE II
The Porosities of PPS Samples with PEG 4000
(PPS is 30 wt %)

PEG concentration	0.5 wt %	2 wt %	8 wt %
Porosity	76.0%	80.2%	81.3%

overmuch nucleating agent, the concentration of PEG is better to choose about 2 wt % in this system.

CONCLUSIONS

1. In the process of phase separation, the nucleating agent can change the nucleation density, so the pore density increases and the pore size decreases. Moreover, the nucleating agent also can result in the change of surface energy, and thereby the mechanism of phase separation may be changed.
2. The addition of PEG changes the mechanism of phase separation and pore structure. For different molecular weight PEG 800/PEG 1000/PEG 4000/ the PEG 4000 is the best nucleating agent because the branch-like pore can be obtained, the pore size is about 0.5 ~ 0.05 μm and the porosity is above 70%.
3. When the concentration of PEG is too high, the pore will be destroyed because the gather of overmuch nucleating agent. For the better pore structure and pore size, the proper concentration of nucleating agent should be chosen. Therefore, the concentration of PEG is better to choose about 2 wt %, based on the experimental data.

References

1. Castro, A. J. U.S. Pat. 4,247,498[P] (1981).
2. Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. *J Membr Sci* 1990, 52, 239.
3. Lloyd, D. R.; Kim, S. S.; Kinzer, K. E. *J Membr Sci* 1991, 64, 1.
4. Kim, S. S.; Lloyd, D. R. *J Membr Sci* 1991, 64, 13.
5. Lim, G. B. A.; Kim, S. S.; Ye, Q.; Wang, Y. F.; Lloyd, D. R. *J Membr Sci* 1991, 64, 31.
6. Kim, S. S.; Lim, G. B. A.; Alwattari, A. A.; Wang, Y. F.; Lloyd, D. R. *J Membr Sci* 1991, 64, 41.
7. Alwattari, A. A.; Lloyd, D. R. *J Membr Sci* 1991, 64, 55.
8. McGuire, K. S.; Lloyd, D. R.; Lim, G. B. A. *J Membr Sci* 1993, 79, 27.
9. Matsuyama, H.; Berghmans, S.; Lloyd, D. R. *J Membr Sci* 1998, 142, 213.
10. Matsuyama, H.; Teramoto, M.; Kudari, S.; Kitamura, Y. *J Appl Polym Sci* 2001, 82, 169.
11. Matsuyama, H.; Hayashi, K.; Maki, T.; Teramoto, M.; Kubota, N. *J Appl Polym Sci* 2004, 93, 471.
12. Matsuyama, H.; Maki, T.; Teramoto, M.; Asano, K. *J Membr Sci* 2002, 204, 323.
13. Matsuyama, H.; Yuasa, M.; Kitamura, Y.; Teramoto, M.; Lloyd, D. R. *J Membr Sci* 2000, 179, 91.
14. Matsuyama, H.; Iwatani, T.; Kitamura, Y.; Tearamoto, M. *J Appl Polym Sci* 2001, 79, 2456.
15. Matsuyama, H.; Iwatani, T.; Kitamura, Y.; Tearamoto, M.; Sugoh, N. *J Appl Polym Sci* 2001, 79, 2449.
16. Matsuyama, H.; Kobayashi, K.; Maki, T.; Tearamoto, M. *J Appl Polym Sci* 2001, 82, 2583.
17. Matsuyama, H.; Ohga, K.; Maki, T.; Tearamoto, M.; Nakatsuka, S. *J Appl Polym Sci* 2003, 89, 3951.
18. Hua, F. J.; Park, T. G.; Lee, D. S. *Polymer* 2003, 44, 1911.
19. Shin, K. C.; Kim, B. S.; Kim, J. H.; Park, T. G.; Nam, J. D.; Lee, D. S. *Polymer* 2005, 46, 3801.
20. Kim, D. H.; Bae, E. H.; Kwon, I. C.; Pal, R. R.; Nam, J. D.; Lee, D. S. *Biomaterials* 2004, 25, 2319.
21. Caplan, M. R.; Chiang, C. Y.; Lloyd, D. R.; Yen, L. Y. *J Membr Sci* 1997, 130, 219.
22. Ramaswamy, S.; Greenberg, A. R.; Krantz, W. B. *J Membr Sci* 2002, 210, 175.
23. Mehta, R. H.; Madsen, D. A.; Kalika, D. S. *J Membr Sci* 1995, 107, 93.
24. Mehta, R. H.; Kalika, D. S. *J Appl Polym Sci* 1997, 66, 2347.
25. Matsuyama, H.; Kakemizu, M.; Maki, T.; Tearamoto, M.; Mishima, K.; Matsuyama, K. *J Appl Polym Sci* 2002, 83, 1993.
26. Ding, H.; Zeng, Y.; Meng, X.; Tian, Y.; Shi, Y.; Jiao, Q.; Zhang, S. *J Appl Polym Sci* 2006, 102, 2959.
27. Ding, H.; Zhang, Q.; Tian, Y.; Shi, Y. Q.; Liu, B. Q. *J Appl Polym Sci* 2007, 104, 1523.
28. McGuire, K. S.; Lloyd, D. R.; Lim, G. B. A. *J Membr Sci* 1993, 79, 27.
29. Luo, B. Z.; Zhang, J.; Wang, X. L.; Zhou, Y.; Wen, J. Z. *Desalination* 2006, 192, 142.