

In Situ Cross-linked-PDMS/BPPO Membrane for the Recovery of Butanol by Pervaporation

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ABSTRACT: In this study, an *in situ* crosslinked polydimethylsiloxane/brominated polyphenylene oxide (*c*-PDMS/BPPO) membrane on ceramic tube has been prepared for the recovery of butanol by pervaporation. A series of BPPO with different bromide-substituted ratio were firstly synthesized through Wohl–Ziegler reaction. BPPO and PDMS were sequentially assembled and *in situ* crosslinked to form the final *c*-PDMS/BPPO membrane. The results of solid-state NMR and Differential Scanning Calorimeter demonstrated that the *c*-PDMS/BPPO copolymer has a crosslinking structure and the SEM result proved the coverage of ceramic tube by copolymer layer. The effects of preparation conditions including dipping time and bromide-substituted ratio of BPPO on the membrane performance were studied. The pervaporation experiments of butanol–water mixture indicated that the *c*-PDMS/BPPO membrane exhibited an acceptable flux of $220 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and high separation factor of 35 towards butanol, when the bromide-substituted ratio was 34 wt % and the dipping time was 1.33 h. Moreover, the *c*-PDMS/BPPO membrane performed excellent stability in an about 200 h continuous butanol recovery, as compared to the PDMS membrane. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40004.

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INTRODUCTION

Utilization of renewable biomass sources can significantly reduce the dependence on fossil resources.¹ As one of the particular interesting bio-alcohols, butanol has several advantages such as higher energy content, low vapor pressure, higher octane rating, and better adaptability for the existing gasoline supply system than bioethanol.^{2–6} However, butanol has a severe inhibition to the traditional fermentation process in making it, which results in its low productivity.¹ Therefore, a number of techniques for continuous butanol recovery have been proposed, such as vacuum distillation,⁷ solvent extraction,⁸ gas stripping,⁹ and membrane pervaporation,¹⁰ to make the fermentation process economically attractive, thereby enhance its yield. Currently, the application of membrane pervaporation has received great amount of attention in industry, including butanol recovery mentioned above due to its economical, safe, and clean behavior. In the membrane pervaporation, the property of the membrane material plays an important role in its separation performance.

Polydimethylsiloxane (PDMS) is the most representative pervaporation membrane material for the removal of alcohols from their aqueous solutions, due to its advantages of thermostability, hydrophobicity, low-surface tension, biocompatibility, and

commercial availability. However, the application of PDMS is limited for its bad membrane-forming property, poor cohesion, and low glass transition temperature, which induce the cumbersome curing process of PDMS and poor anti-swelling capacity.¹¹ Several modification strategies of assembling PDMS with other rigid polymers, such as blending, interpenetrating polymer network, block or graft copolymerization have been adopted to overcome these shortages of PDMS.^{12,13} For example, Nagase et al.¹⁴ modified PDMS by poly(1-phenyl-1-propyne) (PPP) to improve the anti-swelling capacity of PDMS. They prepared PPP/PDMS graft copolymer membranes by the metalation of PPP with *n*-butyl lithium, followed by treating with hexamethylcyclotrisiloxane and trimethylchlorosilane. The resulting membrane was used in the removal of organic solvents from their aqueous solutions. PPP chains are rigid and have a good anti-swelling capacity in its membrane and PDMS has good affinity with organic solvent, therefore, PPP/PDMS membrane showed excellent permselectivity towards ethanol, acetone, dioxane, acetonitrile, and pyridine. The similar work about the modification of PDMS including poly(dimethylsiloxane)-*block*-polymethylmethacrylate copolymer membranes,¹⁵ poly(dimethylsiloxane)-*graft*-polymethylmethacrylate copolymer membranes,¹⁶ and polydimethylsiloxane/polystyrene interpenetrating polymer network membranes have also been fabricated

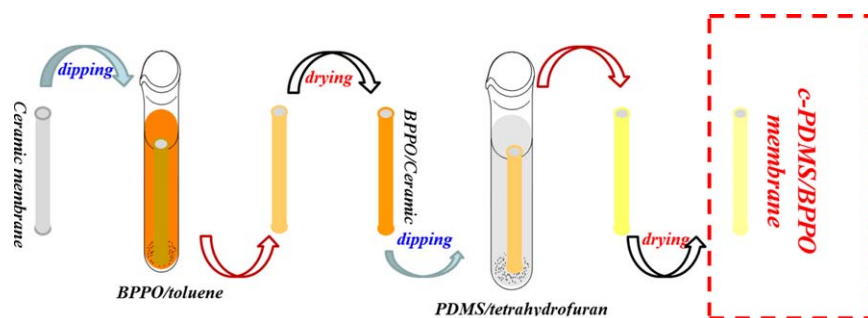


Figure 1. Detailed process for the preparation of c-PDMS/BPPO membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and used in separation of alcohol/water mixtures by pervaporation.¹³ These successful examples demonstrated that the bad membrane-forming property of PDMS and the poor anti-swelling capacity of PDMS membrane can be overcome by assembling PDMS with other rigid polymers.

On the other hand, brominated polyphenylene oxide (BPPO) is a thermoplastic polymer exhibiting a stable physical and chemistry properties.¹⁷ The BPPO could be used to improve the membrane-forming ability and anti-swelling capacity of PDMS by crosslinking with each other. In this study, a series of BPPO with different bromide-substituted ratio were first synthesized. BPPO and aminopropyl-terminated PDMS were sequentially assembled on ceramic tube and then *in situ* crosslinked to form the PDMS/BPPO membrane. The crosslinked-PDMS/BPPO (c-PDMS/BPPO) membrane was applied in the separation of butanol/water mixture by pervaporation, which exhibited a high flux of $220 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and separation factor of 35 towards butanol. The effects of preparation conditions such as dipping time and bromide-substituted ratio of BPPO on pervaporation performance were also studied. Moreover, the operation stability of c-PDMS/BPPO membrane was tested and compared with PDMS membrane.

EXPERIMENTAL

Materials

PDMS (KF-8012, dual-terminated by aminopropyl group) was purchased from Shin-Etsu Chemical Industry Company (Japan). Polyphenylene oxide (PPO; $M_w \approx 16,000 \text{ g/mol}$) was provided by Hao Di Chemical Trading Company (Kun Shan City, China). *N*-Bromosuccinimide (NBS) was provided by Capot Chemical (Shang Hai, China). All the chemicals, such as Carbon tetrachloride, methanol, toluene, tetrahydrofuran, ethanol, isopropanol, *n*-butyl alcohol, ethyl acetate, tetraethoxysilane (TEOS), and dibutyltin dilaurate (DBTDL), with analytical grade, were purchased from Beijing Chemical Company (Bei Jing, China).

Synthesis of BPPO

BPPO was synthesized via a Wohl-Ziegler reaction.¹⁸ In a typical experiment, about 10 g of PPO was added to a 500 mL reaction kettle containing 150 mL of carbon tetrachloride. After the solution had been refluxed for 15 min, 15 g of NBS was added in the reaction kettle over a 5 min period of time. And then the solution was irradiated with a 150 W flood lamp for 3 h, after

which the lamp and heat were removed and the solution was stirred at room temperature overnight. Finally, the solution was filtered to remove the solid-state by-product of succinimide, and then the product was precipitated by the addition of methanol. Similarly, a series of BPPO with different bromide-substituted ratio were synthesized by changing the illumination time.

Preparation of c-PDMS/BPPO Membrane

The c-PDMS/BPPO membrane was prepared by a procedure as shown in Figure 1. The Al_2O_3 ceramic tube (provided by Jiexi Lishun Company, Guangdong, China) with pore size of 0.1–0.2 μm was first dipped in a 10 wt % BPPO/toluene solution for 10 s, and was pulled by a Dip Coater (SYDC-200, San-Yan Experimental Equipment Company, Shanghai, China) with pulling rate of $5000 \mu\text{m s}^{-1}$. The resulting BPPO/ceramic composite membrane was then dried in a vacuum oven at 50°C for 48 h, and then it was dipped in a 10 wt % PDMS/tetrahydrofuran solution for a given period of time and further dried at 50°C for 48 h.

Characterizations

FTIR spectra were measured by a Nicolet 5DX instrument fourier transform infrared spectroscopy. The BPPO was dissolved in toluene and then the solution was cast onto KBr windows. The solvent was evaporated in vacuum oven at 60°C to obtain the specimen of films for the FTIR characterization. The BPPO was dissolved in chloroform-*d* to carry out its $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ on a Bruker Avance 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal reference. The solid-state $^{13}\text{C-NMR}$ of c-PDMS/BPPO membrane was measured on a Bruker AVANCE III NMR spectrometer. The bromide-substituted ratio of BPPO (mass fraction of bromine element) was confirmed by XRF (XRF-1800 X-Ray Fluorescence from SHIMADZU Corporation). The differential scanning calorimeter (DSC) analysis of the samples were carried out at a DSC-60 Differential Scanning Calorimetry from SHIMADZU Corporation. The carrier gas is nitrogen and the flow rate is 50 mL min^{-1} . The temperature rate is $10^\circ\text{C min}^{-1}$. Scanning electron microscopes (SEM; Hitachi-4700, Japan) was used to observe the top surface and cross section of the c-PDMS/BPPO membranes obtained. All the c-PDMS/BPPO membrane samples were dried under vacuum, fractured in liquid nitrogen, and gold-coated before SEM experiment. The crosslinking degree was tested by the Gel-fraction experiment,¹⁹ the c-PDMS/BPPO

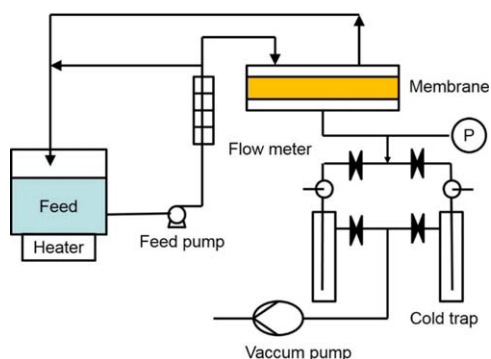


Figure 2. The experimental apparatus of pervaporation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membranes were respectively immersed in *n*-heptane and toluene solvent for 12 h at room temperature and then dried in a vacuum oven at 100°C. The crosslinking degree, which is equal to the gel fraction, was calculated using equation:

$$\text{Gel fraction (\%)} = [(W_a - W_c) / (W_0 - W_c)] \times 100,$$

Where W_c is the weight of ceramic membrane, W_0 and W_a are the weights of the *c*-PDMS/BPPO membrane before and after immersion into the two solvents, respectively.

Pervaporation Experiments

The pervaporation apparatus used in this study is shown in Figure 2. The membrane was installed in a glass pervaporation cell with an effective area of 49 cm². The feed was circulated through the pervaporation cell by a peristaltic pump. The downstream pressure was maintained at approximately 0.1 kPa by a vacuum pump. Permeate was collected through the condensation by liquid nitrogen. All the feeds are butanol/water mixture with a ratio of 1 : 20 (5 wt % of the butanol), and the operating temperature is 40°C. The feed and permeate compositions were analyzed by gas chromatography (GC7900, Tianmei, Shanghai, China), when the operating temperatures were 160°C in injector, 150°C in column, and 160°C in detector. The separation factor was calculated from the quotient of the weight ratio of butanol and water in the permeate, $Y_{\text{butanol}}/Y_{\text{water}}$, and in the feed, $X_{\text{butanol}}/X_{\text{water}}$: $\alpha = \frac{Y_{\text{butanol}}/Y_{\text{water}}}{X_{\text{butanol}}/X_{\text{water}}}$. The flux was calculated through weight of permeate (W) at unit time (t) and unit area (A): $J = \frac{W}{t \cdot A}$, g·m⁻²·h⁻¹.

RESULTS AND DISCUSSION

The Chemical Structure of BPPO

As shown in Figure 3, BPPO was synthesized via a Wohl–Ziegler reaction of PPO with radical mechanism. In Wohl–Ziegler reaction, succinimide and bromine free radicals were generated by NBS in the presence of illumination. The succinimide free radicals could capture one methyl hydrogen atom of benzyl and simultaneously the bromine free radicals combine with the resulting methylene to form bromide-substituted polyphenylene oxide.

The FTIR spectra of the PPO and BPPO are shown in Figure 4. Compared with that of PPO, the FTIR spectrum of

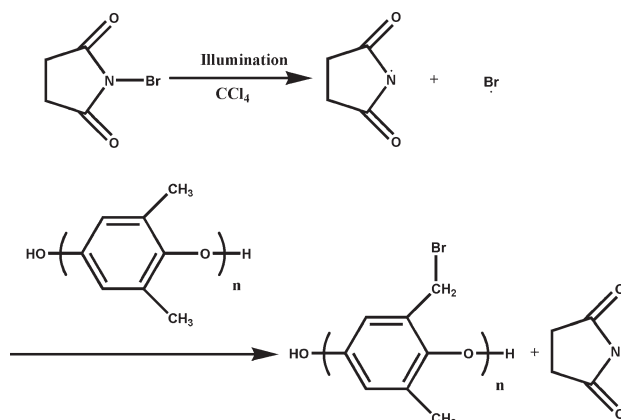


Figure 3. The mechanism of benzylic bromination.

BPPO shows a new peak appeared at 650 cm⁻¹ besides of that of PPO, which is ascribed to the characteristic peak of brominated aliphatic hydrocarbons group.²⁰ The result of FTIR spectra showed that the bromination of PPO is achieved.

Additionally, the NMR results further demonstrated the structure of BPPO. Appearance of the characteristic peaks of hydrogen atoms at 2.130 and 4.371 ppm [Figure 5(a)], and those for carbon atoms at 16.88 and 26.77 ppm [Figure 5(b)] on benzylic methyl group and methylene, respectively shows the formation of BPPO by the Wohl–Ziegler reaction.

The Effect of Illumination Time on Bromide-substituted Ratio of BPPO

Figure 6 shows the X-ray fluorescence results of bromide-substituted ratio of BPPO prepared with different illumination time. In the bromination reaction of this study, the amount of bromosuccinimide was excess. When the illumination time is 0.5 h, the bromide-substituted ratio of BPPO is about 23 wt %. When the illumination time increases to 6 h, the bromide-substituted ratio of BPPO closes to 78 wt %. Theoretically, the illumination time can control the amount of generated bromine free radicals, which determine the final bromide-substitution.

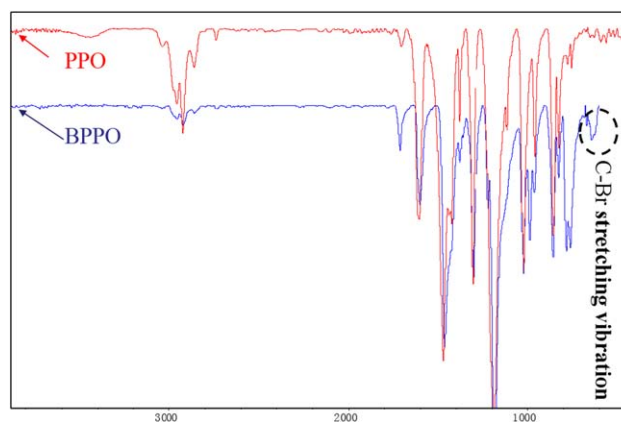


Figure 4. Experimental results from FTIR spectra of PPO and BPPO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

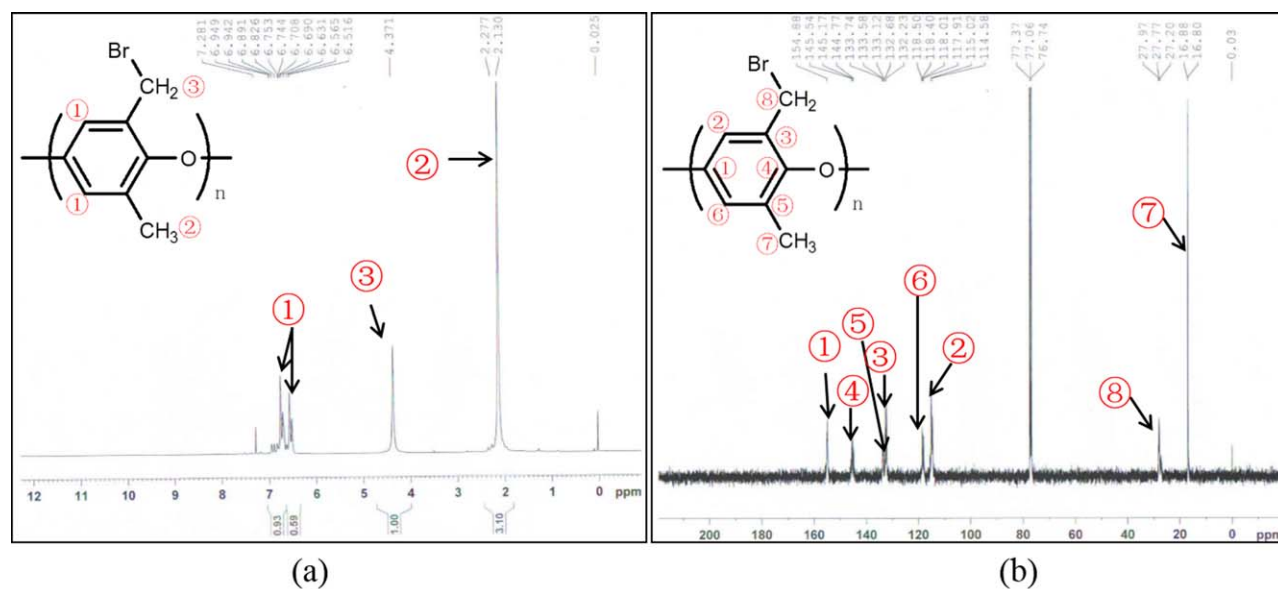


Figure 5. The NMR spectra of BPPO (a) ^1H -NMR and (b) ^{13}C -NMR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The bromide-substituted ratio of BPPO could thus be controlled by adjusting the illumination time.

The Formation of c-PDMS/BPPO Membrane

The BPPO and aminopropyl-terminated PDMS were cross-linked through the reaction between aminopropyl group and bromine atom. As shown in Figure 7, based on the reaction of amino group with bromine, a BPPO chain could graft several PDMS chains, and a PDMS chain could link with two BPPO chains. Thus, the resulting c-PDMS/BPPO membrane has a network structure, being composed of crosslinked-PDMS/BPPO copolymers. On the other hand, the ceramic tube has been used as the substrate, which is resistant to organic solvent (better than other organic substrates). Moreover, the BPPO/ceramic composite membrane can swell when dipping in PDMS/tetrahydrofuran solution, which results in the penetration of PDMS into the BPPO layer. The crosslinking reaction happened thus when the dipped-BPPO/ceramic composite membrane was heated in an oven at 50°C and the c-PDMS/BPPO membrane formed.

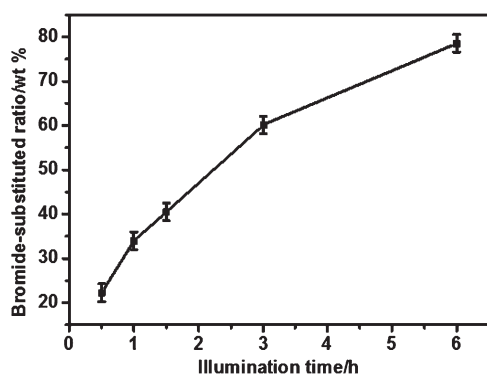


Figure 6. The effect of illumination time on bromide-substituted ratio of BPPO.

The Solid-State NMR, DSC, and SEM Characterizations of c-PDMS/BPPO Membrane

As shown in Figure 8, the peak at $\delta = 5.53$ ppm can be ascribed to the carbon atom of methyl in the side group of PDMS. The peaks at $\delta = 31.59$ and 37.33 ppm can be ascribed to the carbon atoms of $-\text{CH}_2\text{Br}$ in BPPO, which means that there are some unreacted $-\text{Br}$ existed in the membrane. Moreover, several new peaks arise in the range of 60–100 ppm, which should be corresponded to the carbon atoms of $-\text{CH}_2-\text{NH}-\text{CH}_2$, indicating the occurrence of the crosslinking reaction.

The DSC analysis was also conducted for further demonstrating the formation of c-PDMS/BPPO copolymer. As shown in Figure 9, the glass transition peak of BPPO appeared at 220°C . And the characteristic peaks of PDMS appeared at -128 , -95 , and -65°C , which corresponding to glass transition peak, cold crystallization peak, and melting peak, respectively. In the DSC curve of c-PDMS/BPPO copolymer, the peaks at -127 , -95 , and -58°C were basically corresponding to the characteristic peaks of PDMS segments. Moreover, there was a new peak appeared at 30°C , corresponding to the glass transition peak of BPPO segment. The change of the glass transition peak of BPPO can attributed to the substitution of BPPO by multiple PDMS chains. Therefore, the crosslinking reaction between PDMS and BPPO is definitely happened.

Furthermore, a series of c-PDMS/BPPO membranes were fabricated by changing the dipping time of BPPO/ceramic composite membrane in PDMS/tetrahydrofuran solution, when keeping the bromide content of BPPO at 34 wt %. The surface and cross-section morphologies of these membranes were characterized by SEM. As can be seen in Figure 10, the surface of ceramic tube is porous and the surface of these three c-PDMS/BPPO membranes are dense, due to the surface coverage of ceramic tube by the polymer layer. The thickness of c-PDMS/

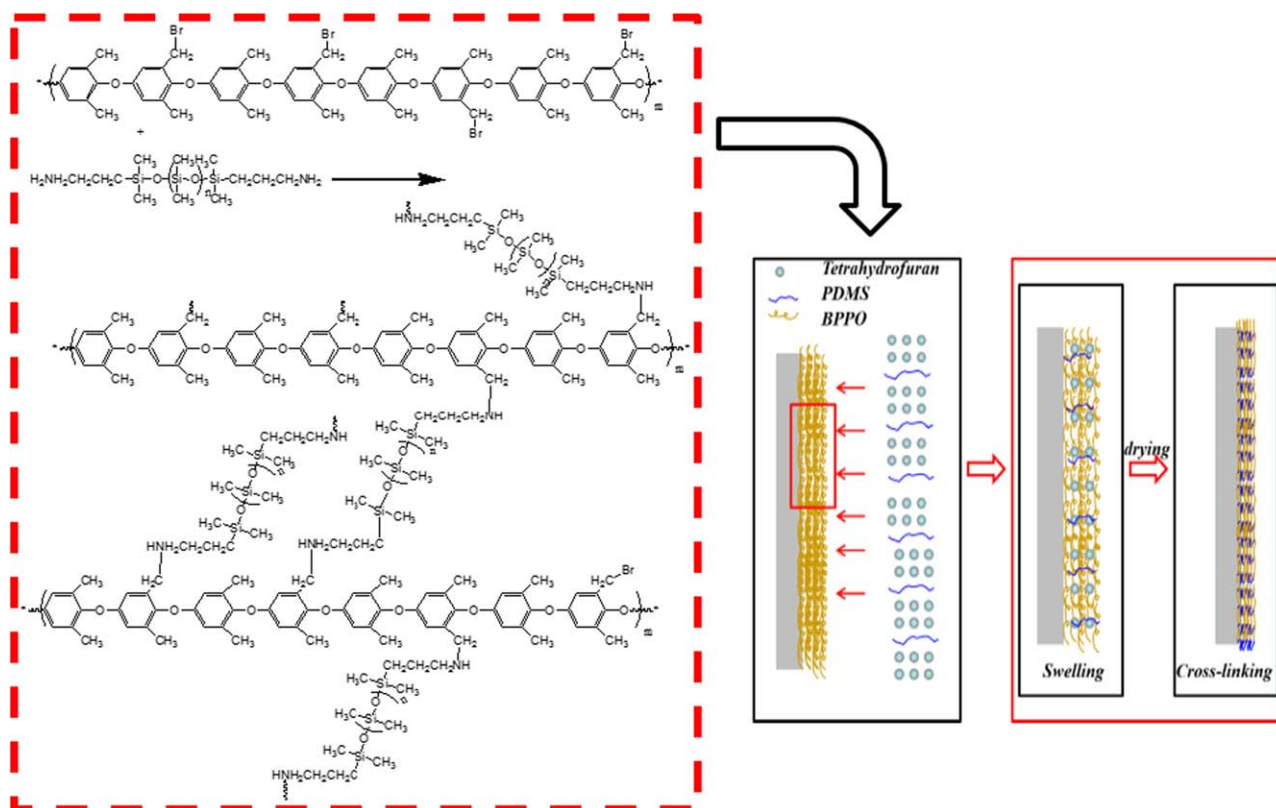


Figure 7. The mechanism of crosslinking reaction between α,ω -diaminopropyl PDMS and BPPO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

BPPO layer increased from 6 to 11 μm when the dipping time increased from 1.33 to 36 h. It is because that with the extension of dipping time, more PDMS penetrated into the BPPO layer, thereby increasing its thickness.

The Effects of Dipping Time and Bromide-substituted Ratio of BPPO on the Pervaporation Performance of *c*-PDMS/BPPO Membrane towards Butanol Recovery

The effect of dipping time on pervaporation performance of resulting *c*-PDMS/BPPO membrane was studied. As shown in Figure 11, the separation factor of *c*-PDMS/BPPO membrane decreased from 35 to 18 while the flux increased from 220 to 450

$\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, when the dipping time increased from 1.33 to 36 h. This is because as the increase of dipping time, the PDMS content in polymer layer increased and the crosslinking degree decreased, which led to more uncrosslinked PDMS existed in the polymer layer and the mass transfer resistance decreased. The effect of dipping time on crosslinking degree of *c*-PDMS/BPPO membrane was also studied to support this viewpoint. As shown in Figure 12, when the dipping time is 1.33 h, the crosslinking degree was 97.34%. As the dipping time increased from 1.33 to

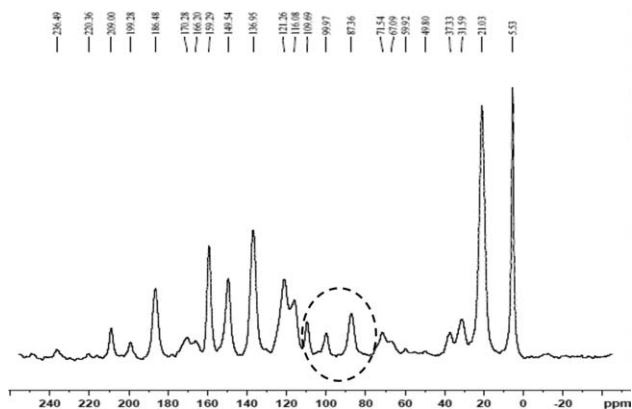


Figure 8. The solid-state ^{13}C -NMR of *c*-PDMS/BPPO membrane.

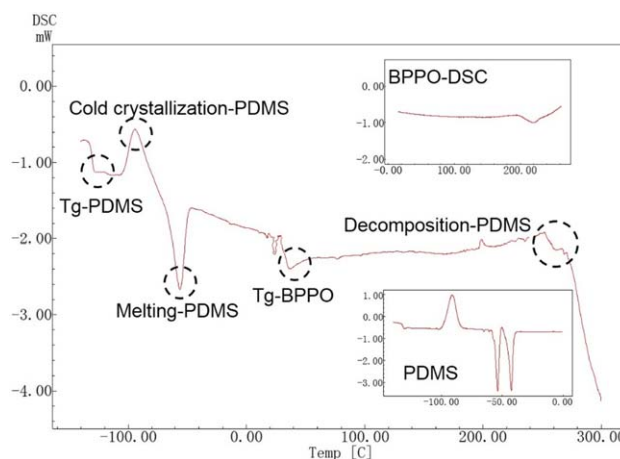


Figure 9. The DSC analysis of *c*-PDMS/BPPO copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

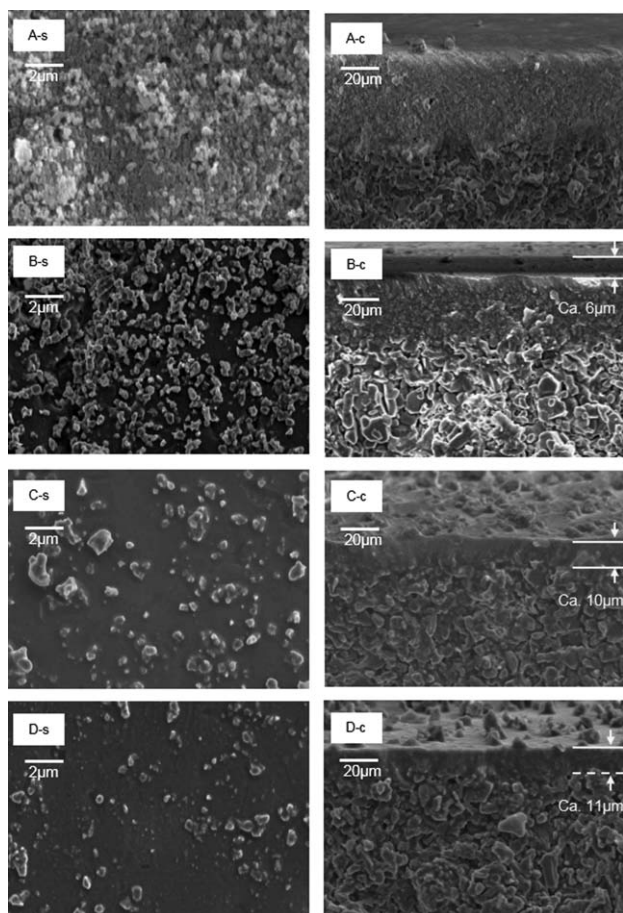


Figure 10. The surface and cross-section morphologies of ceramic-supported c-PDMS/BPPO membrane prepared with different dipping time in PDMS/tetrahydrofuran solution, (A) ceramic membrane; (B) 1.33 h; (C) 10 h; (D) 36 h. s: surface; c: cross section. The mark layer in cross section, (A) Al₂O₃ layer, 40 μm; (B) c-PDMS/BPPO layer, 6 μm; (C) c-PDMS/BPPO layer, 10 μm; (D) c-PDMS/BPPO layer, 11 μm.

36 h, the crosslinking degree decreased from 97.34% to 74.79%. Therefore, the crosslinking degree of c-PDMS/BPPO membrane decreased as the increase of dipping time.

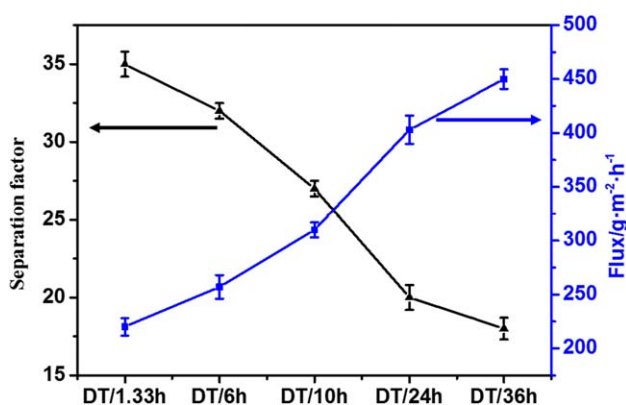


Figure 11. The effect of dipping time in PDMS solution (DT) on pervaporation performance of c-PDMS/BPPO membranes. All the c-PDMS/BPPO membranes were prepared when the bromide-substituted ratio of BPPO is 34 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

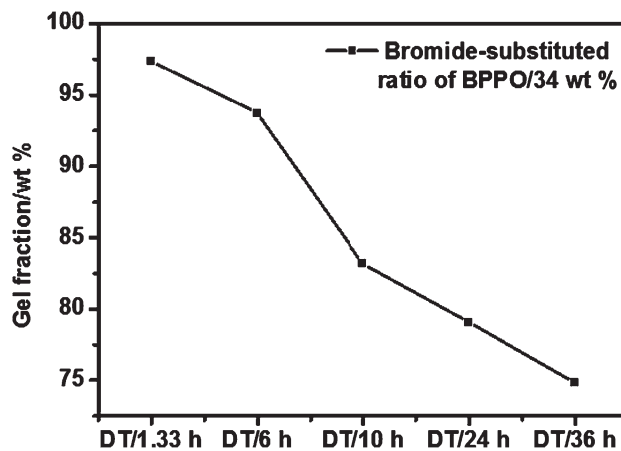


Figure 12. The effect of dipping time in PDMS solution on crosslinking degree of c-PDMS/BPPO membrane.

The effect of bromide-substituted ratio of BPPO on pervaporation performance of c-PDMS/BPPO membrane is also explored. As shown in Figure 13, the separation factor showed a trend of first increase and then decrease. For example, the separation factors on the bromide-substituted ratio of 22 and 34 wt % were 25 and 35, respectively. This suggested that the PDMS cannot be completely crosslinked by BPPO in the case of the bromide-substituted ratio being 22 wt %. When the bromide-substituted ratio of BPPO increased to 34 wt %, a high crosslinking degree c-PDMS/BPPO copolymer formed. However, the separation factor decreased from 35 to 18 while the flux increased from 220 to 479 g·m⁻²·h⁻¹ when bromide-substituted ratio increase from 34 to 78.53 wt %. This indicated that excessive bromine groups would not benefit for the pervaporation performance of the membrane. When the bromide-substituted ratio is lower than 34 wt %, PDMS cannot be crosslinked completely, which result in the decrease of crosslinking degree. However, when the bromide-substituted ratio is higher than 34 wt %, the crosslinking degree maintained in a constant level as the increase of

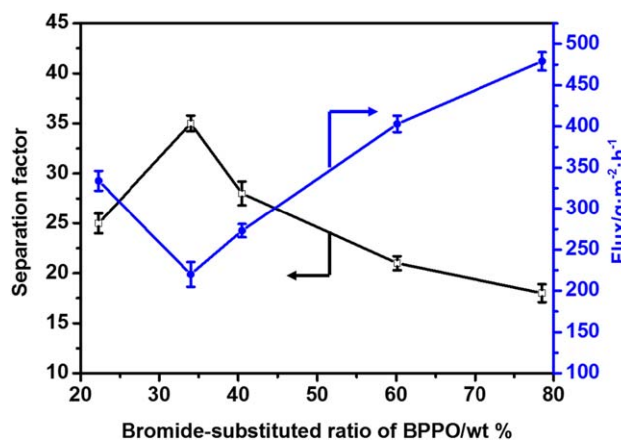


Figure 13. The effect of bromide-substituted ratio of BPPO on pervaporation performance of c-PDMS/BPPO membranes towards butanol/water separation. All the c-PDMS/BPPO membranes were prepared when the dipping time in PDMS solution is 1.33 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bromide-substituted ratio (Figure 14), and meanwhile, the excessive bromine groups enhanced the polarity of c-PDMS/BPPO membrane, which results in the decrease of affinity between membrane and butanol.

In order to investigate the optimum pervaporation performance of c-PDMS/BPPO membrane, series of experiments were designed. Figure 15 shows the comparison of pervaporation performance of c-PDMS/BPPO membranes prepared by different dipping time and bromide-substituted ratio of BPPO. As shown in Figure 15, when the bromide-substituted ratio of BPPO was 22.27 wt %, the separation factor showed a decrease and the flux showed an increase because of the incompletely crosslinking. When the bromide-substituted ratio of BPPO was 40.49 wt %, the separation factor showed a trend of first increase and then decrease as the increase of dipping time, and the preferable separation factor of 33 appeared when the dipping time was 6 h due to the completely crosslinking of the two polymers. As the

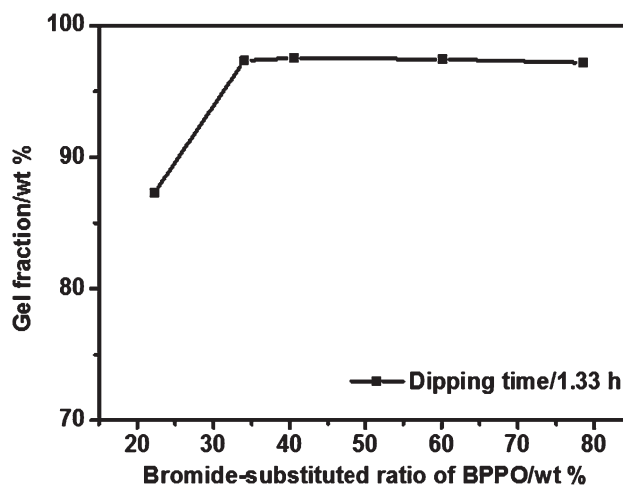


Figure 14. The effect of bromide-substituted ratio of BPPO on crosslinking degree of c-PDMS/BPPO membrane.

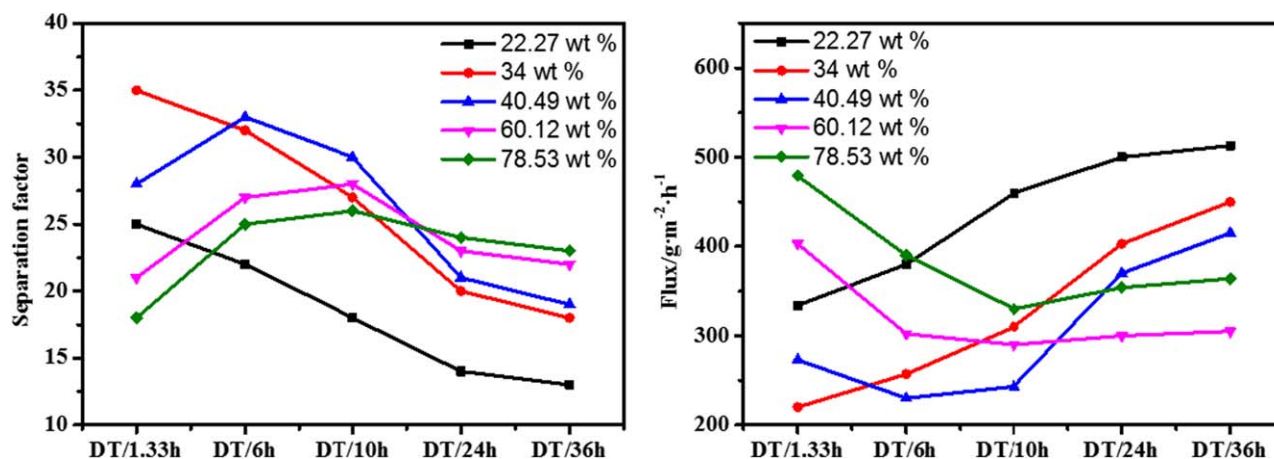


Figure 15. Comparison of pervaporation performance of c-PDMS/BPPO membranes prepared by different dipping time and bromide-substituted ratio of BPPO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

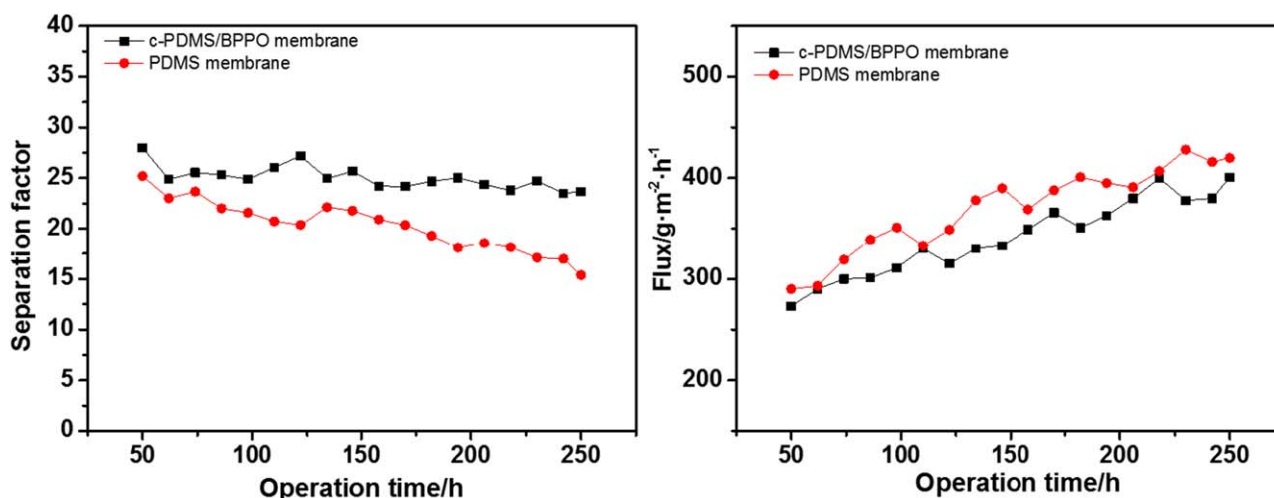


Figure 16. Comparison of operation stability of c-PDMS/BPPO and PDMS membrane in a period of 200 h. Preparation conditions of c-PDMS/BPPO membrane: dipping time—1.33 h; bromide-substituted ratio—40.49 wt %. Preparation conditions of PDMS membrane: casting solution—PDMS/heptane solution with 1 wt % of PDMS, 0.1 wt % of TEOS, and 0.005 wt % of DBTDL; dipping time—10 s; pulling rate—5000 $\mu\text{m}\cdot\text{s}^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Comparison of Different Membranes in Literature and c-PDMS/BPPO Membrane

Type of membrane	Feed concentration	Temperature (°C)	Total flux (g·m ⁻² ·h ⁻¹)	Separation factor	References
PDMS/ceramic composite membrane	1 wt %	40	457.4	26.1	21
PDMS/ceramic composite membrane	4 wt %	40	720	23.2	21
Poly(ether- <i>block</i> -amide)	0.4 wt %	40	250	20	22
Poly(ether- <i>block</i> -amide)	0.4 wt %	60	490	32	22
Perv. 2200	11 g/L	33	33	10	23
5% ZSM-5-Poly(ether- <i>block</i> -amide)	0.5	35	200	21.5	24
PTMSP	0.002	25	60	52	25
c-PDMS/BPPO ^a	5	40	220	35	This study

All the data were obtained when the feed was simulated butanol/water solution.

^aPreparation conditions: dipping time, 1.33 h; bromide-substituted ratio, 40.49 wt %.

dipping time increased, the crosslinking degree decreased and the separation factor decreased from 33 to 19. As same as 40.49 wt % of bromide-substituted ratio of BPPO, the c-PDMS/BPPO membrane showed the same variation tendency of separation factor when the bromide-substituted ratio of BPPO was 60.12 and 78.53 wt %, respectively. According to the results of experiments, the optimum pervaporation performance of c-PDMS/BPPO membrane were 35 of separation factor and 220 g·m⁻²·h⁻¹ of flux, when the dipping time was 1.33 h and the bromide-substituted ratio of BPPO was 34 wt %.

Stability of c-PDMS/BPPO Membrane in Butanol Recovery

In order to investigate the stability of c-PDMS/BPPO membrane in butanol/water mixture, the continuous pervaporation experiments of c-PDMS/BPPO membrane and PDMS membrane in a period of 200 h were tested and compared. As shown in Figure 16, as the operating time reach to 200 h, the separation factor of c-PDMS/BPPO membrane decreased slightly from 28 to 23.67 and that of PDMS membrane was down from 22.45 to 15.38, while the flux of both membranes increased simultaneously. The decline of separation factor could be attributed to the swelling of the membrane. This observation suggested also that the anti-swelling capacity of c-PDMS/BPPO is better than that of PDMS membrane. Although both c-PDMS/BPPO membrane and PDMS membrane have crosslinking structures, the c-PDMS/BPPO membrane exhibited more stable pervaporation performance than that of PDMS membrane because of the existence of rigid-BPPO segment in the former.

Comparison of Reported Membranes with c-PDMS/BPPO Membrane

The recovery of butanol from its aqueous solution by pervaporation has been studied by several other groups, Table I gives a comparison of the pervaporation performance of reported membranes in literature with our c-PDMS/BPPO membrane in this work. Liu et al.²¹ studied the pervaporation performance of PDMS/ceramic composite membrane. The effects of operating conditions on the membrane pervaporation performance were investigated. The PDMS/ceramic composite membrane showed a flux of 720 g·m⁻²·h⁻¹ with the separation factor of 23.2 when the feed concentration was 4 wt % and the operating tempera-

ture was 40°C. Furthermore, the PDMS/ceramic composite membrane showed a decrease of separation factor and an increase of flux with the increase of butanol concentration in the feed. In this study, c-PDMS/BPPO membrane has a total flux of 220 g·m⁻²·h⁻¹ and a separation factor of 35 at 40°C for a 5 wt % butanol in water. With addition of BPPO, the c-PDMS/BPPO membrane performed an enhanced separation factor while the flux maintained in an acceptable level. With observed high separation performance, together with the benefits of easy membrane fabrication, our c-PDMS/BPPO membrane is a promising candidate for the application in practical butanol recovery.

CONCLUSIONS

In conclusion, Wohl-Ziegler reaction was used to synthesize series of BPPO and their bromide-substituted ratio was controlled by adjusting the illumination time. The *in situ* crosslinked PDMS/BPPO membrane on ceramic tube was successfully prepared by sequentially assembling BPPO and aminopropyl-terminated PDMS. The resulting c-PDMS/BPPO membrane was applied in the recovery of butanol from its aqueous solution by pervaporation. The results showed that as the increase of dipping time in membrane fabrication, the separation factor showed a trend of decrease, while the flux showed a trend of increase. As the increase of bromide-substituted ratio of BPPO, the separation factor firstly increased and then decreased. When the dipping time was fixed 1.33 h and the bromide-substituted ratio of BPPO was 34 wt %, the c-PDMS/BPPO membrane exhibited a high separation factor of 35 and an acceptable flux of 220 g·m⁻²·h⁻¹. It is clear that BPPO enhanced the membrane-forming ability and anti-swelling capacity of PDMS, and the c-PDMS/BPPO membrane achieved a more stable pervaporation performance in butanol/water mixtures than that of PDMS membrane even in a period of 200 h. In addition, this study demonstrated that the *in situ* crosslinking method is feasible in the preparation of copolymer membrane, taking advantage of combining the synthesis of copolymer, and process of membrane-forming.

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