



New fluorinated siloxane-imide block copolymer membranes for application in organophilic pervaporation

Xue Jiang^a, Jian Gu^a, Yan Shen^b, Shugen Wang^a, Xiuzhi Tian^{a,*}

^a College of Textiles & Clothing, Key Laboratory of Eco-Textile, Ministry of Education, Jiangnan University, Wuxi 214122, PR China

^b Jiangsu Environmental Monitoring Center, Nanjing, 210036, PR China

ARTICLE INFO

Article history:

Received 6 March 2010

Received in revised form 10 July 2010

Accepted 13 July 2010

Available online 8 August 2010

Keywords:

Organophilic pervaporation

Membrane

Siloxane-imide block copolymers

ABSTRACT

New siloxane-imide block copolymers (PSI) were designed and synthesized from 2,2'-bis[4-(4-aminophenoxy) phenyl] hexafluoropropane (BDAF), 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and diamine-terminated poly(dimethyl siloxane)s (SIDA, average molecular weight = 900, 1680 and 4600) for application in organophilic pervaporation. The chemical structure of the copolymer was confirmed by FT-IR and ¹H NMR spectra. In addition, its good thermal stability and micro-phase separated amorphous structure were confirmed by TGA, DSC, WXR and AFM analyses. The content of siloxane blocks in the copolymer decreased, and thus the micro-phase separation became more serious with decreasing the molecular weight of SIDA used for copolymerization. The PSI membrane prepared from the lowest molecular weight of SIDA (900) was fragile. The siloxane blocks in the copolymer mainly contributed to the pervaporation properties of the copolymer membranes. Their increase made an improvement of the separation properties including permeate flux and selectivity. But simultaneously, it would lead to a drop of mechanical strength of the corresponding copolymer membrane.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Trace volatile organic compounds (VOCs) i.e. toluene, trichloroethylene, chloroform and phenol, which are toxic or even carcinogenic, are always existing in several industrial wastewaters including chemistry, pharmacy, electron, petroleum, printing, dope and textile. Removal of such VOCs from wastewater is a long-standing topic for environmental protection. Organophilic pervaporation (O-PV) using hydrophobic membranes has been demonstrated to be potentially a remediation for such applications. Relative to other conventional technologies, such as air stripping and adsorption with activated carbon, it has obvious advantages, especially high efficiency, energy-saving and eco-friendly aspects, and simple equipment and operation [1]. Nevertheless, to the best of our knowledge no industrial breakthrough has yet been made. One of the main restrictions relates to a lack of membranes providing the best combination of properties with respect to flux, selectivity and stability for the removal of most organics [2].

In fact, membrane, especially the polymeric one is the core of a pervaporation process and its separation properties are depended on the nature of the corresponding membrane material. Hereby, design and development of new membrane materials are a key to realize the industrial applications of O-PV.

So far, very limited materials are used for O-PV, including poly(dimethylsiloxane)s (PDMS), polyether-block-polyamides (PEBA), polyurethane (PUR), nitrile-butadiene copolymer (NBR), poly[bis(phenoxy)phosphazene] (BPOP), styrene-butadiene (SBS), poly[bis(phenoxy)phosphazene] (BPOP), ethylene propylene diene rubber (EPDM), poly(1-trimethylsilyl-1-propyne) (PTMSP), polyvinylidene fluoride (PVDF), poly(vinylidene fluoride-co-hexafluoropropene) (P(VDF-co-HFP)), etc. [3–6]. Among them, PDMS are the most widely used membrane material for O-PV due to their high permeating flux and moderate selectivity. However, the scope of their applications is somehow limited by two factors. Firstly, PDMS have intrinsic bad mechanical strength, poor film-forming ability and hence need to be cross-linked, leading either to rather thick films or to composite membranes. Secondly, it is difficult to tailor their chemical-physical properties for a given separation [7]. As a result, the modification of PDMS to overcome the above mentioned shortcomings is an effective way to realize the industrial applications of PDMS membranes for O-PV. Currently, graft or block copolymerization seems to be the most hopeful method in this area [7–11], although apart from which dip-coating [12–14], physical filling [15–20], alteration of molecular backbone [21,22], and incorporation of functionalized groups [23,24] were also attractive. That is, by means of graft or block copolymerization, the aimed membrane material with comprehensively good properties containing penetrability, selectivity, membrane-forming ability, chemical stability and thermal stability should be obtained. And accordingly the choice of segments to be grafted or blocked with PDMS is significantly important.

* Corresponding author. Tel./fax: +86 510 85919920.
E-mail address: xzhtian@yahoo.com.cn (X. Tian).

Aromatic polyimides (PI) are well known engineering plastics with excellent thermal and mechanical properties [25]. Otherwise, multiple PI can be gained based on various diamine and dianhydride. Therefore, a new membrane material with high separation properties can be obtained for the aimed separating system by tailoring the PI structure. Nevertheless, PI membranes can not be directly applied for O-PV due to their chain rigidity. The fluorinated PI synthesized from fluorine-containing (especially with bulky side groups, CF_3) monomers are suitable membrane materials for O-PV because of their unique hydrophobicity and relatively high free volume, which are important factors governing preferential sorption and diffusion of organics over water.

As discussed above, the reciprocally complementary advantages of each other will be acquired by rod-coil block copolymerization between PDMS and fluorinated PI. Namely, copolymers with alternating blocks of siloxane and fluorinated imide (PSI) have the potential for improving the mechanical strength of conventional PDMS membranes without sacrificing many separation properties. Whereas, studies on the fluorinated PI and its related polymers used in O-PV have rarely been reported [7–11,26].

In this work, new fluorinated PSI were synthesized from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF) and diamine-terminated poly(dimethyl siloxane) (SIDA) by condensation polymerization. They were firstly reported to be used in O-PV of chlorinated organics from water. Particularly, correlation between their structural parameters which were characterized by FT-IR, ^1H NMR, wide-angle X-ray diffraction (WAXD), DSC and the pervaporation properties were evaluated.

2. Experimental

2.1. Materials

4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) (99%) was purchased from Fluro Chemical Co. and was re-crystallized

from acetic anhydride before use. 2,2'-Bis[4-(4-amino-phenoxy)phenyl]hexafluoropropane (BDAF) (97%) was purchased Fluro Chemical Co. and dried before use. Diamine-terminated poly(dimethyl siloxane)s (SIDA, average molecule weight = 900, 1680, 4600) were obtained from the Shinetsu Co. (Japan). Tetrahydrofuran (THF) was distilled from molten sodium using benzophenone as an indicator until a dark blue color was obtained. The N-methylpyrrolidinone (NMP) used was distilled under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). All the drying procedures were performed under dry nitrogen gas. Trichloroethylene (TCE), spectroscopy grade, was purchased from Shanghai Chemical Corporation. Other reagents were used as received without purification.

2.2. Copolymer synthesis

Fig. 1 outlined the synthetic route to new PSI. The polymerization was carried out in flowing nitrogen, and equimolar diamine and dianhydride were used. Namely, the mol ratio of BDAF/6FDA/SIDA was 1/2/1. Three SIDA with different molecular weights (900, 1680, 4600) were used. Since SIDA did not dissolve in NMP, a co-solvent system was essential. NMP and THF were used as the co-solvent in a weight ratio of 1/1. The polymerization procedure was as follows. The THF solution of the appropriate amount of SIDA was added dropwise to a magnetically stirred NMP solution of excess 6FDA under dry nitrogen. The reaction proceeded at room temperature for 24 h and then the requisite amount of BDAF was added. The reaction was continued for another 24 h to yield the precursor, poly(siloxane amic acid), a solution with a solid content of 15 wt.%.

Thereafter, the chemical imidization was carried out with a prescribed volume of pyridine and acetic anhydride (1/1) at room temperature for 48 h. Finally, the reaction mixture was then poured into ethanol solution. The precipitate was collected by filtration and dried in vacuum at 60 °C for 24 h.

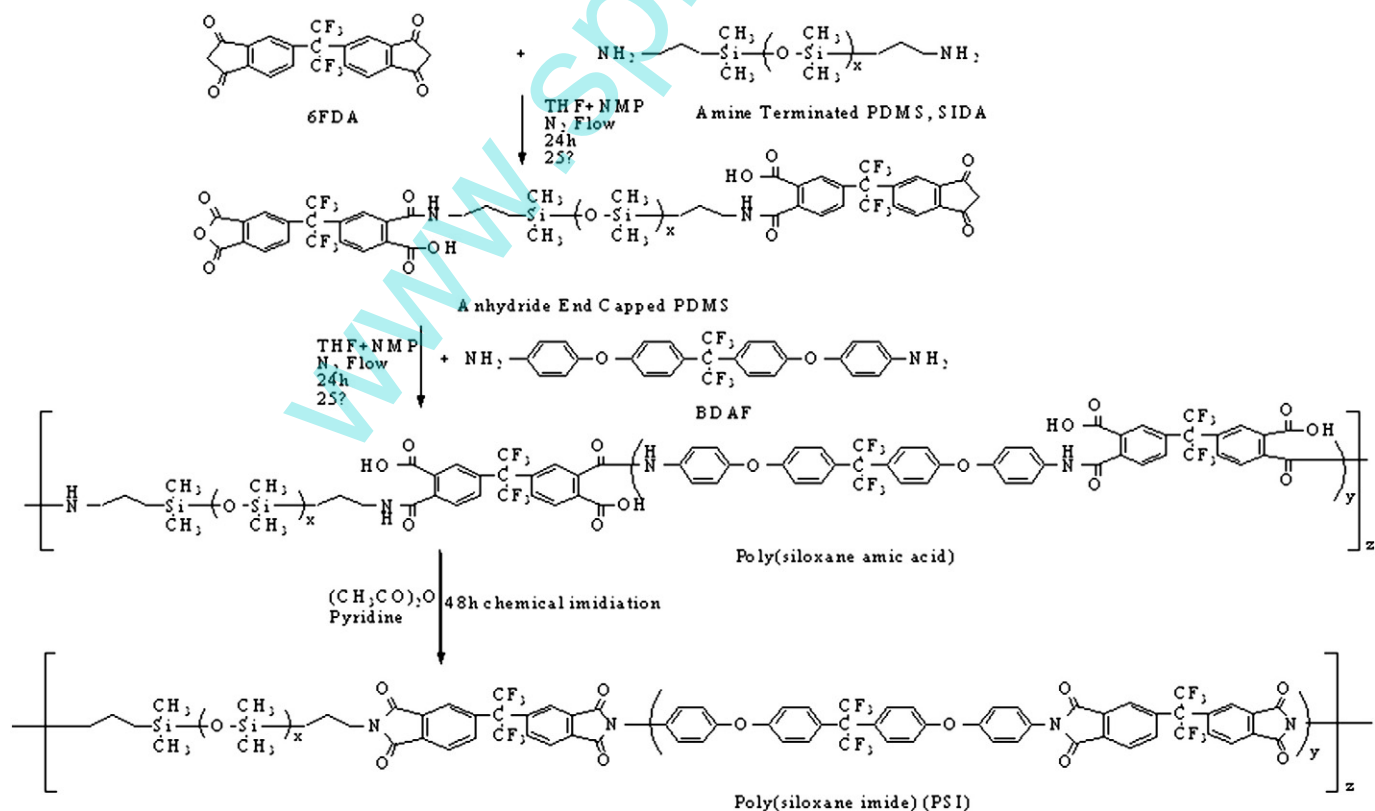


Fig. 1. Schematic route to synthesizing the PSI.

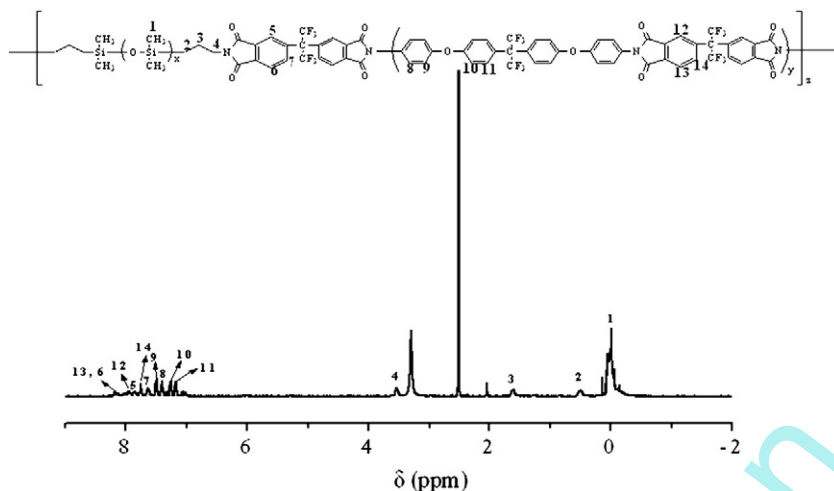


Fig. 2. ^1H NMR spectrum of the PSI.

The fluorinated PSI synthesized from the three different molecular weights of SIDA (900, 1680, 4600) were abbreviated as PSI-1, PSI-2 and PSI-3, respectively.

2.3. Copolymer characterization

^1H NMR spectrum was carried on a Bruker AMX400 NMR spectrometer using DMSO- d_6 as a solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 470 spectrometer in the range of 400–4000 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1} . Gel permeation chromatography (GPC) analysis was performed using THF as eluant. Thermogravimetric analyses (TGA) was carried out in a TA® DSC Q100 calorimeter with a heating rate of 10 $^\circ\text{C}/\text{min}$ in N_2 . DSC tests were carried out by using of a TA® DSC Q600 analyzing system connected to a cooling system. Wide-angle X-ray diffraction (WAXD) patterns were recorded on an X-ray Diffractometer (Model D/MAX-IIIB).

2.4. Membrane preparation and characterization

The synthesized PSI were dissolved in NMP at 10 wt.%. The homogeneous membranes were prepared by casting the copolymer solution onto the glass plate and vacuum-dried at 60 $^\circ\text{C}$. The surface morphologies of the copolymer membranes were examined using atomic force microscopy (AFM). The AFM used in this study was a CSPM 4000 provided by Benyuan Co., LTD. Scanning was carried out in a contact mode AFM with a silicon cantilever and all images were obtained at ambient conditions. Break strength of the fabricated membrane was tested on an AG-1 (Japan) electronic serimeter.

2.5. Pervaporation experiments

A traditional pervaporation apparatus was used in this study [26]. The circular flat membrane was clamped into a sealed stainless steel test cell above a porous sintered metal support with a viton 'o' ring arrangement forming a leak free seal, giving a pervaporation area of 28.26 cm^2 . The cell was filled with the feed solution and stirred at 1000 rpm by a magnetic agitator. The cell temperature was controlled at 25 ± 0.5 $^\circ\text{C}$ with a thermocouple and electronic temperature control system. A vacuum pump maintained the downstream pressure at 300–400 Pa. The permeate was condensed and frozen with the cold trap, which was cooled with liquid nitrogen. The permeation rate was determined by measuring the weight of the permeate. The compositions of the

feed solutions, permeates were measured by gas chromatography (GC, China Chromatography 120).

Permeate flux, J , was calculated using the expression

$$J(\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}) = \frac{Q}{AT} \quad (1)$$

where Q (g) was the total amount of permeate passed through the membrane during an experimental time interval T (h) at a steady state and A (m^2) was the effective area of the membrane.

The separation factor was calculated from

$$\alpha_{O/W} = \frac{Y_O/Y_W}{X_O/X_W} \quad (2)$$

where Y_O , X_O were the weight fractions of TCE in permeate and feed, respectively. And Y_W , X_W were the weight fractions of water in permeate and feed, respectively.

3. Results and discussion

3.1. Copolymer characterization

The PSI was prepared by the conventional two-step polymerization method, involving ring-opening polyaddition forming poly(siloxane amic acid) and subsequently chemical cyclodehydration forming poly(siloxane imide). ^1H NMR spectrum of the PSI was presented in Fig. 2.

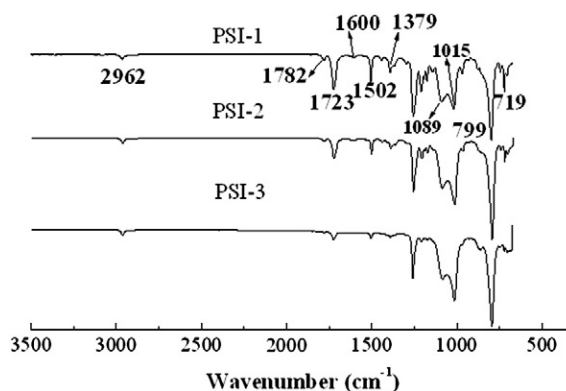


Fig. 3. FT-IR spectra of the PSI.

Table 1

Some parameters of the PSI obtained from GPC, TGA, DSC, WXRd and membrane-forming characterizations.

PSI (abbreviation)	SIDA \bar{M}_n	M_n	M_w	Polydispersity	T, (°C)	T_{g1} (°C)	T_{g2} (°C)	d-spacing (Å)	Membrane quality
PSI-1	900	24,267	31,384	1.29	446.85	-99.07	153.22	6.50	Fragile
PSI-2	1680	21,401	26,708	1.25	442.14	-114.32	168.30	7.05	Good
PSI-3	4600	27,136	37,663	1.39	439.92	-122.45	170.36	7.27	Good

As expected, the aromatic protons were detected around 6.5–8.5 ppm (H_5 – H_{14}), depending on the position in the aromatic ring. The characteristic peak at 3.6 ppm corresponded to the protons H_4 of the methylene group adjacent to the terminated imide ring. And two other characteristic peaks at 1.6 ppm and 0.6 ppm corresponded to the protons H_3 and H_2 of the methylene groups from the siloxane blocks, respectively. The protons of the methyl group from the siloxane blocks (H_1) appeared at around 0 ppm. As discussed above, the peaks of all protons in the 1H NMR spectrum were in good accordance with the proposed copolymer structure, as schemed in Fig. 1.

FT-IR spectra of the PSI were exhibited in Fig. 3. Characteristic absorption bands for the imide ring (CO_2N) at 1782, 1723 cm^{-1} due to the asymmetrical and symmetrical carbonyl stretching vibrations, respectively, and at 719 cm^{-1} due to ring deformation were clearly seen. Besides, the absorption band arisen from the stretching vibration of the C–N group in the imide ring also appeared at 1379 cm^{-1} [27]. On the contrary, absorption bands at 1650–1690 cm^{-1} (–CO–NH–, amida I), 1530–1560 cm^{-1} (–CO–NH–, amida II), 1260–1280 cm^{-1} (–CO–NH–, amida III) and 2900–3400 cm^{-1} (amide –NH– and acid –OH) were not detected [28,29]. All these confirmed the complete conversion of o-carboxy-amide groups to the imide rings.

Other absorption bands at 2962 cm^{-1} (aliphatic C–H), 1600, 1502 cm^{-1} (aromatic C=C), 1089, 1015 cm^{-1} (Si–O–Si) and 799 cm^{-1} (Si–C) [30] were also observed in Fig. 3. But that at 3300–3500 cm^{-1} (amine), 1760–1830 cm^{-1} (anhydride) were absent, implying that no un-reacted components consisting of BDAF SIDA and 6FDA were mixed in the synthesized PSI.

Moreover, a decrease of the bands' intensity at 1782, 1723, 1600, 1502, 1379 cm^{-1} (but an increase of that at 1089, 1015 cm^{-1}) from PSI-1, PSI-2 to PSI-3 explained that the content of imide blocks in the PSI decreased (but that of siloxane ones in the PSI increased) with increasing the molecular weight (or longer chain length) of SIDA used for copolymerization.

Results from GPC analysis based on linear polystyrene (PSt) standards were listed in Table 1, which gave a weight-averaged molecular weight (M_w) of 26,708–37,663 and a relatively narrow polydispersity of 1.29–1.39 for the PSI.

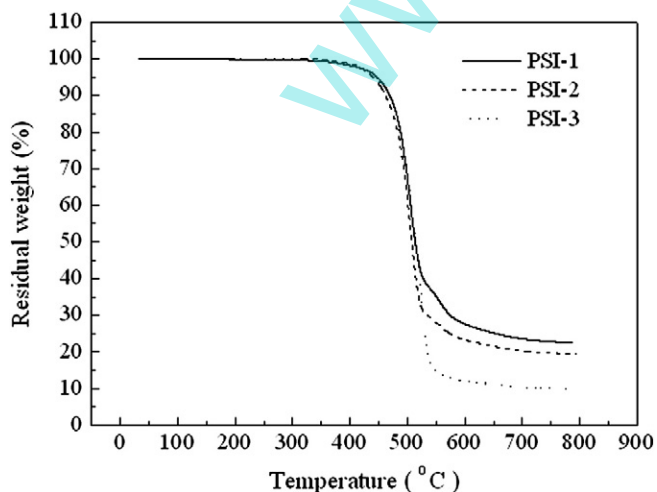


Fig. 4. TGA curves of the PSI.

Thermal decomposition kinetics and stability of the PSI were investigated using TGA under a nitrogen atmosphere and the results were shown in Fig. 4.

It could be seen that both the PSI-1 and PSI-2 membranes underwent two-step degradation, but this behavior for PSI-3 membranes did not show clearly in Fig. 4. The first step occurred between 370 °C and 450 °C, which was attributed to the scission of aliphatic amino propyl linkages of the PDMS units incorporated into the copolymer. The second one occurred between 500 °C and 600 °C, and it was due to the degradation of imide groups.

The decomposition temperature (T_5) at 5% mass loss was used to compare the relative thermal stability of the copolymer samples, as listed in Table 1. An increase of siloxane blocks (or a decrease of imide ones) in the PSI resulted in a somewhat decreased decomposition temperature. Nevertheless, the good thermal stability of all the samples could be testified by T_5 at about 439–447 °C.

The thermal behavior of the PSI evaluated using a DSC was presented in Fig. 5. The found glass transition temperatures (T_g) were listed in Table 1 too.

A double T_g but no crystallization or melting transition observed for all the copolymer samples indicated that the PSI had an amorphous but two micro-phase separated structure. The lower T_g (T_{g1} , -122–100 °C) corresponded to the flexible siloxane blocks dropped when the content of siloxane blocks in the PSI increased, but it was always higher than that of pure PDMS, -123 °C. In contrast, the higher T_g (T_{g2} , 153–171 °C) corresponded to the hard imide blocks increased with increasing the content of siloxane blocks in the PSI. This opposite behavior of the two glass transition temperatures could be explained in terms of the different phase morphologies of the copolymers. In the case of the relatively lower content of siloxane blocks in the copolymer, the two phases were clearly separated due to the heterogeneity existing between the PDMS and fluorinated PI moieties (i.e., phase demixing). This might be just the reason why the PSI-1 membrane was fragile. Otherwise, as the content of siloxane blocks in the copolymer increased, in some way the copolymer became homogeneous (i.e. phase mixing) and the two glass transition temperatures were influenced by each other, in such a way that T_{g1} decreased, while T_{g2} increased.

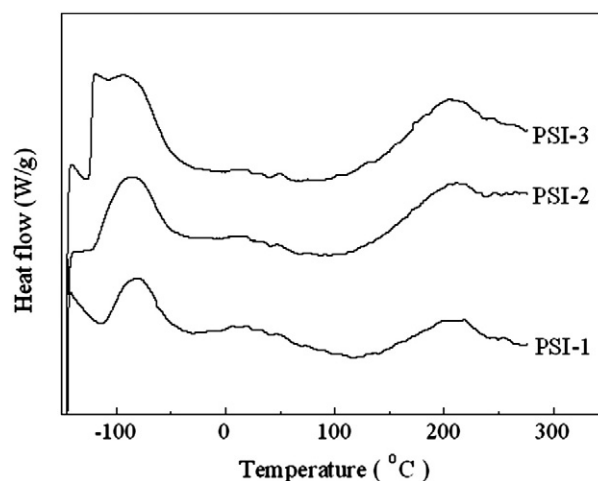


Fig. 5. DSC curves of the PSI.

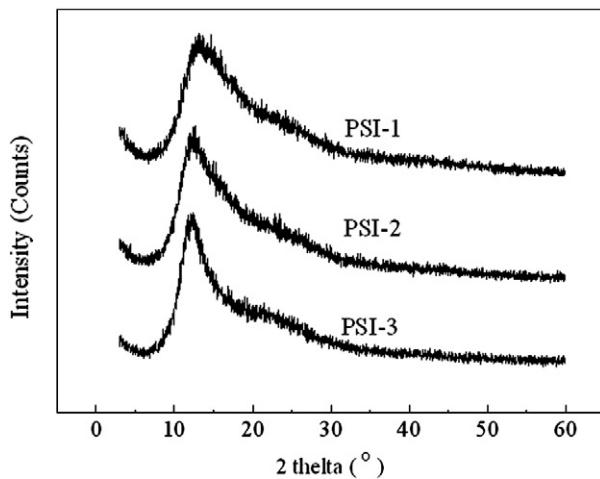


Fig. 6. WAXRD patterns of the PSI.

Actually, the presence of the crystalline phase in the polymer matrix influences both the sorption of components into and their transport through the membrane [31]. All of the steps involved in the permeation process through a crystalline polymer, namely sorption, diffusion, and desorption, take place in the amorphous regions. Under this condition, the crystal entities act as impermeable barriers. Consequently, the permeating molecules have to detour from the crystalline regions and thus 'travel' a much longer distance through a crystalline polymer than through a fully amorphous polymer.

Fig. 6 compared the WAXRD patterns of the copolymer samples. Positively, the broad peaks indicated that all the copolymer samples

were basically amorphous, which would be in favor of the diffusion of components.

3.2. Morphologies, mechanical and pervaporation properties of the PSI membranes

It was found in this work that the PSI-1 was difficult to form membranes; in other words, the PSI-1 membranes were fragile, but the other PSI-2 and PSI-3 had good membrane-forming ability, which was also registered in Table 1. To analyze the reasons, we adopted the AFM images of the other two PSI-2 and PSI-3 membranes to compare their surface morphologies, as presented in Fig. 7.

The similar surface morphologies of the two PSI membranes were testified by the AFM images in Fig. 7. Namely, rough surfaces accompanied with some discontinued regions were observed. Relatively bright and dark parts in the AFM images implied the existence of a micro-phase separation in the PSI membranes. However, a more distinct micro-phase separation was found in the PSI-2 membrane, implying that a more homogeneous membrane would be prepared from the copolymer with a higher content of siloxane blocks which was synthesized from SIDA of a higher molecular weight.

Results from AG-1 electronic serimeter were listed in Table 2. It could be seen that a higher siloxane block contained copolymer membrane (PSI-3) had a relatively poorer mechanical strength compared with the PSI-2 one. Nevertheless, both the PSI-2 and PSI-3 membranes had a higher break strength than the pure PDMS membrane (0.2–0.3 Mpa) [15], which was necessary for their applications in O-PV.

To test the separation properties of the synthesized copolymer membranes used for O-PV, TCE was chosen as the representative of

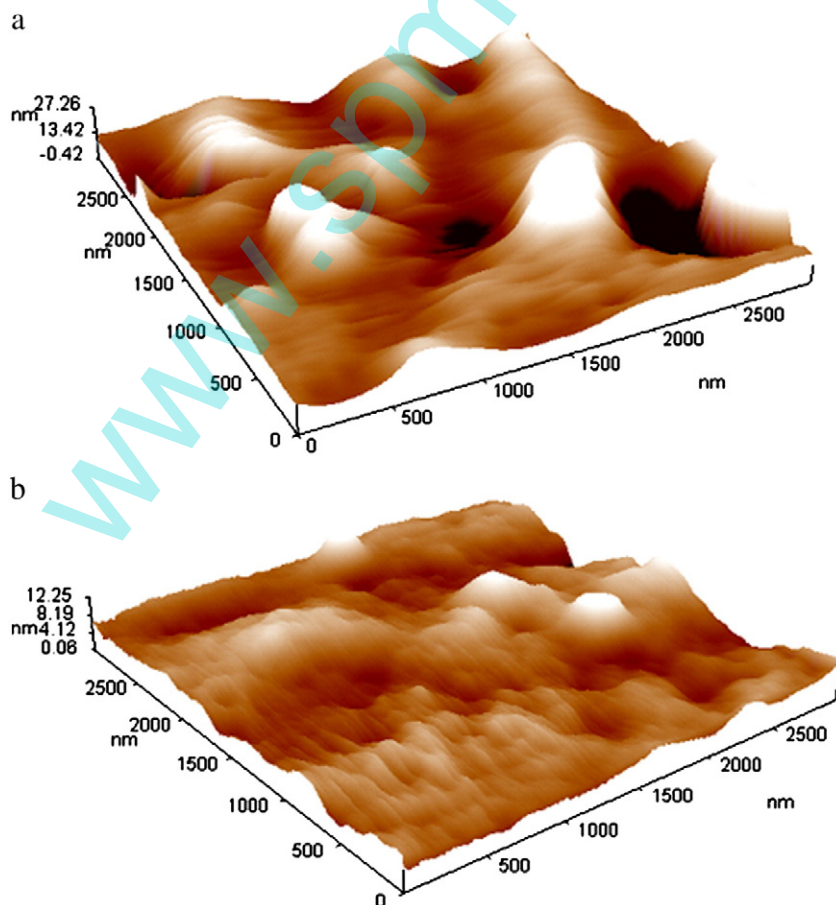


Fig. 7. AFM topography images of the PSI-2(a) and PSI-3(b) membranes.

Table 2
Mechanical and pervaporation properties of the PSI membranes.

Sample	Break strength (Mpa)	Permeate flux (10^3 kg/(m^2 h))	Separation factor
PSI-1	–	–	–
PSI-2	8.5	25.4	2580
PSI-3	1.8	27.6	3270

Note: The pervaporation test was done at 25 °C and 500 ppm TCE concentration.

VOCs. The results were also shown in Table 2. It could be seen that both the permeate flux and selectivity of the PSI-3 membrane was higher than that of the PSI-2 one. The reason could be correlated to the structure parameters of the copolymer (T_g and d -spacing).

On the one hand, the premise for transport almost exclusively through the amorphous phase is conformational transitions which create voids for diffusion of the permeating molecules. So T_g is an important factor to effect the diffusion of components through a given copolymer matrix. It is well known that a lower T_g of the polymer certainly will in favor of diffusion through the polymer matrix. Because in this case, more free volume for diffusion is produced due to the expanded amorphous regions (the macromolecular chains inside them can move more easily). As the afore-discussion, with the content of siloxane blocks in the copolymers increasing, T_{g1} related to the flexible siloxane blocks decreased but T_{g2} related to the hard imide ones increased. Thereby, the better pervaporation properties of the PSI-3 membrane which had a higher content of siloxane blocks indicated that the siloxane blocks in the copolymer did make a main contribution to the pervaporative separating properties of the copolymer membranes.

On the other hand, the d -spacing value determined by wide-angle X-ray scattering and calculation using the Bragg's equation (listed in Table 1) characterizes the chain-to-chain distance in the copolymer matrix [27], and further provides an indication of the resistance to diffusion. It could be seen that the d -spacing value was reduced when the content of the imide blocks in the copolymer increased. As a matter of fact, an increase in the imide blocks in some sense increased the rigidity in the copolymer matrix. This certainly would somewhat weaken the inter-segmental motion and chain rotation, bringing on a higher efficiency of chain packing within the copolymer matrix. Finally, diffusion resistance of components through the copolymer matrix increased. That was, both the VOC and water molecules would permeate more difficultly through the PSI-2 membrane than through the PSI-3 membrane.

4. Conclusions

A series of new siloxane-imide block copolymers (PSI) were prepared by varying the average molecular weight of flexible siloxane diamine (SIDA, 900, 1680 and 4600) and their membranes fabricated by means of solvent evaporation were adopted for pervaporation of trichloroethylene (TCE) from water. To increase the hydrophobicity and free volume of the resulted PSI membranes, apart from SIDA, both the diamine (4,4'-(hexafluoroisopropylidene) diphthalic anhydride, 6FDA) and dianhydride (2,2'-bis[4-(4-amino-phenoxy) phenyl] hexafluoropropane, BDAF) containing bulky CF_3 group were applied to synthesize the PSI using the conventional two-step polymerization method, involving ring-opening polyaddition and subsequently chemical cyclodehydration. 1H NMR spectrum confirmed the successful preparation of the PSI. FT-IR spectra indicated increasing siloxane blocks in the copolymer with increasing molecular weight of SIDA used for copolymerization.

DSC and TGA analyses showed that the PSI had a good thermal stability but micro-phase separation. In addition, tensile tests demonstrated its higher breaker strength than the pure PDMS membrane. AFM observation further testified that the higher content of imide blocks in the copolymer resulted in a more serious micro-

phase separation, so that the PSI prepared from the lowest molecular weight (900) of SIDA was difficult to form the membrane.

Siloxane blocks in the copolymer mainly contributed to the pervaporation properties of the membrane. PSI with a higher content of siloxane blocks had dropped T_g (correlated to the flexible siloxane blocks) and larger d -spacing, which were in favor of improving the pervaporation properties of the corresponding copolymer membrane. But at the same time the mechanical properties of the PSI membrane having a high content of siloxane blocks became poorer.

Acknowledgements

This research was financially supported by the National Natural Science Fund of China (No. 20704018), the Open Project Program of Key Laboratory of Eco-Textiles, Ministry of Education, China (No. KLET0607) and the Fundamental Research Funds for the Central Universities (No. JUSRP10902, JUSRP10904).

References

- [1] F. Lipnizki, S. Hausmanns, P.-K. Ten, R.W. Field, G. Laufenberg, Organophilic pervaporation: prospects and performance, Chem. Eng. J. 73 (2) (1999) 113–129.
- [2] J.H.A. Willemsen, B.H. Dijkink, A. Togtema, Organophilic pervaporation for aroma isolation – industrial and commercial prospects, Membrane Technol. 2004 (2) (2004) 5–10.
- [3] P. Ming, M.V. Leland, X.L. Sean, Recent advances in VOCs removal from water by pervaporation, J. Hazard. Mater. B98 (2003) 69–90.
- [4] S. Claesa, P. Vandezande, S. Mullensa, R. Leysena, K. De Sitter, A. Andersson, F.H.J. Maurer, H. Van den Rulb, R. Peetersd, M.K. Van Baelb, High flux composite PTMSP-silica nanohybrid membranes for the pervaporation of ethanol/water mixtures, J. Membrane Sci. 351 (2010) 160–167.
- [5] X. Tian, X. Jiang, B. Zhu, Y. Xu, Effect of the casting solvent on the crystal characteristics and pervaporative separation performances of P(VDF-co-HFP) membranes, J. Membrane Sci. 279 (2006) 479–486.
- [6] X. Tan, S.P. Tan, W.K. Teo, K. Li, Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water, J. Membrane Sci. 271 (2006) 59–68.
- [7] M. Krea, D. Roizard, N. Moulai-Mostefa, D. Sacco, New polyimide membranes with high siloxane content designed to remove polar organics from water by pervaporation, J. Membrane Sci. 241 (1) (2004) 55–64.
- [8] Y. Nagase, T. Ando, C.M. Yun, Syntheses of siloxane-grafted aromatic polymers and the application to pervaporation membrane, React. Func. Polym. 67 (11) (2007) 1252–1263.
- [9] T. Uragami, H. Yamada, T. Miyata, Removal of dilute volatile organic compounds in water through graft copolymer membranes consisting of poly(alkylmethacrylate) and poly(dimethylsiloxane) by pervaporation and their membrane morphology, J. Membrane Sci. 187 (1–2) (2001) 255–269.
- [10] B.-J. Chang, Y.-H. Chang, D.-K. Kim, J.-H. Kim, S.-B. Lee, New polyimide membranes for the pervaporation of trichloroethylene from water, J. Membrane Sci. 248 (1–2) (2005) 99–107.
- [11] S. Schnabel, D. Roizard, T. Nguyen, P. Lochon, P. Aptel, Synthesis of novel block siloxane polymers for the removal butanols from aqueous feed solutions, Colloid Surface A. 138 (1998) 335–343.
- [12] F. Xiali, W. Wei, Y. Chen, W. Jin, N. Xu, Optimization of preparation conditions for polydimethylsiloxane (PDMS)/ceramic composite pervaporation membranes using response surface methodology, J. Membrane Sci. 311 (1–2) (2008) 23–33.
- [13] L. Li, Z. Xiao, S. Tan, L. Pu, Z. Zhang, Composite PDMS membrane with high flux for the separation of organics from water by pervaporation, J. Membrane Sci. 243 (1–2) (2004) 177–187.
- [14] D. Panek, K. Konieczny, Preparation and applying the membranes with carbon black to pervaporation of toluene from the diluted aqueous solutions, Sep. Purif. Technol. 57 (3) (2007) 507–512.
- [15] L. Li, Z. Xiao, Z. Zhang, S. Tan, Pervaporation of acetic acid/water mixtures through carbon molecular sieve-filled PDMS membranes, Chem. Eng. J. 97 (15) (2004) 83–86.
- [16] F. Peng, Z. Jiang, C. Hu, Y. Wang, H. Xu, J. Liu, Removing benzene from aqueous solution using CMS-filled PDMS pervaporation membranes, Sep. Purif. Technol. 48 (3) (2006) 229–234.
- [17] T. Uragami, T. Meotoiwa, T. Miyata, Effects of morphology of multicomponent polymer membranes containing calixarene on permselective removal of benzene from a dilute aqueous solution of benzene, Macromolecules 36 (6) (2003) 2041–2048.
- [18] T. Uragami, T. Meotoiwa, T. Miyata, Effects of the addition of calixarene to microphase-separated membranes for the removal of volatile organic compounds from dilute aqueous solutions, Macromolecules 34 (19) (2001) 6806–6811.
- [19] H. Wu, L. Liu, F. Pan, C. Hu, Z. Jiang, Pervaporative removal of benzene from aqueous solution through supramolecule calixarene filled PDMS composite membranes, Sep. Purif. Technol. 51 (3) (2006) 352–358.
- [20] K. Konieczny, M. Bodzek, D. Panek, Removal of volatile compounds from the wastewaters by use of pervaporation, Desalination 223 (1–3) (2008) 344–348.

- [21] Y. Luo, S. Tan, H. Wang, F. Wu, X. Liu, L. Li, Z. Zhang, PPMS composite membranes for the concentration of organics from aqueous solutions by pervaporation, *Chem. Eng. J.* 137 (3) (2008) 496–502.
- [22] M. Bennett, B.J. Brisdon, R. England, R.W. Field, Performance of PDMS and organofunctionalised PDMS membranes for the pervaporative recovery of organics from aqueous streams, *J. Membrane Sci.* 137 (1–2) (1997) 63–68.
- [23] P. Wu, R.W. Field, R. England, B.J. Brisdon, A fundamental study of organofunctionalised PDMS membranes for the pervaporative recovery of phenolic compounds from aqueous streams, *J. Membrane Sci.* 190 (2) (2001) 147–157.
- [24] W.-C. Liaw, K.-P. Chen, The influence of diphenyl siloxane on morphology and physical properties in the poly(imide siloxane) (PIS) copolymer, *J. Polym. Res.* 14 (2007) 5–21.
- [25] J.-H. Kim, B.-J. Chang, S.-B. Lee, S.Y. Kim, Incorporation effect of fluorinated side groups into polyimide membranes on their pervaporation properties, *J. Membrane Sci.* 169 (2) (2000) 185–196.
- [26] A. Higuchi, B.-O. Yoon, T. Asano, K. Nakaegawa, S. Miki, M. Hara, Z. He, I. Pinnau, Separation of endocrine disruptors from aqueous solutions by pervaporation, *J. Membrane Sci.* 198 (2002) 311–320.
- [27] M. Simionescu, M. Marcu, M. Cazacu, New poly(amide-imide) siloxane copolymers by polycondensation, *Eur. Polym. J.* 39 (4) (2003) 777–784.
- [28] A. Ghosh, S. Banerjee, Synthesis, characterization, and comparison of properties of novel fluorinated poly(imide siloxane) copolymers, *J. Appl. Polym. Sci.* 107 (3) (2008) 1831–1841.
- [29] A. Ghosh, S. Banerjee, Thermal, mechanical, and dielectric properties of novel fluorinated copoly(imide siloxane)s, *J. Appl. Polym. Sci.* 109 (4) (2008) 2329–2340.
- [30] U. Senthilkumar, B.S.R. Reddy, Polysiloxanes with pendent bulky groups having amino-hydroxy functionality: structure–permeability correlation, *J. Membrane Sci.* 292 (1–2) (2007) 72–79.
- [31] R.B. Long, Liquid permeation through plastic films, *Ind. Eng. Chem. Res.* 4 (4) (1965) 445–451.