Gas Permeation Properties of Poly(2,5-benzimidazole) Derivative Membranes

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ABSTRACT: In this article, three novel polymers based on poly(2,5-benzimidazole) (ABPBI) were synthesized by introducing propyl, isobutyl or *n*-butyl groups to its side chain through an alkyl substitution reaction. FTIR and ^{13}C NMR were applied to confirm the formation of corresponding chemical groups. Their physical properties including crystallinity, thermal stability, mechanical strength, and micro-morphology were also characterized. Their solubility in common solvents were also tested to see if the modification will bring any improvement. Gas permeation properties of three derivative membranes prepared by a casting and solvent-evaporation method were tested with pure gases including H_2, N_2, O_2, CH_4, and CO_2. It has been revealed that gas with a smaller molecular size owned a larger permeability. This means gas permeation in all prepared membranes should be diffusivity selective. Among all three modified ABPBI membranes, isobutyl substitution modified ABPBI (IBABPBI) showed the best selectivity of H_2 over other gases such as N_2 (~185) and CO_2 (~6.3) with a comparable permeability (~9.33 barrer) when tested at 35°C and 3.0 atm. Testing temperature increase facilitated gas permeation for all three membranes obviously; while in term of gas selectivity temperature increase showed diverse alteration because it brought variable impact on gas solubility of different gases. Even so, IBABPBI membrane still owned acceptable selectivity of H_2 over N_2 (~118) and CO_2 (~6.3) with an almost doubled permeability (~17.5 barrer) when tested at 75°C and 3.0 atm. Additional tests showed that running at high pressure did not bring any obvious deterioration to gas separation performance of IBABPBI membrane. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40440.

INTRODUCTION

Hydrogen is attracting attention from the researchers all over the world as it is such a green gas as well as a promising energy source in the foresee future in fossil industry, fuel cell applications, and some other fields like single-crystal silicon producing process.[1–3] The main way of producing hydrogen is coal gasification,[4] and as a result hydrogen always accompanied with carbon dioxide is produced. There also a demanding need for hydrogen recovery from purge gas that in most cases hydrogen is accompanied by nitrogen.

In recent years, gas separation membrane has an obvious increase in market share because of lower cost, higher efficiency, and easiness to operate in contrast with conventional methods such as absorption, adsorption, distillation, etc.[5] A lot of efforts are currently being made on developing new polymeric materials since it will directly determine the performance of prepared separation membrane.[6] 6FDA-4MPD (4,4′hexafluoroisopropylidene diphthalicanhydride-2,3,5,6–tetramethyl-1,4-phenylene diamine) has extremely large free volume, however, its intrinsic perm-selectivity of H_2 over CO_2 is as low as 1.0 with a H_2 permeability of 540 barrer.[7,8] Polyaniline membrane with a doping-undoping-doping process obtaining a H_2/CO_2 selectivity around 8.0 has been reported elsewhere, while unfortunately this selectivity improvement was realized by sacrificing the H_2 permeability (as low as 4.4 barrer).[9] As another newly developed membrane material for H_2 separation poly (vinyl chloride) is also suffering from the same problem.[10] Thus the main direction for new material development should be aiming at finding a balance between permeability and selectivity for H_2 separation.

Aromatic polybenzimidazoles (PBI), generally poly 2,2′-(m′phenylene)-5,5-bibenzimidazole, is thermally and mechanically stable, thus it has been widely used as high performance material such as proton exchange membranes.[11–13] Like those polymers that we mentioned above when serving as a membrane material for gas separation its dense membrane has a

high selectivity of H_2 over CO_2 but extremely low H_2 permeability. To enhance the gas permeation performance of PBI, many investigations have been carried out to study the effect of N-substitution.[14–19]

Compared with PBI, poly (2,5-polybenzimidazole) (ABPBI) is easier to be synthesized since it is produced by a simple self-polymerization process. What should be also pointed out is that the monomer, 3,4-diaminobenzoicacid(DABA), is much more economically available and environmental friendly since it is being widely used in pharmaceutical industry.[12] However, though similar to PBI its structure is more rigid as a result of eliminating two sigma bonds thus ABPBI shows very poor solubility in common organic solvents. So how to improve its solubility will be a key issue that determines if it is going to be a good candidate as membrane material. Generally, there are different methods including blending, doping, chemical crosslinking, copolymerization, group substitution being used to modify the polymer structures. Among them group substitution shows better performance for improving the solubility of polymers in solvents without major compromise in thermal stability.[6,8,9,20–22]

Proper alterations made to polymer backbone would inhibit chain packing and suppress chain mobility that will help achieving permeability increase while acceptable selectivity decrease.[22,23] This has been confirmed by some reports regarding tetramethyl or tert-butyl group being introduced to the backbone of polycarbonate, polysulfone, polyester, poly(aryl ether ketone)s and PBI.[24]

While there are not complete researches on the gas permeation properties of ABPBI-based polymers, and less is known about the effect of introducing alkyl on the solubility and gas permeability of ABPBI. According to group contribution prediction, isobutyl is superior than tert-butyl and n-butyl for H_2/CO_2 separation.[25] In addition, the alkylation reagent, isobutyl bromide, and n-butyl bromide are much cheaper than 4-tert-butylbenzyl and methylene trimethylsilyl bromide. Thus it should worth a

detailed investigation to incorporate different groups to the polymer to facilitate free volume formation while simultaneously maintaining its chain rigidity.

The present work is focusing on how to improve the solubility of ABPBI in common solvents by a substitution reaction. Different groups including propyl, isobutyl, and n-butyl were incorporated to show the effects. Then investigations on the solubility, physical properties and gas permeation performance of three modified ABPBI dense membranes were carried out. Temperature dependence of gas permeability was examined, and its influence on diffusivity and solubility coefficient was also covered to find out if the membrane will be applicable at a higher temperature. At the end pressure dependence of gas permeability for IBABPBI was also discussed.

EXPERIMENTAL

Materials

The 3,4-diaminobenzoic acid was purchased from Acros Organics with a purity of 99%. N-methyl-2-pyrrolidinone (NMP), N,N-dimethyl acetamide (DMAc), dichloromethane ($CHCl_2$), tetrahydrofuran (THF), methyl sulfonic (CH_3SO_3H), sodium bicarbonate ($NaHCO_3$), formic acid (HCOOH), sodium hydride (NaH), and some other solvents were from Tianjin Kermel Company. Propyl bromide, isobutyl bromide, and n-butyl bromide were from Shanghai Chemical. All the reagents are of analytical grade and were used without any treatment. Polyphosphoric acid (PPA) was from Sinopharm Chemical Reagent and Dimethyl sulfoxide (DMSO) was from Tianjin Kermel Company. They both were treated with molecular sieves before use for dehydration. Deionized water was house made. High purity gases (not lower than 99.9%) were bought from Dalian Special Gas Company.

ABPBI Synthesis and its Modification by Substitution

Our synthesis route was shown in Figure 1 that has been described by other references.[19,23,26] At first, 2.012 g DABA and
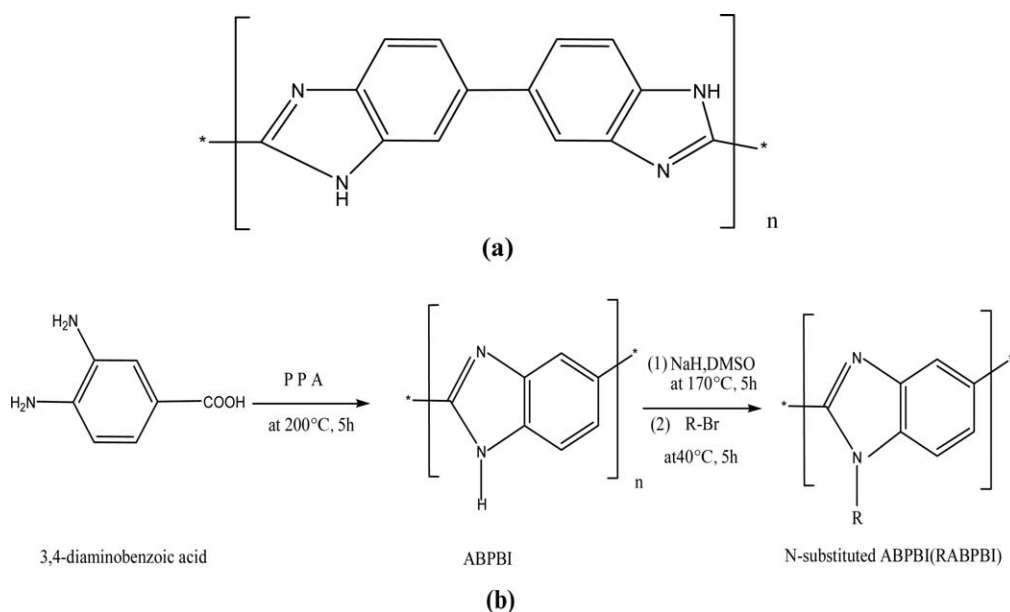

Figure 1. Structure of (a) poly 2,2′-(m′phenylene)-5,5-bibenzimidazole(PBI); (b) synthetic route of Poly(2,5-polybenzimidazole) (ABPBI) and its derivatives.

52.68 g PPA were added into a three-necked bottle loaded with a drying tower and nitrogen gas inlet. Then it was heated to 200°C and kept for 5 h. After that the solution was precipitated in de-ionized water. The newly synthesized polymer was neutralized with NaHCO₃, then washed with de-ionized water completely and dried at 120°C in a vacuum oven.

Then 1.208 g ABPBI with 0.478 g NaH were added to 65.0 mL DMSO in the same three-necked bottle as above, kept at 120°C for 5 h with stirring. To get different modified ABPBI, corresponding Alkyl halide was added by drops respectively with certain amount (propyl bromide: 1.491 g, isobutyl bromide: 1.661 g, butyl bromide: 1.661 g). After a reaction duration of 24 h, the solution was poured into the deionized water and light brown solid was seen. It was washed thoroughly with de-ionized water and dried in a vacuum oven at 110°C for 48 h.

Dense Membrane Casting

Certain amount of modified ABPBI was dissolved in HCOOH to form a homogeneous solution with a concentration of 3.0% (w/w) at first, and then the dope was slowly filtered with fine mesh, degassed with a vacuum pump for 2 h before it was poured onto a clean and leveled glass plate at 40°C to form a dense membrane. Solvent evaporation time was kept as long as 12 h to allow the evaporation happening as much as possible. After that the formed dense membrane was peeled off the plate by immersing it into the de-ionized water bath. Membrane was kept at 110°C in vacuum for 72 h before use. Its thickness was measured with a micrometer (Chengdu Cheng Liang). In most cases the measured membrane thickness varied between 30 and 40 μm with an accuracy of ± 1 μm.

Characterization

Chemical Structure Change After Modification Examined by FTIR and ^{13}C NMR. ATR-FTIR spectra of the polymers in thin film form were recorded on a NEXUS Fourier Transform infrared spectrophotometer at ambient temperature. The wave number was from 800 to 4000 cm^{-1}.

All samples of ABPBI and its three derivatives were dried and cut into small particles. The ^{13}C NMR tests were carried out on Varian Infinity-plus 400 MHz (WB) (6000 kHz).

Solubility Measurement. The solubility of ABPBI, propyl-substituted poly (2,5-benzimidazole) (PABPBI), IBABPBI and n-butyl-substituted poly (2,5-benzimidazole) (BABPBI) in common organic solvents were measured at a concentration of 10.0% (w/w) with continuous stirring for 10 h at room temperature, if not soluble, further heated to 80°C to see whether there was any change.

Inherent Viscosity Test. The inherent viscosities of base polymer ABPBI and its three derivatives were tested with a Ubbelohde viscometer at 30°C with a concentration of 0.5 g dL^{-1} in concentrated sulfuric acid.

Thermal Stability Tests by Gravimetric Analysis (TGA). TGA of polymers in film form were investigated by a NETZSCH STA 449F3 thermal gravimetric analyzer. The sample performance was recorded with a heating rate of 10°C min^{-1} and nitrogen

flow rate at 20 mL min^{-1}, and the temperature range was from 25 to 700°C.

Mechanical Strength Test. Film mechanical strength tests were carried out on a PARAM auto tensile tester. For each membrane three samples were used that had thickness around 30–40 μm. The 40 mm × 10 mm samples were held in the grips and pulled by a movable head containing the load cell of 20 N with a constant rate of 25 mm min^{-1} at room temperature.

Wide Angle X-ray Diffraction (WAXD). To find out the crystallinity degree of prepared polymers, wide angle X-ray diffraction (5°–80°) of three polymer samples including ABPBI, IBABPBI, and BABPBI were carried out on an X'pert Pro diffractometer at a scan rate 2°C min^{-1} and with Cu Kα (wave length = 1.54) radiation.

Scanning Electron Microscopy (SEM). Samples in film form were immersed into liquid nitrogen for 2 min and fractured with care. Then they were golden-sprayed in vacuum condition to get conductive surface for SEM imaging. Surface and cross section images of the films were recorded by JSM- 6360LV.

Gas Permeation Test

Gas permeation apparatus was self-made based on constant volume method similar with description in Refs. 27 and 28. Briefly, permeability is calculated by following eq. (1) when the gas transport reaches a steady state:

$$P = \frac{V_m \times V \times l}{A \times RT \times p_0} \times \frac{dp}{dt} \tag{1}$$

where P is the permeability coefficient of a gas, in unit of barrer (1 barrer = 1 × 10^{-10} cm^3 (STP) cm/cm^2 s cmHg); A is the permeation area (cm^2); p_0 is the upstream pressure of the permeation chamber (cmHg); V is the volume of the downstream chamber (cm^3), V_m is the molar volume of ideal gas at standard condition (cm^3(STP)/mol); l is thickness of the membrane (cm); T is the absolute temperature (K); dp/dt is the permeation rate (cmHg/s); R is the universal gas constant (6236.56 cm^3 cmHg mol^{-1} K^{-1}).

D is the apparent diffusion coefficient that can be calculated according to the eq. (2):

$$D = \frac{l^2}{6\theta} \tag{2}$$

where l is thickness of the membrane (cm), and θ is the time lag of the defined gas (s).

According to "solution-diffusion" mechanism, the solubility of a gas (S) can be calculated by eq. (3):

$$S = \frac{P}{D} \tag{3}$$

And ideal selectivity of gas A over gas B is simply defined as eq. (4):

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{4}$$

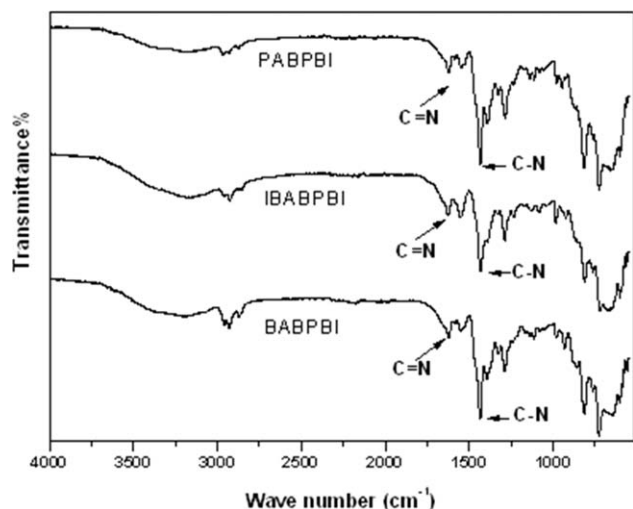For each polymer sample, at least three films were tested to make sure a reproduced result could be achieved.

Figure 2. ATR-FTIR spectra of synthesized PABPBI, IBABPBI, and BABPBI.

RESULTS AND DISCUSSION

Substitution Confirmation by FTIR and ^{13}C NMR

As ABPBI is difficult to be ground into powder or cast into film, its FTIR spectra is not available in this article. The ATR-FTIR spectra of PABPBI, IBABPBI and BABPBI in film form were pictured in Figure 2. The wave number at 1626, 1557 cm^{-1} indicated the formation of C=N, C-N bonds, respectively. Complete substitution of the nitrogen atom by alkyl was

implied by the vanishing of free nonhydrogen-bonded N-H stretching (characterized by bands at 3434 cm^{-1}).[29]

To further confirm the formation of three derivatives a continued ^{13}C NMR examination was applied to all four samples. As we can see from Figure 3, all peaks were marked and types of carbon were determined following reference.[30] The main difference between ABPBI and its derivatives was the peaks in the range of 0–65 ppm, which indicated the presence of substituted alkyl groups. Detailedly, substituted propyl was manifested by the -C-N (6b, 62.3 ppm), secondary carbon (7b, 22.1 ppm), primary carbon (8b, 10.4 ppm); compared with the existence of isobutyl can be confirmed by the appearance of -C-N (6c, 50.0 ppm), secondary carbon (7c, 20.1 ppm), primary carbon (8c, 10.1 ppm); analogically, buthyl was shown by the -C-N (6d, 64.9 ppm), secondary carbon (7d, 30.4 ppm), secondary carbon (8d, 19.0 ppm), primary carbon (8d, 12.7 ppm). So based on the spectra difference and corresponding analysis it could be concluded that the proposed substitution reaction has been realized without any doubt.

Solubility Improvement by Substitution Reaction

As we mention before, solubility of a polymer is very important since it will directly determine its suitability as membrane material. As shown in Table I, the original ABPBI cannot be dissolved by common solvents including m-cresol, DMF, pyridine, DMSO, etc. It is only partially soluble in Formic acid. It is expected that the introduction of side chain to the main structure of ABPBI could improve the solubility and processing
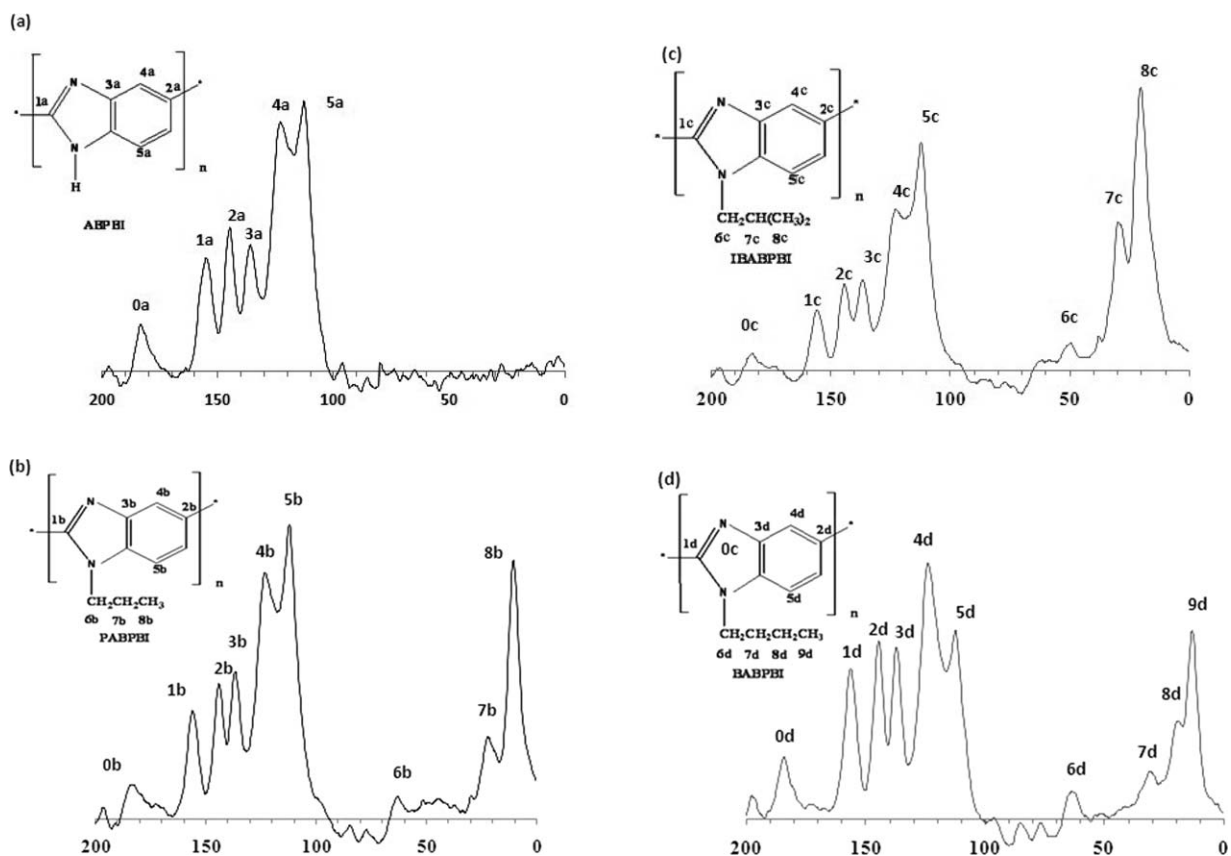

Figure 3. ^{13}C NMR spectra of ABPBI and its three derivatives.

Table I. Solubility of ABPBI and Three Derivatives in Organic Solvents

Polymers	m-cresol	DMF	Pyridine	CH_2Cl_2	THF	DMSO	NMP	DMAc	HCOOH	CH_3SO_3H	H_2SO_4
ABPBI	−	−	−	−	−	−	−	−	±	+	+
PABPBI	±	±	±	−	−	±	±	±	+	+	+
IBABPBI	±	±	±	−	−	±	±	±	+	+	+
BABPBI	±	±	±	−	−	±	±	±	+	+	+

+: soluble at ambient temperature; ±: partially soluble or swelling; −: insoluble

capability. As exhibited in Table I, compared with the original ABPBI, all modified polymers including PABPBI, IBABPBI, and BABPBI showed a significant solubility improvement in organic solvents, especially in HCOOH. This could be attributed to the disruption of molecular hydrogen bond and decline of chain packing density by incorporating propyl, isobutyl, and *n*-butyl groups to the side chain of ABPBI.

So based on the solubility test results formic acid was selected as the solvent for modified ABPBI polymers to develop a homogenous casting solution for dense membrane preparation.

Physical Properties of Original and Modified ABPBI

Degree of Polymerization (DP). DP is an important factor since it will affect polymer's characteristics to some extent. As we already know DP can be estimated by the Mark Houwink Equation listed as below:

$$[\eta] = 8.7^3 \times DP^{1.10} \tag{5}$$

where $[\eta]$ is the intrinsic viscosity of the polymer with a unit of dL g^{-1}.[31] The inherent viscosity of synthesized ABPBI has been measured to be 2.27 dL g^{-1}, and this value was approximately as high as reference reported.[31] Thus according to eq. (5) ABPBI synthesized in our lab owns a DP about 150.

What's more, the intrinsic viscosities of the three modified polymers were also measured. Test results showed that PABPBI, IBABPBI, and BABPBI exhibited close viscosities of 1.93, 1.82, and 1.96 dL g^{-1}, respectively. This could partially reveal that all three modified polymers owned comparable molecular weights.
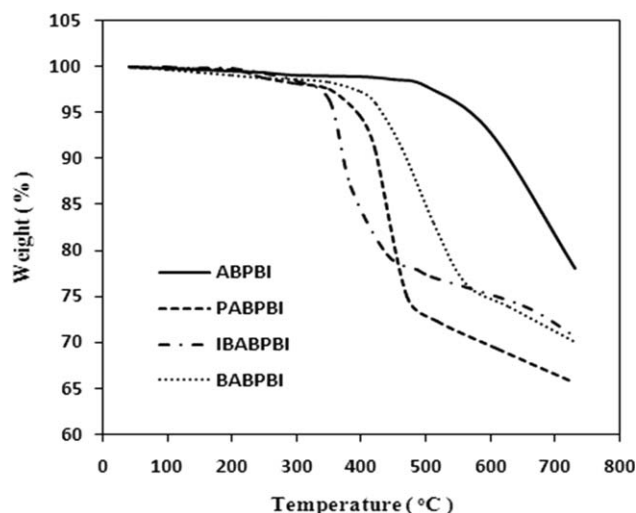

Figure 4. TGA of ABPBI and its three derivatives.

Table II. Mechanical Properties of PABPBI, IBABPBI, and BABPBI films

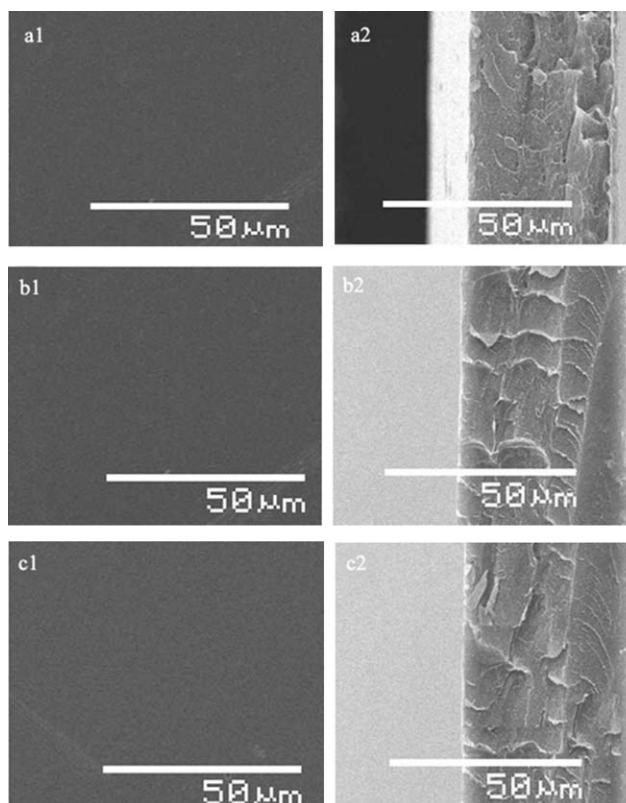| Sample	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
PABPBI	104.3	47.5	2610
IBABPBI	64.3	15.0	2134
BABPBI	77.4	47.5	2577
Polysulfone (Udel) [32]	70.3	~50.0	2480

Figure 5. SEM micrograph of different membranes: surfaces of PABPBI (a1), IBABPBI (b1); BABPBI (c1); cross sections of PABPBI (a2), IBABPBI (b2), and BABPBI (c2).

Thermal Stability. From Figure 4 an obvious drop of degradation temperature was clearly seen after substitution. This may be due to the alkylation of the side chain of ABPBI and less dense chain packing density, which cut off the tough chain stiffness. Compared with original ABPBI that had a degradation temperature about 520°C, all three modified polymers showed a similarly lower degradation temperature around 375°C that should be acceptable since their thermal stability are still better than typical commercial polymers such as polysulfone ($T_d = 275$°C) and polyetherimide ($T_d = 350$°C).

Mechanical Property. The tensile strength and the elongation at break of PABPBI, IBABPBI, and BABPBI film were exhibited in Table II. All films had a little bit lower but comparable mechanical strength comparing with commercially available and widely used gas separation membrane material of polysulfone.[32] In term of elongation at break, IBABPBI owned the lowest value around 15.0% that meant its molecular structure could be the stiffest among all samples. We believe this difference may show

an effect on their gas permeability and selectivity that will be discussed in the next section.

Membrane Morphology. As shown in Figure 5, surface and cross section of all three films showed homogeneously dense structure and all sample thickness was in the range of 30–40 µm that was quite close to the values we measured with a micrometer for gas permeability calculation.

Gas Permeation Performance
Comparison of Gas Permeability of Three Modified ABPBI Membranes and Proposed Explanation. Pure gas permeability including H_2, O_2, N_2, CH_4, and CO_2 were measured for all three modified ABPBI dense membranes and the results were shown in Table III. There were also some reported data for other polymers we used to make a comparison.

If we examine the data in Table III carefully, it could be easily concluded that among all three modified ABPBI membranes, IBABPBI showed the best performance for hydrogen purification. Firstly, in term of hydrogen permeability, it owned a value

Table III. The Gas Permeation Performance of Three ABPBI Derivatives (Tested at 35°C and 3.0 atm)

| Polymer | Permeability (barrer) | | | | $\alpha(H_2/CO_2)$ | $\alpha(H_2/N_2)$ | $\alpha(O_2/N_2)$ | Reference |
	H_2	N_2	O_2	CO_2				
PABPBI	11.24	0.14	0.84	3.21	3.5	74.9	6.0	This work
IBABPBI	9.33	0.05	0.42	1.48	6.3	185.0	8.4	This work
BABPBI	11.80	0.23	1.19	5.13	2.3	51.3	5.2	This work
BZABPBI	5.12	0.080	0.37	0.94	5.4	64.0	4.6	23
SABPBI	15.9	0.161	1.18	5.3	3.0	94.1	7.3	23
PBI-I	0.6	0.0048	0.015	0.16	3.8	131	3.1	16
DBPBI-I	6.54	0.09	0.36	1.79	3.7	73	4.0	16

Notes:

SABPBI

BzABPBI

DBPBI-I

PBI-I
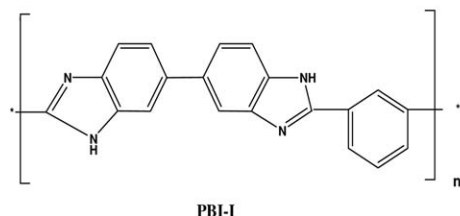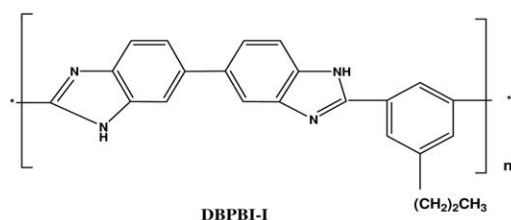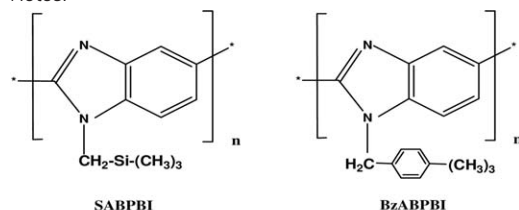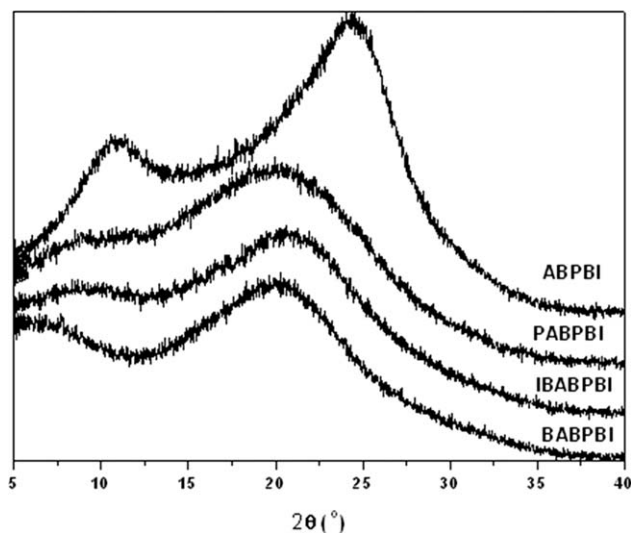
Figure 6. Wide-angle X-ray diffraction spectra of ABPBI and its derivatives.

Figure 7. Temperature dependence of gas permeation in three modified ABPBI membranes.

of 9.33 barrer. This was a little bit lower than PABPBI and IBABPBI but much higher than reference reported value for other polymers from the same category including BZABPBI, SABPBI, PBI-I, and DBPBI-I. Now let us have a look at the selectivity of hydrogen over CO_2 and N_2: IBABPBI membrane showed the highest selectivity for both gas pairs among all five polymers without any doubt. What should be specially pointed out is that its selectivity of hydrogen over nitrogen was as high as 185 that may be among the highest level for all reported polymers according to our knowledge.

So here comes a following question for us: since all three modified ABPBI membranes own very similar molecular structure, why we see such an obvious difference in both gas permeability and selectivity? Next we are attempting to make a possible explanation for this difference from the angle of crystallinity degree that usually can be calculated from WAXD spectra which was shown in Figure 6.[30,33] It turned out that the original ABPBI owned a highest crystallinity degree around 63.5%. Substitution modification obviously reduced crystallinity degree for all three derivatives. Among them IBABPBI showed a crystallinity degree about 59.1% that was larger than the other two that owned very similar value around 51.0%. No need to say, crystallinity degree could partially reveal polymers' packing density and then correspondingly influence their gas permeability. So based on this assumption, it can be easily explained why IBABPBI showed the slightly lower gas permeability with a much higher selectivity than the other two derivatives.

From Table III it could also be clearly seen that the permeability coefficients of tested gases were in the order of H_2, CO_2, O_2, N_2, and CH_4 that was actually opposite to their kinetic diameters (H_2: 2.89Å; CO_2: 3.30 Å; O_2: 3.46 Å; N_2: 3.64 Å; and CH_4: 3.80 Å). This meant gas permeation in all three modified ABPBI membranes was mainly controlled by diffusivity.

Tables IV and V presents the diffusivity and solubility coefficients for all three modified polymers. According to these values it can be summarized that their gas selectivity was mainly contributed by the diffusivity selectivity that could double confirm our conclusion above. What's more, compared with gas pair of H_2/N_2 that owned a much higher separation factor, the obviously lower value for gas pair of H_2/CO_2 was due to the much larger solubility of condensable CO_2 in polymers.

Effect of Temperature on Gas Permeation Performance. Because in some cases hydrogen purification may need to be carried out at a higher temperature, thus it is very important for us to investigate the gas permeation performance of modified ABPBI membranes under different temperatures. In this section gas permeation tests were carried out at 3.0 atm and with a temperature range from 35 to 75°C. The results were shown in Figure 7.

As we can see from Figure 7, for all three tested membranes, their gas permeability showed obvious increase with test temperature. This sounds quite reasonable since at a higher temperature molecular vibration frequency will be larger that enables gas permeation happening much easier. What should also be pointed out is that for all gases BABPBI owned the highest gas

Table IV. The Diffusivity Coefficients of Three ABPBI Derivatives (Tested at 35°C and 3.0 atm)

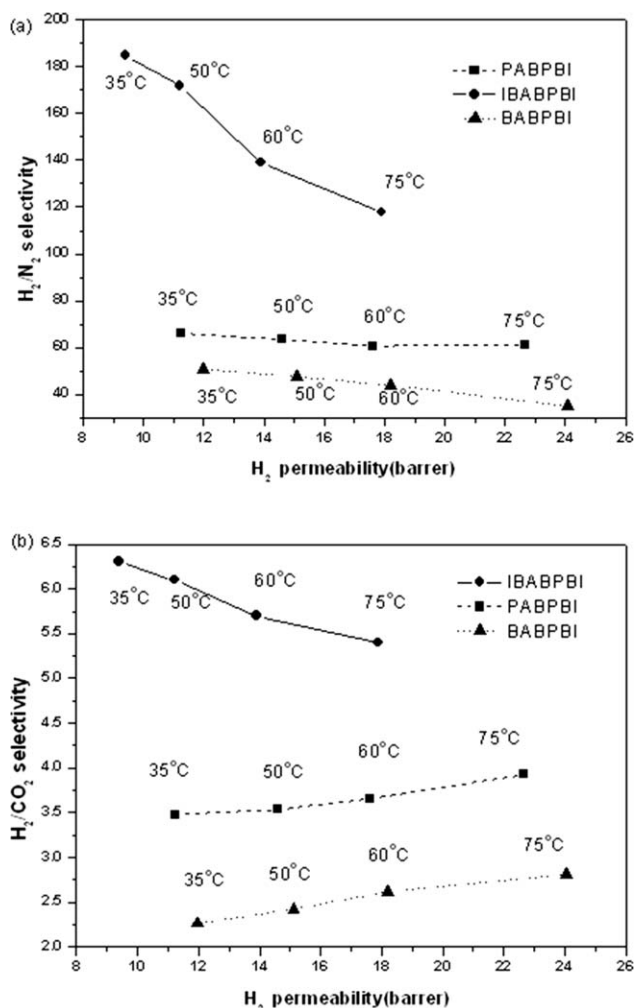| Polymer	Diffusivity coefficient (cm^2 s^{-1})			D_{H2}/D_{N2}	D_{H2}/D_{CO2}
	H_2	N_2	CO_2		
PABPBI	4.29E-07	2.27E-09	2.68E-09	1.89E+02	1.60E+02
IBABPBI	1.96E-07	4.83E-10	8.80E-10	4.06E+02	2.23E+02
BABPBI	7.07E-07	7.74E-09	7.78E-09	9.14E+01	9.09E+01

Figure 8. Temperature dependence of gas selectivity in three modified ABPBI membranes: (a) H2/N2; (b) H2/CO2.

permeability, then PABPBI, IBABPBI showed the lowest value. Same as shown in Table III, H_2 permeation was the fastest, second was CO_2 and N_2 was the slowest.

In term of gas selectivity, as shown in Figure 8, for IBABPBI, separation factors of H_2 over both N_2 and CO_2 showed obvious decrease with temperature increase. For diffusivity controlled polymeric membrane higher temperature will show much more influence on larger gas like N_2 than smaller gas as H_2. This could possibly explain why there was a selectivity decrease of H_2 over N_2 with temperature increase. In case of separation factor

of H_2 over CO_2, one aspect may be same reason as explained regarding of diffusivity, on the other hand what should be noticed was that as we already know higher temperature will bring larger impact on more condensable gas of CO_2 than H_2 (this will increase the solubility selectivity actually), while from the final results we saw a decreased selectivity of H_2 over CO_2 at higher temperature that meant the former effect was playing a more important role for determining the final selectivity. What should be pointed out is IBABPBI membrane still owned separation factors around 118 for H_2 over N_2 and 5.4 over CO_2 even at as high as 75°C. These values should be thought as definitely acceptable that means the prepared IBABPBI membrane owns satisfactory potential to be applied at high temperatures.

From Figure 8 it can also be clearly seen that selectivity of H_2 over N_2 for both PABPBI and BABPBI showed obvious decrease with temperature increase. As we mentioned above since both H_2 and N_2 are same kind of noncondensable gases, temperature increase would show similar effects on their solubility while the diffusivity was differently changed. In tem of selectivity of H_2 over CO_2, oppositely with H_2/N_2 pairs, for both modified membranes the values increased with a temperature increase and we believe gas solubility effect should play a controlling role here.

Effect of Pressure on Gas Permeation Performance. Because most gas separation by membrane is a pressure-driving process thus it is necessary to study gas permeation performance of modified membrane at a higher pressure. As we already know among all three modified ABPBI membranes, IBABPBI membrane showed the best performance thus in this Section we are going to investigate pressure influence only focusing on IBABPBI membrane. What should be mentioned here is that restricted by the highest enduring pressure for our permeation test setup the feed pressure will only go up to 2.0 MPa. The detailed results for gas permeability were shown in Figure 9. When tested at 35°C and with feed pressure in the test range of 0.5–2.0 MPa, for all three tested pure gases of H_2, CO_2 and N_2, we did not see any obvious permeability changes. Usually because CO_2 is kind of condensable gas thus its permeation in polymers under high pressure will cause so called "plasticization" that means gas permeability will show sharp increase because of the presence of large amount of dissolved CO_2 in polymers. The phenomena may happen at a higher test pressure while currently we do not have a suitable setup so this investigation will have to be carried out at a later time. In term of gas selectivity, as shown in Figure 10, stable selectivity around 178–185 for H_2 over N_2 and slightly increase from 6.5 to 7.1 for H_2 over CO_2 in the test pressure range could be seen.

Table V. The Solubility Coefficients of Three ABPBI Derivatives (Tested at 35°C and 3.0 atm)

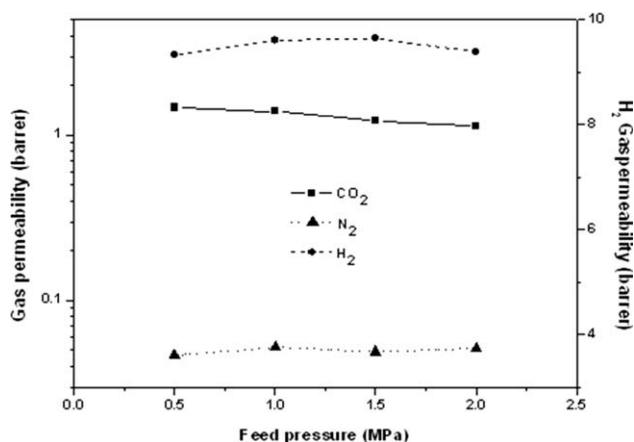| Polymer	Solubility coefficient (cm^3(STP)/cm^3 cmHg)			S_{H2}/S_{N2}	S_{H2}/S_{CO2}
	H_2	N_2	CO_2		
PABPBI	2.61E-03	6.17E-03	1.20E-01	4.23E-01	2.18E-02
IBABPBI	4.41E-03	9.40E-03	1.67E-01	4.69E-01	2.64E-02
BABPBI	1.67E-03	3.01E-03	6.60E-02	5.55E-01	2.53E-02

Figure 9. Effect of feed pressure on permeability of gases for IBABPBI (35°C).

CONCLUSIONS

Three novel modified ABPBI membranes by *N*-substitution (propyl, isobutyl, and *n*-butyl) were developed in this study. It was confirmed that after modification solubility of all three polymers in common solvents have been greatly improved. At the same time, they still maintained similarly excellent thermal and mechanical properties as the original ABPBI. Among all the three modified membranes, IBABPBI showed the best gas separation performance with comparable gas permeability that could possibly explained by their crystallinity degree difference calculated from WAXD spectra. Continued high temperature tests showed that temperature increase led to a corresponding permeability increase for all tested gases in three modified membranes. While IBABPBI membrane still owned separation factors around 118 for H_2 over N_2 and 5.4 over CO_2 even at as high as 75°C. At the end, high-pressure tests were carried out with IBABPBI that owned the best performance. It turned out that pressure did not show too much influence since IBABPBI membrane showed quite stable gas permeability and selectivity at high pressure up to 2.0 MPa. In conclusion, we believe the
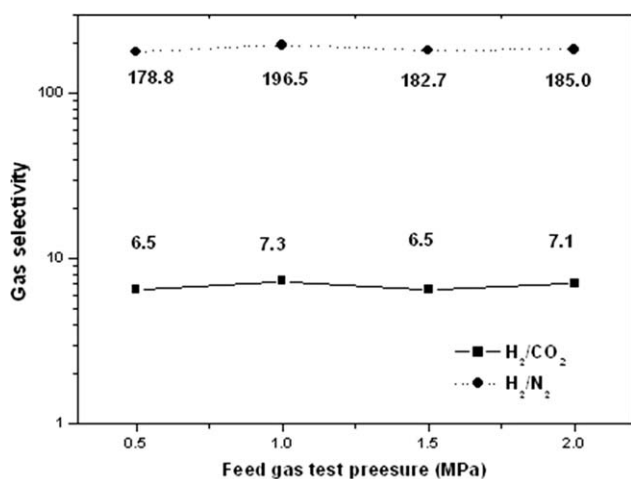
prepared material IBABPBI owns great application potential for H_2 purification.

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Figure 10. Effect of feed pressure on selectivity of gases for IBABPBI (35°C).

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