

Synthesis, Properties, and Gas Permeation Performance of Cardo Poly(arylene ether sulfone)s Containing Phthalimide Side Groups

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ABSTRACT: Novel bisphenol monomers (**1a-d**) containing phthalimide groups were synthesized by the reaction of phenolphthalein with ammonia, methylamine, aniline, and 4-*tert*-butylaniline, respectively. A series of cardo poly(arylene ether sulfone)s was synthesized via aromatic nucleophilic substitution of **1a-d** with dichlorodiphenylsulfone, and characterized in terms of thermal, mechanical and gas transport properties to H₂, O₂, N₂, and CO₂. The polymers showed high glass transition temperature in the range 230–296°C, good solubility in polar solvents as well as excellent thermal stability with 5% weight loss above 410°C. The most permeable membrane studied showed permeability

coefficients of 1.78 barrers to O₂ and 13.80 barrers to CO₂, with ideal selectivity factors of 4.24 for O₂/N₂ pair and 28.75 for CO₂/CH₄ pair. Furthermore, the structure–property relationship among these cardo poly(arylene ether sulfone)s had been discussed on solubility, thermal stability, mechanical, and gas permeation properties. The results indicated that introducing 4-*tert*-butylphenyl group improved the gas permeability of polymers evidently. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2808–2816, 2007

Key words: poly(arylene ether sulfone)s; gas permeation; phthalimide; cardo; synthesis

INTRODUCTION

Poly(arylene ether sulfone)s are useful in numerous applications such as coatings, adhesives, composites, molded parts, toughening agents, engineering plastics, and membrane materials for their excellent mechanical toughness, electrical/insulating, thermal and environmental stability, and high glass-transition temperature (T_g).¹ A number of heat-resistant poly(arylene ether sulfone)s and their copolymers have been obtained by nucleophilic substitution of various bisphenols with activated aromatic dihalide compounds in polar aprotic solvents, and some of them had been commercialized.^{2–4}

The term “cardo polymers” refers to polymers containing bulky side groups.⁵ It has been known that the introduction of cardo groups along the polymer backbone disrupts crystallinity, increases their glass transition temperature, and improves their solubility. For example, phenolphthalein-based cardo poly(aryl ether sulfone) (PES-C) has been noted for its excellent solubil-

ity, mechanical toughness, thermoxidative stability, and high glass transition temperature. It has been used as membrane materials for gas separation,⁶ water desalination,⁷ and fuel cells applications.⁸ As gas separation membranes, PES-C membrane possesses better gas transport properties than hydroquinone-based poly(arylene ether sulfone) membranes,^{9,10} but from the viewpoint of further practical application, its gas selectivity and permeability coefficient must be further improved.

Several cardo poly(aryl ether sulfone) based on phenolphthalein derivatives have been investigated as candidate gas separation materials. Chen and co-workers^{6,11} reported the synthesis and gas permeation properties of modified PES-C containing pendant alkyl, amide and carboxyl groups. In this article, we report the synthesis of the modified cardo PES containing phthalimide (PES-N). The systematic variations in chemical structure were expected to result in interesting and unique variations in physical properties, e.g., packing density and segmental motion of the polymer chain, which would significantly affect the gas permeation behavior of polymer membranes.

EXPERIMENTAL

Materials

Phenolphthalein (PPH) was purchased from Beijing Chemical Reagent Company, and purified by

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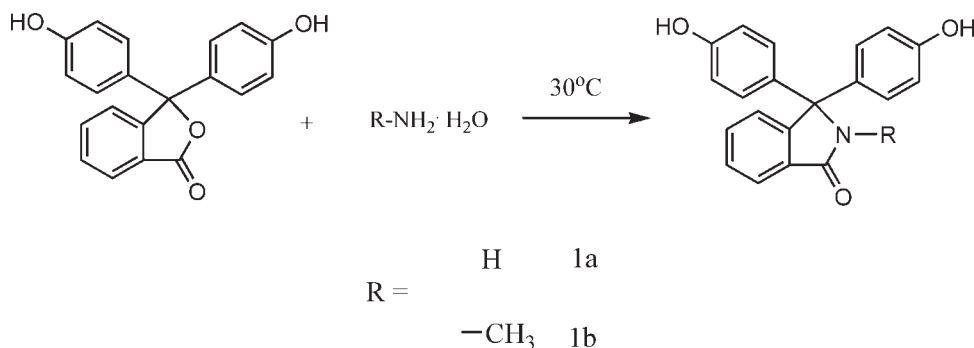
recrystallization from mixed solvent of ethanol and water. Bis(4-chlorophenyl)sulfone, aniline (99%), aniline hydrochloride and 4-*tert*-butylaniline were purchased from Across and used as received. Dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP) were firstly dried with CaH₂ and then distilled under reduced pressure before use. Anhydrous potassium carbonate was finely powdered prior to use.

Measurements

¹H NMR was recorded on a Varian Unity spectrometer at 300 MHz at 30°C with tetramethylsilane (TMS) as the internal standard and DMSO-*d*₆ as the solvent, respectively. Fourier transform infrared (FTIR) spectra were determined using a Bio-Rad Digilab Division FTS-80 spectrometer. Inherent viscosities of all polymers were determined at 30°C using Ubbelohde viscometer with 0.5 g/dL concentration in DMAc. Solubility was determined at a 5% (w/w) concentration. Thermogravimetric analysis (TGA) was conducted with a SDT 2960 thermal analysis station in flowing nitrogen at a heating rate of 10°C/min. Dynamic mechanical thermal analysis (DMTA) were performed on a dynamic mechanical thermal analyzer (Rheometric Scientific, USA) in a tensile mode at a heating rate of 5°C/min and a frequency of 1 Hz. Wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku Max 2500V PC X-ray diffract meter (Japan) with Cu-Kα radiation at a wavelength of 1.54 Å (40 kV, 200 mA) with a scanning rate of 5°/min. Different scanning calorimetry (DSC) was conducted on a Perkin-Elmer DSC-7 at a heating rate of 20°C/min under nitrogen. The mean interchain distance or *d* spacing can be calculated with Bragg's equation:

$$\lambda = 2d \sin \theta$$

where θ refers to the angle of the peak maxima.



Scheme 1 Synthesis of monomers **1a** and **1b**.

The tensile measurements were carried out on an Instron Model 1122 with an average cross head speed of 5.0 mm/min at room temperature. Generally, five samples were tested and the results were averaged. The fractional FFV (FFV) of each of polymers was given by the equation below:

$$\text{FFV} = (V - V_0)/V$$

where V is the specific volume at 30°C, $V_0 = 1.3V_w$ and V_w is the van der Waals volume of the repeating unit estimated by the method outlined by Bondi.¹²

Permeability coefficient of inert gas $P(X_2)$ was measured using an apparatus described in the literature.⁶ The permeability coefficient was obtained from the slope of pressure-time plots after steady state had been reached. The ideal selectivity is calculated from the ratio of permeability coefficients:

$$\alpha(A/B) = P_A/P_B$$

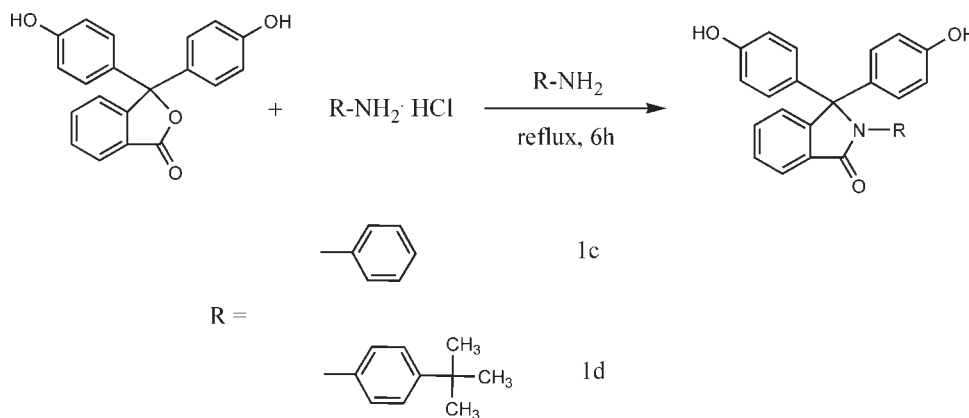
where P_A and P_B refer to the permeability coefficients of pure gases A and B , respectively.¹³ The diffusion coefficient (D) can be estimated from membrane thickness (l) and the time lag (θ) from the transient permeation measurement according to the relation^{14,15}

$$D = l^2/6\theta$$

The solubility coefficients (S) were calculated from $S = P/D$.

Synthesis of 3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (**1a**)

The monomer **1a** was prepared by the same method reported by Wang et al.¹⁶ Mp: 284–285°C, yield 88%. ¹H NMR (DMSO-*d*₆) δ (ppm): 9.44 (2H, s, NH), 9.39 (2H, s, OH). FTIR (KBr): 3172 cm⁻¹ ($\nu_{\text{N-H}}$), 1653



Scheme 2 Synthesis of monomers **1c** and **1d**.

cm^{-1} ($\nu_{\text{C=O}}$), 3319 cm^{-1} ($\nu_{\text{O-H}}$). Elemental analysis (%) for $\text{C}_{20}\text{H}_{15}\text{NO}_3$ (molecular weight, 317.34): calculated: C, 75.73; H, 4.75; N, 4.42; Found: C, 75.69; H, 4.74; N, 4.35.

Synthesis of *N*-methyl-3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (**1b**)

The monomer **1b** was synthesized according to the following procedure. A 1000-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, gas inlet and condenser was charged with 50.9 g (0.16 mol) of PPH and 500 mL of an aqueous methylamine (40%). The mixture was stirred vigorously at 30°C for 24 h. After the solution was poured into a mixture of ice and concentrated hydrochloric acid, white precipitation was obtained by filtration. The crude product was recrystallized from a mixture of ethanol and water. Mp: $264\text{--}265^\circ\text{C}$, yield 82%. ^1H NMR (DMSO- d_6) δ (ppm): 2.70 (3H, s, CH_3), 9.55 (2H, s, OH). FTIR (KBr): 1663 cm^{-1} ($\nu_{\text{C=O}}$). Elemental analysis (%) for $\text{C}_{21}\text{H}_{17}\text{NO}_3$ (molecular weight, 331.4) calculated: C, 76.16; H, 5.17; N, 4.43; Found: C, 75.75; H, 5.30; N, 4.31.

Synthesis of *N*-phenyl-3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (**1c**)

The monomer **1c** was prepared according to the method reported.¹⁷ Mp: $279\text{--}280^\circ\text{C}$, yield: 68%. ^1H NMR (DMSO- d_6) δ (ppm): 9.54 (2H, s, OH). FTIR (KBr): 1703 cm^{-1} ($\nu_{\text{C=O}}$). Elemental analysis (%) for $\text{C}_{26}\text{H}_{19}\text{NO}_3$ (molecular weight, 393.4) calculated: C, 79.38; H, 4.87; N, 3.56; Found: C, 79.32; H, 4.82%; N, 3.60.

Synthesis of *N*-(4-*tert*-butylphenyl)-3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (**1d**)

4-*tert*-Butylaniline hydrochloride was prepared by the hydrochlorination of 4-*tert*-butylaniline using

diethyl ether as solvent, and white solid was obtained by filtration. The crude product was washed with diethyl ether, and then quickly filtered out and dried in a vacuum oven at 100°C for 12 h.

After a 250-mL, three-necked, round-bottom flask, equipped with a mechanical stirrer, thermometer, condenser, and nitrogen inlet, was flame-dried, it was charged with 44.8 g (0.30 mol) of 4-*tert*-butylaniline, followed by 15.9 g (0.05 mol) of phenolphthalein and 22.3 g (0.12 mol) of 4-*tert*-butylaniline hydrochloride. The mixture was refluxed for 6 h under a slow nitrogen flow and cooled to 100°C . The mixture was then poured into 250 mL of aqueous HCl solution (6M) and stirred for 1 h, and white solid precipitate formed. The precipitate was filtered and washed with distilled water for the removal of unreacted hydrochloric acid and then dried at 120°C in vacuo for 12 h. The product was dissolved in 150 mL of aqueous NaOH solution (10%) and filtered to remove the solid residue. The solution was then cooled to $0\text{--}5^\circ\text{C}$ with an ice bath and acidified with

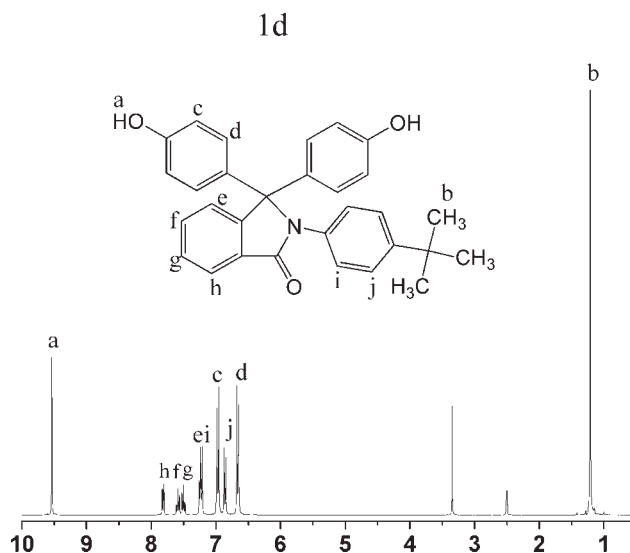
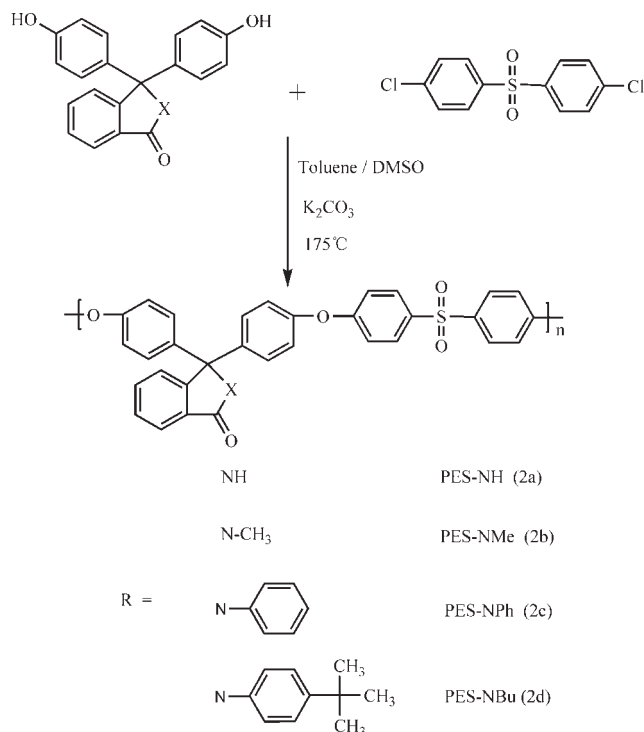


Figure 1 ^1H NMR spectrum of **1d**.



Scheme 3 Synthesis of polymers.

aqueous HCl solution (6M). White precipitate was obtained and washed with ice-cold distilled water, and dried in a vacuum oven at 200°C for 12 h. The crude product was recrystallized from ethanol and water mixture after charcoal treatment, and white crystals were obtained. Mp >300°C, yield: 60%. ¹H NMR (DMSO-d₆) δ (ppm): 1.21 (9H, s, CH₃), 9.53 (2H, s, OH). FTIR (KBr): 1668 cm⁻¹ (ν_{C=O}). Elemental analysis (%) for C₃₀H₂₇NO₃ (molecular weight, 449.5) calculated: H, 6.05; C, 80.16; N, 3.12; Found: C, 80.24; H, 6.03; N, 3.08.

Polymer synthesis

The polymer PES-NBu (**2d**) was given as an example: To a 100-mL three-necked round-bottomed

flask equipped with a Dean-Stark trap, N₂ inlet, mechanical stirrer and thermometer, were added **1d** (4.4954 g, 0.01 mol), dichlorodiphenylsulfone (2.8717 g, 0.01 mol), anhydrous K₂CO₃ (3.04 g, 0.022 mol), 10 mL toluene and 12 mL DMSO, followed by strongly stirring at 145°C. After toluene and water had been distilled off, the temperature was raised gradually to 175°C and allowed to react at this temperature for 10 h to give a viscous solution. A slow stream of nitrogen was maintained. The product was diluted with DMSO and then precipitated in mixture of ethanol and concentrated hydrochloric acid to give a white polymer. The polymer was washed successively with boiling water to remove the inorganic salt and dried in vacuum at 120°C for 12 h.

Spectroscopic data of the polymers

Polymer PES-NH (**2a**)

The polymer **2a** was synthesized from **1a** and dichlorodiphenylsulfone. The polycondensation was carried out at 170°C for 7 h. The yield was 93%. ¹H NMR (DMSO-d₆) δ (ppm): 9.79 (1H, s, NH), 7.09–7.12 (8H, d, Ar), 7.88–7.91 (4H, d, Ar), 7.35–7.51 (4H, d, Ar). FTIR (KBr): 3470 cm⁻¹ (ν_{N-H}), 1643 cm⁻¹ (ν_{C=O}), 1263 cm⁻¹ (ν_{Ar-O-Ar}).

Polymer PES-NMe (**2b**)

The polymer **2b** was synthesized from **1b** and dichlorodiphenylsulfone at 175°C. The yield was 98%. ¹H NMR (DMSO-d₆) δ (ppm): 3.35 (3H, s, CH₃), 7.11–7.14 (8H, d, Ar), 7.38–7.40 (4H, d, Ar), 7.89–7.91 (4H, d, Ar). FTIR (KBr): 1698 cm⁻¹ (ν_{C=O}), 1242 cm⁻¹ (ν_{Ar-O-Ar}).

Polymer PES-NPh (**2c**)

The polymer **2c** was synthesized from **1c** and dichlorodiphenylsulfone at 175°C. The yield was

TABLE I
Synthesis and Characters of the Polymers

Polymer	Yield (%)	Reaction time (h)	Temperature (°C)	(η) ^a (dL/g)	T _g ^b (°C)	T _{5%} ^c (°C)	d spacing (Å)	FFV ^d
PES-C	98	10	175	0.76	251.6	505.2	4.97	0.143
2a	93	7	170	0.86	296.2	483.8	4.60	0.117
2b	98	10	175	0.68	245.7	478.4	5.04	0.132
2c	97	10	175	0.70	235.7	522.6	5.09	0.138
2d	95	10	175	0.64	230.1	470.1	5.42	0.161

^a Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

^b Obtained by defining the peak of Tan_delta curves from DMTA at the heating rate of 5°C/min at 1 Hz.

^c By TGA in N₂, 5% weight loss temperature in nitrogen at 10°C/min.

^d FFV = (V - V₀)/V, where V is the specific volume at 30°C, V₀ = 1.3 V_w and V_w is the van der Waals volume of the repeating unit estimated by the method outlined by Bondi.

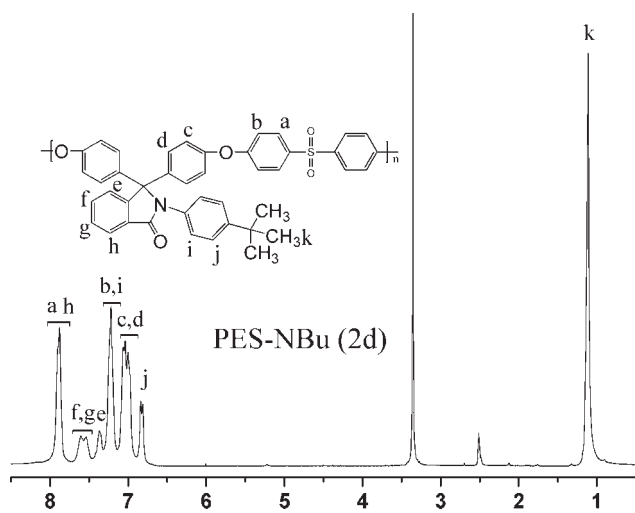


Figure 2 ^1H NMR spectrum of 2d.

97%. ^1H NMR (DMSO- d_6) δ (ppm): 7.01–7.06 (8H, m, Ar). FTIR (KBr): 1703 cm^{-1} ($\nu_{\text{C=O}}$), 1242 cm^{-1} ($\nu_{\text{Ar-O-Ar}}$).

Polymer PES-NBu (2d)

This polymer was synthesized from **1d** and dichlorodiphenylsulfone at 175°C . The yield was 95%. ^1H NMR (DMSO- d_6) δ (ppm): 1.11 (9H, s, CH_3), 7.00–7.06 (8H, m, Ar). FTIR (KBr): 1704 cm^{-1} ($\nu_{\text{C=O}}$), 1242 cm^{-1} ($\nu_{\text{Ar-O-Ar}}$).

Preparation of PES-N films

About 10% wt solutions of PES-N in NMP were cast onto glass substrate and dried at 80°C for 6 h. The semidry polymer films were removed from the substrate and then heated at 120°C , 200°C for 24 h in vacuum, respectively. All films were transparent, flexible and $\sim 25\ \mu\text{m}$ in thickness. These films were cut into strips of about 4 cm length and 5 mm width for stress–strain and thermal measurements.

RESULTS AND DISCUSSION

Monomers synthesis

The synthetic route of the monomers is outlined in Schemes 1 and 2. All modified cardo phthalimide bisphenols were synthesized from PPH with series of amines and ammonia. Monomers **1a** and **1c** were prepared according to the literature method. In a similar manner with the synthesis of **1a**, monomer **1b** was synthesized from phenolphthalein and methylamine at room temperature (Scheme 1). Monomer **1d** was prepared from phenolphthalein and 4-*tert*-butylaniline hydrochloride via refluxing in 4-*tert*-butylaniline (Scheme 2). Elemental analyses and ^1H NMR spectro-

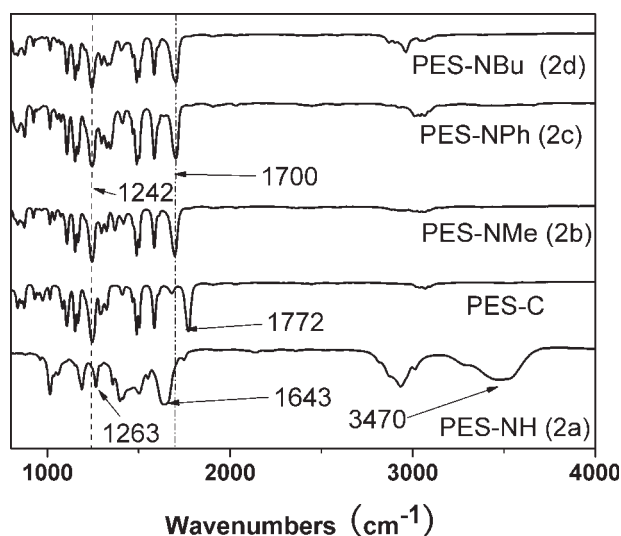


Figure 3 FTIR spectra of PES-N and PES-C.

scopic techniques were used to identify the structures of the target monomers. The FTIR spectra of the modified monomers showed that the characteristic absorption of ester carbonyl (C=O) at 1772 cm^{-1} was disappeared, and strong *N*-phthalimidine carbonyl absorptions (C=O) were detected at 1653 cm^{-1} for **1a**, 1698 cm^{-1} for **1b**, 1704 cm^{-1} for **1c**, and 1668 cm^{-1} for **1d**, which indicated the successful synthesis of monomers. The ^1H NMR spectrum of **1d** was illustrated in Figure 1. Assignment of each proton was also given in this Figure and this spectrum agrees well with the proposed molecular structure of **1d**.

Synthesis of polymers

Poly(arylene ether sulfone)s (PES-N) (**2a–d**) containing phthalimide with different *N*-substituents were easily synthesized by a solution of nucleophilic polycondensation of bisphenols **1a–d** with dichlorodiphenylsulfone (Scheme 3). For comparison study, poly(arylene ether sulfone) (PES-C) from phenolphthalein and dichlorodiphenylsulfone was also synthesized. Polymer **2a** was prepared via polycondensation for less time at lower temperature than another three polymers in order to avoid cross-linking. The N–H

TABLE II
Solubility^a of PES-N and PES-C

Polymer	DMAc	NMP	DMF	DMSO	CHCl_3	THF
PES-C	++	++	++	++	++	–
2a	++	++	++	++	–	–
2b	++	++	++	++	++	+
2c	++	++	++	++	++	++
2d	++	++	++	++	++	++

^a Solubility: (++) soluble; (+) partially soluble, –: insoluble.

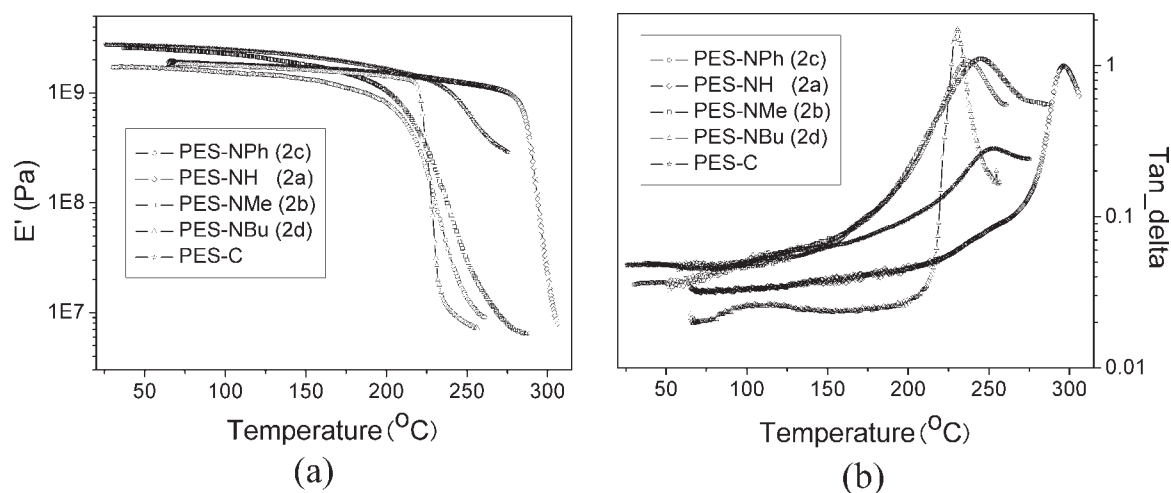


Figure 4 DMTA curves of the PES-N and PES-C. (a) The curves of storage modulus (E') versus temperature of polymers. (b) The curves of Tan_delta versus temperature of polymers.

group contained in **1a** could participate in nucleophilic polycondensation with dichlorodiphenylsulfone at high temperature, and then generated cross-linked polymers which precipitated from the solvent system. As can be seen from Table I, all polymers exhibited inherent viscosities in the range of 0.64–0.86 dL/g in DMAc. The structures of PES-N were confirmed by ^1H NMR (Fig. 2) spectrum and FTIR spectra (Fig. 3). The polymers exhibited absorption at 1244 or 1263 cm^{-1} (Ar–O–Ar), and the disappearance of broad peak at 3340 cm^{-1} (O–H) and strong stretching at 1772 cm^{-1} (ester carbonyl, C=O) demonstrated a successful polycondensation reaction between modified bisphenols and dichlorodiphenylsulfone.

Polymer properties

The solubility of the polymers was tested in various solvents, and the results are summarized in Table II. Polymers **2b–d** exhibited outstanding solubility in common organic solvents, such as NMP, DMAc, DMF, THF, and CHCl_3 . In general, these polymers revealed an enhanced solubility as compared with conventional poly(arylene ether sulfone). This can be attributed in part to the incorporation of alkyl or

aryl groups into polymer backbone, which retard dense chain packing and lead to a decreased chain–chain interaction, hence, increased the solubility. Polymer **2a** revealed a slightly decreased solubility, possibly due to denser chain packing and aggregation induced by the N–H bond.

The thermal properties of these polymers were assessed with thermogravimetric analysis (TGA). As shown in Table I, the 5% weight loss temperatures of the polymers ($T_{5\%}$) in nitrogen ranged from 470 to 523 $^{\circ}\text{C}$, depending on the bisphenol monomers used. Among all the polymers synthesized, polymer **2c** showed the highest thermal stability ($T_{5\%} = 523^{\circ}\text{C}$), which can be attributed to its wholly aromatic structure. Polymer **2d** had relative lower $T_{5\%}$ (470 $^{\circ}\text{C}$) than that of PES-C (505 $^{\circ}\text{C}$) because of incorporation of

TABLE III
Mechanical Properties of the PES-N and PES-C

Polymer	Strength (MPa)	Elongation at break (%)	Modulus (GPa)
PES-C	101.1	10.6	2.8
2a	100.7	18.3	2.6
2b	95.2	10.2	2.5
2c	84.0	8.3	2.0
2d	69.2	5.7	1.8

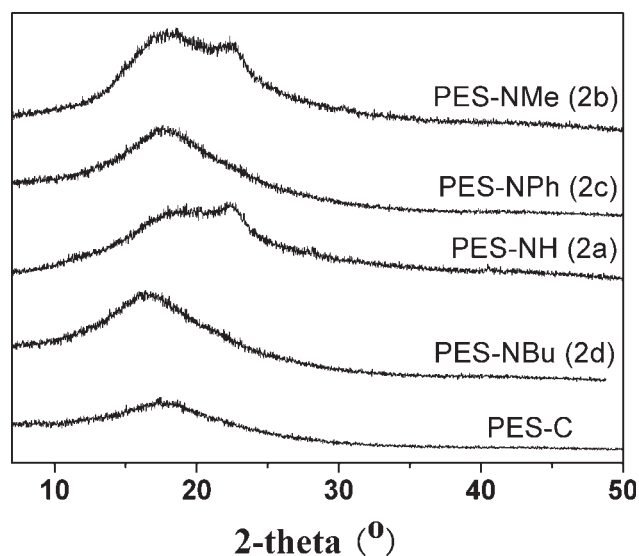


Figure 5 X-ray curves of the PES-N and PES-C.

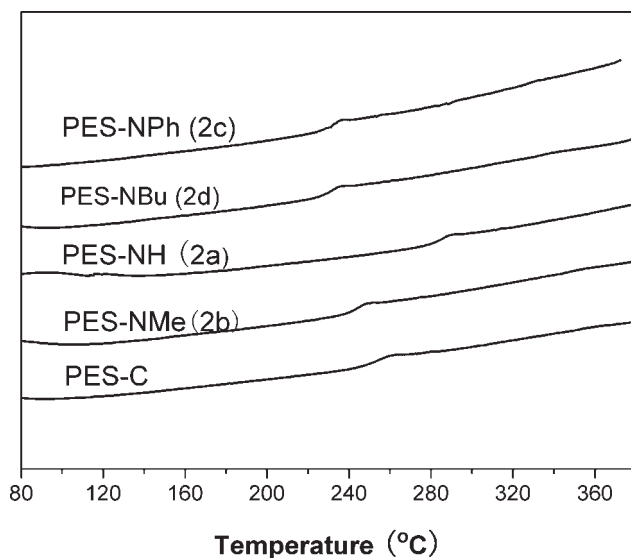


Figure 6 DSC curves of the PES-N and PES-C.

tert-butyl groups. The glass transition temperatures (T_g) of the synthesized PES-N were characterized by DMTA measurement at a heating rate of 5°C/min, and the results were summarized in Table I. The polymers showed T_g in the range of 230–300°C, and the T_g value of **2a** was the highest among the polymers because of the presence of N–H bond which resulted in compact packing and hindered the segment motion. As can be seen from Figure 4, the T_g order of another four kinds of polymers was PES-C > **2b** > **2c** > **2d**, which indicated that T_g values were decreased slightly with increasing size of the N-substituent.

Transparent, flexible, and almost colorless films could be cast from the NMP solutions of all the PESs and were subjected to a tensile test by an Instron machine. The tensile properties of these polymers were summarized in Table III. These films showed tensile strengths of 69.2–101.1 MPa, elongation to break of 5.7–18.3%, and an initial modulus of 1.8–2.8 GPa. The strength of polymers decreased with introducing of N-substituent, and the more bulky of the substituent led to the lower strength (Table III). Any-

way, all of the polymers yielded high enough toughness for gas permeation experience.

Figure 5 displayed the wide-angle X-ray diffractions of PES-N films. Most of the films exhibited typical Gaussian distribution curves, broad and structureless, suggesting that all the polymers tested were amorphous nature. This probably due to the presence of bulky pedant groups which hindered the packing of polymer chains. Different scanning calorimetry (DSC) was also conducted and the results were shown in Figure 6. All the DSC curves for polymers showed a single T_g transition, which indicated that all polymers were amorphous.

Gas transport

It is well-known that permeation of gas molecules in polymers occurs via the “solution–diffusion” mechanism,¹⁸ and the permeability coefficient (P) is determined by the solubility coefficient (S) and the diffusion coefficient (D), $P = D \cdot S$. For the uncondensable gases, which have no obvious interactions between gases and polymers, the P is mainly determined by the diffusion coefficient (D).^{4,6} The diffusivity coefficients (D) correlate very well with the FFV of the polymers according to the following relation⁶:

$$D = Ae^{-B/FFV}$$

where A and B are characteristic parameters for each gas that may also depend to some degree on the polymer family and type of gas. To explain different gas permeability of polymers, the fraction free volume (FFV) of polymers was calculated by using the bondi's group contribution method and listed in Table I. The diffusion coefficient (D) of gas molecules in polymers was obtained from the time-lag method, and S was calculated with equation mentioned above, and the results were listed in Table IV. The gas permeability and selectivity of the dense PES membranes for H₂, O₂, N₂, CO₂, and CH₄ were determined at 30°C and 1 atm (Table V). The

TABLE IV
Gas Diffusivity Coefficients and Solubility Coefficients of PES-N and PES-C

Polymer	Diffusivity (D) (10 ⁻⁸ cm ² /s)				Solubility (S) (cm ³ STP)/(cm ³ atm)			
	O ₂	N ₂	CO ₂	CH ₄	O ₂	N ₂	CO ₂	CH ₄
PES-C	3.03	0.697	1.18	0.128	0.156	0.228	4.42	1.30
2a	1.22	0.166	0.314	0.0496	0.218	0.233	5.57	1.31
2b	2.38	0.583	0.98	0.0883	0.166	0.121	2.02	0.757
2c	2.86	0.618	1.12	0.108	0.149	0.121	2.16	0.690
2d	10.53	3.56	5.80	0.558	0.128	0.0897	1.81	0.654

TABLE V
Gas Permeability and Permselectivity of PES-N and PES-C

Polymer	Permeability (P) barrer ^a					Permselectivity α^a		
	P(O ₂) ^a	P(H ₂)	P(N ₂)	P(CO ₂)	P(CH ₄)	$\alpha(\text{O}_2/\text{N}_2)$	$\alpha(\text{H}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{CH}_4)$
PES-C	0.62	13.96	0.21	6.87	0.22	2.95	66.48	31.22
2a	0.35	5.59	0.051	2.30	0.086	6.86	109.61	26.74
2b	0.52	7.11	0.093	2.61	0.088	5.59	76.45	29.66
2c	0.56	8.08	0.098	3.18	0.098	5.71	82.44	32.45
2d	1.78	23.43	0.42	13.80	0.48	4.24	55.79	28.75

^a Gas permeation coefficient (barrers) 1 barrer = 10^{-10} cm³ (STP) · cm/cm² s cmHg.

permeability coefficients of H₂, O₂, and CO₂ are in the range 5.6–23.4, 0.4–1.8, and 2.3–13.8 barrers, respectively. Figure 7 shows the curves of gas permeability (*P*) versus 1/FFV. It can be seen from Figure 7, the gas permeability increased with increasing of FFV of polymers. Compared with another four kinds of PESs, the polymer **2a** exhibited the lowest gas permeability because of strongly hydrogen bond interaction between polymer chains caused by N–H groups. This hydrogen bond interaction results in an increase in packing density of polymers and a decrease in FFV. Additionally, the polymer **2d** shows about three times higher *P*(X₂) than PES-C accompanying with increase of the separation coefficients of $\alpha(\text{O}_2/\text{N}_2)$ from 2.95 to 4.24. It was owing to the presence of the bulky pedant 4-*tert*-butylphenyl group in polymer backbone which hindered the compact packing of polymer chains and resulted in increase of FFV from 0.143 to 0.161. However, the gas permeabilities of **2c** and **2b** were lower than that of PES-C, although there was pedant methyl, or phenyl groups in polymer side chains. The possible reason explained by Chen coworkers⁶ was that the pendants

on the side chains would play two opposite roles on the polymer chains packing density. One was to open up the polymers chains, and it was favorable for the FFV. On the other hand, the relatively small methyl and planar structure of phenyl might occupy the space between polymer chains and decrease the FFV of polymers. For **2b** and **2c**, the latter effect was more evident, leading to theirs decreased FFV. Moreover, another reason for decreased FFV of **2c** might be the packing mode, which would form $\pi \sim \pi$ conjugated interaction among *N*-phenyl belonging to different polymer chains when the chains accumulated together. Compared with PES-C and **2c**, polymer **2d** exhibited higher gas permeability by introducing of 4-*tert*-butylphenyl instead of phenyl because that the former effect was evident, and *tert*-butyl hindered the formation of $\pi \sim \pi$ conjugated interaction among polymer chains. Compared with modified PES-C containing pendant alkyl groups reported by Chen and coworkers,⁶ polymer **2d** showed higher *P*(X₂) than PES-C containing pendant methyl groups, but lower *P*(X₂) than PES-C containing pendant isopropyl groups.

In gas separation application, a tradeoff generally existed between permeability and permselectivity resulted in any improvement in permeability accompanied with a decrease permselectivity, and vice versa. As can be seen from Table IV, the results of this series of PES-N almost followed the above rules. Compared with PES-C, the *P*(O₂) of **2a**, **2c**, and **2b** decreased from 0.62 to 0.35, 0.52 and 0.56 barrers, respectively, but the $\alpha(\text{O}_2/\text{N}_2)$ increased about two times. Furthermore, the $\alpha(\text{H}_2/\text{N}_2)$ of **2a** reached 109 that was significantly higher than that of commercial bisphenol-A polysulfone (PSF).¹⁹ The increase in $\alpha(\text{H}_2/\text{N}_2)$ of **1a** might be due to compact stack and restricted segmental motion^{20–23} caused by hydrogen bonds.

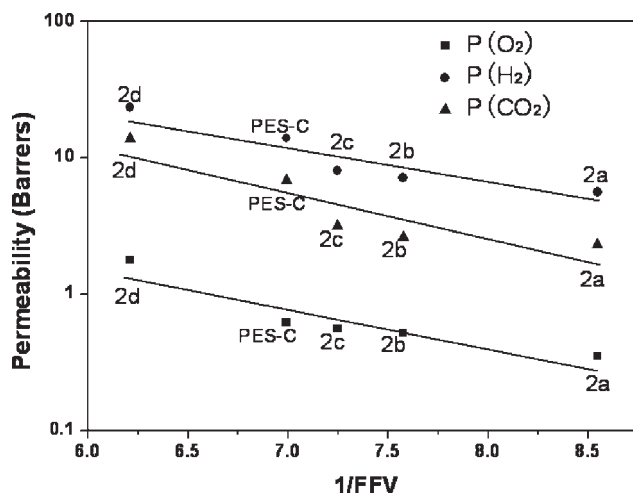


Figure 7 The curves of gas permeability versus 1/FFV of polymers.

CONCLUSION

Novel cardo poly(arylene ether sulfone)s containing phthalimide side groups were successfully synthe-

sized from the modified phenolphthalein and dichlorodiphenylsulfone. All synthesized polymers displayed good solubility in aprotic polar solvents, high thermal stability, and good mechanical properties.

Gas transport properties for H₂, CO₂, CH₄, N₂, and O₂ had been investigated. Introduction of bulky phthalimides moieties increase the FFV, thus resulted in increased gas permeability. In comparison with PES-C membrane, the modified polymer **2d** membrane showed higher gas permeability and permselectivity of O₂ over N₂ which increased from 2.95 to 4.24. The O₂ permeability increased from 0.62 to 1.78 barrers, and the CO₂ permeability increased from 6.87 to 13.80 barrers. The results indicated that the introduction of 4-*tert*-butylphenyl group into PES-C backbone is highly effective to improve the gas permeability of membranes.

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