

# Synthesis and Gas Permeability of Novel Fluorinated Poly(phenylene-co-naphthalimide)s

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**ABSTRACT:** A new class of high-performance polymers [poly(phenylene-co-naphthalimide)s] was prepared through the Ni(0) catalytic coupling of *N*-(4-chloro-2-trifluoromethylphenyl)-5-chloro-1,8-naphthalimide and 2,5-dichlorobenzophenone. The resulting copolymers exhibited high molecular weights (high inherent viscosities) and a combination of desirable properties such as good solubility in dipolar aprotic solvents, film-forming capability, and mechanical properties. The glass-transition temperatures of the copolymers ranged from 320 to 403°C and increased as the content of the naphthalimide moiety increased. Tough polymer films, obtained via casting from *N*-methylpyrrolidone

solutions, had tensile strengths of 64–107 MPa and tensile moduli of 3.4–4.7 GPa. The gas permeability coefficients of the copolymers were measured for H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. They showed oxygen permeability coefficients and permeability selectivity of oxygen to nitrogen (permeability coefficient for O<sub>2</sub>/permeability coefficient for N<sub>2</sub>) in the ranges of 1.39–4.31 and 4.92–5.38 barrer, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2395–2402, 2007

**Key words:** gas permeation; high performance polymers; polyimides

## INTRODUCTION

Aromatic polyimides represent a class of materials that combine outstanding mechanical and electrical properties and high thermal and chemical stability. They are widely used in many applications such as dielectrics, coatings, composite materials, and membranes.<sup>1,2</sup> Recently, sulfonated naphthalenic polyimides have been suggested to be promising candidates for novel proton-exchange membrane fuel cells because of their superior chemical and thermal stability.<sup>3–5</sup> In some cases, the introduction of a rigid naphthalene ring into the polymer backbone contributes to increased thermal stability of the polymer, even yielding materials with glass-transition temperatures ( $T_g$ 's) greater than 400°C.<sup>6–10</sup>

However, most polyimides also encounter processing difficulty because of their infusibility and poor solubility in organic solvents. The most common method used for preparing polyimides is a two-step polymerization method that allows the use of a soluble precur-

sor, poly(amic acid), to deposit thin films, followed by a thermal treatment to obtain polyimide films. This kind of two-step process cannot be taken to process naphthalenic polyimides. This is because bis(naphthalenic anhydride)s have reduced electrophilic reactivity, so their polycondensation reactions with diamines require high reaction temperatures (>180°C) with an organic acid or base as a catalyst. Under these conditions, the formation of poly(amic acid) and imidization essentially occur spontaneously. Therefore, their synthesis and process are more difficult than those for common five-membered ring polyimides.<sup>11–13</sup> It is of particular interest to develop processable naphthalenic polyimides without sacrificing their thermal stability and mechanical properties.<sup>14–16</sup>

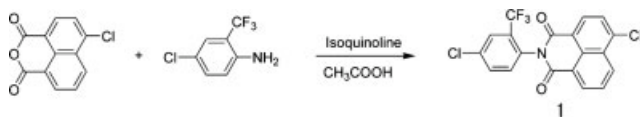
The Ni(0)-catalyzed coupling of bis(aryl halide)s is one of the most recent approaches to the development of high-performance materials.<sup>17–20</sup> In a previous article,<sup>21,22</sup> we reported the successful synthesis of a polyimide by the Ni(0) catalytic coupling of bis(chlorophthalimide). The monomer was easily prepared from chlorophthalic anhydride and diamines and was also copolymerized with other macromonomers, such as dichlorodiphenylsulfone<sup>23</sup> and 2,5-dichlorobenzophenone (2).<sup>24</sup> In similar manner, the naphthalimide dichloride monomer can be easily synthesized from 5-chloro-1,8-naphthalic anhydride. The preparation of polymers containing naphthalimide structures with the Ni(0) catalytic coupling method is more attractive

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Scheme 1 Synthesis of 1.

because of the accessibility of the monomer, the mild reaction conditions, and the high degree of polymerization. This method also avoids using low-reactivity bis(naphthalenic anhydride)s and the formation of the imide cycle as the polyimide-forming reaction. With this Ni(0) catalyst system, the resulting polymer should be soluble in the polymerization solution to obtain high-molecular-weight polymers and give satisfactory processability of the products. However, naphthalimide dichloride is a rigid macromonomer. Our previous investigation revealed that the polymerization of rigid phthalimide dichloride gave low-molecular-weight polymers because of the formation of a polymer precipitate.<sup>21</sup>

Copolymerization is one of the most effective methods for synthesizing a polymer with desirable properties. Many researchers have synthesized various copolymers from known homopolymers as an alternative to the synthesis of new polymers.<sup>25,26</sup> The copolymers are intended to optimize the properties of the homopolymers. Monomer 2 is potentially inexpensive because it can be synthesized from 1,4-dichlorobenzene and benzoyl chloride. Poly(2,5-benzophenone) (PBP), synthesized from 2, displays good solubility in common organic solvents and excellent thermal and mechanical properties. The tensile modulus of commercial PBP (Poly-X-1000), produced by Maxdem, Inc. (San Dimas, CA), far exceeds those of other high-performance polymers, including poly(phenylene sulfide), poly(ether ether ketone), and poly(ether imide).<sup>27</sup> However, PBP forms very brittle films.<sup>28</sup> The inability to form flexible films has greatly limited its applications, such as gas-separation membranes and organic electronics.

In this article, we report a successful synthesis of novel poly(phenylene-*co*-naphthalimide)s by the Ni(0)-catalyzed coupling of 2 and aromatic dichlorides containing naphthalimide components. The objective of this work was to design and synthesize a copolymer having improved thermooxidative stability and film-forming ability by taking advantage of polyimides and poly(*p*-phenylene)s. The introduction of naphthalimide moieties into the macromolecular chain was intended to improve the film-forming ability of the soluble polymers. Hence, the goal of better thermal stability together with good processability may be achieved by the preparation of polyimides bearing both benzophenone and naphthalimide units. The properties of the copolymers are also discussed.

## EXPERIMENTAL

### Materials

5-Chloro-1,8-naphthalic anhydride was used as received from Beijing Multi Technology Co., Ltd. 4-Chloro-2-trifluoromethylaniline, received from JS Chemical & Metallurgical Co., Ltd. (Tianjin, China), was distilled before use. *N,N*-Dimethylacetamide was dried over CaH<sub>2</sub>, distilled under reduced pressure, and stored over 4-Å molecular sieves. Reagent-grade anhydrous NiBr<sub>2</sub> was dried at 220°C *in vacuo*. Triphenylphosphine (PPh<sub>3</sub>) was recrystallized from hexane. Zinc dust was stirred with acetic acid, filtered, washed thoroughly with ethyl ether, and dried *in vacuo*. Other chemicals were used as received.

### Measurements

<sup>13</sup>C-NMR spectra were measured at 300 MHz on an AV300 spectrometer. Fourier transform infrared (FTIR) spectra were obtained with a Bio-Rad Digilab Division FTS-80 FTIR spectrometer. Elemental analyses were performed on an Elemental Analyses MOD-1106. The inherent viscosities were determined at a 0.5% concentration of the polymer in *N*-methyl-2-pyrrolidone with an Ubbelohde capillary viscometer at 30 ± 0.1°C. The thermogravimetric analyses (TGAs) were obtained in nitrogen with a PerkinElmer TGA-2 thermogravimetric analyzer, and the experiments were carried out with samples (10 ± 2 mg) at a heating rate of 10°C/min. The mechanical properties of the films were measured on an Instron 1211 mechanical tester.

Dynamic mechanical analysis (DMTA; DMTA IV, Rheometric Scientific) was used to analyze the mechanical stability of each sample. All measurements were carried out from 50 to 200°C in a strain-con-

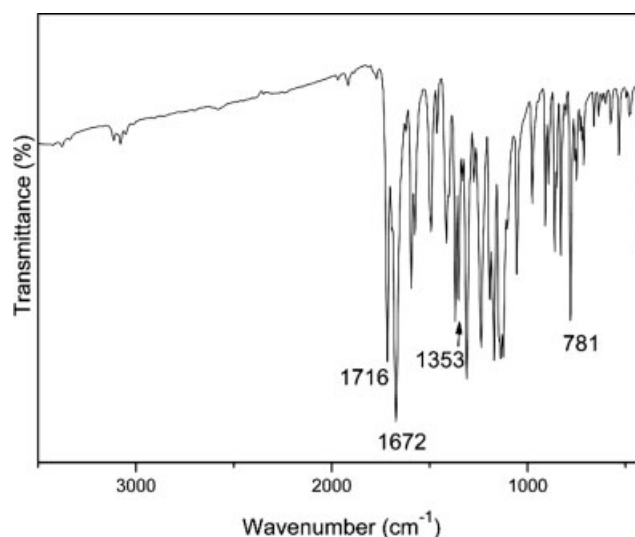


Figure 1 FTIR spectrum of 1.

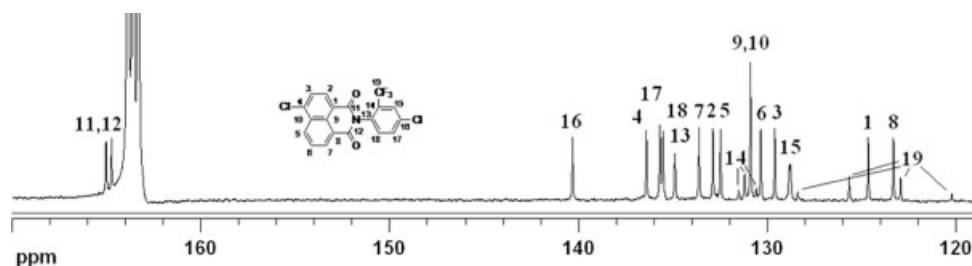


Figure 2  $^{13}\text{C}$ -NMR spectrum of 1.

trolled mode. The strain was 0.01%. The scanning rate was  $3^\circ\text{C}/\text{min}$ , and the frequency was 1 Hz. The areas of the measured samples were  $1\text{ cm} \times 3\text{ cm}$ .

The permeability was determined in the sequence of  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ . They were tested at  $25^\circ\text{C}$  at 1 atm. The design of the permeation apparatus and the experimental procedure are described in detail elsewhere.<sup>29</sup> In short, the gas permeability was determined from the rate of the pressure increase in the permeation (downstream) side in the steady state with the following equation:

$$P = \frac{VL}{ART\Delta p} \left( \frac{\Delta p}{\Delta t} \right)$$

where  $P$  is the permeability coefficient of a membrane to gas in barrers ( $1\text{ barrer} = 10^{-10}\text{ cm}^3\text{ [STP] cm cm}^{-2}\text{ s}^{-1}\text{ cmHg}^{-1}$ ),  $V$  is the downstream volume,  $L$  is the membrane thickness,  $A$  is the effective area of the film,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $\Delta p$  is the transmembrane pressure ( $\Delta p = p_2 - p_1$ , where  $p_2$  and  $p_1$  are the upstream and downstream pressures, respectively), and  $\Delta p/\Delta t$  is the steady rate at which the pressure increases on the downstream side. The temperature was controlled within  $\pm 1^\circ\text{C}$  with a thermal regulator connected to a heater in the permeation cell wall.

The density [ $\rho$  ( $\text{g}/\text{cm}^3$ )] was determined by the flotation method in a mixture of carbon tetrachloride and xylene at  $20^\circ\text{C}$ . The specific volume [ $V_{sp}$  ( $\text{cm}^3/\text{g}$ )] was calculated as follows:

$$V_{sp} = 1/\rho$$

The fraction free volume (FFV) was calculated with the following equation:

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

where  $V_{sp}$  is the volume of polyimide calculated from the measured value of  $\rho$  and  $V_0$  is the occupied volume calculated from the correlation  $V_0 = 1.3V_w$ .  $V_w$  is the van der Waals volume, which is estimated with Bondi's group contribution method.<sup>30</sup> The specific free volume,  $V_f = (V_{sp} - V_0)$ , is defined as the differ-

ence between the observed values of  $V_{sp}$  and  $V_0$ . Both FFV and  $V_f$  are useful guides for interpreting permeation characteristics.

### Monomer synthesis

Synthesis of *N*-(4-chloro-2-trifluoromethylphenyl)-5-chloro-1,8-naphthalimide (1)

1 was synthesized according to a previously described procedure.<sup>31</sup>

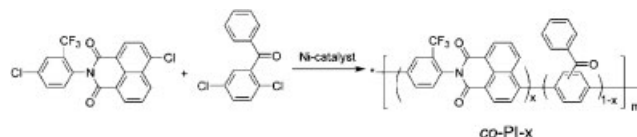
mp:  $278\text{--}279^\circ\text{C}$ . Yield: 76.8%.  $^{13}\text{C}$ -NMR (dimethylformamide- $d_7$ ,  $\delta$ ): 165.0, 164.7, 140.3, 136.4, 135.7, 135.5, 134.9, 133.6, 132.9, 132.5, 131.5, 131.2, 130.9, 130.6, 130.3, 129.6, 128.8, 128.4, 125.7, 124.7, 123.3, 122.9, 120.2 ppm.

Synthesis of 2,5-dichlorobenzophenone (2)

2 was prepared by the Friedel–Crafts acylation of 1,4-dichlorobenzene and benzoyl chloride according to a previously described procedure.<sup>24</sup> The yield was 62%, and the melting point was  $90\text{--}91^\circ\text{C}$ .

### General procedure for the syntheses of the copolyimides

*co*-PI-50 is given as an example.  $\text{NiBr}_2$  (0.32 g, 1.42 mmol),  $\text{PPh}_3$  (2.60 g, 9.98 mmol), and zinc dust (5.20 g, 80.00 mmol) were placed in a 250-mL, three-necked, round-bottom flask. The flask was evacuated and filled with nitrogen three times. Then, dry *N,N*-dimethylacetamide (20 mL) was added via syringe. The mixture became red-brown in 20 min. Then, 7.20 g (10.00 mmol) of the monomers was added and stirred at  $90^\circ\text{C}$  for 4 h. The resulting viscous mixture was diluted with 50 mL of *N,N*-dimethylacetamide, filtered, and then poured into 200 mL of 10 wt %  $\text{HCl}/$



Scheme 2 Synthesis of the copolymers derived from 1 and 2.

TABLE I  
Properties of the Copolymers and Homopolymers

Polymer	[ $\eta$ ] <sup>a</sup>	Yield	$T_g$ (°C) <sup>b</sup>	$T_{d,5\%}$ (°C) <sup>c</sup>	Water uptake	Elemental analysis			
						C		N	
						Calcd	Found	Calcd	Found
PBP	1.23	96	169	524	—	86.65	86.23	0	—
co-PI-30	1.54	94	320	526	1.65	77.94	77.16	1.84	1.78
co-PI-40	1.57	95	336	530	1.31	75.83	75.07	2.30	2.23
co-PI-50	1.78	96	361	528	1.14	73.96	73.53	2.70	2.62
co-PI-60	1.98	97	375	534	1.03	72.30	71.87	3.05	2.96
co-PI-80	1.45	93	403	527	0.80	69.51	69.02	3.64	3.57
PI	—	95	—	537	—	67.26	67.14	4.13	4.07

<sup>a</sup> Inherent viscosity measured in an *N*-methyl-2-pyrrolidone solution at a concentration of 0.5 dL/g at  $30 \pm 0.1^\circ\text{C}$ .

<sup>b</sup> Defined by the peak temperature in the  $\tan \delta$  curve.

<sup>c</sup> Temperature at which a 5% weight loss occurred when the polymer was subjected to TGA at a heating rate of  $10^\circ\text{C}/\text{min}$ .

acetone. The polymer was collected by filtration, washed with acetone, and dried *in vacuo* at  $200^\circ\text{C}$  for 24 h.

co-PI-30, co-PI-40, co-PI-60, and co-PI-80 were prepared with the same procedure, except that the feed ratios of monomer **1** to **2** were 3 : 7, 4 : 6, 6 : 4, and 8 : 2, respectively.

As for the homopolymers, PBP was synthesized from **2**, and polynaphthalimide (PI) was synthesized from **1** according to the aforementioned method.

### Casting of the membranes

The copolymers were dissolved in *N*-methyl-2-pyrrolidone to form a 2–3% solution at  $80^\circ\text{C}$  under an argon atmosphere for several days. Then, the *N*-methyl-2-pyrrolidone solution was filtered and cast onto a glass sheet. The solvent was evaporated via heating at  $70^\circ\text{C}$  until the membranes were dry, and then they were dried in a vacuum oven at  $200^\circ\text{C}$  for 24 h.

## RESULTS AND DISCUSSION

### Monomer syntheses

Recently, a novel fluorinated dichloride monomer containing naphthalimide was synthesized with acetic acid as the reaction medium through the reaction of 5-chloro-1,8-naphthalic anhydride and 2-amino-5-chlorobenzotrifluoride in the presence of isoquinoline, as shown in Scheme 1. The rate of the reaction was very low. This was attributed to the low reactivity of the naphthalenic anhydride in comparison with its phthalic counterpart. In addition, 2-amino-5-chlorobenzotrifluoride has reduced nucleophilic reactivity because of strong electron-withdrawing and steric hindrance effects of the  $\text{CF}_3$  group ortho to the imide nitrogen. Despite the low activity of the naphthalenic anhydride and hindered aniline monomers, naphthalimide dichloride could be obtained in a moderate yield.

The chemical structure of monomer **1** was confirmed by FTIR and  $^{13}\text{C}$  spectroscopy. FTIR (Fig. 1) showed the characteristic absorption bands of the imide ring near 1716 and 1672 (asymmetrical and symmetrical C=O stretching vibration), 1353 (C–N stretching vibration), and  $781\text{ cm}^{-1}$  (imide ring deformation).<sup>31</sup> The  $^{13}\text{C}$ -NMR spectrum of the dichloride monomer exhibited 23 peaks in the range of 120–166 ppm for carbon atoms, as shown in Figure 2. C19 and C14 showed clear quartet absorptions at 120–128 and 130–132 ppm, respectively, probably because of the  $^2J_{\text{C-F}}$  and  $^3J_{\text{C-F}}$  couplings of the carbon and fluorine atoms in the molecule.<sup>31</sup>

### Synthesis and characterization of the copolymers

The copolymerization of **2** with bis(chlorophthalimide)s was previously examined.<sup>24</sup> The main side reactions in the nickel-catalyzed coupling of aryl chlorides were minimized with thoroughly dried sol-

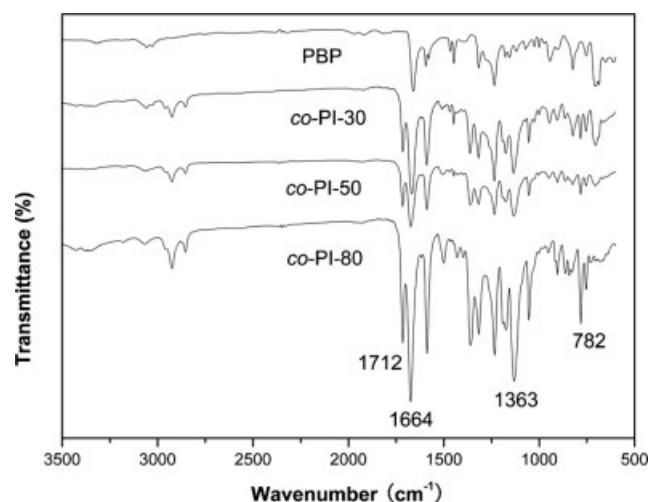


Figure 3 FTIR spectra of the copolymers.



TABLE II  
Solubility of the Copolymers and Homopolymers

Polymer	Acetone	THF	DMF	DMSO	DMAc	NMP	CHCl <sub>3</sub>	<i>m</i> -Cresol
PBP	–	–	+	+	+	+	+	+
<i>co</i> -PI-30	–	–	+-	–	+	+	–	+
<i>co</i> -PI-40	–	–	+-	–	+	+	–	+
<i>co</i> -PI-50	–	–	+-	–	+	+	–	+
<i>co</i> -PI-60	–	–	+-	–	+	+	–	+
<i>co</i> -PI-80	–	–	+-	–	+-	+-	–	+
PI	–	–	–	–	–	–	–	+-

+ = soluble; +- = partially soluble; – = insoluble; DMF = dimethylformamide; THF = tetrahydrofuran; DMSO = dimethyl sulfoxide; DMAc = *N,N*-dimethylacetamide; NMP = *N*-methyl-2-pyrrolidone.

vents in which the water concentration was less than 30 ppm and with excess amounts of PPh<sub>3</sub> with respect to NiBr<sub>2</sub>. The effects of the temperature, solvent volume, and amount of the nickel catalyst on the molecular weight were investigated to obtain high-molecular-weight copolymers. In this study, a series of copolymers was synthesized from **1** and **2** by Ni(0)-catalyzed coupling with our previously optimized reaction conditions (Scheme 2). The homopolymerization of monomer **1** proceeded rapidly with polymer precipitation because of the crystalline polymers and gave insoluble materials, whereas the copolymerization of **1** with **2** took place homogeneously. The results of the polymerizations are summarized in Table I. The copolymers are labeled *co*-PI-*x*, where *x* is the molar fraction of monomer **1** in the feed. The formation of the copolymers was confirmed by elemental analysis and FTIR spectroscopy. As shown in Figure 3, the FTIR spectra of *co*-PI-30, *co*-PI-50, and *co*-PI-80 exhibited characteristic absorption bands of the imide ring at 1712 and 1664 (asymmetrical and symmetrical C=O stretching vibration), 1363 (C–N stretching vibration), and 782 cm<sup>-1</sup> (imide ring deformation).<sup>10</sup>

The intensity of these peaks increased with an increase in the amount of monomer **1**, suggesting an increase in the incorporation of naphthalimide groups. The inherent viscosities of the copolymers were 1.23–1.98 dL/g, indicating fairly high molecular weights. The elemental analysis values of these polymers were in agreement with their respective structures. Their solubility behavior is shown in Table II. All the copolymers were soluble in polar organic solvents such as *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone but not soluble in less polar solvents such as tetrahydrofuran and chloroform. In comparison with the insoluble homopolymer derived from **1**, the copolymers displayed improved solubility because of the introduction of benzophenone moieties into the polymer backbone, which served to solubilize the materials. It is well known that PBP displays good solubility in common organic solvents and excellent thermal and mechanical properties but poor film-forming capability. In this study, the copolymers could form flexible and tough films via casting from the solution. The excellent film-forming ability of the copolymers could be attributed to the introduction of naphthalimide moieties, which increased interchain

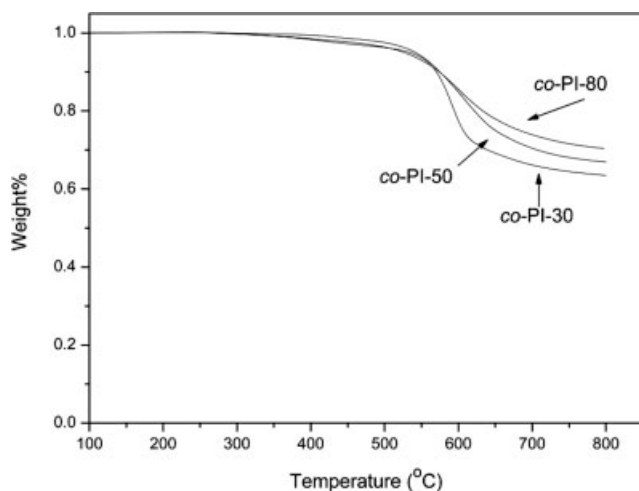


Figure 4 TGA curves of the copolymers.

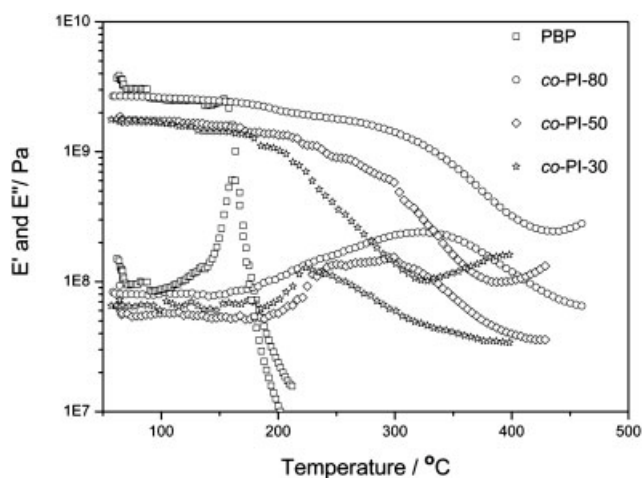


Figure 5 Temperature dependence of  $E'$  and  $E''$ .

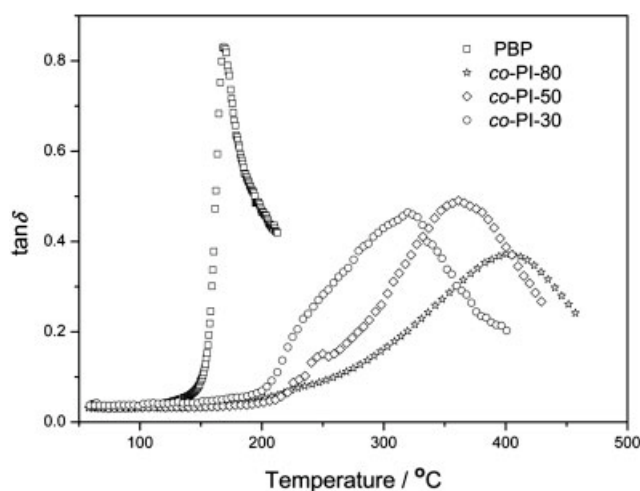


Figure 6 Temperature dependence of  $\tan \delta$ .

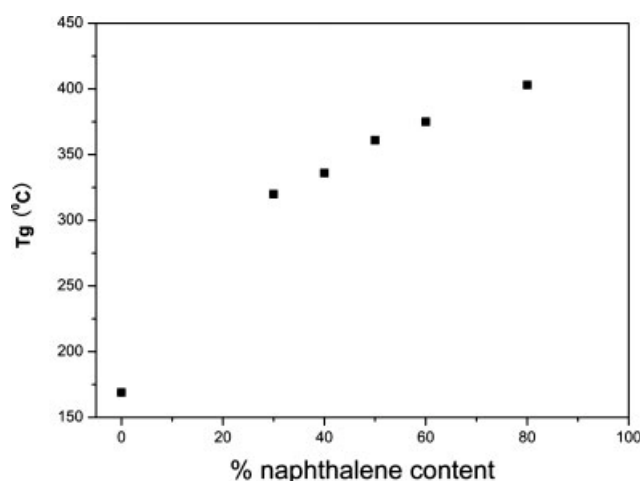


Figure 7 Variation of  $T_g$  as a function of the naphthalene content.

interactions because of strong charge-transfer interactions between the naphthalimide moieties.

The thermal and thermooxidative stability of the polyimides were evaluated by TGA with 5 wt % loss values for comparison, and the results are tabulated in Table I. Typical TGA curves of the copolymers are illustrated in Figure 4. The temperature at 5% weight loss of the copolymers stayed within 526–534°C. The

TABLE III  
Mechanical Properties of the Copolymer Films

Polymer	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
PBP	22	1.1	2.6
co-PI-30	64	2.5	3.4
co-PI-40	83	4.7	4.0
co-PI-50	91	4.3	4.3
co-PI-60	107	6.7	4.7
co-PI-80	68	3.0	3.5

results indicate that these copolymers all had high thermal stability.

The dynamic mechanical properties of all the copolymer membranes were investigated with DMTA. The temperature dependence of the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) is presented in Figure 5. All the membranes showed high  $E'$  values. The  $E'$  values dropped gradually at high temperatures. The  $\tan \delta$  (maximum) values (Fig. 6) were taken to estimate the  $T_g$  values of these polymers, and the results are listed in Table I. The  $T_g$  values of the copolymers were not detectable by differential scanning calorimetry (DSC) in either normal or oscillating modes. The  $T_g$ 's of some rigid, rodlike polyimides have also been reported to be very weak or not detectable.<sup>10</sup> The  $T_g$  value of PBP (164°C) observed by DMTA was comparable to that previously determined by DSC (167°C).<sup>18</sup>  $T_g$  of the copolymers could be tuned from 320 to 403°C. As expected, the  $T_g$  values of all the copolymers were much higher than that of homopolymer PBP (167°C) and increased with increasing content of the naphthalimide moieties. As shown in Figure 7, the increase in  $T_g$  with the naphthalimide content was linear. Apparently, the rigidity of the naphthalimide moiety increased the  $T_g$  values of these copolymers.

Table III shows the mechanical properties of the polymer membranes. The copolymer membranes had a tensile strength, elongation at break, and Young's modulus in the ranges of 64–107 MPa, 2.5–6.7%, and 3.4–4.7 GPa. All the copolymers exhibited better mechanical properties than PBP under the same test conditions. The tensile strength and Young's modulus of the copolymers increased with increasing imide content in the polymer backbone. Again, this can be

TABLE IV  
Gas Permeability of the Copolymers at 25°C and 1 atm

Polymer	$P_{H_2}$	$P_{O_2}$	$P_{N_2}$	$P_{CO_2}$	$P_{CH_4}$	$\alpha_{H_2/N_2}$	$\alpha_{O_2/N_2}$	$\alpha_{CO_2/CH_4}$
co-PI-30	16.3	1.39	0.258	6.81	0.256	63.3	5.38	26.6
co-PI-40	29.7	2.93	0.567	13.8	0.559	52.4	5.16	24.7
co-PI-50	39.7	4.31	0.875	20.0	0.848	45.4	4.92	23.6
co-PI-60	36.5	3.71	0.743	17.3	0.716	49.1	4.99	24.2
co-PI-80	35.5	3.61	0.710	17.1	0.688	50.0	5.09	24.9

$P$  is the permeability coefficient in barrers (1 barrer =  $10^{-10}$  cm<sup>3</sup> [STP] cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>);  $\alpha_{A/B} = P_A/P_B$ .

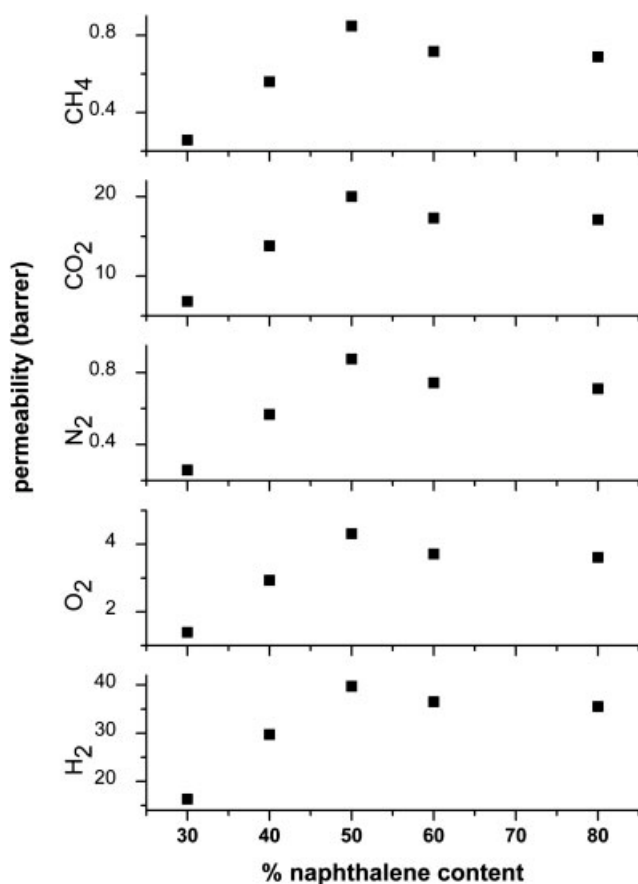


Figure 8 Permeability versus the naphthalene content.

explained by the rigidity and strong interactions of naphthalimide. However, *co*-PI-80 displayed lower mechanical properties than the other copolymers. This was probably due to the lower molecular weight of *co*-PI-80 in comparison with the other copolymers because it had the lowest inherent viscosity.

The water uptake of the copolymers is listed in Table I. The copolymers also showed very low water uptake in the range of 1.65–0.80%, which could be calculated from the weight change of the vacuum-dried polymer membranes after they were placed in water at room temperature for 3 days. *co*-PI-80 exhibited the lowest water uptake (0.80%) in comparison with *co*-PI-30 (1.65%). Apparently, the low water uptakes were mainly attributable to the polymer hydrophobicity

derived from the trifluoromethyl groups in the polyimide backbones.

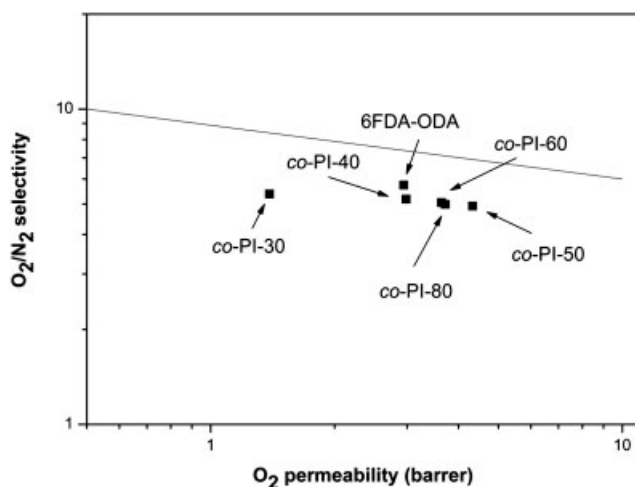
Good solubility, rigidity, and a large free volume of the polymers are vital for applications in gas-separation membranes. Bulky groups in the main chain generally tend to increase the free volume and hence the permeability coefficients. High chain stiffness is expected to result in relatively high permselectivities. In this study, the copolymers contained bulky trifluoromethyl groups and rigid polyphenylene main chains. Because of the unique properties of poly(phenylene-*co*-naphthalimide), it was interesting to investigate the gas-separation behavior of these copolymer membranes. Table IV summarizes the permeabilities and permselectivities of the copolymers determined from pure gas at 1 atm and 25°C. The gas-transport properties for the homopolymers were not measured because their membranes were too brittle.

Figure 8 illustrates the H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> permeability coefficients of the copolymers as functions of the content of the naphthalimide component. When the content of the naphthalimide component was increased from 30 to 50%, the permeability coefficients for all the tested gases increased with an increasing content of the naphthalimide component. It has been previously reported that **1** is an unsymmetrical monomer that results in enhanced free volume.<sup>31</sup> The bulky CF<sub>3</sub> group of monomer **1** also inhibits efficient chain packing and increases the permeability. For example, the permeability of O<sub>2</sub> increased from 1.39 to 4.31, and that of CO<sub>2</sub> increased from 6.81 to 20.0. However, the gas permeability of *co*-PI-60 and *co*-PI-80 was lower than that of the *co*-PI-50 membranes. This was due to increased interchain interactions along with increasing naphthalimide content.

To explain the different gas permeability values of the copolymer membranes, the FFV values of the copolymers were calculated with Bondi's group contribution method, and they are given in Table V.  $\rho$  (g/cm<sup>3</sup>) of the copolymers was measured by the flotation method in a mixture of carbon tetrachloride and xylene at 20°C and used for calculating the FFV values of the copolymers. The copolymers exhibited increased  $\rho$  with the content of the naphthalimide moieties. When the content of the naphthalimide component was increased from 30 to 50%, the FFV value

TABLE V  
FFV Values of the Copolymers

Polymer	$\rho$ (g/cm <sup>3</sup> )	$V_{sp}^{V_0}$ (cm <sup>-3</sup> g <sup>-1</sup> )	$V_w^{V_0}$ (cm <sup>-3</sup> mol <sup>-1</sup> )	$V_0^{V_0}$ (cm <sup>-3</sup> g <sup>-1</sup> )	$V_f^{V_0}$ (cm <sup>-3</sup> g <sup>-1</sup> )	FFV
<i>co</i> -PI-30	1.3680	0.731	111.79	0.638	0.093	0.127
<i>co</i> -PI-40	1.3850	0.722	117.34	0.625	0.097	0.134
<i>co</i> -PI-50	1.3986	0.716	122.89	0.615	0.101	0.141
<i>co</i> -PI-60	1.4265	0.701	128.44	0.606	0.095	0.136
<i>co</i> -PI-80	1.4663	0.682	139.54	0.590	0.092	0.135



**Figure 9** Permeability/permeability diagram for the  $O_2/N_2$  gas pair.

increased from 0.125 to 0.141. However, the FFV value decreased from 0.141 to 0.135 when the content of the naphthalimide component increased from 50 to 80%.

The ideal gas selectivities for  $H_2/N_2$ ,  $O_2/N_2$ , and  $CO_2/CH_4$ , based on the ratios of the pure gas permeability coefficients, are presented in Table IV. For all the copolymers, the selectivity decreased as the permeability increased and vice versa. This result was consistent with the well-known tradeoff. To provide some perspective on the performance of these copolymers, a permeability/selectivity map is present in Figure 9 for the  $O_2/N_2$  pair. The solid lines represent the upper bound lines of Robeson.<sup>32</sup> All the experimental ideal gas selectivities for the copolymers were lower than the upper bound values. The data for polyimide 6FDA-ODA, from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 4,4'-diaminodiphenyl ether (ODA), are shown for comparison.<sup>33</sup> The gas-separation performance of the copolymers was similar to that of 6FDA-ODA. The results suggest that the copolymers are attractive materials for industrial gas separation.

## CONCLUSIONS

A new class of novel high-performance copolymers were synthesized and characterized in this study. The copolymers were soluble in conventional solvents such as *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, and *m*-cresol and easy to process to form films by the solution-casting method. They were very stable until the temperature was higher than 500°C and exhibited high  $T_g$  values. Moreover, increasing the naphthalene content in the copolymers caused a linear increase in  $T_g$ .

The gas-transport properties for  $H_2$ ,  $CO_2$ ,  $CH_4$ ,  $N_2$ , and  $O_2$  were investigated. The gas permeability of the copolymer membranes was related to their chemical

compositions. The introduction of fluorinated naphthalimide moieties increased the fractional free volume and thus resulted in increased gas permeability. However, when the concentration of the naphthalimide moieties was more than 50%, the copolymer membranes showed decreased gas permeability because of increased interchain interactions.

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