Synthesis and Characterization of Highly Soluble and Oxygen Permeable New Polyimides Bearing a Noncoplanar Twisted Biphenyl Unit Containing *tert*-Butylphenyl or Trimethylsilyl Phenyl Groups[†]

Hyung-Sun Kim, Yun-Hi Kim, Seung-Kuk Ahn, and Soon-Ki Kwon*

Department of Polymer Science & Engineering and Engineering Research Institute, Gyeongsang National University, Chinju 660-701, Korea

Received September 9, 2002

ABSTRACT: The two new dianhydrides, 2,2'-bis(4"-tert-butylphenyl)-4,4',5,5'-biphenyltetracarboxylic dianhydride (BBBPAn) and 2,2'-bis(4"-trimethylsilylphenyl)-4,4',5,5'-biphenyltetracarboxylic dianhydride (BTSBPAn), composed of a noncoplanar twisted biphenyl unit containing *tert*-butylphenyl or trimethyl-silylphenyl groups were prepared. Two series of new organosoluble polyimides were prepared from the dianhydride and aromatic diamines by the conventional polyamide acid reaction followed by chemical imidization as well as high-temperature one-step polymerization. The structures of polymers were confirmed by various spectroscopic techniques. The weight-average molecular weight and polydispersities of resulting polymers were in the ranges 60 400–332 400 and 1.87–3.51, respectively. The polyimides showed good solubility in various organic solvents such as chloroform and THF. The polyimides exhibited 5% weight loss at 540–550 °C in nitrogen as measured by thermogravimetric analysis. The polyimides showed high T_{g} 's and good mechanical properties. The oxygen permeability coefficient (P_{O_2}) and permselectivity of oxygen to nitrogen (P_{O_2}/P_{N_2}) of the films were in the ranges 31–110 barrer and 2.8–4.3, respectively.

Introduction

Aromatic polyimides are widely used in the semiconductor and electronic packaging industry because of their outstanding thermal stability, good insulation properties with low dielectric constant, good adhesion to common substrates, and superior chemical stability.^{1,2} However, their applications were limited in many fields because the early polyimides were insoluble and intractable. Therefore, considerable research has been undertaken to devise new ways to circumvent these restrictions.

To circumvent these problems, solutions of polyimides would be desirable instead of precursors. Flexible links (e.g., -O-, $-SO_2-$, $-CH_2-$) or bulky groups (hexafluoroisopropylidene, isopropylidene, etc.) are commonly employed as solubilizing moieties, but it often costs in thermal stability and chain stiffness of polyimides. Alternatively, the solubilizing units may be derived from substituted biphenyls, increasing entropy factors due to rotational isomerism of benzene rings relative to an aryl-aryl bond.^{3,4} The relevant compounds of this class are biphenyltetracarboxylic dianhydrides. Among them, 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA) was commercialized in the early 1980s and is widely used at present.^{5,6}

It has been known that polymers containing a *tert*butyl group or trimethylsilyl groups have excellent gas permeability.^{7–13} Soluble polyimides containing a bulky *tert*-butylphenyl group or trimethylsilylphenyl groups offer particular promise in gas separation membrane application due to their superior mechanical property, high permeability, and permselectivity. Thus, we synthesized new *s*-BPDA-based polyimides containing a bulky *p-tert*-butylphenyl group and/or *p*-trimethylsi-

 † This article is dedicated to professor Won-Jei Cho on the occasion of his retirement.

lylphenyl, which are expected to give good solubility, high permeability, and permselectivity with good thermal stability and mechanical property. In this article, we report the synthesis and characterization of new polyimides derived from *s*-BPDA containing a bulky *p*-tert-butylphenyl group or *p*-trimethylsilylphenyl group and conventional aromatic diamines, and oxygen permeability (P_{O_2}) and permselectivity of oxygen to nitrogen (P_{O_2}/P_{N_2}) are also studied.

Experimental Section

Materials. *N*,*N*-Dimethylformamide (DMF) was dried over CaH₂ and distilled under nitrogen prior to use. *m*-Cresol was dried over CaCl₂ and then over 4 Å Linde type molecular sieves, distilled under reduced pressure, and stored under nitrogen in the dark. 4,4'-Oxydianiline (ODA, mp 192 °C), 4,4'-methylenediamine (MDA, mp 90 °C), and 4,4'-(hexafluoroisopropylidene)dianiline (FDA, mp 196 °C; all diamines from Aldrich) were used without additional purification. Other chemicals were purchased from Aldrich Chemical Co. or Fluka. and used as received.

Measurements. A Genesis II FT-IR spectrometer was used to record IR spectra. ¹H NMR and ¹³C NMR spectra were recorded with a DRX 500 MHz NMR spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA instruments 2050 thermogravimetric analyzer. The sample was heated using a 20 °C/min heating rate from 50 to 800 °C. Differential scanning calorimetry (DSC) was conducted under nitrogen on a TA instruments 2100 differential scanning calorimeter. The sample was heated at 20 °C/min from 30 to 400 °C. Inherent viscosities were measured with a Cannon Fenske viscometer in chloroform solution (0.5 g/dL, 25 °C). Tensile properties were determined from stress-strain curves obtained with a universal testing machine (UTM) (LR-10K, Lloyd Instrument Ltd.) with a load cell of 10 kgf. A gauge of 2 cm and a strain rate of 0.5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (1 cm wide, 5 cm long, and $30-80 \ \mu m$ thick). Gas permeabilities for the polymer membrane with about $30-60 \,\mu\text{m}$ of thickness

^{*} To whom all correspondence should be addressed.

were measured with a conventional permeability apparatus, which consists of upstream and downstream parts separated by a membrane.^{14–17} The upstream part was maintained to a constant pressure of 3 kgf/cm² of either pure O_2 or N_2 gas during the experimental period, and the downstream part was opened to the atmosphere. A bubble gas flowmeter was employed to measure the steady-state permeation flux, from which the gas permeability was calculated.

Monomer Synthesis. 3,3',4,4'-Tetramethylbiphenyl (TMBP). NiCl₂ (0.68 g, 0.05 mol), 2,2'-bipyridyl (0.84 g, 0.05 mol), triphenylphosphine (5.38 g, 0.19 mol), and Zn (16.24 g, 0.248 mol) were dissolved in 100 mL of DMF. The solution was heated to 60 °C for 1 h. 4-Bromo-o-xylene (20 g, 0.108 mol) was added with a syringe, and the flask was heated to 90 °C for another 24 h. After being cooled to room temperature, the product was poured into 500 mL of 2 N HCl solution, and then the organic layer was extracted twice with 200 mL portions of diethyl ether. The combined organic layer was washed twice with NaHCO₃ solution and dried over MgSO₄. The solvent was evaporated, and product was recrystallized from methanol to give a white product. Yield after recrystallization: 18 g (80%); mp: 75 °C. Anal. Calcd for C₁₆H₁₈ (210.31): C, 91.37%; H, 8.63%. Found: C, 91.22%; H, 8.54%. ¹H NMR (CDCl₃/TMS): δ 2.35-2.38 (d, 12H, Ar-CH₃), 7.22-7.24 (d, 1H, Ar-H), 7.36-7.37 (d, 1H, Ar-H), 7.41 (s, 1H, Ar-H). FT-IR (KBr pellet): 3040 (aromatic C-H), 2912 cm⁻¹ (aliphatic C-H),

2,2'-Dibromo-4,4',5,5'-tetramethylbiphenyl (DBTMBP). TMBP (50 g, 0.237 mol), FeCl₃ (0.58 g, 15.3 mmol), and methylene dichloride (300 mL) were charged into a threenecked round-bottom flask, equipped with a magnetic stirrer, addition funnel, condenser, drying tube, and thermometer. The solution was cooled to below -5 °C with an ice/salt bath, followed by adding bromine (79.41 g, 0.495 mol) dropwise over a period of 3-4 h under vigorous stirring. After reacting overnight, the product was poured into cooled 2 N NaOH solution, and then the organic layer was extracted twice with 200 mL portions of diethyl ether. The combined organic layer was washed twice with water and dried over MgSO4. The solvent was evaporated, and product was recrystallized from hexane to give a white product. Yield after recrystallization: 65.7 g (75%); mp: 115 °C. Anal. Calcd for C₁₆H₁₆Br₂ (368.11): C, 52.21%; H, 4.38%. Found: C, 52.35%; H, 4.45%. ¹H NMR (CDCl₃/TMS): δ 2.27–2.32 (d, 12H, Ar–CH₃), 7.02 (s, 1H, Ar-H), 7.45 (s, 1H, Ar-H). FT-IR (KBr pellet): 3073 (aromatic C-H), 2995 cm⁻¹ (aliphatic C-H).

p-tert-Butylbenzeneboronic Acid (TBBBA) and p-Trimethylsilylbenzeneboronic Acid (TSBBA). Magnesium turnings (6.72 g, 0.28 mol) were weighed into 500 mL threenecked round-bottom flask, equipped with a magnetic stirrer and activated with iodine. The solution of 46.9 g of bromo compound (0.22 mol) in dry THF (500 mL) was added at a rate that kept the reaction mixture refluxing. Finally, the reaction mixture was refluxed for 4-5 h until consumption of almost all magnesium turnings. After being cooled to room temperature, the trimethylborate (0.33 mol) was added dropwise to a cooled (-78 °C) solution with a syringe. After complete addition the mixture was allowed to warm to room temperature and stirred overnight. Subsequently, 2 N HCl solution (300 mL) was added. The organic layer was separated, and the aqueous layer was extracted twice with 200 mL of diethyl ether. The combined organic layer was washed with water and dried over MgSO₄. The solvent was evaporated, and the white powdered boronic acid derivative was washed several times with hexane to remove any impurity. Yield of TBBBA: 31 g (80%); mp: 209.8 °C. Anal. Calcd for C₁₀H₁₅BO₂ (178.04): C, 67.46%; H, 8.49%. Found: C, 67.32%; H, 8.39%. ¹H NMR (CDCl₃/TMS): δ 1.32 (s, 9H, Ar-tert-butyl), 7.42-7.47 (d, 2H, Ar-H), 7.83-7.89 (d, 2H, Ar-H). FT-IR (KBr pellet): 3336 (B-OH stretching), 3000 (aromatic C-H), 2966 cm⁻¹ (aliphatic C-H). TSBBA: 32 g (76%); mp 179.40 °C. Anal. Calcd for C₉H₁₅BO₂Si (194.11): C, 55.69%; H, 7.79%. Found: C, 55.91%; H, 7.70%. ¹H NMR (CDCl₃/TMS): δ 0.31 (s, 9H, Si-CH₃), 7.72-7.77 (d, 2H, Ar-H), 8.21-8.26 (d, 2H, Ar-H). FT-IR (KBr pellet): 3217 (B-OH stretching), 3050 (aromatic C-H), 2955 (aliphatic C–H), 1101 cm⁻¹ (C–Si stretching).

2,2'-Bis(4"-tert-butylphenyl)-4,4',5,5'-tetramethylbiphenyl (BBTMBP). The TBBBA (21.3 g 0.15 mol), DBTMBP (18.4 g, 0.05 mol), and tetrakis(triphenylphosphine)palladium-(0) (1 g, 0.87 mmol) were dissolved in dry toluene (300 mL). A solution of 2 M Na₂CO₃ (75 mL) was added, and the mixture was refluxed with stirring for 24 h in an atmosphere of nitrogen. After being cooled, the organic phase was separated, and the water phase was extracted twice with 200 mL portions of chloroform. The combined organic layer was washed twice with NaHCO₃ solution and dried over MgSO₄. The solvent was evaporated, and product was recrystallized from methanol to give a white product. Yield after recrystallization: 17 g (73%); mp: 161 °C. Anal. Calcd for C₃₆H₄₂ (474.72): C, 91.08%; H, 8.92%. Found: C, 91.23%; H, 8.85%. ¹H NMR (CDCl₃/TMS): δ 1.21 (s, 18H, Ar-*tert*-butyl), 2.21-2.25 (d, 12H, Ar-CH₃), 6.29-6.30 (d, 2H, Ar-H), 6.81-6.83 (d, 2H, Ar-H), 6.84 (s, 1H, Ar-H), 7.13 (s, 1H, Ar-H). FT-IR (KBr pellet): 3018 (aromatic C–H), 2975 cm⁻¹ (aliphatic C–H).

2,2'-Bis(4''-trimethylsilylphenyl)-4,4',5,5'-tetramethylbiphenyl (BTSTMBP). The synthesis of BTSTMBP was conducted as described above. Yield after recrystallization: 18 g (72%); mp: 160 °C. Anal. Calcd for $C_{34}H_{42}Si_2$ (506.87): C, 80.57%; H, 8.35%. Found: C, 80.63%; H, 8.44%. ¹H NMR (CDCl₃/TMS): δ 0.14 (s, 18H, Si-CH₃), 2.18–2.22 (d, 12H, Ar-CH₃), 6.32–6.33 (d, 2H, Ar-H), 6.79 (s, 1H, Ar-H), 6.92– 6.93 (d, 2H, Ar-H), 7.10 (s, 1H, Ar-H). FT-IR (KBr pellet): 3018 (aromatic C-H), 2975 (aliphatic C-H), 1119 cm⁻¹ (C-Si stretching).

2,2'-Bis(4"-tert-butylphenyl)-4,4',5,5'-biphenyltetracarboxylic Acid (BBBPTA). The oxidation was performed using BBTMBP (5 g, 10.5 mmol), pyridine (240 mL), distilled water (40 mL), and $KMnO_4$ (16.59 g 0.105 mol). The reaction mixture was refluxed for 24 h. For the second reaction step NaOH (8 g, 0.2 mol), distilled water (200 mL), and KMnO₄ (8.29 g, 0.053 mol) were used. The residual manganese dioxide was filtered and washed several times with hot water. After treatment of the cooled solution with excess concentrated HCl a white solid precipitated slowly, which was collected and dried in vacuo at 90 °C for 24 h. Yield: 5 g (80%); mp: 214 °C. Anal. Calcd for C₃₆H₃₄O₈ (594.65): C, 72.71%; H, 5.76%. Found: C, 72.52%; H, 5.61%. ¹H NMR (DMSO-*d*₆/TMS): δ 1.05 (s, 18H, Ar-*tert*butyl), 6.11-6.15 (d, 2H, Ar-H), 6.75-6.82 (d, 2H, Ar-H), 7.19 (s, 1H, Ar-H), 7.58 (s, 1H, Ar-H). FT-IR (KBr pellet): 3777 (carboxylic C-OH stretching), 3020 (aromatic C-H), 2980 (aliphatic C–H), 1721 cm⁻¹ (C=O stretching).

2,2'-Bis(4''-trimethylsilylphenyl)-4,4',5,5'-biphenyltetracarboxylic Acid (BTSBPTA). The synthesis of BTSBPTA was conducted as described above. Yield: 4.5 g (72%); mp: 210 °C. Anal. Calcd for $C_{34}H_{34}O_8Si_2$ (626.80): C, 65.15%; H, 5.47%. Found: C, 65.32%; H, 5.55%. ¹H NMR (DMSO-*d*₆/TMS): δ 0.02 (s, 18H, Si–CH₃), 6.18–6.19 (d, 2H, Ar–H), 6.88–6.92 (d, 2H, Ar–H), 7.29 (s, 1H, Ar–H), 7.57 (s, 1H, Ar–H). FT-IR (KBr pellet): 3500 (carboxylic C–OH stretching), 3020 (aromatic C–H), 2980 (aliphatic C–H), 1720 cm⁻¹ (C=O stretching).

Dianhydrides. In 100 mL round-bottom flask, tetracarboxylic acid (12 mmol) was dissolved in acetic acid (35 mL) and acetic anhydride (35 mL). The solution was refluxed for 4 h. After the solution was cooled to room temperature and filtered, the product was recrystallized for 1 day. The product was filtered and washed with toluene and dried at 120 °C under vacuum. Yield of 2,2'-bis(4"-tert-butylphenyl)-4,4',5,5'biphenyltetracarboxylic dianhydride (BBBPAn): 4.5 g (67%); mp: 310 °C. Anal. Calcd for C₃₆H₃₀O₆ (558.62): C, 77.40%; H, 5.41%. Found: C, 77.25%; H, 5.36%. ¹H NMR (DMSO-d₆/ TMS): δ 1.27 (s, 18H, Ar-*tert*-butyl), 6.36-6.39 (d, 2H, Ar-H), 6.97-7.03 (d, 2H, Ar-H), 7.81 (s, 1H, Ar-H), 8.33 (s, 1H, Ar–H). FT-IR (KBr pellet): 3015 (aromatic C–H), 2980 (aliphatic C–H), 1770 cm⁻¹ (C=O stretching). Yield of 2,2'bis(4"-trimethylsilylphenyl)-4,4',5,5'-biphenyltetracarboxylic dianhydride (BTSBPAn): 5 g (73%); mp: 300 °C. Anal. Calcd for $C_{34}H_{30}O_6Si_2$ (590.77): C, 69.12%; H, 5.12%. Found: C, 69.02%; H, 5.06%. ¹H NMR (DMSO-*d*₆/TMS): δ 0.007 (s, 18H, Si-CH₃), 6.16-6.19 (d, 2H, Ar-H), 6.86-6.89 (d, 2H, Ar-H), 7.59 (s, 1H, Ar-H), 8.11 (s, 1H, Ar-H). FT-IR (KBr pellet):



Polyimides 2329



3017 (aromatic C–H), 2982 (aliphatic C–H), 1770 cm⁻¹ (C=O stretching).

Polymer Synthesis. Polymerization procedures were as follows. Corresponding diamine (1 mmol) was dissolved in *m*-cresol in a 25 mL flask. After the diamine was dissolved completely, 1 mmol of dianhydride was added. The mixture was stirred at room temperature for 2 h. The temperature of the mixture was gradually elevated to 200 °C and then stirred for 5 h. An excess *m*-cresol was added to the mixture, and the mixture was cooled. The obtained polymer was precipitated in methanol. The precipitation procedure was carried out several times. Yield: 93–98%.

Preparation of Dense Film. A 5–7 wt % solution of polymer in chloroform was prepared and filtered through a 0.2 μ m syringe filter to remove the nondissolved materials and dust particles. The solution was then poured into a casting ring on a leveled clean glass plate. The casting ring was covered with a piece of filter paper. The casting process took about 8 h at room temperature. The cast films were dried in an oven at 40 °C for 6 h without vacuum and for another 6 h with vacuum, and the film samples were dried at 80 °C for 6 h and then at 100 °C for 10 h. Dense films were obtained at 150 °C in a vacuum oven for an additional 24 h before the gas permeability measurement.

Results and Discussion

The synthetic routes for monomers are shown in Scheme 1. 3,3',4,4'-Tetramethylbiphenyl was obtained

by Ni-coupling reaction of 4-bromo-o-xylene. The bromination of 3,3',4,4'-tetramethylbiphenyl gave 2,2'dibromo-4,4',5,5'-tetramethylbiphenyl, which was reacted with *p-tert*-butylbenzene boronic acid or *p*-trimethylsilylphenyl boronic acid to generate 2,2'-bis(4"-tertbutylphenyl)-4,4',5,5'-tetramethylbiphenyl and 2,2'-bis-(4"-trimethylsilylphenyl)-4,4',5,5'-tetramethylbiphenyl, respectively. 2,2'-Bis(4"-tert-butylphenyl)-4,4',5,5'-biphenyltetracarboxylic dianhydride (BBBPAn) and 2,2'bis(4"-trimethylsilylphenyl)-4,4',5,5'-biphenyltetracarboxylic dianhydride (BTSBPAn) were obtained by oxidation and dehydration of 2,2'-bis(4"-tert-butylphenyl)-4,4',5,5'-tetramethylbiphenyl and 2,2'-bis(4"-trimethylsilylphenyl)-4,4',5,5'-tetramethylbiphenyl. The yields in each step were very high, and the obtained products in each steps were confirmed by spectroscopic techniques. The structures of obtained monomers, BBBPAn and BTSBPAn, were also analyzed by ¹H NMR, FT-IR, and elemental analysis. For BBBPAn, the proton peaks of *tert*-butyl and aromatic ring appeared at 1.2 and 6.3-8.2 ppm, respectively. In the case of BTSBPAn, those of trimethylsilyl and aromatic ring appeared at 0.2 and 6.2-8.2 ppm, respectively. In the FT-IR spectrum, instead of the broad acid peak, a peak characteristic of a carbonyl group of dianhydrides appeared at 1770 and 1860 cm⁻¹.

It is known that there are two general methods for the preparation of polyimides. One procedure involves

				-	-				
	vield	inh visc ^d	M_{w}^{e}	PDI		elemental	analysis		moisture
polymer code	ັ(%)	(dL/g)	(GPC)	$(M_{\rm w}/M_{\rm n})$		С	Н	Ν	intake (%) f
polyimide 1	94	1.43	332 400	2.16	calcd	79.76	5.30	3.88	1.89
(BBBPAn-ODA ^a)					found	80.80	5.03	3.83	
polyimide 2	96	0.56	141 500	2.33	calcd	81.64	5.59	3.89	0.88
(BBBPAn-MDA ^b)					found	82.19	6.23	3.96	
polyimide3	96	0.41	138 000	1.87	calcd	71.49	4.47	3.27	0.38
(BBBPAn-FDAc)					found	70.49	4.57	3.42	
polyimide 4	96	0.59	110 400	3.51	calcd	73.18	5.07	3.71	0.14
(BTSBPAn-ODA)					found	74.06	4.74	3.95	
polyimide 5	98	0.58			calcd	74.97	5.35	3.72	0.93
BTSBPAn-MDA)					found	76.52	5.92	4.07	
polyimide 6	93	0.38	60 400	1.92	calcd	66.20	4.31	3.15	0.26
(BTSBPAn-FDA)					found	65.15	4.39	3.32	

Table 1. Yields and Properties of the Polyimides

^{*a*} 4,4'-Oxydianiline. ^{*b*} 4,4'-Methylenediamine. ^{*c*} 4,4'-(Hexafluoroisopropylidene)dianiline. ^{*d*} Inherent viscosity measured at a concentration of 0.5 g/dL in DMAc at 25 °C. Relative to polystyrene. ^{*e*} Moisture intake (%) = 100 × ($W - W_0$); W = weight of polymer sample after standing at room temperature for 3 days; W_0 = weight of polymer sample after being dried in a vacuum at 100 °C for 10 h.



Figure 1. FT-IR and ¹H NMR spectra of polyimide 1 (above) and polyimide 4 (below).

two steps and proceeds via poly(amic acid)s intermediate. The other is one-step solution polymerization. The one-step method has some advantages over the two-step method. Polyimides in bulk are more easily produced, and polyimides with higher crystallinity can be more readily obtained.¹⁸ The one-step method is also useful for unreactive diamines and dianhydrides which cannot form high-molecular-weight poly(amic acid)s by the two-

Table 2. Solubility of Polyimides^a

	solvent									
polyimide	<i>m</i> -cresol	NMP	DMF	DMAc	DMSO	pyridine	1,2-dichlorobenzene	chloroform	THF	acetone
polyimide I	+ -	++	+ -	+ +		+ +	+ +	+ +	++	
polyimide 2	+ +	+ +	++	+ +		+ +	+ +	+ +	+ +	
polyimide 3	+ +	+ +	++	+ +		+ +	+ -	+ +	+ +	
polyimide 4	+ -	+ +	++	+ -		+ +	+ +	+ +	+ +	
polyimide 5	++	+ +	++	+ +		++	+ +	+ +	+ -	
polyimide 6	+ +	++	++	+ -		+ +	+ -	+ +	++	

a + + = soluble, + - = partially soluble, - - = insoluble.

step method.^{19,20} The disadvantage of the one-step method is that insoluble polyimides cannot form highmolecular-weight polyimides because of premature precipitaion. We tried two general methods (Scheme 2). When polyimides were synthesized by the conventional two-step procedure involving a ring-opening polyaddition and subsequent thermal cyclodehydration, the polymer molecular weights were not enough for preparing of free-standing films. It may be suggested that dianhydrides are deactivated by steric hindrance due to bulky *tert*-butylphenyl or trimethylsilylphenyl substituents in the 2,2'-position of the s-BPDA unit. Otherwise, the one-step polymerization at high temperature resulted in high viscosity. The yields of polymerization were 93-98%. The results of the polymerization are summarized in Table 1. The inherent viscosities of polyimides are 0.38-1.43 dL/g. The gel permeation chromatography (GPC) measurements demonstrated that polymers exhibited $M_{\rm w}$ and polydispersities $(M_{\rm w}/M_{\rm n})$ in the ranges 60 400–332 400 and 1.87–3.51, respectively. The inherent viscosity decreased in the following order: polyimide 1 > polyimide 2 > polyimide 3 for BBBPAn and polyimide 4 > polyimide 5 > polyimide 6 for BTSBPAn. From the results, it appears that a diamine with an electron-donating group is active for imidization; thus, polyimides from diamines with an electron-donating group have higher molecular weights. The elemental analysis values agreed quite well with calculated values for the proposed structures of polyimides. The structures of obtained polyimides were also confirmed by IR and ¹H NMR spectroscopies. Figure 1 showed IR and ¹H NMR spectra of polyimide 1 and polyimide 4, respectively. The IR spectra supported the formation of polyimides. The characteristic absorption bands of the polyimides rings appeared near 1778 (asym C=O str), 1722 (sym C=O str), 1371 (C-N str), and 742 cm^{-1} (imide ring deformation). The proton peaks are assigned for the obtained polyimide 1 and polyimide 4, respectively.

The solubility of polyimides was studied in various solvents (Table 2). Regardless of the nature of substituents introduced in dianhydride and diamine, the synthesized polyimides showed good solubility in common organic solvents such as chloroform and THF. It is supposed that this is due to the noncoplanar twisted biphenyl structure and the bulkiness of introduced substituents.

The thermal properties of the polyimides were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in a nitrogen atmosphere (Table 3). The polyimides exhibited 5% weight loss at 540–550 °C in nitrogen as measured by thermogravimetric analysis. The thermal transitions (T_g 's) of polyimides were observed between 348 and 381 °C. The high T_g 's of polyimides can be explained by the fact that noncoplanar twisted biphenyl and steric hindrance

Table 3. Thermal Behavior of Polyimides

polyimide	$T_{g}{}^{a}$ (°C)	$T_{\mathbf{d}}{}^{b}$ (°C)	char yield ^c (%)
polyimide 1	370	550	65
polyimide 2	360	540	58
polyimide 3	381	549	57
polyimide 4	348	552	62
polyimide 5	348	542	65
polyimide 6	365	543	57

^{*a*} From the second heating trace of DSC measurements conducted with a heating rate of 20 °C/min under a nitrogen atmosphere. ^{*b*} 5% weight loss temperature in TGA at 20 °C/min heating rate. ^{*c*} Residual yield in TGA at 800 °C under a nitrogen atmosphere.

Table 4. Mechanical Properties of Polyimides

	tensile	elongation at	tensile
polyimide	strength (MPa)	break (%)	modulus (MPa)
polyimide 1	58	9	805
polyimide 2	54	9	630
polyimide 3	44	6	780
polyimide 4	94	11	1129
polyimide 5	63	10	696
polyimide 6	38	7	656

of the bulky substituents restricts the segmental motion. The polyimides derived from BBBPAn showed higher T_g 's than those derived from BTSBPAn. The result can be explained in terms of the flexibility and low rotation barrier of the trimethylsilyl group and (or) the rigidity of the *tert*-butyl group. The results of the TGA and DSC analyses showed an excellent thermal stability of the polyimides even though the polyimides showed high solubility.

The mechanical properties of the two series of polyimides prepared by solution casting from chloroform solution are summarized in Table 4. The polyimide films had tensile strengths of 38-94 MPa, elongation at break of 6-11%, and tensile modulus of 0.63-1.13 GPa. The polyimides derived from BBBPAn showed higher elongation at break than those derived from BTSBPAn. It may be due to the flexibility of the trimethylsilylphenyl group. The polyimide 3 and polyimide 6 derived from hexafluoroisopropylidenediamine (FDA) showed lower elongation at break than those derived from 4,4'methylenedianiline (MDA) and 4,4'-oxydianiline (ODA). The result can be explained by the rigidity of FDA having trifluoromethyl groups. The results of mechanical properties of films are relatively low for highmolecular-weight polyimides. It may result from low intermolecular interaction due to bulky and twisted molecular structure.

From such good solubility, good thermal stability, and mechanical properties, it is suggested that the obtained polyimides have adequate properties for gas permeability. Therefore, the oxygen gas permeation of films of obtained polyimides was studied (Table 5). The newly synthesized polyimides showed a high oxygen permeability coefficient [P, cm³ (STP) cm/(cm² scmHg)] (P_{O_2}

Table 5. Gas Transport Properties of Polyimides

	permea	ıbility ^a	permselectivity		
polyimide	O_2	N_2	$(P_{\rm O_2}/P_{\rm N_2})$		
polyimide 1	43	12	3.58		
polyimide 2	31	8	3.9		
polyimide 3	110	35	3.14		
polyimide 4	61	18	3.4		
polyimide 5	52	12	4.3		
polyimide 6	105	37	2.84		

^{*a*} 1 barrer = 10^{-10} cm³(STP) cm/(s cm² cmHg).

= 31–110 barrer) and the permselectivity of oxygen to nitrogen ($P_{O_2}/P_{N_2} = 2.8-4.3$). The results showed that the newly obtained polyimides had the highest oxygen permeability ever reported.²¹ The results may be explained by the fact that the highly twisted main chain with bulky *p-tert*-butylphenyl or *p*-trimethylsilylphenyl inhibits intermolecular packing, and this provides high free volume. The polyimides derived from BTSBPAn containing trimethylsilylphenyl showed better oxygen permeability than the polyimides derived from BBBPAn containing a tert-butylphenyl group. It is possible that BTSBPAn with a bulky and flexible trimethylsilyl group has a high solubility toward oxygen, and (or) it can afford the high free volume. Changing the diamine part from FDA to MDA, the permeability for oxygen increased in the order MDA, ODA containing flexible oxygen linkage, FDA containing bulky and highly oxygen soluble hexafluoroisopropylidene linkage.

Conclusions

Two new dianhydride monomers composed of a noncoplanar twisted biphenyl unit containing *tert*-butylphenyl or trimethylsilylphenyl groups were prepared by various organic reactions. A series of polyimides with high molecular weights were obtained from such dianhydride monomers and three commercially available diamines. The obtained polymers showed high thermal stability with high T_g 's, good mechanical properties, and high solubility in common organic solvents such as chloroform and THF. In addition, the newly obtained

polyimides showed the highest oxygen permeability ever reported. Thus, these new polyimides could be considered as newly processable and for varied uses in highperformance polymeric material.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2000-005-E00005).

References and Notes

- (1) Ghosh, M. K.; Mittal, K. L. Polyimides: Fundamentals and Applications, Marcel Dekker: New York, 1996. de Alajo, J.; de la Campa, J. G. Adv. Polym. Sci. **1999**, 140,
- 23.
- (3) Li, F.; Fang, S.; Ge, J. J.; Honigfort, P. S.; Chen, J. C.; Harris, F. W.; Cheng, S. Z. D. *Polymer* **1999**, *40*, 4571. Li, F.; Ge, J. J.; Honigfort, P. S.; Fang, S.; Chen, J. C.; Harris,
- (4) F. W. Cheng, S. Z. D. *Polymer* **1999**, *40*, 4987.
 (5) Itaaki, H.; Yoshimoto, H. *J. Org. Chem.* **1973**, *38*, 76.
 (6) Rozhanskii, I.; Okuyama, K.; Goto, K. *Polymer* **2000**, *41*, 7057.
- (7) Kim, Y. H.; Kim, H. S.; Ahn, S. K.; Kwon, S. K. J. Polym. Sci., Polym. Chem. 2002, 40, 4288.
- Kim, Y. H.; Kwon, S. K.; Choi, S. K. Macromolecules 1997, 30. 6677
- Ahn, S. K.; Kim, Y. H.; Shin, D. C.; Kwon, S. K. Bull. Korean (9) Chem. Soc. 2000, 21, 377.
- Masuda, T.; Hamano, T.; Tsuchihara, K.; Higashimura, T. Macromolecules **1990**, 23, 1374. (10)
- Tsuchihara, T.; Masuda, T.; Higashimura, T. J. Am. Chem. Soc. **1991**, *113*, 8549. (11)
- (12) Seki, H.; Masuda, T.; Higashimura, T. J. Polym. Sci., Polym. *Chem. Ed.* **1995**, *33*, 117.
- (13)Kim, Y. H.; Shin D. C.; Ha, C. S.; Cho, W. J.; Kwon, S. K. J. *Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 937. (14) Kim, Y. H.; Kwon, S. K. *Korea Polym. J.* **1997**, *5*, 100. (15) Ryoo, M. S.; Lee, W. C.; Choi, S. K. *Macromolecules* **1990**,
- *23*, 3029.
- (16) Han, S. H.; Kim, U. Y.; Kang, Y. S.; Choi, S. K. Macromolecules 1991, 24, 973.
- Koo, K. M.; Han, S. H.; Kang, Y. S.; Kim, U. Y.; Choi, S. K. *Macromolecules* **1993**, *26*, 2485. (17)
- (18)Masao, T.; Cheng, S. Z. D.; Harris, F. W. Polym. Prepr. 1992, 33. 396.
- (19) Yoshida, S.; Hay, A. S. Macromolecules 1997, 30, 5979.
- (20)Yi, M. H.; Huang, W.; Jin, M. Y.; Choi, K. Y. Macromolecules 1997, 30, 5606.
- Masri, M. A.; Kricheldorf, H. R.; Fritsch, D. *Macromolecules* 1999, *32*, 7853. (21)

MA0214557