# Synthesis and Characterization of Polyamideimide-Branched Siloxane and Its Gas-separation

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ABSTRACT: Polyamideimide-branched siloxanes (PAIBrSs) were synthesized from 4. 4'-(hexafluoroisopropyllidene)diphthalic anhydride (6FDA), p,p'-oxydianiline (ODA), and aminopropyl-terminated oligomeric dimethylsiloxane (ODMS). In this investigation, a mixture of N-methylpyrrolidinone (NMP) and tetrahydrofuran (THF) was used as a cosolvent for the homogeneous mixing of poly(amic acid) (PA) and the ODMS solution. Thionyl chloride (SOCl<sub>2</sub>) was used for the acylation of PA to activate the reaction between PA and ODMS. FTIR spectra showed an increase in the intensity of characteristic absorption peaks of dimethylsiloxane units with the amount of ODMS reacted. From thermogravimetric analysis (TGA), PAIBrSs showed good thermal stability, but relatively low thermal stability when compared with that of block poly(imide siloxane) (PIBIS) or poly(amideimide siloxane) (PAIBIS). A solubility test showed that dipolar aprotic solvents were relatively good solvents for the polymer. Gas separation was performed by single gas-permeation equipment. The permeabilities of PAIBrS membranes are higher than those of PIBlS membranes and the selectivities of PAIBrS membranes are lower than those of PIBIS membranes. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 965-973, 1999

Key words: polyamideimide; branched polymer; siloxane; gas separation

# INTRODUCTION

Polyimides and related polymers, when synthesized from aromatic reactants, have generally rigid-chain structures resulting in low gas permeability.<sup>1</sup> The rigidity of the polymer chains reduces the segmental motion of the chains and plays a role in being a good barrier against gas transport. To overcome the limit for use as materials of gas-separation membranes due to low gas permeability, block copolymers with incorporation of flexible segments such as siloxane<sup>2</sup> and ether linkage<sup>3</sup> have been studied. Especially, siloxane polymers have a much higher permeability to gases than that of most other rubbery materials. Therefore, these polymers have been of interest for gas-separation membranes, the goal being to vary the basic siloxane structure to improve selectivity without decreasing permeability. Polymers such as polyimide, polyamideimide, and polyetherimide can be included in these categories.

Additionally, an incorporation of the siloxane unit to polyimides and related polymers<sup>3–20</sup> makes it possible to increase the solubility and processibility and, furthermore, to impart impact resistance, biocompatibility, low moisture uptake, low dielectric constant, thermooxidative resistance, low surface energy, and good adhesion properties to the substrate. In our laboratory,<sup>11</sup> the thermal kinetics of poly(imide siloxane)s prepared from aromatic dianhydrides [4,4'-(hexafluoroisopropyllidene)diphtalic anhydride (6FDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride

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(BTDA) and pyromellitic dianhydride (PMDA)] and aminopropyl-terminated oligomeric dimethylsiloxane (ODMS) having different molecular weights were studied. Various kinetic parameters for the thermal decomposition reaction of polymers were examined by dynamic thermogravimetric analysis (DTGA). In addition to the case of polyimide and related polymers, incorporation of siloxane units to other polymers such as polystyrene,<sup>20</sup> polyamide,<sup>21,22</sup> polysulfone,<sup>23–25</sup> polyurethane,<sup>26</sup> polyurea,<sup>27</sup> and epoxy resin<sup>28</sup> have been widely investigated by many research groups.

However, one of the difficulties in the synthesis of this class of polymers is the low reactivity of a siloxane diamine when compared to the aromatic diamines. Oishi et al.<sup>29,30</sup> used trimethylsilyl chloride (TMSCl) as an activating agent for the synthesis of aromatic polyamide, and later they reported the synthesis of PDMS containing multiblock copolyamide.<sup>31</sup> In our laboratory,<sup>32</sup> poly(amideimide siloxane) based on trimellitic anhydride chloride (TMAC), 4,4'-oxydianiline (ODA), and ODMS was previously synthesized using TM-SCl as an activating agent. Polyamideimide exhibits solubility in many organic solvents in itself. An incorporation of ODMS to polyamideimide enhances the solubility of polyamideimide and the property of ODMS at the same time.

Several kinds of synthetic methods to incorporate siloxane groups into the polyimides and related polymers or other polymers have been achieved by many research groups. Especially, block copolymerization<sup>3–8,11–14,16–18,20,31,32</sup> based on ODMS, aromatic dianhydride, or with an aromatic diamine as a chain extender has been usually used. Other methods such as the incorporation of siloxane groups into the side chain of the polymer<sup>9,10,25</sup> and polymerization through monomers containing the silicone or siloxane unit<sup>8,15,18</sup> were less explored for the block copolymerization.

In the separation membrane area, Stern et al.<sup>8</sup> elucidated the structure/permeability relationships of silicone-containing polyimides. They synthesized two types of polymers: one type synthesized from an aromatic dianhydride, an aromatic diamine and ODMS (silicone-polyimide), and the other synthesized from aromatic dianhydride containing a silicon atom and an aromatic diamine (silicone-modified polyimide). The gas permeability and selectivity of poly(imide siloxane) were rather similar to the silicone components' characteristics than to those of polyimides. Also, permselectivity of silicone-modified polyimides was quite close to that of polyimides. Lai et al.<sup>2,12,13</sup> synthesized poly(imide siloxane)s from PMDA, ODA, and ODMS and then utilized them in gas separation and pervaporation. Polyimides in gas separation show high selectivity and very low permeability. Therefore, research has been focused mainly on the increase of permeability with a minimal loss of selectivity.

This study shows the preparation procedure and characterization of polyamideimide containing the ODMS segment in the side chain to prepare ODMS-branched PAs (PAIBrSs) (see Fig. 1). This polymer will be compared with a block type of polymers in terms of the gas-separation property.

# **EXPERIMENTAL**

### Materials

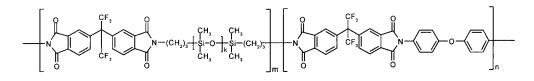
6FDA was obtained from Hoechst Chemikalien Co. and ODA was obtained from TCI Co. 6FDA was used after drying in a vacuum oven without further purification and ODA was used after crystallizing from water. ODMS ( $M_n = 900$ ) was kindly donated by Shinetsu Chemical Co. (Tokyo, Japan) and used after vacuum drying overnight at 110°C. N-Methylpyrrolidinone (NMP; Tedia Co., Fairfield, OH) and tetrahydrofuran (THF; J. T. Baker, Phillipsburg, NJ) were used after distillation in a vacuum and atmospheric pressure, respectively, over calcium hydride. All solvents were stored in a bottle sealed carefully under a nitrogen atmosphere. Triethylamine (TEA; Kanto Chemical Co., Tokyo, Japan) and thionyl chloride (Fluka Co., Switzerland) were used as received.

### Synthesis of Poly(amic acid) (PA)

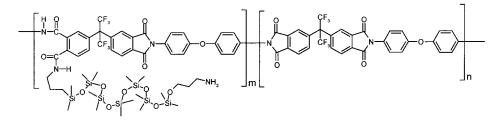
ODA (1.0 g, 5 mmol) was dissolved in a predetermined volume of NMP and THF with magnetic stirring in a three-necked round-bottomed flask equipped with a nitrogen inlet and outlet. After ODA was dissolved completely, 6FDA (2.22g, 5 mmol) was added in the solid state, and the reaction was performed for 10 h at room temperature under a nitrogen atmosphere. PAs were obtained with a clean solution.

#### Synthesis of PABrSs

PABrSs were prepared by a reaction of PA solution with ODMS. After lowering the temperature of a PA solution to 0°C, an excess equivalent of



Block polyimidesiloxane (PIBIS)



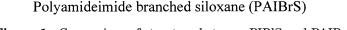


Figure 1 Comparison of structure between PIBIS and PAIBrS.

SOCl<sub>2</sub> (0.01mol in the case of PAIBrS 5) in THF for the complete acylation was dropped into the PA solution and the reaction was continued until no acidic gas was evolved. Into this solution, ODMS, prepared by dissolving ODMS in predetermined volume of THF and mixing TEA, was added by dropping. After the dropping was completed, the temperature was increased to room temperature again, and the reaction was continued for another 10 h. After the reaction was completed, a polymer solution (PABrS) was precipitated into a methanol/*n*-hexane mixture. The precipitates were washed with methanol and distilled water several times and then dried at 60°C in a vacuum oven for 24 h. In all the reactions, the solid content and the ratio of NMP/THF were varied (see Table I).

# Synthesis of Polyamideimide-branched Siloxanes (PAIBrSs)

PAIBrSs were prepared through thermal imidization of a PABrS solution. Imidization was performed with a 5(w/v)% polymer solution in NMP on a glass plate by the following thermal curing steps:

1. 100°C in a drying oven for 2 h.

Sample	Mol Ratio (6F/O/OD) <sup>a</sup>	NMP/THF	Solid Content [(w/v) %]	$M_n^{\mathrm{\ b}}~( imes 10^5)$	$M_w^{\mathrm{b}}~( imes 10^5)$	$M_w/M_n{}^{ m b}$
PA	10/10/0	1/0	10	3.35	3.33	1.094
PABrS 1	10/10/1	2/1	9	2.09	2.96	1.416
PABrS 2	10/10/2.5	3/2	8.5	1.99	2.84	1.426
PABrS 3	10/10/5	4/3	8	2.39	3.17	1.325
PABrS 4	10/10/7.5	5/4	7.5	2.43	3.25	1.337
PABrS 5	10/10/10	1/1	7	2.72	3.76	1.305

Table I Sample Designation and Molecular Weight

<sup>a</sup> 6F, 6FDA; O, ODA; OD, ODMS.

<sup>b</sup> From GPC. Solvent: NMP; temperature: 50°C; flow rate: 1.0 mL/min.

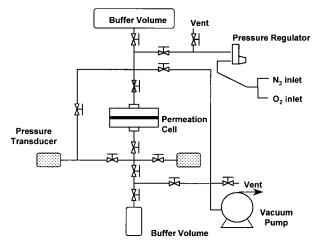


Figure 2 Apparatus of gas-permeation measurement.

- 2. 150°C in a drying oven for 1 h.
- 3. 200°C in a vacuum oven for 1 h.
- 4. 250°C in a vacuum oven for 2 h.

The resulting thicknesses of the membranes were in the range of  $30-100 \ \mu m$ .

#### Characterization

FTIR spectra of the synthesized polymer were obtained using a Nicolet Model Magna IR550. Thermogravimetric analysis (TGA) was done using a Perkin-Elmer System 7 to study the thermal stability of the polymer. The heating rate was 10°C/min. X-ray diffraction patterns of the polymer were obtained using a Rigaku Denki Model RAD-C with a scanning rate of 10°/min for both PABrSs and PAIBrSs. The molecular weight and distribution of PABrSs were obtained by the relative elution time to monodisperse polystyrene standards from a GPC apparatus (Waters Model 510 HPLC pump, Milford, MA) at 50°C. The mobile phase was NMP with a flow rate of 1 mL/min. The injection volume was 100 mL of stock solutions [0.5(w/v)%]. The calibration curve was prepared before measurements by using standard polystyrene. Eventually, the densities of each polymer were measured by using an SD 120L electronic densitimeter (Mirage Co.).

#### **Gas-Separation Experiments**

Gas-separation performance of the prepared membrane was measured using a single gas-permeation method at a feed pressure of 200 Torr and the feed temperature of 25°C (see Fig. 2). Before the gas-permeation measurements, both the upper and lower sides were evacuated below 5 mTorr. The pressure versus time transient of the lower side equipped with a pressure transducer (MKS's baraton type 146) was recorded on a personal computer. The slopes of the linear part of the transient pressure curves provide the flux rates of permanent gases. The gas permeability coefficient was determined by the following equation:

$$P = \frac{dp}{dt} \times \frac{273 \ V}{760 \ (273 + T)} \times \frac{1}{\Delta p} \times \frac{l}{60}$$
(1)

where *P* denotes gas permeability  $[\text{cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ s cmHg, barrer}]$ , dp/dt, the pressure gradient during *t* in the steady state (Torr/s); *T*, temperature (°C); *V*, calibrated lower volume (124.8 cm<sup>2</sup>); *A*, an effective membrane area (14.5 cm<sup>2</sup>); *l*, the membrane thickness, and  $\Delta p$ , the pressure difference between the high- and low-pressure sides of the membrane. When a mixture of gases is separated, an ideal separation factor for the components is defined as the ratio of permeability of each component as follows:

$$\alpha = \frac{P_{O_2}}{P_{N_2}} \tag{2}$$

In this experiment, the operating pressure was 200 Torr for  $O_2$  and  $N_2$ , respectively, and the feed temperature was 25°C.

## **RESULTS AND DISCUSSION**

Cosolvent systems of dipolar aprotic solvents such as NMP, DMF, or DMAc and THF have been usually used for the synthesis of polydimethylsiloxane block copolyimide or copolyamideimide because of their differences in solubility to PA and ODMS. Generally, solvents such as methylene chloride, THF, chloroform, and ethers can easily solvate the ODMS, but they cannot readily dissolve aromatic dianhydrides or aromatic diamines and PAs resulting from the solubility difference. Dipolar aprotic solvents are good solvents for aromatic monomers and PAs but not for ODMS.

From this viewpoint, a cosolvent system of NMP as a dipolar aprotic solvent and THF was employed in this study. The amount and the ratio of NMP and THF were varied according to the

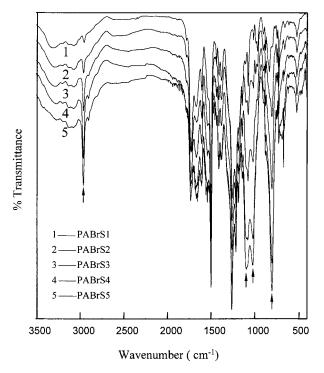


Figure 3 FTIR spectra of synthesized PABrS.

amount of ODMS to be reacted. For homogeneous mixing of PA solutions and ODMS solutions, higher THF contents and low solid contents were required as the amount of ODMS was increased.

In this experiment, we used thionyl chloride (SOCl<sub>2</sub>) for the acylation of PA to activate the amidation reaction with ODMS. An excess equivalent of SOCl<sub>2</sub> was used to complete the acylation and to improve the probability of the incorporation of ODMS. According to Oishi et al.<sup>30,31</sup> and Ha et al.,<sup>32</sup> *N*-trimethylsilylated amines from the reaction between diamines and TMSCl showed the high reactivity to acid chloride. This comes from the fact that organosilicon compounds have a strong affinity for oxygen, fluoride, or chloride, and the carbocation on the  $\beta$ -position can be stabilized through a silicone  $\sigma - \pi$  effect.<sup>33</sup> On the other hand, Higashi et al.<sup>34,35</sup> reported a direct polyamidation of aromatic dicarboxylic acids and diamines with SOCl<sub>2</sub> in NMP. They proposed that the reaction proceeded via the formation of SOCl<sub>2</sub>/NMP complexes. According to their result, the inherent viscosity of the polymer was the highest at 70°C, and this value was acquired even though a HCl scavenger was not used. We refer to the result of Higashi et al. except the reaction temperature (at room temperature in this case) for the continuous reaction.

In all the reaction steps, when all the reagents are used, the resulting polymers and their intermediates are susceptible to hydrolytic decomposition. Therefore, all solvents were kept in a bottle filled with a molecular sieve under a nitrogen atmosphere before and after use and after purification by distillation. Other reagents were also kept sealed carefully under a nitrogen atmosphere. In Table I, the mol ratio of the reagents and the molecular weight of the resulting polymer are presented. Figure 1 illustrates the difference between block poly(imide siloxane) (PIBIS) and PAIBrS.

### **FTIR Analysis**

Figure 3 exhibits the FTIR spectra for synthesized polymers (PABrSs) from 6FDA, ODA, and ODMS. Strong absorption bands at 1090 and 1020  $\text{cm}^{-1}$ (Si-O-Si stretching) and 800cm<sup>-1</sup> (Si-C) are the characteristic peaks of a siloxane group. Strong and sharp absorption bands at 2968 cm<sup>-1</sup> (C—H stretching) were attributed to methyl or methylene groups attached to silicon molecules in ODMS. Their intensity increases with the amount of ODMS reacted. Absorption bands by an amide linkage (1670 and 1543cm<sup>-1</sup>) also increase in intensity, resulting from the formation of an amide linkage by the reaction between PA and ODMS. On the other hand, the absorption intensity of hydroxyl groups  $(3100-3500 \text{ cm}^{-1})$  decreases with the formation of an amide linkage.

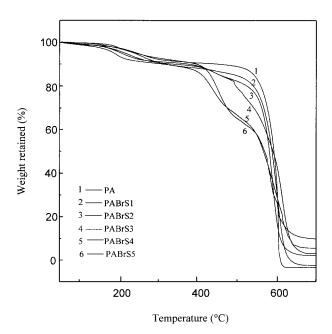
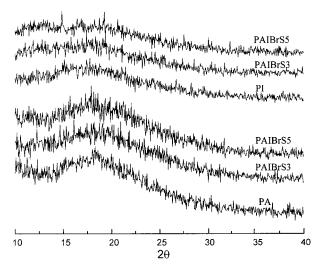


Figure 4 TGA of PA and ODMS-branched PA.

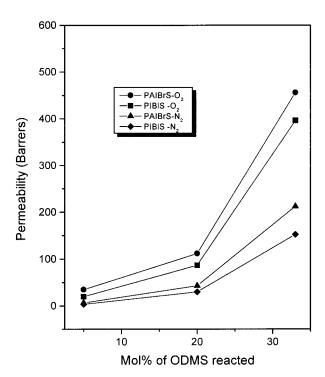


**Figure 5** X-ray diffraction patterns of PA, PABrS, polyimide, and PAIBrS.

# TGA

The thermal stability of PAIBrSs varies with the amount of the incorporated ODMS (Fig. 4). A 10% decomposition temperature of all PAIBrS samples appeared at around 330°C. This decomposition temperature is lower than that of poly(imide siloxane)  $(around 460^{\circ}C)^{10}$  or poly(amideimide siloxane) (around 355°C).<sup>10</sup> A tendency toward lower thermal stability of the branched polymer is expected because PAIBrSs have free chain ends compared to block-type polymers. Therefore, those free chain ends are susceptible to thermal degradation. The char contents at a high temperature of over 600°C, however, increased with the amount of ODMS reacted. In the synthesis of a block copolymer, ODMS reacts with monomers, whereas, in the case of PAIBrS, ODMS reacts with PA. Therefore, ODMS has a better reactivity for block copolymerization. Furthermore, thermal degradation begins at the

Table II Result of Solubility Tes	Table II	Result	of Solu	ability	Test
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**Figure 6** Permeability of oxygen and nitrogen through PIBIS and PAIBrS.

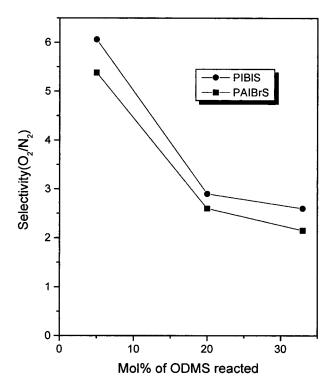
Si—C bonds of ODMS because the bond dissociation energy is lower than that of the other bonds.

# X-ray Diffraction Patterns (XRD)

Figure 5 shows wide-angle X-ray diffraction (WAXD) patterns of PA, PABrSs, polyimide, and PAIBrSs. The effect of ODMS on the membrane was qualitatively observed through X-ray diffraction. Diffraction patterns of both PABrSs and PAIBrSs that appeared at  $2\theta = 18^{\circ}$  did not show any remarkable changes irrespective of the increase of the ODMS portion in the polymers. In

						NMP/THF			
Sample	DMF	DMAc	NMP	THF	1:1	2:1	3:2	$\mathrm{CHCl}_3$	DMSO
PA	$\mathbf{S}$	$\mathbf{S}$	$\mathbf{S}$	$\mathbf{SH}$	S	$\mathbf{S}$	$\mathbf{S}$	IS(H)	$\mathbf{S}$
PABrS1	$\mathbf{S}$	$\mathbf{S}$	$\mathbf{S}$	$\mathbf{SH}$	$\mathbf{S}$	$\mathbf{S}$	$\mathbf{S}$	IS(H)	$\mathbf{S}$
PABrS2	$\mathbf{S}$	$\mathbf{S}$	$\mathbf{S}$	$\mathbf{SH}$	$\mathbf{S}$	$\mathbf{S}$	$\mathbf{S}$	IS(H)	$\mathbf{S}$
PABrS3	$\mathbf{SH}$	$\mathbf{SH}$	$\mathbf{SH}$	PSH	$\mathbf{SH}$	$\mathbf{SH}$	$\mathbf{SH}$	IS(H)	$\mathbf{SH}$
PABrS4	$\mathbf{SH}$	$\mathbf{SH}$	$\mathbf{SH}$	PSH	$\mathbf{SH}$	$\mathbf{SH}$	$\mathbf{SH}$	IS(H)	$\mathbf{SH}$
PABrS5	$\mathbf{SH}$	$\mathbf{SH}$	$\mathbf{SH}$	PSH	PSH	$\mathbf{SH}$	$\mathbf{SH}$	IS(H)	$\mathbf{SH}$

PA state. S: soluble; IS: insoluble; ISH: insoluble in heat; SH: soluble in heat; PSH: partially soluble in heat.



**Figure 7** The selectivity of oxygen and nitrogen through block polyimidesiloxane (PIBIS) and polyamideimide branched siloxane (PAIBrS).

the case of PI and PAIBrSs, the intensity at around  $2\theta = 18^{\circ}$  decreased compared with those of PABrSs. It is thought that the amorphous portion in the polymer increased during the course of the imidization processes.

#### Solubility of the PABrSs

Table II shows the result of solubility of PABrSs. The polar aprotic solvents showed relatively good solubility to the polymers. As the amount of reacted ODMS increased, the solubility unexpectedly decreased. In the case of a block type of poly(imide siloxane)s or poly(amideimide siloxane)s, siloxane units are incorporated into the polyimide or polyamide backbone and increased the chain flexibility, contributing to ease of the polymer to solvent attack. However, as we have seen from the WAXD result of the polymer, PABrSs exhibit no changes in intermediates at  $2\theta = 18^{\circ}$  with increase of the ODMS content, meaning that an increased amount of ODMS in the polymer does not contribute to the crystallinity.

#### **Gas-permeation Performance**

Figures 6 and 7 show the permeability and the selectivity of the PIBIS and PAIBrS membranes on oxygen and nitrogen, respectively. For both membranes, the gas permeability of oxygen and nitrogen increased with the amount of the reacted ODMS and the selectivity of oxygen over nitrogen decreased. In all cases, the permeabilities of the PAIBrS membranes are higher than those of the PIBIS membranes. However, the selectivities of the PAIBrS membranes toward oxygen are lower than those of the PIBIS membranes. This is because the incorporation of ODMS as side chain into the backbone of polyamideimide may decrease the packing density, leading to more free volume within the polymer than within the block copolymer. As shown in Table III, comparison of the density data of PIBIS and PAIBrS confirms this assumption. Because ODMS chains have a very flexible linkage and can rotate freely, the incorporation of ODMS interferes with the chain packing more in the side chain than in the main chain of a polymer. This enlarges the distance between the chains, resulting in increase of the free volume of a polymer.<sup>36–38</sup>

Table IV shows the permeability and selectivity of several kinds of silicone-containing polymers. PAIBrSs showed high gas permeability for oxygen and a slightly low oxygen selectivity over nitrogen compared with those of other silicone (or siloxane)-containing polymers. Also polymers having ODMS in their side chains showed relatively good gas-permeation properties rather than those of the polymers having ODMS in their main chains.

# **CONCLUSIONS**

PAIBrSs were successfully prepared by incorporating ODMS into the side chains of the PAs and then thermally imidizing the polymers. In the synthesis,

Table III Densities of I	PIB1S	and PAIBrS
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Sample	Density
PIB1S 1	1.31
PIB1S 3	1.29
PIB1S 5	1.28
PAIBS 1	1.26
PAIBS 3	1.24
PAIBS 5	1.22

Sample	${P}_{\mathrm{O}_2}$	$P_{\mathbf{N}_2}$	$\alpha_{\rm O2/N2}$
Polvimide (PI) <sup>a</sup>	4.34	0.83	5.2
PTMSP <sup>b</sup>	10,040	6693.3	1.5
$PDMS^{b}$	600	272.7	2.2
Silicone-modified PI <sup>c</sup>	0.69	0.15	4.6
Silicone–PI <sup>c</sup>	43.4	18.87	2.3
Poly(imide siloxane) <sup>d</sup>	1.1	0.26	4.3
Poly(imide siloxane) <sup>e</sup>	7.5	3.41	2.2
PSF-g-PDMS <sup>f</sup>	140	55.12	2.5
Poly(amideimide siloxane) <sup>g</sup>	120	51.72	2.3
PAIBrS 5	456	231	2.1

Table IV Comparison of Gas Permeability and Selectivity of the Polymers

<sup>a</sup> PI from 6FDA–ODA, 35°C, 2 atm, ref. 33.

<sup>b</sup> Poly[1-(trimethylsilyl)-1-propyne], ref. 34.

<sup>c</sup> Silicone-modified PI from bis(3,4-dicarboxy-phenyl)dimethylsilan-g-ODA, silicone-PI from 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, *m*-phenylenediamine, and amine-terminated PDMS, ref. 5.

<sup>d</sup> PI from BTDA and 1,3-bis(3-aminopropyl)tetramethyldisiloxane, ref. 4.

<sup>e</sup> PI from PMDA and methylene diamine, ref. 1.

<sup>f</sup> Polysulfone (PSf), 60 wt % PDMS, ref. 23.

<sup>g</sup> PAI from TMAC, ODA, and ODMS, ref. 35.

a cosolvent system of NMP and THF was necessary for the homogeneous mixing of PA and ODMS solutions for the reaction to proceed. A careful control of the ratios of NMP/THF and the concentrations of the solution was essential to the successful synthesis of PAIBrSs. From TGA analysis, PAIBrSs showed a good thermal stability. The char contents at over 600°C increased with the amount of ODMS incorporated. PAIBrSs showed rather low thermal stability compared with that of block poly(imide siloxane) or poly(amideimide siloxane). During the process of thermal curing, the amorphous region of the polymers increased as evidenced from the WAXD patterns. The solubility of PABrSs was relatively good for dipolar aprotic solvents such as NMP, DMAc, DMF, and DMSO, but deteriorated with increase of the ODMS contents. Gas-separation experiments of PAIBrSs showed that the permeability of oxygen increased and the selectivity of oxygen over nitrogen decreased with the amount of ODMS incorporated. PAIBrSs exhibit good gas-permeation properties compared with those other silicone-containing polymers.

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