

Polymers of Intrinsic Microporosity with Dinaphthyl and Thianthrene Segments †

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ABSTRACT: Novel intrinsically microporous homopolymers and copolymers derived from PIM-1 monomers (5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethylspirobisindane and 2,3,5,6-tetrafluoroterephthalonitrile) with two additional monomers-tetrahydroxydinaphthyl and tetrafluorotetraoxide thianthrene-are reported as potential materials for membrane-based gas separations. The resulting copolymers prevent efficient space packing of the stiff polymer chains and consequently exhibit analogous behavior to that of PIM-1, the most widely reported polymer in this class of materials. In addition, the copolymerization provides high molecular weight copolymers and low polydispersity if the polymerization reactions were conducted at elevated temperature for an extended period of time. Detailed structural characterization of the new monomers and polymers was determined by ¹H and ¹⁹F nuclear magnetic resonance spectroscopy (NMR). The thermal properties were detected by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Polymer free volume was calculated from the polymer density and specific van der Waals volume. Under the same testing conditions, the homopolymer containing thianthrene units and most of the analogous copolymers have an excellent combination of properties with good film-forming characteristics. The gas transport properties show higher selectivity for gas pairs such as O_2/N_2 , CO_2/N_2 , and H_2/N_2 with a corresponding decrease in permeability compared to PIM-1. This work also demonstrates that significant improvements in properties may be obtained through copolymers of intrinsic microporosity (CoPIM)s. Furthermore, this work extends the spectrum of high molecular weight soluble PIMs beyond those reported previously.

Introduction

Since 2004, a novel class of polymers, termed "polymers of intrinsic microporosity" (PIMs), have been prepared that reveal unusually high free volume and high surface areas.¹⁻⁴ Different from other polymeric microporous materials, such as solvent swollen polymers,^{5,6} polymer networks with rigid units,^{7–11} or polymers with bulky groups,^{12,13} PIMs have special ladder-type main-chain structures with contorted or kinked centers which prevent efficient space packing and pore collapse, resulting in intrinsically microporosity materials. Even compared with traditional microporous materials, such as zeolites or activated carbons which are widely used industrially, PIMs present a unique advantage due to the combination of processability with a high degree of microporosity, which are attractive for applications such as adsorbents and catalysis. Solvent-soluble film-forming PIMs of high molecular weight are particularly promising as gas separation materials on account of their high gas permeability. A number of published examples of PIMs have shown gas permeability data that lie above the Robeson upper bound for the separation of important gas pairs $(O_2/N_2, \dot{CO}_2/N_2)$, moderate to good selectivity, and high permeability.¹⁻⁴ In addition, PIMs also exhibit excellent performance for hydrocarbon/methane and hydrocar-bon/hydrogen separation.¹⁴ The most well-known polymer of this type is referred to as PIM-1, which is derived by step-growth polymerization of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethylspirobisindane (TTSBI), and 2,3,5,6-tetrafluoroterephthalonitrile

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(TFTPN). Although PIM-1 has a spiro-contorted center and a rigid ladder-like structure (Scheme 1), it can be readily cast from solution into mechanically strong free-standing films. To date, a number of studies on PIMs have been reported by several research groups;^{4,15–17} however, there are still a limited number of reported monomers which include spiro/contorted sites or tetrafluoro groups similar to PIM-1 monomers and which provide high molecular weight solvent-soluble PIMs suitable for membrane fabrication and gas permeability measurement.

It is well-known that gas transport properties of polymeric membrane can be tuned by modifying or tailoring the polymer structure.^{12,19–21} In our previous work, we reported several soluble high molecular weight PIMs derived from TTSBI and new tetrafluoro monomers which contain trifluoromethyl or sulfone groups as full or partial replacement of the tetrafluorodinitrile monomer.^{4,18} Although the distance between the spiro centers on the chains was the same as PIM-1, the gas permeability and selectivity of the new PIMs could be tuned by the type of pendent groups as a consequence of space filling and rigidity

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Scheme 2. Synthetic Route to Copolymers (DNPIMs, TOTPIMs, and DNTOTPIMs) Based on PIM-1 Monomers (B, C) and THDN (A) and TFTOT (D)





K₂CO₃ Ar A + B + C + D → DNTOTPIMs

increase. In the present work, we focus on the design of new ladder-type PIM structures which contain other highly kinked units and/or those having a longer distance between the twist or spiro centers to improve the understanding of structure-property relationships. The new PIMs are derived from TTSBI, TFTPN, 2,2'3,3'-tetrahydroxy-1,1'-dinaphthyl (THDN), and a newly reported tricyclic monomer: 2,3,7,8-tetrafluoro-5,5',10,10'tetraoxide thianthrene (TFTOT). In an earlier communication, we reported a single copolymer composition based on THDN (DNPIM-33).²² Attempts will be made to correlate the structure of these new PIMs with the degree of microporosity achieved, as assessed by gas adsorption, and gas permeability. The spatially twisted dinaphthyl unit has a different contortion angle compared with the spirobisindane unit, whereas the tricyclic TFTOT unit provides a longer distance between the centers of contortion than the TFTPN unit.

Experimental Section

Materials. 2,3-Naphthalenediol (Acros), ferric chloride hexahydrate (FeCl₃ \cdot 6H₂O, Anachemia), and 1,2-difluorobenzene (Oakwood) were used as received. Sulfur monochloride, anhydrous aluminum chloride, chromium oxide (CrO₃), anhydrous potassium carbonate (K_2CO_3), tetrahydrofuran (THF), acetic acid, and toluene were all obtained from Sigma-Aldrich and were used as received. The monomer 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-spirobisindane (Sigma-Aldrich) was purified by crystallization from methanol. The monomer 2,3,5,6-tetrafluoroterephthalonitrile (Matrix scientific) was purified by vacuum sublimation at 150 °C under an inert atmosphere.

Characterization Methods. The structures of the two synthesized monomers and PIMs were fully characterized using NMR spectroscopy. NMR analyses were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ¹H and 376.276 MHz for ¹⁹F. ¹H and ¹⁹F NMR spectra were obtained from samples dissolved in CDCl₃ or DMSO- d_6 using a 5 mm pulsed field gradient indirect detection probe. The solvent signals (CDCl₃ ¹H 7.25 ppm; DMSO- d_6 ¹H 2.50 ppm) were used as the internal references. An external reference was used for ¹⁹F NMR: CFCl₃ 0 ppm.

Elemental analysis was carried out with a Thermoquest CHNS-O elemental analyzer.

Molecular weight and molecular weight distributions were measured by GPC using Ultrastyragel columns and THF as the

polymers	THDN (mol ratio)	TTSBI (mol ratio)	TFTPN (mol ratio)	TFTOT (mol ratio)	$M_{\rm n}$	$M_{ m w}$	$M_{ m w}/M_{ m p}$	
DNPIM-100 ^a	1	0	1	0	32 000	99 000	3.1	
DNPIM-66 ^a	2	1	3	0	45 000	135 000	3.0	
DNPIM-50	1	1	2	0	47 000	118 000	2.5	
DNPIM-33	1	2	3	0	56 000	129 000	2.3	
DNPIM-25	1	3	4	0	65 000	137 000	2.1	
TOTPIM- 100^{b}	0	1	0	1				
TOTPIM-66	0	3	1	2	35000	74 000	2.1	
TOTPIM-50	0	2	1	1	41 000	89 000	2.2	
TOTPIM-33	0	3	2	1	30 000	70 000	2.3	
TOTPIM-25	0	4	3	1	42,000	84 000	2.0	
TOTPIM-20	0	5	4	1	40 000	81 000	2.1	
DNTOTPIM-50	1	1	1	1	14 000	32,000	2.3	
DNTOTPIM-33	1	2	2	1	38,000	74 000	1.9	
DNTOTPIM-25	1	3		1	56,000	113 000	2.0	
DNTOTPIM-20	1	4	4	i	42 000	110 000	2.6	
$PIM-1 (40 min)^4$	0	1	1	0	55,000	85,000	1.6	

^a After purification. ^b The molecular weight of TOTPIM-100 was not tested by GPC, since the polymer was not soluble in the THF eluent.

eluent at a flow rate of 1 mL/min. The values obtained were determined by comparison with a series of polystyrene standards.

Polymer thermal degradation curves were obtained from TGA (TA Instruments model 2950). Polymer samples for TGA were initially heated to 120 °C under nitrogen gas and maintained at that temperature for 1 h for moisture removal and then heated to 600 at 10 °C/min for degradation temperature measurement. The polymers were tested for the occurrence of glass transition temperatures (T_g) from DSC measurements (TA Instruments model 2920); the samples were heated at 10 °C/min under a nitrogen flow of 50 mL/min, then quenched with liquid nitrogen, and reheated at 10 °C/min for observation of the presence of T_g .

Dense polymer films for gas permeability measurements were prepared from 1 to 2 wt % polymer solutions in chloroform. Polymer solutions were filtered through 0.45 μ m poly-(tetrafluoroethylene) filters and then cast into Teflon Petri dishes in a glovebox and slowly evaporated for 1 day. The films were boiled in water for 1 h, then soaked in methanol, and dried in the vacuum oven at 100 °C for 24 h. The resulting membranes with thickness in the range of 60–80 μ m were flexible and bright yellow. The absence of residual solvent in the films was confirmed by a weight loss test using TGA.

Surface adsorption was evaluated by Brunauer–Emmett– Teller measurements (BET) using an ASAP 2020 (Accelerated Surface Area and Porosimetry System) instrument from Micromeritics Instrument Corp., and data analysis was performed using ASAP 2020 version 3 software Rev H. Samples were initially degassed conditions under vacuum at 80 °C for 24 h.

Density measurements of polymeric membranes were by a standard gravimetric method in ethanol. The polymers membranes having thickness in the range of $70-90 \,\mu\text{m}$ were initially dried under vacuum 100 °C for 24 h.

The mechanical properties of polymers were tested on a model 5565 Instron materials tester. Film samples having thickness in the range of 70–90 μ m were cut by a standard dumbbell-shaped die.

Permeability coefficients (*P*) of N₂, O₂, H₂, and CO₂ were determined at 25 °C with a feed pressure of 50 psig and atmospheric permeate pressure (0 psig) using the constant-pressure/variable-volume method. The permeate gas flow rate was measured by a mass flow meter (Agilent ADM 2000) or a bubble flowmeter. The permeability (*P*) was calculated by using a following equation:

$$P = \left(\frac{273}{T}\right) \left(\frac{\mathrm{d}V}{\mathrm{d}t}\right) \left(\frac{l}{\Delta pA}\right)$$

where dV/dt is the permeate-side flow rate (cm³/s) and *T* is the operation temperature (K). The membrane effective area was 9.6 cm².

Preparation of 2,2',3,3'-Tetrahydroxy-1,1'-dinaphthyl. A literature procedure was employed,²³ whereby a mixture of 2,3naphthalenediol (16 g, 0.1 mol) and FeC1₃·6H₂O (27 g, 0.2 mol) was ground to a finely divided powder using an agate mortar and pestle. The mixture was placed in a test tube and sonicated with ultrasound at 50 °C for 4 h. Decomposition of the reaction product with dilute HC1 gave crude 2,2'3,3'-tetrahydroxy-1,1'dinaphthyl in 85% yield. The tetrol was recrystallized three times from THF to give white needle crystals in 53% yield; mp > 300 °C. ¹H NMR (DMSO-*d*₆) δ : 6.80–6.82 (d, *J* = 8.0 Hz, 2H), 6.94–6.98 (t, *J* = 8.0 Hz, 2H), 7.14–7.18 (t *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 7.64–7.62 (d, *J* = 8.0 Hz, 2H), 8.41 (s, OH), 10.07 (s, OH). Elem. Anal. Calcd for C₂₀H₁₄O₄ (318.32 g/mol): C, 75.46%; H, 4.43%. Found: C, 75.41%; H, 4.56%.

Preparation of 2,3,7,8-Tetrafluoro-5,5',10,10'-tetraoxide Thianthrene. 2,3,7,8-Tetrafluorothianthrene was synthesized according to a modified procedure.²⁴ Into a 250 mL three-neck flask equipped with a magnetic stirrer, an argon inlet and a condenser, difluorobenzene (20 mmol), AlCl₃ (60 mmol), and dry dichloromethane (50 mL) were added. The reaction mixture was cooled to 0 to -20 °C in an ice salt bath (NaCl/ice = 3:1, w/w) and stirred for 1 h. Thereafter, the reaction mixture was added dropwise into S_2Cl_2 (20 mmol), and the temperature was gradually increased to room temperature. After stirring at room temperature for 2 h, the reaction mixture was refluxed for 20 min and then poured into water. The crude product was washed with 8 N hydrochloric acid and extracted with dichloromethane and dried over MgSO₄. After removal of the dichloromethane, the 2,3,7,8-tetrafluorothianthrene (5 g) was recrystallized from hexane to give white needle crystals in a yield of 49%; mp = $108 \degree C$. ¹H NMR (chloroform-d) δ : 7.309 (t, J = 8.0 Hz, 4H). ¹⁹F NMR (chloroform-d) δ : -136.4 (t, J = 8.0 Hz, 4F).

20 g of 2,3,7,8-tetrafluorothianthrene was oxidized using CrO₃ (excess) in acetic acid (100 mL) at a reaction temperature maintained at 100 °C for 24 h. The resulting white 2,3,7,8-tetrafluoro-5,5',10,10'-tetraoxide thianthrene was collected and recrystallized from DMF to give white flake crystals in a yield of 92%; mp > 300 °C. ¹H NMR (DMSO-*d*₆) δ : 8.087 (t, *J* = 8.0 Hz, 4H). ¹⁹F NMR (DMSO-*d*₆) δ : -123.185 (t, *J* = 8.0 Hz, 4F). Elem. Anal. Calcd for C₁₂H₄F₄O₄S₂ (352.28 g/mol): C, 40.91%; H, 1.14%, S 18.20%. Found: C, 41.09%; H, 1.14%; S 18.36%.

Preparation of PIM-1. PIM-1 was synthesized by polycondensation of TTSBI and TFTPN using the procedure reported previously.⁴ The reactions were run for 40 min.

Preparation of DNPIMs, TOTPIMs, and DNTOTPIMs. Two homopolymers and three series of CoPIMs were synthesized by polycondensation of TTSBI, TFTPN, THDN, or TFTOT (with different molar ratios) using a procedure similar to that of PIM-1,⁴ but for a longer reaction time (120 min). The properties of the homopolymers and CoPIMs are summarized in Table 1. DNPIM-100, ¹H NMR (chloroform-d) δ (ppm): 7.88–6.67 (10H).

TOTPIM-100, ¹H NMR (chloroform-d) δ (ppm): 7.54 (s, 2H), 7.45 (s, 2H), 6.67 (s, 2H), 6.31 (s, 2H), 2.33 (s, 2H), 2.12 (s, 2H), 1.33 (s, 6H), 1.23 (s, 6H).

Results and Discussion

The synthesis of THDN reported by Toda in 1989 is unexpectedly simple. It was carried out with 2,3-naphthalenediol in the presence of a catalyst²³ at 50 °C under ultrasonic conditions for 4 h. In the present work, it was found the optimum temperature for this reaction is in the range of 50-70 °C. Higher temperatures led to more insoluble side products.

To the best of our knowledge, there is only one article that mentions the synthesis of the monomer precursor 2,3,7,8-tetra-fluorothianthrene; however, structural characterization of the monomer is lacking.²⁴ Although Budd et al. reported 2,3,7,8-tetrachloro-5,5',10,10'-tetraoxide thianthrene as a potential PIM monomer in a patent,¹⁵ the reactivity of this monomer is considerably lower than the tetrafluoro analogue. As a result, the tetrachlorotetraoxide thianthrene monomer is unsuitable for preparing PIMs with sufficiently high molecular weight. The 2,3,7,8-tetrafluorothianthrene precursor was oxidized using CrO₃/acetic acid instead of conventional oxidation reagents, such as H₂O₂/acetic acid, because the solubility of the resulting 2,3,7,8-tetrafluoro-5,5',10,10'-tetraoxide thianthrene is poor, and it was found that H₂O₂/acetic acid is too weak to effect complete oxidation.

Two homopolymers and three series of copolymers were synthesized by polymerization of combinations of TTSBI, TFTPN, THDN, or TFTOT, using a modified procedure similar to the synthesis of PIM-1. The homopolymers are referred to as DNPIM-100 or TOTPIM-100, where PIM denotes polymer of intrinsic microporosity, DN denotes dinaphthyl groups, and TOT denotes tetraoxide thianthrene groups. The copolymers are identified as DNPIM, TOTPIM, or DNTOTPIM with suffixes, -66, -50, and -33, -25, -20, which refer to dinaphthyl groups to TFTPN or tetraoxide thianthrene groups to TTSBI ratio in the copolymers (see Table 1).

We previously reported in a communication a single CoPIM (DNPIM-33) based on TTSBI, TFTPN, and THDN.²² The reaction was carried out at 160 °C for 120 min in contrast with the synthesis of PIM-1 under the same conditions; copolycondensation led to high molecular weight and low polydispersity. It is interesting to note that the same phenomena were observed in other copolymerizations based on TTSBI, TFTPN, and TFTOT, with or without THDN. It is shown in Table 1 and Figure 1 that for all the copolymers a high $M_{\rm p}$ can be obtained, with a narrow molecular weight distribution. There is no evidence of crosslinking or the formation of cyclics. Thus, a conclusion can be made that under the same reaction conditions (160 °C, 120 min) molecular weight distribution broadening (cyclics or crosslinking) is effectively reduced by introducing a certain ratio of other comonomers into the PIM chain, leading to high molecular weight CoPIMs. PIM-1 prepared under similar conditions (extended reaction time) results in a cross-linked product. One conceivable explanation is that the comonomers disrupt chain uniformity and change the ladder structures; a more unfolded structure could result in less cross-linking and cyclics. Another explanation is that they have different reactivity, and the comonomers with high reactivity in the polymerization system were changed in concentration by introducing other comonomers with low reactivity.

The homopolymers derived from THDN and TFTPN or from TFTOT and TTSBI can be obtained under the same reaction conditions as the CoPIMs. The first reported synthesis of DNPIM-100 at 80 °C and 72 h reaction time gave only a low



Figure 1. GPC curves for the DNPIM polymer series and PIM-1.



Figure 2. MALDI-TOF mass spectrum of DNPIM-100.

molecular weight material having M_n of 3000 Da.¹⁷ A higher molecular weight of DNPIM-100 homopolymer (after purification, $M_{\rm n} = 32\,000$ Da) was obtained under reaction conditions of 160 °C and 2 h with polar solvents, but there were still numerous low molecular weight cyclics and oligomers present. Although $M_{\rm n}$ of DNPIM-100 would appear to be sufficiently high molecular weight, strong free-standing films could not be obtained due to the extremely rigid and contorted polymer chain. It is likely that the steric hindrance over short segmental chain lengths of dinaphthyl leads to difficulty in two such monomer segments accessing a single TFTPN monomer and excessive spatial contortion increases the possibility of cyclic formation from spatially close reactive groups. As shown in Figure 1, DNPIM-100 (without purification) and DNPIM-66 (without purification) have a significant amount of low molecular weight fractions. From the MALDI-TOF mass spectrum (Figure 2), it can be seen that DNPIM-100 contains a high level of cyclics and oligomers, which have two -F and two -OH groups at the polymer chain terminus, which is in good agreement with the explanation. In the case of TOTPIM-100 homopolymer, cross-linking occurs easily during the reaction. According to the different electronic activation power of electron withdrawing groups $(-SO_2R > -CF_3 >$ -CN),²⁵ the reactivity of -F activated by $-SO_2$ is much higher than by -CN. The polymerization to give TOTPIM-100 proceeded rapidly in N-methylpyrrolidone (NMP), providing high molecular weight polymer within 2 h, and the resulting polymer could be cast into free-standing films from chloroform solution. However, the same polymerization for TOTPIM-100 run in DMAc resulted in cross-linked white insoluble product within a short time.



Figure 3. ¹H NMR spectra of PIM-1, DNPIM-50, TOTPIM-50, and DNTOTPIM-50.

NMR Analysis. All three CoPIMs-50 were fully characterized by ¹H and ¹⁹F NMR spectroscopy. The ¹H spectra of CoPIMs-50 were quite similar to those of PIM-1 at high field due to their identical aliphatic protons occurring in the TTSBI monomer segment. The additional signals at low field due to aromatic protons in the different comonomer segments were readily assigned in the ¹H NMR spectra (Figure 3). Furthermore, the experimental ratio of intensity values for aromatic protons H-6 to H-11 compared with aliphatic protons H-2,3 was found to be exactly as expected. For example, the experimental ratio of intensity values for protons on the aromatic rings of dinaphthyl segments in DNPIM-50 compared with $-CH_3$ is exactly 10H:12H, as expected for one repeat unit of dinaphthyl group in copolymers.

Table 2. Thermal Properties of the DNPIMs, TOTPIMs, DNTOTPIMs Series and PIM-1

polymers	$T_{\rm d} (^{\circ}{\rm C})^b$	$T_{\rm d} (^{\circ}{\rm C})^c$	$T_{d5} (^{\circ}\mathrm{C})^d$	$RW(\%)^e$
DNPIM-100 ^a	485.1	510.5	516.5	85.0
DNPIM-50	476.7	507.2	514.9	75.3
DNPIM-33	466.1	504.3	509.5	72.1
DNPIM-25	457.3	499.1	502.7	70.3
FOTPIM-100	472.3	471.6	483.2	70.4
FOTPIM-50	469.1	470.2	481.3	71.1
FOTPIM-33	362.6	474.5	485.8	74.7
FOTPIM-25	333.0	479.8	487.2	76.1
ONTOTPIM-50	343.9	490.6	494.6	76.6
ONTOTPIM-33	338.9	486.9	493.1	77.4
ONTOTPIM-25	298.9	481.9	490.5	77.5
PIM-1 (40 min)	429.6	492.6	495.4	68.2

^{*a*}After purification. ^{*b*}Actual onset temperature of decomposition. ^{*c*}Extrapolated onset temperature of decomposition measured by TGA. ^{*d*}5% weight loss temperature measured by TGA. ^{*e*}Residue weight at 600 °C under N₂.

The ¹H NMR spectra of CoPIMs can be explained better by three-dimensional representation. In the 3-D image it is observed that the four methyl groups (H-1) are not equivalent. Two of them are very close to H-5, and the electron cloud of the -CH₃ group is shielding this proton-hence its very low chemical shift (6.4 ppm) for an aromatic proton. Another two methyl groups are more distant from the H-4, and a higher chemical shift (6.8 ppm) is observed due to absence of shielding. This explains the reason that the four methyl groups (H-1) do not appear as a singlet but as two singlets. The same principle also applies to H-2 and H-3. For H-4 and H-5 protons in PIM-1 and DNPIM-50, respectively, they appear at the same position because their environment is almost the same. However, in TOTPIM-50 and DNTOTPIM-50, different nearby electron-withdrawing groups (-CN and $-SO_2-$) cause different chemical shifts for H-4 and H-5 protons. The integral ratio of the four signals is 1:1:1:1, which indicates 50% H-4 and H-5 are affected by $-SO_2$ groups and are shifted to low field. This is additional proof indicating these two CoPIMs were obtained as the expected structures. Although they are randomly polymerized, the ratio of tetraoxide thianthrene to TFTPN groups is 1:1 in the resulting copolymers.

Finally, the ¹⁹F NMR spectra (not shown) were collected for all PIMs homo- and copolymers. It is worth mentioning that no aromatic F signal was detected in all these PIM-1 homo- and copolymers.

Thermal Analysis. Thermal analyses results for the three new PIMs series and PIM-1 are compared in Table 2. All the polymers are amorphous, remaining glassy up to their decomposition temperatures, and have excellent thermal stabilities. No glass transitions were detected at temperatures up to 350 °C. Actual onset temperatures of decomposition in nitrogen for DNPIMs, TOTPIMs, and DNTOTPIM were in the range of 457–485, 333–472, and 298–344 °C respectively. The thermal stabilities of copolymers were slightly reduced by tetraoxide thianthrene segments but improved significantly by introducing dinaphthyl segment on the main chain.

Mechanical Properties. The mechanical properties of three CoPIMs-50 series and PIM-1 are listed in Table 3. Tensile stress at break and tensile strain at break decreased obviously due to the introduction of dinaphthyl groups into the polymer chain. Compared with PIM-1 (tensile strain at break: 11.2%; tensile stress at break: 47.1 MPa), the tensile strain at break of DNPIM-50 is only 5.67%, while the tensile stress at break is 38.6 MPa. This could be possibly attributed to the polymer being more contorted and less amenable to chain

Table 3. Physical Properties of the DNPIM-50, TOTPIM-100, TOTPIM-50, DNTOTPIM-50, and PIM-1^a

polymers	P (g/cm ³)	$V_{\rm sp}~({\rm cm}^3/{\rm g})$	M (g/mol)	$V_{\rm w}$ (cm ³ /mol)	$V_{\rm f}({\rm cm}^3/{\rm g})$	FFV	$S_{\rm BET} ({ m m}^2~{ m g}^{-1})$	tensile stress at break (MPa)	tensile strain at break (%)
DNPIM-50	1.11	0.90	449	233	0.227	0.25	709	38.6	5.67
TOTPIM-100	1.28	0.78	630	302	0.157	0.20	560	48.3	24.1
TOTPIM-50	1.19	0.84	545	274	0.186	0.22	601	45.8	20.9
DNTOTPIM-50	1.30	0.77	533	263	0.129	0.17	408	38.2	4.75
PIM-1	1.06	0.94	460	246	0.244	0.26	729	47.1	11.2
a Tha diamantia		1	In FEV		1 f . 11		$1 \dots V = (V$	1.2U), EEV $-U/$	IZ and and IZ in

^{*a*} The disruption in chain packing, validated by FFV, was calculated using the following relationship: $V_f = (V_{sp} - 1.3V_w)$; FFV = V_f/V_{sp} , where V_f is the free volume and V_{sp} is the specific volume. Film samples had a density in the range 1.06–1.21 g cm⁻³, as determined by measurements of their weight in air and in ethanol. V_w is the specific volume are Waals volume calculated using the group contribution method of Bondi.

Table 4. Gas Permeabilities and Ideal Selectivities of the DNPIM, TOTPIM, DNTOTPIM Series and PIM-1

		P (barrers ^{<i>a</i>})			α^b			
polymers	O ₂	N_2	H_2	CO_2	O_2/N_2	CO_2/N_2	H_2/N_2	
DNPIM-50	522	132	1478	2627	3.96	19.9	11.2	
DNPIM-33	907	242	2347	4646	3.75	19.2	9.7	
DNPIM-25	1139	321	3049	5799	3.55	18	9.5	
TOTPIM-100	642	190	1368	3056	3.40	16.1	7.2	
TOTPIM-50	1198	413	2616	4756	2.90	11.5	6.3	
TOTPIM-33	1247	436	2854	5320	2.86	12.2	6.5	
TOTPIM-25	1596	570	3567	6441	2.80	11.2	6.3	
DNTOTPIM-50	621	172	1703	3065	3.61	18.0	10.0	
DNTOTPIM-33	773	228	2077	3693	3.39	16.2	9.1	
DNTOTPIM-25	973	287	2695	4814	3.30	16.8	9.4	
PIM-1	1717	629	3847	7108	2.73	11.3	6.1	
PIM-1 (40 min)	1133	353	3042	5366	3.20	15.2	8.6	

^{*a*} Permeability coefficients measured at 25 °C and 50 psig pressure. 1 barrer = 10^{-10} [cm³ (STP) cm]/(cm² s cmHg). ^{*b*} Ideal selectivity $\alpha = (P_a)/(P_b)$.

packing due to the incorporation of bulky dinaphthyl segments. In contrast, mechanical properties were enhanced significantly by the incorporation of tetraoxide thianthrene segments. The tensile strain at break for TOTPIM-50s is more than double that of PIM-1, which indicates that polymer chain assumed a more open-chain conformation that allowed greater chain packing after incorporating the tetraoxide thianthrene segments.

Transport Properties of Pure Gases. The porosities of TOTPIM-100 and CoPIMs-50 (DNPIM-50, TOTPIM-50, and DNTOTPIM-50) were probed by nitrogen sorption BET analysis at 77 K. The polymers were precipitated from chloroform into methanol, followed by extensive washing with methanol prior to sorption measurements. PIM-1 was tested under the same conditions and used as a reference material. Nitrogen sorption measurements on these polymers revealed that the samples were microporous. As shown in Table 3, compared with PIM-1, BET surface area of TOTPIM-100 and CoPIM-50 decreased from 729 m² g⁻¹ for PIM-1 to 408 m² g⁻¹ for DNTOTPIM-50, which is consistent with the calculated frac-tional free volume (FFV).²⁶⁻²⁸ Table 3 also shows DNPIM-50 chain packing is the least efficient among the three CoPIMs, which FFV is close to PIM-1. A detailed study on the comparison of structures for DNPIMs and PIM-1 was reported elsewhere.²² Dinaphthyl segments provide a shorter distance between contorted centers and a smaller twist angle, resulting in a more compact polymer chain. The molecular conformation is more zigzag compared with the offset-linear structure of PIM-1 containing the spirobisindane segment. These two factors combine to give a high FFV in dinaphthyl-containing PIM. In contrast, tetraoxide thianthrene segments provide a longer distance between contorted centers and an offset-linear structure, which results in a more efficient packing and less FFV.

In general, there is a trade-off relationship in glassy or rubbery polymers between gas permeability and selectivity for common gases. Higher permeability is gained at the cost



O₂ Permeability, barrer

Figure 4. Relationship between O₂ permeability and O₂/N₂ selectivity of TOTPIM-100, CoPIMs, and PIM-1. PIM-1 (∇) [1, reported by Budd et al. (2005) at 200 mbar (2.90 psia) feed pressure at 30 °C;¹⁵ 2, reported by Budd et al. (2008) at 1 atm (14.7 psig) feed pressure at 23 °C;¹⁵ 3, reported by Staiger et al. at 4 atm (58.8 psia) feed pressure 35 °C;¹⁶ 4, reported by Du et al. at 4.4 atm (50 psig) feed pressure 25 °C; 5, the membrane was prepared by the same procedure as other CoPIMs and tested at 4.4 atm (50 psig) feed pressure 25 °C]. TOTPIM-100 and CoPIMs at 4.4 atm (50 psig) feed pressure 25 °C (\Box) [6, DNPIM-50; 7, DNPIM-33; 8, DNPIM-25]. (\diamondsuit) [9, DNTOTPIM-50; 10, DNTOTPIM-30; 11, DNTOTPIM-25]. (\diamondsuit) [12, TOTPIM-100, 13, TOTPIM-50; 14, TOTPIM-33; 15, TOTPIM-25].

of lower selectivity, and vice versa. An upper bound performance for this trade-off relationship was proposed by Robeson.^{29,30} Pure-gas permeability coefficients (P) were measured on dense polymer films of PIM-1, TOTPIM-100, and three series of CoPIMs for O2, N2, H2, and CO2. A summary of these P values and ideal selectivities for various gas pairs is shown in Table 4. According to numerous reported gas separation data for PIM-1 and our own labora-tory testing experience,^{15,16} it is evident that the gas transport properties of PIMs are quite sensitive to the testing conditions, such as ambient surroundings, pretreatment, and different film fabrication techniques. However, all the PIM data are above the Robeson upper bound (1991) with the expected "trade-off" behavior between permeability and selectivity, as shown in Figure 4. TOTPIM-100 and three series of CoPIMs exhibit higher selectivity, coupled with some reduction in gas permeabilities, compared with PIM-1 (no. 5 tested under the same conditions). The overall permeabilityselectivity performance combines to exceed the Robeson upper bound (1991) for O_2/N_2 . For all three series of CoPIMs, gas permeabilities are observed to increase with decreasing ratios of dinaphthyl or/and tetraoxide thianthrene groups in the polymer chain. For the same ratio of dinaphthyl or/and



Figure 5. Models of the segments based on TTSBI, TFTPN, THDN, and TFTOT as calculated with energy minimization.

tetraoxide thianthrene groups, the gas permeabilities are observed to be in the sequence of TOTPIM > DNTOTPIM > DNPIM. From a materials viewpoint, a shorter interchain distance combined with the more contorted zigzag polymer chain structure imparts higher selectivity but lower permeability, and vice versa. Dinaphthyl has a shorter distance between contorted centers, and the chain has a more compact zigzag structure; hence, selectivity increased. Compared with PIM-1 and TOTPIMs, the permeability is decreased because of a shorter segmental length and smaller twist angle. For TOTPIMs, tetraoxide thianthrene units have a longer segmental length between spiro centers and a more offset-linear structure, which leads to a more efficient chain packing and reduction of the permeability but increasing selectivity.

Molecular Modeling. Molecular modeling results may help to explain why, as compared to PIM-1, the coeffects of the three CoPIMs exhibit improved gas selectivity without overall loss of performance relative to the upper bound. Conformational analysis of four segments comprising two repeat unit lengths derived from TTSBI, TFTPN, THDN, and TFTOT was modeled to study the effect and distribution of dinaphthyl and tetraoxide thianthrene groups on chain geometry and steric interaction. The calculation results of geometry optimization with energy minimization using the AMBER method provides a visualization of major conformational changes occurring in the polymers, as shown in Figure 5. The chains containing tetraoxide thianthrene units have a relatively linear and long ladder structure, which presumably leads to more efficient chain packing. The chains containing dinaphthyl units resulting in a zigzag and short ladder segment would lead to less efficient chain packing and more contortion. For example, compared with PIM-1 (the fragment including of TTSBI, TFTPN), the TTSBI + TFTOT segment shows a similarly unperturbed coil conformation, but the distance between the spiro center is longer, resulting in a more open-chain structure and increased chain-packing. On the other hand, the TFTPN + THDN segment is observed to be a

more contorted structure when viewed from the "x", "y", and "z" axes perspective, but the angle at the spatially twisted dinaphthyl center (~60°) is considerably smaller than that at the spirobisindane (~90°); in addition, the distance between the twist center is shorter. This is in good agreement with their mechanical properties and gas permeation results of DNPIM, which exhibits the lowest permeability and highest selectivity.

Conclusions

Novel PIMs homopolymers and copolymers derived from TTSBI, TFTPN, TFTOT, and THDN extend the spectrum of possible soluble polymeric structures having high molecular weight that are suitable as film-forming membrane materials. Reaction conditions of elevated temperature and reaction times of 120 min led to polymers having high molecular weight and low polydispersity. Incorporation of high molar ratios of TFTOT and/or THDN monomers resulted in polymers exhibiting analogous gas transport properties to that of conventional PIM-1. The structures of the new monomers, homopolymers, and copolymers were confirmed by ¹H and ¹⁹F NMR spectroscopy. The intrinsic microporosities of these polymers are supported by FFV, BET data, and gas permeability measurements. Thermal properties of the new homopolymers and copolymers indicate they have high thermal stability, with DNPIMs containing the dinaphthyl segment showing the highest stability. TOTPIM-100 and the Co-PIMs have an excellent combination of properties and were more gas/N₂ selective than PIM-1. The increased selectivity coupled with high permeability combines to exceed the Robeson upperbound line for O_2/N_2 . These results suggest that these polymers are potential candidates for gas separation membrane materials and have a good combination of physical properties, similar to PIM-1. The incorporation of the dinaphthyl and tetraoxide thianthrene monomers into a copolymer system allows the gas permeability, selectivity, and other properties to be tuned.

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References and Notes

- Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* 2004, 230–231.
- (2) Budd, P. M.; Elabas, E. S.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E.; Wong, D. *Adv. Mater.* 2004, *16*, 456–459.
- (3) McKeown, N. B.; Budd, P. M.; Msayib, K. J.; Ghanem, B. S.; Kingston, H. J.; Tattershall, C. E.; Makhseed, S.; Reynolds, K. J.; Fritsch., D. Chem.—Eur. J. 2005, 11, 2610–2620.
- (4) Du, N.; Robertson, G. P.; Song, J.; Pinnau, I.; Thomas, S.; Guiver, M. D. Macromolecules 2008, 41, 9656–9662.
- (5) Davankov, V. A.; Tsyurupa, M. P. React. Polym. 1990, 13, 27-42.
- (6) Tsyurupa, M. P.; Davankov, V. A. React. Funct. Polym. 2002, 53, 193–203.
- Budd, P. M.; Ghanem, B.; Msayib, K.; McKeown, N. B.; Tattershall, C. J. *Mater. Chem.* **2003**, *13*, 2721–2726.
- (8) McKeown, N. B.; Gahnem, B.; Msayib, K. J.; Budd, P. M.; Tattershall, C. E.; Mahmood, K.; Tan, S.; Book, D.; Langmi, H. W.; Walton, A. Angew. Chem., Int. Ed. 2006, 45, 1804–1807.
- (9) Webster, O. W.; Gentry, F. P.; Farlee, R. D.; Smart, B. E. Makromol. Chem., Macromol. Symp. 1992, 54, 477–482.
- (10) Urban, C.; McCord, E. F.; Webster, O. W.; Abrams, L.; Long, H. W.; Gaede, H.; Tang, P.; Pines, A. Chem. Mater. 1995, 7, 1325–1332.
- (11) Wood, C. D.; Tan, B.; Trewin, A.; Niu, H. J.; Bradshaw, D.; Rosseinsky, M. J.; Khimyak, Y. Z.; Campbell, N. L.; Kirk, R.; Stockel, E.; Cooper, A. I. *Chem. Mater.* **2007**, *19*, 2034–2048.
- (12) (a) Dai, Y.; Guiver, M. D.; Robertson, G. P.; Kang, Y. S. Macromolecules 2005, 38, 9670–9678. (b) Dai, Y.; Guiver, M. D.; Robertson, G. P.; Kang, Y. S.; Lee, K. J.; Jho, J. Y. Macromolecules 2004, 37, 1403–1410.

- (13) (a) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau,
 I. Prog. Polym. Sci. 2001, 26, 721–798. (b) Pinnau, I.; Toy, L. G.
 J. Membr. Sci. 1996, 116, 199–209.
- (14) (a) Thomas, S.; Pinnau, I.; Du, N.; Guiver, M. D. J. Membr. Sci. 2009, 333, 125–131. (b) Thomas, S.; Pinnau, I.; Du, N.; Guiver, M. D. J. Membr. Sci. 2009, 338, 1–4.
- (15) (a) Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Reynolds, K. J.; McKeown, N. B.; Fritsch., D. J. Membr. Sci. 2005, 251, 263–269.
 (b) Budd, P. M.; McKeown, N. B.; Ghanem, B. S.; Msayib, K. J.; Fritsch, D.; Starannikova, L.; Belov, N.; Sanfirova, O.; Yampolskii, Y.; Shantarovich., V. J. Membr. Sci. 2008, 325, 851–860.
- (16) (a) Staiger, C. L.; Pas, S. J.; Hill, A. J.; Cornelius, C. J. *Chem. Mater.* **2008**, *20*, 2606–2608. (b) Ghanem, B. S.; Hashem, M.; Harris, K. D. M.; Msayib, K. J.; Xu, M.; Budd, P. M.; Chaukura, N.; Book, D.; Tedds, S.; Walton, A.; McKeown, N. B. *Macromolecules* **2010**, *43*, 5287–5294. (c) McKeown, N. B.; Budd, P. M. *Macromolecules* **2010**, *43*, 5163–5176. (d) Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Al-Harbi, N. M.; Fritsch, D.; Heinrich, K.; Starannikova, L.; Tokarev, A.; Yampolskii, Y. *Macromolecules* **2009**, *42*, 7881–7888.
- (17) McKeown, N. B.; Budd, P. M.; Msayib, K.; Ghanem, B. Microporous Polymer. Material, WO 2005/012397 A2.
- (18) Du, N.; Robertson, G. P.; Pinnau, I.; Guiver, M. D. Macromolecules 2009, 42, 6023–6030.
- (19) Aoki, T. Prog. Polym. Sci. 1999, 24, 951–993.
- (20) George, S. C.; Thomas, S. Prog. Polym. Sci. 2001, 26, 985-1017.
- (21) Du, N.; Robertson, G.; Song, J.; Pinnau, I.; Guiver, M. D. Macromolecules 2009, 42, 6038–6043.
- (22) Du, N.; Robertson, G. P.; Pinnau, I.; Thomas, S.; Guiver, M. D. Macromol. Rapid Commun. 2009, 30, 584–588.
- (23) Toda, F.; Tanaka, K.; Iwata, S. J. Org. Chem. 1989, 54, 3007-3009.
- (24) Bock, V. H.; Stein, U.; Rittmeyer, P. Angew. Chem. 1982, 94, 540-541.
- (25) March, J. Advanced Organic Chemistry; McGraw-Hill: New York, 1970; p 253.
- (26) Bondi, A. J. Phys. Chem. 1964, 68, 441-451.
- (27) Van Krevelen, D. W. Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions; Elsevier: Amsterdam, The Netherlands, 1990.
- (28) Chern, R. T.; Sheu, F. R.; Jia, L.; Stannett, V. T.; Hopfenberg, H. B. J. Membr. Sci. 1987, 35, 103–115.
- (29) Robeson, L. M. J. Membr. Sci. 1991, 62, 165-185.
- (30) Robeson, L. M. J. Membr. Sci. 2008, 320, 390-400.