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# Copolymers of Intrinsic Microporosity Based on 2,2′,3,3′-Tetrahydroxy-1,1′-dinaphthyl[a]

Naiying Du, Gilles P. Robertson, Ingo Pinnau, Sylvie Thomas, Michael D. Guiver*

A series of new copolymers with high molecular weight and low polydispersity, prepared from tetrahydroxydinaphthyl, tetrahydroxyspirobisindane, and tetrafluoroterephthalonitrile monomers, prevent efficient space packing of the stiff polymer chains and consequently show intrinsic microporosity. One copolymer, DNPIM-33, has an excellent combination of properties with good film-forming characteristics and gas transport performance, and exhibits higher selectivity than the corresponding spirobisindane-based homopolymer PIM-1 for gas pairs, such as $O_2/N_2$, with a corresponding small decrease in permeability. This work demonstrates that significant improvements in properties may be obtained through development of copolymers with intrinsic microporosity (CoPIMs) that extends the spectrum of high-molecular-weight ladder structures of poly(dibenzodioxane)s.
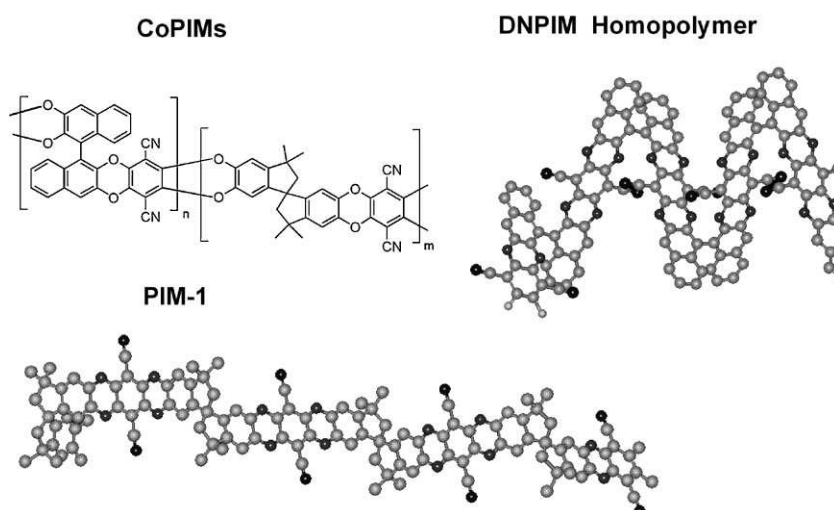
## Introduction

Microporous polymeric materials, such as solvent-swollen polymers,[1,2] polymer networks with rigid units,[3–8] and polymers with extremely bulky structural units,[9,10] are of considerable interest in applications such as adsorbents, separation materials, and catalysis. This is because of the combined advantages of polymer processability and high internal surface area, which is comparable with conventional inorganic microporous materials such as zeolites or activated carbons. Recently, Budd, McKeown, and co-workers reported a novel class of polymeric microporous material—polymers of intrinsic microporosity (PIMs).[8,11,12] These rigid ladder homopolymers have contorted structures that prevent efficient chain packing and provide high free volume and high surface areas. Meanwhile, they can be readily cast from solution into robust free-standing films that show great promise for membrane-based gas separations.

One important structural feature of PIMs is the presence of bulky kinks in the repeat units. For example, PIM-1, the most studied PIM that has a high molecular weight, is
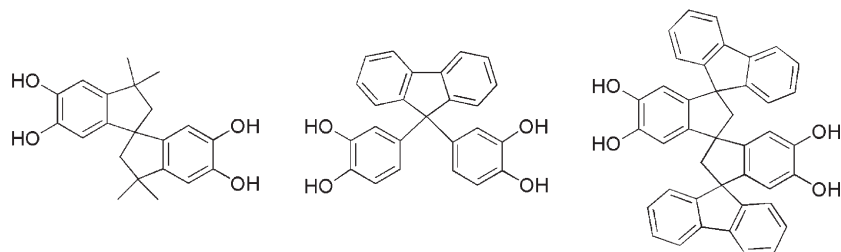
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**Figure 1.** Some spiro-monomers for high-molecular-weight PIMs reported previously.

prepared from a dioxane-forming reaction between commercially available 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (TTSBI), and 2,3,5,6-tetrafluoro-terephthalonitrile (TFTPN). McKeown and Budd suggested several monomers for the preparation of PIMs having spiro-contorted centers;[13] however, only a few reported monomers provide high-molecular-weight PIMs suitable for film formation and advanced gas permeation properties (Figure 1).[14–16] It is of great interest to expand the spectrum of available high-molecular-weight PIM structures that have contorted chains to tailor membranes with high-performance gas separation properties.

To gain insight into the effect of other contorted centers on polymer chain conformation, we investigated PIMs derived from a tetrahydroxy dinaphthyl monomer by computational molecular modeling. The 2,2′,3,3′-tetrahydroxy-1,1′-dinaphthyl (THDN) monomer is fully aromatic and has a highly kinked unit that originates from the spatially twisted dinaphthyl bond between two ring systems. The presence of this center might be expected to result in less efficient space packing and higher thermal stability. In addition, the remarkably simple synthesis of the THDN dinaphthyl monomer, first reported by Toda et al. in 1989, consists of a short reaction time of 2,3-naphthalenediol in the presence of a catalyst at 50 °C.[17]

The initially reported synthesis of a PIM homopolymer derived from THDN dinaphthyl monomer and TFTPN at 80 °C and 72 h reaction time gave only a low-molecular-weight material that had a $\overline{M}_n$ of 3 000 Da, which is too low for adequate film formation and good mechanical properties necessary to measure gas permeabilities.[13] The most likely reason for the low molecular weight of the THDN-based PIM homopolymer is an excessive spatial contortion and steric hindrance over short segmental chain lengths,

which leads to difficulty in two dinaphthyl monomers accessing a single TFTPN dinitrile monomer. This problem could be alleviated by incorporating THDN into a PIM copolymer structure together with the spirobisindane mono-mer, thereby providing space for one THDN monomer to react with TFTPN. In order to investigate the effect of the spatially twisted structure in the poly-mer chain, the present work focuses on CoPIMs derived from TTSBI, TFTPN, and THDN. A relationship between copolymer properties and the observation of intrinsic microporosity is discussed.

## Results and Discussion

PIM copolymers derived from various feed ratios of TTSBI/THDN/TFTPN monomers were prepared by aromatic nucleophilic polycondensation at 160 °C for 120 min. ^{1}H NMR spectra and matrix-assisted laser desorption–ionization time-of-flight (MALDI-TOF) mass spectra were consistent with the expected structures. For comparison, PIM-1 was prepared under identical reaction conditions from TTSBI and TFTPN. It should be noted that PIM-1 prepared under the newly reported conditions of 160 °C produced high-molecular-weight polymer with a narrow polydispersity.[18] Figure 2 gives an overview of the resulting DNPIM copolymer structure. Table 1 reports the molecular weights and polydispersities of DNPIM-33 copolymer, as determined by gel permeation chromato-graphy (GPC) against polystyrene standards. The designa-tion '33' in the DNPIM-33 copolymer refers to the percentage of THDN/TFTPN (molar ratio) in the polymer chain.
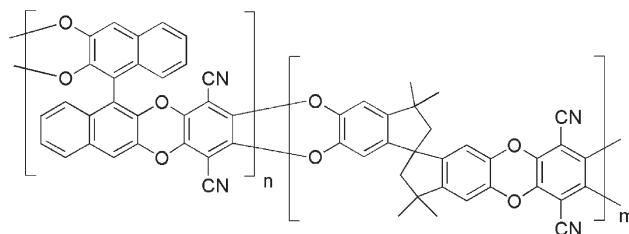


**Figure 2.** DNPIM copolymers.

**Table 1.** Properties of DNPIM-33 copolymer and PIM-1 polymerized at 160 °C for 120 min.

| Polymers | THDN | TTSBI | TFTPN | $\overline{M}_n$ | $\overline{M}_w$ | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|---|
| | mol ratio | mol ratio | mol ratio | | | |
| DNPIM-33 | 1 | 2 | 3 | 116 000 | 273 000 | 2.3 |
| PIM-1 (120 min) | 0 | 1 | 1 | 58 000 | 625 000 | 10.8 |
| PIM-1 (40 min)[18] | 0 | 1 | 1 | 55 000 | 85 000 | 1.6 |

In our earlier work on the preparation of PIMs,[18] we note that cyclic oligomers and cross-linking can be effectively reduced by using polycondensation reaction conditions of elevated temperature at 160 °C and high monomer concentrations. Toluene was also added to increase the solubility of the growing polymer chain. Within 40 min, the PIM-1 polymerization under optimum reaction conditions (160 °C and monomers: DMAc = 1 mmol : 2 mL) proceeded smoothly and no evidence of cross-linking was detected. When the reaction time exceeded 90 min under the same conditions, it was observed that the conditions were prone to produce high-molecular-weight fractions and possible cross-linked polymer (polydispersity values up to 15), which resulted in limited $\overline{M}_n$. In the absence of toluene in the reaction system, cross-linking occurred rapidly, typically within 30 min. In the present study, PIM-1 was prepared under the same conditions as the DNPIM copolymer. In the GPC trace (not shown), several shoulder peaks in the high-molecular-weight region occurred around the main peak, which indicates the presence of high-molecular-weight fractions and possible cross-linking in PIM-1 prepared at a reaction time of 120 min. In general, the polydispersities of the DNPIM copolymers are in the range of 1.8–2.3, compared with >10 for PIM-1 prepared at the extended 120 min reaction time. It is interesting to note that as the molar ratio of THDN/TFTPN in the DNPIM copolymers is increased to 50, a high $\overline{M}_n$ can be obtained with low polydispersity. Even at molar ratios beyond 50, $\overline{M}_n$ values above 10 000 could still be obtained under these conditions, with low polydispersities. In the case of DNPIM-33, a high molecular weight and low polydispersity was obtained, with no evidence of cross-linking. Thus, under the same reaction conditions (160 °C, 120 min), molecular weight broadening and cross-linking are efficiently reduced by introducing a certain ratio of THDN into the polymer chain, and high-molecular-weight copolymers can be obtained. A plausible explanation is that TTSBI has a higher reactivity than THDN, and its concentration was decreased by introducing THDN into the copolymerization system, which results in less cross-linking. On the other hand, although high temperature and high concentration polymerization conditions were applied in this reaction, the high-molecular-weight homopolymer from TFTPN and THDN still could not be obtained. Although the $\overline{M}_n$ of the DNPIM homopolymer obtained was higher ($\overline{M}_n$ = 10 000 Da) than that previously reported ($\overline{M}_n$ = 3 000),[13] it consists of mainly of cyclics and oligomers as shown by MALDI-TOF analysis, and is insufficient to fabricate mechanically strong films for gas permeability measurements. The copolymers were readily soluble in chloroform and tetrahydrofuran, and those with up to 50% DN had adequately good mechanical properties to provide solution-cast self-supporting membranes. The present communication reports on the most promising copolymer of this series, DNPIM-33. Comprehensive details of the complete copolymer series, the new homopolymer structure, and the MALDI-TOF mass spectroscopic analysis will be published elsewhere.

### Thermal Analysis

All synthesized polymers are amorphous and have excellent thermal stabilities, remaining glassy up to their decomposition temperatures (>430 °C). No glass transitions were detected up to 350 °C. Actual onset temperatures of decomposition in nitrogen were in the range of 466–479 °C, which is high compared to that of PIM-1 (430 °C). The dinaphthyl group imparts improved thermal stability, as shown by the increasing thermal stability with dinaphthyl monomer molar ratio.

### Pure-Gas Permeability

In glassy and rubbery polymers, there is typically a trade-off relationship between gas permeability and selectivity for common gases. In general, higher permeability is gained at the cost of lower selectivity and vice versa. An upper boundary performance for this trade-off relationship was proposed by Robeson.[19,20] Single-gas permeability coefficients ($P$) were measured on polymer dense films of PIM-1 and DNPIM-33 for $O_2$, $N_2$, He, $H_2$, and $CO_2$ following the same procedure reported previously.[18] A summary of these $P$ values and ideal selectivities for various gas pairs is shown in Table 2. DNPIM-33 exhibits higher selectivity, coupled with a reduction in gas permeability when compared with a PIM-1 film fabricated and measured under the same conditions. The overall permeability/selectivity performance combines to exceed the Robeson upper boundary for $O_2/N_2$. From a material viewpoint, a shorter interchain distance imparts higher selectivity, but lower permeability. In this case, THDN units effectively shorten the distance between contorted centers, while maintaining a zig-zag structure, hence increasing selectivity. Molecular modeling analyses of DNPIM-100 and PIM-1 provide insight as to why gas permeabilities for DNPIM-33 were not reduced excessively, even though the THDN structure is more compact and has a shorter distance between contorted centers and a smaller twist angle. Energy minimized structural analysis of DNPIM-100 and PIM-1 of four repeat units was performed by using HyperChem 7.0 software. A visual indication of major conformational changes in the polymer chain units was obtained by the calculated results of geometry optimization with minimum energy using the AMBER method. In Figure 3, it is observed that PIM-1 and DNPIM-100 have similarly unperturbed zig-zag coil structures when viewed from the 'x' and 'y' axes perspective. The angle at the spatially twisted dinaphthyl center in DNPIM-

*Table 2.* Gas permeabilities and ideal selectivities of DNPIM-33 and PIM-1.

| Polymers | $P$[a] | | | | | $\alpha$[b] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Barrer | | | | | $O_2/N_2$ | $CO_2/N_2$ | $He/N_2$ | $H_2/N_2$ |
| | $O_2$ | $N_2$ | $He$ | $H_2$ | $CO_2$ | | | | |
| DNPIM-33 | 907 | 242 | 968 | 2347 | 4646 | 3.75 | 19.2 | 4.0 | 9.7 |
| PIM-1 (120 min) | 1560 | 547 | 1531 | 3364 | 7329 | 2.85 | 13.4 | 2.8 | 6.7 |
| PIM-1 (40 min)[18] | 1133 | 353 | 1114 | 3042 | 5366 | 3.2 | 15.2 | 3.1 | 8.6 |

[a]Permeability coefficients measured at 25 °C and 50 psi pressure; 1 Barrer $= 10^{-10}$ cm$^3$ (STP) $\cdot$ cm $\cdot$ cm$^{-2} \cdot$ s$^{-1} \cdot$ cmHg$^{-1}$; [b]Ideal selectivity $\alpha = (P_a)/(P_b)$.

100 (approximately 60°) is considerably smaller than that at the spirobisindane center in PIM-1 (approximately 90°). However, it is notable that when both polymers are compared from the 'z' axis perspective, PIM-1 has an offset-linear conformation, whereas DNPIM-100 has a zig-zag structure. This suggests that DNPIM-100 is potentially even more contorted than PIM-1, which may result in even less efficient chain packing. The incorporation of THDN units into copolymers would also have the same effect. This is in good agreement with the gas permeability results. Although the distance between the twisted dinaphthyl units is shorter and the kink angle is smaller than PIM-1, there was little apparent change observed in interchain spacing throughout the DNPIM copolymer series.

Figure 4 shows the gas permeability/selectivity trade-off plot for the $O_2/N_2$ gas pair in relation to the Robeson upper-boundary.[19,20] The ▽ symbols show previous data reported by Budd et al.[21,22] and Staiger et al.[23] for PIM-1. Compared to data reported by Budd et al. for films cast from tetrahydrofuran and measured at very low gas feed pressure, the oxygen permeability of chloroform-cast films of PIM-1 (reaction time: 120 mins; high polydispersity material) reported in the present work (≈1 560 Barrer) is about four times higher, but with a reduction in oxygen/

nitrogen selectivity from 4.0 to 2.8. We also show the comparative PIM-1 data of our previous work (reaction time: 40 min, low polydispersity).[18] The disparity in results is not surprising as the gas permeation properties of highly rigid glassy polymers depend strongly on film formation protocols, such as casting solvent type and drying conditions.[22,24] As shown in Table 2 and Figure 4, the DNPIM-33 copolymer had an excellent combination of properties and was more gas-selective than PIM-1. The selectivity and high permeability combine to exceed the Robeson upper-boundary for $O_2/N_2$. The results imply that THDN can be incorporated as a co-monomer for the syntheses of high-molecular-weight PIMs and is effective in tuning the gas permeability, selectivity, and other properties of PIM copolymers.
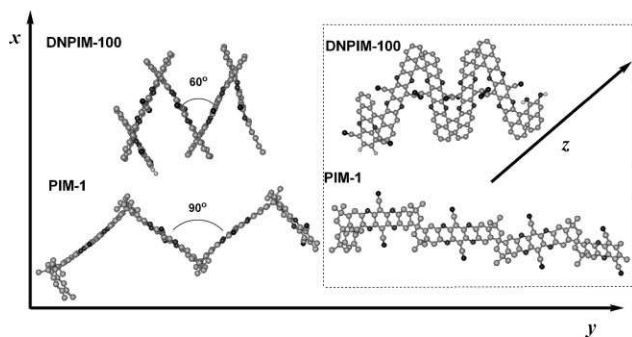


*Figure 3.* Models of PIM-1 and DNPIM-100 as calculated with energy minimization.
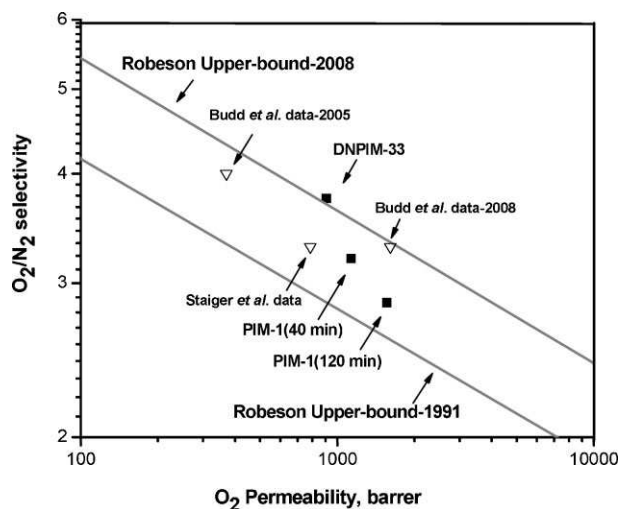


*Figure 4.* Trade-off between $O_2$ permeability and $O_2/N_2$ selectivity of DNPIM-33 and PIM-1 membranes relative to the Robeson's upper boundary. ▽ The data from Budd et al. (2005) were reported at 200 mbar (2.90 psia) feed pressure at 30 °C. [21] ▽ The data from Budd et al. (2008) were reported at 1 atm (14.7 psia) feed pressure at 30 °C. [22] ▽ The data from Staiger et al. were reported at 4 atm (58.8 psia) feed pressure 35 °C. [23]

## Conclusion

High-molecular-weight copolymers that have intrinsic microporosity are prepared by inclusion of up to 50% of a dinaphthyl comonomer. The dinaphthyl monomer contains a spatially twisted contorted center that extends the spectrum of possible structures of the PIM polymers. Reaction conditions of an elevated temperature and reaction times of 120 min led to low polydispersity copolymers. The intrinsic microporosity of these polymers is supported by pure-gas permeability data and molecular modeling. The reported copolymer, DNPIM-33, had high molecular weight and provided mechanically strong films that have pure-gas permeabilities and selectivities different to the corresponding homopolymer PIM-1. The $O_2/N_2$ selectivity coupled with high permeability combines to exceed the Robeson upper-boundary. Computational molecular modeling suggests the effect of the contorted center in the dinaphthyl unit results in a considerable change in chain conformation. In conclusion, this work illustrates that the inclusion of a monomer that has a contorted center, while not yielding a high-molecular-weight homopolymer, can be effectively incorporated into high-molecular-weight copolymers at certain monomer ratios, thereby extending the range of new structures and properties for polymers with intrinsic microporosity.

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