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Soluble aromatic polyamides containing the phenylindane group and their gas transport characteristics

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Abstract

A series of new polyamides containing the phenylindane moiety was synthesized from 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid and aromatic diamines by the direct phosphorylation polymerization method. The phenylindane moiety containing polyamides are highly soluble in polar aprotic solvents, such as DMF, DMAc, and NMP, and exhibit very high glass transition temperatures and attractive gas separation characteristics, i.e. high gas permeability coefficients combining with high gas separation factors. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It has been established that stiffening the polymeric backbone while simultaneously inhibiting chain packing can lead to improved gas permeability combined with an increase in gas selectivity for certain gas mixtures [1–7]. Based on these findings, aromatic polyamides and polyimides have attracted extensive attention as candidate materials for gas separation membrane preparation due to their rigid backbone structure and superior mechanical and thermal properties. Polyimides have been studied as candidate materials more extensively for gas separations as compared to polyamides [8–12], largely because they can be processed into membranes from solution-based systems. Most recently, we have advanced polyimide membrane preparation methodology by using polyamic acid salts as precursors. These precursors are soluble in alcohol-based solvents and can be completely imidized at a relatively low temperature [13–15]. Compared to polyimides, aromatic polyamides have been studied less extensively [16–21]. This, most probably, can be attributed the fact that polyamides are generally intractable due to their rigid backbone structure and inter-chain hydrogen bonding. Our work had two objectives: first to synthesize a series of new soluble, rigid backbone polyamides and

second to study the relationship between the polyamide structure and gas transport properties.

The phenylindane group has been shown to impart improved solubility to a polymer while simultaneously leading to an improvement in gas transport characteristics, i.e. increase in both gas separation factors and permeability coefficients [6,22–25]. A typical example is the commercially available polyimide, Matrimid[®], which is derived from a phenylindane diamine and the benzophenone dianhydride [26]. Matrimid is highly soluble in a variety of organic solvents, exhibits a high T_g and excellent gas transport characteristics. Consequently, it finds application as a commercial gas separation membrane material. A number of soluble polyamides containing the phenylindane group have been synthesized from 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane and dicarboxylic chlorides [22]. Surprisingly, few polyamides has been prepared from 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid. To our knowledge, only one such polyamide was prepared from 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid and from 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane [22]. We reasoned that polyamides derived from 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid should be organo-soluble and possess attractive gas transport properties. A series of new polyamides containing the phenylindane moiety was

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synthesized from 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid and their structure was correlated with gas transport characteristics.

2. Experimental section

2.1. Instruments

ATR–FT-IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument equipped with an Omni-ATR attachment. Differential scanning calorimetry (DSC) data were obtained with a Seiko DSC 6200 instrument under nitrogen atmosphere. The heating rate was 10 °C/min. Inherent viscosities were measured at 25.0 ± 0.1 °C with an Ubbelohde viscometer. Film densities were determined with a Metler density kit 33360 in water. It was determined independently that water take up/swelling of polyamides during density measurements was negligible by soaking polyamide film samples in water for time period identical to the duration of density measurement experiments and measuring weight increase. The reported density value was an average of three measurements. H NMR spectra were recorded on a Bruker 500 NMR instrument and DMSO-*d*₆ was used as the solvent.

2.2. Materials

All solvents were purchased from Aldrich and used as received. Anhydrous calcium chloride, 1,4-phenylene diamine, 1,3-phenylene diamine, 4,4'-(4,4'-isopropylidene-diphenyl-1,1'-diyl-dioxy)dianiline and triphenyl phosphite were also purchased from Aldrich. The dicarboxylic acid, 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid, was purchased from Acros Organics. 4,4'-Hexafluoroisopropylidenedianiline, 2,2'-bis(trifluoromethyl)benzidine, 4,4'-oxydianiline (ODA) and 3,3'-diaminodiphenyl sulfone were purchased from Chriskev Company, Inc. 1,5-Diaminonaphthalene was purchased from TCI.

2.3. General procedure of polyamide synthesis

The synthesis of phenylindane moiety containing polyamide **3a** provides a representative example of preparation methodology. A 500 ml four neck round flask equipped with a nitrogen inlet, a thermometer, and a mechanical stirrer was charged with 8.11 g (0.025 mol) of 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid, 2.70 g (0.025 mol) of 1,3-phenylene diamine, 3.0 g of calcium chloride, 16 ml of pyridine, 20 ml of triphenylphosphite and 50 ml of NMP. The mixture was heated under nitrogen to 110 °C and stirred for 3 h. The viscous solution was then cooled down and precipitated into 2 l of methanol. The stringy polymer was washed thoroughly with hot water and methanol, collected by filtration, and dried at 100 °C

under vacuum. The inherent viscosity of this polymer was 0.63 dl/g, measured at 25 °C with polymer solution concentration of 0.4 g/dl in NMP.

2.4. Preparation of polyamide films

The polyamide films were cast from their solutions in DMF (ca. 10% solid) in an oven set at 70 °C using the ring technique described by Moe et al. [27]. The films were then released from the glass plates and dried under vacuum at 160 °C for 24 h. The dried films were stored in a desiccator under nitrogen atmosphere prior to testing. The thickness of the dense flat sheet films studied was about 30 μm.

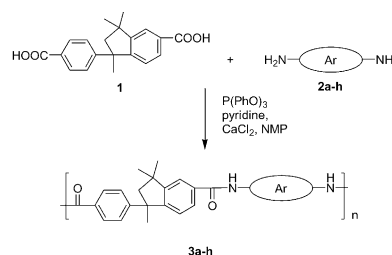
2.5. Gas permeation measurements

The permeation testing apparatus and procedures that were utilized to measure the gas permeability of flat sheet films were the same as described by Koros et al. [28]. All measurements were made using an upstream pressure of 1–2 atm, while the down stream pressure was effectively zero. The pressure in the receiver was monitored with a MKS Baratron pressure transducer. The gas permeability coefficients are reported in Barrers (1 Barrer = 10⁻¹⁰ cm³(STP) cm/cm² cmHg s).

3. Results and discussion

3.1. Synthesis of polyamides

In total eight new polyamides containing the phenylindane moiety were synthesized in this study. The schematics of the synthesis and the structure of polyamides synthesized are shown in Fig. 1. The polyamides were synthesized by



Polymer	Ar	Polymer	Ar
3a		3e	
3b		3f	
3c		3g	
3d		3h	

Fig. 1. Schematics of polyamide synthesis.

Table 1
Solubility characteristics of phenylindane containing polyamides

Polymer	CHCl ₃	THF	DMF	NMP	DMAc	η_{inh} (dl/g) ^a
3a	–	–	+	+	+	0.63
3b	–	–	+	+	+	0.48
3c	–	–	+	+	+	0.39
3d	–	–	+	+	+	0.41
3e	–	–	+	+	+	0.45
3f	–	–	+	+	+	0.41
3g	–	–	+	+	+	0.53
3h	–	–	+	+	+	0.67

+, Soluble; –, insoluble.

^a Measured at 25 °C in NMP at the concentration of 0.4 g/dl.

direct polycondensation of aromatic diamines with 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid using triphenyl phosphite and pyridine as condensation agents. High molecular weight polymers were readily available in 3 h. The inherent viscosities of the resultant polyamides were in the range 0.39–0.67 dl/g measured at 20 °C in NMP (Table 1). Tough and creasible films were obtained from all polyamides that allowed measurements of gas transport characteristics.

The formation of aromatic amide linkage was confirmed by FT-IR. Fig. 2 shows the ATR-FT-IR spectra of polymers **3b** and **3h**. The IR spectra show the characteristic amide group absorptions at 3310 and 1660 cm⁻¹, corresponding to –NH– and carbonyl groups, respectively. The structures of two representative polyamides **3b** and **3h** were also confirmed by H NMR spectroscopy. The H NMR spectra of these polymers, as well as peak assignments, are shown in Figs. 3 and 4, respectively. The polyamide **3b**

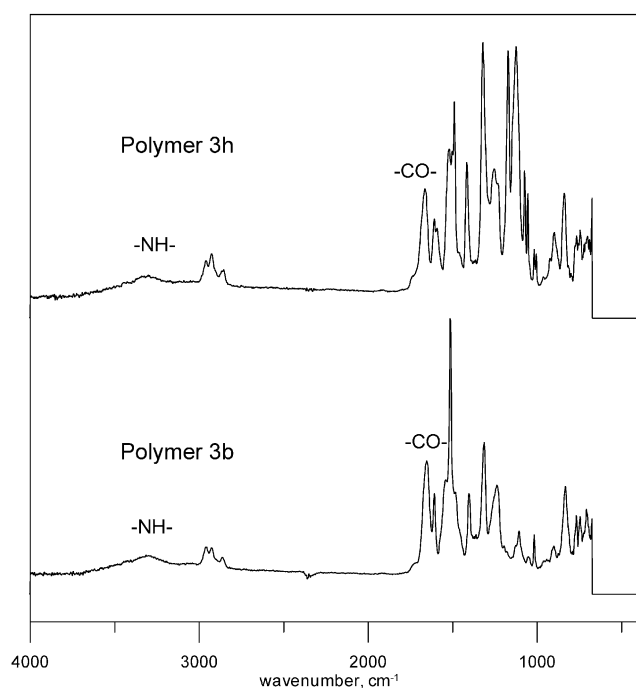


Fig. 2. ATR-FT-IR spectra of polyamides **3b** and **3h**.

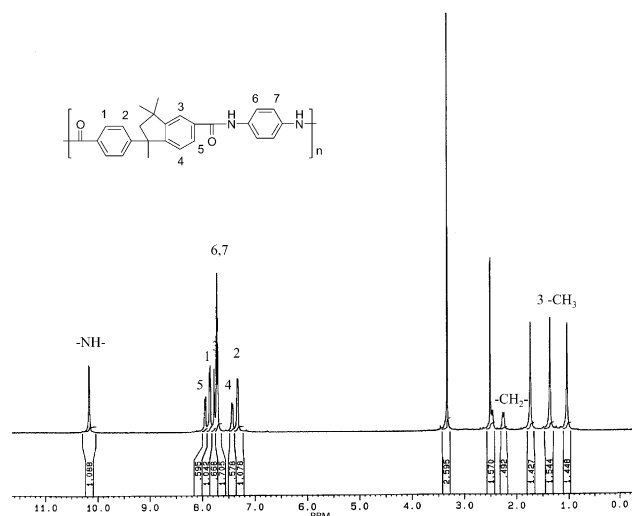


Fig. 3. H NMR spectrum of polymer **3b**.

exhibits a single peak at δ 10.2 ppm that is assigned to protons in the amide linkage. The polymer **3h** exhibits two peaks at δ 10.6 and 10.7 ppm, respectively, which are also assigned to the protons in the amide linkages. The doublet peak is due to the combination of asymmetric structure of the phenylindane group and the diamine used. Both polymers exhibit three singlets at δ 1.02, 1.35 and 1.73 ppm, respectively, which are assigned to protons of three methyl groups in the phenylindane moiety.

3.2. Physical properties of polyamides

All of the newly synthesized polyamides containing the phenylindane moiety are readily soluble in polar aprotic solvents, such as DMF, DMAc, and NMP (Table 1). The high solubilities are attributed to the phenylindane moiety, which has a rigid bent structure [29]. The bent structure of phenylindane disrupts strong hydrogen bonding between amide linkages.

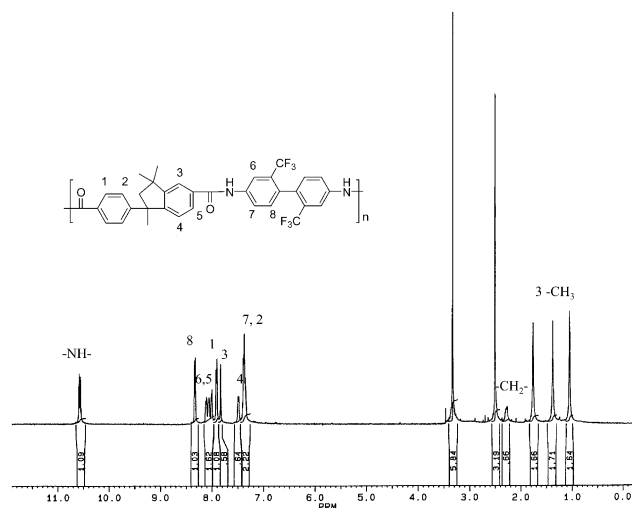


Fig. 4. H NMR spectrum of polymer **3h**.

Table 2
Physical properties of phenylindane containing polyamides

Polymer	T_g (°C)	Density (g/cm ³)	FFV	FFV(O ₂)
3a	346	1.170	0.188	0.086
3b	357	1.171	0.187	0.124
3c	302	1.183	0.180	0.115
3d	251	1.159	0.174	0.121
3e	381	1.200	0.168	0.096
3f	323	1.250	0.168	0.084
3g	>400	1.296	0.185	0.128
3h	>400	1.271	0.203	0.174

FFV = $(V_s - V_0)/V_s$, V_s : specific volume obtained by measurement; V_0 : specific volume at 0 K.

Even though phenylindane moiety containing polyamides are highly soluble, they exhibit very high glass transition temperatures. As shown in Table 2, all polymers exhibit glass transition temperature above 300 °C, except for polymer **3d**, which exhibits a glass transition temperature of 251 °C. It can be seen that polymers **3c**, **3d**, and **3f** have a lower glass transition temperature than polymers **3a**, **3b**, and **3e**. This can be attributed to the fact that polymers **3c**, **3d**, and **3f** possess flexible linkages in the polymer backbone, such as –O–, isopropylidene, and –SO₂–. Flexible linkages are frequently introduced into high performance polymers deliberately to impart improved solubility to the polymer. However, at the same time, these flexible linkages tend to lower the glass transition temperature. Polymers **3g** and **3h** exhibit glass transition temperatures above 400 °C, which is attributed to the presence of the bulky rigid –CF₃ group. The –CF₃ group not only imparts good solubility but a high glass transition temperature as well.

The measured density of all polyamides is relatively low (between 1.17 and 1.30 g/cm³, Table 2), which can be attributed to a reduced polymer chain packing density imparted by the bulky phenylindane groups. Fractional free volume, FFV, of each polyamide was calculated from the polymer density following the method of Bondi and Van Krevelen [30,31]. Fractional free volume for oxygen, FFV(O₂), for each polyamide was calculated following the procedure described by Park and Paul [32]. The later methodology accounts for the fact that the gas molecules of

different size can access different amounts of free volume. For example, the fractional free volume for oxygen, FFV(O₂), is different from the fractional free volume for nitrogen, FFV(N₂). The calculated FFV and FFV(O₂) are listed in Table 2.

3.3. Gas transport characteristics of polyamides

Gas transport properties of O₂, N₂, He, CO₂ and CH₄ in polyamides were measured at 30 °C and are summarized in Table 3. The calculated ideal gas separation factors for several selected gas pairs are also shown in Table 3. It can be concluded that polyamides containing the phenylindane moiety exhibit excellent gas separation characteristics. These high gas separation factors are combined with high gas permeability coefficients. Polymer **3f** exhibits a gas permeability coefficient of 0.53 Barrer for O₂ and an O₂/N₂ separation factor of 8.8. Polymer **3e** exhibits a gas permeability coefficient of 0.94 Barrer for O₂ and an O₂/N₂ separation factor of 8.0.

The relationship between oxygen/nitrogen separation factor and oxygen permeability coefficient for the series of phenylindane containing polyamides is shown in Fig. 5. It can be seen that all phenylindane containing polyamides exhibit gas transport properties close to the so-called upper bound, while most fall into the region classified by Koros as very attractive [4,33]. The oxygen permeability coefficient increases in the following sequence: **3f**, **3e**, **3a**, **3c**, **3b**, **3d**, **3h**, **3g**.

The results indicate that 3,3'-phenylsulfone, 1,5-naphthene, and 1,3-phenylene groups dramatically decrease gas permeability coefficients while simultaneously increasing gas separation factors. On the other hand, the trifluoromethyl group increases gas permeability coefficients while only modestly lowering gas separation factors. These gas transport properties can be attributed to the effect each group imparts on chain packing. The difference in chain packing leads to a difference in free volume and thus influences the gas transport properties of an individual polymer. However, the correlation between the FFV and gas permeability coefficients is rather poor. It has been noted that gas molecules of different size can access different amounts of the free volume in a polymeric material [32].

Table 3
Gas transport properties of phenylindane containing polyamides measured at 30 °C

Polymer	P(He)	P(O ₂)	P(N ₂)	P(CH ₄)	P(CO ₂)	P(O ₂)/P(N ₂)	P(CO ₂)/P(N ₂)	P(CO ₂)/P(CH ₄)
3a	17.7	1.16	0.15	0.09	5.2	7.6	34	58
3b	18.3	1.67	0.25	0.18	8.9	6.8	36	49
3c	19.2	1.67	0.24	0.21	8.4	6.8	34	39
3d	16.9	1.91	0.31	0.33	9.6	6.1	31	29
3e	15.8	0.94	0.12	0.09	4.1	8.0	34	48
3f	11.9	0.53	0.06	0.04	2.2	8.8	35	55
3g	65.8	7.35	1.36	0.91	35.3	5.4	26	39
3h	63.2	7.23	1.30	0.90	31.2	5.5	24	35

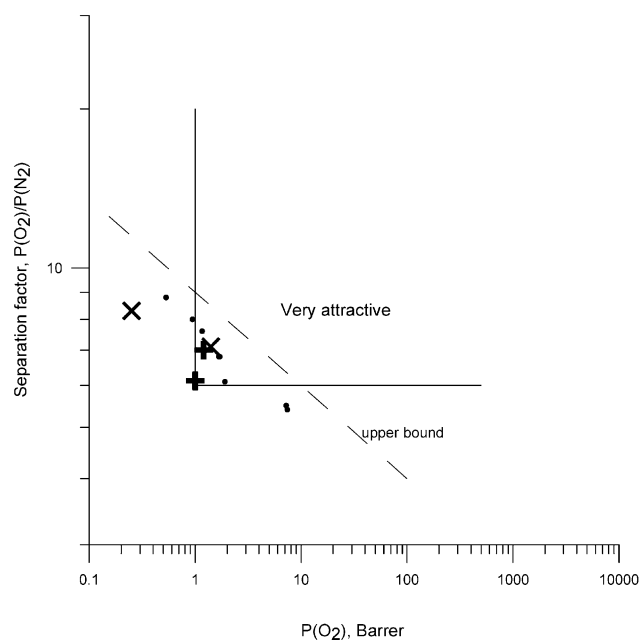


Fig. 5. Relationship between separation factor $\alpha(\text{O}_2/\text{N}_2)$ and oxygen permeability $P(\text{O}_2)$. (■, new polyamides; reference: +, polyamides and ×, polyimides from Table 4).

When the $\text{FFV}(\text{O}_2)$ is plotted against $P(\text{O}_2)$, a much better correlation is observed (Fig. 6). Polymers **3a**, **3e**, and **3f** exhibit the smallest fractional free volumes for oxygen among the series of polyamides and these polymers exhibit the lowest permeability coefficients. On the other hand, polymers **3g** and **3h** exhibit the highest $\text{FFV}(\text{O}_2)$, both polymers also exhibit much higher gas permeability coefficients.

By comparing the gas transport properties of the eight novel polyamides to gas transport properties of polyamides reported in the literature, it can be concluded that the phenylindane moiety imparts significant improvement to gas transport properties. In general, aromatic polyamides exhibit low gas permeability coefficients even to gas molecules with small kinetic diameters due to the high cohesive energy density [34]. Introduction of a bulky *t*-butyl

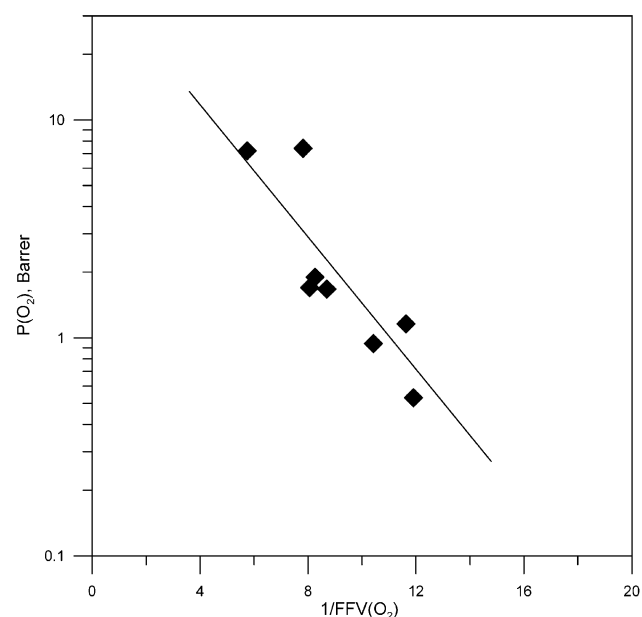


Fig. 6. Oxygen permeability coefficient as function of $\text{FFV}(\text{O}_2)$ for series of phenylindane containing polyamides.

group into the polyamide chain was reported to produce polyamides with improved gas transport properties [21,35]. The gas transport properties of two representative polyamides containing the bulky *t*-butyl group, as reported in the literature, are listed in Table 4. The entries 1 and 2 are polyamides derived from 5-*t*-butyl isophthaloyl chloride (BIPC) and diamines 1,5-diaminonaphthalene (DAN) and ODA, respectively. Compared to these polyamides, polymers **3c** and **3e**, derived from the same ODA and DAN diamines, respectively, exhibit both a higher $P(\text{O}_2)$ and a higher separation factor, $\alpha(\text{O}_2/\text{N}_2)$. As shown in Fig. 5, the novel phenylindane containing polyamides exhibit properties that are closer to the so-called upper bound than the reference polymers listed in Table 4. The introduction of the phenylindane moiety into polyimide backbone also leads to a significant improvement in gas transport properties as compared to conventional polyimides [36]. For example,

Table 4
Gas transport properties of structurally related polyamides and polyimides

Polymer ^a	$P(\text{O}_2)$ (Barrer)	$P(\text{O}_2)/P(\text{N}_2)$	Temperature (°C)	Reference
1	1.2	7.0	25	33
2	1	6.12	25	33
3	1.4	7.1	25	34
4	0.25	8.25	30	35, 36

^a 1, BIPC–DAN; 2, BIPC–ODA; 3, Matrimid[®]; 4, Ultem[®].

phenylindane containing polyimide, Matrimid[®], exhibits superior gas transport characteristics to that of a commercially available polyether imide Ultem[®]1000 (Table 4). There is a genuine need in the industry to employ membrane materials that exhibit an O₂/N₂ separation factor above 8 and oxygen permeability coefficient above 0.5 Barrer. Ultem[®]1000 exhibits a high O₂/N₂ separation factor of 8.25 but an oxygen permeability coefficient of only 0.25 Barrer [37,38]. The oxygen permeability coefficient of the polymer **3f** is twice as high as that of Ultem, while the O₂/N₂ separation factor is also higher. The oxygen permeability coefficient of the polymer **3e** is almost four times as high as that of Ultem, while the O₂/N₂ separation factor of polymer **3e** is still 8.0. Thus, polyamides **3e** and **3f** are attractive materials for gas separation membrane preparation.

4. Conclusions

A series of novel aromatic polyamides containing the phenylindane moiety was synthesized. These polyamides are highly soluble in polar aprotic solvents and exhibit high glass transition temperatures. It has been further found that these polyamides exhibit excellent gas transport properties, i.e. high gas permeability coefficients combined with high gas separation factors. The improved gas transport properties of polyamides are imparted by the presence of the phenylindane moiety. The polyamides formed from diamine co-monomers with a non-linear structure, such as 1,3-phenylene, tend to exhibit both lower gas permeability coefficients and gas separation factors for most gas pairs, as compared to polyamides derived from diamine co-monomers with a linear structure, such as 1,4-phenylene. On the other hand, polyamides derived from diamines containing the trifluoromethyl group exhibit higher gas permeability coefficients combining with only modestly lower gas separation factors, as compared to polyamides derived from diamines that have no substituents.

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