CrossMark

Synthesis, characterization, and structure-property relationships of aromatic polyimides containing 4,4′-diaminotriphenylmethane

C. Aguilar-Lugo[1] · J. L. Santiago-García[2] · M. I. Loría-Bastarrachea[2] ·
D. Guzmán-Lucero[3] · L. Alexandrova[1] · M. Aguilar-Vega[2]

Abstract This work reports two series of structurally different aromatic polyimides based on 4,4′-diaminodiphenylmethane (DPM) and 4,4′-diaminotriphenylmethane (TPM) and three commercial dianhydrides. All TPM-based polyimides formed membranes due to their high molecular weight (inherent viscosities ~0.93–1.14 dl/g), they exhibited high thermal stability (5 %: 490–544 °C), glass transition temperatures between 269 and 293 °C, and reasonable mechanical properties. The incorporation of pendant phenyl moieties in the TPM-based polyimides has a strong effect producing an improvement in solubility, thermal stability, density and gas permeability coefficient in comparison with DPM-based polyimides. The most interesting polyimide TPM-6FDA, containing phenyl and trifluoromethyl as bulky pendant groups, showed higher gas permeability coefficient for CO_2 (23.73 Barrer) and the best ideal selectivity to the gas pair CO_2/CH_4 ($\alpha = 28.93$).

Keywords 4,4′-diaminotriphenylmethane · Aromatic polyimides · Structure-property relationships · Membranes

✉ M. Aguilar-Vega
mjav@cicy.mx

1 Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, 04510 México, D.F., México

2 Unidad de Materiales, Centro de Investigación Científica de Yucatán, A.C. Chuburna de Hidalgo, Calle 43 No.130, 97200 Mérida, Yucatán, México

3 Gerencia de Transformación de la Biomasa, Instituto Mexicano del Petróleo, Eje Central L. Cárdenas 152, Col. San Bartolo Atepehuacan, 07730 México, D.F., México

Introduction

The development of advanced technologies requires of high performance polymers for use in especially harsh environments with the expectation of a long life span, ease of maintenance and low production cost. Aromatic polyimides (PIs) are a kind of high performance polymers owing their outstanding set of thermal and mechanical properties [1–3]. However, the main problem of aromatic polyimides is associated with their insolubility due to their rigid backbones and strong interchain interactions, leading to processing difficulties [4, 5]. To overcome this problem, several approaches have been evaluated to produce soluble aromatic polyimides through structural modification of their monomers [6–12].

The use as monomers based on aromatic diamines or dianhydrides with bulky pendant groups could generate aromatic polyimides with good solubility without compromising their thermal and mechanical stability. Moreover, the inclusion of bulky pendant groups increases the interchain spacing and reduces the packing efficiency, thereby increasing the fractional free volume (FFV) [13, 14]. This ultimate behavior finds application in gas separation membrane technology, where a considerable amount of effort has been focused to enhance gas permeability through an increment in the FFV which could be achieved by chemical modifications of the polymer backbone [15–17].

4,4′-Diaminotriphenylmethane (TPM) and its derivatives, have attracted the attention of our research group as monomers for synthesis of various rigid-rod polyamides (PAs) and polyimides (PIs) [18, 19]. The pendant phenyl ring and practically free internal rotation for the triphenylmethane bridging group, predicted from theoretical calculations, makes it an excellent candidate for synthesis of processable PAs and PIs without sacrificing the high thermal stability [19]. Earlier research carried out for the structurally similar N,N-diamine

triphenylamine showed that the incorporation of a pendant phenyl group into the polymer backbone is a successful approach to increase solubility and processability of PIs [20–23]. The synthesis of TPM developed in our group is simple and highly efficient using commercially available and cheap starting materials such as aniline and benzaldehyde, this is a big advantage in comparison to 4,4′-diaminotriphenylamine, whose synthesis is a lot more complicated and required expensive reagents. Besides, the use of microwave irradiation instead of traditional heating allows reducing the reaction times as well as the amount of aniline employed, that facilitates the purification process. A wide variety of diamines derived from TPM using different substituted anilines and benzaldehydes have been successfully synthesized [24].

In spite of all these advantages, there was only one report on the use of TPM as monomer for polyimides, PIs, preparation from Koton et al., dated by 1980 [25], where PI's based on TPM and two anhydrides, pyromellitic and 4,4′-oxydiphthalic, had been obtained by the traditional two-stage method using thermal-imidization. However, the PIs synthesized presented relatively low molecular weights and because of it, their mechanical and thermal properties were not as good as those reported for other PI's based on traditional 4,4′-diaminodiphenylmethane (DPM) [26]. Additionally, TPM-based polyimides containing bulky pendant groups in their structure would be more soluble and would have the potential for other applications such as gas separation membrane materials.

In this article we report a comparative study between a series of PI's based on 4,4′-diaminotriphenylmethane (TPM) that are compared to PI's based on a traditional 4,4'diaminodiphenylmethane (DPM). We discuss the effect that the presence of the pendant phenyl ring has on their solubility, thermal stability, mechanical properties and gas permeability.

Experimental

Materials

Benzophenone-3,3′-4,4′-tetracarboxylic dianhydride (BZP, Aldrich, 96 %), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, Aldrich, 99 %), and 4,4′-oxydiphthalic anhydride (ODP, Aldrich, 97 %) were recrystallized from acetic anhydride (Ac$_2$O). 4,4′-diaminodiphenylmethane (DPM, Aldrich, ≥97.0 %) was recrystrallized from ethanol. 4,4′-diaminotriphenylmethane (TPM) was synthesized from aniline (Aldrich, ≥99.5 %) and benzaldehyde (Aldrich, ≥99.5 %), and purified according to a previously described procedure [19]. N-methyl-2-pyrrolidinone, (NMP, Aldrich, anhydrous 99.5 %), N,N-dimethylformamide (DMF, Aldrich, anhydrous 99.8 %) were dried and stored over molecular sieves. Nitrobenzene (Aldrich, ≥99.0 %) was distilled under vacuum prior to use. Solvents for solubility test were used as received.

Polyimides synthesis

A series of aromatic polyimides were synthesized from TPM diamine and aromatic dianhydrides, i.e. ODP, BZP, and 6FDA, respectively. For comparison another series of aromatic polyimides were synthesized from DPM diamine employing the same aromatic dianhydrides. All aromatic polyimides were prepared by a two-step method. In a typical polymerization for TPM-6FDA which was derived from TPM diamine and 6FDA dianhydride, was carried out as follows: In the first step, TPM diamine (2.0 mmol, 548.72 mg) was dissolved in 5.6 mL freshly distilled NMP at 0 °C in nitrogen atmosphere. 6FDA dianhydride (2.0 mmol, 888.48 mg) was then added all at once to the reaction solution to obtain a 25 wt% solids solution. Whereas continuously stirring, the mixture was gradually heated to room temperature and allowed to stir for another 5 h to form the corresponding poly(amic acid). In the second step, a thermal cyclization was applied for conversion of poly(amic acid) to polyimide. The obtained poly(amic acid) solutions were cast onto glass plates and dried at 60 °C overnight to slowly eliminate the casting solvent. The dried poly(amic acid) membranes were stripped of the glass plates, placed into metal frames and transformed into TPM-6FDA polyimide by sequential heating at 80 °C for 24 h under vacuum, 270 °C for 30 min, and 300 °C for 30 min. The complete removal of solvents was confirmed by TGA. All other polyimides were prepared by the same procedure.

Characterizations

Fourier transform infrared (FT-IR) spectra of the polyimide membranes were recorded on a Nicolet 510P FTIR spectrophotometer using 32 scans at a resolution of 4 cm^{-1} in the transmittance mode covering a wave number range from 4000 to 400 cm^{-1}. ^{1}H-NMR spectra were acquired on a Varian VNMRS 600 MHz NMR instrument using DMSO-d_7 as solvent and TMS as internal standard. Inherent viscosities (η_{inh}) were determined in 0.5 g/dL N,N-dimetylformamide (DMF) solutions using a Cannon Ubbelohde viscometer No. 0B K642 at 25 °C. A Du Pont, high resolution Thermogravimetric Analyzer, TGA 2950, was used for the thermal analysis. All measurements were performed under a nitrogen atmosphere (20 mL/min) from 50 to 600 °C at a heating rate of 5 °C/min. The glass transition temperature, T_g, was determined by a film-elongation technique using a Du Pont Thermo-mechanical Analyzer, Model TA 2940 under nitrogen atmosphere and a heating rate of 5 °C/min. Mechanical tests of polymer films (about 25 μm thickness) were performed by using an INSTRON Tester Machine, Model 111, at a separation rate 50 mm/min, on samples of 20 mm × 5 mm × 0.025 mm. The polymer densities were measured in a jacketed density gradient column filled with a well-degassed aqueous potassium iodide solution at

23.0 ± 0.1 °C. Each dried polymer sample was first wetted in the low-density solution and then transferred to the column. Two samples of each material were used to determine the density. Although they stabilized rapidly in the column, the measurements were performed after 12 h to ensure that they had reached equilibrium.

The gas permeability coefficient, P, for five different pure gases, helium (He), oxygen (O_2), nitrogen (N_2), methane (CH_4), and carbon dioxide (CO_2), were determined using a constant volume permeation cell built in our laboratories as described elsewhere [27]. The purity of all gases used was >99.99 % (Praxair Corp). P was calculated from slope of the downstream pressure versus time plot (dp/dt), under steady-state conditions at 2.0 atm upstream pressure and 35 °C for each gas pure gas, by using the following equation:

$$P = \frac{Vl}{ART\Delta p}\left(\frac{dp}{dt}\right)_{ss} \tag{1}$$

where V is the downstream volume (cm^3 STP) of the cell, l and A are the membrane thickness (cm) and the effective area of the membrane exposed to the gas (cm^2), respectively. R is the gas constant, T is the absolute temperature (°K), Δp is the pressure difference between upstream and downstream (cm Hg) and $\left(\frac{dp}{dt}\right)_{ss}$ is the steady state increase of pressure in the downstream (cm Hg/s). The permeability coefficient is reported in Barrer [1 Barrer $= 1 \times 10^{-10}$ (cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)].

The ideal separation factor, a measure of the selectivity toward each gas pair of PI membranes, was calculated from the ratio of pure gas permeability coefficients as:

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{2}$$

where P_A and P_B are the permeability coefficients of the pure gases A and B, respectively [28].

Results and discussion

### Polyimides synthesis and characterization

The chemical structure of the polyamides and the reaction scheme for their preparation are shown in Fig. 1. The chemical structures of the PIs synthesized by conventional two-step procedure involving the synthesis of poly(amic acid) followed by thermal imidization were confirmed by FTIR and ^{1}H-NMR spectroscopy. Figure 2 shows the FTIR spectrum of the TPM-6FDA polyimide. As expected, the intensive characteristic absorptions of the imide group at approximately 1785 and 1716 cm^{-1}

(imide I ν(C = O)), 1365 cm^{-1} (imide II ν(OC–N–CO)), 1088 cm^{-1} (imide III ν(OC–N–CO)) and 707 cm^{-1} (imide IV γ(CNC)) were observed. Moreover, the characteristic vibrations of amide groups (N-H) present in the poly(amic acid) at around 3300–300 were not detected in the spectra of all PIs [29]. All these results clearly indicated that the thermal imidization was completed successfully. Furthermore, the complete imidization of the PIs was also confirmed by ^{1}H-NMR. As an example, the ^{1}H-NMR spectrum from TPM-6FDA is presented in Fig. 3. ^{1}H-NMR (400 MHz, DMF-$d7$): 5.88 (s, 1H), 7.32 (m, 3H), 7.39 (d, $J = 7.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 4H), 7.58 (d, $J = 8.4$ Hz, 4H), 7.94 (s, 2H), 8.05 (d, $J = 8.3$ Hz, 2H), 8.19 (d, $J = 8.1$ Hz, 2H). These results confirm that the poly(amic acid) precursors have been completely converted into PIs due to the nonappearance at downfield of the shift in amide protons.

It is known that the aromatic polyimides generally have poor solubility in common organic solvents because aromatic rings give rise to molecular stiffness, high polarity and high internal molecular association forces [4]. The solubility behavior of PIs synthesized in this study is summarized in Table 1. The PIs obtained from DPM diamine were partially soluble in polar aprotic organic solvents [30]. However, polyimides based on TPM diamine displayed good solubility in polar aprotic solvents such as NMP, DMF and DMAc owing to the presence of the bulky pendant phenyl group. Due to the bulkiness and free internal rotation of TPM moieties, the chain packing of the polymer was disturbed, and consequently, the solvent molecules find an easier solvation pathway.

Inherent viscosities and mechanical properties of the PIs are given in Table 2. All the polyimides exhibited high inherent viscosity values, between 0.93 and 1.12 dL/g, indicating that they are high molecular weight polymers. These results were confirmed by the ability of the polyimides to form flexible membranes, which were subjected to tensile tests. Additionally, Young's Modulus, (E_0), and tensile strength, (σ_b) in the TPM-based polyimides increases in the follow order TPM-6FDA > TPM-ODP > TPM-BZP. This behavior was also observed in DPM-based polyimides. However, E_0 and σ_b values were slightly higher for TPM-based polyimides. Generally, the Young's modulus (E_0) and tensile strength (σ_b) decrease, and the elongation at break increases with increasing chain flexibility [31]. Nevertheless, the elongation at break of the DPM and TPM-based polyimides did not show large a difference that is attributed to their rigid backbone structure.

Thermal stability of the all PIs was evaluated by TGA under a nitrogen atmosphere. The TGA curves are shown in Fig. 4. These PIs exhibit excellent thermal stability and have high degradation temperatures. The decomposition temperatures (T_d) at 5 wt% weight loss in nitrogen determined in original TGA curves, are tabulated in Table 3. The 5 % weight loss of all polyimides was recorded in the range 490–544 °C. For the same dianhydride PI's, TMP based polyimides show

Fig. 1 Synthesis of polyimides
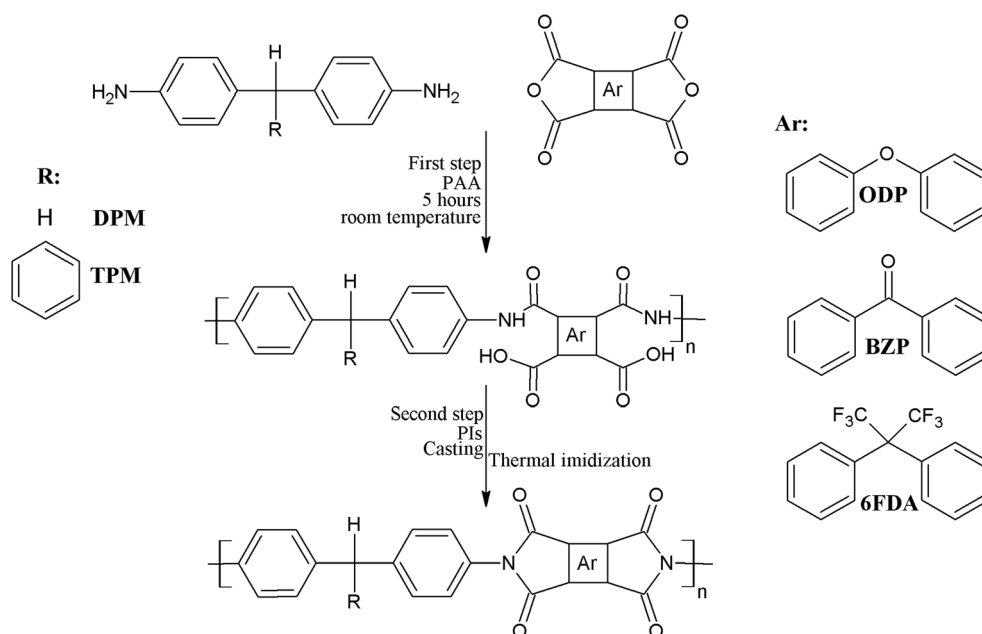
higher thermal resistance. Moreover, the carbonized residues (char yield) of these polyimides in nitrogen atmosphere was more than 70 % at 600 °C. In Table 3 the glass transition temperatures (T_g), determined by film elongation using thermomechanical analysis, are also listed. Flexible linkages, such as –O– in TPM-ODP, tend to present lower T_g while the presence of the -CF_3 moieties in the dianhydride tend to increase it. All the PIs have glass-transition temperature (T_g) values in the range of 262 to 301 °C. T_g values for TPM and DPM based PIs are close and mainly related to the anhydride used [18]. An increase in T_g generally corresponded to an increase in rigidity of the dianhydride monomer. Bridging groups, such as –O– and >C = O (ODP, BZP), between the two phenyl rings present in the dianhydrides clearly facilitate bond rotation and consequently lower the T_g [32]. In contrast, 6FDA moieties have higher T_g values because molecular motions are inhibited due to the bulkiness of the 6FDA motifs.
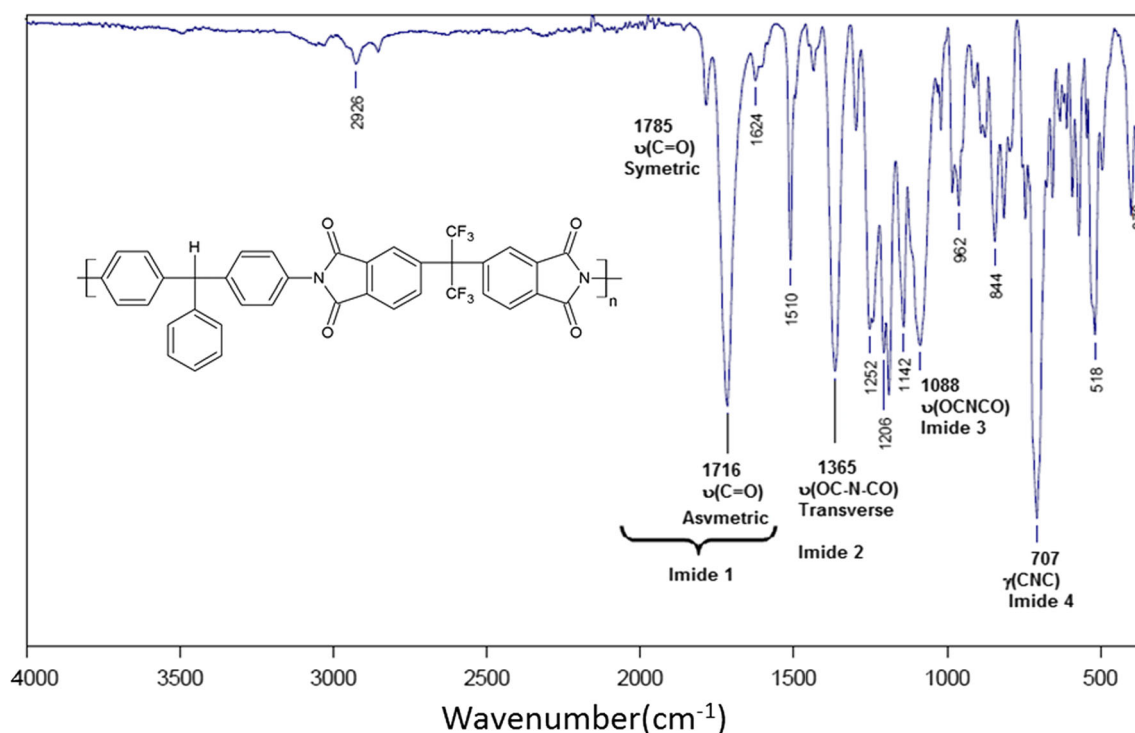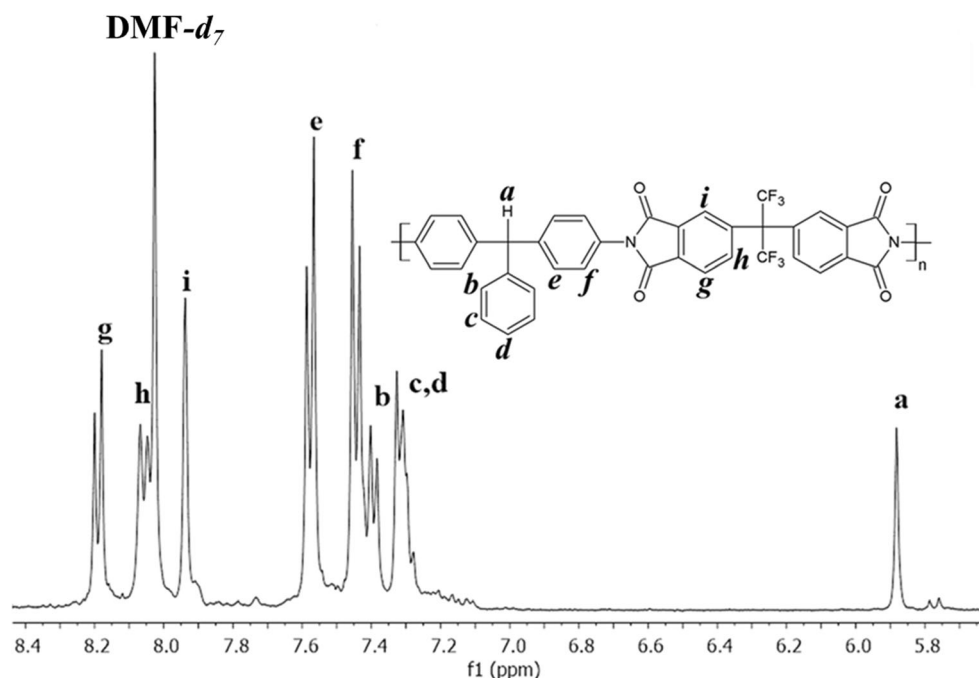

Fig. 2 FTIR spectrum of the polyimide TPM-6FDA

Fig. 3 ¹H-NMR spectrum of the polyimide TPM-6FDA in DMF-*d₇*

4,4′-diaminotriphenylmethane (TPM) consist of three phenyl rings that converge in a tertiary carbon, in which a phenyl group is present as pendant group. Because of its noncoplanar structure (Fig. 5), it is expected that, this diamine decreases the tight stacking producing a high fractional free volume. The polyimides (PI) obtained from this diamine should be good candidates to develop gas separation membranes with both high permeability and selectivity [13, 33]. Consequently, gas permeability test were performed in thin film membranes of the synthesized PI's from DPM and TPM diamines and the three commercial anhydrides ODP, BZP and 6FDA.

Densities and fractional free volume (FFV) values of the polyimides in film form are also reported in the Table 3. For polyimides that were obtained from the TPM diamine, the phenyl pendant group makes the chain packing less efficient, and consequently, the TPM-

based polyimides showed lower densities compared with DPM-based polyimides. Moreover, the results showed the following order for the density depending upon the dianhydride used ODP < BZP < 6FDA. A measure of chain packing of a polymer could be given by the amount of fractional free volume available in the polymer. Fractional free volume (FFV) of PIs in Table 3 was determined following Bondí's group contribution method, as reported by van Krevelen [34] as:

$$FFV = \frac{V - (1.3 V_w)}{V} \qquad (3)$$

where, V is the specific volume (cm³/g), and V_w is the van der Walls volume (cm³/g). In all cases the results indicate that TPM-based polyimides have highest FFV (lower packing density) than DPM-based polyimides. It is also clearly seen

Table 1 Solubility of polyimides based on DPM and TPM diamines

Polyimide	DMF	NMP	THF	CH₃Cl	DMAc
TPM-BZP	+	+	−	−	±
TPM-ODP	+	+	−	−	±
TPM-6FDA	+	+	−	±	+
DPM-BZP	±	±	−	−	−
DPM-ODP	±	±	−	−	−
DPM-6FDA	+	±	−	±	±

+ Soluble, ± Partially soluble, − Insoluble: *NMP* N-methyl-2-pyrrolidinone, *CH₃Cl* chloroform, *DMF* N,N-dimethyl formamide, *THF* tetrahydrofuran, *DMAc* N,N-dimethyl acetamide

Table 2 A comparison of mechanical properties of polyimide membranes based on DPM and TPM diamines

Polyimide	η_{inh} dL/g	Young's modulus (E_0) MPa	Tensile strength (σ_b) MPa	Elongation at break (ε_b)%
TPM-BZP	0.93	630	21.5	5
TPM-ODP	0.96	850	23.6	6
TPM-6FDA	1.14	950	27.8	8
DPM-BZP	1.04	740	20.7	5
DPM-ODP	1.03	820	21.8	6
DPM-6FDA	1.12	890	24.4	6

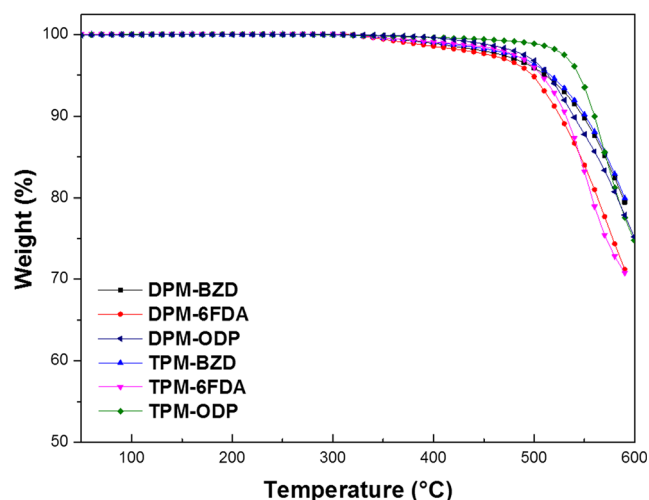**Fig. 4** TGA thermograms of the polyimides under nitrogen atmosphere

that the presence of the –CF₃ groups in the 6FDA dianhydride contribute to increase the amount of FFV in the PIs, being the largest for the TPM-6FDA (FFV = 0.164).

Gas permeability

Table 4 shows the pure gas permeability coefficient, P, and ideal permselectivity, α, values for polyimide membranes measured at 2.0 atm and 35 °C. In general, the permeability order was, in all cases, $P_{He} > P_{co_2} > P_{O_2} > P_{N_2} \geq P_{CH_4}$. On the other hand, P coefficient in TPM-based polyimides showed the following order TPM-6FDA > TPM-BZP > TPM-ODP. This same behavior was also observed in the series of DPM-based polyimides, indicating that the order has a strong correlation with the dianhydride used. Nevertheless, P coefficients were slightly higher for all gases in TPM-based polyimides in comparison with the DPM-based polyimides. This result is attributed to the fact that TPM-based polyimide presents the higher FFV values, indicating that TPM moieties induce the formation of a less densely packed structure, and therefore, presents an increasing in the gas permeability coefficient. In
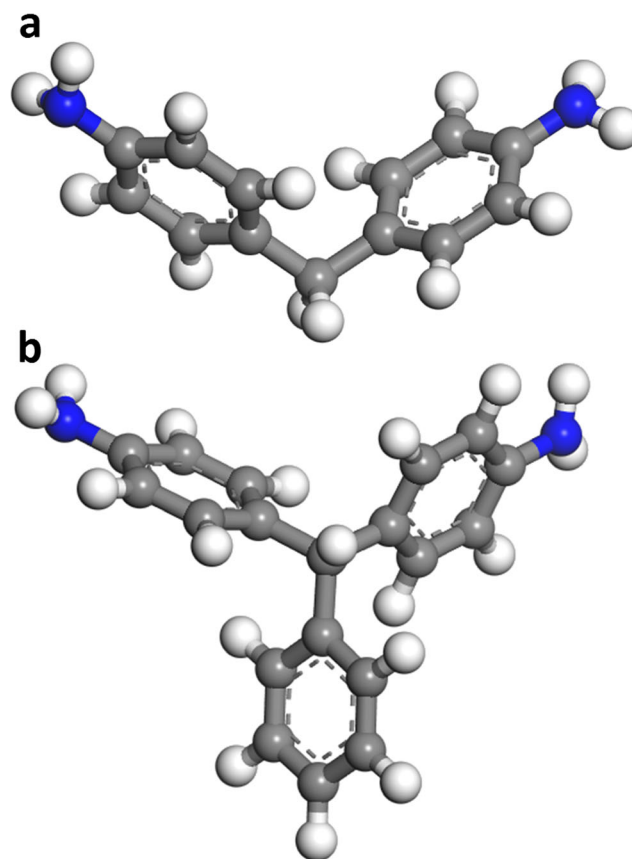

Fig. 5 Schematic representation of minimum energy structures (COMPASS forcefield) of a) 4,4′-diaminodiphenylmethane (DPM) and b) 4,4′-diaminotriphenylmethane (TPM)

fact a correlation of the effect of FFV with permeability coefficients is given by relationship [35]

$$P = P_o \exp\left[\frac{-B}{FFV}\right] \quad (4)$$

where P_o is a pre-exponential factor and B is a constant that depends on the type and physical characteristics of the gas

Table 3 Thermal properties, density, and fractional free volume data of the polyimides

Polyimides	T_g [°C]	Weight loss [°C] 5 %	ρ (g/cm³)	FFV
TPM-BZP	278	510	1.299	0.132
TPM-ODP	269	544	1.294	0.141
TPM-6FDA	293	500	1.361	0.164
DPM-BZP	276	511	1.329	0.124
DPM-ODP	262	513	1.331	0.129
DPM-6FDA	301	490	1.405	0.157

Table 4 Gas permeability coefficient, P, and ideal selectivity, α, of TPM and DPM diamine based polyimide thin film membranes at 2.0 atm and 35 °C

Polyimides	P (Barrer)[a]					α(P_A/P_B)	
	He	CO₂	O₂	N₂	CH₄	CO₂/N₂	CO₂/CH₄
TPM-BZP	11.10	3.95	0.79	0.23	0.15	17.17	26.33
TPM-ODP	10.04	2.46	0.72	0.32	0.33	7.68	7.45
TPM-6FDA	41.89	23.73	4.47	0.93	0.82	25.51	28.93
DPM-BZP	6.83	1.49	0.73	0.55	0.37	2.70	4.02
DPM-ODP	6.80	1.90	0.72	0.28	0.34	6.78	5.58
DPM-6FDA	39.44	14.47	3.33	0.92	0.99	15.72	14.61

[a] 1 Barrer: 1×10^{-10} [cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹]
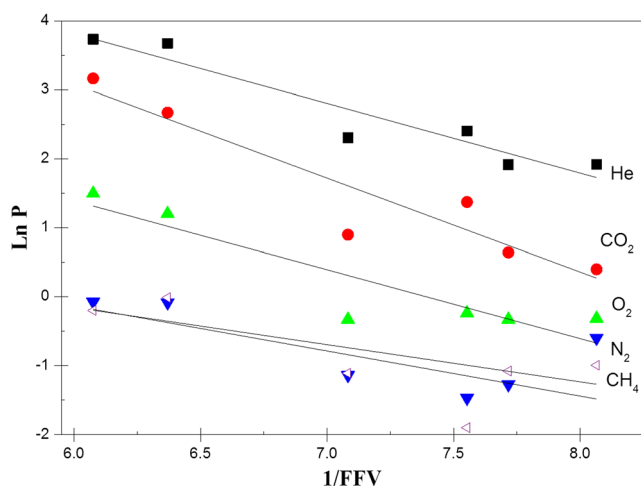
Fig. 6 Gas permeability coefficient and 1/FFV relationships of polyimides

Fig. 8 Selectivity versus permeability with the Robeson's trade off curve for CO_2/N_2 [38]

tested and the particular polymer. Figure 6 shows a plot of P as a function of FFV according to Eq. 4. The results show that P for the different gases adjust closely to Eq. 4. It is also seen that as FFV increases the polyimides with the highest FFV, TPM-6FDA and DPM-6FDA, present the largest permeability while the polyimide with the lower FFV, DPM-BZP, shows the lowest permeability coefficients for all gases [36, 37].

An important fact is that polyimide chemical structures determine gas permeation and separation properties. In particular for gas separations, Robeson [38] has established that there exists a trade-off between gas permeability, P, and selectivity, α; in such a way that as gas permeability coefficients increase the selectivity or gas separation factor, α, for a given pair of gases decreases. In the polyimides studied here the substitution of a phenyl group, TPM, in place of a hydrogen atom present in DPM-based polyimides, enhances both P and α, see Figs. 7 and 8. These results of gas permeability in the polyimides reported here clearly indicate that in all cases the
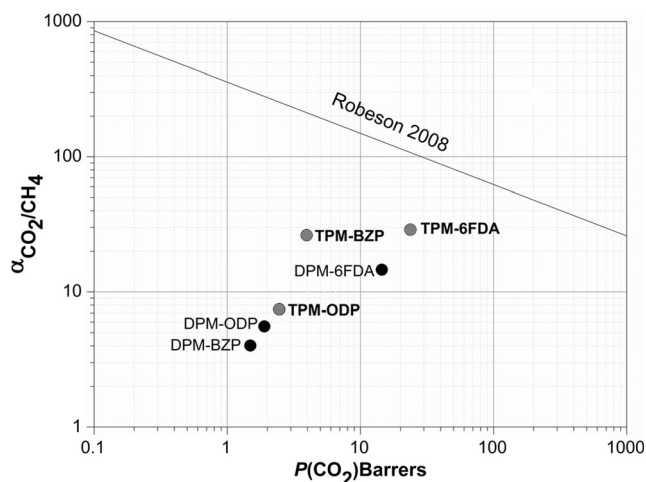
substitution of the phenyl group instead of the hydrogen atom in polyimides with the same diahnhydride structure produces an increase in permeability and an increase in selectivity.

Conclusions

In this work, the three polyimides obtained from 4,4′-diaminotriphenylmethane (TPM) showed good solubility in organic solvents, higher thermal stability, reasonable mechanical properties, and higher gas permeability coefficient. The enhancement of these properties, particularly gas permeability and thermal resistance behavior, is ascribed to the presence of the bulky pendant phenyl group, which is not present in the three polyimides synthesized with 4,4′-diaminodiphenylmethane (DPM). In here clearly, we found an advantage of an alternative design for processable polyimides by introducing bulky lateral substituents, in order to hinder molecular packaging, and therefore, increase solubility in organic solvents and gas permeability in the polyimide membranes prepared from TPM-based polyimides. This approach also shows that the combination of two bulky pendant groups, a phenyl group (C_6H_6) present in the TPM diamine, and trifluoromethyl groups ($-CF_3$) present in the 6FDA dianhydride affords the best results. The polyimide membrane obtained using such monomers, TPM-6FDA, showed higher gas permeability coefficient for CO_2 (23.73 Barrer) and the best ideal selectivity for the gas pair CO_2/CH_4 ($\alpha = 28.93$).

Fig. 7 Selectivity versus permeability with the Robeson's trade off curve for CO_2/CH_4 [38]

References

1. Liaw DJ, Wang KL, Huang YC, Lee KR, Lai JY, Ha CS (2012) Advanced polyimides materials: Synthesis, physical properties and applications. Prog Polym Sci 37:907–974
2. Mittal V (2011) High performance polymers and engineering plastics. Wiley-Scrivener, New Jersey
3. Ree M (2006) High performance polyimides for applications in microelectronics and flat panel displays. Macromol Res 14:1–33
4. Ghosh A, Sen SK, Banerjee S, Voit B (2012) Solubility improvements in aromatic polyimides by macromolecular engineering. RSC Adv 2:5900–5926
5. de Abajo J, de la Campa JG (1999) Processable aromatic polyimides. Adv Polym Sci 140:23–59
6. Yao P, Gu J, Lei X, Sun W, Chen Y, Zhang Q (2014) Highly soluble and thermally stable copolyimides modified with trifluoromethyl and siloxane. J Appl Polym Sci 132:41713
7. Zhuo L, Kou K, Wang Y, Yao P, Wu G (2014) Synthesis of soluble and thermally stable polyimides with phthalimide as pendent group from pyridine-containing triamine. J Mater Sci 49:5141–5150
8. Chen JC, Rajendran K, Chang YH, Huang SW, Chern YT (2011) Highly transparent and organosoluble polyimides derived from 2, 2′-disubstituted-4,4′-oxydianilines. J Appl Polym Sci 120: 3159–3170
9. Yi L, Li C, Huang W, Yan D (2014) Soluble aromatic polyimides with high glass transition temperature from benzidine containing *tert*-butyl groups. J Polym Res 21:572–581
10. Kin SD, Lee S, Heo J, Kim SY, Chung IS (2013) Soluble polyimides with trifluoromethyl pendent groups. Polymer 54: 5648–5654
11. Hou Y, Chen G, Pei X, Fang X (2012) Synthesis and characterization of novel optically transparent and organosoluble polyimides based on diamines containing cyclohexane moiety. J Polym Res 19:9955
12. Chen G, Pei X, Liu J, Fang X (2013) Synthesis and properties of transparent polyimides derived from trans- and cis-1,4-bis(3,4-dicarboxyphenoxy)cyclohexane dianhydrides. J Polym Res 20:159
13. Calle M, Lozano AE, de Abajo J, de la Campa JG, Álvarez C (2010) Design of gas separation membranes derived of rigid aromatic polyimides. 1. Polymers from diamines containing di-tert-butyl side groups. J Membr Sci 365:145–153
14. Xiao Y, Low BT, Hosseine SS, Chung TS, Paul DR (2009) The strategies of molecular architecture and modification of polyimide-based membranes for CO$_2$ removal from natural gas- A review. Prog Polym Sci 34:561–580
15. Budd PM, McKeown NB, Fritsch D (2005) Free volume and intrinsic microporosity in polymers. J Mater Chem 15:1977–1986
16. Nagel C, Gunther-Schade K, Fritsch D, Strunskus T, Faupel F (2002) Free volume and transport properties in highly selective polymer membranes. Macromolecules 35:2071–2077
17. Thran A, Kroll G, Faupel F (1999) Correlation between fractional free volume and diffusivity of gas molecules in glassy polymers. J Polym Sci: Part B: Polym Phys 37:3344–3335
18. Likhatchev D, Alexandrova L, Tlenkopatchev M, Martinez-Richa A, Vera-Graziano R (1996) One-step synthesis of aromatic polyimides based on 4,4′-diaminotriphenylmethane. J Appl Polym Sci 61:815–818
19. Likhatchev D, Alexandrova L, Tlenkopatchev M, Vilar R, Vera-Graziano R (1995) Soluble aromatic polyimides and polyamides based on 4,4′-diaminotriphenylmethane. J Appl Polym Sci 57:37–44
20. Liaw DJ, Hsu PN, Chen WH, Lin SL (2002) High glass transitions of new polyamides, polyimides, and poly(amide − imide)s containing a triphenylamine group: Synthesis and characterization. Macromolecules 35:4669–4676
21. Liaw DJ, Liaw BY, Yang CM (1999) Synthesis and properties of new polyamides based on bis[4-(4-aminophenoxy)phenyl]diphenylmethane. Macromolecules 32:7248–7250
22. Oishi Y, Ishida M, Kakimoto M, Imai Y, Kurosaki T (1992) Preparation and properties of novel soluble aromatic polyimides from 4,4′-diaminotriphenylamine and aromatic tetracarboxylic dianhydrides. J Polym Sci: Part A: Polym Chem 30:1027–1035
23. Vasilenko NA, Akhmet'eva YI, Sviridov YB, Berendyayev VI, Rogozhkina YD, Alkayeva OF, Koshelev KK, Izyumnikov AL, Kotov BV (1991) Soluble polyimides based on 4,4′-diaminotriphenylamine. Synthesis, molecular mass characteristics and solution properties. Polym Sci U.S.S.R. 33:1439–1450
24. Guzmán-Lucero D, Guzmán J, Likhatchev D, Martínez-Palou R (2005) Microwave-assisted synthesis of 4,4′-diaminotriphenylmethane. Tetrahedron Lett 46:1119–1122
25. Koton MM, Romanova MS, Laius LA, Sazanov YN, Fjodorova GN (1980) Aromatic polyimides based on 4,4′-diaminodiphenylmethane and some of its derivates. J Appl Sci USSR 53:1591–1593
26. Ren L, Fu W, Luo Y, Lu H, Jia D, Shen J, Pang B, Ko TM (2004) Thermal degradation of the polyimides from 4,4′-(hexafluoroisopropylidene) diphthalic dianhydride and 4,4′-diaminodiphenylmethane. J Appl Polym Sci 91:2295–2301
27. Loría-Bastarrachea MI, Aguilar-Vega M (2013) Membranes from rigid block hexafluoro copolyaramides: Effect of the block lengths on gas permeation and ideal separation factors. J Membr Sci 443: 36–44
28. Díaz K, Vargas J, Del Castillo LF, Tlenkopatchev MA, Aguilar-Vega M (2005) Polynorbornene dicarboximides with cyclic pendant groups: Synthesis and gas transport properties. Macromol Chem Phys 206:2316–2322
29. Ayala D, Lozano AE, de Abajo J, de la Campa JG (1999) Synthesis and characterization of novel polyimides with bulky pendant groups. J Polym Sci: Part A: Polym Chem 37:805–814
30. Kaneda T, Katsura T, Nakagawa K, Makino H, Horio M (1986) High-strength–high-modulus polyimide fibers II. Spinning and properties of fibers. J Appl Polym Sci 3:3151–3176
31. Clair TLS (1990) In: Wilson D, Stenzenberger HD, Hergenrother PM (eds) Polyimides. New York, Springer
32. Ragosta G, Abbate M, Musto P, Scarinzi G (2012) Effect of the chemical structure of aromatic polyimides on their thermal aging, relaxation behavior and mechanical properties. J Mater Sci 47: 2637–2647
33. Kothawade SS, Kulkarni MP, Kharul UK, Patil AS, Vernekar SP (2008) Synthesis, characterization, and gas permeability of aromatic polyimides containing pendant phenoxy group. J Appl Polym Sci 108:3881–3889
34. Van Krevelen DW, Hoftyzer PJ (1972) Properties of Polymers. Correlation with Chemical Structure, Elsevier, New York
35. Pixton MR, Paul DR (1994) In: Paul DR, Yampol'skii YP (eds) Polymeric Gas Separation Membranes. Boca Raton, CRC press
36. Bandyopadhyay P, Bera D, Ghosh S, Banerjee S (2014) Synthesis, characterization and gas transport properties of cardobis(phenylphenyl)fluorine based on semifluorinated poly(ether amide)s. RSC Adv 4:28078–28092
37. Ayala D, Lozano AE, de Abajo J, García-Pérez C, de la Campa JG, Peinemann KV, Freeman BD, Prabhakar R (2003) Gas separation properties of aromatic polyimides. J Membr Sci 215:61–73
38. Robeson LM (2008) The upper bound revisited. J Membr Sci 320: 390–400