Synthesis, Characterization, and Evaluation of Novel Polyhydantoins as Gas Separation Membranes

Rubén Tejero, Ángel E. Lozano, Cristina Álvarez, Javier de Abajo

Departamento de Química Macromolecular Aplicada, Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas (ICTP-CSIC), Madrid 28006, Spain

Correspondence to: J. de Abajo (E-mail: deabajo@ictp.csic.es)

Received 1 April 2013; accepted 25 May 2013; published online 23 July 2013

DOI: 10.1002/pola.26806

ABSTRACT: Novel polyhydantoins (**PHYs**) were synthesized from original aromatic diisocyanates and bisiminoacetates by a two-step polycondensation procedure, which involved the cyclization of polyurea intermediates promoted by acid catalysis. The physical properties of the novel **PHYs** were evaluated by comparing them with a classical PHY derived from 4,4′-methylenediphenyl diisocyanate. All **PHYs** were soluble and could be processed into dense films, which showed good mechanical properties (tensile strength up to 110 MPa) and thermal stability of >400 °C. High glass transition temperatures (T_gs), ranging from 260 to 410 °C, were observed. Fractional free volume (FFV) was strongly dependent on the chemical structure, and a linear correlation between gas permeability and FFV of **PHYs** could be found. The gas separation properties were comparable to those of the commercial polyimide Matrimid®, with the exception of one of the **PHYs** which exhibited very promising properties as its gas productivity was comparable to the gas separation performance of well-established experimental polyimides. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4052–4060

KEYWORDS: diisocyanate; fractional free volume; heteroatom-containing polymers; high performance polymers; membrane gas separation; polyhydantoin; structure-property relations; thermal properties

INTRODUCTION Heterocylic polymers such as polyimides, polybenzimidazoles and polybenzoxazoles have generated a significant level of interest in both industry and academia in recent decades.[1] Particularly, aromatic polyimides have found application in aeronautics and electrical–electronic industries, thanks to their outstanding mechanical and thermal properties. In recent years, they have received special attention as membrane-forming polymers for gas separation operations, which are directly related to environmental protection and energy-saving challenges.[2–4] In fact, there are many examples of polyimides with high fractional free volume (FFV) and which are consequently highly permeable to vapor and gases.[5–8] Aromatic polyhydantoins (**PHYs**) are a class of polyheterocycles which underwent short but important technical developments in the 1970s, but they have not received special interest in recent years.[9–12] **PHYs**, which are commonly synthesized by the polycondensation of bisiminoacetates and diisocyanates, have been used successfully as copper-wire enamel insulators and high-temperature adhesives.[13–17] These polymers are mainly notable owing to their mechanical properties, chemical resistance and their exceptional thermal stability. As with other polyheterocycles, **PHYs** possess attractive structural characteristics to be considered as film-forming polymer materials for gas separation and purification. Nevertheless, it seems that no significant research effort has been devoted to this application so far. The absence of research on this field in recent years has moved us to initiate a study to assess the suitability of **PHYs** for gas separation applications. In this regard, an advantageous characteristic of these polymers relies on their high chemical versatility as both monomers, diisocyanates and bisiminoacetates, can be produced from a widespread number of commercial diamines.

As has been well established, for a polymer to exhibit promising properties for gas separation, it should show a relatively high free volume, to permit the easy transportation of gas molecules. Additionally, it should possess the capability to efficiently separate gases of different molecular sizes, which is mainly determined by chain rigidity, that is molecular stiffness.

Herein, **PHYs** have been synthesized from newly designed monomers, which contain the structural elements which predictably would work in terms of both good selectivity and

Additional Supporting Information may be found in the online version of this article.

high permeability. Thus, monomers were prepared containing fluorene units, which provide favorable chain stiffness and improve gas selectivity. Furthermore, bulky side groups were incorporated which can inhibit the dense packing of polymer chains and improve the permeability.[18] To investigate the effect of these "cardo" bridging units and bulky groups on the chain stiffness and free volume, a classical PHY from methylene diphenyl diisocyanate (MDI) was also prepared and evaluated as a reference.

Particular attention was paid to characterize and conveniently evaluate the set of synthesized polymers, and a study has been accomplished to find out structure–property relationships to figure out the real capabilities of these **PHYs** as special polymer materials, and in particular as polymer membranes for gas separation This approach allowed for the critical evaluation of the prepared **PHYs** in terms of special polymer materials, specifically for this application. For this assessment, their separation performances were compared to that of a commercial polyimide, Matrimid®,[19] which is a polymer widely used in gas separation. Furthermore, the present **PHYs** were also compared with the experimental polyimide 6FDA-6FpDA,[20] which is a highly fluorinated polyimide considered as a reference for experimental, high-performance gas polymer membranes. The modulation of the composition of these **PHYs** allowed for the study of the effects of the chemical structure on general properties such as solubility, thermal resistance, crystallization ability, and mechanical strength.

EXPERIMENTAL

Materials

Methyl bromoacetate (97%), ethyl bromoacetate (98%), *m*-phenylenediamine (MPD, 99%), triethylamine (TEA, 99%), triphosgene (98%), and anhydrous 1-methyl-2-pyrrolidinone (NMP, 99.5%) were purchased from Aldrich and were used without further purification. 9,9-*Bis*(4-aminophenyl) fluorene (98%) was purchased from TCI Europe and 1,4-*bis*(2-trifluoromethyl-4-aminophenoxy)−2,5-*bis*-*tert*-butylbenzene was purchased from Aurora Fine Chemicals and were used as received; *m*-cresol (99%) was purchased from Aldrich and was distilled before use. 4,4'-Methylene-bis(phenylisocyanate) (4,4′-MDI) was purchased from Aldrich and was sublimated before use. Other solvents and reactants were all purchased from Aldrich and were used without further purification.

Synthesis of Aromatic Bisiminoacetates

Diethyl 2,2′-[(1,3-phenylenebis(azanediyl))] diacetate

A mixture of MPD (5.0 g, 0.046 mol) and ethyl bromoacetate (11.7 mL, 0.106 mol) was refluxed in TEA (60 mL) for 30 min under a nitrogen atmosphere. After cooling, the solvent was evaporated under vacuum and the residue was purified by column chromatography over silica gel (hexane–ethyl acetate, 1:1 v/v) to yield 7.5 g (58%) of diethyl 2,2′-[(1,3-phenylenebis(azanediyl))] diacetate (**BIS-1**) as a white solid. mp: 70–71 °C.

^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.98 (dd, $J = 8.1$ Hz, 1H; Ar), 6.03 (dd, $J = 2.2$, 8.1 Hz, 2H; Ar), 5.84 (dd, $J = 2.3$ Hz, 1H; Ar), 4.21 (c, $J = 7.2$ Hz, 4H; 2OCH$_2$), 3.84 (s, 4H; 2CH$_2$), 1.27 (t, $J = 7.2$ Hz, 6H; 2CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, δ): 171.6 (2C═O), 148.6 (2C), 130.6 (2C), 104.1 (2C), 61.7 (2C), 46.3 (2C), 14.7 (2C); HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{14}H_{20}N_2O_4$, 281.1423; found, 281.1501. Anal. calcd for $C_{14}H_{20}N_2O_4$: C 60.40, H 7.14, N 10.00; found: C 60.00, H 7.21, N 9.54.

Dimethyl 2,2′-[((9H-fluorene-9,9-diyl)bis(4,1-phenylene))bis(azanediyl)] diacetate

Over a stirred mixture of 9,9-*bis*(4-aminophenyl)fluorene (10.7 g, 0.030 mol) and 2,6-lutidine (8.4 mL, 0.072 mol) dissolved in acetonitrile (500 mL) methyl bromoacetate (7.3 mL, 0.066 mol) was added dropwise and the reaction mixture was refluxed for 8 h. The final reaction mixture was partitioned with ethyl acetate/water, the combined organic layers were dried over magnesium sulfate, and the solvent was removed under vacuum. The residue was purified by column chromatography over silica gel (hexane–ethyl acetate, 2:1 v/v), to yield 8.0 g (53%) of dimethyl 2,2′-[((9H-fluorene-9,9-diyl)-*bis*(4,1-phenylene))*bis*(azanediyl)] diacetate (**BIS-2**) as a white solid. mp: 132–133 °C.

^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.65 (dd, $J = 7.6$ Hz, 2H; Ar), 7.32 (d, $J = 7.3$ Hz, 2H; Ar), 7.29 (dd, $J = 1.3$, 7.6 Hz, 2H; Ar), 7.16 (dd, $J = 1.3$, 7.3 Hz, 2H; Ar), 6.97 (d, $J = 8.6$ Hz, 4H; Ar), 6.36 (d, $J = 8.6$ Hz, 4H; Ar), 3.97 (s, 2H; 2NH), 3.74 (s, 4H; 2CH$_2$), 3.64 (s, 6H; 2OCH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, δ): 171.5 (2C═O), 152.1 (2C), 145.4 (2C), 139.8 (2C), 135.6 (2C), 128.9 (4C), 127.4 (2C), 126.9 (2C), 125.9 (2C), 119.8 (2C), 112.5 (4C), 63.9, 52.0 (2C), 45.5 (2C); HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{31}H_{28}N_2O_4$, 493.2049; found, 493.2131. Anal. calcd for $C_{31}H_{28}N_2O_4$: C 75.59, H 5.73, N 5.69; found: C 75.37, H 5.46, N 5.76.

Synthesis of Aromatic Diisocyanates

9,9-Bis(4-isocyanatophenyl)−9H-fluorene

Over a stirred mixture of triphosgene (2.08 g, 0.007 mol) in anhydrous toluene (50 mL) at 0 °C under a nitrogen atmosphere, a solution of 9,9-*bis*(4-aminophenyl)fluorene (5.0 g, 0.014 mol) in anhydrous toluene (50 mL) was dropped for 1 h. Then, the mixture was refluxed for 10 h. After cooling, the solvent was evaporated under vacuum and the residue was extracted several times with anhydrous hexane. The combined organic layers were dried over magnesium sulfate. Removal of the solvent under vacuum yielded a residue which was sublimated under vacuum at 180 °C to yield 2.3 g (83%) of 9,9-*bis*(4-isocyanatophenyl)−9H-fluorene (**DII-1**) as a white solid. mp: 140–141 °C; Attenuated total reflectance-Fourier transform infrared (ATR-FTIR): 3046 (═CH), 2258 (N═C═O) cm^{-1}

^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.74 (d, $J = 8.5$ Hz, 2H; Ar), 7.35 (m, $J = 1.5$, 6.9 Hz, 2H; Ar), 7.29-7.25 (m, $J = 1.5$, 6.9, 8.5 Hz, 4H; Ar), 7.09 (d, $J = 8.6$ Hz, 4H; Ar), 6.92 (d, $J = 8.6$ Hz, 4H; Ar); ^{13}C NMR (75 MHz, CDCl$_3$, δ): 149.9 (2NCO), 142.8 (2C), 139.6 (2C), 131.6 (2C), 128.7 (6C), 127.5 (2C), 127.4 (2C), 125.3 (2C), 124.2 (4C), 119.9 (2C), 64.1. Anal. calcd for $C_{27}H_{16}N_2O_2$: C 80.99, H 4.03, N 7.00; found: C 81.03, H 4.25, N 6.98.

4,4′-[(2,5-Di-tert-butyl-1,4-phenylene)bis(oxy)]bis(1-isocyanato-3-trifluoromethylbenzene)

In a similar way, 4,4′-[(2,5-di-*tert*-butyl-1,4-phenylene) *bis*(oxy)]*bis*(1-isocyanato-3-trifluoromethylbenzene) (**DII-2**) was synthesized from 1,4-*bis*(2-trifluoromethyl-4-aminophenoxy)−2,5-*bis*-tertbutylbenzene and triphosgene. It was isolated in 72% of yield after purification by sublimation under vacuum at 220 °C. mp: 166–167 °C.

ATR-FTIR: 3025 (=CH), 2990 (—CH), 2980 (—CH), 2270 (N=C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.43 (d, $J = 2.6$ Hz, 2H; Ar), 7.18 (dd, $J = 2.6$, 8.9 Hz, 2H; Ar), 6.85–6.75 (m, 4H; Ar), 1.27 (s, 18H; $6CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.2 (4C), 137.9 (2C), 129.3 (2C), 129.0 (2C), 128.9 (q, $^1J_{C\text{—}F} = 271.4$ Hz, 2C; CF_3), 128.2 (4C), 120.1 (q, $^2J_{C\text{—}F} = 33.1$ Hz, 2C; CF_3), 118.8 (4C), $C_{30}H_{26}F_6N_2O_4$: C 60.81, H 4.42, N 4.73; found: C 60.53, H 4.32, N 4.47.

Synthesis of PHYs

As an example of the general synthetic route to **PHYs**,[21–24] the preparation of the homopolymer **PHY-3** is described here in detail: A mixture of **BIS-2** (2.46 g, 0.005 mol) and **DII-1** (2.00 g, 0.005 mol) in 5 mL of freshly distilled *m*-cresol was heated to 50 °C and stirred under a nitrogen atmosphere for 4 h. As the reaction progressed, the solution became very viscous. The second stage of the reaction (chemical cyclization) was carried out by the addition of 0.5 mL of concentrated HCl and 5 mL of *m*-cresol. Then, the reaction was heated at 50 °C for 3 h. The viscous solution obtained was poured into 400 mL of ethanol (EtOH), the precipitated polymer was filtered, and washed several times with EtOH, and it was finally dried to constant weight in a vacuum oven at 200 °C for 12 h. The yield was quantitative.

ATR-FTIR: 3056 (=CH), 1776 (C=O), 1718 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.95 (m, $J = 8.4$ Hz, 2H; Ar), 7.55 (d, $J = 7.8$ Hz, 4H; Ar), 7.46–7.28 (m, $J = 7.8$ Hz, 8H; Ar), 7.14 (d, $J = 8.4$ Hz, 2H; Ar), 4.55 (s, 2H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 168.5, 153.5, 150.8, 150.3, 145.6, 141.2, 139.9, 136.9 (2C), 130.9 (2C), 128.6 (4C), 128.4 (4C), 128.2, 127.4, 126.6, 126.4, 121.1, 118.9 (2C), 64.9, 50.3; Anal. calcd for $(C_{28}H_{18}N_2O_2)_n$: C 81.14, H 4.38, N 6.76; found: C 78.93, H 4.36, N 6.62.

Film Preparation

PHYs dense films were prepared as follows: a 10% solution of polymer in NMP (w/v) was filtered through a 3.1-μm fiberglass Symta® syringe filter and, after degassing, the polymer solution was poured into a glass ring placed on a leveled glass plate, and the solvent was slowly evaporated at 60 °C for 8 h, and then at 80 °C for 3 h. Polymer films were peeled off from the glass and the residual solvent was evaporated under vacuum for 12 h at 250 °C. Thicknesses of the films ranged from 50 to 80 μm.

Characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer operating at 300 and 75 MHz. Melting points were determined using a Büchi 504392-S instrument. Microanalyses were made with a Carlo Erba EA1108 elemental analyzer. ATR-FTIR spectra were recorded on a Perkin Elmer RX-1 instrument with Universal ATR Sampling Accessory module. Inherent viscosities were measured at 25 °C with an Ubbelohde viscometer using NMP as solvent at a concentration of 0.5 $g{\cdot}dL^{-1}$. Differential scanning calorimetry (DSC) data were recorded on a TA Q-2000 device in nitrogen at 20 $°C{\cdot}min^{-1}$. Thermogravimetric analysis (TGA) data were recorded on a TA Q-500 analyzer using Hi-Res™ option. Hi-Res scans were run at 50 $°C{\cdot}min^{-1}$ with resolution and sensitivity parameters of 4.0 and 1.0, respectively, in the temperature range of 25–850 °C. The purge gas was nitrogen (60 $mL{\cdot}min^{-1}$) and the sample mass was about 5 mg. Tensile strength, elongation at break, and Young's module of the membranes were measured with a MTS Synergie 200 apparatus fitted with a 100 N load cell at room temperature. The samples of 5 mm width and 5 cm length were clamped at both ends with an initial gauge length of 10 mm at an elongation rate of 5 mm min^{-1}. At least eight samples were tested for each film. Wide-angle X-ray scattering (WAXS) patterns were recorded in the reflection mode at room temperature, using a Bruker D8 Advance diffractometer provided with a Goebel Mirror and a PSDVantec detector. CuKα (wavelength, $\lambda = 1.54$ Å) radiation was used. A step-scanning mode was used for the detector, with a 2θ step of 0.024° and 0.5 s per step.

Fractional Free Volume

FFV was calculated from the density (ρ) of polymer films using the following relation:

$$FFV = \frac{V - 1.3V_w}{V} \tag{1}$$

where $V = 1/\rho$ is the polymer-specific volume ($cm^3{\cdot}mol^{-1}$), V_w is the van der Waals volume, which was estimated by using the Hyperchem 7.0 computer program.[25] This program considers the dependence of van der Waals volume on the chemical environment and it can estimate V_w for the structural unit of a polymer chain.

The density was determined experimentally using a top-loading electronic XS105 Dual-Range Mettler Toledo balance coupled with a density kit based on Archimide's principle. The samples were weighed in air and into a known-density liquid (high-purity isooctane). The measurement was performed at room temperature and the density was calculated as follows:

$$\rho = \rho_{\text{liquid}} \left[\frac{\omega_{\text{air}} - \omega_{\text{liquid}}}{\omega_{\text{air}}} \right] \tag{2}$$

where ρ_{liquid} is the density of isooctane, ω_{air} is the weight of the sample in air, and ω_{liquid} is its weight when is submerged in isooctane.

Permeability Measurements

The gas permeation properties were determined for pure gas feeds using a constant volume/variable pressure

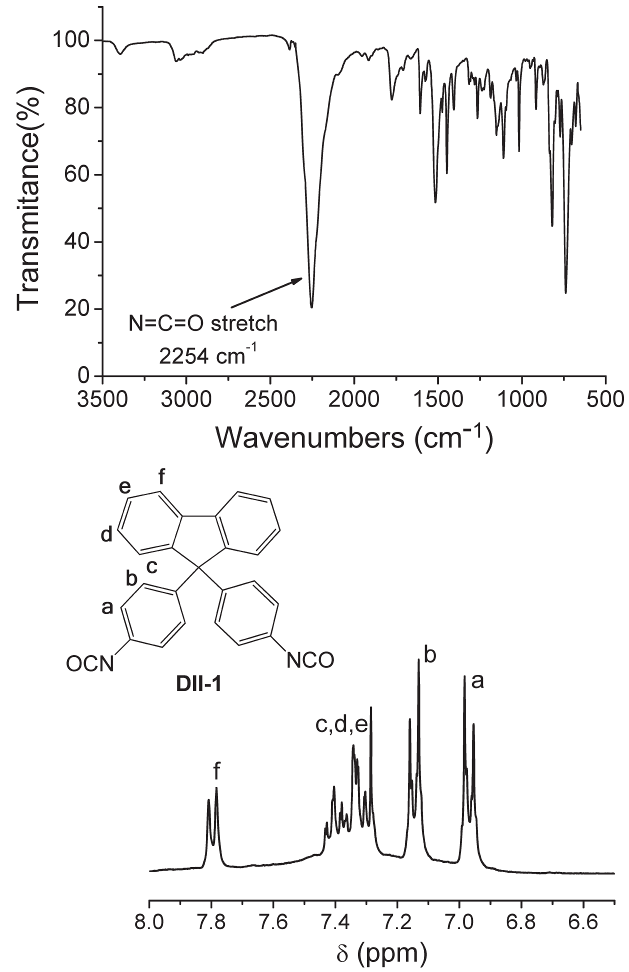


FIGURE 1 ATR-FTIR (top) and ^{1}H NMR (bottom, $CDCl_3$) spectra of **DII-1**.

apparatus at 30 °C. The downstream pressure was kept below 10^{-2} mbar, whereas the upstream pressure was maintained at 3 bar.

Permeability coefficients (P) were determined from the slope of downstream pressure versus time, plotted once steady state had been achieved, according to the equation:

$$P = \frac{273}{76}\frac{Vl}{ATp_0}\frac{dp(t)}{dt} \tag{3}$$

where A and l are, respectively, the effective area and the thickness of the film, T is the measurement temperature in K, and p_0 is the pressure of the feed gas in the upstream chamber. P is usually expressed in barrers [1 barrer = 10^{-10} (cm^3 (STP)·cm)·(cm^{-2}·s^{-1}·$cmHg^{-1}$)]. To evaluate the possible existence of micropores (pinholes) in the membranes, they were subjected to a preliminary test to measure the permeability to Helium at different pressures, from 1 to 5 bar. To ensure reproducibility of results, each membrane was measured three times. The ideal selectivities of the O_2/N_2 and CO_2/CH_4 gas pairs were calculated from the ratio of pure gas permeabilities ($\alpha P_A/P_B$).

RESULTS AND DISCUSSION

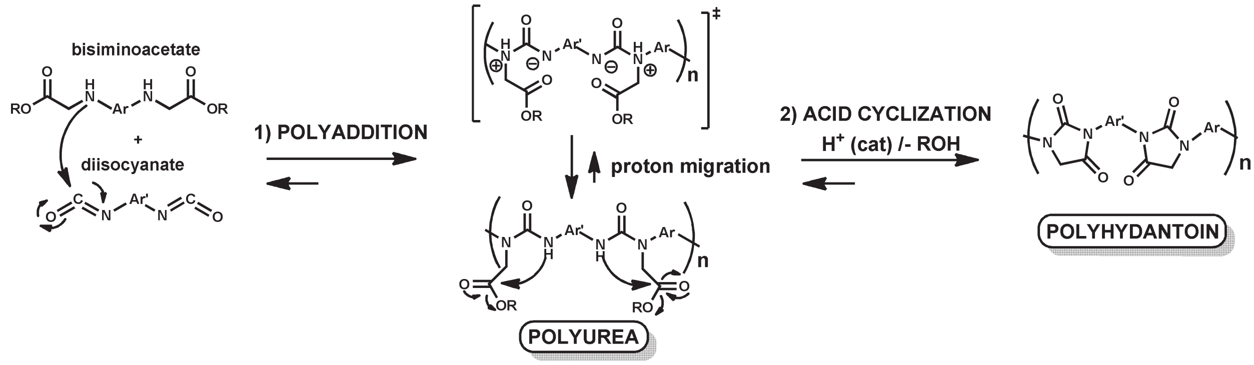
Monomers and Polymers

Bisiminoacetates **BIS-1** and **BIS-2** were prepared from the corresponding diamines and alkyl bromoacetates by the general method reported previously.[26,27] Unreported diisocyanates **DII-1** and **DII-2** were prepared by the method reported elsewhere from diamines and using triphosgene as the acylation agent.[28] These electrophilic monomers were obtained in high yield and could be purified to monomer grade by sublimation. **DII-1** and **DII-2** were identified by spectroscopic methods. Data of IR and NMR were consistent with the proposed structures as shown in Figure 1, where the spectra of **DII-1** are shown as examples. The appearance of the characteristic band of the isocyanate group in the ATR-FTIR spectra, around 2200 cm^{-1} (N=C=O), confirmed the chemical structure of the monomer; in the same way, all peaks of the NMR spectra could be easily assigned to the protons of the monomer. Additional data on the spectroscopic characteristics of all the monomers have been summarized in Supporting Information material.

The polycondensations of diisocyanates and bisiminoacetates were carried out using the classical method in solution in *m*-cresol as shown in Scheme 1. The precursor polyureas, which were formed in the first step of the reaction, were converted into the final **PHYs** by an acid-catalyzed cyclization at moderate temperature (approx., 50 °C). The complete cyclization of precursors to **PHYs** was confirmed by the appearance in the ATR-FTIR spectra of two characteristics bands of the carbonyls in the hydantoin ring at 1770 and 1710 cm^{-1} (C=O), and by the absence of bands around 3300 (N—H) and 1690 (C=O) cm^{-1} of the urea groups. As an example, Figure 2 shows the ATR-FTIR and ^{1}H-NMR spectra of **PHY-3**. ATR-FTIR, ^{1}H and ^{13}C NMR spectra, and elemental analyses confirmed that **PHYs** were successfully synthesized in high yield (91–98%) and with full conversion via the polyurea chemical cyclization method (Supporting Information).

The polymer's chemical composition and the results of the polycondensation reactions have been listed in Table 1, along with inherent viscosities measured for the set of polymers and their solubility in organic solvents. All polymers showed good solubility in highly polar organic solvents such as *m*-cresol, NMP and DMAc. Polymers **PHY-3** and **PHY-4** were soluble even in THF and $CHCl_3$. Inherent viscosities in the range of 0.40–0.70 dL·g^{-1} should correspond to medium to high molecular weights.

Consistent with this assumption, films of good quality with high mechanical resistance could be attained by the casting of polymer solutions in all cases (Table 2). Polymer films showed elastic moduli close to 2.0 GPa and tensile strength values of between 50 and 110 MPa, indicating that these polymers have excellent mechanical properties, comparable to other polyheterocycles and engineering thermoplastics.[29] These values allow these polymers to be considered as



SCHEME 1 Synthesis of **PHYs**.

suitable candidates for the preparation of dense membranes able to withstand high gas pressures for long periods of time.

TGA was used to investigate the thermal resistance (Fig. 3). Data summarized in Table 2 reveal that these materials possess high temperatures of initial decomposition, T_d, with two of them, **PHY-2** and **PHY-3**, showing T_d higher than 440 °C. All of them left char residues close to 50% at 800 °C.

DSC was used to determine the glass transition temperature, T_g, of these polymers. The samples were subjected to a heating–cooling–heating cycle, the first heating until 300 °C to ensure the removal of water and traces of solvent. T_gs are listed in Table 2 where it can be seen that all of the **PHYs** have T_gs higher than 250 °C. This agrees well with the chemical composition of these polymers, where only aromatic and hydantoin rings are present. The trend observed in the T_gs was consistent with the chain stiffness that was predicted. Thus, **PHY-2** and **PHY-3** have T_g values of 345 and 405 °C, respectively, as corresponds to the presence of bulky fluorene moieties. On the other hand, **PHY-1** and **PHY-4** do not reach such high values of T_g because both polymer have —CH_2— and —O— linkages between the phenylene rings, which work for a higher conformational freedom and lower T_g. Endothermic peaks, which could be associated with enthalpy of fusion, were not observed in any case (Fig. 4), therefore these polymers should be considered as amorphous in nature.

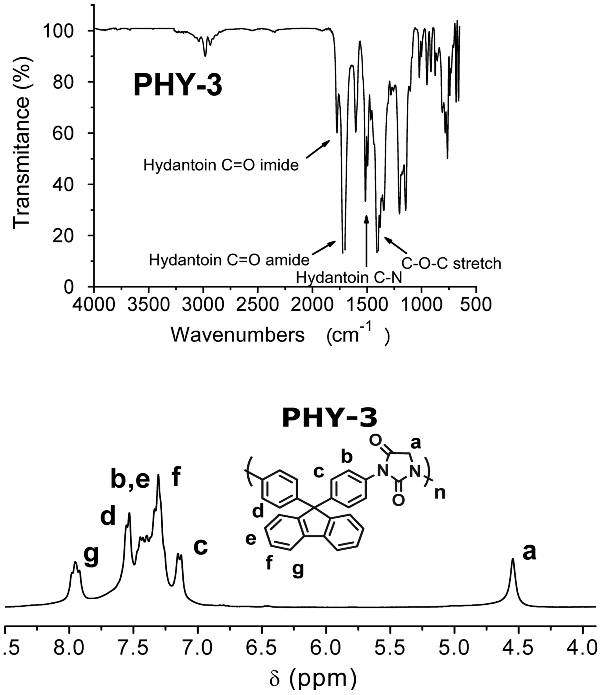


FIGURE 2 ATR-FTIR (top) and ^{1}H NMR (bottom, DMSO-d_6) spectra of **PHY-3**.

To confirm this, the molecular order of the current **PHYs** was also investigated by WAXS. As expected, the X-ray patterns showed the typical halo seen in amorphous polymers (Fig. 5). Moreover, **PHYs** containing fluorene units exhibited a more or less defined maximum, close to 14°, which corresponds to an intersegmental distance of 6.3 Å, indicating that these bulky units cause chain separation and hinder efficient chain packing.

Evaluation of PHYs as Gas Separation Membranes

On applying eq (1), values of FFV were obtained through the experimental density of the polymer films (Table 3). **PHY-1** presented the lowest value of FFV (0.081), whereas **PHY-4** showed the highest FFV (0.194). The values of FFV followed a trend just opposite to that of densities, according to a correct application of eq (1). **PHY-1** was the only polymer with no bulky fluorene moiety in its repeating unit and it also did not have side substituents, which made it in terms of efficient molecular packing and high density. **PHY-2** and **PHY-3** showed similar values of FFV although their chemical compositions were very different. The presence of diphenylmethane units in **PHY-2** should not give as high FFV as the fluorene unit does in **PHY-3**, but the molecular heterogeneity provided by the different nature of the starting diisocyanate and bis-iminoacetate of **PHY-2** can explain the reason why both polymers exhibit similar values of density and FFV. The high FFV of **PHY-4** can be attributed to the presence of bulky groups such as tert-butyl and trifluoromethyl along with the fluorene units. One could presume that the molecular mobility that generally impart the —O— linkages to aromatic polymers would allow for good molecular packing and a higher

TABLE 1 Yield, Inherent Viscosity (η_{inh}) and Solubility of **PHYs**

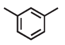
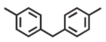
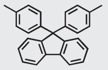
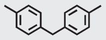
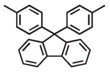
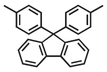
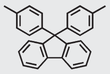
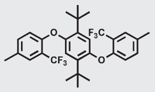
	Ar-R-Ar′				Solvent			
Polymer	Ar (Bisiminoacetate)	Ar′ (Diisocyanate)	Yield (%)	η_{inh} (dL g^{-1})	*m*-Cresol	NMP	THF	$CHCl_3$
PHY-1			98	0.69	+	+	−	−
PHY-2			96	0.72	+	+	−	−
PHY-3			91	0.42	+	+	+	+
PHY-4			94	0.52	+	+	+	+

TABLE 2 Thermal and Mechanical Properties of **PHYs** Films

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Young's Module (GPa)	T_g (°C)	T_d[a] (°C)	Char Yield[b] (%)
PHY-1	110 ± 10	10 ± 1	2.0 ± 0.2	265	430	52
PHY-2	100 ± 10	14 ± 4	1.8 ± 0.2	345	450	48
PHY-3	50 ± 10	2.5 ± 0.4	2.3 ± 0.7	405	490	55
PHY-4	60 ± 10	3.5 ± 0.3	2.0 ± 0.3	310	440	49

[a] Onset temperature at which decomposition begins.

[b] Char yield at 800 °C.

density for **PHY-4**, but it is not so because the presence of tert-butyl groups placed *ortho* to the —O— linkage greatly restricts the rotation around the Ph—O—Ph bonds, as it has been reported previously.[20]

The gas permeabilities and selectivities of **PHYs** are listed in Table 4. **PHY-2** showed values similar to Matrimid®, whereas those of **PHY-1** were considerably lower in agreement with its lower FFV. **PHY-3** exhibited higher permeability than Matrimid® although CO_2/CH_4 and O_2/N_2 selectivities were lower.

PHY-4 presented the best permeability, even higher than that of 6FDA-6FpDA, as could be expected of a polymer that has a very high FFV. However, the selectivity CO_2/CH_4 was significantly lower than that of the reference polymer. Their properties are actually also fairly comparable with those of some recently reported polyimides.[30,31] As it has been reported, it is possible to establish a correlation between log P and 1/FFV for a wide variety of macromolecular structures.[32–34]

Park and Paul[35] reported that this correlation is accurate when a specific family of polymers is studied. Also, they

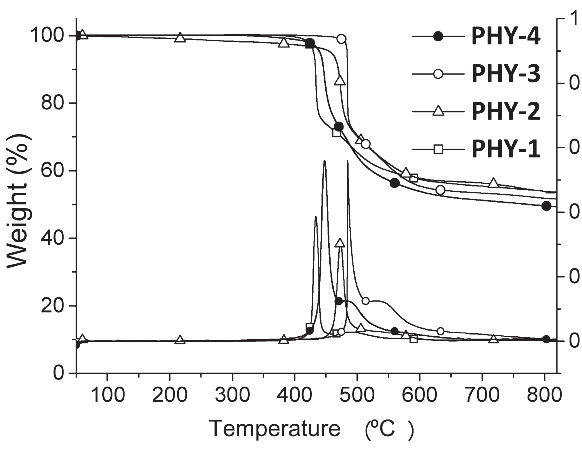


FIGURE 3 TGA thermograms of **PHYs**.

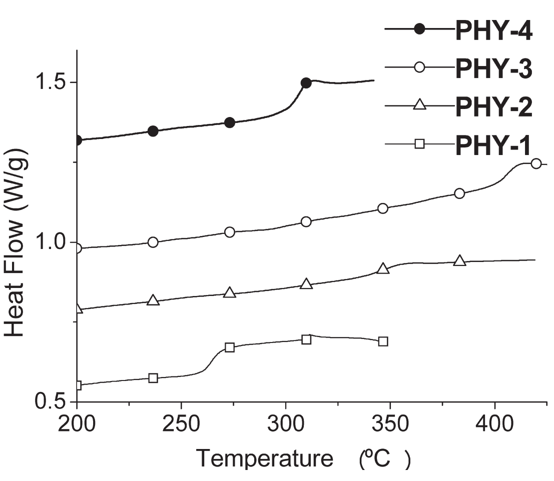


FIGURE 4 DSC thermograms of **PHYs**.

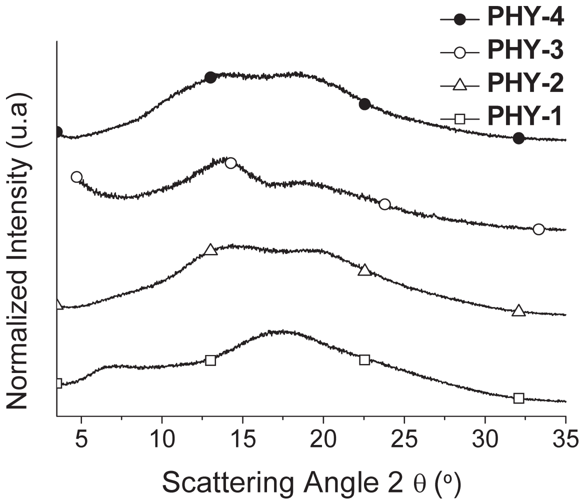


FIGURE 5 WAXS patterns of **PHYs**.

found a much better correlation when FFV was calculated considering the occupied volume, which is specific for each gas, irrespective of the polymer studied. To find out whether **PHYs** fit the classical correlation between gas permeability and FFV, a graph is shown in Figure 6, where the values of Matrimid® and 6FDA-6FpDA are also included. A fairly good correlation for the **PHYs** and reference polyimides could be observed, both for CO_2 and for O_2.

This relationship could be employed for further research on these polymers which should be accomplished in the near future.

TABLE 3 Densities and FFV of **PHYs**, Matrimid®,[19] and 6FDA-6FpDA[20]

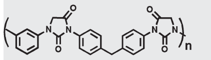
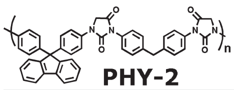
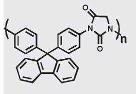
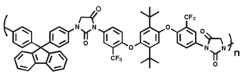
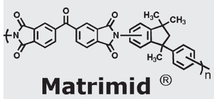
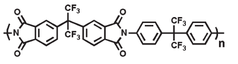
Polymer	ρ (g cm^{-3})	FFV
 **PHY-1**	1.345	0.081
 **PHY-2**	1.256	0.102
 **PHY-3**	1.249	0.112
 **PHY-4**	1.217	0.194
 **Matrimid ®**	1.266	0.110
 **6FDA-6FpDA**	1.466	0.208

TABLE 4 Permeabilities and Selectivities of **PHYs**, Matrimid®,[19] and 6FDA-6FpDA[20]

	Permeability (barrer)					Selectivity	
Polymer	PHe	PN_2	PO_2	PCH_4	PCO_2	$\alpha PCO_2/PCH_4$	$\alpha PO_2/PN_2$
PHY-1	4.6	0.025	0.17	0.015	0.85	57	6.8
PHY-2	16	0.33	1.9	0.32	10	31	5.8
PHY-3	29	0.75	4.2	0.77	14	18	5.6
PHY-4	120	5.2	25	5.2	110	21	4.8
Matrimid®	22	0.27	1.9	0.24	8.7	36	7.0
6FDA-6FpDA	151	3.6	18	2.0	70	35	5.0

On plotting selectivity (α) against permeability (P) in a chart, which includes the upper bound limits of Robeson (1991 and 2008)[36,37] for a given pair of gases, a promising behavior of these polymers in this kind of separation could be observed.

The productivity of gas separation for this family of **PHYs** is shown in Figure 7, which also includes the values of Matrimid® and 6FDA-6FpDA. **PHY-1** showed a moderate permeability/selectivity balance for the gas pairs CO_2/CH_4 and O_2/N_2. **PHY-2** had similar values to Matrimid® for the

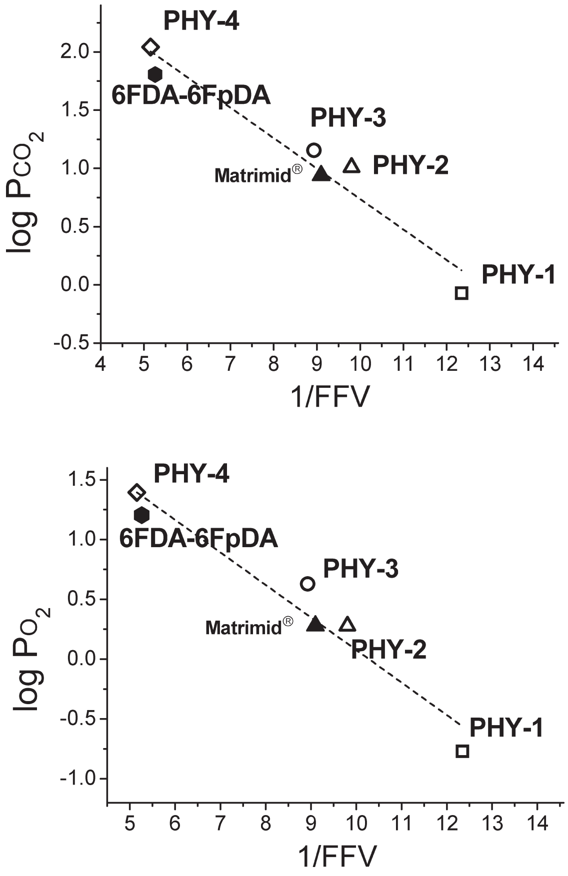


FIGURE 6 Log $P-1$/FFV diagram for CO_2 (top) and O_2 (bottom).

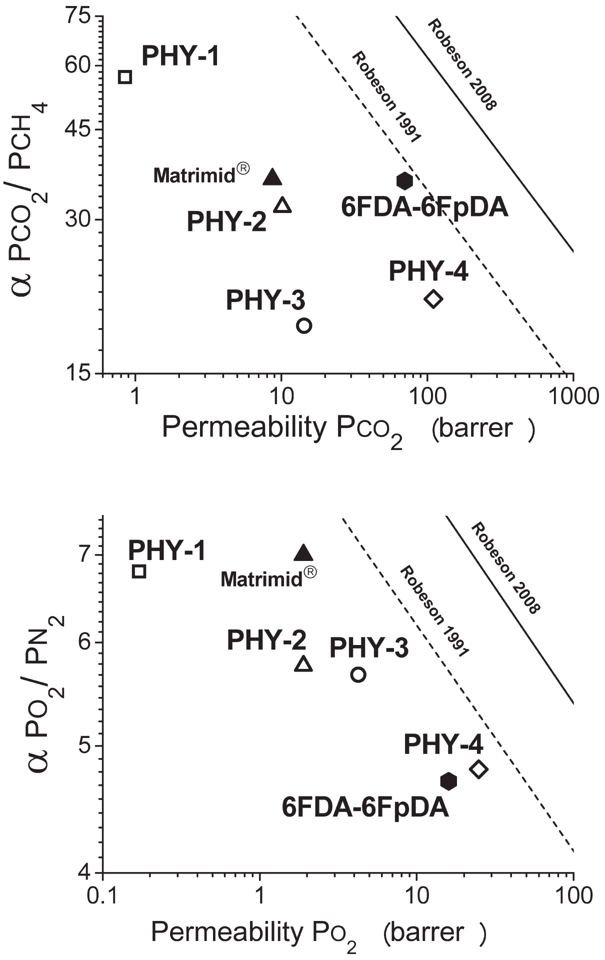


FIGURE 7 Selectivity–permeability (*α-P*) diagram for CO_2/CH_4 pair (top) and O_2/N_2 pair (bottom).

CO_2/CH_4 separation, O_2/N_2 pair. **PHY-3** had lower selectivity for CO_2/CH_4 although its permeability was better than that of Matrimid®. The best results, with a high permeability to O_2 and CO_2 along with a good selectivity, were by far for **PHY-4**. Furthermore, it showed better performance in terms of permeability/selectivity than 6FDA-6FpDA for the O_2/N_2 pair as it lays closer to the Robeson limit. However, for the CO_2/CH_4 pair, **PHY-4** presented lower productivity than 6FDA-6FpDA. Nonetheless, this PHY was better for gas separation than many glassy polymers reported so far.[38,39]

CONCLUSIONS

It has been demonstrated that it is possible to prepare new **PHYs** in high yield based on an optimized synthetic approach by using new monomers derived from commercial aromatic diamines. These **PHYs** can be processed into dense films with good mechanical properties. Furthermore, these **PHYs** are amorphous materials, soluble in many organic solvents, which have high thermal stability.

This research has also proved that **PHYs** containing fluorene bridging groups have high T_gs. The additional presence of bulky side groups, such as tert-butyl and trifluoromethyl, gave comparatively high FFV as well.

The presence of fluorene units in the backbone of **PHYs** significantly improves the gas permeabilities, with acceptable losses in selectivity, in accordance with the highest FFV disposable for gas transport. Nonetheless, it was necessary to introduce additional bulky side groups in the monomers to get gas separation properties comparable to those of the reference 6FDA-6FpDA polyimide.

Data reported here indicate that the convenient modification of the starting monomers can lead to **PHYs** with outstanding physical properties and with gas permeation capabilities superior to those of many polyimides. This study should be considered as an original approach to reach valuable information to design new materials, with improved gas separation properties for selected applications, mainly related to CO_2 capture and air component separation.

ACKNOWLEDGMENTS

The authors are indebted to the Ministry of Economy and Competitiveness of Spain (MINECO) for the economic support of this work (MAT2010–20668/MAT and MAT2011–25513/MAT). The authors also acknowledge financial support from the program Consolider Ingenio 2010 (project CSD-0050-MULTICAT). The help provided by Sara Rodriguez and Alberto Tena in measuring gas permeability is greatly appreciated. R. Tejero thanks CSIC for a predoctoral JAE fellowship. The Authors acknowledge Maria Nash for the revision of this manuscript.

REFERENCES AND NOTES

1 T.-S. Chung, *J. Polym. Sci. Part C: Polym. Rev.* **1997**, *37*, 277–301.

2 B. Sedlacek, J. Kahovec, *J. Polym. Sci. Part C: Polym. Lett.* **1987**, *26*, 242.

3 M. Mulder, Basic Principles of Membrane Technology; Kluwer Academic Publishers: London, **1991**.

4 K. Scott, Handbook of Industrial Membranes; Elsevier: Oxford, **1995**.

5 C. E. Sroog, *Prog. Polym. Sci.* **1991**, *16*, 561–694.

6 R. Wang, C. Cao, T.-S. Chung, *J. Membr. Sci.* **2002**, *198*, 259–271.

7 J. de Abajo, J. G. De la Campa, A. E. Lozano, J. Espeso, C. García, *Macromol. Symp.* **2003**, *199*, 293–305.

8 Y. Xiao, B. T. Low, S. S. Hosseini, T.-S. Chung, D. R. Paul, *Prog. Polym. Sci.* **2009**, *34*, 561–580.

9 R. Merten, W. Dünwald, K.-H. Mielke, E. Reese (Bayer AG). U.S. 3,397,253, **1965**.

10 R. Merten, W. Zecher (Farbenfabriken Bayer AG). U.S. 3,448,170, **1969**.

11 J. A. Preston, F. Wayne (Essex International). U.S. 3,681,282, **1972**.

12 K. B. Wagener, B. W. Spivey, J. M. Chapman (Akzona Incorporated). U.S. 4,053,441, **1977**.

13 E. Reese, J. Wank, R. Binsack, (Bayer Aktiengesellschaft). U.S. 4,206,110, **1980**.

14 W. Zecher, R. Merten, W. Dünwald (Bayer Aktiengesellschaft). U.S. 4,517,353, **1985**.

15 G. Heywang, F. Jonas, R. Merten, W. Schmidtberg (Bayer Aktiengesellschaft). U.S. 4,849,492, **1989**.

16 F. Jonas, R. Merten (Bayer Aktiengesellschaft). U.S. 5,006,641, **1991**.

17 C.-I. Tseng (Lonza). U.S. 5,785,963, **1998**.

18 Y. Yampolskii, *Macromolecules* **2012**, *45*, 3298–3311.

19 M. D. Guiver, G. P. Robertson, Y. Dai, F. Bilodeau, Y. S. Kang, K. J. Lee, J. Y. Jho, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 4193–4204.

20 M. Calle, A. E. Lozano, J. de Abajo, J. G. de la Campa, C. Álvarez, *J. Membr. Sci.* **2010**, *365*, 145–153.

21 R. H. Sallé, B. J. Sillion, G. P. Gaudemaris, *J. Polym. Sci. Part A: Polym. Chem.* **1966**, *4*, 2903–2906.

22 Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.* **1967**, *5*, 2289–2296.

23 M. M. Koton, *Vysokomol. Soyed.* A18, **1976**, *9*, 2092.

24 R. Merten, *Angew. Chem. Int. Ed.* **1971**, *10*, 294–301.

25 Hyperchem, Computational Chemistry, version 7.0, Hypercube Inc., Gainesville, Florida, **2002**.

26 H. Kwon, *Bull. Korean Chem. Soc.* **1997**, *18*, 476–480.

27 K. Yasuda (Kokai Tokkyo Koho), JP 133483, **2006**.

28 W. Xiang-Hui, H. Yong-Ning, *Appl. Chem. Ind.* **2008**, *37*, 1019.

29 J. M. Margolis, Ed. Engineering Thermoplastics; Dekker: New York, **1985**.

30 Y. Yampolskii, B. D. Freeman, I. Pinnau, Materials Science of Membranes for Gas and Vapor Separation; John Wiley & Sons Ltd: New York, **2006**.

31 H. Lin, B.D. Freeman, *J. Mol. Struct.* **2005**, *739*, 57–74.

32 C. L. Aitken, W. J. Koros, D. R. Paul, *Macromolecules* **1992**, *25*, 3651.

33 T. H. Kim, W. J. Koros, G. R. Husk, K. C. O'Brien, *J. Membr. Sci.* **1988**, *37*, 45.

34 D. H. Weinkauf, D. R. Paul, *J. Polym. Sci. Part B: Polym. Phys.* **1992**, *30*, 837.

35 J. Y. Park, D. R. Paul, *J. Membr. Sci.* **1997**, *125*, 23–39.

36 L. M. Robeson, *J. Membr. Sci.* **1991**, *62*, 165–185.

37 L. M. Robeson, *J. Membr. Sci.* **2008**, *320*, 390–400.

38 M. M. Dal-Chin, A. A. Kumar, A. Layton, *J. Membr. Sci.* **2008**, *323*, 299–308.

39 L. M. Robeson, B. D. Freeman, D. R. Paul, B. W. Rowe, *J. Membr. Sci.* **2009**, *341*, 178–185.