Designed Monomers and Polymers

Synthesis and characterization of novel polyamides containing dibenzobarrelene pendant groups

José Luis Santiago-García[a], José Manuel Pérez-Francisco[a], María Isabel Loría-Bastarrachea[a] & Manuel Aguilar-Vega[a]

[a] Unidad de Materiales, Centro de Investigación Científica de Yucatán, A.C., Calle 43, No. 130, C.P., 97200 Mérida, Yucatán, Mexico
Published online: 03 Mar 2015.

CrossMark

Click for updates

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of novel polyamides containing dibenzobarrelene pendant groups

José Luis Santiago-García*, José Manuel Pérez-Francisco, María Isabel Loría-Bastarrachea and Manuel Aguilar-Vega

Unidad de Materiales, Centro de Investigación Científica de Yucatán, A.C., Calle 43, No. 130, C.P., 97200 Mérida, Yucatán, Mexico

The 5-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido) isophthalic acid (DEAIA) monomer, containing a dibenzobarrelene pendant group, was synthesized by the condensation of 5-aminoisophthalic acid and 9,10-dihydroanthracene-9,10-α,β-succinic anhydride (DASA). The DEAIA monomer was reacted with four structurally different aromatic diamines to synthesize four novel polyamides. All aromatic polyamide based in the DEAIA monomer showed very good solubility in aprotic polar solvents and excellent thermal stability with onset of decomposition at 430 °C. They readily form membrane by the casting method. Moreover, the most interesting polyamide was DEAIA-6F that showed high thermal stability, good film formation, and the largest gas permeability coefficients in comparison with a reported polyhexafluoroisophthalamide, HFAISO; this confirms the advantage of inserting a dibenzobarrelene pendant group.

Keywords: bulky pendant groups; aromatic polyamides; dibenzobarrelene

1. Introduction

Aromatic polyamides are an important group of high-performance polymers. They are well known for their outstanding properties, which meet the demands at end-use conditions for technological applications. However, one of the disadvantages presented by aromatic polyamides is their low solubility in common organic solvents that restrict their solution processability, while their high thermal and mechanical properties require high energy for other processing methods. Therefore, the aromatic polyamides that can be processed from solution have received considerable attention recently; with work directed toward chemical modification of backbone that allows their enhanced solubility.[1]

Modification of polymers by incorporating bulky pendant groups might bring more chemical versatility and it will extend their field of applications.[2–4] In particular, the introduction of bulky pendant groups has been performed to promote chain separation, increase amorphous character, and produce a higher free volume. Their introduction also improves solubility and processability on aromatic polymers while maintaining their outstanding properties.[5] Some bulky pendant groups such as trimethylsilyl (–Si(CH$_3$)$_3$),[6] trifluoromethyl (–CF$_3$), [7] tert-butyl (–C(CH$_3$)$_3$), and phenyl (–C$_6$H$_5$) are preferred because their introduction promotes chain separation and improves processability.[2]

High-performance aromatic polyamides tend to be quite insoluble and therefore, there is a strong need to increase their solubility.[8,9] Carja et al. [10] synthesized aromatic polyamides containing phthalonitrile pendant groups, these polymers exhibited good solubility in organic solvents. Serna et al. [11] reported several modified chemical structures of aromatic polyisophthalamides, with the incorporation of different pendant groups, using the monomer 5-aminoisophthalic acid as a basis.[12,13] The amine group in this aminated monomer has attracted great attention for its potential to modify highly aromatic polyamides after the polycondensation reaction [4,14,15] or the possibility to use it as a basis to synthesize new monomers.[16–18] In the later approach, taking advantage of the Diels–Alder reaction between anthracene and maleic anhydride, it is possible to prepare bulky dibenzobarrelene groups,[19] this fact and the reactivity of the amine group in 5-aminoisophthalic acid could be combined with the anhydride to synthesize maleimides.[20–22]

In this work, the synthesis and properties of four novel polyamides containing dibenzobarrelene pendant groups are investigated. The dibenzobarrelene group has been described by the concept of geometrically designed roof-shaped molecules [23]; which presents a rigid, bulky, and three-dimensional moiety composed by a bicyclic aromatic structure. Similar structures reported in the literature produce polymers with high internal free volume where local cavities are formed due to the inability of such structures to pack efficiently.[24] To the best of our knowledge, so far there are no reports on the

---

*Corresponding author. Email: jlsantia@cicy.mx

synthesis and properties of aromatic polyamides bearing the dibenzobarrelene unit as a pendant group. Here, we report the synthesis of four aromatic polyamides by reacting 5-(9,10-dihydro-9,10-ethanoanthracene-11,12-di-carboximido) isophthalic acid, **DEAIA**, with four different aromatic diamines; 4,4′-(hexafluoroisopropylidene) dianiline, **6F**, 4,4′-methylenebis(2-isopropyl-6-methylaniline), **MIMA**, 2,3,5,6-tetramethyl-1,4-phenylenediamine, **TEMPD**, and 2,4,6-trimethyl-*m*-phenylenediamine, **TMPD**. Consequently, the detailed synthesis of the monomer DEAIA and its characterization as well as the physicochemical properties of the new aromatic polyamides and their gas permeability coefficients are reported.

2. Experiment

2.1. Materials

Anthracene, maleic anhydride (Fluka), xylene (Vetec), 5-aminoisophthalic acid, 4,4′-(hexafluoroisopropylidene)dianiline, **6F**, 4,4′-methylenebis(2-isopropyl-6-methylaniline), **MIMA** (Across Organics), 2,3,5,6-tetramethyl-1,4-phenylenediamine, **TEMPD**, 2,4,6-trimethyl-*m*-phenylenediamine, **TMPD**, *N*-methyl-2-pirrolidone, NMP, pyridine, Py, triphenyl phosphite, TPP, and anhydrous calcium chloride, $CaCl_2$ (Baker) which was dried under vacuum at 200 °C for 24 h before use. Methanol, MeOH (Baker), *N,N*-dimethylformamide, DMF, dimethyl sulfoxide, DMSO, *N,N*-dimethylacetamide, DMAc, 1,1,2,2-tetrachloroethane, TCE, chloroform, CCl_3, dichloromethane, DCM, tetrahydrofuran, THF. All chemical reactants and solvents were purchased from Sigma-Aldrich.

2.2. Synthesis of 9,10-dihydroanthracene-9,10-α,β-succinic anhydride (DASA)

A solution of anthracene (5.0 g, 28 mmol) and maleic anhydride (2.5 g, 25.5 mmol) in xylene (60 mL) was placed in a 100-mL flask and refluxed for 8 h. The reaction mixture was then cooled to room temperature. The precipitated solid was collected by filtering, thoroughly washed with xylene and diethyl ether, and then dried in vacuum to afford the compound DASA, which was recrystallized in xylene. Yield: 90.19%. Anal. Calc. for $C_{18}H_{12}O_3$ (276.28 g mol^{-1}): C, 78.25%; H, 4.38%; found: C, 78.36%; H, 4.46%. FTIR-KBr-pellets (cm^{-1}): v (=C–H) asymmetric 3075, v (=C–H) symmetric 3026, v (C–H) 2968, v (C=O) asymmetric 1862, v (C=O) symmetric 1782, v (C=C) 1463, v (C–O) asymmetric 1229, v (C–O) symmetric 1069. ^{1}H NMR: (600 MHz, ppm): 7.46 (2H, s), 7.32 (2H, s), 7.17 (4H, m), 4.86 (2H, s), 3.64 (2H, s).

2.3. Synthesis of 5-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido) isophthalic acid (DEAIA)

Into a round-bottom flask equipped with a condenser and a magnetic stirrer, 5.52 g (20 mmol) of DASA, 3.62 g (20 mmol) of 5-aminoisophthalic acid, and 50 mL of DMF were placed. The reaction mixture was refluxed for 8 h and after this time, it was cooled to room temperature. The resulting solution was carefully added into 500 mL of cold water. The white solid precipitated obtained was collected, thoroughly washed with water, and then dried under vacuum. The product DEAIA (yield: 80.71%) was purified by recrystallization in isopropanol. Anal. Calc. for $C_{26}H_{17}NO_6$ (439.41 g mol^{-1}): C, 71.07%; H, 3.9%; N, 3.19%; found: C, 70.83%; H, 4.02%; N, 3.25%. FTIR-KBr pellets (cm^{-1}): v (COOH) Key peak 3400–2500, v (C=O) asymmetric 1780, v (C=O) symmetric 1700, v (C=O) aromatic 1610, (C=C) 1460, v (C–N) 1380. ^{1}H NMR (600 MHz, ppm): 13.43 (s, br. COOH), 8.36 (1H, s), 7.51 (2H, s), 7.31 (4H, m), 7.18 (4H, m), 4.87 (2H, s), 3.42 (2H, s).

2.4. Synthesis of aromatic polyamides

The preparation of the novel polyamides was carried out following the traditional Yamazaki′s method.[25] The synthesis of polyamide **DEAIA-MIMA** provides a representative example of this methodology. A mixture of 5-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido) isophthalic acid (**DEAIA**, 0.88 g, 2.0 mmol), 4,4′-methylenen(2-isopropyl-6-methylaniline) (MIMA, 0.62 g, 2.0 mmol), anhydrous calcium chloride ($CaCl_2$, 0.63 g), triphenyl phosphite (TPP, 1.15 mL), pyridine (Py, 1.14 mL), and *N*-methyl-2-pirrolidone (NMP, 4.44 mL) was stirred and heated for 24 h at 110 °C under nitrogen atmosphere. After this time, the reaction mixture was poured into 1.0 L of methanol, and the stringy precipitated polymer was collected by filtration, washed thoroughly with methanol and hot water, and dried under vacuum at 120 °C for 24 h. The other polyamides DEAIA-TEMPD, DEAIA-TMPD, and DEAIA-6F were synthesized following the same steps.

DEAIA-MIMA. Yield: 1.27 g (86.8%); η_{inh} : 0.39 dL/g, FTIR-ATR (film, cm^{-1}): 3300, 2960, 2928, 2866, 1780, 1712, 1666, 1595, 1488, 1436, 1253, 1177, 758.

DEAIA-TEMPD, Yield: 1.03 g (98.6%); η_{inh} : 0.18 dL/g, FTIR-ATR (film, cm^{-1}): 3276, 2960, 2925, 2866, 1780, 1708, 1663, 1496, 1436, 1375, 1250, 1179, 1016, 758.

DEAIA-TMPD, Yield: 0.81 g (70.5%); η_{inh} : 0.25 dL/g, FTIR-ATR (film, cm^{-1}): 3300, 2960, 2934, 2866, 1780, 1711, 1663, 1594, 1494, 1441, 1375, 1250, 1177, 1024, 759.

DEAIA-6F, Yield: 1.44 g (95.1%); η_{inh} : 0.27 dL/g, FTIR-ATR (film, cm^{-1}): 3330, 2928, 1780, 1711, 1680, 1595, 1515, 1377, 1329, 1245, 1170, 966, 927, 827, 759.

2.5. Characterizations

Elemental analyses were carried out on a Carlo Erba EA1108 elemental analyzer (C, H, N). An FTIR spectrometer Thermo Nicolet Nexus 8700 was used to confirm both the monomer and polyamide synthesis. Samples were prepared using KBr pellets for intermediate and the diacid monomer; the spectra were acquired with 32 scans using a resolution of 4 cm^{-1} in the transmittance mode covering the wavenumber range of 4000–400 cm^{-1}. The polyamide films were analyzed on ATR accessory (Diamond Golden Gate) and the spectra were obtained in the region 4000–600 cm^{-1} with 32 scans using a resolution of 4 cm^{-1} in the transmittance mode. ^{1}H NMR spectra were recorded on a Varian VNMRS 600 MHz NMR instrument using DMSO-d_6 as solvent for intermediate and diacid monomer, DMF-d_7 as solvent for polyamides, and TMS as internal standard.

Solubility was determined by dissolving 5 mg of polymer in 1 mL of solvent at room temperature for 24 h. Gel permeation chromatography (GPC) analysis of the polyamides was performed on an HP Agilent 1100 HPLC system equipped with a differential refractive index detector. DMF was used as the mobile phase at a flow rate of 1 mL/min and the injection volume was 20 μL. Calibration was accomplished with polystyrene standards (Polymer Laboratories) and molecular weights ranged from 5.8×10^2 to 1.7×10^5. Two columns Zorbax PSM 60-S and Zorbax PSM 1000-S were used for calibration and molecular weight determination.

Wide-angle X-ray Diffraction measurements were performed on polyamide films using a SIEMENS 5000 X-ray diffractometer with CuKα radiation of wavelength 1.54 Å and operated at 40 kV and 15 mA. Data were collected in the angular range of 2–60° (2θ) with 1.0°/min scan increments.

Thermogravimetric analyses (TGA) were performed on a TGA-7 thermobalance (Perkin Elmer, Inc) under nitrogen atmosphere in the temperature range between 50 and 700 °C at 10 °C/min heating rate. Differential scanning calorimetry (DSC) analyses were performed on a Diamond (Perkin Elmer, Inc) differential scanning calorimeter, using 7.0 mg samples at 10 °C/min with a heating rate of 10 °C/min over the temperature range of 50–310 °C. The determination of the glass transition temperature (T_g) was carried out taking of the slope change from the base line for the second DSC heat scan.

3. Results and discussions

3.1. Synthesis and characterization of monomers

The elemental analysis, IR spectrum, and ^{1}H NMR supported the synthesis of the diacid monomer 5-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido) isophthalic acid (DEAIA), from the reaction between 5-aminoisophthalic acid and 9,10-dihydroanthracene-9,10-α,β-succinic anhydride, DASA, following the reaction scheme described in Figure 1. The intermediate DASA compound was obtained readily in good yield by the Diels–Alder reaction between anthracene and maleic anhydride. DASA was essential for the preparation of dibenzobarrelene units as pendant group, when reacted with 5-aminoisophthalic acid to give DEAIA. The amine group in the 5-aminoisophthalic acid is a very valuable synthetic moiety, which can be utilized to incorporate a number of different pendant groups, bearing interesting molecular as well as material properties.[18,26–29]

3.2. Synthesis of novel aromatic polyamides based on DEAIA

The aromatic polyamides were prepared by the reaction of DEAIA diacid with four structurally different aromatic diamines using NMP as solvent and triphenyl phosphite and pyridine as condensing agents [25] as shown schematically in Figure 2. Figure 3 shows the IR spectrum of the polyamide DEAIA-MIMA. The characteristic bands of the amide group (–CONH–) appeared at 3300 cm^{-1} and 1666 cm^{-1}, whereas a strong absorption band about 2960–2866 cm^{-1} was attributed to the CH stretching (CH, CH$_2$, and CH$_3$) presents in the diamine monomer. Moreover, the bands of the carbonyl groups corresponding to the imide group present in the diacid monomer appeared at 1780 cm^{-1} (asymmetric stretching of C=O) and 1712 cm^{-1} (symmetric stretching of C=O). The FTIR spectra of all other polyamides synthesized were comparable in the specific amine, methyl, methylene, and carboxylic bands present as well as the ones belonging to benzene and fluorine groups (see supporting information). ^{1}H NMR spectroscopy was used to confirm the chemical structure of the aromatic polyamide. The singlet at 10.00 ppm was attributed to the amide bond proton (–CONH–), which was present in all polyamides. As an example, the ^{1}H NMR spectrum of DEAIA-MIMA polyamide has been reproduced in Figure 4. These findings suggest that the expected novel polyamides had been synthesized as described in the scheme shown in Figure 2.

3.3. Properties of DEAIA-based aromatic polyamides

The solubility of the novel polyamides incorporating dibenzobarrelene units was evaluated dissolving 5.0 mg of
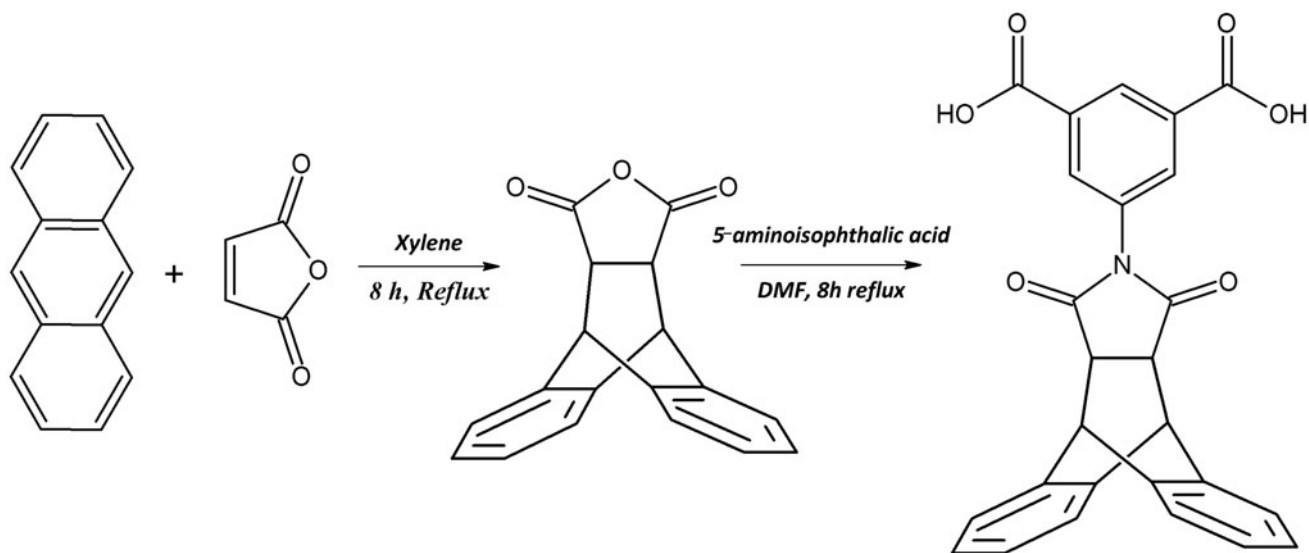
Figure 1. Scheme of synthesis of the diacid DEAIA.
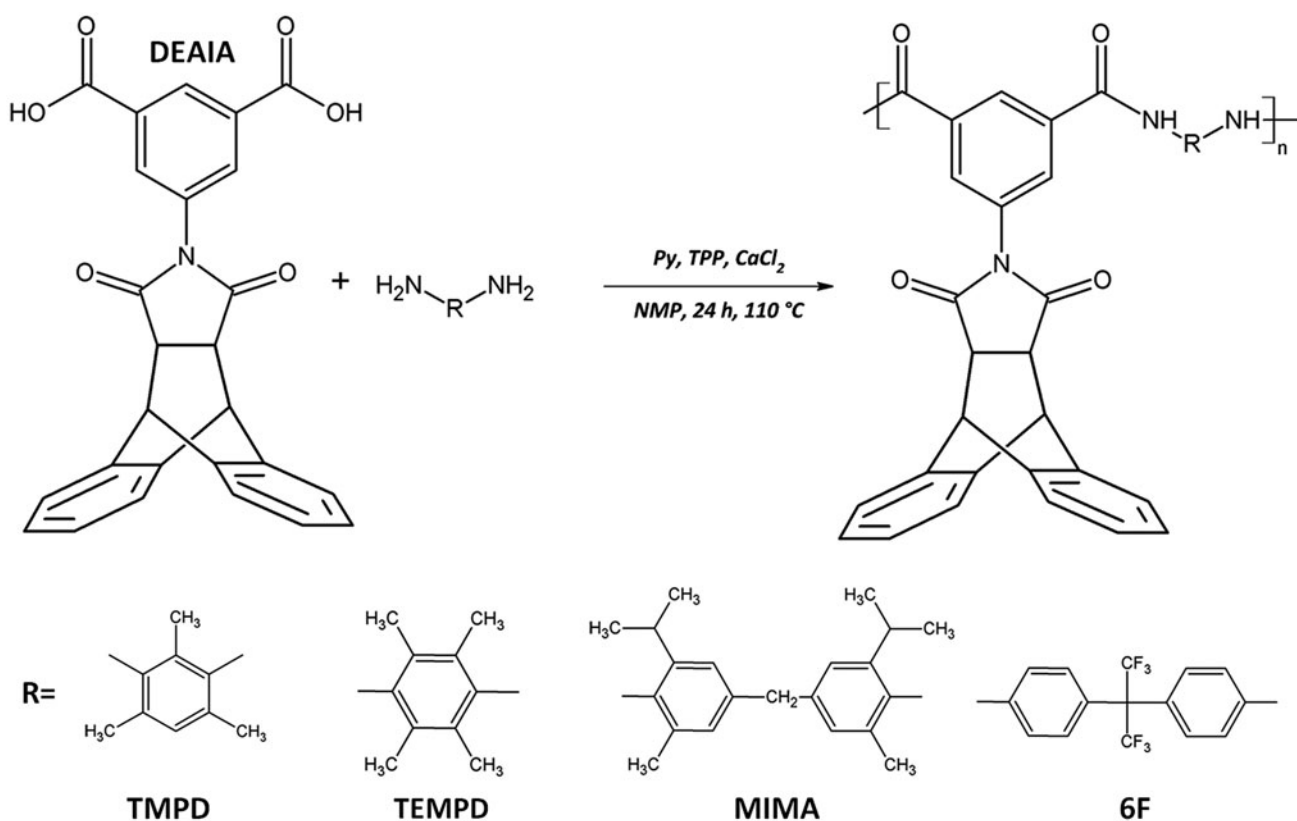
Figure 2. Scheme of synthesis of the DEAIA-based polyamides.

polymer in 1 mL of solvent (0.5% w/v) at room temperature. The four polyamides were readily dissolved in polar aprotic solvents such as NMP, DMAc, DMSO, and DMF; however, the polyamide DEAIA-MIMA exhibited better solubility than the others (Table 1). The enhanced solubility exhibited by DEAIA-MIMA is due the presence of *ortho* methyl and isopropyl substituents on the phenylene moieties bringing steric hindrance and
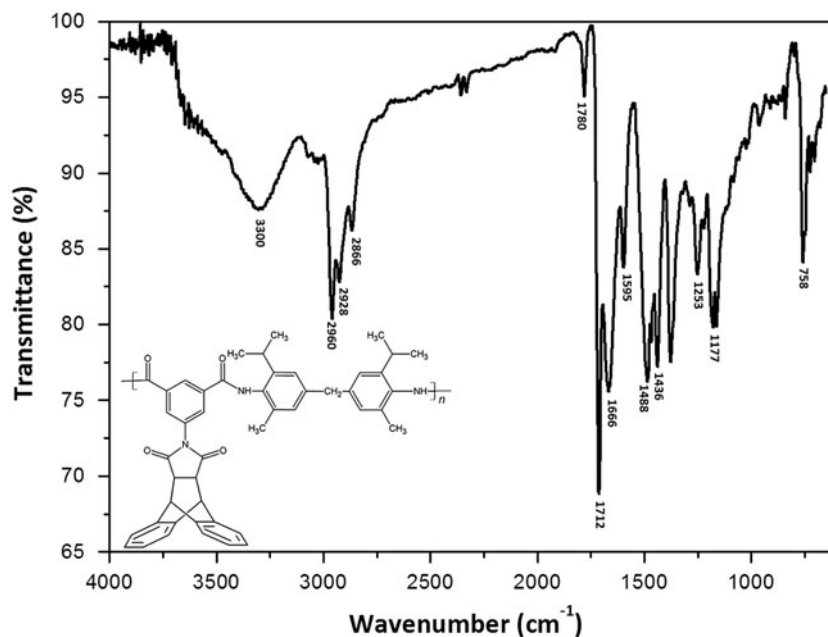
Figure 3.   FTIR spectrum of the polyamides DEAIA-MIMA.
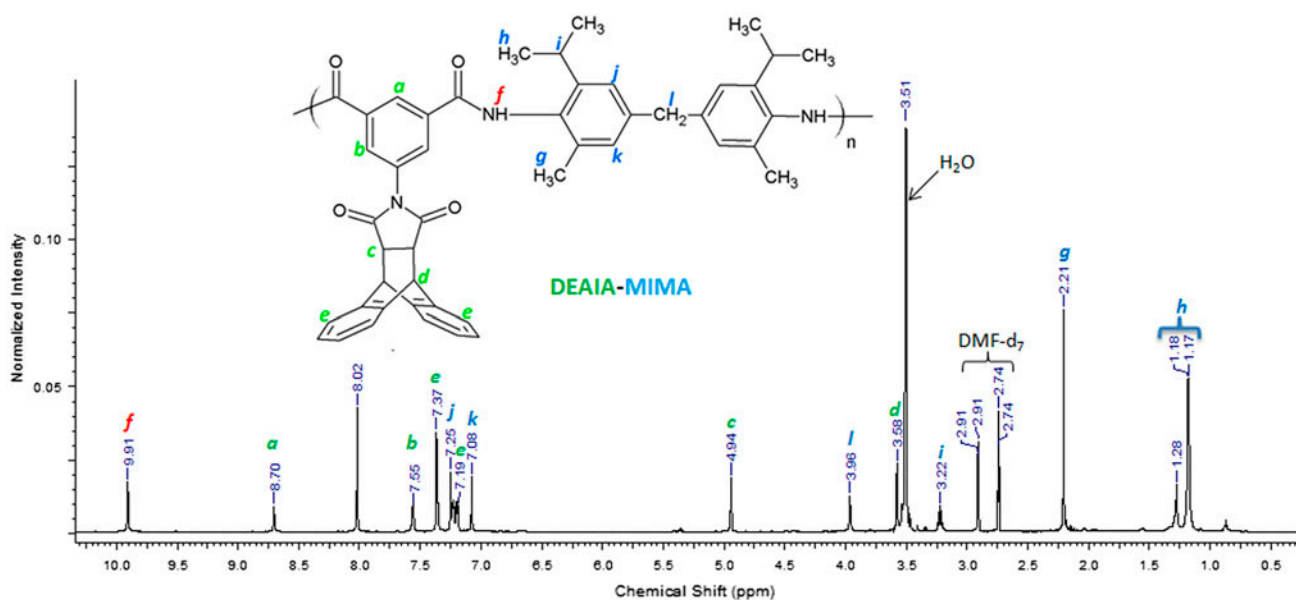
Figure 4.   ^{1}H NMR spectrum of the polyamides DEAIA-MIMA.

Table 1.   Solubility of aromatic polyamides with dibenzobarrelene pendant group.

Polyamide	NMP	DMAc	DMF	DMSO	DCE	TCE	CCl$_3$	THF
DEAIA-6F	+	+	+	+	−	−	−	−
DEAIA-MIMA	+	+	+	+	−	+	+	+
DEAIA-TMPD	+	+	+	+	−	−	−	−
DEAIA-TEMPD	+	+	+	+	−	−	−	−

Note: Solubility test: 5 mg/mL at room temperature. +, soluble; −, insoluble.

Figure 5.   Dense membrane of the polyamide DEAIA-MIMA.

Figure 6.   XRD patterns of the DEAIA-based polyamides.

providing an easier solvation pathway.[30] The solubility test suggests to utilize DMF as solvent for GPC analysis and to evaluate its ability to form cast-films by this solvent. Flexible and continuous polyamide films of DEAIA-MIMA (Figure 5), DEAIA-TEMPD, and DEAIA-6F were obtained by casting from a homogeneous polymer solution of them in DMF (10.0% p/v). However, the DEAIA-TMPD polyamide was not able to form continuous films. The number average molecular weight ($\overline{M}_n$), the weight average molecular weight ($\overline{M}_w$), and polydispersity index (PDI) of the aromatic polyamides bearing the dibenzobarrelene moiety are reported in Table 2. $\overline{M}_n$ are broadly similar among all polyamides with PDI around 3 with the exception of DEAIA-6F. The dibenzobarrelene polyamides that showed good film-forming ability were suitable for XRD analysis and considered to test its thermal properties as well as evaluation of gas permeability coefficient in dense membranes.

3.4.   X-ray diffraction analysis of the polyamides

Figure 6 displays X-ray diffraction (XRD) patterns of novel polyamides based on DEAIA monomer. The resulting patterns indicated that all polyamides are
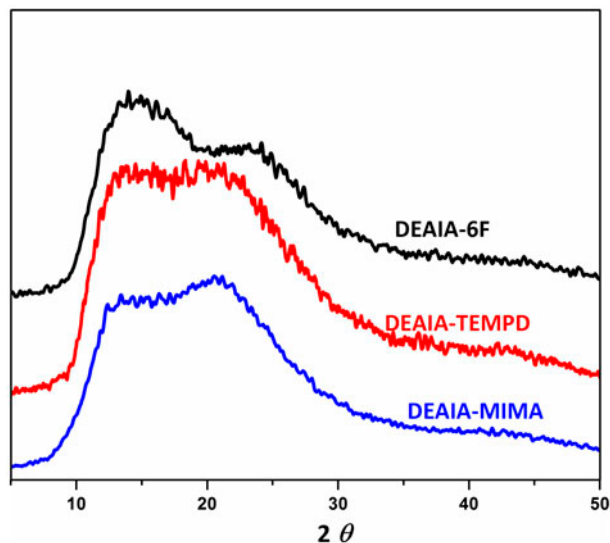
amorphous with two broad maxima. This behavior could be associated to the bulky dibenzobarrelene pendant groups, which significantly increase chain disorder and therefore, modify the chain packing.[31] Although all dibenzobarrelene polyamides showed a typical amorphous halo, it can be seen that in general two peaks were observed at about $2\theta = 14.0$ and $2\theta = 22$; using Bragg′s equation, the *d*-spacing was calculated at around 6.1 Å and 4.0 Å, respectively (Table 3). The polyamides DEAIA-TEMPD and DEAIA-MIMA showed similar diffraction patterns, while in the polyamide DEAIA-6F, the *d*-spacing peak at 6.0 have a higher intensity; this behavior is due to the fact that repeat unit contains –CF$_3$ as bulky pendant group, which was observed to give a similar pattern previously in similar type of polymers.[32]

3.5.   Thermal properties of the polyamides

DSC and TGA, were used to evaluate the thermal properties of the novel polyamides based on DEAIA, and the results are summarized in Table 4. Confirming the amorphous nature of the DEAIA polyamides in the DSC analysis no melting peaks (T_m) were observed in the range of 50–310 °C (see Figure 7). The glass transition temperature (T_g) showed for these dibenzobarrelene polyamides was in the range of 261–288 °C. Among these three polyamides, DEAIA-6F showed the highest T_g due to the presence of bulky –CF$_3$ groups which increases the rotational barrier and inhibits the local segmental motions making it more rigid.[33] TGA thermograms are shown in Figure 8 and decomposition data are reported in Table 4. All DEAIA polyamides were thermally stable up to 300 °C without significantly weight loss and they displayed char yields above 40% at 700 °C under N_2

Table 2.   GPC analysis of aromatic polyamides.

Polyamide	$M_n \times 10^3$ (g/mol)	$M_w \times 10^3$ (g/mol)	PDI
DEAIA-6F	25.6	144.0	5.6
DEAIA-MIMA	31.0	87.7	2.8
DEAIA-TMPD	19.0	53.0	2.7
DEAIA-TEMPD	19.2	30.8	1.6

Note: DMF as mobile phase and polystyrene as a standard.

Table 3.   X-ray scattering data of polyamides based on DEAIA monomer.

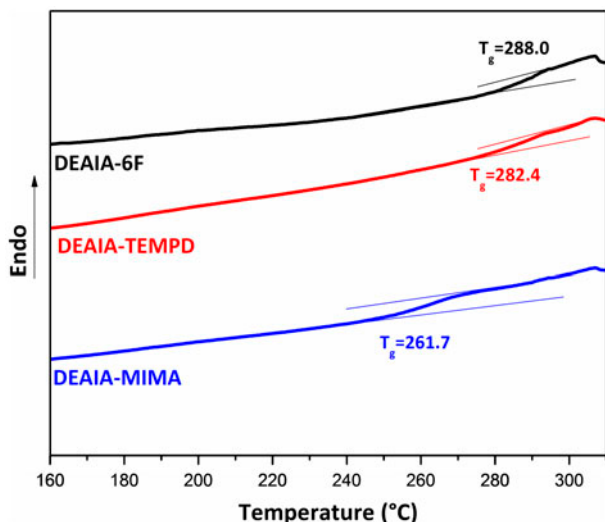| Polyamide	$2\theta_1$ (°)	$2\theta_2$ (°)	d_1-spacing (Å)	d_2-spacing (Å)
DEAIA-6F	14.6	24.04	6.0	3.7
DEAIA-TEMPD	14.4	20.88	6.1	4.2
DEAIA-MIMA	14.2	20.68	6.2	4.3

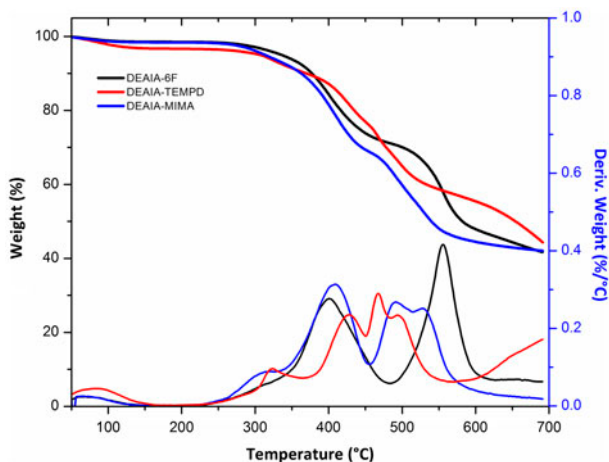Figure 7.   DSC thermograms of the DEAIA-based polyamides.

Figure 8.   TGA thermograms of the DEAIA-based polyamides.

atmosphere. Their temperature at 5% weight loss (T_5) is in the range of 306–334 °C, with the following stability order   DEAIA-TEMPD < DEAIA-MIMA < DEAIA-6F an indication that the first decomposition involves the elimination of –CH$_3$ and > CH$_2$ groups present in the polyamide backbone. Moreover, TGA thermograms of

these polyamides showed two degradation steps under nitrogen. The first weight loss appeared around 400 °C, which is attributed to the degradation of the dibenzobarrelene pendant group, whereas the second weight loss was in the range of 490–553 °C due to decomposition of main chain with the following stability order DEAIA-TEMPD < DEAIA-MIMA < DEAIA-6F.

3.6.   Gas permeability of the polyamide membranes

The facts described above, good solubility, ability to form continuous films, good thermal stability, and amorphous nature, suggest evaluating gas permeability coefficient in the DEAIA polyamides. Furthermore, to the best of our knowledge, gas transport properties of aromatic polyamides containing dibenzobarrelene pendant groups have not been reported in open literature. Pure gas permeability coefficients were measured at 35 °C and 2.0 atm for He, O_2, N_2, CH_4, and CO_2, using the constant-volume variable-pressure method. Their values of permeability coefficients are reported in Table 5. The gas permeability order was, in all cases, $P_{He} > P_{CO_2} > P_{O_2} > P_{N_2} > P_{CH_4}$, which correlate with the kinetic diameters reported for each gas molecule (He, 2.6 Å; CO_2, 3.3 Å; O_2, 3.46 Å; N_2, 3.64 Å; CH_4, 3.8 Å).[34] This tendency is observed in most glassy polymer membranes.[35] For some gases (He, CO_2, and O_2), the permeability coefficient values in dibenzobarrelene polyamide membranes followed the order DEAIA-TEMPD < DEAIA-MIMA < DEAIA-6F. To visualize the effect on gas permeability coefficients of bearing a dibenzobarrelene group in aromatic polyamides, a comparison has been made with the gas permeability coefficient for polyamide HFA-ISO, using the data obtained from the literature, see Table 5.[33] As it is shown, the incorporation of the dibenzobarrelene group increases the permeability coefficient, for all five gases. This result confirmed that pendant dibenzobarrelene groups inhibit chain packing and improve the permeability coefficients on aromatic polyamides. On the other hand, ideal selectivity obtained as the ratio of pure gas permeability coefficients, for gas pairs CO_2/N_2 and CO_2/CH_4, shows a decrease for all dibenzobarrelene polyamides, which is consistent with the observed trade-off between gas permeability and ideal selectivity reported in polymeric membranes [36]; however, the ideal selectivity of the

Table 4. Thermal properties of aromatic polyamides.

Polyamide	T_g (°C)	$T_{5\%}$ (°C)	$T_{1\ max}$ (°C)	$T_{2\ max}$ (°C)	Char yield (%)
DEAIA-6F	288.0	334.5	404.1	553.6	41.0
DEAIAI-TEMPD	282.4	306.6	431.4	465.2	44.3
DEAIA-MIMA	261.7	313.8	406.9	490.5	42.0

Table 5. Gas permeability coefficients of novel aromatic polyamides with dibenzobarrelene pendant groups.

Polyamide	Permeability (Barrer)					Selectivity (α)		
	He	CO_2	O_2	N_2	CH_4	CO_2/CH_4	CO_2/N_2	CO_2/O_2
DEAIA-TEMPD	12.09	2.96	0.82	0.35	0.33	8.9	8.4	3.6
DEAIA-MIMA	19.13	6.94	2.00	1.00	0.87	8.0	6.9	3.5
DEAIA-6F	30.18	9.66	2.38	0.71	0.65	14.9	13.6	4.0
HFA-ISO [33]	34.5	6.5	1.68	0.25	0.13	50.0	26.0	3.9

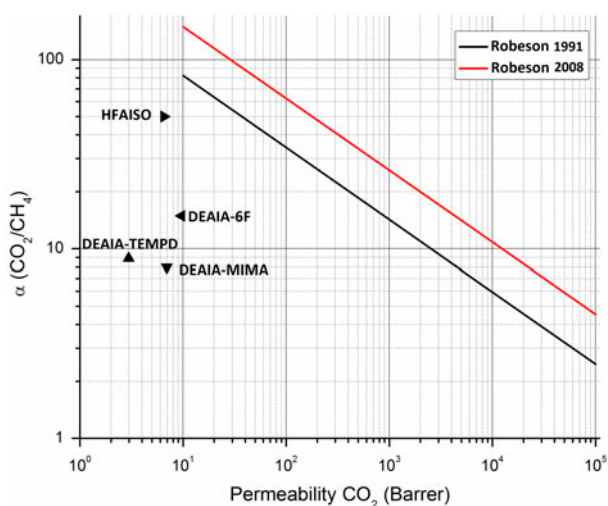Note: 1 Barrer: 1×10^{-10} cm^3(STP) cm cm^{-2}s cm Hg^{-1}.

Figure 9. Trade-off plot for CO_2/CH_4 gas pair defined by Robeson.[36,37]

CO_2/O_2 gas pair does not changes significantly. The performance of DEAIA-based polyamides for CO_2/CH_4 gas pair in a Robeson plot, where the upper bound limits are shown, is compared with the performance of HFAISO membrane reported elsewhere [33] in Figure 9.[36,37] Here, in the plot of the DEAIA-based polyamides series, the comparison is favorable to the DEAIA-6F which has higher CO_2 permeability coefficient and it is closer to the upper bound. However, the introduction of dibenzobarrelene as pendant groups increases the permeability coefficient but it follows the usual trade-off as the ideal selectivity decreases, when it is compared with HFAISO membrane which is less permeable to CO_2 but presents a higher selectivity.

3.7. Structural modification

In order to take advantage of the properties that have been reported in the aromatic polyamide HFAISO,[33] efforts toward enhancing both their solubility in organic solvents and gas permeability coefficient through the incorporation of pendant groups on the diacid monomer are shown in Figure 8. Liu et al. [15] reported that incorporation of maleimide functional group on aromatic polyisophthalamide, HFAISO, provides an opportunity to increase the solubility of aromatic polyamides in polar aprotic solvents; however, the membrane preparation as well as other properties such as T_g and gas permeability coefficients were not reported. For comparison, the membrane of HFAISO was casted utilizing DMAc (*boiling point:* 165 °C) as solvent, and their gas permeability coefficients were reported. On the other hand, the aromatic polyamide, DEAIA-6F, synthesized in this study was soluble in polar aprotic solvents, and its membrane was elaborated using DMF (*boiling point*: 153 °C) as solvent. The result of this modification allowed a better performance by maintaining thermal properties plus an increase in CO_2 gas permeability coefficient of almost 50% on the polyamide DEAIA-6F in comparison with membrane HFAISO (T_g: 294 °C, T_d: 492 °C, $P_{CO_2} = 6.5$ Barrer). These results confirmed that incorporation of bulky dibenzobarrelene pendant groups increases the gas permeability coefficients while maintain the advantages of high T_g and increasing solubility in organic polar aprotic solvents. This behavior is due to the fact that the dibenzobarrelene group presents a higher van der Waals volume (see Figure 10) as compared to the Hydrogen and maleimide groups, as calculated using the COMPASS force field in Materials Studio 7.0 (Accelrys Software, Inc.)
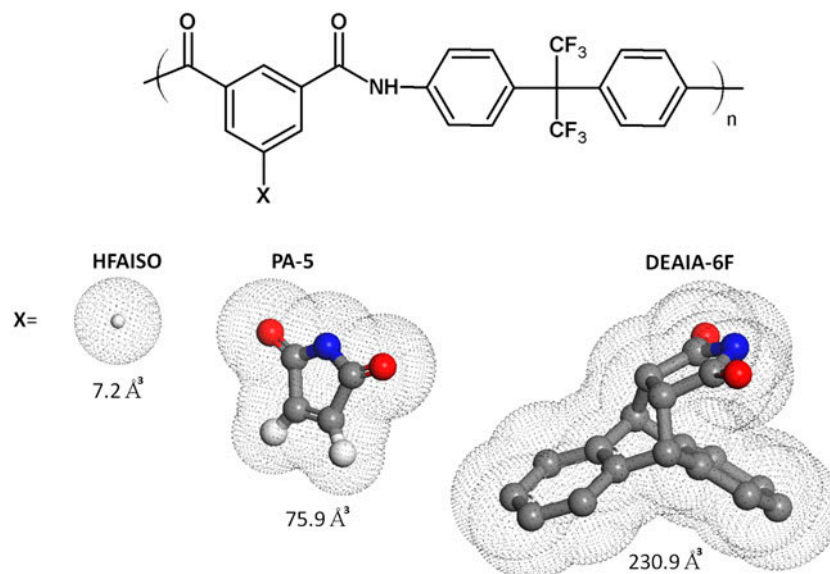
Figure 10. Sequence of chemical modification of the polyisophthalamides in the position 5 from isophthalic acid. (a) HFAISO,[33] (b) PA-5,[15] and (c) DEAIA-6F (this study).

4. Conclusions

Four novel aromatic polyamides containing dibenzobarrelene pendant groups were successfully synthesized using the monomers 5-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido) isophthalic acid (DEAIA) and four different aromatic diamines. Incorporation of the dibenzobarrelene pendant group resulted in aromatic polyamides with good solubility in polar aprotic solvents. Polyamides bearing dibenzobarrelene pendant groups showed T_g above 250 °C and onset of thermal decomposition above 300 °C. This chemical modification was especially useful to achieve an increase in the gas permeability coefficients of the membranes obtained by solution casting, without modify significantly its thermal stability. The best result was achieved for DEAIA-6F. It showed higher permeability coefficient for CO_2 (9.66 Barrer) and it maintained the ideal selectivity for carbon dioxide with respect to oxygen ($CO_2/O_2 = 4$) in comparison with the values reported for polyisophthalamide HFAISO.

Acknowledgments

Funding

References

[1] Banerjee S, Maji S High performance polymers and engineering plastics. In: Mittal V editor. Chapter 5, High-performance processable aromatic polyamides. Hoboken (NJ): Wiley, Scrivener Publishing; 2011, p. 111–166.

[2] Ayala D, Lozano AE, De Abajo J, De La Campa JG. Synthesis and characterization of novel polyimides with bulky pendant groups. J. Polym. Sci. Part A. Polym. Chem. 1999;37:805–814.

[3] Bailey GC, Swager TM. Masked Michael acceptor in poly (phenyleneethynlene) for facile conjugation. Macromolecules. 2006;39:2815–2818.

[4] Trigo-López M, Pablos JL, García FC, Serna F, García JM. Functional aramides: aromatic polyamides with reactive azido and amido groups in the pendant structure. J. Polym. Sci. Part A. Polym. Chem. 2014;52:1469–1477.

[5] Huang W, Yin J. Synthesis, photophysical properties, and electron paramagnetic resonance studies of new poly(bis-benzothiazole)s containing bulky pendant groups. Polym. Eng. Sci. 2007;47:429–438.

[6] Dai Y, Guiver MD, Robertson GP, Bilodeau F, Kang YS, Lee KJ, Jho JK, Won J. Modified polysulfones 5: synthesis and characterization of tetramethyl polysulfones containing trimethylsilyl groups and their gas transport properties. Polymer. 2002;43:5369–5378.

[7] Jin HS, Chang JH, Kim JC. Synthesis and characterization of colorless polyimide nanocomposite films containing pendant trifluoromethyl groups. Macromol. Res. 2008;16:503–509.

[8] García JM, García FC, Serna F, De la Peña JL. High-performance aromatic polyamides. Prog. Polym. Sci. 2010;35:623–686.

[9] Carretero P, Sandín R, Molina S, Martinez A, De la Campa JG, Lozano AE, De Abajo J. Linear polyisophthalamides from the trifunctional monomer 5-hydroxyisophthalic acid. A convenient approach towards functionalized aromatic polymers. Eur. Polym. J. 2011;47:1054–1064.

[10] Carja ID, Hamciuc C, Hamciuc E, Vlad-Bubulac T, Lisa G. New highly thermostable aromatic polyamides with pendant phthalonitrile groups. Macromol. Res. 2012;20:1011–1020.

[11] Serna F, García F, De la Peña JL, García JM. Aromatic polyisophthalamides with mononitro, dinitro and trinitro-iminobenzoyl pendant groups. High Perform. Polym. 2008;20:19–37.

[12] Diakoumakos CD, Mikroyannidis JA. Modified polyisophthalamides bearing furamido pendant groups. Eur. Polym. J. 1995;31:761–767.

[13] Spiliopoulos IK, Mikroyannidis JA. Modified polyisophthalamides bearing pendent benzoyamino and/or (phenylamino)carbonyl groups. J. Polym. Sci. Part A. Polym. Chem. 1996;34:1685–1691.

[14] Galvin CJ, Genzer J. Applications of surface-grafted macromolecules derived from post-polymerization modification reactions. Prog. Polym. Sci. 2012;37:871–906.

[15] Liu YL, Li SH, Lee HC, Hsu KY. Selective reactivity of aromatic amines toward 5-maleimidoisophthalic acid for preparation of polyamides bearing N-phenylmaleimide moieties. React. Funct. Polym. 2006;66:924–930.

[16] Liaw DJ, Hsu PN, Chen JJ, Liaw BY, Hwang CY. Synthesis and characterization of new soluble polyamides containing phthalaimide pendant group. J. Polym. Sci. Part A. Polym. Chem. 2001;39:1557–1563.

[17] Hassan HH, Elhusseiny AF, Elkony YMA, Mansour ESME. Synthesis and characterization of thermally stable aromatic polyamides and poly(1,3,4-oxadiazole-amide)s nanoparticles containing pendant substituted bezamides. Chem. Cent. J. 2013;7:13.

[18] Espeso JF, Lozano AE, de la Campa JG, García-Yoldi I, de Abajo J. Synthesis and properties of new aromatic polyisophthalamides with adamantyl pendant group. J. Polym. Sci. Part A. Polym. Chem. 2010;48:1743–1751.

[19] Jones S, Wilson I. Synthesis of substituted 3-furan-2(5H)-ones via anthracene Diels–Alder sequence. Tetrahedron Lett. 2006;47:4377–4380.

[20] Smet M, Corens D, Van Meervelt L, Dehaen W. Synthesis of the formal Diels–Alder adducts of N-substituted dehydromaleimides and anthracene. Molecules. 2000;5:179–188.

[21] Shanes D, Favier I, Saffon N, Teuma E, Gómez M. Stereospecific synthesis of hydroanthracene-dicarboximides. Tetrahedron Lett. 2008;49:6720–6723.

[22] Khalil AM, Berghot MA, Gouda MA. Synthesis and study of some new 1,3-isoindoledione derivatives as potential antibacterial agents. Eur. J. Med. Chem. 2010;45:1552–1559.

[23] Weber E, Csoeregh I, Ahrendt J, Finge S, Czugler M. Design of roof-shaped clathrate hosts. Inclusion properties and x-ray crystal structures of a free host and of inclusion compounds with 1-butenol and DMF. J. Org. Chem. 1988;53:5831–5839.

[24] Chen C-F, Ma Y-X. Iptycenes chemistry. Berlin Heidelberg: Springer-Verlag; 2013.

[25] Yamazaki N, Matsumoto M, Higashi F. Studies on reactions of the N-phosphonium salts of pyridines. XIV. Wholly aromatic polyamides by the direct polycondensation reaction by using phosphites in the presence of metals salt. J. Polym. Sci. Polym. Chem. Ed. 1975;13:1373–1380.

[26] Matsunaga D, Tamaki T, Ichimura K. Azo-pendant polyamides which have the potential to photoalign chromonic lyotropic liquid crytals. J. Mater. Chem. 2003;13:1558–1564.

[27] Zarchi MAK, Tayefi M, Tirgir F, Sabzalian MR. An environmentally compatible synthesis of polyesters derived from 5-(2-phthalimidoethanesulfonamido) isophthalic acid as a novel diacid monomer. J. Appl. Polym. Sci. 2011;121:2573–2583.

[28] Wang H-N, Meng X, Qin C, Wang X-L, Yang G-S, Su Z-M. A series of pillar-layer metal-organic frameworks based on 5-aminoisophthalic acid and 4,4′-bipyridine. Dalton Trans. 2012;41:1047–1053.

[29] Chandrasekhar V, Mohapatra C, Metre R. Reactions of (E)-5-(pyridine-4-yl-methyleneamino)isophthalic acid (LH₂) with triorganotin oxides and -chloride. Formation of one-dimensional- and two-dimensional-coordination polymers. Cryst. Growth Des. 2013;13:4607–4614.

[30] Huertas RM, Maya EM, de Abajo J, de la Campa JG. Effect of 3,5-diaminobenzoic acid content, casting solvent, and physical aging on gas permeation properties of copolyimides containing pendant acid groups. Macromol. Res. 2011;19:797–808.

[31] Bera D, Bandyopadhyay P, Ghosh S, Banerjee S. Gas transport properties of aromatic polyamides containing adamantly moiety. J. Membr. Sci. 2014;453:175–191.

[32] Vaughn J, Koros WJ. Effect of the amide bond diamine structure on the CO₂, H₂S, and CH₄ transport properties of a series of novel 6FDA-Based polyamide-imides for natural gas purification. Macromolecules. 2012;45:7036–7049.

[33] Carrera-Figueiras C, Aguilar-Vega M. Gas permeability and selectivity of hexafluoroisopropylidene aromatic isophthalic copolyamides. J. Polym. Sci. Part B. Polym. Phys. 2005;43:2625–2638.

[34] Breck DW. Zeolite molecular sieve: structure, chemistry, and use. New York, NY: Wiley; 1974.

[35] Espeso J, Lozano AE, de la Campa JG, de Abajo J. Effect of substituents on the permeation properties of polyamide membranes. J. Membr. Sci. 2006;280:659–665.

[36] Robeson LM. Correlation of separation factor versus permeability for polymeric membranes. J. Membr. Sci. 1991;62:165–185.

[37] Robeson LM. The upper bound revisited. J. Membr. Sci. 2008;320:390–400.