

**SYNTHESIS AND GAS PERMEATION PROPERTIES
OF RING-OPENED POLYNORBORNENE
DICARBOXIMIDES BEARING
2,2,6,6-TETRAMETHYLPYPERIDYL
MOIETIES**

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Abstract

The *N*-2,2,6,6-tetramethylpiperidyl-norbornene-5,6-dicarboximide (**2a**), *N*-4-hydroxy-phenyl-norbornene-5,6-dicarboximide (**2b**), and *N*-pentafluorophenyl-norbornene-5,6-dicarboximide (**2c**) mixtures of *exo* and *endo* monomers were synthesized and polymerized via ring opening metathesis polymerization (ROMP) using bis(tricyclohexylphosphine) benzylidene ruthenium (IV) dichloride (**I**) and tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidene] ruthenium dichloride (**II**) to produce the corresponding polynorbornene dicarboximides **PTMPiNDI**, **PHPhNDI**, and **PPFPhNDI**, respectively. The transport of five gases He, N₂, O₂, CO₂, and CH₄ across membranes prepared from these polynorbornenes were determined at 35°C by using a constant volume permeation cell. Gas permeability, diffusion, and solubility coefficients of **PTMPiNDI** classify it as a low permeability polymer for oxygen and carbon dioxide with possibilities of use in packaging applications. It was also found that gas permeation is lower in **PTMPiNDI** due to a lower fractional free volume (FFV), which difficulties the diffusion through it as compared to **PHPhNDI** and **PPFPhNDI** that present more open structures. The permeability coefficients for all gases in the fluorine-containing **PPFPhNDI** membrane are much more larger than those in the non-fluorinated **PHPhNDI** and **PTMPiNDI** membranes. The sorption process and not the diffusive step is responsible for this increase in the permeability of the **PPFPhNDI** membrane. A molecular dynamics simulation of each polynorbornene was performed to estimate the density value. The results are in good agreement with the experimentally measured densities and allow to corroborate FFV determinations.

1. Introduction

The use of polymeric materials for preparation of membranes has received widespread attention for the separation of gases and liquids [9]; thus, there is an interest in different polymeric materials that can be used for preparation of membranes. For example, in gas separation processes, the ideal membrane material should show large permeability

to the gases as well as a high selectivity for gas separation. Furthermore, the polymeric material should be easy to process and form films with good mechanical and physical properties [10]. Polynorbornenes with different substituent in the cyclic group have been studied and their gas transport properties reported [2, 4, 7]. In particular, gas permeability for polynorbornene dicarboximide groups with different substituents in the *N*-alkyl or *N*-phenyl norbornene dicarboximide has been reported [5, 8, 11, 14]. The latter materials show good thermal and mechanical properties as well as gas permeabilities and gas separation factors that depend strongly on the substituent nature.

For improving the permeability of membranes based on this type of polymers, fluorocarbon moieties, characterized by having very weak intermolecular attractive forces, have been introduced in the substituted dicarboximide group moieties thus increasing the free volume and raising substantially the permeability of the membranes with the fluorine content at expense of only a slight decrease in permselectivity [15, 16].

Taking into account that, the chemical structure of ring-opened polynorbornenes can be easily modified in order to prepare a series homologous functionalized polymers, in here we report the synthesis of polynorbornenes with lateral imide groups that contain pendant piperidyl, hydroxyphenyl, and pentafluorophenyl moieties, respectively, with the aim of finding out how slight differences in the chemical backbone affect the gas permeability process in membranes. Hence, thermal, mechanical, and gas transport properties of these polynorbornenes were determined and compared to those found for a perfluorinated one measured at the same conditions. Gas transport properties as a function of pressure for the piperidyl-containing polynorbornene are also reported.

2. Experimental Section

2.1. Techniques

^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Varian spectrometer at 300, 75, and 300MHz, respectively, in deuterated

chloroform (CDCl_3). Tetramethylsilane (TMS) and trifluoroacetic acid (TFA) were used as internal standards. FT-IR spectra were obtained on a Thermo Nicolet 6700 spectrometer. Glass transition temperature, T_g , was determined in a DSC-7 Perkin Elmer Inc., at scanning rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The sample was encapsulated in a standard aluminum DSC pan. The sample was run twice in the temperature range 30°C to 300°C under a nitrogen atmosphere. Onset of decomposition temperature, T_d , was determined by using thermogravimetric analysis, TGA, which was performed at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere with a DuPont 2100 instrument. Mechanical properties under tension, elastic modulus (E), and stress (σ), were measured in a universal mechanical testing machine Instron 1125-5500R using a 50Kg cell at a crosshead speed of $10\text{mm}/\text{min}$ according to the method ASTM D1708 in film samples of 0.5mm of thickness at room temperature. Molecular weights and molecular weight distributions were determined with reference to polystyrene standards on a Waters 2695 ALLIANCE GPC at 35°C in tetrahydrofuran using a universal column and a flow rate of 0.5mL min^{-1} .

Films of poly(*N*-2,2,6,6-tetramethylpiperidyl-*exo-endo*-norbornene-5,6-dicarboximide), **PTMPiNDI** and poly(*N*-4-hydroxyphenyl-*exo-endo*-norbornene-5,6-dicarboximide), **PHPhNDI**, were cast from solution of each polymer in chloroform at room temperature and they were left standing overnight in the same solvent atmosphere at room temperature. Films of the perfluorinated poly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide) **PPFPhNDI**, were cast from chloroform under the same conditions. Later, the films were dried in a vacuum oven at 80°C to completely eliminate the solvent. The thickness of the films used for the determination of thermal and gas transport properties were between 0.04mm and 0.07mm . Density of the polynorbornene dicarboximides was measured by the density gradient column method at 23°C . The gradient was established using $\text{Ca}(\text{NO}_3)_2$ solutions and glass

standards of known density. Dynamic mechanical analysis, damping factors as a function of temperature for **PTMPiNDI**, **PHPhNDI**, and **PPFPhNDI** was performed in a DMA-7 (Perking Elmer Inc.) between 40°C and 300°C at a scanning rate of 5°C/min under nitrogen atmosphere. The test coupons for DMA measurements were cut from the as cast films and they were dried at 100°C under vacuum in the form of strips with dimensions $15 \times 3 \times 0.04$ to 0.07mm.

Gas transport properties were measured in a permeation cell of the constant volume type as described elsewhere [5]. Gas permeability coefficients, P , were determined under steady state conditions, using a transient permeation method for pure gases He, O₂, N₂, CH₄, and CO₂ measured at 35°C between 2 and 10atm upstream pressure. From the same transient permeation experiment, the apparent diffusion coefficients, D , were calculated by using the time lag method for CO₂, O₂, N₂, and CH₄ under the same conditions. Apparent solubility coefficients, S , were calculated as the ratio between permeability and apparent diffusion coefficients.

Molecular dynamic simulations for the three polynorbornenes were performed on a HP-Z400 workstation by using Material Studio (version 5.5) software package from Accelrys Inc.. The simulation of densities was carried out by using the DISCOVER package employing the COMPASS force field. The amorphous cell module was employed to fold one polynorbornene chain (with and 20 repeating units) into a periodic unit cell at 298K to generate 10 low density configurations (0.02g/cm^3). Then, the configuration that had lowest energy was selected to apply an energy minimization using the method of steepest descent followed by the conjugate gradient method. After minimization, the molecular dynamic (MD) simulations were carried out using NVT (600 and 298K) and NPT (1000, 5000, 30000, and 1 bar at 50-ps and 298K) protocol described by Karayiannis et al. [6] in order to obtain an optimized polymer cell. In the last step, a total of 1000-ps NPT MD simulation at 1.0 bar and 298K was performed to check the course of the density.

2.2. Reagents

Exo(90%)-*endo*(10%) mixture of norbornene-5,6-dicarboxylic anhydride (**NDA**) was prepared via Diels-Alder condensation of cyclopentadiene and maleic anhydride according to literature [13]. 2,2,6,6-tetramethylpiperidylamine, 4-hydroxyaniline, 2,3,4,5,6-pentafluoroaniline, and other chemicals were purchased from Aldrich Chemical Co.. 1,2-dichloroethane and dichloromethane were dried over anhydrous calcium chloride and distilled over CaH₂. Bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride (**I**) and tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidene] ruthenium dichloride (**II**) were purchased from Aldrich Chemical Co. and used as received.

2.3. Synthesis of monomers

2.3.1. Synthesis and characterization of *exo*(90%)-*endo*(10%) monomer mixture of *N*-2,2,6,6-tetramethylpiperidyl-norbornene-5,6-dicarboximide (**2a**)

NDA (5.0g, 30.5mmol) was dissolved in 50mL of dichloromethane. An amount of 4.75g (30.4mmol) of 2,2,6,6-tetramethylpiperidylamine in 5mL of dichloromethane was added dropwise to the stirred solution of **NDA**. The reaction was maintained at reflux for 2h and then cooled to room temperature. The precipitate was recovered by filtration and dried to give 9.4g of amic acid **1a**. The obtained amic acid **1a** (9.4g, 29.3mmol), anhydrous sodium acetate (2.0g, 24.3mmol) and acetic anhydride (29.0g, 284.3mmol) were heated at 60-70°C for 24h and then cooled. The solid which is crystallized out on cooling was filtered, washed several times with cold water, and dried in a vacuum oven at 50°C overnight. A mixture of *exo*(90%) and *endo*(10%) monomers **2a** (Scheme 1) was obtained after two recrystallizations from hexane: yield = 89%.

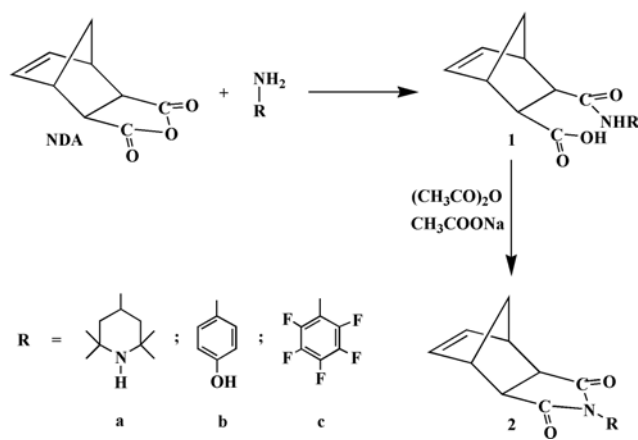
m.p. = 193-195°C.

FT-IR (KBr): ν 3242 (N-H str), 2968 (C=C-H asym str), 1765 (C=O), 1697 (C=O), 1631 (C=C str), 1474 (C-H), 1389 (C-N), 1319, 1292 (C=C-H), 1207, 1159, 1127, 1090, 1044, 979, 915, 846 (C-C str), 741, 683, 625 cm^{-1} .

^1H NMR (300MHz, CDCl_3 , ppm): δ 6.33 (2H, s), 4.39-4.28 (1H, m), 3.39 (2H, m), 3.22 (2H, m), 2.48 (2H, t), 2.26 (2H, s), 1.75-1.71 (1H, m), 1.58-1.46 (14H, m).

^{13}C NMR (75MHz, CDCl_3 , ppm): δ 177.7, 174.2, 134.3, 57.9, 51.9, 45.5, 45.0, 43.8, 42.7, 33.1, 29.8, 27.8.

Anal. Calcd. (%) for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{N}_2$ (302): C, 71.52; H, 8.60; O, 10.59; N, 9.27; Found C, 72.02; H, 8.35; N, 9.64.



Scheme 1. Synthesis route of monomers **2a**, **2b**, and **2c**.

2.3.2. Synthesis and characterization of *exo*(90%)-*endo*(10%) monomer mixture of *N*-4-hydroxyphenyl-norbornene-5,6-dicarboximide (**2b**)

NDA (5.0g, 30.5mmol) was dissolved in 20mL of dichloromethane. An amount of 3.32g (30.4mmol) of 4-hydroxyaniline in 10mL of dichloromethane was added dropwise to the stirred solution of **NDA**. The reaction was maintained at reflux for 2h and then cooled to room temperature. The precipitate was recovered by filtration and dried to give

8.1g of amic acid **1b**. The obtained amic acid **1b** (8.1g, 29.6mmol), anhydrous sodium acetate (1.7g, 20.7mmol) and acetic anhydride (25.0g, 245mmol) were heated at 60-70°C for 12h and then cooled. The solid which is crystallized out on cooling was filtered, washed several times with cold water, and dried in a vacuum oven at 50°C overnight. A mixture of *exo*(90%) and *endo*(10%) monomers **2b** (Scheme 1) was obtained after two recrystallizations from methanol: yield = 92%.

m.p. = 177-179°C.

FT-IR (KBr): ν 3068 (C=C-H asym str), 2997, 1761 (C=O), 1702 (C=O), 1631 (C=C str), 1510, 1503, 1382 (C-N), 1288 (C=C-H), 1231, 1188, 907cm⁻¹.

¹H NMR (300MHz, CDCl₃, ppm): δ 7.33-7.16 (4H, m), 6.34 (2H, s), 3.39 (2H, s), 2.85 (2H, s), 2.29 (1H, s), 1.79-1.42 (2H, m).

¹³C NMR (75MHz, CDCl₃, ppm): δ 176.7, 168.8, 150.2, 137.9, 134.5, 129.1, 127.2, 122.1, 52.1, 47.7, 45.7, 42.8.

Anal. Calcd. (%) for C₁₅H₁₃O₃N (255): C, 70.58; H, 5.09; O, 18.82; N, 5.49; Found C, 71.08; H, 4.97; N, 5.81.

2.3.3. Synthesis and characterization of *exo*(90%)-*endo*(10%) monomer mixture of *N*-pentafluorophenyl-norbornene-5,6-dicarboximide (**2c**)

Monomer **2c** was synthesized by reacting 2,3,4,5,6-pentafluoroaniline with **NDA** to the corresponding amic acid, which was cyclized to imide using acetic anhydride as dehydrating agent (Scheme 1) [16]. **NDA** (5.0g, 30.5mmol) was dissolved in 40mL of CH₂Cl₂. An amount of 5.58g (30.5mmol) of 2,3,4,5,6-pentafluoroaniline in 20mL of CH₂Cl₂ was added dropwise to the stirred solution of **NDA**. The mixture was boiled for 3h and then cooled to room temperature. Solvent removal gave a white solid of amic acid. The obtained amic acid **1c** (10.3g, 29.7mmol), anhydrous sodium acetate (2.50g, 30.47mmol) and acetic anhydride (21.0g, 205.7mmol) were heated at 80°C for 24h. The mixture was washed with

dilute HCl and extracted into ether. The ether layer was washed with dilute HCl, saturated NaHCO₃ and H₂O. Solvent was evaporated and a mixture of *exo*(90%) and *endo*(10%) monomers **2c** was obtained after twice recrystallization from hexane and dried in a vacuum oven at 50°C overnight: yield = 75%.

m.p. = 112-113°C.

FT-IR (KBr): ν 3076, 2949 (C-H asym str), 2880 (C-H sym str), 1782 (C=O), 1724, 1644 (C=C str), 1519, 1356, 1299 (C-F), 1172, 1157, 984, 793cm⁻¹.

¹H NMR (300MHz, CDCl₃): δ (ppm) = 6.36 (1H, s), 6.25 (1H, s), 3.53 (1H, s), 3.42 (1H, s), 2.96 (2H, s), 1.70-1.54 (2H, m).

¹³C NMR (75MHz, CDCl₃): δ (ppm) = 174.7 (C=O), 147.8-139.6 (C-F), 137.8 (C=C), 134.4 (C=C), 107.1 (C-N), 52.1, 48.4, 45.8, 45.6, 42.9.

¹⁹F NMR (300MHz, CDCl₃, ref. TFA [-77ppm]): δ (ppm) = -142.2, -142.4, -150.1, -150.6, -160.1, -160.4.

2.4. Metathesis polymerization of monomer

Polymerizations were carried out in glass vials under a dry nitrogen atmosphere. They were quenched by adding a small amount of ethyl vinyl ether and the solutions were poured into an excess of methanol. The polymers were purified by solubilization in chloroform and precipitation into methanol containing a few drops of 1N HCl. The obtained polymers were dried in a vacuum oven at 40°C to constant weight.

2.4.1. Polymerization of **2a**

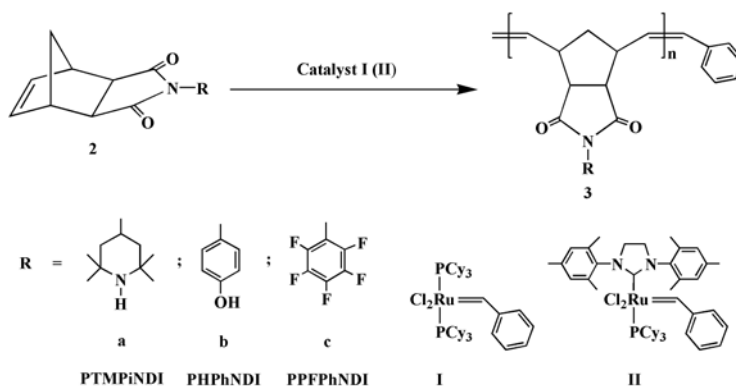
Monomer **2a** (1.0g, 3.31mmol) and catalyst **I** (2.72×10^{-3} g, 0.0033mmol) were stirred in 3.3mL of 1,2-dichloroethane at 45°C for 2h (Scheme 2). The obtained polymer **3a** (PTMPiNDI) was soluble in chloroform and dichloromethane. The values of the number-average molecular weight (M_n), molecular weight distribution (MWD), glass transition

temperature (T_g), decomposition temperature (T_d), elastic modulus (E), and stress in tension (σ_u) of poly(*N*-2,2,6,6-tetramethylpiperidyl-*exo*-*endo*-norbornene-5,6-dicarboximide) were, respectively, $M_n = 235000$, $MWD = 1.18$, $T_g = 151^\circ\text{C}$, $T_d = 415^\circ\text{C}$, $E = 1220\text{MPa}$, $\sigma_u = 45.0\text{MPa}$.

FT-IR (film): ν 3241 (N-H str), 2960 (C=C-H asym str), 1769 (C=O), 1698 (C=O), 1628 (C=C str), 1478 (C-H), 1384 (C-N), 1310, 1286 (C=C-H), 1212, 1162, 1129, 1087, 1047, 976, 911, 849 (C-C str), 746, 680, 622cm^{-1} .

^1H NMR (300MHz, CDCl_3 , ppm) δ : 5.69 (1H, s, *trans*), 5.62 (1H, s, *cis*), 4.49 (1H, m), 3.19 (2H, s), 2.95 (2H, m), 2.60 (2H, s), 2.26 (2H, s), 1.90 (1H, s), 1.60-1.26 (14H, m).

^{13}C NMR (75MHz, CDCl_3 , ppm) δ : 176.5, 175.8, 174.2, 169.6, 132.0 (*cis*), 129.3 (*trans*), 123.6, 58.0, 53.0, 48.3, 44.1, 43.2, 40.3, 33.3, 29.8, 27.6, 25.3, 24.3, 18.2.



Scheme 2. ROMP of norbornene dicarboximides **2a**, **2b**, and **2c**.

2.4.2. Polymerization of **2b**

Monomer **2b** (1.0g, 3.92mmol) and catalyst **II** ($3.32 \times 10^{-3}\text{g}$, 0.0039mmol) were stirred in 4.0mL of 1,2-dichloroethane at 45°C for 2h (Scheme 2). The obtained polymer **3b** (**PHPhNDI**) was soluble in chloroform and

dichloromethane. The values of the number-average molecular weight (M_n), molecular weight distribution (MWD), glass transition temperature (T_g), decomposition temperature (T_d), elastic modulus (E), and stress in tension (σ_u) of poly(*N*-4-hydroxyphenyl-*exo-endo*-norbornene-5,6-dicarboximide) were, respectively, $M_n = 216000$, $MWD = 1.32$, $T_g = 225^\circ\text{C}$, $T_d = 390^\circ\text{C}$, $E = 1400\text{MPa}$, $\sigma_u = 52.0\text{MPa}$.

FT-IR (film): ν 3076 (C=C-H asym str), 2992, 1766 (C=O), 1710 (C=O), 1635 (C=C str), 1511, 1498, 1387 (C-N), 1280 (C=C-H), 1237, 1190, 905cm^{-1} .

^1H NMR (300MHz, CDCl_3 , ppm): δ 7.33-7.02 (4H, m), 5.77 (1H, s, *trans*), 5.52 (1H, s, *cis*), 3.13 (2H, s), 2.84 (2H, s), 2.29 (1H, s), 1.96-1.40 (2H, m).

^{13}C NMR (75MHz, CDCl_3 , ppm): δ 176.9, 168.9, 150.1, 131.7 (*cis*), 129.2 (*trans*), 127.6, 122.0, 50.8, 46.1, 41.8.

2.4.3. Polymerization of **2c**

Monomer **2c** (1.0g, 3.04mmol) and catalyst **I** ($2.49 \times 10^{-3}\text{g}$, 0.0030mmol) were stirred in 4.3mL of 1,2-dichloroethane at 45°C for 2h (Scheme 2). The obtained polymer **3c** was soluble in chloroform and dichloroethane. The values of the number-average molecular weight (M_n), molecular weight distribution (MWD), glass transition temperature (T_g), decomposition temperature (T_d), elastic modulus (E), and stress in tension (σ_u) of poly(*N*-pentafluorophenyl-norbornene-5,6-dicarboximide) were, respectively, $M_n = 307000$, $MWD = 1.62$, $T_g = 193^\circ\text{C}$, $T_d = 425^\circ\text{C}$, $E = 1226\text{MPa}$, $\sigma_u = 48.7\text{MPa}$.

FT-IR (film): ν 3002, 2930 (C-H asym str), 2855 (C-H sym str), 1790 (C=O), 1725, 1647 (C=C str), 1513, 1356, 1297 (C-F), 1165, 1138, 984, 785, 767, 624cm^{-1} .

^1H NMR (300MHz, CDCl_3): δ (ppm) = 5.78 (1H, s, *trans*), 5.56 (1H, s, *cis*), 3.28 (2H, s), 2.88 (2H, s), 2.24 (1H, s), 1.70 (1H, s).

^{13}C NMR (75MHz, CDCl_3): δ (ppm) = 174.7, 147.0, 146.1, 141.0, 135.3, 133.3 (*cis*), 131.9 (*trans*), 107.1, 51.4, 46.6, 41.9.

^{19}F NMR (300MHz, CDCl_3 , ref. TFA [-77ppm]): δ (ppm) = -142.2, -142.5, -143.2, -150.0, -150.3, -159.8, -160.2, -160.7.

3. Results and Discussion

Monomers **2a**, **2b**, and **2c** were prepared in high yields. 2,2,6,6-tetramethylpiperidylamine, 4-hydroxyaniline, and 2,3,4,5,6-pentafluoroaniline reacted with **NDA** to the corresponding amic acids (**1a**, **1b**, and **1c**), which were cyclized to imides by using acetic anhydride as dehydrating agent (Scheme 1). ^1H , ^{13}C , and ^{19}F NMR spectra as well as elemental analysis confirmed monomer structure and purity. The infrared spectra of monomer showed characteristic peaks at 1765cm^{-1} and 1702cm^{-1} (asymmetric and symmetric C=O stretching), 1382cm^{-1} (C-N stretching). ROMP of **2a**, **2b**, and **2c** using ruthenium catalysts **I** and **II** were carried out in 1,2-dichloroethane at 45°C (Table 1). Table 1 summarizes the results of the polymerizations of **2a**, **2b**, and **2c**. The monomers reacted in 2h giving polymer in high yield (94-96%, entries 3, 6, and 8). The results obtained by GPC analysis show that the number average molecular weights (M_n) were between 95,000 and 307,000. The experimental number average molecular weights are in agreement with the theoretical ones. As shown in Table 1, the molecular weight distribution (*MWD*) of the polymers **3a**, **3b**, and **3c** obtained using **II** is about $M_w/M_n = 1.32$ -1.62, which is broader than polymers prepared using **I** ($M_w/M_n = 1.15$ -1.30).

Table 1. Polymerization conditions of *N*-2,2,6,6-tetramethylpiperidyl-*exo*-*endo*-norbornene-5,6-dicarboximide (**2a**), *N*-4-hydroxyphenyl-*exo*-*endo*-norbornene-5,6-dicarboximide (**2b**), and *N*-pentafluorophenyl-*exo*-*endo*-norbornene-5,6-dicarboximide (**2c**)

Entry	Monomer ^a	Catalyst	M/Cat ^b	<i>Cis</i> content in polymer (%) ^c	Yield (%) ^d	$M_n \times 10^{-5e}$	<i>MWD</i> ^e
1	2a	I	500	18	87	1.13	1.22
2	2a	I	1000	17	83	2.35	1.18
3	2a	II	1000	55	94	2.68	1.38
4	2b	I	500	19	91	0.95	1.20
5	2b	I	1000	21	89	2.07	1.15
6	2b	II	1000	52	96	2.16	1.32
7	2c	I	1000	17	85	2.15	1.30
8	2c	II	1000	54	96	3.07	1.62

^a1,2-Dichloroethane as solvent, Temperature = 45°C, Time = 2h, Initial monomer concentration $[M_0] = 1.0\text{mol/L}$.

^bMolar ratio of monomer to catalyst.

^cDetermined by ^1H NMR.

^dMethanol insoluble polymer.

^eGPC analysis in tetrahydrofuran with polystyrene calibration standards.

Changing the pendant moiety did not affect the stereochemistry of the double bonds in the polymer. Catalyst **I** gave polymers with predominantly *trans* configuration of the double bonds (79-83%), whereas catalyst **II** produced polymers with a mixture of *cis* and *trans* double bonds (52-55% of *cis* structure).

Figure 1 shows the ^1H NMR spectra of (a) monomer **2a** and (b) polymer **3a** prepared using **II**. The *exo* and *endo* monomer olefinic signals at $\delta = 6.33\text{-}6.13\text{ppm}$ are replaced by new signals at $\delta = 5.69\text{-}5.62\text{ppm}$,

which correspond, respectively, to the *trans* and *cis* H at the double bonds of the product polymer.

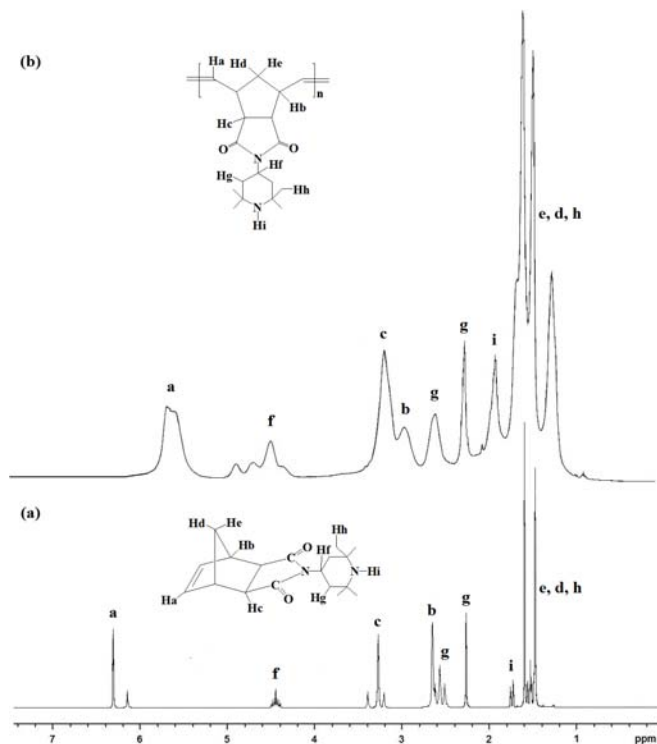


Figure 1. ^1H NMR spectra of (a) monomer **2a** and (b) **PTMPiNDI** prepared using **II**.

The films cast from **PTMPiNDI** and **PHPhNDI** were transparent and once dried they were used to determine the density, thermal, and mechanical properties. The effect that fluorine-containing pendant groups in the polynorbornene dicarboximide (**PPFPhNDI**) had on the physical properties of polynorbornenes with similar structures is compared in Table 2.

Thermal properties indicate that these polynorbornenes **PTMPiNDI** and **PHPhNDI** are rigid amorphous polymers with T_g 's at 151°C and 225°C as determined by DSC measurements, respectively. The lower T_g found for

PTMPiNDI in comparison with polymer **PHPhNDI** could be attributed to the presence of the bulky $-\text{CH}_3$ groups pending on the piperidyl ring, which inhibit the ability of the polymer chains for packaging. The non-fluorinated polynorbornene dicarboximide **PHPhNDI** has a higher T_g than the previously reported poly (*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide) **PPFPhNDI** [16]. The lowering of T_g for the perfluorinated polymer is attributed to a diminished ability to pack of the phenyl ring due to the presence of the fluorine atoms, which decrease the temperature to attain the relaxation process, while **PHPhNDI** could form some interaction with the terminal $-\text{OH}$ groups, which increases rigidity and therefore T_g . The thermal stability of the polymers was studied by TGA under N_2 , the onsets of thermal decomposition, T_d 's of these polynorbornene dicarboximides are around 400°C showing the relatively high thermal stability of these kinds of polymers. Density measurements, reported also in Table 2, indicate that the presence of fluorine atoms increases density of the polynorbornene dicarboximide, (**PPFPhNDI**), as compared to the non-fluorine substituted polynorbornene dicarboximides, **PTMPiNDI** and **PHPhNDI**, respectively. Figure 2 shows the damping factors, $\tan \delta$, for the three polynorbornene dicarboximides. The α -transition, T_α , which is the result of similar molecular motion processes that give rise to the T_g , for each polynorbornene was taken as the maximum in the transition peak. The results indicate that T_α is lower for **PTMPiNDI** followed for the one of **PPFPhNDI** and the higher T_α corresponds to **PHPhNDI**. The indication of a larger T_α and T_g for the polynorbornenes with pendant phenyl groups indicates that they possess higher rigidity in their structures, due to the planar phenyl groups, while the piperidyl pending group in **PTMPiNDI** gives more flexibility to the structure.

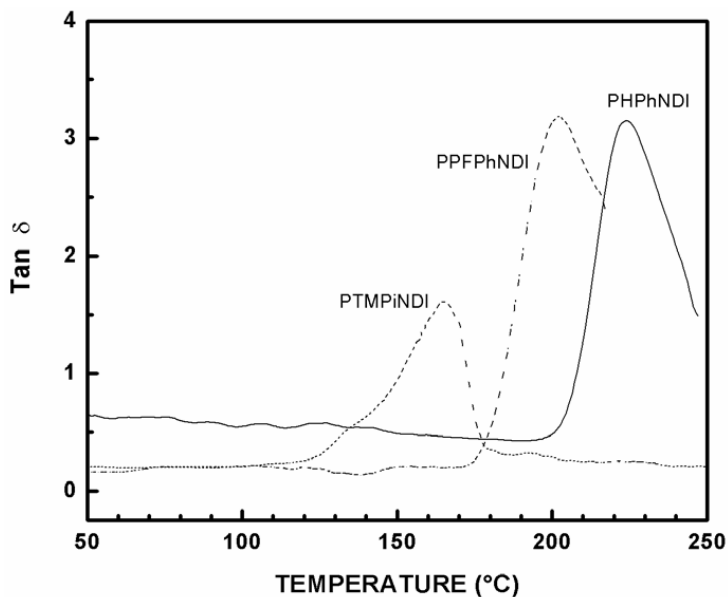
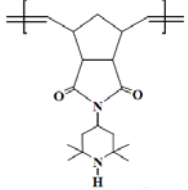
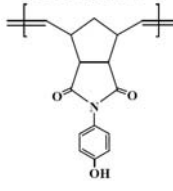
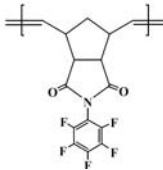


Figure 2. Damping factor, $\tan \delta$, from dynamic mechanical analysis as a function of temperature for **PHPhNDI**, **PTMPiNDI**, and **PPFPhNDI**.

Stress-strain measurements in tension for the films of the synthesized polynorbornenes were performed. The experiments were stopped at the maximum stress and indicate that the elastic modulus ($E = 1400\text{MPa}$) as well as the stress ($\sigma = 52.0\text{MPa}$) for the sample **PHPhNDI**, which bears the smallest substituent, are higher than those mechanical properties determined for the sample **PTMPiNDI** ($E = 1220\text{MPa}$ and $\sigma = 45.0\text{MPa}$). The latter could be attributed to the ability of the phenyl ring in **PHPhNDI** to chain packaging, which results in an increase of rigidity; whereas the contrary effect is observed for **PPFPhNDI**, which exhibits lower mechanical properties ($E = 1226\text{MPa}$ and $\sigma = 48.7\text{MPa}$) in comparison with the former polymer. The physical properties results are summarized in Table 2.

Table 2. Physical properties of polynorbornene dicarboximides

Polynorbornene	T_g (°C)	T_d (°C)	T_a (°C)	ρ (g/cm ³)	$\rho^{\text{th}(d)}$ (g/cm ³)	FFV	σ (MPa)	E (MPa)
PTMPiNDI^a 	151	415	165.8	1.165	1.084	0.1344	45.0	1220
PHPhNDI^b 	225	390	224.0	1.212	1.219	0.1772	52.0	1400
PPFPhNDI^c 	193	425	201.6	1.457	1.456	0.1999	48.7	1226

^apoly(*N*-2,2,6,6-tetramethylpiperidyl-*exo-endo*-norbornene-5,6-dicarboximide).^bpoly(*N*-4-hydroxyphenyl-*exo-endo*-norbornene-5,6-dicarboximide).^cpoly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide).^dFrom molecular dynamics simulations.

Gas permeability coefficients, P , for amorphous polymers are known to be the product of a diffusion and solubility coefficients

$$P = DS. \quad (1)$$

Using a single transient experiment, the permeability coefficient, P , and the apparent diffusion coefficient, D , can be determined by the time lag method as described elsewhere [1], where D is found from the equation

$$D = \frac{l^2}{6\theta}, \quad (2)$$

where l is the thickness of the membrane and θ is the time lag. This method has the advantage of allowing us to determine P and D from one single experiment. The solubility coefficient is then calculated as the ratio of P/D from Equation (1).

A measure of the capacity of a polymer membrane to separate a gas mixture is given by the ideal separation factor, α_B^A , which is calculated as the ratio of pure gas permeability coefficients for gas A and B

$$\alpha_B^A = \frac{P_A}{P_B}. \quad (3)$$

Gas permeability coefficients, P , for pure gases He, O₂, N₂, CH₄, and CO₂ in membranes prepared from **PTMPiNDI** and **PHPhNDI** are given in Table 3 at 35°C and 5atm upstream pressure and compared with those for **PPFPhNDI** at the same conditions. Apparent diffusion, D and solubility coefficients, S , are given for the three polynorbornenes.

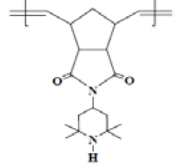
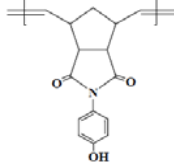
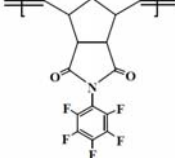
The P results indicate that **PHPhNDI** presents P values that are larger than those presented by **PTMPiNDI**, particularly those for the larger kinetic diameter gases O₂, N₂, and CH₄, which indicates that diffusion of these gases is lower in **PTMPiNDI** as compared to **PHPhNDI**. The result is attributed to a lower free volume between the molecules of **PTMPiNDI** as indicated by the fractional free volume, FFV , reported in Table 2, where it is calculated from Bondi's group contribution method as indicated by van Krevelen [12] from the following equation:

$$FFV = \frac{(V - V_o)}{V}, \quad (4)$$

where V is the specific volume ($1/\rho$), V_o is the specific occupied volume that according to Bondi's method can be calculated from the van der Waals volume, V_w , as $V_o = 1.3(V_w)$.

Table 3 shows that the presence of fluorine atoms in the substituted imide side groups hinders chains packaging increasing the *FFV*, and hence the permeability of the polynorbornene membranes increases, as revealed by the fact that the permeability coefficients for all gases in the **PPFPhNDI** membrane are two to four times larger than those in the non fluorinated **PHPhNDI** membrane, and fourteen to thirty times larger than those in the non fluorinated **PTMPiNDI** membrane. The difference is particularly large for the gases with the higher kinetic diameter (N_2 and CH_4). However, the sorption process and not the diffusive step is responsible for this increase in the permeability of the **PPFPhNDI** membrane.

Table 3. Gas transport properties of fluorinated and non fluorinated polynorbornene dicarboximides at 35°C and 5atm upstream pressure

Polynorbornene	$P(\text{Barrer})$					$D \times 10^8 \left(\frac{\text{cm}^2}{\text{S}} \right)$				$S \times 10^3 \left(\frac{\text{cm}^3 \text{STP}}{\text{cm}^3 \text{cmHg}} \right)$			
	He	O ₂	CO ₂	N ₂	CH ₄	O ₂	CO ₂	N ₂	CH ₄	O ₂	CO ₂	N ₂	CH ₄
PTMPiNDI^a 	12.4	0.43	1.79	0.058	0.046	11.1	2.6	1.9	0.88	0.38	6.6	0.30	0.52
PHPhNDI^b 	15.5	1.71	10.3	0.32	0.35	29.6	10.5	7.98	2.54	0.57	9.80	0.40	1.38
PPFPhNDI^c 	63.5	8.98	46.8	3.0	2.69	182.9	29.7	24.4	8.81	0.49	15.7	1.23	3.05

^apoly(*N*-2,2,6,6-tetramethylpiperidyl-*exo-endo*-norbornene-5,6-dicarboximide).

^bpoly(*N*-4-hydroxyphenyl-*exo-endo*-norbornene-5,6-dicarboximide).

^cpoly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide).

On the other hand, it is surprising in a sense that a polynorbornene with the substitutions of four bulky methyl groups in the piperidyl moiety presents lower *FFV* than the one that bears a phenyl ring with an $-OH$ pending from the phenyl in *para* position which, according to the results, opens further the *FFV*. A molecular dynamics simulation with a model bearing 20 repeating units of each polynorbornene is given in Figure 3. We performed a density calculation using the COMPASS force field and a NPT ensemble for the final density at room temperature (298K) and atmospheric pressure. The results indicate a very good agreement with the experimentally measured densities as reported in Table 2 as ρ^{th} the density values are close to the second significant figure with those found by density gradient column. In Figure 4, a graph of the predicted density and the equilibration time during the NPT molecular dynamics step indicates that the average density value is reached in 4×10^5 ps for **PHPhNDI** with very small variation after this time.

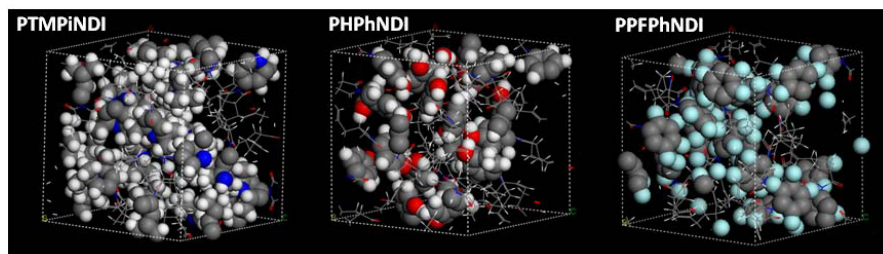


Figure 3. Polynorbornene structures in three-dimensional periodic cells after full equilibration using molecular dynamics simulation.

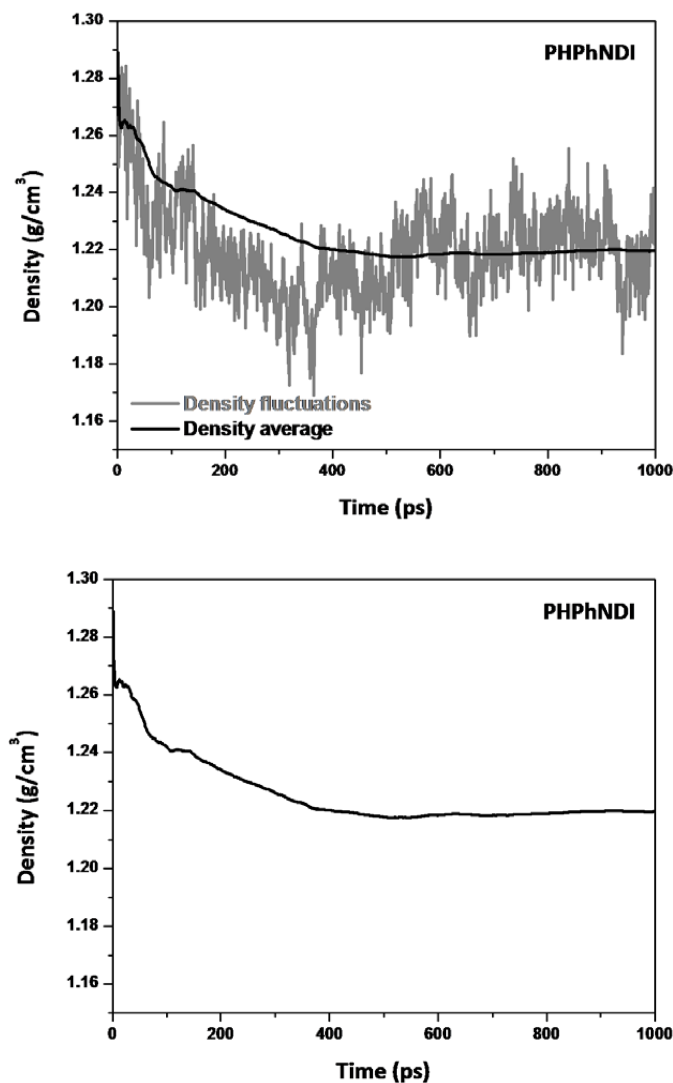


Figure 4. Predicted density equilibration versus NPT molecular dynamic time for polynorbornene **PPhNDI**.

The results in Figure 3 agrees with the fact that the structure of **PTMPiNDI** has lower *FFV* due to the volume occupied by methyl groups that come in closer contact to methyl groups in the adjacent unit. The structure also indicates that the planar structure, π bonds, of the phenyl ring helps to open the volume between adjacent units, while the *sp*

hybridization on the piperidyl moiety contributes to a lower *FFV* and difficulties the permeation of the gas through it. It is also important to notice that *P* coefficients for **PTMPiNDI** are low for O₂, N₂, and CH₄, which situate this polynorbornene as a low permeability polymer just one order of magnitude over the range of polyethylene terephthalate, PET, [1], and some aromatic polyamides [3] that are important in packaging and food storage.

Taking into account the possibility of using **PTMPiNDI** in packaging applications, Figure 5 shows the behaviour of *P* between 2 and 10atm for this polymer. The results indicate that *P* remains constant for the interval measured for He, CO₂, and O₂. *P* values for N₂ and CH₄, not shown in the graph, are quite low and they are close to the base line of the permeation cell. As a result, the last two gases presented long times to establish steady state permeation, > 24h, which in the case of nitrogen and methane are just above the base line in order of magnitude, around 9×10^{-3} Barrer.

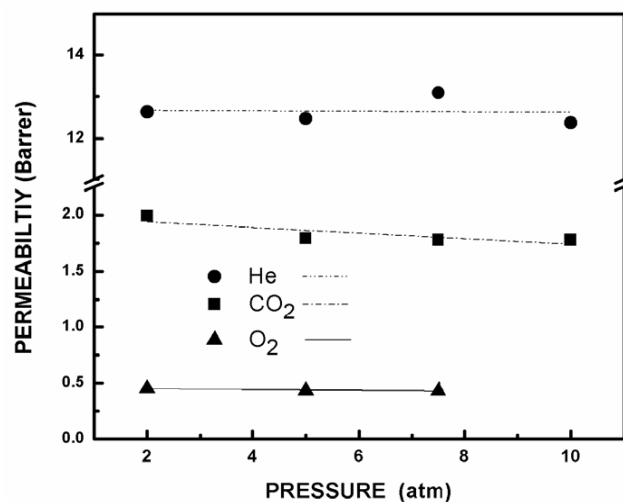
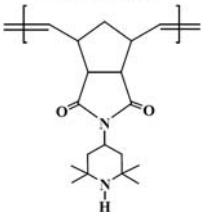
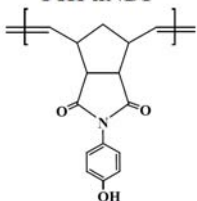
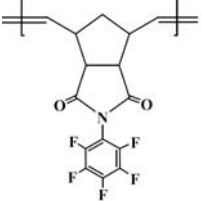


Figure 5. Permeability coefficients as a function of pressure for **PTMPiNDI**.

Ideal gas separation factors, α , for the industrially important gas pairs O_2/N_2 , CO_2/CH_4 , and CO_2/N_2 are given in Table 4 for **PTMPiNDI**, **PHPhNDI**, and **PPFPhNDI**. The results indicate that **PTMPiNDI**, which presents the lowest P , shows the largest separation factors for all gas pairs, in contrast, the **PPFPhNDI** membrane exhibits the highest P , but the lowest α for the gas pairs of all the polymers compared here. This is a common trade off observed in glassy polymers since as the gas permeability coefficient increases the ideal separation factor decreases. While separation factor for the pair O_2/N_2 is attractive because, it is above the average for the gas pairs for **PTMPiNDI** the low permeability coefficients could make it unattractive for actual use in membranes separation, but could find use in packaging applications.

Table 4. Ideal gas separation factors of fluorinated and non fluorinated polynorbornene dicarboximides at 35°C and 5atm upstream pressure

Polynorbornene	$\alpha_B^A = \frac{P_A}{P_B}$		
	O ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
<p>PTMPiNDI^a</p> 	7.4	38.9	30.8
<p>PHPhNDI^b</p> 	5.3	29.4	32.1
<p>PPFPhNDI^c</p> 	2.99	17.3	15.6

^apoly(*N*-2,2,6,6-tetramethylpiperidyl-*exo-endo*-norbornene-5,6-dicarboximide).^bpoly(*N*-4-hydroxyphenyl-*exo-endo*-norbornene-5,6-dicarboximide).^cpoly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide).

4. Conclusion

Exo(90%)-*endo*(10%) monomer mixtures of **2a**, **2b**, and **2c** were synthesized and polymerized via ROMP using well defined ruthenium alkylidene catalysts **I** and **II**. The former catalyst produced polymers with

predominantly *trans* configuration of the double bonds, whereas the latter catalyst gave polymers with a mixture of *cis* and *trans* double bonds. All the polynorbornenes are amorphous polymers with glass transitions temperatures above 150°C and good thermal stability up to at least 350°C as well as similar mechanical properties. Pure gas permeability, diffusion, and solubility coefficients determined by transient measurements in a constant volume cell for He, CO₂, O₂, N₂, and CH₄ show that the polynorbornene **PTMPiNDI** presents gas transport properties that classify it as a low gas permeability polymer with possibilities of use in packaging applications. It was also found that gas permeation is lower in this polynorbornene due to a lower fractional free volume, which difficulties the diffusion through it as compared to **PHPhNDI** that presents a more open structure. The presence of fluorine atoms in the phenyl substituted dicarboximide side group as in the case of **PPFPhNDI** is more effective to increase gas permeability than the presence of bulky moieties such as the piperidyl group.

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