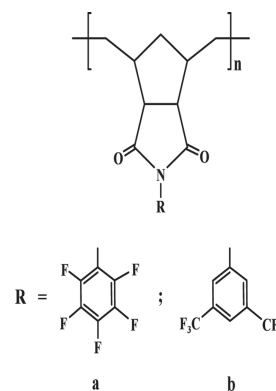


# Gas Transport Properties of Hydrogenated and Fluorinated Polynorbornene Dicarboximides

Joel Vargas, Arlette A. Santiago, Jorge A. Cruz-Morales, Mikhail A. Tlenkopatchev,\* Tomás de Lys, Mar López-González,\* Evaristo Riande

The synthesis and further hydrogenation of fluorinated polynorbornene dicarboximides is reported, using *p*-toluenesulfonyl hydrazide and Wilkinson's catalysts, respectively. Despite improving the resistance to thermo-oxidative degradation, it is observed that the hydrogenation of the backbone double bonds in the polymer also decreases the thermomechanical properties. Afterward, a comparative study of gas transport in membranes based on these hydrogenated polynorbornenes, as well as in their unsaturated analogues, is carried out. The gases studied are hydrogen, oxygen, nitrogen, carbon dioxide, methane, ethane, ethylene, and propylene. After hydrogenation, the gas permselectivity of the membranes is enhanced as a consequence of the decrease of both the gas solubility and the gas diffusion.



## 1. Introduction

Several pieces of research have focused on norbornene since this monomer can be easily modified, thus facilitating the way to prepare a homologous functionalized series of norbornene derivatives that may be subjected to different polymerization reactions yielding materials whose structures and properties depend on the kind of catalyst employed.<sup>[1,2]</sup> In this regard, the ring-opening metathesis polymerization (ROMP) is a unique tool for synthesizing macromolecules that cannot be prepared by conventional methods: it generates unsaturated macromolecular architectures that can undergo further functionalization and also provides well-controlled polymers owing to its living nature.<sup>[3,4]</sup>

Nowadays, substituted polynorbornenes have been gathering much attention as interesting functional and high-performance polymers, especially with respect to their suitable thermomechanical and chemical properties, which allow potential applications not only as gas and ionic separation membranes<sup>[5–9]</sup> but also as optical films and flexible substrates for optoelectronics, among others.<sup>[10]</sup>

In this sense, the presence of fluorine-containing moieties in the polynorbornene dicarboximide structures has shown to be effective to improve gas permeability due to an increase of the interactions between the gases and the polar fluorinated moieties, as well as in the free volume, which in turns facilitates the diffusion of the gas molecules through the polymer.<sup>[11,12]</sup> Recently, sorption studies carried out on membranes of polynorbornene with pentafluorophenyl moieties attached to the dicarboximide side groups showed a significant increase in gas solubility.<sup>[13]</sup>

Taking into account that some commercially available cycloolefin polymers synthesized by ROMP bear saturated backbones, it is highly desired to afford hydrogenated polynorbornene derivatives that exhibit improved thermal and chemical stability for practical applications.<sup>[14]</sup> Hence, the transformation of the rigid double bonds into single bonds would increase the conformational mobility of

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polymer chains and new polynorbornene dicarboximides with enhanced gas permselectivity can be obtained. Thus, in order to provide novel materials with tailored properties, the ROMP-prepared polymers can be hydrogenated either by applying the method based on metallic catalysts such as Pd,<sup>[15]</sup> Rh,<sup>[16,17]</sup> or Ir,<sup>[18]</sup> among others, or by applying the *p*-toluenesulfonyl hydrazide (tosyl hydrazide) decomposition method.<sup>[19–21]</sup>

Therefore, this research deals with the synthesis of fluorine-containing polynorbornene dicarboximides via ROMP and their quantitative hydrogenation by employing an optimal method along with the investigation of the gas transport properties in polynorbornene membranes obtained before and after the hydrogenation process. The thermomechanical properties together with the structural and physical properties of the formed polymers are also studied.

## 2. Experimental Section

### 2.1. Techniques

<sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>19</sup>F NMR spectra were recorded on a Varian spectrometer at 300, 75, and 300 MHz, respectively, in deuterated chloroform CDCl<sub>3</sub>. Tetramethylsilane (TMS) and trifluoroacetic acid (TFA) were used as internal standards, respectively. The glass transition temperatures, *T*<sub>g</sub>, were determined using a DSC-7 instrument (Perkin–Elmer Inc.) at scanning rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. The samples were encapsulated in standard aluminum DSC pans. Each sample was run twice on the temperature range between 30 and 300 °C under nitrogen atmosphere. The *T*<sub>g</sub> values obtained were confirmed by TMA from the first heating cycle conducted at a rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere using a TA Instruments TMA 2940 Thermomechanical Analyzer. The onset of decomposition temperature, *T*<sub>d</sub>, was determined using thermogravimetric analysis (TGA), which was performed at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere using a DuPont 2100 instrument. The molecular weights and molecular-weight distributions were determined with reference to polystyrene standards on a Waters 2695 ALLIANCE gel-permeation chromatography (GPC) instrument at 35 °C, with tetrahydrofuran (THF), a universal column, and a flow rate of 0.5 mL min<sup>-1</sup>. The mechanical properties under tension, Young's modulus (*E*) and tensile strength ( $\sigma_u$ ), were measured using an Instron 1125–5500R universal mechanical testing machine, with a 50 kg cell at a crosshead speed of 10 mm min<sup>-1</sup>, according to ASTM D1708, with film samples of 0.5 mm of thickness at room temperature. Wide-angle X-ray diffraction (WAXD) measurements of the polymer films as cast were carried out using a Siemens D-5000 diffractometer between  $2\theta = 4^\circ$  and  $70^\circ$ , at 35 kV 25 mA, using Cu K $\alpha$  radiation (1.54 Å).

### 2.2. Reagents

An *exo*(90%)–*endo*(10%) monomer mixture of *N*-pentafluorophenyl-norbornene-5,6-dicarboximide (**1a**) and an *exo*(90%)–*endo*(10%)

monomer mixture of *N*-3,5-bis(trifluoromethyl)phenyl-norbornene-5,6-dicarboximide (**1b**) were prepared as described previously.<sup>[13,17]</sup> Tripropylamine (<sup>n</sup>Pr<sub>3</sub>N) and 3,5-di-*tert*-4-butylhydroxytoluene (BHT) were purchased from Aldrich Chemical Co., and used without further purification. 1,2-Dichloroethane, chlorobenzene, dichloromethane, and *p*-dioxane were dried over anhydrous calcium chloride and distilled over CaH<sub>2</sub>. Tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene] ruthenium dichloride (**I**), Wilkinson's catalyst, ClRh(PPh<sub>3</sub>)<sub>3</sub>, and *p*-toluenesulfonyl hydrazide (tosyl hydrazide) were purchased from Aldrich Chemical Co., and used as received.

### 2.3. Metathesis Polymerization of Monomers

Polymerizations were carried out in glass vials under dry nitrogen atmosphere. They were inhibited 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 containing a few drops of 1 N HCl and precipitation into methanol. The obtained polymers were dried in a vacuum oven at 40 °C to constant weight.

#### 2.3.1. Polymerization of **1a**

Monomer **1a** (1.0 g, 3.04 mmol) and catalyst **I** ( $2.58 \times 10^{-3}$  g, 0.0030 mmol) were stirred in 4.3 mL of 1,2-dichloroethane at 45 °C for 2 h (Scheme 1). The obtained poly(*N*-pentafluorophenyl-*exo*(90%)–*endo*(10%)–norbornene-5,6-dicarboximide) (**2a**) was soluble in chloroform and dichloroethane.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 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). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 174.7, 147.0, 146.1, 141.0, 135.3, 133.3 (*cis*), 131.9 (*trans*), 107.1, 51.4, 46.6, 41.9. <sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>, ref. TFA (–77 ppm),  $\delta$ ): –142.2, –142.5, –143.2, –150.0, –150.3, –159.8, –160.2, –160.7. FTIR (thin film, cm<sup>-1</sup>): 3002, 2930 (C–H asym str), 2855 (C–H sym str), 1790 (C=O), 1725, 1647 (C=C str), 1513, 1356 (C–N), 1297 (C–F), 1165, 1138, 984, 785, 767, 624.

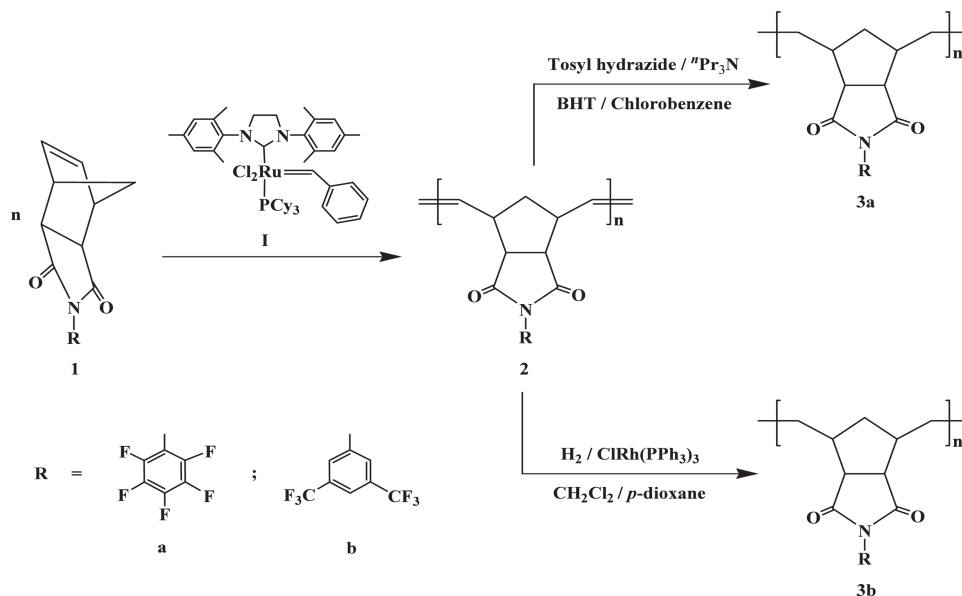
#### 2.3.2. Polymerization of **1b**

Monomer **1b** (1.0 g, 2.66 mmol) and catalyst **I** ( $2.70 \times 10^{-3}$  g, 0.0023 mmol) were stirred in 3.8 mL of 1,2-dichloroethane at 45 °C for 2 h (Scheme 1). The obtained poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo*(90%)–*endo*(10%)–norbornene-5,6-dicarboximide) (**2b**) was soluble in chloroform and dichloroethane.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.88–7.69 (3H, m), 5.82 (1H, s, *trans*), 5.60 (1H, s, *cis*), 3.47 (1H, s), 3.24 (2H, s), 2.90 (1H, s), 2.23 (1H, s), 1.69 (1H, s). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 176.0, 133.0 (*cis*), 132.1 (*trans*), 126.7, 124.5, 122.1, 120.9, 50.9, 46.4, 42.1. <sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>, ref. TFA [–77 ppm],  $\delta$ ): –62.0. FTIR (thin film, cm<sup>-1</sup>): 3034, 2938 (C–H asym str), 2879 (C–H sym str), 1775 (C=O), 1733, 1598 (C=C str), 1459, 1365 (C–N), 1295 (C–F), 1165, 790.

### 2.4. Hydrogenation of **2a**

0.5 g (15.19 mmol) of **2a**, 1.0 g (5.36 mmol) of *p*-toluenesulfonyl hydrazide, 0.76 g (5.30 mmol) of tripropylamine, and 10 mg of 3,5-di-*tert*-4-butylhydroxytoluene were added to 60 mL of chlorobenzene in a round-bottom flask charged with a stir bar. The

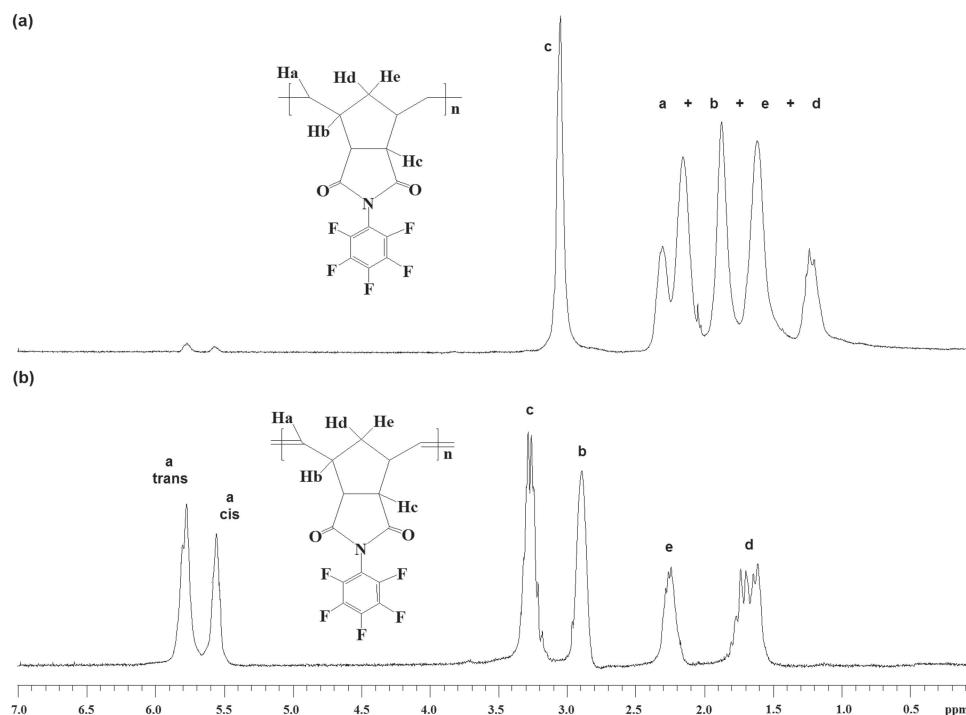


■ Scheme 1. ROMP of norbornene dicarboximides and further hydrogenation of the polymers.

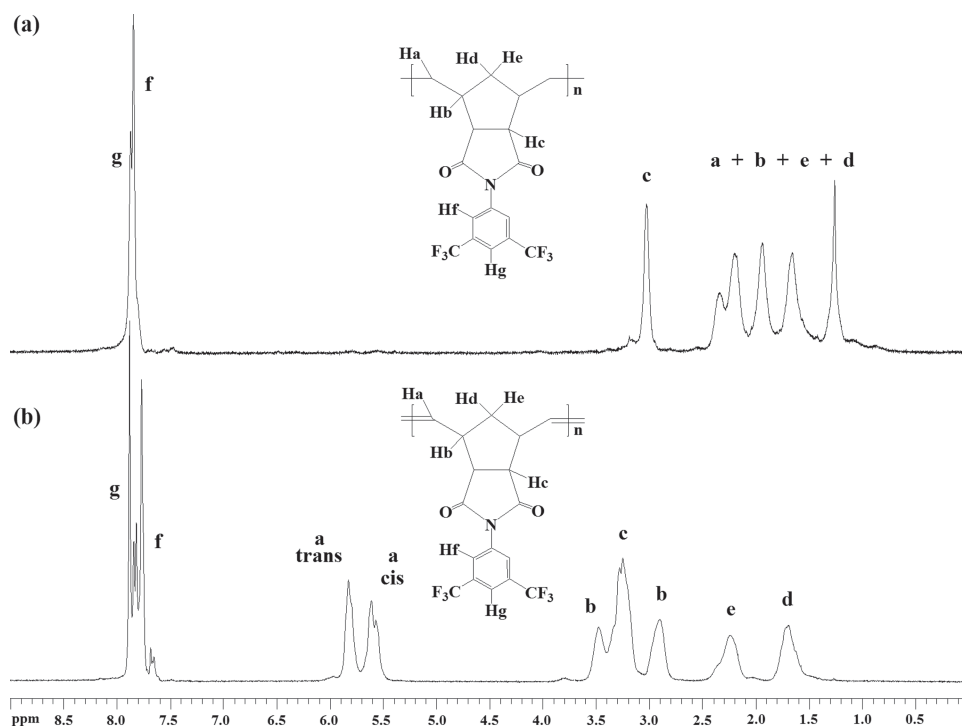
mixture was degassed by pulling high vacuum on the solution for about 60 s. Under a nitrogen atmosphere, the flask was fitted with a reflux condenser, and the reaction was heated to 130 °C for 24 h. The reaction mixture was then cooled to room temperature and precipitated into hot stirring methanol. The product **3a** (Scheme 1) was purified by solubilization in chloroform and precipitation into methanol and finally dried in a vacuum oven at 50 °C overnight. A 97% of hydrogenation for **3a** was determined

by  $^1\text{H}$  NMR spectroscopy (Figure 1). The obtained polymer **3a** was soluble in chloroform and dichloromethane.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 3.06, 2.31, 2.17, 1.88, 1.62, 1.25.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 175.6 (C=O), 146.1, 144.7, 140.8, 135.8, 132.4, 107.2, 51.9, 44.6, 44.0, 42.2.  $^{19}\text{F}$  NMR (300 MHz,  $\text{CDCl}_3$ , ref. TFA [-77 ppm],  $\delta$ ): -142.2, -143.1, -150.2, -159.9, -160.2. FTIR (thin film,  $\text{cm}^{-1}$ ): 2902 (C–H asym str), 2861 (C–H sym str), 1794 (C=O), 1720, 1502, 1460 (C–N), 1367, 1279 (C–F), 1161, 1147, 1000.



■ Figure 1.  $^1\text{H}$  NMR spectra of: a) hydrogenated polymer **3a** and b) its unsaturated analogous polymer **2a**.



■ Figure 2.  $^1\text{H}$  NMR spectra of a) hydrogenated polymer **3b** and b) its unsaturated analogous polymer **2b**.

## 2.5. Hydrogenation of **2b**

0.5 g of **2b** was added to 60 mL of solvent (dichloromethane-*p*-dioxane 1:1) in a Schlenk tube. The catalyst (5 wt%) was previously introduced into a Parr shaker reactor. The solution was degassed and charged into the reactor under  $\text{N}_2$ . Then, hydrogen was added. A 99% of hydrogenation product **3b**, determined by  $^1\text{H}$  NMR spectroscopy (Figure 2), was achieved using a Wilkinson's catalyst,  $\text{ClRh}(\text{PPh}_3)_3$ , at room temperature and 115 bar (Scheme 1). The obtained polymer **3b** was soluble in chloroform and dichloromethane.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.88–7.69 (3H, m), 3.03, 2.35, 2.22, 1.95, 1.68, 1.28.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 176.9 (C=O), 133.2, 132.6, 126.5, 124.5, 121.8, 120.9, 51.5, 44.3.  $^{19}\text{F}$  NMR (300 MHz,  $\text{CDCl}_3$ , ref. TFA (–77 ppm),  $\delta$ ): –62.0. FTIR (thin film,  $\text{cm}^{-1}$ ): 2968, 2870 (C–H sym str), 1785 (C=O), 1726, 1480, 1412 (C–N), 1287 (C–F), 1163, 830.

## 2.6. Membranes Preparation and Permeation Experiments

Membranes were cast from polymer solutions in chloroform at room temperature. The density of the membranes was measured at room temperature by the flotation method using ethanol as liquid. The values of the density are shown in Table 1.

Permeation experiments were carried out in a cell made of two semicells separated by the membrane. After making vacuum in the two semicells, gas at a given pressure is introduced into the high pressure or upstream semicell, which is coupled to a Gometric pressure transducer. The gas flowing across the membrane to the low pressure or downstream semicell is monitored as a function of time with a MKS 628/B pressure transducer via

a PC. The permeation cell is kept inside a water thermostat at the temperature of interest. If the volume  $V$  of the downstream semicell is given in  $\text{cm}^3$ , the area  $A$  of the exposure membrane in  $\text{cm}^2$ , its thickness in cm and the pressure in cm Hg, the permeability coefficient  $P$  of the gases in the membranes in barrer [ $1 \text{ barrer} = 10^{-10} \text{ cm}^3(\text{STP})\text{cm}/(\text{cm}^2 \text{ s cmHg})$ ] is given by:

$$P = 3.59 \frac{Vl}{p_0 AT} \lim_{t \rightarrow \infty} \left( \frac{dp}{dt} \right) \quad (1)$$

where  $T$  is the absolute temperature and  $p_0$  and  $p$  are the upstream and downstream gas pressures, respectively. The  $p$  versus  $t$  isotherms present a transitory followed by a straight line ( $t \rightarrow \infty$ ) corresponding to steady-state conditions. The intersection of the straight line with the abscissa axis of the plot is the time lag  $\theta$ , related to the apparent gas diffusion coefficient by:<sup>[22]</sup>

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

The diffusion coefficient,  $D$ , is currently given in  $\text{cm}^2 \text{ s}^{-1}$  units. The apparent solubility coefficient,  $S$ , is given by:

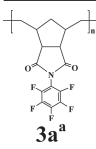
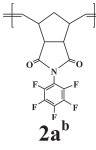
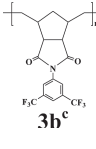
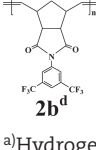
$$S = P/D \quad (3)$$

The usual units of  $S$  are  $\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ cmHg})$ .

## 3. Results and Discussion

Monomers **2a** and **2b** were readily prepared in high yields (87–89%). 2,3,4,5,6-Pentafluoroaniline and

Table 1. Physical properties of saturated and unsaturated polynorbornene dicarboximides.

Polymer	$T_g$ [°C]	$T_d$ [°C]	$E$ [ $\times 10^3$ MPa]	$\sigma$ [MPa]	$\bar{M}_n$ [ $\times 10^5$ g mol $^{-1}$ ]	$\bar{M}_w/\bar{M}_n$	$\rho$ [g cm $^{-3}$ ]	FFV	$d$ -spacing [Å]
 <b>3a<sup>a</sup></b>	144	448	1.2	43	3.22	1.87	1.468	0.177	5.353
 <b>2a<sup>b</sup></b>	171	425	1.2	48	3.07	1.62	1.457	0.199	5.368
 <b>3b<sup>c</sup></b>	121	472	1.3	54	3.37	1.56	1.493	0.140	4.381
 <b>2b<sup>d</sup></b>	168	393	1.4	59	3.27	1.22	1.414	0.199	4.464

<sup>a</sup>)Hydrogenated poly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide); <sup>b</sup>)Poly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide);<sup>[13]</sup> <sup>c</sup>)Hydrogenated poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide); <sup>d</sup>)Poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide).<sup>[13]</sup>

3,5-bis(trifluoromethyl)aniline reacted with an *exo*(90%)–*endo*(10%) mixture of norbornene-5,6-dicarboxylic anhydride to the corresponding amic acids, which were cyclized to imides using acetic anhydride as dehydrating agent according to the literature.<sup>[13,17]</sup> Figure 1 and 2 show the  $^1\text{H}$  NMR spectra of: a) hydrogenated polymer **3a** (**3b**) and b) its unsaturated analogous polymer **2a** (**2b**) of poly(*N*-pentafluorophenyl-) and poly(*N*-bis(trifluoromethyl)phenyl-) derivatives, respectively. The olefinic signals regarding to the *trans* and *cis* double bonds of the polymers are observed at  $\delta = 5.78$  and 5.56 ppm (**2a**) and  $\delta = 5.82$  and 5.60 ppm (**2b**), respectively. After the hydrogenation step, the signals mentioned above become weak and new signals corresponding to the methylene protons arise in the region of  $\delta = 2.35$ –1.25 ppm. The hydrogenation level for polymer **3a** was estimated in the  $^1\text{H}$  NMR spectrum from the integrated peak area of the olefinic proton region relative to the proton attached to the tertiary carbon appearing at  $\delta = 3.06$  ppm. Likewise, the hydrogenation level for polymer **3b** was determined by integrating the area of the olefinic proton region relative to aromatic proton region ( $\delta = 7.88$ –7.69 ppm). A 97% of hydrogenation for polymer **3a** was achieved by using tosyl hydrazide whereas a 99% of hydrogenation for polymer **3b** was achieved by using a Wilkinson's catalyst  $\text{ClRh}(\text{PPh}_3)_3$ .

The effect that the hydrogenation of the backbone double bonds in the polynorbornene dicarboximides

had on the physical properties of polynorbornenes with similar structures is compared in Table 1. The  $T_g$ s for **3a** and **3b** were observed at 144 and 121 °C, nearly 30 and 50 °C less than the corresponding unsaturated polymers **2a** and **2b**, respectively. The latter could be attributed to the highest conformational mobility of the polymer chains in the saturated backbones. The slightly higher  $T_g$  of **3a** in comparison with that of **3b** suggests an increase of rigidity due to the ability of the pentafluorophenyl rings of **3a** to chain packing. The thermal stability of the polymers was studied by TGA under  $\text{N}_2$ . The onset temperature for decomposition of **2a** and **2b** is about 425 and 393 °C that were enhanced by almost 23 and 79 °C after the hydrogenation step, respectively, showing that the hydrogenation of polynorbornene dicarboximides yields materials of relatively high thermal stability that is even heightened in polymers bearing  $\text{CF}_3$  moieties.

The stress–strain measurements in tension for the films of the synthesized saturated polymers indicate that the hydrogenated polymer bearing the larger substituent, **3b**, exhibits higher elastic modulus ( $E = 1300$  MPa) and tensile strength ( $\sigma_u = 54$  MPa) in comparison with the hydrogenated polymer **3a** (1200 and 43 MPa). This fact suggests that the presence of the bulky  $\text{CF}_3$  moieties pending at positions 3 and 5 of the phenyl ring in **3b** restricts the ability to attain the relaxation process. On the other hand, besides lowering the  $T_g$ s, the increase



ability of the polymer chains to adopt different conformations in the saturated backbones of **3a** and **3b** was also reflected in a lesser elastic modulus and tensile strength as compared with their unsaturated analogues **2a** and **2b**, respectively.

The results obtained by GPC analysis show that the number-average molecular weights ( $\bar{M}_n$ ) were between 307 000 and 337 000 g mol<sup>-1</sup>. The experimental  $\bar{M}_n$  are in agreement with the theoretical ones. As shown in Table 1, the molecular weight distribution (MWD) of the hydrogenated polymers **3a** and **3b** is about  $\bar{M}_w/\bar{M}_n = 1.56$ – $1.87$ , which is broader than that of the unsaturated polymers **2a** and **2b** ( $\bar{M}_w/\bar{M}_n = 1.22$ – $1.62$ ).

The GPC analysis performed on the polymers before and after being subjected to the hydrogenation process do not show low-molecular-weight compounds. Moreover, the molecular weights of the hydrogenated polymers are greater than those of their precursors, which indicate that there was not chain degradation or other side reactions during the hydrogenation stage. The presence of by-products after the hydrogenation reaction was neither able to be detected by <sup>1</sup>H NMR spectroscopy.

The density,  $\rho$ , of the membranes was measured at room temperature by the flotation method using ethanol as liquid. Density measurements, reported in Table 1, show that the hydrogenation of the unsaturated polynorbornene dicarboximides promotes chain-packing efficiency that is reflected in higher density values and lower fractional free volume, FFV, as compared with those of the starting unsaturated analogues. The fractional free volume was calculated by the Bondi group contribution method<sup>[23]</sup> from:

$$\text{FFV} = (V - V_0)/V \quad (4)$$

where  $V$  is the specific volume ( $1/\rho$ ),  $V_0$  is the specific occupied volume that according to Bondi's method can be calculated from the van der Waals volume  $V_w$  as  $V_0 = 1.3 V_w$ , estimated using van Krevelen's data.<sup>[24]</sup>

WAXD measurements of the as-cast hydrogenated and unsaturated polymer films show typical polynorbornene dicarboximide patterns with one broad diffraction peak with a maximum around  $2\theta = 20^\circ$ .<sup>[12,16]</sup> The latter evidences that all these polymers as cast are amorphous since no crystallinity was detected either by WAXD or in the thermal measurements described previously. Because of the short-range order exhibited by amorphous polymers, a maximum is observed in the diffraction patterns and a measure of their mean intersegmental distance or chain-packing density could be obtained from the  $d$ -spacing value at the angle of maximum reflective intensity in the amorphous trace using the Bragg's equation,  $n\lambda = 2d\sin\theta$ .<sup>[25]</sup> A comparison on the average  $d$ -spacing indicates that there is a slightly reduction in this

parameter after the hydrogenation step that correlates fairly good with the decrease in FFV considered a measure of the  $d$ -spacing.

Values of the permeability, diffusion, and apparent solubility coefficients for several gases in the membranes of **3a**, **3b**, **2a**, and **2b**, at 30 °C and 1 atm of pressure, are shown in Table 2. In the same table and for comparative purposes, the values of these coefficients for the hydrogenated (P-HPhNDI) and unsaturated (P-PhNDI) poly(*N*-phenyl-*exo-endo*-norbornene-5,6-dicarboximide), reported earlier,<sup>[5]</sup> are also shown. It is worth noting that after the hydrogenation step, the permeability coefficients of the gases in the membranes decrease as a consequence of the decrease of both the gas solubility and the gas diffusion. The lowering in the solubility coefficient could be attributed to the loss of the electronic density associated with the backbone double bonds, which vanishes after the saturation of the main chain. On the other hand, the lesser gas diffusion coefficients in the hydrogenated polynorbornenes are related to the lesser FFV, which in turn hinders the diffusion of the gas molecules through the polymer. However, there are situations in which membranes with similar fractional free volume exhibit different diffusivities and thus a lack of correlation between the diffusion coefficient and the FFV may arise. This issue was examined by Wang et al.<sup>[26]</sup> using simulation techniques finding that not only the free volume but also the distribution of cavities affects the diffusive process.

In general, the permeability coefficients follow the trends  $P(\text{H}_2) > P(\text{CO}_2) > P(\text{O}_2) > P(\text{C}_2\text{H}_4) > P(\text{N}_2) > P(\text{CH}_4) \geq P(\text{C}_3\text{H}_6) > P(\text{C}_2\text{H}_6)$  that differ from those for the diffusion coefficient, which decrease in the order  $D(\text{H}_2) > D(\text{O}_2) > D(\text{N}_2) > D(\text{CO}_2) > D(\text{CH}_4) > D(\text{C}_2\text{H}_4) > D(\text{C}_2\text{H}_6) > D(\text{C}_3\text{H}_6)$ . Evidently,  $\text{CO}_2$  and the most condensable hydrocarbon gases exhibit the larger apparent solubility coefficients in such a way that  $S(\text{C}_3\text{H}_6) > S(\text{CO}_2) > S(\text{C}_2\text{H}_4) > S(\text{C}_2\text{H}_6) > S(\text{CH}_4) > S(\text{O}_2) > S(\text{N}_2) > S(\text{H}_2)$ . From Table 2, it is seen that the presence of fluorine atoms in the substituted imide side groups increases the permeability of the hydrogenated polynorbornene membranes as reveals the fact that the permeability coefficients of the gases in the fluorinated **3a** membrane are one to two times larger than those in the non-fluorinated P-HPhNDI membrane. This effect is much more marked when the gas permeability coefficients of the fluorinated **3b** membrane are compared with those of the non-fluorinated one. The results show that gas permeability coefficients in the former membrane are five to ten times larger than those of the latter membrane. The increase in permeability in the hydrogenated and fluorinated **3a** and **3b** membranes with regard to that of the hydrogenated and non-fluorinated P-HPhNDI membrane arise from both the diffusive process and

**Table 2.** Values of the permeability, diffusion, and apparent solubility coefficients of different gases, at 30 °C and 1 atm upstream pressure, in membranes of saturated and unsaturated polynorbornene dicarboximides.

Gas	3a <sup>a)</sup>			2a <sup>b)</sup>		
	<i>P</i> [barrer]	<i>D</i> [× 10 <sup>8</sup> ]	<i>S</i> [× 10 <sup>3</sup> ]	<i>P</i> [barrer]	<i>D</i> [× 10 <sup>8</sup> ]	<i>S</i> [× 10 <sup>3</sup> ]
H <sub>2</sub>	12.8	110.2	1.16	38.5	112.1	3.43
N <sub>2</sub>	0.30	1.53	1.98	1.55	2.51	6.15
O <sub>2</sub>	1.34	4.23	3.16	6.08	7.64	7.96
CO <sub>2</sub>	6.12	0.79	77.3	25.1	1.50	170.6
CH <sub>4</sub>	0.27	0.35	7.72	1.37	0.64	21.3
C <sub>2</sub> H <sub>6</sub>	0.12	0.03	41.4	0.70	0.05	141.9
C <sub>2</sub> H <sub>4</sub>	0.57	0.10	55.8	3.06	0.21	147.3
C <sub>3</sub> H <sub>6</sub>	0.30	0.02	197.2	1.24	0.05	229.5
Gas	3b <sup>c)</sup>			2b <sup>d)</sup>		
H <sub>2</sub>	37.5	47.1	7.98	57.4	351.5	1.63
N <sub>2</sub>	1.32	4.56	2.90	4.20	8.27	5.08
O <sub>2</sub>	5.94	11.1	5.33	13.5	18.6	7.24
CO <sub>2</sub>	26.1	3.14	83.2	67.2	4.81	139.7
CH <sub>4</sub>	1.24	1.16	10.7	4.28	3.29	13.0
C <sub>2</sub> H <sub>6</sub>	0.61	0.11	56.3	2.62	0.32	82.7
C <sub>2</sub> H <sub>4</sub>	2.06	0.33	61.6	6.91	0.74	93.0
C <sub>3</sub> H <sub>6</sub>	1.20	0.05	222.1	3.79	0.16	239.5
Gas	P-HPHNDI <sup>e)</sup>			P-PhNDI <sup>f)</sup>		
H <sub>2</sub>	7.22	116.4	0.62	11.0	132.0	0.83
N <sub>2</sub>	0.12	0.94	1.28	0.31	2.23	1.39
O <sub>2</sub>	0.66	3.11	2.12	1.44	6.30	2.29
CO <sub>2</sub>	4.51	0.72	62.6	11.4	1.81	63.2
CH <sub>4</sub>	0.15	0.18	8.33	0.54	0.72	7.50
C <sub>2</sub> H <sub>6</sub>	—	—	—	0.09	0.40	2.25
C <sub>2</sub> H <sub>4</sub>	—	—	—	0.58	0.30	19.3
C <sub>3</sub> H <sub>6</sub>	—	—	—	—	—	—

<sup>a)</sup>Hydrogenated poly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide); <sup>b)</sup>Poly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide);<sup>[13]</sup> <sup>c)</sup>Hydrogenated poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide); <sup>d)</sup>Poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide);<sup>[13]</sup> <sup>e)</sup>Hydrogenated poly(*N*-phenyl-*exo-endo*-norbornene-5,6-dicarboximide);<sup>[5]</sup> <sup>f)</sup>Poly(*N*-phenyl-*exo-endo*-norbornene-5,6-dicarboximide).<sup>[5]</sup>

the gas-sorption step. Furthermore, a comparison between the gas transport properties of the hydrogenated **3a** and **3b** membranes indicates that the more fluorine atoms in the dicarboximide moiety the larger the gas permeability coefficient of the hydrogenated polynorbornene membrane.

The effect of the hydrogenation of the backbone double bonds in the polynorbornene dicarboximide membranes was estimated from the permselectivity coefficient, a measure of the capacity of a polymer membrane to carry out the separation for a given gas pair mixture, given by:

$$\alpha\left(\frac{A}{B}\right) = \frac{P(A)}{P(B)} \quad (5)$$

The comparison of the permselectivities of different pairs of gases in the membranes is collected in Table 3. As it is seen, the hydrogenated polynorbornene dicarboximides with the lower gas permeability coefficients show the best ideal separation factors,  $\alpha$ , defined as the ratio of pure gas permeability coefficients  $P(A)/P(B)$ , a trade-off that is commonly found in glassy polymers.

In general, the results show that the lower the permeability the higher the permselectivity. For example,

Table 3. Permselectivity coefficients for different pair of gases in the membranes, at 30 °C.

Polymer	$\alpha_{\text{O}_2/\text{N}_2}$	$\alpha_{\text{CO}_2/\text{CH}_4}$	$\alpha_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_6}$	$\alpha_{\text{H}_2/\text{CH}_4}$	$\alpha_{\text{H}_2/\text{C}_2\text{H}_6}$	$\alpha_{\text{H}_2/\text{C}_2\text{H}_4}$	$\alpha_{\text{H}_2/\text{C}_3\text{H}_6}$
<b>3a</b> <sup>a)</sup>	4.42	22.59	4.75	47.38	107.0	22.52	42.94
<b>2a</b> <sup>b)</sup>	3.93	18.42	4.40	28.18	55.39	12.56	31.04
<b>3b</b> <sup>c)</sup>	4.50	21.05	3.37	30.29	61.59	18.23	31.30
<b>2b</b> <sup>d)</sup>	3.22	15.71	2.63	13.41	21.91	8.30	15.14
P-HPhNDI <sup>e)</sup>	5.50	30.06	—	48.13	—	—	—
P-PhNDI <sup>f)</sup>	4.64	21.18	6.44	20.37	122.2	18.96	—

<sup>a)</sup>Hydrogenated poly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide); <sup>b)</sup>Poly(*N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide);<sup>[13]</sup> <sup>c)</sup>Hydrogenated poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide); <sup>d)</sup>Poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide);<sup>[13]</sup> <sup>e)</sup>Hydrogenated poly(*N*-phenyl-*exo-endo*-norbornene-5,6-dicarboximide);<sup>[5]</sup> <sup>f)</sup>Poly(*N*-phenyl-*exo-endo*-norbornene-5,6-dicarboximide).<sup>[5]</sup>

the schematic replacement of the phenyl group in the hydrogenated P-HPhNDI membrane by the bis(trifluoromethyl)phenyl to yield the hydrogenated **3b** membrane increases the permeability coefficient of nitrogen in 1000%, in detriment of the permselectivity coefficient  $\alpha_{\text{O}_2/\text{N}_2}$  that decreases about 18%. Similarly, the replacement of the phenyl group in the hydrogenated P-HPhNDI membrane by the perfluorinated phenyl moiety, yielding the hydrogenated **3a** membrane augments the permeability coefficient of nitrogen in the latter membrane in 150%, but decreases  $\alpha_{\text{O}_2/\text{N}_2}$  nearly 20%. In fact, the permeability coefficients of the gases in the hydrogenated **3a** membrane are increased 70–150% in comparison with those of the hydrogenated **3b** membrane that are increased 400–1000%. Both hydrogenated **3a** and **3b** membranes exhibit fairly good properties to separate CO<sub>2</sub> from CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> from C<sub>2</sub>H<sub>6</sub> as well as H<sub>2</sub> from low-molecular-weight hydrocarbon gases.

As usual, the temperature dependence of the permeability, diffusion and apparent solubility coefficients follows Arrhenius behavior as the illustrative plots of the natural logarithm of these parameters against the reciprocal of temperature for H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>6</sub> in the hydrogenated **3b** membrane show (see Figure 3). The activation energies associated with the permeability and diffusive steps obtained from the slopes of the corresponding Arrhenius plots are summarized in Table 4. It can be seen that for all gases the activation energy associated with the permeability coefficient of the gases is positive and  $\Delta H_s = E_p - E_D < 0$ . Therefore, the sorption step is an exothermic process that increases with gas condensability.

## 4. Conclusion

The hydrogenation of a series of unsaturated fluorinated ROMP-prepared polynorbornene dicarboximides was

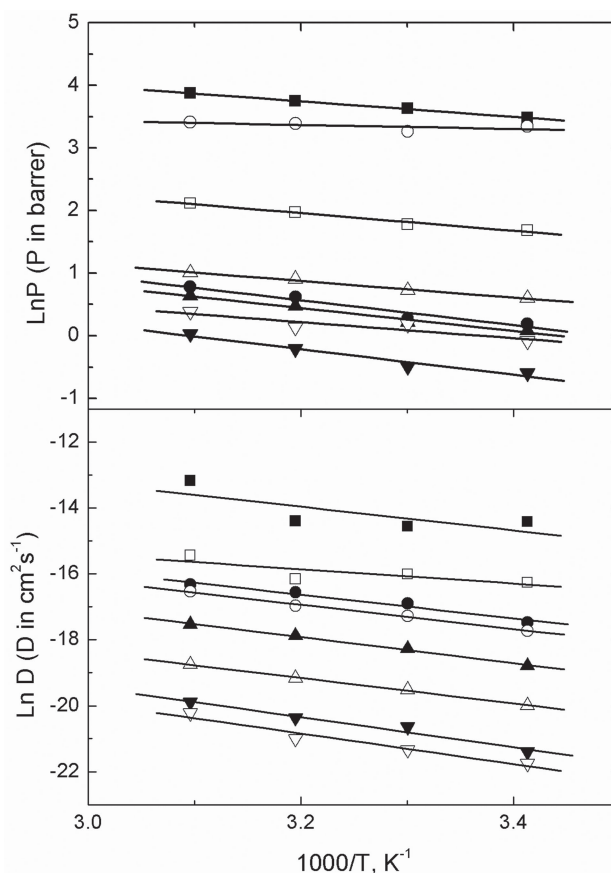


Figure 3. Arrhenius plots for the permeability and diffusion coefficients of hydrogen (■), oxygen (□), nitrogen (●), carbon dioxide (○), methane (▲), ethylene (Δ), ethane (▼), and propylene (▽) in hydrogenated poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide) (**3b**) membrane.

successfully carried out by applying a Wilkinson's catalyst, ClRh(PPh<sub>3</sub>)<sub>3</sub>, and *p*-toluenesulfonyl hydrazide, respectively, yielding new saturated materials. The gas-transport properties of hydrogenated polynorbornenes were compared



**Table 4.** Activation energies associated with the permeability ( $E_p$ ) and diffusion ( $E_D$ ) coefficients and apparent sorption heat ( $\Delta H_s$ ) for different gases in hydrogenated poly(*N*-3,5-bis(trifluoromethyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide) (**3b**), at 1 bar.

Gas	$E_p$ [kcal mol <sup>-1</sup> ]	$E_D$ [kcal mol <sup>-1</sup> ]	$\Delta H_s$ [kcal mol <sup>-1</sup> ]
H <sub>2</sub>	+2.47	+7.18	-4.71
N <sub>2</sub>	+3.98	+7.21	-3.23
O <sub>2</sub>	+2.80	+4.32	-1.52
CO <sub>2</sub>	+0.64	+7.35	-6.71
CH <sub>4</sub>	+3.65	+7.91	-4.26
C <sub>2</sub> H <sub>6</sub>	+4.08	+9.11	-5.03
C <sub>2</sub> H <sub>4</sub>	+2.67	+7.74	-5.07
C <sub>3</sub> H <sub>6</sub>	+2.56	+9.28	-6.72

with their unsaturated analogues. It is observed that membranes prepared from hydrogenated polymers show an enhancement of the gas permselectivity, though the permeability remains low as a consequence of the decrease of both the gas solubility and the gas diffusion coefficients.

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