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ScienceDirect
Polymer 48 (2007) 6546–6553
polymer
www.elsevier.com/locate/polymer

Synthesis and gas permeability of new polynorbornene dicarboximide with fluorine pendant groups

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Received 7 June 2007; received in revised form 23 August 2007; accepted 25 August 2007
Available online 7 September 2007

Abstract

The new *exo-N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide (TFmPhONDI, **2**), was synthesized and polymerized via ring opening metathesis polymerization (ROMP) using tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolilydene] [benzylidene] ruthenium dichloride (**I**) to produce the corresponding PTFmPhONDI (**3**). Gas permeability, diffusion and solubility coefficients of PTFmPhONDI (**3**) were determined by transient permeation for five gases He, CO_2, O_2, N_2 and CH_4. The larger gas permeability and diffusion coefficients of **3** compared to polynorbornene dicarboximides without fluorine pendant groups were attributed to a lower polymer chain packing due to the effect of the CF_3 groups in the lateral phenyl moiety pending at positions 3 and 5.

Keywords: Fluorinated polynorbornene dicarboximide; Ring opening metathesis polymerization; Gas transport properties

1. Introduction

Nowadays there is a growing interest for the search of polymeric materials that can be used as membranes for gas or liquid separation. Particularly in gas separation processes, the ideal membrane should show large permeability coefficients and high selectivity for gas separation. Polymeric materials with bulky pendant groups in their structures may hinder polymeric chain packing that in turn will facilitate gas diffusion without affecting very negatively gas selectivity. Development of membranes based on materials of this type has focused the attention of many researchers in the last decades [1].

Ring opening metathesis polymerization (ROMP) of norbornene dicarboximides with linear aliphatic and aromatic substituents has been described [2–6]. We recently proceeded with the synthesis of new carboximide functionalized polynorbornenes which showed high T_gs, good mechanical properties and high thermal resistance [7,8]. We have also reported gas transport properties of polynorbornenes containing adamantyl, cyclohexyl and cyclopentyl imide side chain groups [9–13]. Membranes prepared from these polymers show an enhancement of the selectivity, though the permeability remains low and does not dependent on the bulkiness of side chain groups. This fact is due to strong intermolecular interactions of polar C=O and C–N bonds in polynorbornene dicarboximides. The imide containing polynorbornenes are very attractive for their application as membranes for various reasons. Thus, it has been reported that introduction of dicarboximide groups into the five-membered ring of the polynorbornene main chain resulted in increase of glass transition temperature, thermal stability and selectivity for some gases [7–10]. It is well known, that in many cases higher permeabilities are found for glassy polymers with higher glass transition temperature [14,15]. It is expected that the combination of distinct properties of polynorbornene and imide containing polymers will allow to control the permeability and selectivity of

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doi:10.1016/j.polymer.2007.08.064

gases changing the structure and composition of polynorbornene dicarboximides.

Introduction of fluorine atoms into the polymer structure can cause significant change in physical and chemical properties of polymers. It is well known that fluorinated polymers are important specialty materials in many applications [16]. Thus, compared to polynorbornene, partially fluorinated polynorbornene membranes exhibit even higher gas permeability and selectivity [17]. The ROMP of norbornene derivatives with various fluorine-containing units is well established [18–21]. It is important to note that fluorinated polymers with low intermolecular and intramolecular interactions are potential candidates for membrane applications. It is expected that the introduction of fluorine atoms into polynorbornene dicarboximides will decrease interchain interactions between polar imide side chain groups and this effect will increase the gas permeability across them without detriment to the selectivity.

With the aim of investigating the effect of the increase of conformational versatility of the chains on gas permeability, poly(*exo*-*N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide) (PTFmPhONDI, **2**) was synthesized and gas transport properties of membranes prepared from the resulting polymer were studied.

2. Experimental part

2.1. Techniques

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Varian spectrometer at 300, 75 and 300 MHz, respectively, in $CDCl_3$. Tetramethylsilane (TMS) and trifluoroacetic acid (TFA) were used as internal standards, respectively.

Molecular weight and molecular weight distribution were determined with reference to polystyrene standards on a Varian 9012 GPC at 30 °C, in chloroform using a universal column and a flow rate of 1 mL/min^{-1}.

Mechanical properties under tension, Young's modulus (E) and stress (σ), were measured in a Universal Mechanical Testing Machine Instron 1125-5500R using a 50 kg cell at a crosshead speed of 10 mm/min according to the method ASTM D1708 in film samples of 0.5 mm of thickness at room temperature.

2.1.1. Film preparation

Films of PTFmPhONDI were cast from 5% by weight polymer solution in chloroform at room temperature. The solution was filtered and poured onto a glass plate and it was allowed to evaporate slowly under controlled chloroform atmosphere. Later, the film obtained was dried under vacuum at 80 °C for 24 h. Film thickness was 100 μm.

2.1.2. Thermal properties

Glass transition temperature, T_g, for PTFmPhONDI (**3**) was determined by differential scanning calorimetry, DSC, in a DSC-7 Perkin Elmer Inc., in 10 mg samples between 40 and 300 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The T_g was calculated as the midpoint on the second heating of the sample. Onset of decomposition temperature, T_d, for PTFmPhONDI was found by thermogravimetric analysis with a TGA-7, Perkin Elmer Inc., using samples around 10 mg. The test was carried out at a heating rate of 10 °C/min, initiating at 40 °C and up to 600 °C under nitrogen atmosphere. Storage modulus and damping factor as a function of temperature for PTFmPhONDI (**3**) was determined by dynamic mechanical analysis in a DMA-7, Perkin Elmer Inc. between −40 and 300 °C at a scanning rate of 5 °C/min under nitrogen atmosphere. The sample for dynamic mechanical measurements was cut from the as cast film and was dried at 100 °C under vacuum in the form of strips with the dimensions $15 \times 3 \times 0.1$ mm. Density for PTFmPhONDI (**3**) film was obtained using the density gradient column method where the gradient was established by calcium nitrate solutions in the range between 1.33 and 1.45 g/cm^3 at 23 °C.

X-ray diffraction measurements of PTFmPhONDI (**3**) film as cast were carried out in a Siemens D-5000 diffractometer between 4 and 50° 2θ, at 35 kV, 25 mA, using Cu Kα radiation (1.54 Å).

2.1.3. Permeation experiments

Gas permeability coefficients, P, for pure gases He, O_2, N_2, CH_4 and CO_2 at 35 °C between 2 and 10 atm were measured in a permeation cell using the constant volume method as described elsewhere [11]. Gas permeability coefficients were determined under steady state conditions, using a transient permeation method. From the same transient experiment, the diffusion coefficients, D, were determined using the time lag method for all gases with the exception of He which has a very short time lag and does not allow for its determination. Solubility coefficients, S, were calculated from the ratio between the permeability coefficients and diffusion coefficients.

2.2. Reagents

3,5-Bis(trifluoromethyl)aniline, *exo*-7-oxanorbornene-5,6-dicarboxylic anhydride (*exo*-ONDA) and other chemicals were purchased from Aldrich Chemical Co. and used without further purification. 1,2-Dichloroethane and dichloromethane were dried over anhydrous calcium chloride and distilled under nitrogen over CaH_2. Catalyst 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene $(PCy_3)Cl_2Ru{=}CHPh$ (**I**) was purchased from Aldrich Chemical Co. and used as received.

2.3. Synthesis and characterization of monomer

2.3.1. Synthesis of exo-N-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide (TFmPhONDI, 2)

exo-7-Oxanorbornene-5,6-dicarboxylic anhydride (5 g, 30 mmol) was dissolved in 50 ml of CH_2Cl_2. An amount of 6.9 g (30.1 mmol) of 3,5-bis(trifluoromethyl) aniline in 10 ml of CH_2Cl_2 is added dropwise to the stirred solution of *exo*-7-oxanorbornene-5,6-dicarboxylic anhydride. The mixture was boiled for 3 h and then cooled to room temperature. Solvent removal gave a white solid of amic acid. The obtained amic acid **1** (11.4 g, 28.8 mmol), anhydrous sodium acetate (1.35 g, 16.45 mmol) and acetic anhydride (14.56 g, 142.6 mmol) were heated at 80 °C for 24 h. The mixture was washed with dilute HCl and extracted into ether. The ether layer was washed with dilute HCl, saturated $NaHCO_3$ and H_2O. Solvent was evaporated and pure TFmPhONDI **2** (Scheme 1) was obtained after twice recrystallization from ethanol and dried in a vacuum oven at 50 °C overnight: yield = 86%, m.p. = 137–139 °C.

FT-IR: 3106.5 (C=C–H asym str), 1791.5 (C=O), 1727.1 (C=O), 1625.9 (C=C str), 1471.6, 1394.6 (C–N str), 1283.0 (C–F), 1175.7, 897.2 (C–C str), 690.9 cm^{-1} (C–H). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.91–7.85 (3H, m), 6.59 (2H, s), 5.42 (2H, s), 3.06 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 174.3, 136.7, 133.0, 132.7, 132.2, 126.7, 124.5, 122.2, 120.8, 81.5, 47.5. ^{19}F NMR (300 MHz, $CDCl_3$, ref. TFA [−77 ppm]), δ (ppm) = −62.1. $C_{16}H_9O_3NF_6$ (377): Calcd C 50.92, H 2.38, O 12.73, N 3.71, F 30.23; Found C 50.76, H 2.15, N 4.06.

2.4. Metathesis polymerization of monomer

Polymerization was carried out in glass vials under nitrogen atmosphere at 45 °C. Polymerization was inhibited by adding a small amount of ethyl vinyl ether and the solution was poured into an excess of methanol. The polymer was purified by solubilization in chloroform containing a few drops of 1 N HCl and precipitation into methanol. The obtained polymer was dried in a vacuum oven at 40 °C to constant weight.

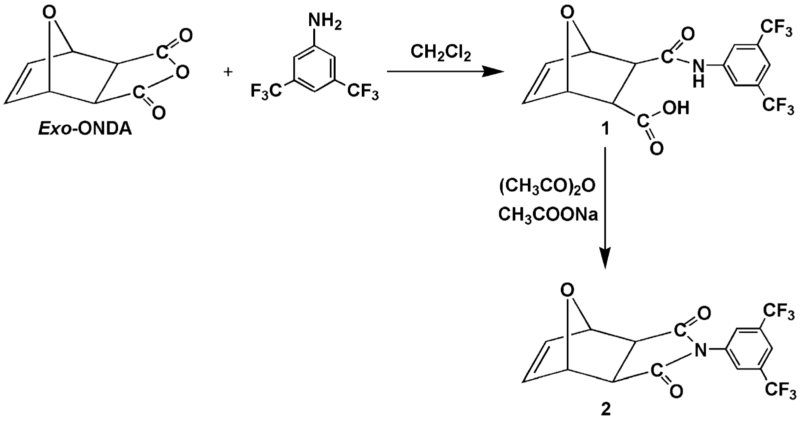
2.4.1. Polymerization of **2**

Monomer **2** (1.0 g, 2.65 mmol) and catalyst **I** (2.25×10^{-3} g, 0.0026 mmol) were stirred in 2.6 mL of 1,2-dichloroethane at 45 °C for 2 h (Scheme 2). The obtained polymer **3** was soluble in chloroform and dichloroethane. $M_n = 315{,}000$; $M_w/M_n = 1.20$.

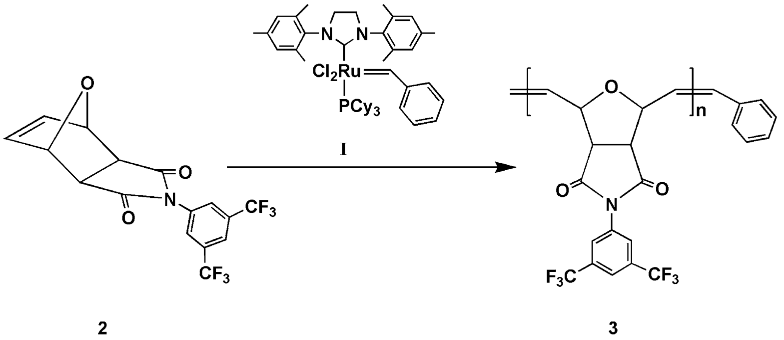
FT-IR: 3102 (C=C–H asym str), 1789 (C=O), 1730 (C=O), 1623 (C=C str), 1473, 1396 (C–N str), 1280 (C–F), 1172, 893 (C–C str), 691 cm^{-1} (C–H). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.92–7.75 (3H, m), 6.15 (2H, s, *trans*), 5.83 (2H, m, *cis*), 5.23 (2H, m), 4.66 (2H, s), 3.53 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 173.5, 133.3, 132.8, 132.5, 132.4, 131.9, 130.9, 127.9, 126.5, 124.3, 122.5, 120.7, 81.1, 53.2, 52.2. ^{19}F NMR (300 MHz, $CDCl_3$, ref. TFA [−77 ppm]): δ (ppm) = −62.4.

3. Results and discussion

Monomer **2** was readily prepared with high yield (86%). 3,5-Bis(trifluoromethyl)aniline reacted with *exo*-ONDA to give the corresponding amic acid which was cyclized to imide using acetic anhydride as dehydrating agent (Scheme 1). ^1H,



Scheme 1. Synthesis route of *exo*-*N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide, **2**.



Scheme 2. Ring opening metathesis polymerization of monomer **2**.

^{13}C and ^{19}F NMR spectra and elemental analysis confirmed monomer structure and purity. The infrared spectra of monomer **2** showed characteristic peaks at 1785 and 1725 cm^{-1} (asymmetric and symmetric C=O stretching), 1390 cm^{-1} (C–N stretching). ROMP of **2** using ruthenium catalyst **I** was carried out in 1,2-dichloroethane at 45 °C.

Fig. 1 shows the ^{1}H NMR spectra of (a) monomer **2** and (b) polymer **3** prepared by **I**. The monomer olefinic signals at $\delta = 6.59$ ppm are replaced by new signals at $\delta = 6.15$ and 5.83 ppm, which corresponds to the *trans* and *cis* Hs at the double bonds of the polymer, respectively.

The as cast PTFmPhONDI (**3**) was a transparent film with slightly yellowish color. The film from the polynorbornene dicarboximide, PTFmPhONDI (**3**) was tough on bending and easy to handle. This film was used for the determination of thermal properties and density as summarized in Table 1. Thermal properties indicate that this polynorbornene is a rigid amorphous polymer with a T_g at 182 °C which is larger than the T_g reported for the poly-*exo*-*N*-phenyl-7-oxanorbornene dicarboximide (PPhONDI) without the substitution of the CF$_3$ groups [8]. This increase in T_g is attributed to the presence of the bulky CF$_3$ groups pending on the phenyl ring which inhibit the ability of the chains to relax. PTFmPhONDI (**3**) shows good thermal stability with the onset of decomposition, T_d at 404 °C that is around 30 °C higher than the one reported for PPhONDI [8] showing the effect of a better thermal stability which has been also observed in other polymers with CF$_3$ groups [22]. Density of PTFmPhONDI (**3**) was found to be 1.43 g/cm^3, and it is larger than that reported for other polynorbornene dicarboximides [11] and it is attributed to the presence of the large and bulky triflouromethyl groups in the lateral phenyl moiety pending at positions 3 and 5. The density of this polymer with fluorine atoms or CF$_3$ groups tends to be higher because of the large atomic molecular weight of the fluorine atom that increases the mass per unit volume of the system [23]. Fractional free volume, FFV, was calculated from a group contribution method [24] and it is found to be 0.230. The large FFV results from the presence of the bulky trifluoro methyl groups in the pendant phenyl of the polynorbornene dicarboximide. This value is higher than that reported for other polynorbornene dicarboximides with cyclopentyl- and cyclohexyl-pendant groups [11] and can be attributed to the presence of the trifluoromethyl groups in the lateral phenyl moiety pending at positions 3 and 5 (Table 1). In fact polynorbornenes bearing trifluoromethyl substituents are reported to have large FFV, two examples are poly(5,5-difluoro-6,6-bis(trifluoromethyl)norbornene), DFHFPNB [23], with a reported FFV of 0.227, and poly(5,5,6-trifluoro-6-(heptafluoropropoxy)norbornene) [17], that has a FFV of 0.187. The large FFV is attributed

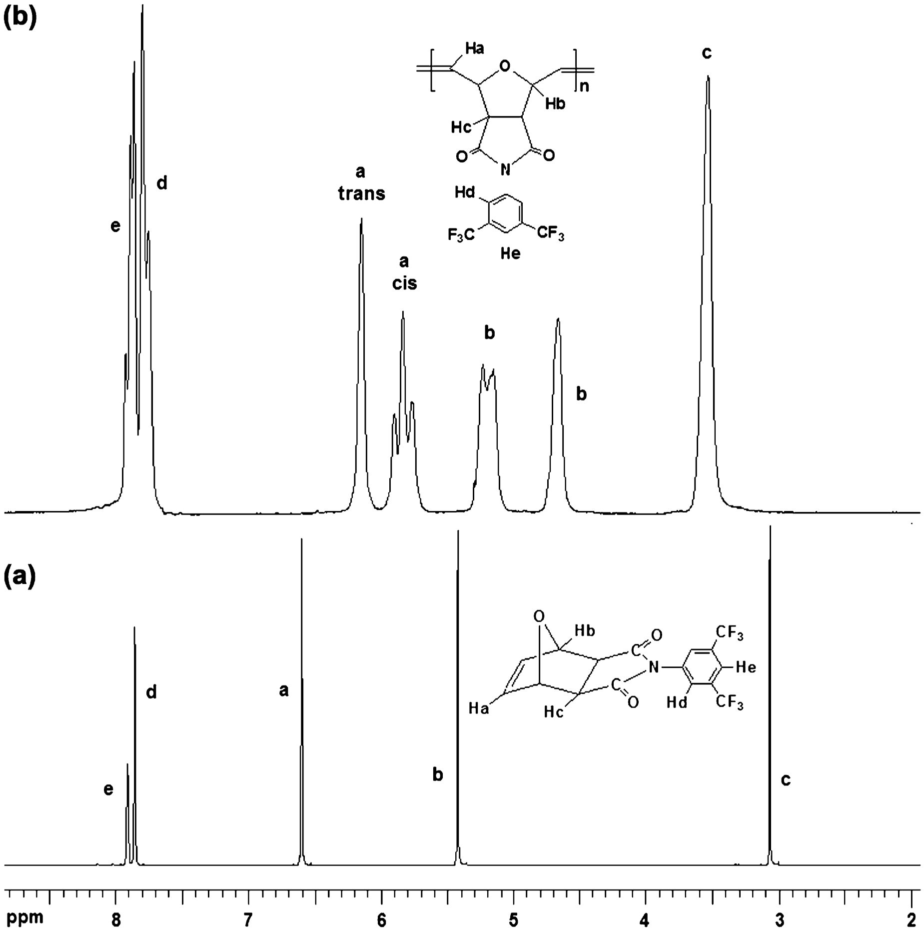
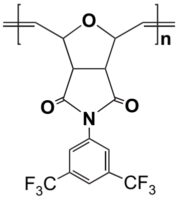
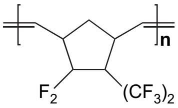
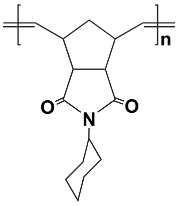


Fig. 1. ^{1}H NMR spectra of (a) monomer **2** and (b) polymer **3** obtained by catalyst **I**.

Table 1
Physical properties of PTFmPhONDI and some selected polynorbornenes

Polymer	T_g (°C)	T_d (°C)	FFV	ρ (g/cm^3)	σ (MPa)	E (MPa)
 PTFmPhONDI[a]	182	404	0.230	1.430	43.2	1512
 DFHFPNB[b]	169	342	0.227[d]	1.55[d]	49.0	1633
 PCyNDI[c]	155	434	0.149	1.156	42.0	1232

[a] Poly(*exo*-*N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide).
[b] Poly(5,5-difluoro-6,6-bis(trifluoromethyl)norbornene) [17].
[c] Poly(*N*-cyclohexyl-*exo*,*endo*-norbornene-5,6-dicarboximide) [11].
[d] Data from Ref. [23].

to the bulkiness of the fluorine moieties which inhibits molecular packing in these polymers. Table 1 compares some physical properties of the fluorinated polynorbornene dicarboximide prepared in this work PTFmPhONDI (**3**) with two other polynorbornenes, one bearing trifluoromethyl substitutions, poly(5,5-difluoro-6,6-bis(trifluoromethyl)norbornene), DFHFPNB, and a polynorbornene dicarboximide without fluorine substitutions poly(*N*-cyclohexyl-*exo*,*endo*-norbornene-5,6-dicarboximide), PCyNDI. The comparison shows that the fluorinated polymers, DFHFPNB and PTFmPhONDI (**3**) present a higher T_g, density and fractional free volume, FFV, and slightly higher mechanical properties than the nonfluorinated polynorbornene dicarboximide PCyNDI. On the other hand, thermal stability, as indicated by the onset of decomposition temperature, T_d under nitrogen atmosphere, is better for the nonfluorinated polynorbornene dicarboximide than for the DFHFPNB.

Fig. 2 shows the storage modulus, E' and damping factor, tan δ, for PTFmPhONDI (**3**) obtained from dynamic mechanical measurements as a function of temperature. The results indicate that the polymer (**3**), is quite rigid with a storage modulus, E' in the order of 10^9 Pa which shows a minimum decrease in rigidity up to the point at which the glass to rubber or alpha transition, T_α, occurs. At this point there is a sharp decrease in modulus in a very short interval of temperature, around 20 °C, of at least three decades. The damping factor, tan δ, does not show the presence of sub-T_g transitions and it has a very sharp transition peak corresponding to T_α with a maximum at 178 °C.

Fig. 3 shows the X-ray diffraction pattern of the as cast PTFmPhONDI (**3**) film. This polymer shows a typical amorphous pattern with one broad diffraction peak with a maximum around 20° 2θ. This indicates that the polymer as cast is amorphous since no crystallinity was detected either by X-ray diffraction or in the thermal measurements described above.

Gas permeability coefficients, P, in amorphous polymers are accepted to be the result of the product of a diffusion coefficient, D, and a solubility coefficient, S.

$$P = DS \tag{1}$$

From a single transient experiment the permeability, P and diffusion coefficient, D, can be obtained using the time lag method as described before [11], where D is given by:

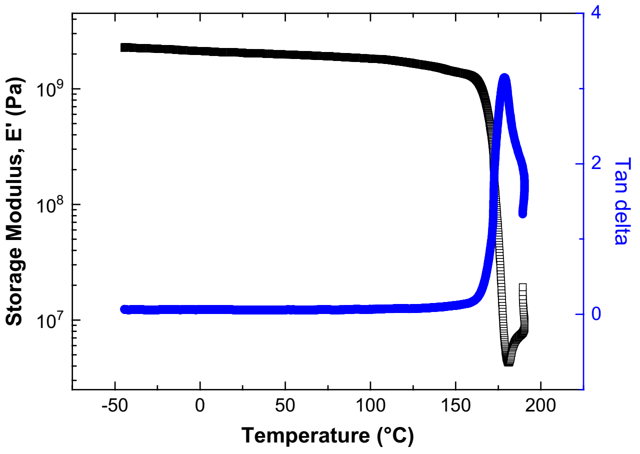


Fig. 2. Storage modulus, E', and damping factor, tan δ, for PTFmPhONDI (**3**) as a function of temperature.

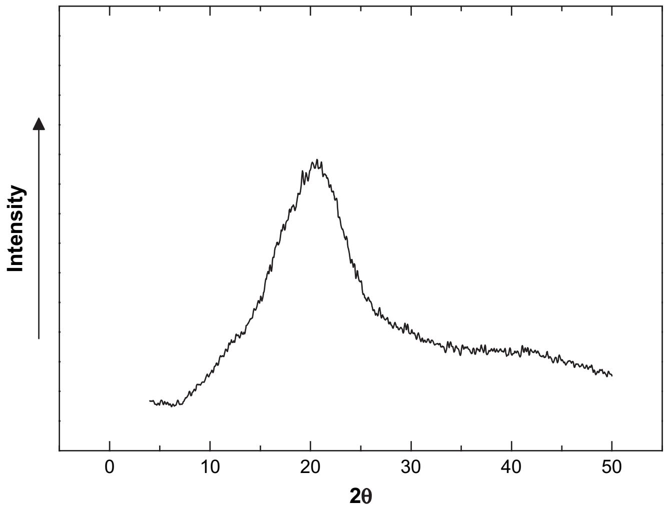


Fig. 3. X-ray diffraction pattern of PTFmPhONDI (**3**).

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

where l is the thickness of the membrane and θ the time lag. The advantage of this technique is that both P and D can be obtained from a single experiment and S can be found from Eq. (1).

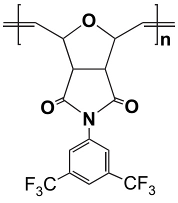
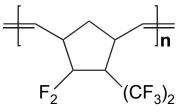
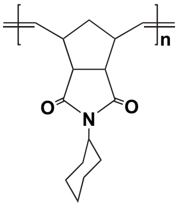
Pure gas permeability coefficients, P, for PTFmPhONDI (**3**) are given in Table 2 at 10 atm and 35 °C for He, CO_2, O_2, N_2 and CH_4 with the exception of O_2 that is given at 5 atm. Diffusion, D, and solubility, S, coefficients are given for the same gases except He. The results indicate that gas permeability coefficients for the polynorbornene dicarboximide studied here are the largest reported for this kind of polymers [10,11,25] and they follow the order of kinetic diameter of the gases $P_{He} > P_{CO_2} > P_{O_2} > P_{N_2} \geq P_{CH_4}$. Diffusion coefficients are also the largest reported for polynorbornene dicarboximides in the order of 10^{-6} cm^2/s for O_2 and 10^{-7} for all other gases (Table 2). Table 2 also shows P, D and S of polynorbornene that bears trifluoromethyl substitutions, poly(5,5-difluoro-6,6-bis(trifluoromethyl)norbornene), DFHFPNB [23]. Permeability and diffusion coefficients for this fluorine substituted polynorbornene is very close to those found for PTFmPhONDI (**3**), an indication that the substitution of the bulky CF_3 groups in general in polynorbornenes decreases the chain packing and increases free volume available for gas permeation. Solubility coefficients are also larger than those reported before for polynorbornene dicarboximides (Table 2) and they are slightly larger than those reported for a polynorbornene dicarboximide with trifluoromethyl pendant groups [12].

A measure of the capacity of a polymer membrane to carry out the separation for a given gas pair mixture can be obtained from the ideal separation factor, α_B^A, which is found by the ratio of pure gas permeability coefficients of each gas;

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

In Table 3 gas separation factors for the pairs O_2/N_2 and CO_2/CH_4 are listed for PTFmPhONDI (**3**) and they are compared to those reported for DFHFPNB [23] and poly(*N*-cyclohexyl-*exo*,*endo*-norbornene-5,6-dicarboximide) (PCyNDI) [11], the comparison indicates that polymer **3** shows slightly larger

Table 2
Gas permeability, diffusion and solubility coefficients of PTFmPhONDI and some selected polynorbornenes at 35 °C and 10 atm upstream pressure

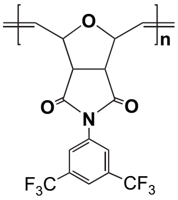
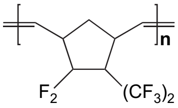
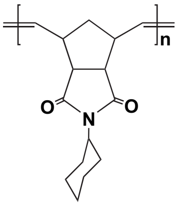
Polymer	P (Barrer)					$D \times 10^8$ (cm^2/s)				$S \times 10^3$ (cm^3(STP)/cm^{3}cmHg)			
	He	CO_2	O_2	N_2	CH_4	CO_2	O_2	N_2	CH_4	CO_2	O_2	N_2	CH_4
 PTFmPhONDI[a]	203.1	164.6	39.4	11.3	10.7	76.0	161	67	20	21.6	2.4	1.6	5.3
 DFHFPNB[b]	185	102.0	27.7	10.5	9.5	29	65	32.5	13.5	35	4.2	3.2	6.9
 PCyNDI[c]	25.1	9.2	2.3	0.43	0.48	15.4	6.6	1.8	2.2	5.9	3.4	2.3	2.1

[a] Poly(*exo*-*N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide).

[b] Poly(5,5-difluoro-6,6-bis(trifluoromethyl)norbornene) [23].

[c] Poly(*N*-cyclohexyl-*exo*,*endo*-norbornene-5,6-dicarboximide) [11].

Table 3
Ideal separation factors for O_2/N_2 and CO_2/CH_4 along with their diffusivity selectivity and solubility selectivity for PTFmPhONDI and some selected polynorbornenes

Polymer	$\alpha_B^A = P_A/P_B$		$\alpha_D = D_A/D_B$		$\alpha_S = S_A/S_B$	
	O_2/N_2	CO_2/CH_4	O_2/N_2	CO_2/CH_4	O_2/N_2	CO_2/CH_4
 PTFmPhONDI[a]	3.4	15.3	2.3	3.8	1.5	4.0
 DFHFPNB[b]	2.6	10.7	2.0	2.1	1.3	5.0
 PCyNDI[c]	5.34	19.1	3.6	7.0	1.4	2.8

[a] Poly(*exo*-*N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide).

[b] Poly(5,5-difluoro-6,6-bis(trifluoromethyl)norbornene) [23].

[c] Poly(*N*-cyclohexyl-*exo*,*endo*-norbornene-5,6-dicarboximide) [11].

ideal separation factor than DFHFPNB even though its permeability coefficients are higher, the polynorbornene with fluorine substitutions. On the other hand, in comparison to polynobornenes with CF_3 substitutions, PCyNDI shows higher ideal separation factors for the gases tested here but lower permeability coefficients. However, this is a common trade off observed in glassy polymers since as the gas permeability coefficient increases the ideal separation factor decreases. Using Eq. (1) it is possible to factorize the ideal separation factor in two different contributions:

$$\alpha_B^A = \frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \tag{4}$$

a diffusivity selectivity contribution, $\alpha_D = D_A/D_B$, and a solubility selectivity contribution, $\alpha_S = S_A/S_B$. These will allow us to determine which one of the factors, α_D or α_S makes the larger contribution to attain the gas pair separation. As it is seen in Table 3, PTFmPhONDI (**3**) diffusivity selectivity factors, α_D, are larger than those of the other fluorinated polynorbornene (DFHFPNB) and the diffusivity selectivity contribution is larger than the α_S for the O_2/N_2 gas pair. One interesting result is that PCyNDI and both polynobornenes DFHFPNB and PTFmPhONDI (**3**) bearing pendant CF_3 groups present lower α_S than α_D for the O_2/N_2 gas pair. This shows that a major contribution to the separation factor is coming from α_D, an indication that their selectivity is controlled by the diffusion coefficients of the gases in the separation of O_2 from nitrogen. In contrast the α_S for the pair CO_2/CH_4 in the fluorinated polymers, DFHFPNB and PTFmPhONDI, is always larger than α_D indicating that the controlling factor is the solubility selectivity. This result is different to the one observed in PCyNDI where α_D is larger than α_S for the same pair of gases. The larger α_S is attributed to an increase in the solubility coefficient of CO_2 and CH_4, see Table 2, which are the gases with the larger solubility coefficient, *S*, in the fluorinated polymers, and they also present *S* values that are, in some cases for CO_2, up to six times larger than those presented for the non fluorinated polynorbornene dicarboximide, PCyNDI. The observed change in controlling factor for selectivity is attributed to an interaction of CO_2 for its higher polarity with the fluorine groups, as well as its inherent condensability which is larger than the one presented for the other three gases tested. On overall the results from gas transport measurements indicate that PTFmPhONDI (**3**) is a polynorbornene with an open structure resulting in one of the largest gas permeability coefficients reported to date in glassy polynorbornene dicarboximides.

4. Conclusions

The synthesis and ROMP of new *exo*-*N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide (TFmPhONDI, **2**) were carried out. Thermal properties of PTFmPhONDI (**3**) as determined here show that the polymer is a rigid material with a storage modulus of 10^9 Pa below the glass to rubber transition, T_α with a T_g as determined by differential scanning calorimetry of 182 °C. Gas permeability, diffusion and solubility coefficients determined by transient permeation for five gases were found to be one of the largest reported to date in glassy polynorbornene dicarboximides and similar to polynorbornenes bearing pendant CF_3 groups reported in the literature. The larger gas permeability and diffusion coefficients are attributed to a lower polymer chain packing due to the effect of the CF_3 groups which results in a larger fraction of free volume available for gas permeability and diffusion.

Acknowledgements

We thank DGAPA-UNAM PAPIIT for generous support with contract ES-104307. We are grateful to Alejandrina Acosta and Gerardo Cedillo for their assistance in NMR analysis. We are also indebted to Maria Isabel Loría for her assistance in permeability coefficients measurements. We are grateful to Dr. Patricia Quintana and M.Sc. Daniel Aguilar for kindly performing the XRD measurement at Cinvestav-Mérida.

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