**Summary:** The synthesis of new *N*-cyclopentyl-*exo,endo*-norbornene-5,6-dicarboximide (CpNDI) (**3a**) and *N*-cyclo-hexyl-*exo,endo*-norbornene-5,6-dicarboximide (ChNDI) (**3b**) monomers was carried out. From these monomers, two polynorbornene dicarboximides with cyclopentyl and cyclohexyl pendant groups, poly(*exo,endo-N*-cyclopentyl norbornene-5,6-dicarboximide) (PCpNDI) and poly(*exo,endo-N*-cyclohexyl norbonene-5,6-dicarboximide) (PChNDI), respectively, were synthesized by ring opening metathesis polymerization (ROMP). PCpNDI, which bears a cyclic pentyl moiety, shows a higher T_g and mechanical properties compared to PChNDI. A comparison of density, fractional free volume, and gas permeability coefficients of the synthesized polynorbornenes shows that PCpNDI presents a slightly higher density and lower fractional free volume than PChNDI. It was also found that gas permeability coefficients for PCpNDI are lower than those of PChNDI. In all cases, the selectivity followed the usual trade-off found in other glassy polymers: as gas permeability coefficients increase selectivity decreases.
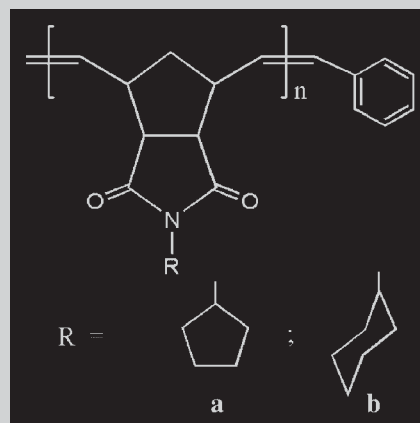
Poly(*exo,endo-N*-cyclopentyl norbornene-5,6-dicarbox-imide) (PCpNDI) was synthesized here by ROMP.

Polynorbornene Dicarboximides with Cyclic Pendant Groups: Synthesis and Gas Transport Properties

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Introduction

In recent times, the use of polymeric membranes to separate gases has received widespread attention, and it is one of the fastest growing technologies for the separation of gases and liquids.[1] Therefore, there is growing interest in the search for 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. The polymeric material should be easy to process and it must be capable of forming highly resistant films with a longer ability to resist ageing.[2]

Gas transport properties of several polynorbornenes with different substituents in the cyclic group, such as silicon

alkyl, fluorine-containing, and different aryl side chains, have been reported.[3–6] The gas permeability of ring-preserved polynorbornenes prepared via an addition polymerization route has also been studied.[7,8] The gas transport of polynorbornenes with lateral imide groups has been tested.[9–11] Membranes prepared from poly(*N*-cycloalkyl-(*N*-phenyl) norbornene-dicarboximide) exhibit a rather high permselectivity for the separation of hydrogen from nitrogen, carbon monoxide, methane, and ethylene.[9–11] These materials show good physical and mechanical properties, and they are soluble in common organic solvents, a fact that allows the preparation of thin polymer membranes that can be used for gas separation.[12,13] The polynorbornenes are obtained via ring opening metathesis polymerization, ROMP, using Grubbs ruthenium alkylidenes of a new generation.[14]

In this work, the synthesis of two polynorbornenes with a lateral imide group that bears a cyclohexyl or a cyclopentyl pendant moiety is described. The synthesis and ROMP of new *N*-cyclopentyl-*exo*,*endo*-norbornene-5,6-dicarboximide (CpNDI) (**3a**) and *N*-cyclohexyl-*exo*,*endo*-norbornene-5,6-dicarboximide (ChNDI) (**3b**) using tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolilydene][benzylidene] ruthenium dichloride (**I**) were studied. The thermal, mechanical, and some physical properties of these polynorbornenes are also determined. A comparison of the pure gas transport properties of both cycloalkyl polynorbornene dicarboximides is performed as a function of pressure and temperature.

Experimental Part

Techniques

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian spectrometer at 300 and 75.5 MHz frequencies, respectively, in CDCl$_3$ with tetramethylsilane (TMS) as an internal standard. Glass transition temperature, T_g, measurements were performed using a DSC-7, Perkin Elmer Inc., at scanning rate of $10\,^\circ\text{C} \cdot \text{min}^{-1}$ under a nitrogen atmosphere. The samples were encapsulated in standard aluminum differential scanning calorimetry (DSC) pans. Each sample was run twice over the temperature range between 30 and 300 °C under a nitrogen atmosphere. Onset of decomposition temperature, T_d, was determined using thermogravimetric analysis, TGA, which was performed at a heating rate of $10\,^\circ\text{C} \cdot \text{min}^{-1}$ under a nitrogen atmosphere with a DuPont 2100 instrument. FT-IR spectra were obtained on a Nicolet 510 p spectrometer. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) with reference to polystyrene standards on a Varian 9012 GPC at 30 °C in chloroform using a universal column and a flow rate of $1\,\text{mL} \cdot \text{min}^{-1}$.

Density of the polynorbornenes was measured by the density gradient column method at 23 °C. The gradient was established by Ca(NO$_3$)$_2$ solutions using glass standards. Mechanical properties under tension were measured in a Universal Mechanical Testing Machine Instron 1125-5500R using a 500 kg cell at a cross-head speed of $10\,\text{mm} \cdot \text{min}^{-1}$ according to the method ASTM D1708 for samples in the form of films with a thickness of 0.5 mm. Wide angle X-ray diffraction (WAXD) was performed using a Bruker AXS D8 Advance diffractometer between $2\theta = 4$ and 60°, using Cu Kα radiation ($\lambda = 1.54$ Å). Films of PChNDA and PCpNDA were cast from 5 wt.-% solutions of each polymer in chloroform at room temperature, and they were dried overnight in the same solvent atmosphere. Later, the films were transferred to a vacuum oven wherein the temperature was maintained at 80 °C to completely eliminate the solvent. The thickness of the films used for thermal analysis and gas transport characterization was 0.07 mm (70 µm).

Gas transport properties were measured in a permeation cell of a constant volume type as described elsewhere.[15] Gas permeability coefficients were determined under steady state conditions (using a transient permeation method) for pure He,

CO$_2$, O$_2$, N$_2$, and CH$_4$ at 35 °C between 2 and 10 atm upstream pressure. From the same transient permeation experiment, the diffusion coefficients were calculated using the time lag method for CO$_2$, O$_2$, N$_2$, and CH$_4$ under the same conditions. Gas permeability coefficients at 45, 55, and 65 °C and 2 atm upstream pressure were also determined in the same cell.

Reagents

Preparation of *exo*-(40%) and *endo*-(60%) norbornene-5,6-dicarboxylic anhydride (NDA, **1**) was carried out via Diels–Alder condensation of cyclopentadiene and maleic anhydride and by the thermal isomerization of the corresponding *endo* isomer according to the literature.[16] Cyclopentylamine, cyclohexylamine, and other chemicals were purchased from Aldrich Chemical Co. 1,2-Dichloroethane and toluene were dried over anhydrous calcium chloride and distilled under nitrogen over CaH$_2$. Catalyst **I** was purchased from Strem Chemicals, Inc. and used as received.

Synthesis and Characterization of Monomers

Synthesis of *N*-Cyclopentyl-*exo*,*endo*-norbornene-5,6-dicarboximide (CpNDI) (**3a**)

exo,*endo*-NDA **1** (12 g, 73 mmol) was dissolved in 120 mL of toluene. An amount of 6.2 g (73 mmol) of cyclopentylamine in 120 mL of toluene was added dropwise to the stirred solution of *exo*,*endo*-NDA. The reaction was maintained at 60 °C for 3 h. The formed precipitate was filtered off and dried to give 17.2 g (69 mmol) of amic acid **2a**. The obtained amic acid (17.2 g, 69 mmol), anhydrous sodium acetate (3.3 g, 40 mmol), and acetic anhydride (65 g, 640 mmol) were heated at reflux for 4 h and then cooled. The solid that crystallized on cooling was filtered off, washed several times with water, and dried in a vacuum oven at 50 °C overnight. Pure monomer **3a** (Scheme 1) was obtained after recrystallizing twice from methanol: yield = 84%, mp = 127–129 °C.

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 6.29$ (2H, *exo*), 6.09 (2H, *endo*), 4.44 (m, 1H), 3.37 (m, 2H), 2.62 (s, 2H), 2.0–1.19 (m, 10H).

^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 177.9$, 137.5, 51.6, 47.1, 45.1, 42.3, 28.3, 25.0.

FT-IR: 3 062 (C=C–H str), 2 951 (C–H asym str), 2 875 (C–H sym str), 1 760 (C=O), 1 692 (C=C str), 1 453 (C–H def.), 1 373 (=CH– def.), 1 291 (C–H def.), 1 221 (C–N str), 1 159, 1 045, 948 (C–C skel), 788 cm^{-1} (=C–H def.).

C$_{14}$H$_{17}$O$_2$N (231): Calcd C 72.73, H 7.36, O 13.85, N 6.06; Found C 73.53, H 7.11, N 6.53.

Synthesis of *N*-Cyclohexyl-*exo*,*endo*-norbornene-5,6-dicarboximide (ChNDI) (**3b**)[12]

exo,*endo*-NDA **1** (12 g, 73 mmol) was dissolved in 120 mL of toluene. An amount of 7.2 g (73 mmol) of cyclohexylamine in 120 mL of toluene was added dropwise to the stirred solution of **1**. The reaction was maintained at room temperature for 1 h. The formed precipitate was filtered off and dried to give 18.6 g (70 mmol) of amic acid **2b**. The obtained amic acid (18.6 g, 70 mmol), anhydrous sodium acetate (3.3 g, 40 mmol), and
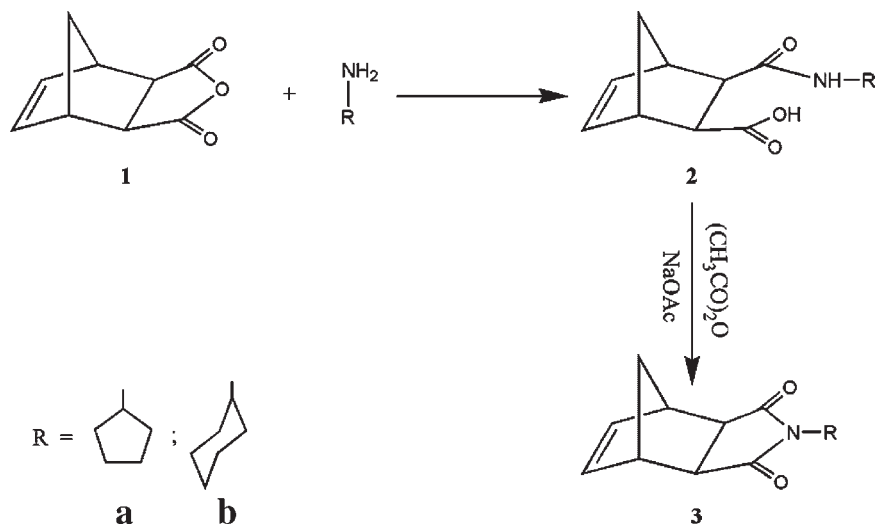
Scheme 1.   Synthesis of monomers **3a** and **3b**.

acetic anhydride (65 g, 640 mmol) were heated at reflux for 2 h and then cooled. The solid that crystallized on cooling was filtered off, washed several times with water, and dried in a vacuum oven at 50 °C overnight. Pure monomer **3b** (Scheme 1) was obtained after recrystallizing twice from methanol: yield = 87%, mp = 130–131 °C.

^{1}H NMR (300 MHz, CDCl$_3$), $\delta = 6.27$ (2H, *exo*), 6.08 (2H, *endo*), 3.94 (m, 1H), 3.25 (d, 2H), 2.60 (d, 2H), 2.12–2.16 (m, 2H), 1.79–1.84 (m, 1H), 1.46–1.60 (m, 2H), 1.33–1.44 (d, 1H).

^{13}C NMR (75 MHZ, CDCl$_3$): $\delta = 178.19$, 137.83, 51.59, 47.38, 45.38, 42.52, 28.74, 25.79, 25.02.

FT-IR: 3 062 (C=C–H str), 2 984 (C–H asym str), 2 857 (C–H sym str), 1 709 (C=O), 1 634 (C=C str), 1 465 (C–H def.), 1 370 (=CH– def.), 1 255 (C–H def.), 1 199 (C–N str), 975 (C–C skel), 784 cm^{-1} (=C–H def.).

C$_{15}$H$_{19}$O$_2$N (245): Calcd C 73.47, H 7.76, O 13.06, N 5.71; Found C 74.27, H 7.51, N 6.18.

Metathesis Polymerization of Monomers

Polymerizations were carried out in glass vials under a dry nitrogen atmosphere at room temperature. Polymerizations 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.
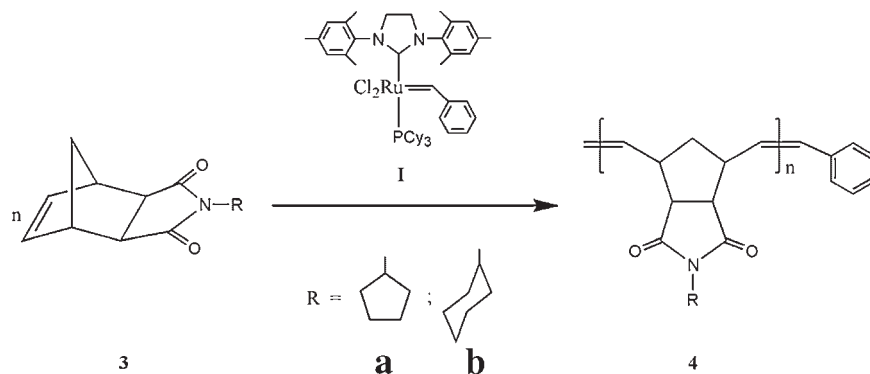
Polymerization of 3a

Monomer **3a** (1 g, 4.33 mmol) and catalyst **I** (0.0036 g, 4.2×10^{-2} mmol) were stirred in 5.4 mL of 1,2-dichloroethane at room temperature for 1 h (Scheme 2). The obtained polymer **4a** was soluble in chloroform and dichloromethane. $T_g = 174$ °C, $T_d = 400$ °C, $\bar{M}_n = 1.86 \times 10^5$, $\bar{M}_w = 2.1 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.13$.

^{1}H NMR (300 MHz, CDCl$_3$) (Figure 1): $\delta = 5.69$ (s, 2H, *trans*), 5.52 (s, 2H, *cis*), 4.42 (s, 1H), 3.15 (s, 2H), 2.94–2.69 (m, 2H), 2.0–1.23 (m, 10H).

^{13}C NMR (75 MHZ, CDCl$_3$): $\delta = 162.2$, 155.7, 71.4, 67.6, 64.0, 57.2, 37.4, 36.2.

FT-IR: 2 967, 2 914, 2 870, 1 768, 1 717, 1 678, 1 450, 1 401, 1 368, 1 321, 1 222, 1 164, 1 068, 967, 768, 632 cm^{-1}.
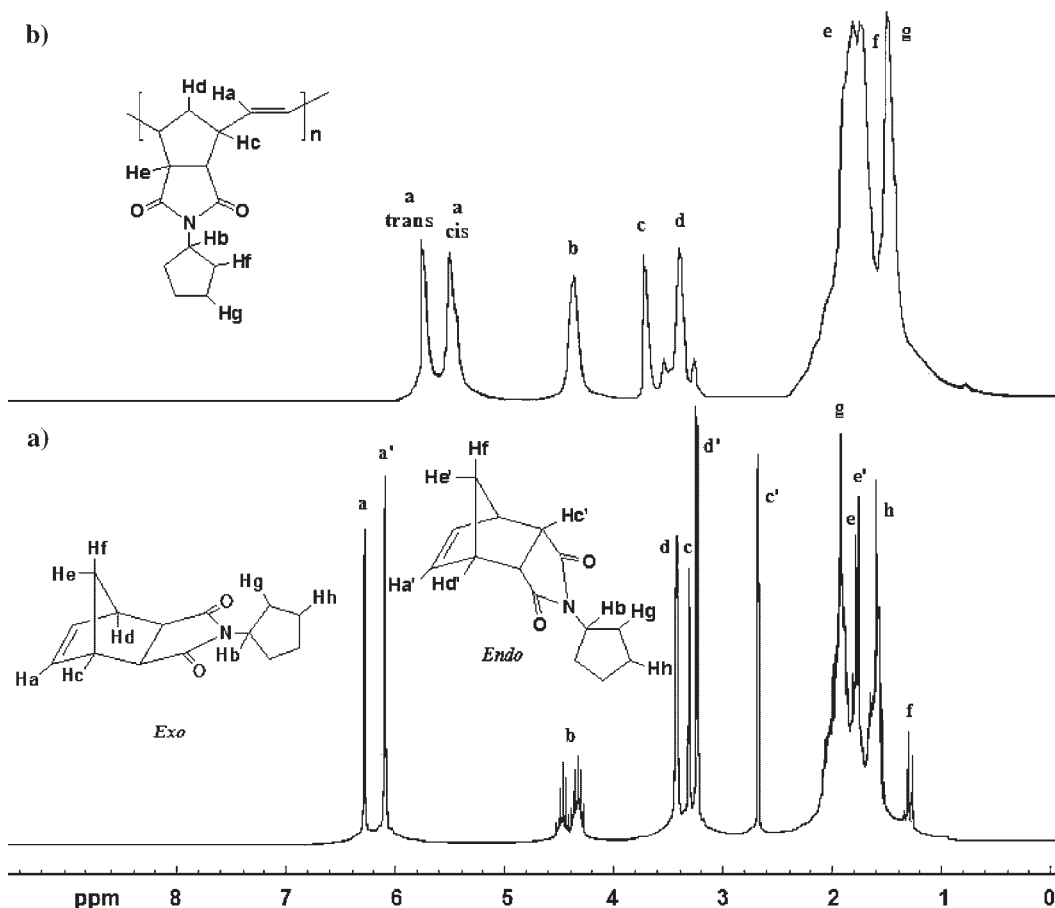

Scheme 2.   ROMP of **3a** and **3b**.

Figure 1. ^{1}H NMR spectra of a) monomer **3a** and b) polymer **4a**.

Polymerization of 3b

The typical polymerization procedure as given above was used Scheme 2). The obtained polymer **4b** was soluble in chloroform and dichloromethane. $T_g = 155\,°C$, $T_d = 434\,°C$ $\bar{M}_n = 2.04 \times 10^5$, $\bar{M}_w = 2.35 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.15$.

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 5.74$ (t, 2H), 5.5 (m, 2H), 3.98 (m, 1H), 2.92 (d, 2H), 2.66 (d, 2H), 2.14–2.11 (d, 2H), 1.80–1.58 (6H, m), 1.27 (4H, m).

^{13}C NMR (75 MHZ, CDCl$_3$): $\delta = 178.49$, 132.05, 51.29, 50.63, 46.10, 42.00, 28.73, 25.81, 25.07.

FT-IR: 3 036, 2 934, 2 893, 1 768, 1 700, 1 665, 1 452, 1 370, 1 346, 1 304, 1 297, 1 186, 987, 762, 748 cm^{-1}.

Results and Discussion

Polynorbornene dicarboximides from *exo,endo*-CpNDI **3a** and *exo,endo*-ChNDI **3b** were prepared using catalyst **I**. It has been demonstrated that the *N*-heterocyclic carbene (NHC)-coordinated ruthenium alkylidenes exhibit dramatically increased olefin metathesis activity compared to

Table 1.   Properties of polynorbornene dicarboximides.

Polymer	T_g	T_d	ρ	FFV	d	σ	E
	°C	°C	g · cm^{-3}		Å	MPa	MPa
PCpNDI	174	400	1.180	0.146	4.978	66.3	1528
PChNDI	155	434	1.156	0.149	5.033	42.0	1232
PNB[a]	31	–	0.98	0.159	–	–	–
PTMSNB[a]	110	–	0.91	0.200	–	–	–

[a] Data from Yampol'skii et al.[7]

Table 2. Gas permeability and diffusion coefficients for PCpNDI and PChNDI at 10 atm and 35 °C.

Polymer	P					$\alpha = P_A/P_B$		$D \times 10^8$			
	barrer[a)]					P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}	cm$^2 \cdot$ s^{-1}			
	He	CO_2	O_2	N_2	CH_4			CO_2	O_2	N_2	CH_4
PCpNDI	15.4	8.8	1.95	0.45	0.54	4.3	16.3	5.9	3.9	2.1	4.1
PChNDI	25.1	9.2	2.3	0.43	0.48	5.3	19.1	15.4	6.6	1.8	2.2
PNB[b)]	–	15.4	2.8	1.4	2.5	1.9	6.3	16	15	4.4	3.6
PTMSNB[b)]	–	165	29.8	11.7	10.9	2.5	15.3	33	42	30	14

[a)] 1 barrer $= 1 \times 10^{-10}$ [(cm^3 (STP) cm) $\cdot$ (cm^2 s cmHg)$^{-1}$].
[b)] Data from Yampol'skii et al.[7]

the bis(phosphine) family of catalysts.[14] The monomers reacted within 2 h to give high-molecular-weight polymers ($\bar{M}_n \sim 10^{-5}$) with high yields (90–95%) and polydispersity 1.1. Figure 1 presents ^{1}H NMR spectra of **3a** (a) and its polymer (b). The monomer olefinic signals at $\delta = 6.25$ ppm (*exo*) and $\delta = 6.09$ ppm (*endo*) are replaced by new signals at $\delta = 5.69$ and 5.52 ppm, which correspond to the *trans* and *cis* double bonds of the polymer, respectively (Figure 1b). The ^{13}C NMR spectra agree with the structure of the obtained polymers.

Mechanical and thermal properties of the polymers are given in Table 1 along with those values for polynorbornene, PNB, and polytrimethylsilylnorbornene, PTMSNB, found in the literature.[4,5] From these results it can be seen that PCpNDI presents a T_g that is higher than that of PChNDI by 20 °C. Both polynorbornene dicarboximides show T_gs that are higher than those reported for PNB, 31 °C, and PTMSNB, 110 °C.[4,5] This could be attributed to an increase in rigidity of the polynorbornene because of the presence of the cyclic dicarboximide with a large pendant cycloalkyl group. The difference in T_g between PCpNDI and PChNDI could be attributed to the ability of the cyclohexyl pendant moiety in PChNDI to adopt different conformations. The increase in rigidity in these cycloalkyl polynorbornene dicarboximides is larger than the effect of a large lateral substitution, such as that of the trimethylsilyl moiety in PTMSNB. It is also seen that PCpNDI and PChNDI show a higher density and lower fractional free volume, FFV, than PNB and PTMSNB. The lower FFV comes from higher chain packing because of the presence of a dicarboximide lateral pendant group in the polynorbornene. FFV was calculated from:

$$FFV = \frac{V - V_o}{V} \tag{1}$$

where V is the specific volume ($1/\rho$), and V_o is the specific occupied volume that can be approximated using Bondi's group contribution method from the van der Waals volume, V_w, as $V_o = 1.3 V_w$.[17]

Finally, both PCpNDI and PChNDI present no crystallinity when a WAXD trace is taken. Since they are amorphous, a measure of their average intermolecular spacing could be obtained from the d-spacing value at the maximum of the amorphous trace using Bragg's equation, $n\lambda = 2d\sin\theta$.[18] A comparison indicates that they have a similar average d-spacing, d (intermolecular distance), which is slightly larger than that for PChNDI.

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.

$$P = DS \tag{2}$$

From a single transient experiment, both permeability, P, and an apparent diffusion coefficient, D, can be obtained from the 'time lag' technique. The advantage of this technique lies in the fact that the two quantities P and D can be evaluated from a single experiment, and S can be deduced from Equation (2). Assuming that D is constant, it has been shown that the amount of permeant, Q_t, passing through a film in time t is given by[19]:

$$Q_t = \frac{Dc_o}{l}\left[t - \frac{l^2}{6D}\right] - \frac{2lc_o}{\pi^2}\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\exp\frac{-Dn^2\pi^2 t}{l^2} \tag{3}$$

where l is the membrane thickness and c_o is the concentration at the upstream side of the membrane. When the steady state is reached, the exponential term becomes negligibly for large t, thus Equation (3) can be written as;

$$Q_t = \frac{Dc_o}{l}\left[t - \frac{l^2}{6D}\right] \tag{4}$$

The conditions of the measurement are that at the beginning the film was gas free, and equilibrium is reached at the gas polymer interface with zero concentration of gas at the outflow face. Under these conditions, a plot of Q_t vs t results in a straight line whose intercept in the t axis is given by the time lag, θ.

$$\theta = \frac{l^2}{6D} \tag{5}$$

The slope of the steady state portion of the experimental data is used to determine the permeability coefficient, P.
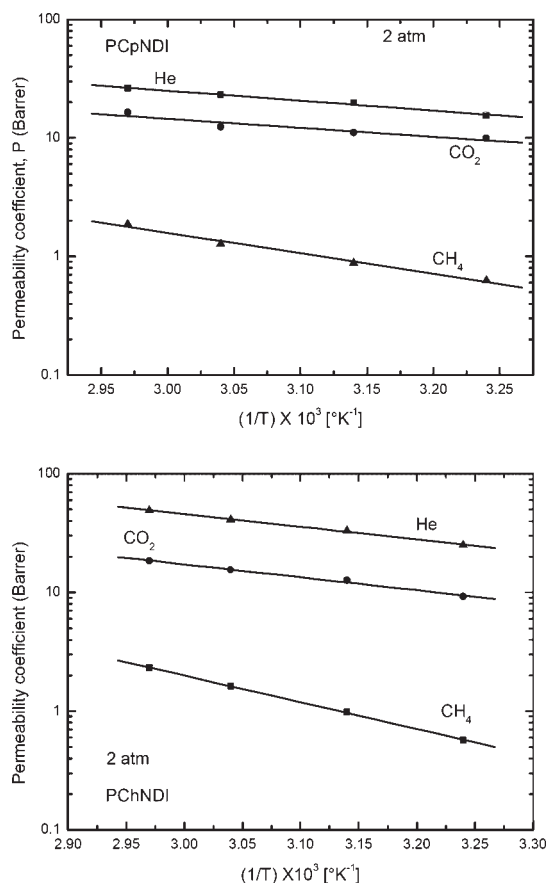
Figure 2. Gas permeability coefficients for PCpNDI and PChNDI as a function of temperature at 2 atm upstream pressure.

Gas permeability and diffusion coefficients for pure He, CO_2, O_2, N_2, and CH_4 in solution-cast membranes of PCpNDI and PChNDI at 10 atm and 35 °C are given in Table 2. These coefficients are compared to those reported in the literature for PNB and PTMSNB. In general, the gas permeability coefficients, P, decrease in the order of increasing kinetic diameter of the gases, $P_{He} > P_{CO_2} > P_{O_2} > P_{CH_4} \approx P_{N_2}$ for all the polynorbornenes listed in Table 2. From Table 2 it is also evident that the polynorbornene dicarboximides with the lower gas permeability coefficients show the best ideal separation factors, α, defined as the ratio of pure gas permeability coefficients P_A/P_B, a trade off that is commonly found in glassy polymers. Gas permeability coefficients for pure He, CO_2, O_2, N_2, and CH_4 in solution-cast membranes of PCpNDI and PChNDI show little dependence on pressure over the range of pressures tested here. Gas permeability coefficients of these two polynorbornene dicarboximides for He and O_2 remain constant in the interval measured. Permeability coefficients of PCpNDI and PChNDI for CO_2, N_2, and CH_4 decrease slightly as the upstream pressure increases, a behavior that is commonly observed in glassy polymers. Solubility coefficients, S, in PCpNDI and PChNDI show the following order $S_{CO_2} > S_{O_2} > S_{N_2} \sim S_{CH_4}$.

It is worth noting that double bonds in the molecular chains impart rigidity to the system, which is alleviated by motions about the two single bonds in the ring-opened units. Conformational transition on the main chain cyclopentyl groups that hinder chain packing cannot be ruled out. However, the polymers used in this study show a rather low permeability in comparison with other glassy polymers containing bulky substituted groups in their structure.[20] It may be explained by strong inter-chain interactions because of the presence of polar C=O and C–N bonds in the tested polymers. It is also worth noting that polymers obtained by ROMP may give rise to the formation of blocks of *cis* and/or *trans* configurations that have different specific chain lengths. The incompatibility between blocks could result in microphase separation that increases the tortuosity of the diffusive path, thus decreasing the diffusion coefficient.

Gas permeability coefficients show an Arrhenius dependence with temperature that follows an equation of the form:[21]

$$P = P_o \exp\left[\frac{-E_p}{RT}\right] \qquad (6)$$

where P_o is a pre-exponential factor, E_p is the energy necessary for the gas to achieve permeation through the membrane, R is the gas constant, and T is the temperature. In particular, E_p gives a measure of the difficulty encountered for a gas to permeate through a polymer film. An increase in E_p will indicate that the gas has a greater difficulty to permeate and diffuse through the polymer. Figure 2 shows permeability coefficients for He, CO_2, and CH_4 as a function of temperature for PCpNDI and PChNDI, respectively. The behavior observed indicates that they adjust closely to an Arrhenius-type behavior. As observed from the values in Table 3, PCpNDI has higher values of E_p than PChNDI.

Conclusion

Two polynorbornene dicarboximides with cyclohexyl and cyclopentyl pendant groups, PChNDI and PCpNDI, respectively, were synthesized by ROMP. PCpNDI, which bears a cyclic pentyl moiety, shows a higher T_g and mechanical properties than PChNDI. A comparison of density,

Table 3. Activation energies for gas permeation and diffusion in polynorbornene dicarboximides.

Polymer	E_P			E_D	
	kcal · mol^{-1}			kcal · mol^{-1}	
	He	CO_2	CH_4	CO_2	CH_4
PCpNDI	4.8	4.9	7.8	5.37	6.21
PChNDI	3.8	4.3	10.2	8.7	16.9

fractional free volume, and gas permeability coefficients of the synthesized polynorbornenes shows that PCpNDI presents a slightly higher density and lower fractional free volume than PChNDI. It was also found that the gas permeability coefficients for PCpNDI are lower than those of PChNDI. This behavior was attributed to a lower fractional free volume and higher rigidity, a fact that was corroborated by the lower diffusion coefficients and higher activation energies found for the permeation of gases through PCpNDI as compared to PChNDI. A comparison with PTMSNB, which bears a large lateral group indicates that the polynorbornene dicarboximides studied here present higher T_gs and densities, as well as lower fractional free volumes and lower gas permeability coefficients. In all cases, the selectivity followed the usual trade off found in other glassy polymers: as gas permeability coefficients increase selectivity decreases.

[1] S. A. Stern, *J. Membr. Sci.* **1994**, *94*, 1.
[2] P. Tiemblo, J. Guzmán, E. Riande, *Macromolecules* **2002**, *35*, 420.
[3] A. P. Contreras, M. A. Tlenkopatchev, T. Ogawa, T. Nakagawa, *Polym. J.* **2002**, *34*, 49.
[4] Y. Kawakami, H. Toda, M. Higashino, Y. Yamashita, *Polym. J.* **1988**, *4*, 285.
[5] V. I. Bondar, Y. M. Kukharskii, Y. P. Yampol'skii, E. S. Finkelshtein, K. L. Makovetskii, *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 1273.
[6] Z. Chun-thian, M. R. Ribeiro, M. N. de Pinho, V. S. Subrahmanyam, C. L. Gil, A. P. de Lima, *Polymer* **2001**, *42*, 2455.
[7] Y. P. Yampol'skii, N. B. Bespalova, E. S. Finkelshtein, V. I. Bondar, A. V. Popov, *Macromolecules* **1994**, *27*, 2872.
[8] E. S. Finkelshtein, M. L. Gringolts, N. V. Ushakov, V. G. Lakhtin, S. A. Soloviev, Y. P. Yampol'skii, *Polymer* **2003**, *44*, 2843.
[9] A. Pineda, M. A. Tlenkopatchev, M. M. López-González, E. Riande, *Macromolecules* **2002**, *35*, 4677.
[10] M. A. Tlenkopatchev, J. Vargas, M. M. López-González, E. Riande, *Macromolecules* **2003**, *36*, 8483.
[11] M. A. Tlenkopatchev, J. Vargas, M. A. Almaraz-Girón, M. M. López-González, E. Riande, *Macromolecules* **2005**, *38*, 2696.
[12] A. Pineda, A. M. Cerda, M. A. Tlenkopatchev, *Macromol. Chem. Phys.* **2002**, *203*, 1811.
[13] J. Vargas, E. Sánchez, M. A. Tlenkopatchev, *Eur. Polym. J.* **2004**, *40*, 1325.
[14] C. W. Bielawski, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2000**, *39*, 2903.
[15] H. J. Bixler, O. J. Sweeting, in: "*The Science and Technology of Polymer Films*", O. J. Sweeting, Ed., Wiley Intersciencie, New York 1971, Chap. 1.
[16] K. F. Kestner, N. J. Calderón, *J. Mol. Catal.* **1982**, *15*, 47.
[17] V. W. Van Krevelen, P. J. Hoftyzer, in: "*Properties of Polymers*", Elsevier, Amsterdam 1976.
[18] S. G. Charati, A. Y. Houde, S. S. Kulkarni, M. G. Kulkarni, *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 921.
[19] R. López-Nava, F. S. Vázquez-Moreno, R. Palí-casanova, M. Aguilar-Vega, *Polym. Bull.* **2002**, *49*, 165.
[20] J. Y. Park, D. R. Paul. *J. Membr. Sci.* **1997**, *125*, 23.
[21] M. Aguilar-Vega, D. R. Paul, *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 1599.