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The effect of fluorine atoms on gas transport properties of new polynorbornene dicarboximides

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ABSTRACT

The new *N*-4-trifluoromethylphenyl-norbornene-5,6-dicarboximide (**2a**) and *N*-3,5-bis(trifluoromethyl)phenyl-norbornene-5,6-dicarboximide (**2b**) 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 **Poly-2a** and **Poly-2b**, respectively. The transport of five gases He, N_2, O_2, CO_2 and CH_4 across membranes prepared from **Poly-2a** was determined at 35 °C using a constant volume permeation cell. The gas transport properties of the fluorine containing polymer **Poly-2a** were compared with those found for membranes from non-fluorinated poly(*N*-phenyl-*exo*-*endo*-norbornene-5,6-dicarboximide) (**P-PhNDI**). Gas permeability, diffusion and solubility coefficients of the fluorine containing polynorbornene **Poly-2a** were up to an order of magnitude larger than those of the non-fluorinated one. **Poly-2a** was found to have one of the largest gas transport coefficients reported to date in glassy polynorbornene dicarboximides.

1. Introduction

Fluorine containing polymers have attracted much attention due to their outstanding properties. These kinds of polymer exhibit high thermostability, chemical inertness and good hydrophobicity. It is important to note that low intermolecular and intramolecular interactions in fluorine containing polymers are important factor for gas permeability properties of membranes. Thus, we have already reported gas transport properties of polynorbornenes containing adamantyl, cyclohexyl and cyclopentyl imide side chain groups [1–5]. These glassy polynorbornene dicarboximides showed high T_g and good physical and mechanical properties. For example, poly(*N*-adamantyl-norbornene-5,6-dicarboximide) (**P-AdNDI**) showed a T_g of 271 °C [6]. Even though polynorbornene dicarboximides, such as **P-AdNDI**, have bulky pendant groups, their gas permeability coefficients are not high but similar to those of amorphous polyesters or polyamides [7–9]. It is well known, that in many cases higher permeabilities are found for glassy polymers with higher glass transition temperature [10–12]. However, this is not the case for polynorbornene with imide side chain groups. Membranes prepared from these polymers show an enhancement of the selectivity, though the permeability remains low and does not depend on the bulk of side chain groups. The low gas permeability of these membranes is due to strong intermolecular interactions of polar C=O and C–N bonds in polynorbornene dicarboximides. 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. The ROMP of norbornene derivatives with various fluorine-containing units is well established [13–16].

With the aim of investigating the effect of fluorine atoms on gas permeability of polynorbornene dicarboximides, the new poly(*N*-4-trifluoromethylphenyl-*exo*-*endo*-norbornene-5,6-dicarboximide) (**Poly-2a**) was synthesized and gas transport properties of membranes prepared from this polymer were studied.

2. Results and discussion

Monomers **2a** and **2b** were prepared in high yields. 4-Trifluoromethyl aniline and 3,5-bis(trifluoromethyl) aniline

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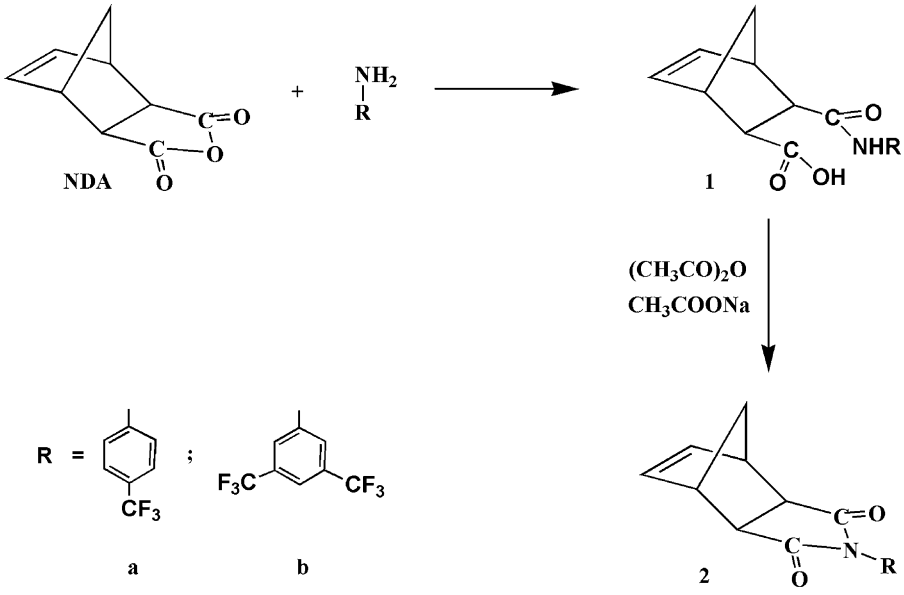

Scheme 1. Synthesis of monomers **2a** and **2b**, respectively.

reacted with **NDA** to the corresponding amic acids (**1a**, **1b**) which were cyclized to imides using acetic anhydride as dehydrating agent (Scheme 1). ^{1}H, ^{13}C and ^{19}F NMR spectra and elemental analysis confirmed monomer structure and purity. The infrared spectra of monomer showed characteristic peaks at 1774 and 1706 cm^{-1} (asymmetric and symmetric C=O stretching), 1383 cm^{-1} (C–N stretching). ROMP of **2a** and **2b** 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 **PhNDI** [5]. The mixture of *exo* and *endo* monomers reacted in 2 h giving polymer in high yield (98–99%, entries 4, 8 and 12). The results obtained by GPC analysis show that the number average molecular weights (M_n) were between 98,000 and 341,000. 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 **Poly-2a**, **Poly-2b** and **P-PhNDI** obtained using **II** is about M_w/M_n = 1.22–1.32 which is broader than polymers prepared using **I** (M_w/M_n = 1.11–1.17) due to the slower initiation of the latter catalyst [18].

Table 1
Polymerization conditions of norbornene dicarboximides.

Entry	Monomer[a]	Catalyst	M/Cat[b]	Yield[c] (%)	*cis*[d] (%)	$M_n \times 10^{-5}$[e]	*MWD*[e]
1	**2a**	**I**	1000	94	16	2.79	1.11
2	**2a**	**I**	500	96	17	1.42	1.12
3	**2a**	**II**	1000	98	53	2.61	1.27
4	**2a**	**II**	500	99	52	1.51	1.26
5	**2b**	**I**	1000	91	18	3.41	1.15
6	**2b**	**I**	500	93	20	1.77	1.17
7	**2b**	**II**	1000	94	51	3.27	1.22
8	**2b**	**II**	500	98	50	1.62	1.23
9	**PhNDI**[f]	**I**	1000	92	22	2.21	1.16
10	**PhNDI**[f]	**I**	500	95	25	1.09	1.17
11	**PhNDI**[f]	**II**	1000	96	55	2.10	1.30
12	**PhNDI**[f]	**II**	500	98	56	0.98	1.32

[a] 1,2-Dichloroethane as solvent, Temperature = 45 °C, Time = 2 h, Initial monomer concentration [M_o] = 0.7 mol/L.
[b] Mole ratio of monomer to catalyst.
[c] Methanol insoluble polymer.
[d] Determined by ^{1}H NMR.
[e] GPC analysis in chloroform with polystyrene calibration standards.
[f] Poly(*N*-phenyl-*exo*,*endo*-norbornene-5,6-dicarboximide) [5].

Catalyst **I** gave polymers with predominantly *trans* configuration of the double bonds (75–84%), whereas catalyst **II** produced polymers with a mixture of *cis* and *trans* double bonds (50–56% of *cis* structure).

Fig. 1 shows the ^{1}H NMR spectra of (a) monomer **2a** and (b) polymer **Poly-2a** prepared using **I**. The *exo* and *endo* monomer olefinic signals at δ = 6.35–6.25 ppm are replaced by new signals at δ = 5.80–5.58 ppm, which correspond respectively to the *trans* and *cis* H at the double bonds of the product polymer.

The effect that CF_3 group substitutions on the pendant phenyl ring in the polynorbornene dicarboximide had on the physical properties of polynorbornenes with similar structures is compared in Table 2. The non-substituted phenyl ring polynorbornene dicarboximide, **P-PhNDI**, has a higher T_g and T_d than the previously reported poly(*exo*-*N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide) **P-TFmPhONDI** [17] with the 3,5 CF_3 substitution on the phenyl ring, or the single CF_3 substitution on the *para* position of the phenyl ring in **Poly-2a**. The latter presents the lowest T_g and T_d values although the T_d's are all above 400 °C which indicates that all these polynorbornenes are of relatively high thermal stability. The lowering of T_g for the fluorine substituted polymers is attributed to a diminished ability to pack of the phenyl ring since the presence of CF_3 moieties in position 3,5 of the phenyl ring inhibits packing and decrease the temperature to attain the relaxation process. The single CF_3 moiety in the *para* position of the phenyl ring, **Poly-2a**, increases mobility mainly because it has the CF_3 group situated on the phenyl ring in a symmetric manner. Density measurements, reported also in Table 2, indicate that the presence of two CF_3 moieties increases density of the polynorbornene dicarboximide (**P-TFmPhONDI**), followed by the one with a single CF_3 substitution, **Poly-2a**, as compared to the non-fluorine substituted polynorbornene dicarboximide, **P-PhNDI**. It is also reported in Table 2 the fractional free volume (*FFV*), as calculated from Bondi's group contribution method from the following equation [19];

$$FFV = \frac{(V - V_O)}{V} \quad (1)$$