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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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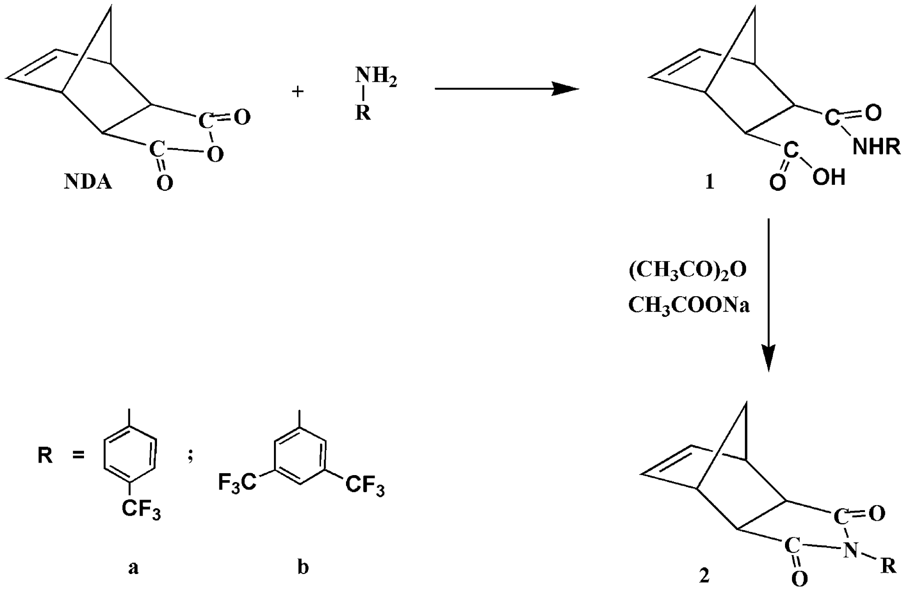


Scheme 1. Synthesis of monomers **2a** and **2b**, respectively.

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] (%)	$M_n \times 10^{-5e}$	*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 $\delta = 6.35–6.25$ ppm are replaced by new signals at $\delta = 5.80–5.58$ 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];

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

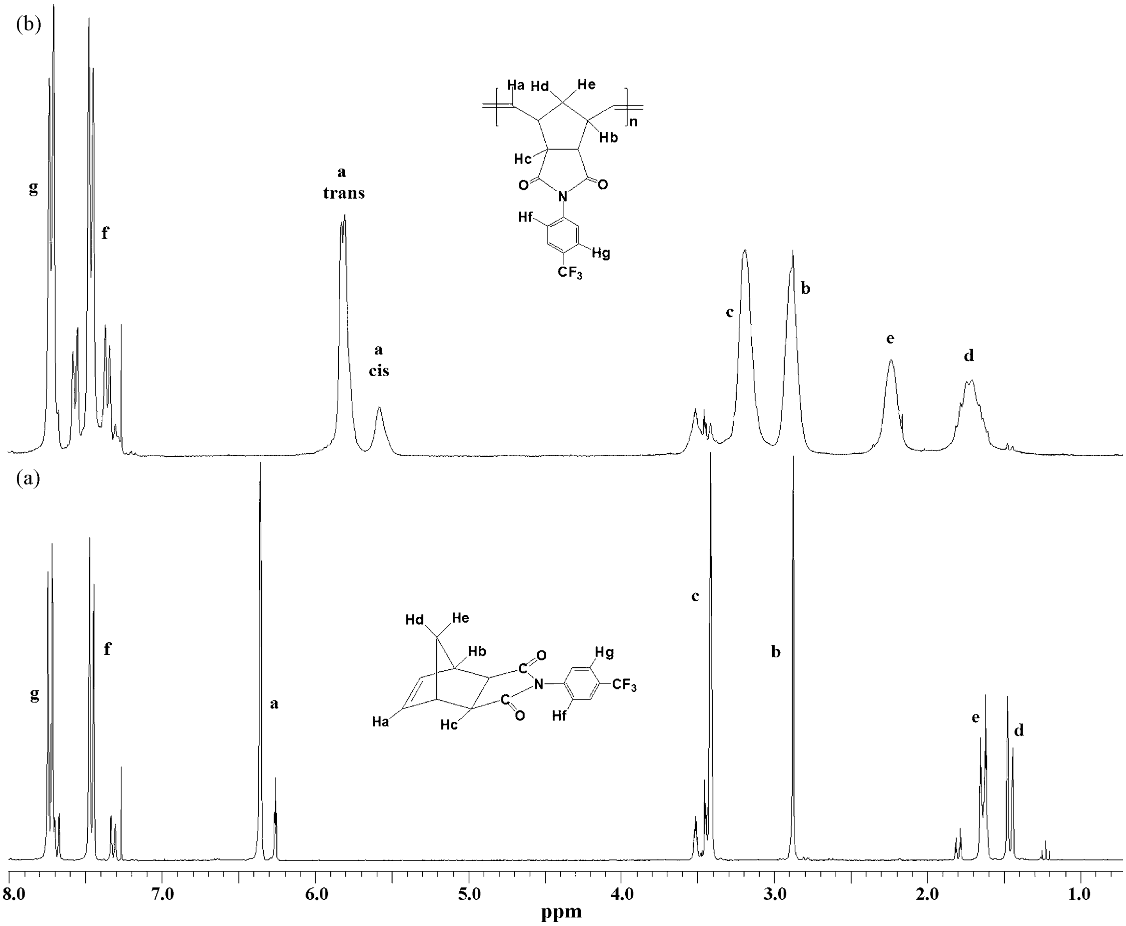


Fig. 1. ^{1}H NMR spectra of monomer **2a** (bottom) and polymer **Poly-2a** (top) obtained using catalyst **I**.

Table 2
Physical properties of polynorbornene dicarboximides.

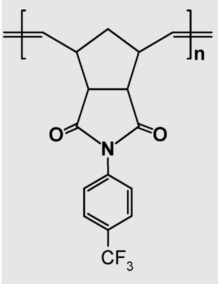
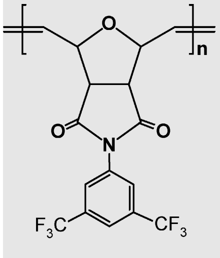
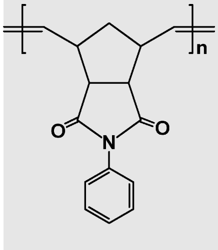
Polymer	T_g (°C)	T_d (°C)	*FFV*	ρ (g/cm^3)	σ (MPa)	E (MPa)
 **Poly-2a**[a]	155	402	0.141	1.368	55.4	1408
 **P-TFmPhONDI**[b]	182	404	0.230	1.430	43.2	1512

Table 2 (*Continued*)

Polymer	T_g (°C)	T_d (°C)	*FFV*	ρ (g/cm^3)	σ (MPa)	*E* (MPa)
 **P-PhNDI**[c]	222	418	0.126	1.241	57.0	1560

[a] Poly(*N*-4-trifluoromethylphenyl-*exo,endo*-norbornene-5,6-dicarboximide).

[b] Poly(*exo*-*N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide) [17].

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

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

FFV is a measure of the intermolecular distance between polymer chains. From Table 2 *FFV* increases drastically with the presence of CF_3 groups on the pendant phenyl moiety in the polynorbornene dicarboximides. *FFV* of **P-TFmPhONDI** is almost twice that of the non-substituted polynorbornene, **P-PhNDI**. The increase in *FFV* is related to a larger intermolecular distance between the polymer chains, which is related to an inhibition of packing by the presence of the CF_3 groups.

The presence of CF_3 moieties in the phenyl ring of the polynorbornene dicarboximide structures becomes important for their gas permeability coefficients, see Table 3. It is seen that the polynorbornene dicarboximide with two CF_3 substitutions and the larger *FFV*, **P-TFmPhONDI**, has around twice the gas permeability coefficients found for the polynorbornene dicarboximide with a single CF_3 substitution, **Poly-2a**. While the latter has gas permeability coefficients that are with the exception of CO_2 an order of magnitude higher than those of the polynorbornene dicarboximide without fluorine groups, **P-PhNDI**. The larger gas permeability coefficients in the CF_3 substituted polynorbornenes are related to the larger *FFV*, which in turn facilitates the diffusion of the gas molecules through the polymer. The latter result is clearly seen by the increase in gas diffusion coefficients, *D*, as the number of CF_3 groups increases in the polynorbornene. As a general trade off when the gas permeability coefficients increase, the gas separation capacity or ideal gas separation factor, as defined for Eq. (2), decreases for a given pair of gases:

$$\alpha_{\mathrm{B}}^{\mathrm{A}} = \frac{P_{\mathrm{A}}}{P_{\mathrm{B}}} \tag{2}$$

where P_{A} and P_{B} are the pure gas permeability coefficients for gases A and B. In Table 3 the ideal gas separation factors for the commercially important gas mixtures O_2/N_2 and CO_2/CH_4 are presented. They follow the expected trend since as the permeability coefficient increases in the polynorbornene dicarboximide, the ideal separation factor decreases. However, since the difference

Table 3

Ideal gas separation factors, gas permeability, diffusion and solubility coefficients of fluorinated and non-fluorinated polynorbornene dicarboximides.

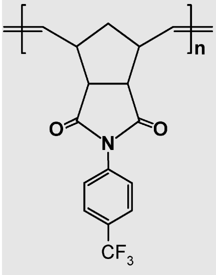
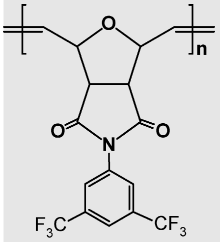
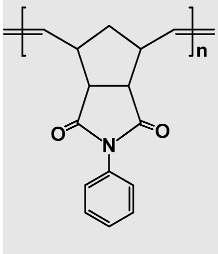
Polymer	*P* (Barrer)					$D \times 10^8$ (cm^2/s)				$S \times 10^3$ cm^3(STP)/cm^3 cmHg				$\alpha_{\mathrm{B}}^{\mathrm{A}} = \frac{P_{\mathrm{A}}}{P_{\mathrm{B}}}$	
	He	CO_2	O_2	N_2	CH_4	CO_2	O_2	N_2	CH_4	CO_2	O_2	N_2	CH_4	O_2/N_2	CO_2/CH_4
 **Poly-2a**[a]	80.8	77.5	15.5	3.69	4.09	11.4	15.0	9.1	5.1	70.5	10.4	4.0	9.7	4.21	18.9
 **P-TFmPhONDI**[b]	203.1	164.6	39.4	11.3	10.7	76.0	161	67	20	21.6	2.4	1.6	5.3	3.40	15.3

Table 3 (*Continued*)

Polymer	P (Barrer)					$D \times 10^8$ (cm^2/s)				$S \times 10^3$ cm^3(STP)/cm^3 cmHg				$\alpha^A_B = \frac{P_A}{P_B}$	
	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	O_2/N_2	CO_2/CH_4
 **P-PhNDI**[c]	–	11.4	1.44	0.31	0.54	1.81	6.3	2.2	0.72	63.2	2.2	1.3	7.5	4.64	21.1

[a] Poly(*N*-4-trifluoromethylphenyl-*exo,endo*-norbornene-5,6-dicarboximide).
[b] Poly(*exo-N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide) [17].
[c] Poly(*N*-phenyl-*exo,endo*-norbornene-5,6-dicarboximide) [5].

in gas permeability coefficients is at least one order of magnitude higher in **P-TFmPhONDI**, as compared to **P-PhNDI** the CF_3 substituted polynorbornene may present an advantage for developing a technical separation where the large gas permeability coefficients will compensate for the loss in selectivity for the gas separation because the loss in selectivity is not large than 1.2.

3. Conclusions

Exo(90%)-*endo*(10%) monomer mixtures **2a** and **2b** were synthesized and polymerized via ROMP using well defined ruthenium alkylidene catalysts **I** and **II**. T_g for **Poly-2a** was observed at 155 °C. The catalyst **I** produced polymers with predominantly *trans* configuration of the double bonds whereas catalyst **II** gave polymers with a mixture of *cis* and *trans* double bonds. A comparison of **Poly-2a** physical and gas transport properties with a non-fluorinated analogous **P-PhNDI** and a polynorbornene with two CF_3 groups in the phenyl ring, **P-TFmPhONDI**, was performed. Thermal properties such as T_g and T_d are lower in **Poly-2a** as compared to those of the analogous non-fluorinated **P-PhNDI**, a fact that was attributed to a larger polymer interchain distance. Density and fractional free volume are larger in the fluorine substituted polymers due to the presence of the bulky CF_3 groups. The large fractional free volume found in **Poly-2a** as compared to the non-fluorine substituted polynorbornene, **P-PhNDI**, produces one of the largest permeability and diffusion coefficients found in polynorbornene dicarboximides.

4. Experimental

4.1. 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. FT-IR spectra were obtained on a Nicolet 510 p spectrometer. Glass transition temperature, T_g, was determined in a DSC-7 Perkin Elmer Inc., at scanning rate of 10 °C/min under nitrogen atmosphere. The sample was encapsulated in a standard aluminum DSC pan. The sample was run twice in the temperature range 30–300 °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 °C/min under a nitrogen atmosphere with a DuPont 2100 instrument. 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. Molecular weights and molecular weight distributions 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}. Density of the polynorbornenes was measured by the density gradient column method for films cast from solution. The gradient was established by $Ca(NO_3)_2$ solutions at 23 °C using glass standards. Films of **Poly-2a**, **P-TFmPhONDI** and **P-PhNDI** were cast from chloroform solutions, 5 wt.%, of each polynorbornene at room temperature. The solutions were dried overnight in a solvent atmosphere until a self-standing film developed. The films were transfer to a vacuum oven and kept at 80 °C to insure that chloroform was totally eliminated. The thickness of the films used for gas transport properties was around 75 μm.

Gas transport properties were measured in a constant volume type gas permeation cell as described elsewhere [3]. Gas permeability coefficients, P, were determined for pure He, CO_2, O_2, N_2 and CH_4 under steady state conditions at 35 °C and 2 atmospheres upstream pressure. From this transient permeation experiment, diffusion coefficients, D, for CO_2, O_2, N_2 and CH_4 were obtained using the time lag method as described before [3]. Solubility coefficients, S, were obtained from the ratio between permeability and diffusion coefficients, $S = P/D$, for each pure gas.

4.2. Reagents

Exo(90%)-*endo*(10%) mixture of norbornene-5,6-dicarboxylic anhydride (**NDA**) was prepared via Diels-Alder condensation of cyclopentadiene and maleic anhydride according to literature [5]. 4-Trifluoromethylaniline, 3,5-bis(trifluoromethyl) aniline and other chemicals were purchased from Aldrich Chemical Co. 1,2-Dichloroethane and dichloromethane were dried over anhydrous calcium chloride and distilled over CaH_2. Bis(tricyclohexylphosphine) benzylidene ruthenium(IV) dichloride (**I**) and tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene] ruthenium dichloride (**II**) were purchased from Aldrich Chemical Co. and used as received.

4.3. Synthesis and characterization of exo(90%)-endo(10%) monomer mixture of N-4-trifluoromethylphenyl-norbornene-5,6-dicarboximide (2a)

NDA (5 g, 30.5 mmol) was dissolved in 50 mL of dichloromethane. An amount of 4.9 g (30.4 mmol) of 4-trifluoromethylaniline in 5 mL of dichloromethane is added dropwise to the stirred solution of **NDA**. The reaction was maintained at reflux for 2 h and then cooled to room temperature. The precipitate was recovered by filtration and dried to give 9.7 g of amic acid **1a**. The obtained amic acid **1a** (9.7 g, 29.8 mmol), anhydrous sodium acetate (1.1 g, 13.6 mmol) and acetic anhydride (12.0 g, 117 mmol) were heated at 70–80 °C for 7 h and then cooled. The solid which is crystallized out on cooling was filtered, washed several times with cold water and dried in a vacuum oven at 50 °C overnight. A mixture of *exo*(90%) and *endo*(10%) monomers **2a** (Scheme 1) was obtained after two recrystallizations from ethanol: yield = 89%. m.p. = 181–183 °C.

FT-IR (KBr): ν 3029 (C=C–H str), 2978 (C–H asym. str.), 2945 (C–H sym. str.), 1774 (C=O), 1706 (C=O), 1519 (C=C str), 1460 (C–H def), 1394 (C–N), 1195, 1169 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.74–7.26 (4H, m), 6.35 (1H, s), 6.25 (1H, s), 3.41 (2H, m), 2.87 (2H, s), 1.81–1.20 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 176.3, 137.9, 134.6, 126.1, 52.2, 47.8, 45.8, 45.5, 42.9.

^{19}F NMR (300 MHz, $CDCl_3$, ppm): δ – 62.0.

Anal. Calcd. (%) for $C_{16}H_{12}O_2F_3N$ (307): C, 62.54; H, 3.90; O, 10.42; F, 18.56; N, 4.56. Found: C, 62.84; H, 3.62; N, 4.95.

4.4. Synthesis and characterization of exo(90%)-endo(10%) monomer mixture of N-3,5-bis(trifluoromethyl)phenyl-norbornene-5,6-dicarboximide (2b)

NDA (5 g, 30.5 mmol) was dissolved in 50 mL of dichloromethane. An amount of 7.0 g (30.5 mmol) of 3,5-bis(trifluoromethyl) aniline in 5 mL of dichloromethane is added dropwise to the stirred solution of **NDA**. The reaction was maintained at reflux for 2 h and then cooled to room temperature. The precipitate was recovered by filtration and dried to give 11.5 g of amic acid **1b**. The obtained amic acid **1b** (11.5 g, 29.2 mmol), anhydrous sodium acetate (2.2 g, 26.8 mmol) and acetic anhydride (34.0 g, 333 mmol) were heated at 90–100 °C for 4 h and then cooled. The solid which is crystallized out on cooling was filtered, washed several times with cold water and dried in a vacuum oven at 50 °C overnight. A mixture of *exo*(90%) and *endo*(10%) monomers **2b** (Scheme 1) was obtained after two recrystallizations from hexane: yield = 92%. m.p. = 105–108 °C.

FT-IR (KBr): ν 3073 (C=C–H str), 2977 (C–H asym str), 2877 (C–H sym str), 1781 (C=O), 1712 (C=O), 1627 (C=C str), 1470 (C–H def), 1405 (C–N), 1337, 1286, 1181, 1129, 922, 872, 844, 751 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.86–7.69 (3H, m), 6.21 (2H, s), 6.31 (2H, t), 3.55–3.48 (2H, m), 2.82 (2H, s), 1.85–1.63 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 175.8, 134.7, 132.6–120.9, 52.4, 45.6, 37.6.

^{19}F NMR (300 MHz, $CDCl_3$, ppm): δ – 62.2.

Anal. Calcd. (%) for $C_{17}H_{11}O_2F_6N$ (375): C, 54.40; H, 2.93; O, 8.53; F, 30.40; N, 3.93. Found: C, 54.80; H, 2.70; N, 4.06.

4.5. Metathesis polymerization of monomer

Polymerizations were carried out in a glass vial under a dry nitrogen atmosphere. After terminating the polymerization by addition of a small amount of ethyl vinyl ether, the solution was poured into an excess of methanol. The polymer was purified by precipitation in methanol from chloroform containing a few drops of 1N HCl. The obtained polymer was dried in a vacuum oven at 40 °C to constant weight.

4.5.1. Polymerization of 2a

Monomer **2a** (1.0 g, 3.25 mmol) and catalyst **I** (2.68×10^{-3} g, 0.0032 mmol) were stirred in 4.6 mL of 1,2-dichloroethane at 45 °C for 2 h (Scheme 2). The obtained polymer **Poly-2a** was soluble in chloroform and dichloromethane. The values of the number-average molecular weight, M_n, polydispersity, M_w/M_n, glass transition (T_g) and decomposition (T_d) temperature of poly(*N*-4-trifluoromethyl-phenyl-*exo*-*endo*-norbornene-5,6-dicarboximide) were, respectively, M_n = 279,000, M_w/M_n = 1.11, T_g = 155 °C, T_d = 402 °C.

FT-IR (film): ν 3090 (C=C–H ar.str), 2953 (C–H asym str), 2886 (C–H sym str), 1782 (C=O), 1714, 1617, 1519 (C=C), 1452, 1374 (C–N), 1171, 1125 cm^{-1}.

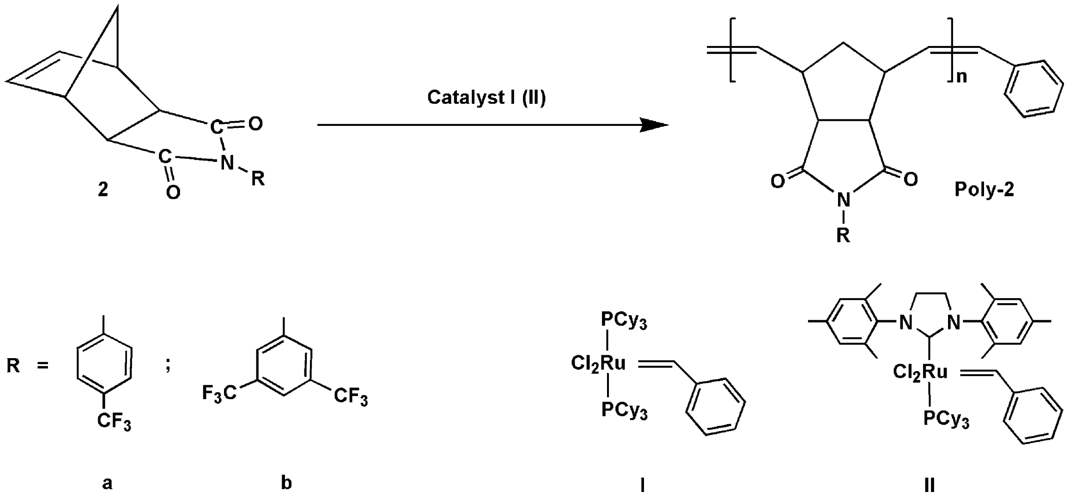
^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.73–7.26 (4H, m), 5.80 (1H, s, *trans*), 5.58 (1H, s, *cis*), 3.18 (2H, s), 2.87 (2H, s), 2.23 (1H, s), 1.70 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 176.5, 134.8, 131.8, 130.4, 130.0, 126.4, 121.7, 50.8, 46.1.

^{19}F NMR (300 MHz, $CDCl_3$, ppm): δ – 67.3.

4.5.2. Polymerization of 2b

Monomer **2b** (1.0 g, 2.66 mmol) and catalyst **I** (2.19×10^{-3} g, 0.0026 mmol) were stirred in 3.8 mL of 1,2-dichloroethane at 45 °C for 2 h (Scheme 2). The obtained polymer **Poly-2b** was soluble in chloroform and dichloromethane. The values of the number-average molecular weight, M_n, polydispersity, M_w/M_n, glass transition (T_g) and decomposition (T_d) temperature of poly(*N*-3,5-bis(trifluoro-



Scheme 2. Synthesis of polynorbornene dicarboximides **Poly-2a** and **Poly-2b** via ROMP.

methyl)phenyl-*exo-endo*-norbornene-5,6-dicarboximide) were, respectively, M_n = 341,000, M_w/M_n = 1.15, T_g = 168 °C, T_d = 393 °C.

FT-IR (film): ν 3034 (C═C–H ar.str), 2938 (C–H asym str), 2879 (C–H sym str), 1775 (C═O), 1598 (C═C), 1459, 1365 (C–N), 1295, 1165, 790 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.89–7.69 (3H, m), 5.85 (1H, s, *trans*), 5.67 (1H, s, *cis*), 3.46 (2H, s), 3.09 (2H, s), 2.02 (1H, s), 1.51 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 174.0, 133.2, 132.6, 129.1, 126.4, 122.1, 120.9, 48.9, 45.3, 40.6.

^{19}F NMR (300 MHz, $CDCl_3$, ppm): δ − 62.0.

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