

# Norbornene Dicarboximides with Fluorine Pendant Groups: Synthesis and Ring Opening Metathesis Polymerization

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The synthesis of new *N*-3,5-Bis(trifluoromethyl)phenyl-*endo*-norbornene-5,6-dicarboximide (*endo*-TFMPhNDI, **2a**) and *N*-4-fluorophenyl-*endo*-norbornene-5,6-dicarboximide (*endo*-FPhNDI, **2b**) monomers was carried out. Polynorbornene dicarboximides were obtained via ring opening metathesis polymerization (ROMP) using ruthenium alkylidene catalysts coordinated with N-heterocyclic carbene ligands (NHC). It was found that Poly-*endo*-FPhNDI (**3b**), which bears a *p*-fluorophenyl moiety, exhibit higher  $T_g$  and mechanical properties compared to Poly-*endo*-TFMPhNDI (**3a**). This could be attributed to the ability of the former to chain packing. Thermal stability of Poly-*endo*-TFMPhNDI was enhanced after complete hydrogenation with Wilkinson's catalyst.

## Introduction

Ring-opening metathesis polymerization (ROMP) of norbornene dicarboximides with linear and cyclic aliphatic and aromatic substituents has been described.<sup>[1-5]</sup> The membranes prepared from these polymers exhibit rather high permselectivity for the separation of hydrogen from nitrogen, carbon monoxide, methane and ethylene.<sup>[6-9]</sup>

Introduction of fluorine atoms into polymer structure can cause significant change in physical and chemical properties of polymers. The ROMP of norbornene derivatives with various fluorine-containing units is well established.<sup>[10]</sup> For example, a wide range of thermally stable and solvent resistant fluorinated polynorbornenes using the ROMP classical catalysts have been synthesized by Feast et al.<sup>[11-13]</sup>

The development of NHC ruthenium alkylidene catalysts makes possible to metathesize challenging cyclic and linear olefins with sterically hindered or electronically deactivating groups.<sup>[14]</sup> *Endo*-isomers of norbornene derivatives with polar fluorine substituents are challenging due to the presence of this electron-withdrawing groups.

The goal of this study is the synthesis and ROMP of new *N*-3,5-bis(trifluoromethyl)phenyl-*endo*-norbornene-5,6-dicarboximide (*endo*-TFMPhNDI) (**2a**) and *N*-4-fluorophenyl-*endo*-norbornene-5,6-dicarboximide (*endo*-FPhNDI) (**2b**) using the mesityl-substituted N-heterocyclic carbene Ru-alkylidene catalyst.

One of the objectives of this work also is the hydrogenation of Poly-*endo*-TFMPhNDI (**3a**). The transformation of the rigid double bonds into single bonds would increase the conformational mobility of polymer chains and thermo- and photo-oxidative stability of polynorbornenes.

## Experimental Part

### Reagents

3,5-Bis(trifluoromethyl)aniline, 4-Fluoroaniline, *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (*endo*-NDA) and other chemicals were purchased from Aldrich Chemical Co. and used without further purification. 1,2-Dichloroethane and toluene were dried over anhydrous calcium chloride and distilled under nitrogen over  $\text{CaH}_2$ . Catalyst 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene  $(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{CHPh}$  (**I**) was purchased from Aldrich Chemical Co. and used as received.

## Synthesis and Characterization of Monomers

### (a) Synthesis of *N*-3,5-Bis(trifluoromethyl)phenyl-*endo*-norbornene-5,6-dicarboximide (TFMPhNDI) (**2a**)

**endo-NDA** (5g, 30.5 mmol) was dissolved in 50 mL of toluene. An amount of 7.0 g (30.6 mmol) of 3,5-Bis(trifluoromethyl)aniline in 5 mL of toluene is added dropwise to the stirred solution of **endo-NDA**. The reaction was maintained at 60 °C for 2 h and then cooled to room temperature. A precipitate was filtered and dried to give 11.5 g of amic acid **1a**. The obtained amic acid **1a** (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 °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. Pure monomer **2a** (Scheme 1) was obtained after two recrystallizations from hexane: yield: 87%, m.p. = 105-108 °C.

FT-IR: 3073 (C=C-H str), 3013, 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 (C-H def), 1286 (C-H def), 1181, 1129, 922 (C-C), 872, 844, 751 (C=C-H def), 680, 626 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) (Figure 1): δ (ppm) = 7.87 (1H, s), 7.69 (2H, s), 6.29 (2H, s), 3.55-3.48 (4H, m), 1.85-1.63 (2H, m).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 175.8, 134.7, 132.6, 132.1, 126.7, 124.5, 122.1, 120.9, 52.4, 45.6, 37.6.

<sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>, ref. TFA [-77ppm]): δ (ppm) = -62.2.

C<sub>17</sub>H<sub>11</sub>O<sub>2</sub>F<sub>6</sub>N (375): Calcd C 54.40, H 2.93, O 8.53, F 30.40, N 3.73; Found C 54.80, H 2.70, N 4.06.

### (b) Synthesis of *N*-4-fluorophenyl-*endo*-norbornene-5,6-dicarboximide (FPhNDI) (**2b**)

**endo-NDA** (5g, 30.5 mmol) was dissolved in 50 mL of toluene. An amount of 3.4 g (30.6 mmol) of 4-Fluoroaniline in 5 mL of toluene is added dropwise to the stirred solution of **endo-NDA**. The reaction was maintained at 90 °C for 2 h and then cooled to room temperature. A precipitate was filtered and dried to give 8.1 g of amic acid **1b**. The obtained amic acid **1b** (8.1 g, 29.4 mmol), anhydrous sodium acetate (1.5 g, 18.29 mmol) and acetic anhydride (24 g, 235 mmol) were heated at 90 °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. Pure monomer **2b** (Scheme 1) was obtained after two recrystallizations from toluene: yield: 88%, m.p. = 170-173 °C.

FT-IR: 3072.2 (C=C-H asym. str.), 3005 (C-H asym. str.), 2953.2 (C-H sym. str.), 1771.2 (C=O), 1705.8 (C=O), 1602.7 (C=C str), 1496 (C-H), 1387 (C-N), 1317 (C-F), 615 cm<sup>-1</sup> (C-H).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.12 (4H, m), 6.25 (2H, s), 3.50 (2H, s), 3.43 (2H, s), 1.80-1.6 (2H, m).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 176.7, 163.7, 160.4, 134.5, 128.4, 127.7, 116.2, 52.2, 46.0, 45.5.

<sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>, ref. TFA [-77ppm]): δ (ppm) = -113.09.

C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>FN (257): Calcd C 70.03, H 4.66, O 12.45, F 7.39, N 5.44; Found C 70.53, H 4.41, N 5.81.

## Metathesis Polymerization of Monomers

Polymerizations were carried out in glass vials under 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 or ethyl ether. The obtained polymers were dried in a vacuum oven at 40 °C to constant weight.

#### Polymerization of **2a**

1 g (2.66 mmol) of **2a** and 0.0023 g ( $2.70 \times 10^{-3}$  mmol) of catalyst **I** were stirred in 2.7 mL of 1,2-dichloroethane at 45°C for 3 h (Scheme 2). The obtained polymer **3a** was soluble in chloroform and dichloromethane.  $T_g = 165$  °C,  $T_d = 393$  °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): (Figure 1)  $\delta$  (ppm) = 7.89-7.69 (3H, m), 5.85 (2H, m, trans), 5.67 (2H, m, cis), 3.46 (2H, m), 3.09 (2H, m), 2.02-1.52 (2H, m).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 174.0, 133.2, 132.6, 129.2, 126.5, 124.5, 122.1, 120.9, 48.9, 45.3, 40.6, 37.5.

$^{19}\text{F}$  NMR (300MHz,  $\text{CDCl}_3$ , ref. TFA [-77ppm]):  $\delta$  (ppm) = -62.0.

#### Polymerization of **2b**

1 g (3.89 mmol) of **2b** and 0.0033 g ( $3.89 \times 10^{-3}$  mmol) of catalyst **I** were stirred in 3.9 mL of 1,2-dichloroethane at 45°C for 3 h (Scheme 2). The obtained polymer **3b** was soluble in 1,2-dichloroethane, DMF and DMSO.  $T_g = 180$  °C,  $T_d = 401$  °C.

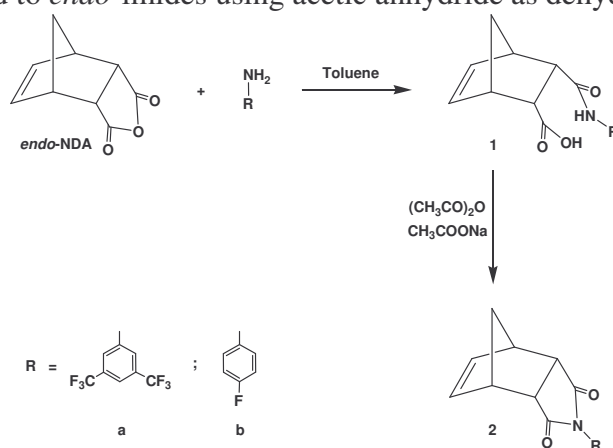
$^1\text{H}$  NMR (300 MHz, DMSO):  $\delta$  (ppm) = 7.32-7.13 (4H, m), 5.70 (2H, s, trans), 5.53 (2H, s cis), 3.86 (2H, m), 3.48 (2H, m), 3.40 (2H, m), 1.76-1.37 (2H, m).

$^{13}\text{C}$  NMR (75 MHz, DMSO):  $\delta$  (ppm) = 176.9, 175.9, 160.0, 134.6, 129.4, 128.9, 116.0, 115.7, 51.9, 48.9, 48.6, 48.3, 48.0, 47.7, 47.5, 47.2, 46.9, 45.5, 44.9.

$^{19}\text{F}$  NMR (300 MHz, DMSO, ref. TFA [-77ppm]):  $\delta$  (ppm) = -112.40.

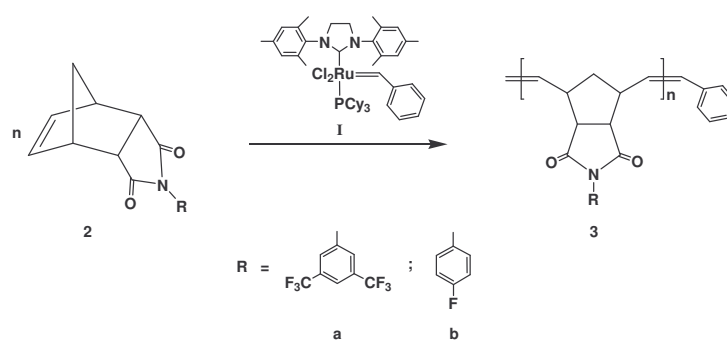
## Results and Discussion

Monomers **2a** and **2b** were readily prepared with high yields (84-88%). 3,5-Bis(trifluoromethyl)aniline and 4-Fluoroaniline reacted with *endo*-NDA to the corresponding amic acids which were cyclized to *endo*-imides using acetic anhydride as dehydrating agent (Scheme 1).



Scheme 1. Synthesis route of monomers **2a** and **2b**.

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra and elemental analysis confirmed monomers structures and purity. ROMP of monomers using ruthenium catalyst **I** were carried out in 1,2 dichloroethane at 45°C for 3h with monomer to catalyst ratio ( $[\text{M}]_0 / [\text{I}]_0 = 1000$  and  $[\text{M}]_0 = 1$  mol/L (Scheme 2).



Scheme 2. Ring Opening Metathesis Polymerization of Monomers **2a** and **2b**.

Changing the pendant moiety did not affect neither the conversion of monomers nor the stereochemistry of the double bonds in the polymer. Catalyst **I** gives polymers with a mixture of *cis* and *trans* double bonds (45-51% of *cis* structure).  $^1\text{H}$  NMR was used to determine the *cis/trans* content in the polymer. Figure 1 shows the  $^1\text{H}$  NMR spectrum of (a) monomer **2a** and (b) its polymer **3a** prepared by **I**. The monomer olefinic signals at  $\delta = 6.29$  ppm are replaced by new signals at  $\delta = 5.85$  and  $5.67$  ppm, which corresponds to the *trans* and *cis* double bonds of the polymer, respectively.

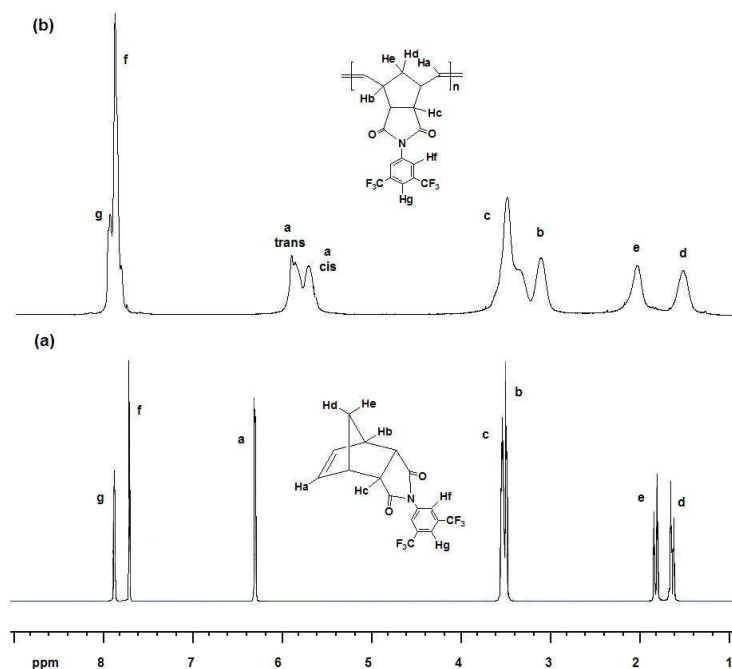


Figure 1.  $^1\text{H}$  NMR spectrum of (a) *endo*-TFMPPhNDI (**2a**) and (b) Poly-*endo*-TFMPPhNDI (**3a**).

Mechanical properties such as tensile strength ( $\sigma_u$ ) and Young's modulus ( $E$ ) of the synthesized polymers were studied on solutions cast films. As expected, all of the polymers studied here show not only much better mechanical properties but also higher  $T_g$ 's than those reported for polynorbornene (31 °C)<sup>[15]</sup>. This could be attributed to an increase in rigidity of the polynorbornene owing to the presence of the dicarboximide with a large pendant group. The  $T_g$  of Poly-*endo*-FPhNDI was observed at 180 °C. Comparison with Poly-*endo*-TFMPPhNDI ( $T_g = 165$  °C) shows a loss of 15 °C in  $T_g$  by introduction of trifluoromethyl substituents. This effect can be explained by the fact that bulky trifluoromethyl groups should increase the average intermolecular spacing and therefore the chain mobility which results in a lower rotational barrier of the polymer chains. The thermal stability of the polymers was studied by TGA under  $\text{N}_2$ . Onset temperature for

decomposition of Poly-*endo*-TFMPhNDI is about 393 °C which was considerably raised after the hydrogenation step with Wilkinson's catalyst.

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## Conclusions

*Endo* isomers of TFMPhNDI (**2a**) and FPhNDI (**2b**) were synthesized and polymerized via ROMP using well-defined N-heterocyclic carbene (NHC) coordinated ruthenium alkylidene catalyst **I**. The tensile strength ( $\sigma_u$ ) and Young's modulus ( $E$ ) of the resultant polymers bearing imide side chain groups are significantly higher compared to those for unsubstituted polynorbornene indicating that the imide substitution leads to restriction in the segmental motion.  $T_g$ 's for Poly-*endo*-FPhNDI and Poly-*endo*-TFMPhNDI were observed at 180°C and 165°C, respectively. Complete hydrogenation of Poly-*endo*-TFMPhNDI was achieved with  $\text{RhCl}(\text{PPh}_3)_3$  catalyst. The onset of decomposition temperature,  $T_d$ , of the hydrogenated polymer was enhanced by almost 20°C nevertheless  $T_g$  was lowered on account of the highest conformational mobility of polymer chains in the saturated backbone.

## References

1. J. Asrar; J. B. Hurlbut *J. Appl. Polym. Sc.* 1993, 50, 1727.
2. J. Asrar *Macromolecules* 1994, 27, 4036.
3. M. Weck; P. Schwab; R. H. Grubbs *Macromolecules* 1996, 29, 1789.
4. A. P. Contreras; A. M. Cerda; M. A. Tlenkopatchev *Macromol. Chem Phys.* 2002, 203, 1811.
5. J. Vargas; E. Sánchez; M. A. Tlenkopatchev *European Polymer Journal* 2004, 40, 1325.
6. K. Díaz; J. Vargas; L. F. del Castillo; M. A. Tlenkopatchev; M. Aguilar-Vega *Macromol. Chem. Phys.* 2005, 206, 2316.
7. J. Vargas; M. A. Tlenkopatchev; M. M. López-González; E. Riande *Macromolecules* 2003, 36, 8483.
8. A. P. Contreras; M. A. Tlenkopatchev; M. M. López-González; E. Riande *Macromolecules* 2002, 35, 4677.
9. M. A. Tlenkopatchev; J. Vargas; M. A. Almaráz-Girón; M. M. López-González; E. Riande *Macromolecules* 2005, 38, 2696.
10. K. J. Ivin; J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997.
11. W. J. Feast; P. M. Blackmore *J. Fluorine Chem.* 1998, 40, 331.
12. W. J. Feast; M. Gimeno; E. Khosravi *Polymer* 2003, 44, 6111.
13. W. J. Feast; M. Gimeno; E. Khosravi *J. Mol. Catal. Chem. A* 2004, 213, 9.
14. C. W. Bielawski; R. H. Grubbs *Angew. Chem. Int. Ed.* 2000, 39, 2903.
15. E. Sh. Finkel'shtein; K. L. Makovetskii; Yu. P. Yampol'skii; E. B. Portnykh; I. Ya. Ostrovskaya; N. E. Kaliuzhnyi; N. A. Pritula; A. I. Gol'berg; M. S. Yatsenko; N. A. Platé *Makromol. Chem.* 1991, 192, 1.