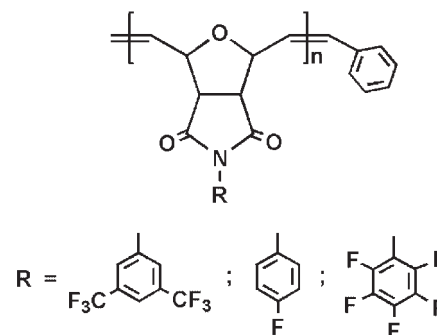


# Synthesis and Ring-Opening Metathesis Polymerization of New Oxanorbornene Dicarboximides with Fluorine Pendant Groups

Arlette A. Santiago, Joel Vargas, Rubén Gaviño, Alfredo Maciel Cerda, Mikhail A. Tlenkopatchev\*

The synthesis of *exo-N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide (TFMPHONDI, **2a**), *exo-N*-4-fluorophenyl-7-oxanorbornene-5,6-dicarboximide (FPhONDI, **2b**), and *exo-N*-pentafluorophenyl-7-oxanorbornene-5,6-dicarboximide (PFPhONDI, **2c**) monomers is described. Poly(norbornene dicarboximide)s were obtained via ROMP using bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (I) and tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolilydene]-[benzylidene] ruthenium dichloride (II). Poly-TFMPHONDI (**3a**) bearing a trifluoromethylaryl moiety showed a higher  $T_g$  and improved mechanical properties as compared to poly-FPhONDI (**3b**) and poly-PFPhONDI (**3c**).



## Introduction

Ring-opening metathesis polymerization (ROMP) of norbornene dicarboximides with linear aliphatic and aromatic substituents has been described.<sup>[1–6]</sup> We recently proceeded with the synthesis of new poly(norbornene dicarboximide)s by ROMP of *exo-N*-(1-adamantyl)-norbornene-5,6-dicarboximide and *exo-endo-N*-cyclohexyl-(cyclopentyl)-norbornene-5,6-dicarboximides using well-defined ruthenium alkylidene (vinylidene) catalysts.<sup>[7–9]</sup>

The carboximide-functionalized polynorbornenes showed high  $T_g$ s, good mechanical properties, and high thermal resistance.<sup>[4,7,8]</sup> The membranes prepared from early synthesized poly(norbornene dicarboximide)s exhibit rather high permselectivity for the separation of hydrogen from nitrogen, carbon monoxide, methane, and ethylene.<sup>[10,11]</sup> Permeation data in membranes prepared from these polymers show an enhancement of the selectivity, though the permeability remains low. Introduction of fluorine atoms into polymer structure can cause a significant change in physical and chemical properties of polymers.<sup>[12]</sup> Thus, compared to polynorbornene, partially fluorinated polynorbornene membranes exhibit much higher gas permeability and selectivity.<sup>[13,14]</sup> Therefore, we have proceeded to the synthesis of new fluorine-containing norbornene dicarboximides and their ROMP using ruthenium alkylidene catalysts. The ROMP of norbornene derivatives with various fluorine-containing units is well established.<sup>[15]</sup> For example, a wide range of

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thermally stable and solvent resistant fluorinated polynorbornenes using the ROMP classical catalysts have been synthesized by Feast et al.<sup>[16–18]</sup>

Development of high functional group tolerance catalysts and different metathesis polymerization methodologies make it possible to control the synthesis and properties of new very important functional polymers.<sup>[19]</sup>

In this work, the syntheses of three polyoxanorbornenes with lateral imide groups that bear fluorine pendant moieties are described. The synthesis and ROMP of new *exo-N*-3,5-bis(trifluoromethyl)phenyl-7-oxanorbornene-5,6-dicarboximide (TFMPhONDI, **2a**), *exo-N*-4-fluorophenyl-7-oxanorbornene-5,6-dicarboximide (FPhONDI, **2b**), and *exo-N*-pentafluorophenyl-7-oxanorbornene-5,6-dicarboximide (PFPhONDI, **2c**) using bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (**I**) and tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolylidene][benzylidene] ruthenium dichloride (**II**) were studied. Thermal and mechanical properties of these polyoxanorbornenes were also determined.

## Experimental Part

### Techniques

<sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>19</sup>F NMR spectra were recorded on a Varian spectrometer at 300, 75, and 300 MHz, respectively, in CDCl<sub>3</sub> or DMSO at 25 °C. Tetramethylsilane (TMS) and trifluoroacetic acid (TFA) were used as internal standards, respectively. Glass transition temperatures, *T*<sub>g</sub>, were determined in a DSC-7 Perkin Elmer instrument at a scanning rate of 10 °C·min<sup>-1</sup> under nitrogen atmosphere. The samples were encapsulated in standard aluminum DSC pans. Each sample was run twice in the temperature range between 30 and 300 °C under nitrogen atmosphere. Obtained *T*<sub>g</sub> values were confirmed by TMA from the first heating cycle. The onset temperature of decomposition, *T*<sub>d</sub>, was determined using thermogravimetric analysis (TGA), which was performed at a heating rate of 10 °C·min<sup>-1</sup> under nitrogen atmosphere with a DuPont 2100 instrument. FTIR spectra were obtained on a Nicolet 510 p spectrometer. Molecular weights and molecular weight distributions were determined with reference to polystyrene standards on a Varian 9012 GPC at 30 °C, in chloroform for polymers **3a** and **3c** and in dimethylformamide for polymer **3b**, using a universal column and a flow rate of 1 mL·min<sup>-1</sup>. The chromatograph was equipped with a column TSK-gel type 64000 H8 containing spherical, cross-linked polystyrene/divinylbenzene particles with diameters of 8–10 μm. Mechanical properties under tension were measured in a Universal Mechanical Testing Machine Instron 1125-5500R using a 50 kg cell at a crosshead speed of 10 mm·min<sup>-1</sup>, according to the method ASTM D1708 in film samples of 0.5 mm of thickness at room temperature.

### Reagents

3,5-Bis(trifluoromethyl)aniline, 4-fluoroaniline, 2,3,4,5,6-pentafluoroaniline, maleic anhydride (MA), *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<sub>2</sub>. Catalysts bis(tricyclohexylphosphine)benzylidene ruthenium(IV)dichloride (**I**) and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (PCy<sub>3</sub>)Cl<sub>2</sub>Ru=CHPh (**II**) were purchased from Aldrich Chemical Co. and used as received.

## Synthesis and Characterization of Monomers

### Synthesis of TFMPhONDI (**2a**)

*exo*-7-Oxanorbornene-5,6-dicarboxylic anhydride (5 g, 30 mmol) was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. An amount of 6.9 g (30.1 mmol) of 3,5-bis(trifluoromethyl)aniline in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was 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 **1a** (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<sub>3</sub>, and H<sub>2</sub>O. Solvent was evaporated and pure TFMPhONDI (**2a**) 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: 3 106.5 (C=C–H asym str), 1 791.5 (C=O), 1 727.1 (C=O), 1 625.9 (C=C str), 1 471.6, 1 394.6 (C–N str), 1 283.0 (C–F), 1 175.7, 897.2 (C–C str), 690.9 cm<sup>-1</sup> (C–H).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.91–7.85 (3H, m), 6.59 (2H, s), 5.42 (2H, s), 3.06 (2H, s).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 174.3, 136.7, 133.0, 132.7, 132.2, 126.7, 124.5, 122.2, 120.8, 81.5, 47.5.

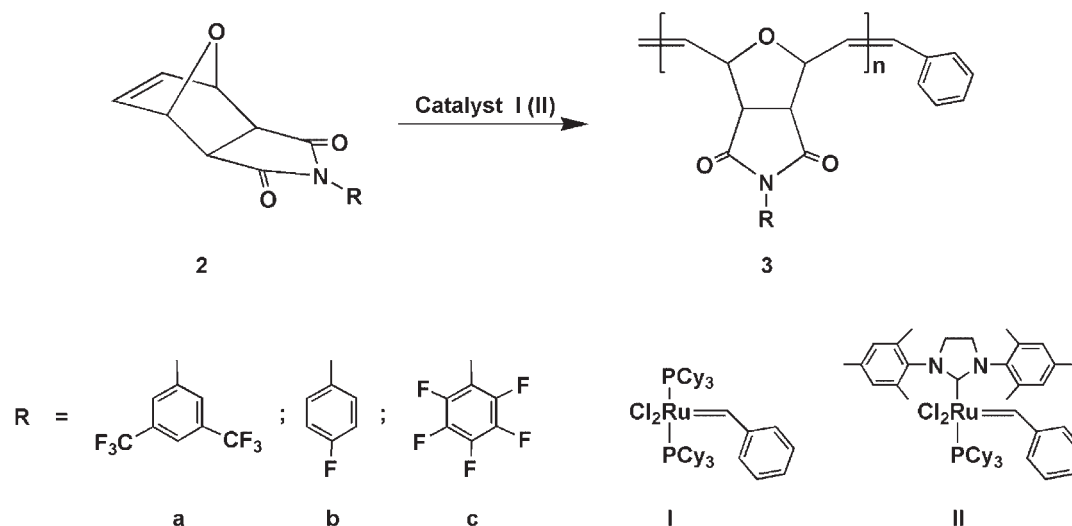
<sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>, TFA = -77), δ = -62.1.

(C<sub>16</sub>H<sub>9</sub>O<sub>3</sub>NF<sub>6</sub>)<sub>n</sub> (377)<sub>n</sub>: 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.

### Synthesis of FPhMI (**1b**)

Maleic anhydride (5 g, 51.0 mmol) was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. An amount of 5.7 g (51.3 mmol) of 4-fluoroaniline in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the stirred solution of maleic anhydride. The mixture was boiled for 10 min and then cooled to room temperature. Solvent removal gave a slightly yellow oil that crystallized to an off-white solid of maleamic acid MAA (**b**). The obtained maleamic acid MAA (**b**) (10.4 g, 49.7 mmol), anhydrous sodium acetate (1.4 g, 17.0 mmol), and acetic anhydride (15.0 g, 146.9 mmol) were heated at 90 °C for 25 min giving a yellow liquid that became semisolid on cooling to room temperature. The mixture was washed with dilute HCl and extracted into ether. The ether layer was washed with dilute HCl, saturated NaHCO<sub>3</sub>, and H<sub>2</sub>O. Solvent was evaporated and pure maleimide **1b** was obtained after twice recrystallization from hexane and dried in a vacuum oven at 50 °C overnight: yield = 90%, m.p. = 150–153 °C.

FT-IR: 3 104.4 (C=C–H asym str), 1 787.8 (C=O), 1 714.5 (C=O), 1 590.4 (C=C str), 1 407.9 (C–N str), 1 300.0 (C–F), 879.02 (C–C str), 729.1 cm<sup>-1</sup> (C–H).



■ Scheme 1. ROMP of monomers **2a**, **2b**, and **2c**, respectively.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.50–6.65 (4H, m), 6.84 (2H, s).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 169.3, 159.8, 143.1, 134.0, 127.5, 115.8.

$^{19}\text{F NMR}$  (300 MHz,  $\text{CDCl}_3$ , TFA =  $-77^\circ\text{C}$ ):  $\delta$  =  $-112.4$ ,  $-112.6$ .

$(\text{C}_{10}\text{H}_6\text{O}_2\text{NF})_n$  (191) $_n$ : Calcd. C 62.82, H 3.14, O 16.75, N 7.32, F 9.94; Found C 63.02, H 2.89, N 7.79.

FT-IR: 3 091.0 (C=C–H asym str), 1 793.3 (C=O), 1 725.0 (C=O), 1 654.7 (C=C str), 1 477.8 (C–H), 1 334.0 (C–F), 1 288.0 (C=C–H), 1 181.8 (C–O–C asym str), 849.37  $\text{cm}^{-1}$  (C–C str).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.59 (2H, s), 5.41 (2H, s), 3.11 (2H, s).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.9, 145.7, 142.1, 140.9, 139.7, 136.6, 81.4, 48.0.

$^{19}\text{F NMR}$  (300 MHz,  $\text{CDCl}_3$ , TFA =  $-77^\circ\text{C}$ ):  $\delta$  =  $-141.3$ ,  $-149.9$ ,  $-159.8$ .

$(\text{C}_{14}\text{H}_6\text{O}_3\text{NF}_5)_n$  (331) $_n$ : Calcd. C 50.75, H 1.81, O 14.50, N 4.22, F 28.7; Found C 51.45, H 1.59, N 4.57.

### Synthesis of FPhONDI (**2b**)

FPhMI (**1b**; 5 g, 26.2 mmol) was dissolved in 50 mL of anhydrous ether. To the stirred solution of FPhMI, 1.80 g of furan (26.4 mmol) in 5 mL of anhydrous ether was added dropwise. The reaction was maintained at room temperature for 4 d. Solvent removal gave a white solid. Pure monomer **2b** was obtained after twice recrystallization from hexane and dried in a vacuum oven at  $50^\circ\text{C}$  overnight: yield = 92%, m.p. =  $125$ – $128^\circ\text{C}$ .

FT-IR: 3 081.2 (C=C–H asym str), 2 960.0 (C–H asym str), 1 779.7 (C=O), 1 714.6 (C=O), 1 603.2 (C–C str), 1 389.0 (C–N str), 1 305.1 (C–F), 1 186.0 (C–O–C asym str), 872.05 (C–C str), 719.42  $\text{cm}^{-1}$  (C–H).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.28–7.09 (4H, m), 6.54 (2H, s), 5.39 (2H, s), 2.99 (2H, s).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 175.1, 160.4, 136.5, 134.5, 128.1, 81.2, 47.3.

$^{19}\text{F NMR}$  (300 MHz,  $\text{CDCl}_3$ , TFA =  $-77^\circ\text{C}$ ):  $\delta$  =  $-112.4$ ,  $-112.6$ .

$(\text{C}_{14}\text{H}_{10}\text{O}_3\text{NF})_n$  (259) $_n$ : Calcd. C 64.86, H 3.86, O 18.53, N 5.4, F 7.33; Found C 65.26, H 3.63, N 5.76.

### Synthesis of PPhONDI (**2c**)

PPhMI<sup>[20]</sup> (**1c**; 5 g, 19.0 mmol) was dissolved in 50 mL of anhydrous ether. To the stirred solution of PPhMI, 1.30 g of furan (19.1 mmol) in 5 mL of anhydrous ether was added dropwise. The reaction was maintained at room temperature for 4 d. Solvent removal gave a white solid. Pure monomer **2c** was obtained after twice recrystallization from hexane and dried in a vacuum oven at  $50^\circ\text{C}$  overnight: yield = 87%, m.p. =  $137$ – $140^\circ\text{C}$ .

### Metathesis Polymerization of Monomers

Polymerizations were carried out in glass vials under nitrogen atmosphere at  $45^\circ\text{C}$ . 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  $40^\circ\text{C}$  to constant weight.

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

Monomer **2a** (1.0 g, 2.65 mmol) and catalyst **II** ( $2.25 \times 10^{-3}$  g, 0.0026 mmol) were stirred in 2.6 mL of 1,2-dichloroethane at  $45^\circ\text{C}$  for 2 h (Scheme 1). The obtained polymer **3a** was soluble in chloroform and dichloroethane.  $T_g = 199^\circ\text{C}$ ,  $T_d = 369^\circ\text{C}$ ,  $E = 1512$  MPa,  $\sigma_u = 43.2$  MPa.

FT-IR: 3 102 (C=C–H asym str), 1 789 (C=O), 1 730 (C=O), 1 623 (C=C str), 1 473, 1 396 (C–N str), 1 280 (C–F), 1 172, 893 (C–C str), 691  $\text{cm}^{-1}$  (C–H).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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.

$^{19}\text{F NMR}$  (300 MHz,  $\text{CDCl}_3$ , TFA =  $-77^\circ\text{C}$ ):  $\delta$  =  $-62.4$ .

Polymerization of **2b**

Monomer **2b** (1.0 g, 3.86 mmol) and catalyst **II** ( $3.27 \times 10^{-3}$  g, 0.0038 mmol) were stirred in 3.8 mL of 1,2-dichloroethane at 45 °C for 2 h (Scheme 1). The obtained polymer **3b** was soluble in DMF, DMSO, and dichloroethane.  $T_g = 176$  °C,  $T_d = 348$  °C,  $E = 1.346$  MPa,  $\sigma_u = 27.6$  MPa.

FT-IR: 3 078 (C=C-H asym str), 2 961 (C-H asym str), 1 777 (C=O), 1 711 (C=O), 1 601 (C-C str), 1 390 (C-N str), 1 306 (C-F), 1 182 (C-O-C asym str), 871 (C-C str), 715  $\text{cm}^{-1}$  (C-H).

$^1\text{H}$  NMR (300 MHz, DMSO):  $\delta = 7.42\text{--}7.06$  (4H, m), 6.02 (2H, s, *trans*), 5.72 (2H, s, *cis*), 5.06 (2H, s), 4.60 (2H, s), 3.054 (2H, s).

$^{13}\text{C}$  NMR (75 MHz, DMSO):  $\delta = 176.2, 160.5, 137.0, 135.0, 129.4, 116.4, 81.4, 48.0$ .

$^{19}\text{F}$  NMR (300 MHz, DMSO, TFA = -77):  $\delta = -112.2$ .

Polymerization of **2c**

Monomer **2c** (1.0 g, 3.02 mmol) and catalyst **I** ( $2.4 \times 10^{-3}$  g, 0.0030 mmol) were stirred in 3.0 mL of 1,2-dichloroethane at 45 °C for 2 h (Scheme 1). The obtained polymer **3c** was soluble in chloroform and dichloromethane.  $T_g = 187$  °C,  $T_d = 361$  °C,  $E = 1.416$  MPa,  $\sigma_u = 35.2$  MPa.

FT-IR: 3 088 (C=C-H asym str), 1 790 (C=O), 1 724 (C=O), 1 652 (C=C str), 1 479 (C-H), 1 336 (C-F), 1 289 (C=C-H), 1 179 (C-O-C asym str), 848  $\text{cm}^{-1}$  (C-C str).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.10$  (2H, s, *trans*), 5.86 (2H, s, *cis*), 5.0 (2H, s), 4.62 (2H, s), 3.55 (2H, s).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 172.2, 146.0, 140.5, 135.4, 130.6, 126.9, 106, 80.9, 53.8, 53.0$ .

$^{19}\text{F}$  NMR (300 MHz,  $\text{CDCl}_3$ , TFA = -77):  $\delta = -142.5, -149.7, -159.7$ .

## Results and Discussion

Monomers **2a**, **2b**, and **2c** were readily prepared with high yields (86–92%). 3,5-bis(trifluoromethyl)aniline reacted with *exo*-ONDA, whereas 4-fluoroaniline and 2,3,4,5,6-pentafluoroaniline reacted with MA to the corresponding amic acids which were cyclized to imides using acetic anhydride as dehydrating agent. *Exo* monomers **2b** and **2c** were synthesized by Diels-Alder reaction between obtained maleimides and furan.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra and elemental analysis confirmed monomers' structures and purity. The infrared spectra of monomers were very similar and showed characteristic peaks at 1 785 and 1 725  $\text{cm}^{-1}$  (asymmetric and symmetric C=O stretching), 1 390  $\text{cm}^{-1}$  (C-N stretching). ROMP of monomers using ruthenium catalysts **I** and **II** was carried out in 1,2-dichloroethane at 45 °C (Table 1). Table 1 summarizes the results of the polymerizations of **2a**, **2b**, and **2c**. The *exo* monomers reacted in 2 h giving polymers with high yields (92–95%, entries 2, 4, and 7). The results obtained by GPC analysis show that the number-average molecular weights ( $\overline{M}_n$ ) are between 227 000 and 340 000. The experimental number-average molecular weights are in agreement with

Table 1. Polymerization conditions of 7-oxanorbornene dicarboximides **2a**, **2b**, and **2c**.

Entry	Monomer <sup>a)</sup>	Catalyst <sup>b)</sup>	Yield <sup>c)</sup>	Cis <sup>d)</sup>	$\overline{M}_n$ <sup>e)</sup>	PDI <sup>e)</sup>
			%	%	$10^5$ Da	
1	<b>2a</b>	<b>I</b>	90	35	3.40	1.12
2	<b>2a</b>	<b>II</b>	92	56	3.15	1.20
3	<b>2b</b>	<b>I</b>	93	33	2.40	1.10 <sup>f)</sup>
4	<b>2b</b>	<b>II</b>	95	48	2.35	1.27 <sup>f)</sup>
5	<b>2c</b>	<b>I</b>	92	34	2.33	1.36
6	<b>2c</b> <sup>g)</sup>	<b>I</b>	89	37	2.27	1.08
7	<b>2c</b>	<b>II</b>	93	52	2.97	1.44
8	<b>2c</b> <sup>g)</sup>	<b>II</b>	88	55	2.86	1.25

<sup>a)</sup>1,2-Dichloroethane as the solvent, temperature = 45 °C, time = 2 h, initial monomer concentration  $[M_0] = 1 \text{ mol} \cdot \text{L}^{-1}$ ; <sup>b)</sup>Molar ratio of monomer to catalyst = 1 000; <sup>c)</sup>Methanol-insoluble polymer; <sup>d)</sup>Determined by  $^1\text{H}$  NMR; <sup>e)</sup>According to GPC analysis in chloroform with polystyrene calibration standards; <sup>f)</sup>GPC analysis in dimethylformamide with polystyrene calibration standards; <sup>g)</sup>Initial monomer concentration  $[M_0] = 0.8 \text{ mol} \cdot \text{L}^{-1}$ .

the theoretical ones. As shown in Table 1, the molecular weight distribution (MWD) of the polymers **3a** and **3b** (entries 1–4) obtained by **II** is about  $\overline{M}_w/\overline{M}_n = 1.20\text{--}1.27$  which is broader compared to polymers prepared by **I** ( $\overline{M}_w/\overline{M}_n = 1.10\text{--}1.12$ ) due to the slower initiation of the latter catalyst.<sup>[21]</sup> When monomer **2c** was polymerized, a precipitate in the early minutes of the reaction was observed resulting in a broader MWD, in comparison with polymers **3a** and **3b** (Table 1, entries 5 and 7).

Changing the pendant moiety affects neither the conversion of monomers nor the stereochemistry of the double bonds in the polymer. Both catalysts give polymers with a mixture of *cis* and *trans* double bonds, 33–37% of *cis* structure by catalyst **I** and 48–56% of *cis* structure by catalyst **II**.  $^1\text{H}$  NMR was used to determine the *cis/trans* content in the polymer. Figure 1 shows the  $^1\text{H}$  NMR spectra of (a) monomer **2a** and (b) polymer **3a** prepared by **II**. The monomer olefinic signals at  $\delta = 6.59$  are replaced by new signals at  $\delta = 6.15$  and 5.83, which correspond to the *trans* and *cis* double bonds of the polymer, respectively. Figure 2 shows the  $^1\text{H}$  NMR spectra of (a) monomer **2c** and (b) polymer **3c** prepared by **I**. The monomer olefinic signals at  $\delta = 6.59$  are replaced by new signals at  $\delta = 6.10$  and 5.82, which correspond to the *trans* and *cis* double bonds of the polymer, respectively.

A clear effect of the size of the substituent on the  $T_g$  is observed. The larger the substituent, the higher the resultant  $T_g$ . The  $T_g$  of poly-FPhONDI (**3b**) was observed

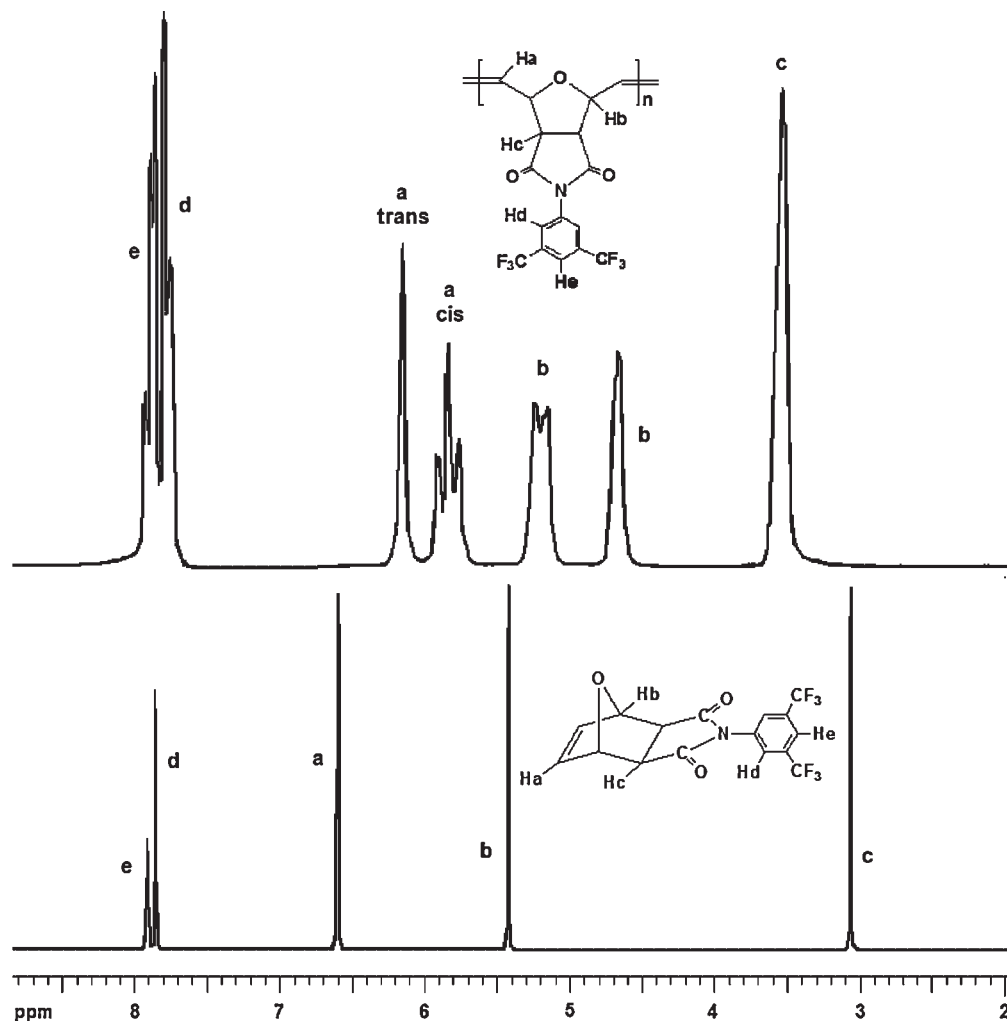


Figure 1.  $^1\text{H}$  NMR spectra of monomer **2a** (bottom) and polymer **3a** (top) obtained by catalyst II.

at  $176^\circ\text{C}$  (Figure 3). The hindered rotation of the phenyl group became higher by the introduction of more fluorine atoms in the moiety which raised the  $T_g$  of poly-PFPhONDI (**3c**) ( $T_g = 187^\circ\text{C}$ ) in comparison with polymer **3b** ( $T_g = 176^\circ\text{C}$ ). Poly-TFMPPhONDI (**3a**) exhibits the higher glass transition temperature of all the polymers studied here ( $T_g = 199^\circ\text{C}$ ). This effect can be explained by the fact that bulky trifluoromethyl groups should decrease the segmental motion of the polymer backbone. The same effect of the size of the substituent on the  $T_g$  has also been observed for alkyl-substituted polynorbornenes.<sup>[7,8]</sup>

The thermal stability of the polymers was studied by TGA under  $\text{N}_2$ . As can be seen from Figure 4, the onset temperature for the decomposition of polymers **3a**, **3b**, and **3c** is about  $369$ ,  $348$ , and  $361^\circ\text{C}$ , respectively. Stress-strain measurements in tension for the films of the synthesized polymers were carried out. The experiments were stopped

at the maximum stress and indicated, for example, that not only the stress ( $43.2\text{ MPa}$ ) but also the elastic modulus ( $1\,512\text{ MPa}$ ) is higher for the sample **3a** (Figure 5). In counterpart, the polymer **3b** has the lowest stress in tension ( $27.6\text{ MPa}$ ) and elastic modulus ( $1\,346\text{ MPa}$ ). Polymer **3c** which bears a pentafluorophenyl moiety has intermediate properties ( $35.2$  and  $1\,416\text{ MPa}$ , respectively).

## Conclusion

*Exo* isomers of TFMPPhONDI (**2a**), FPhONDI (**2b**), and PFPhONDI (**2c**) were synthesized and polymerized via ROMP using well-defined ruthenium alkylidene catalysts I and II.

$T_g$ s for poly-TFMPPhONDI (**3a**), poly-FPhONDI (**3b**), and poly-PFPhONDI (**3c**) were observed at  $199$ ,  $176$ , and  $187^\circ\text{C}$ ,

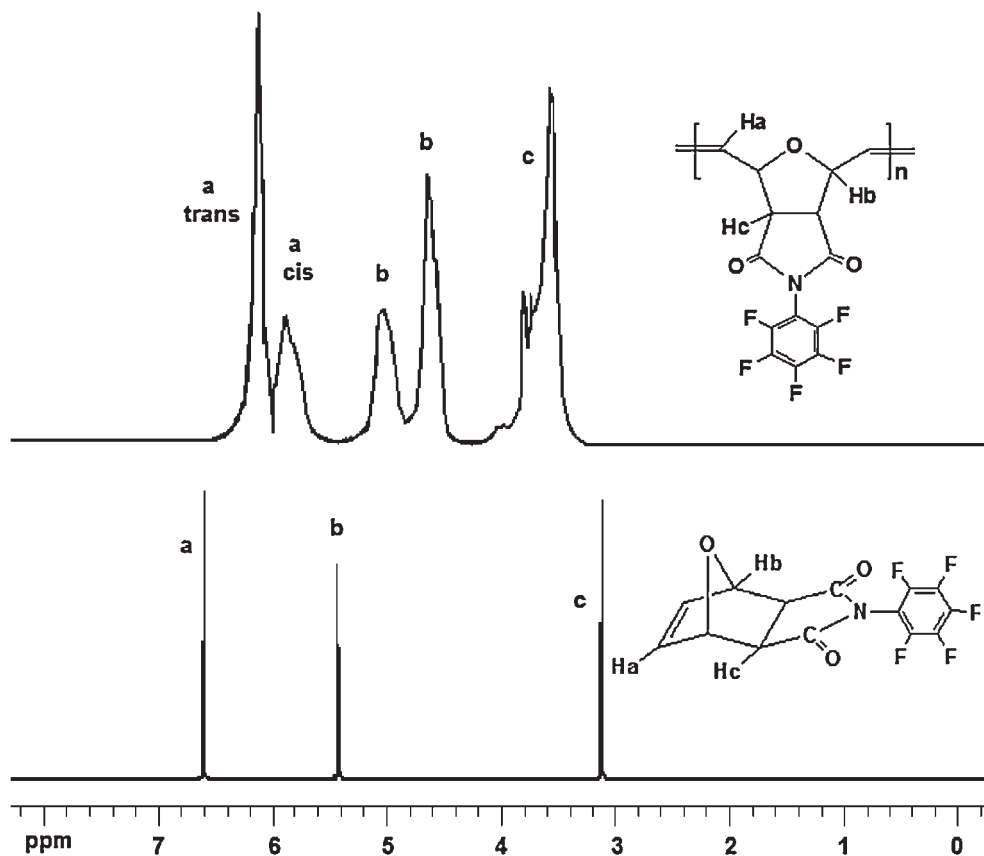


Figure 2. <sup>1</sup>H NMR spectra of monomer 2c (bottom) and polymer 3c (top) obtained by catalyst I.

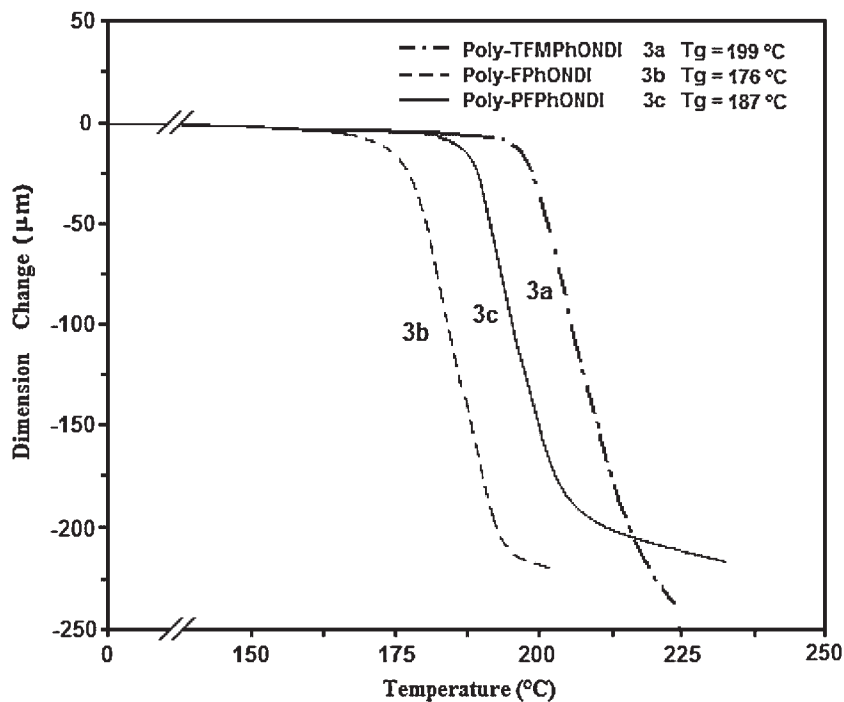


Figure 3. Thermomechanical curves of polymers 3a, 3b, and 3c, respectively.

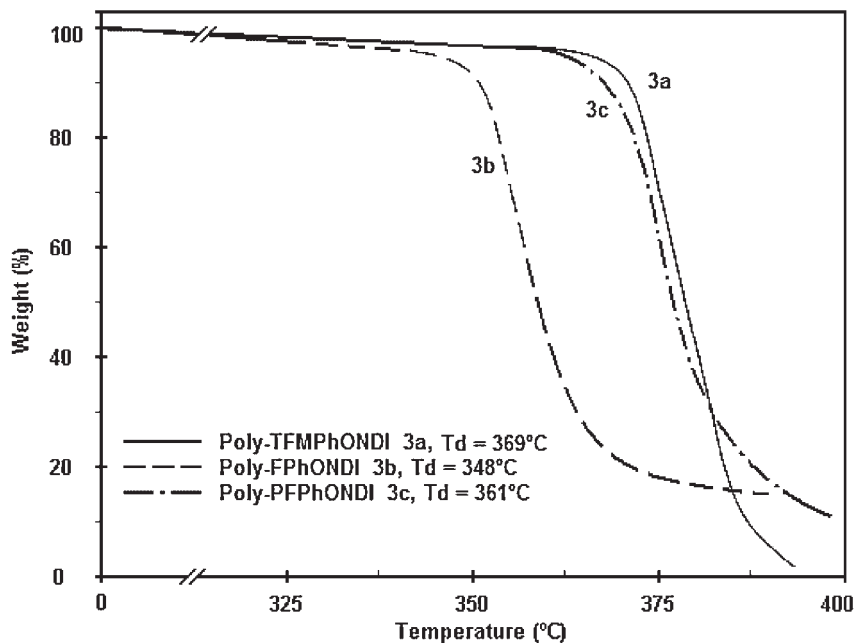


Figure 4. Thermogravimetric analysis of polymers 3a, 3b, and 3c, respectively.

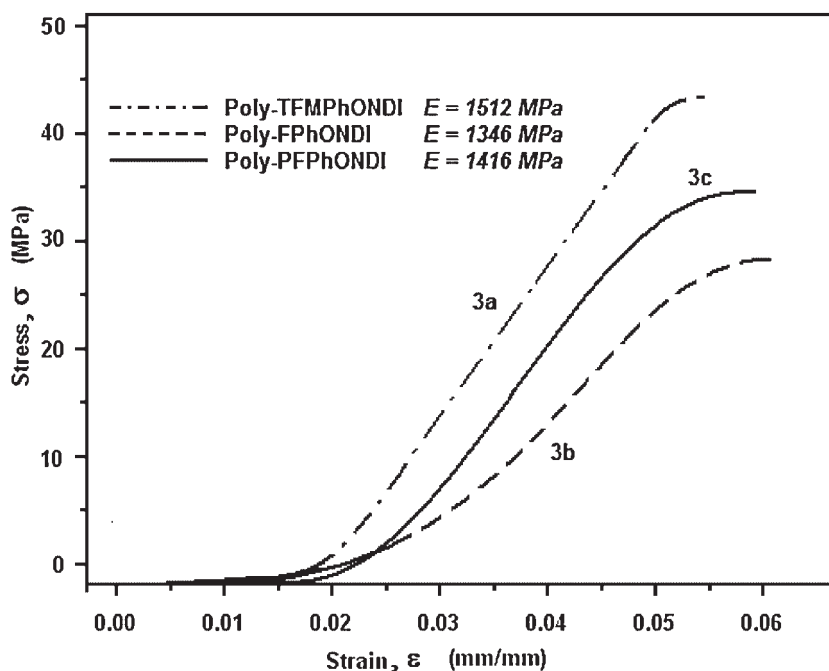


Figure 5. Stress vs. strain plot of polymers 3a, 3b, and 3c, respectively.

respectively. Poly-TFMPPhONDI (**3a**) with bulky trifluoromethyl groups exhibits the highest glass transition temperature of all the polymers studied here ( $T_g = 199^\circ\text{C}$ ). 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.

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