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Synthesis and ring-opening metathesis polymerization (ROMP) of new *N*-fluoro-phenylnorbornene dicarboximides by 2nd generation ruthenium alkylidene catalysts

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Abstract. The synthesis of new *N*-3,5-bis(trifluoromethyl)phenyl-*endo*-norbornene-5,6-dicarboximide (TFMPhNDI, **2a**), *N*-4-fluorophenyl-*endo*-norbornene-5,6-dicarboximide (FPhNDI, **2b**) and *N*-2,2,6,6-tetramethylpiperidyl-*endo*-norbornene-5,6-dicarboximide (TMPNDI, **2c**) monomers was carried out. Polynorbornene dicarboximides were obtained via ring opening metathesis polymerization (ROMP) using a second generation ruthenium alkylidene catalyst (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) ($PCy_3Cl_2Ru = CHPh$) (**I**). Poly-TMPNDI which bears a piperidyl moiety showed the highest T_g and T_d compared to the polymers bearing fluoro-aryl moieties. Thermal stability of Poly-TFMPhNDI (**3a**) was enhanced after hydrogenation with Wilkinson's catalyst.

Keywords: *polymer synthesis, molecular engineering, polynorbornene dicarboximide, ROMP, ruthenium alkylidene, hydrogenation*

1. Introduction

Ring-opening metathesis polymerization (ROMP) of norbornene dicarboximides with linear aliphatic and aromatic substituents has been described [1–6]. We recently proceeded with the synthesis of new polynorbornene dicarboximides 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 [7–9]. The carboximide functionalized polynorbornenes showed high T_g's, good mechanical properties and high thermal resistance [4, 7, 8]. The membranes prepared from these polymers exhibit rather high permselectivity for the separation of hydrogen from nitrogen, carbon monoxide, methane and ethylene [10, 11].

Introduction of fluorine atoms into polymer structure can cause significant change in physical and chemical properties of polymers. It is well known that fluorinated polymers are important specialty materials in many applications [12]. Thus, compared to polynorbornene, partially fluorinated polynorbornene membranes exhibit higher gas permeability and selectivity [13, 14]. The ROMP of norbornene derivatives with various fluorine-containing units is well established [15]. 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.* [16–18].

The development of highly active metal-alkylidene catalysts opens vast opportunities in olefin metathesis and their application to the synthesis of

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well-defined products [19, 20]. The resent generation of ruthenium alkylidene catalysts coordinated with N-heterocyclic carbene ligands makes possible to metathesize challenging cyclic and linear olefins with sterically hindered or electronically deactivating groups [21]. *Endo*-isomers of norbornene derivatives are challenging and few examples of their metathesis exist [22–24].

The goal of this study is the synthesis and ROMP of new *N*-3,5-bis(trifluoromethyl)phenyl-*endo*-norbornene-5,6-dicarboximide (TFMPhNDI) (**2a**), *N*-4-fluorophenyl-*endo*-norbornene-5,6-dicarboximide (FPhNDI) (**2b**) and *N*-2,2,6,6-tetramethylpiperidyl-*endo*-norbornene-5,6-dicarboximide (TMPNDI) (**2c**) using a second generation ruthenium alkylidene catalyst (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) ($PCy_3Cl_2Ru = CHPh$) (**I**). One of the objectives of this work also is the hydrogenation of Poly-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.

2. Experimental

2.1. Techniques

^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Varian spectrometer at 300, 75 and 300 MHz, respectively, in $CDCl_3$ or DMSO. Tetramethylsilane (TMS) and trifluoracetic acid (TFA) were used as internal standards, respectively. Glass transition temperatures, T_g, were determined in a DSC-7 Perkin Elmer Inc., at scanning rate of 10°C/min under nitrogen atmosphere. The samples were encapsulated in standard aluminum DSC pans. Each sample was run twice on the temperature range between 30 and 300°C under 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 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. 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 1 mm/min according to the method ASTM D1708 in film samples of 0.5 mm of thickness at room temperature.

2.2. Reagents

3,5-Bis(trifluoromethyl)aniline, 4-fluoroaniline, 2,2,6,6-tetramethylpiperidylamine, *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 CaH_2. Catalyst 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene ($(PCy_3)Cl_2Ru = CHPh$ (**I**) was purchased from Aldrich Chemical Co. and used as received.

2.3. Synthesis and characterization of monomers

2.3.1. Synthesis of *N*-3,5-bis(trifluoromethyl)phenyl-*endo*-norbornene-5,6-dicarboximide (TFMPhNDI) (2a)

***endo*-NDA** (5 g, 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 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** (Figure 1) was obtained after two recrystallizations from hexane (87% yield).

mp 105–108°C.

FT-IR (KBr): 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,

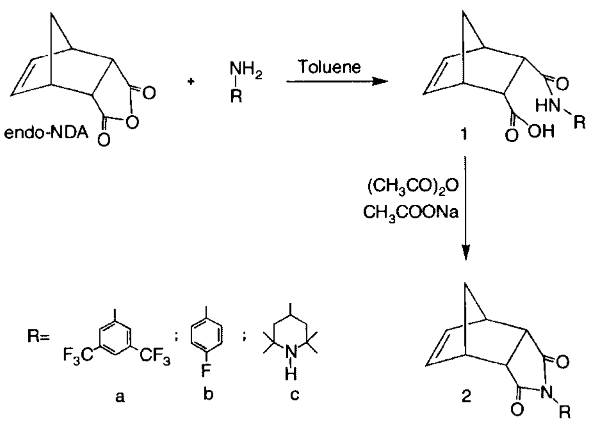

Figure 1. Synthesis route of monomers **2a**, **2b** and **2c**

1129, 922 (C–C), 872, 844, 751 (C=C–H def), 680, 626 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 4) 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).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 175.8, 134.7, 132.6, 132.1, 126.7, 124.5, 122.1, 120.9, 52.4, 45.6, 37.6.

^{19}F NMR (300 MHz, $CDCl_3$, ref. TFA [–77 ppm]) δ (ppm): –62.2.

Anal. Calcd. (%) for $C_{17}H_{11}O_2F_6N$: 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.

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

***endo*-NDA** (5 g, 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 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** (Figure 1) was obtained after two recrystallizations from toluene (88% yield).

mp 170–173°C.

FT-IR (KBr): 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^{-1} (C–H).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.12 (4H, m), 6.25 (2H, s), 3.50 (2H, s), 3.43 (2H, s), 1.80–1.6 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 176.7, 163.7, 160.4, 134.5, 128.4, 127.7, 116.2, 52.2, 46.0, 45.5.

^{19}F NMR (300 MHz, $CDCl_3$, ref. TFA [–77 ppm]) δ (ppm): –113.09.

Anal. Calcd. (%) for $C_{15}H_{12}O_2FN$: 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.

2.3.3. *N*-2,2,6,6-tetramethylpiperidyl-*endo*-norbornene-5,6-dicarboximide (TMPNDI) (2c)

***endo*-NDA** (5 g, 30.5 mmol) was dissolved in 50 ml of toluene. An amount of 4.75 g (30.4 mmol) of 2,2,6,6-tetramethylpiperidylamine in 5 ml of toluene was added dropwise to the stirred solution of ***endo*-NDA**. The reaction was maintained at 60°C for 3 h. A precipitate was filtered and dried to give 9.2 g of amic acid (**1c**). The amic acid obtained (9.2 g, 28.7 mmol), anhydrous sodium acetate (1.8 g, 22.0 mmol) and acetic anhydride (27.2 g, 266 mmol) were heated at reflux for 5 h and then cooled. The solid which crystallized out on cooling was filtered, washed several times with cold water and dried in a vacuum oven at 50°C overnight. Pure monomer **2c** (Figure 1) was obtained after two recrystallizations from hexane (84% yield).

mp 116–119°C.

FT-IR (KBr): 3242 (N–H str), 2968 (C=C–H asym str), 1765 (C=O), 1697 (C=O), 1631 (C=C str), 1474 (C–H), 1369 (C–N), 1319, 1292 (C=C–H), 1207, 1159, 1127, 1090, 1044, 979, 915, 846 (C–C str), 741, 683, 625 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 5) δ (ppm): 6.13 (2H, s), 4.39–4.28 (1H, m), 3.39 (2H, m), 3.22 (2H, m), 2.48 (2H, t), 2.26 (2H, s), 1.75–1.71 (1H, m), 1.58–1.46 (14H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 177.7, 174.2, 134.3, 57.9, 51.9, 45.5, 45.0, 43.8, 42.7, 33.1, 29.8, 27.8.

Anal. Calcd. (%) for $C_{18}H_{26}O_2N_2$: C, 71.52; H, 8.60; O, 10.59; N, 9.27. Found: C, 72.02; H, 8.35; N, 9.64.

2.4. Metathesis polymerization of monomers

Polymerizations were carried out in glass vials under dry nitrogen atmosphere at 45°C. Polymerizations were quenched 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 either methanol or ethyl ether. The obtained polymers were dried in a vacuum oven at 40°C to constant weight.

2.4.1. Polymerization of 2a

1 g (2.66 mmol) of **2a** and 0.0023 g ($2.70 \cdot 10^{-3}$ mmol) of catalyst **I** were stirred in 2.7 ml of 1,2-dichloroethane at 45°C for 3 h (Figure 2). The obtained polymer **3a** was soluble in chloroform and dichloromethane.

T_g = 165°C, M_w/M_n = 1.6, M_n = 25,000.

FT-IR: 3036, 2941, 2880, 1778, 1733, 1598,1462, 1360, 1332, 1298, 1160, 983, 790 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 4) δ (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}C NMR (75 MHz, $CDCl_3$) δ (ppm): 174.0, 133.2 (*cis*), 132.6 (*trans*), 129.2, 126.5, 124.5, 122.1, 120.9, 48.9, 45.3, 40.6, 37.5.

^{19}F NMR (300 MHz, $CDCl_3$, ref. TFA [–77 ppm]) δ (ppm): –62.0.

2.4.2. Polymerization of 2b

1 g (3.89 mmol) of **2b** and 0.0033 g ($3.89 \cdot 10^{-3}$ mmol) of catalyst **I** were stirred in 3.9 ml of 1,2-dichloroethane at 45°C for 3 h (Figure 2). The obtained polymer **3b** was soluble in 1,2-dichloroethane, DMF and DMSO.

T_g = 180°C, M_w/M_n = 1.8, M_n = 34,500.

FT-IR: 3075, 2998, 2947, 1768, 1700, 1597, 1492, 1390, 1320, 611 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6) δ (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).

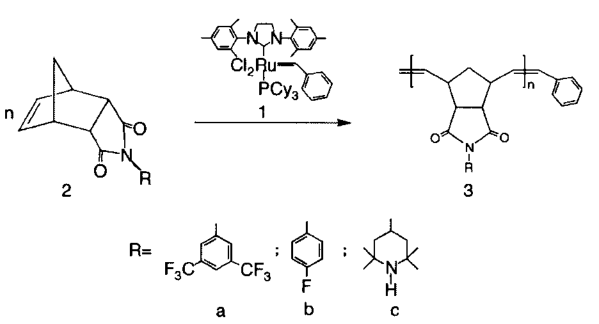

Figure 2. Ring opening metathesis polymerization of monomers **2a**, **2b** and **2c**

^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 176.9, 175.9, 160.0, 134.6 (*cis*), 133.9 (*trans*), 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}F NMR (300 MHz, DMSO-d_6, ref. TFA [–77 ppm]) δ (ppm): –112.40.

2.4.3. Polymerization of 2c

1 g (3.31 mmol) of **2c** and 0.0028 g ($3.29 \cdot 10^{-3}$ mmol) of catalyst **I** were stirred in 3.3 ml of 1,2-dichloroethane at 45°C for 3 h (Figure 2). The obtained polymer **3c** was soluble in chloroform and dichloromethane.

T_g = 189°C, M_w/M_n = 1.9, M_n = 39,300.

FT-IR: 3241, 2960, 1769, 1698, 1628, 1478, 1361, 1310, 1286, 1212, 1162, 1129, 1087, 1047, 976, 911, 849, 746, 680, 622 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) (Figure 5) δ (ppm): 5.69 (2H, s, trans), 5.62 (2H, s, cis), 4.49 (1H, m), 3.19 (2H, s), 2.95 (2H, m), 2.60 (2H, s), 2.26 (2H, s), 1.90 (1H, s), 1.60–1.26 (14H, m).

^{13}C NMR (75 MHZ, $CDCl_3$) δ (ppm): 176.5, 175.8, 174.2, 169.6, 132.0 (*cis*), 129.3 (*trans*), 123.6, 58.0, 53.0, 48.3, 44.1, 43.2, 40.3, 33.3, 29.8, 27.6, 25.3, 24.3, 18.2.

2.5. Polymer hydrogenation

The hydrogenation of poly(*N*-bis(trifluoromethyl) phenyl-*endo*-norbornene-5,6-dicarboximide) (Figure 3) was made using several catalysts. The reaction was investigated at room temperature and pressures ranging from 1–115 bar. The catalysts employed in the reaction were: Pd/C, PtO_2, Al/Ni and Wilkinson catalyst $ClRh(PPh_3)_3$.

A Parr shaker hydrogenator was used. This apparatus provides compact and easily operated systems for the treatment of chemicals with hydrogen in the

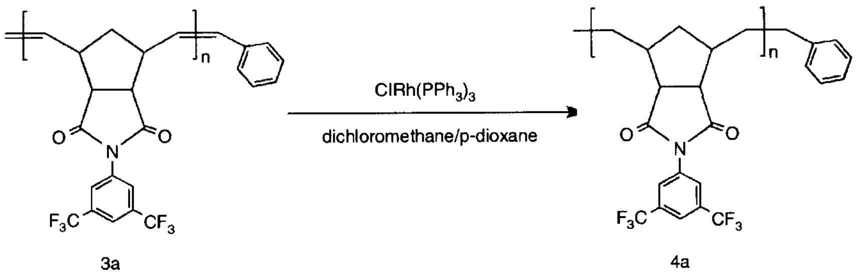

Figure 3. Hydrogenation of Poly-TFMPhNDI (**3a**) by Wilkinson's catalyst

presence of a catalyst at pressure up to 5 bar. The polymer to be treated in a Parr hydrogenator is sealed in a reaction bottle with the catalyst and connected to a hydrogen reservoir. Air is removed by evacuating the bottle. Pressure is then applied from the reservoir and the bottle is shaken vigorously to initiate the reaction. The progress of the reaction was followed by observing the pressure drop in the system and by ^{1}H NMR (Figure 4). The reaction at high pressure was carried out in a stainless steel 160 ml autoclave (Parr).

^{1}H NMR spectra were obtained on a Varian Gemini spectrometer at an observation frequency of 200 MHz with TMS as internal standard.

In a typical procedure, the polymer (0.5 g) was added to 60 ml of solvent in a Schlenk tube. The catalyst was previously introduced into the reactor. The solution was degassed and charged into the reactor under N_2. Hydrogen was added.

The optimum H_2 pressure is higher than 80 bar with $ClRh(PPh_3)_3$ as catalyst. Experiments were carried out using several solvents and the mixture dichloromethane-*p*-dioxane provided the best result. $T_g = 142°C$, $M_w/M_n = 1.9$, $M_n = 25{,}870$.

3. Results and discussion

Monomers **2a**, **2b** and **2c** were readily prepared with high yields (84–88%). 3,5-bis(trifluoromethyl)aniline, 4-fluoroaniline and 2,2,6,6-tetramethylpiperidylamine reacted with ***endo*-NDA** to the corresponding amic acids which were cyclized to *endo*-imides using acetic anhydride as dehydrating agent (Figure 1). ^{1}H, ^{13}C and ^{19}F NMR spectra and elemental analysis confirmed monomers structures and purity. The infrared spectra of monomers were very similar and showed characteristic peaks at 1760 and 1690 cm^{-1} (asymmetric and symmetric C=O stretching), 1400 cm^{-1} (C–N stretching). ROMP of monomers using ruthenium catalyst **I** were carried out in 1,2-dichloroethane at 45°C. The *endo* monomers reacted in 3 h giving polymer with high yields (93–97%). The results obtained by GPC analysis show that the number average molecular weights (M_n) were between 25,000 and 39,300. Polymer yields showed a slightly decrease with increasing the monomer to catalyst ratio. The polydispersity of the polymers is about $M_w/M_n = 1.6$–1.9 which is broader compared to polymers prepared by a living polymerization. This fact is due to slow initiation of this catalyst [25]. It has been also reported that the *endo* norbornene monomers give polymers with broader polydispersity compared to polymers from *exo* monomers [23].

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 (42–49% of *cis* structure). ^{1}H NMR spectra were used to determine the *cis/trans* content in the polymer. Figure 4 shows the ^{1}H NMR spectra of (a) monomer **2a**, (b) polymer **3a** prepared by **I** and (c) its saturated analogous polymer **4a**. 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. After the hydrogenation step, the signals mentioned above become weak and new signals corresponding to the methylene protons arise in the region of $\delta = 1.0$–2.5 ppm. The hydrogenation level was determined by integrating the area, in the ^{1}H NMR spectrum, of the olefinic proton region ($\delta = 5.5$–6 ppm) relative to aromatic proton region ($\delta = 7$–8.5 ppm) (Figure 4). A 98% of hydrogenation for poly-TFMPhNDI (**3a**) was achieved by Wilkinson catalyst $ClRh(PPh_3)_3$ at room temperature.

T_g's for Poly-TFMPhNDI (**3a**), Poly-FPhNDI (**3b**) and Poly-TMPNDI (**3c**) were observed at 165, 180 and 189°C, respectively (Figure 6). Polymer **3c**

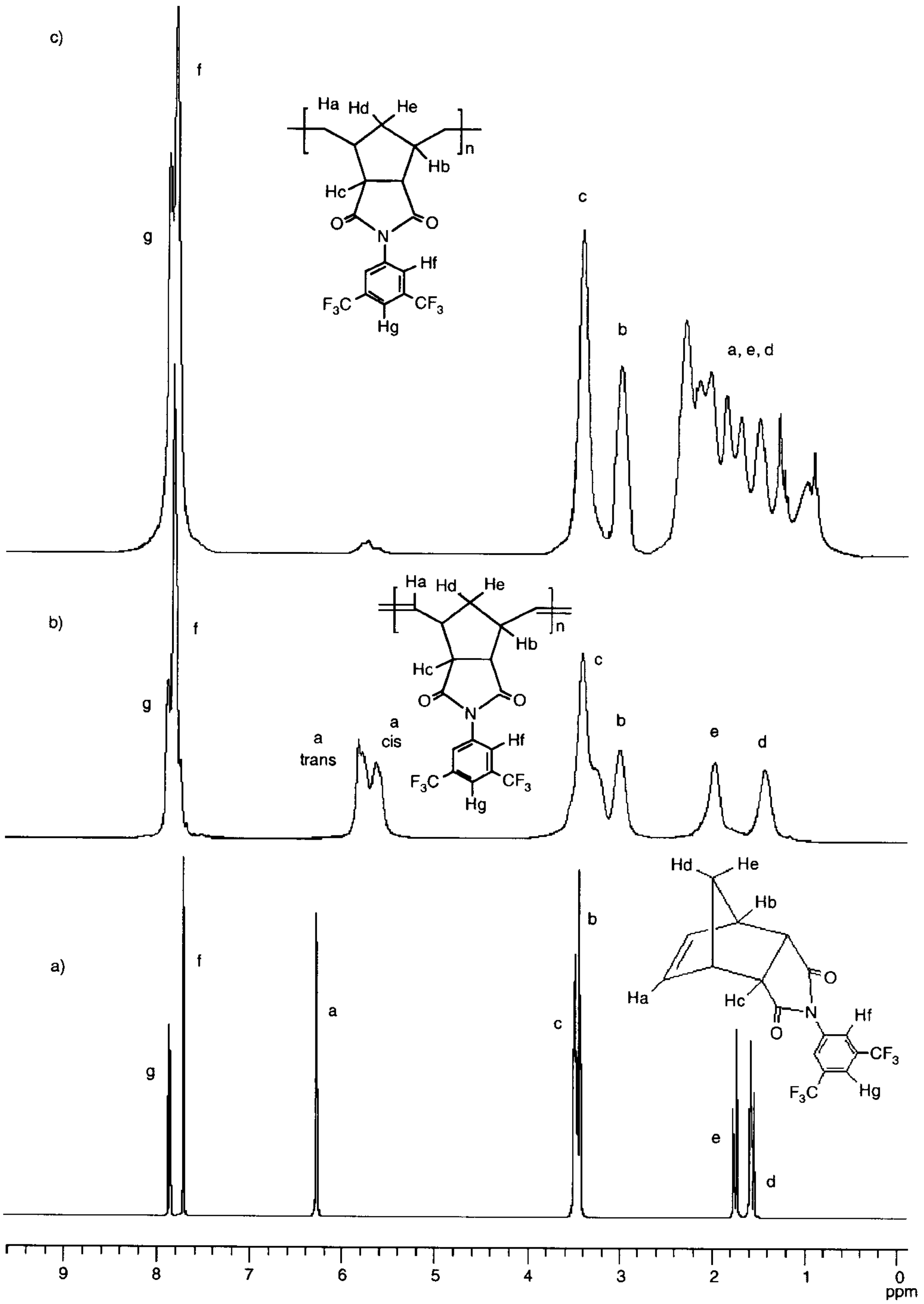

Figure 4. ^{1}H NMR spectra of a) monomer **2a**, b) polymer **3a** and c) its saturated analogous polymer **4a**

with larger substituents exhibits the higher glass transition temperature which indicates that the bulky tetramethyl groups should decrease the segmental motion of the polymer backbone. On the other hand, in spite of bearing the smaller substituent, polymer **3b** shows a T_g higher than polymer **3a**. The latter could be attributed to the ability of Poly-FPhNDI (**3b**) to chain packing which results in an increase in rigidity. The T_g of hydrogenated Poly-TFMPhNDI (**4a**) was lowered to 142°C on account of the highest conformational mobility of polymer chains in the saturated backbone which was also reflected in a lesser elastic modulus and stress in tension, 1567 and 28 MPa, respectively. The same effect of hydrogenation was

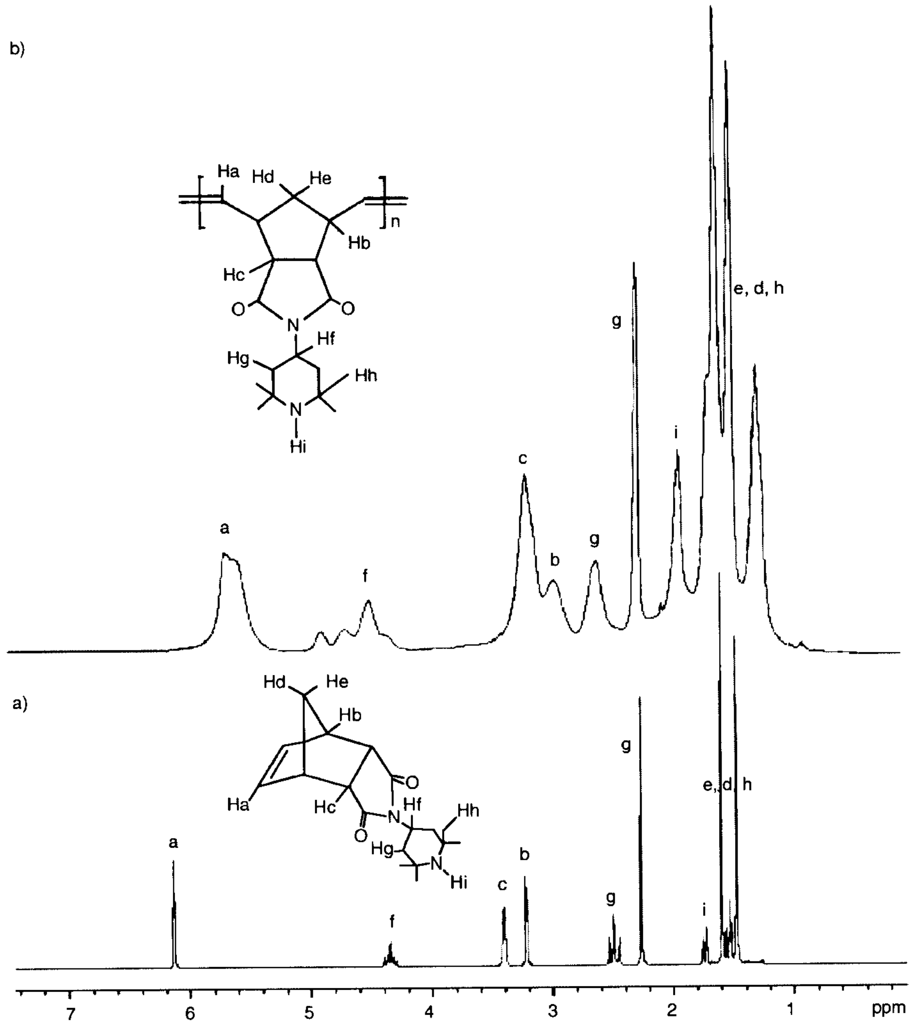

Figure 5. ^{1}H NMR spectra of a) monomer **2c** and b) polymer **3c**

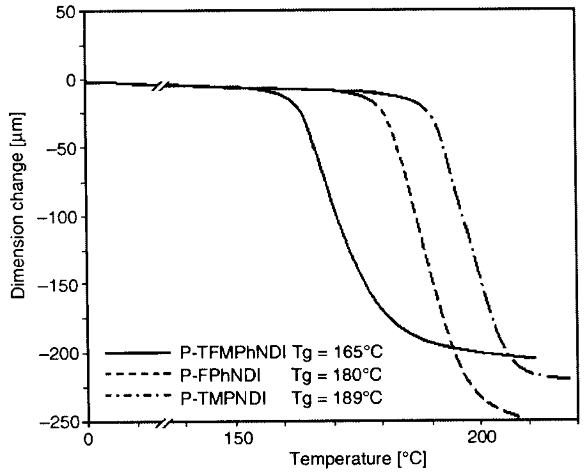

Figure 6. Thermomechanical curves of polymers **3a**, **3b** and **3c**, respectively

observed for other fluorine containing polynorbornenes [17].

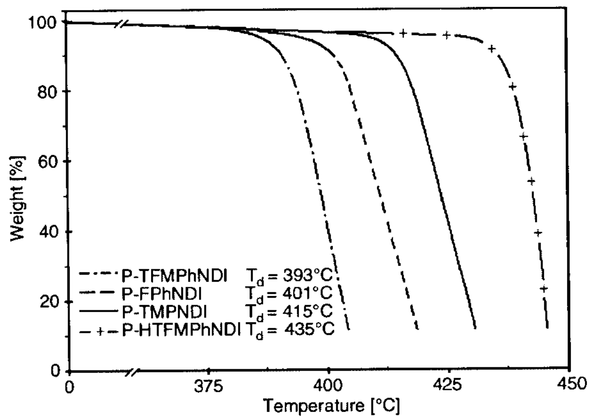

Figure 7. Thermogravimetric analysis of polymers **3a**, **3b**, **3c** and **4a** respectively

The thermal stability of the polymers was studied by TGA under N_2. As can be seen from Figure 7 onset temperature for decomposition of Poly-TFM-PhNDI is about 393°C which was considerably

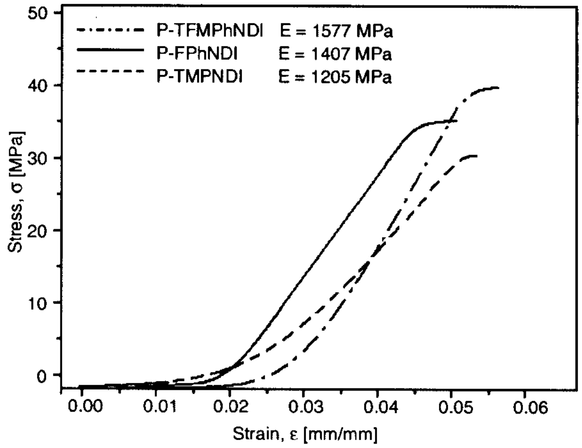

Figure 8. Stress versus strain plots of polymers **3a**, **3b** and **3c**, respectively

raised to 435°C (Poly-HTFMPhNDI, **4a**) after the hydrogenation step. Figure 8 represents, comparatively, the stress-strain curve in tension for the films of the synthesized polymers. The plots were cut at the maximum stress and show, for example, that not only the stress (39.1 MPa.) but also the elastic modulus (1577 MPa) are higher for the sample **3a**. In counterpart, the polymer **3c** has the lowest elastic modulus (1205 MPa) and stress in tension (30 MPa).

4. Conclusions

Endo isomers of TFMPhNDI (**2a**), FPhNDI (**2b**) and TMPNDI (**3c**) were synthesized and polymerized via ROMP using a second generation ruthenium alkylidene catalyst (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) ($PCy_3Cl_2Ru = CHPh$) (**I**). T_g's for Poly-TFMPhNDI, Poly-FPhNDI and Poly-TMPNDI were observed at 165, 180 and 189°C, respectively. Around 98% of hydrogenation for Poly-TFMPhNDI was achieved by $ClRh(PPh_3)_3$ catalyst. The onset of decomposition temperature, T_d, of the hydrogenated polymer was enhanced by almost 42°C nevertheless T_g was lowered to 142°C on account of the highest conformational mobility of polymer chains in the saturated backbone.

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