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Synthesis of new fluorine containing ring-opened polynorbornene dicarboximides using ruthenium alkylidene catalysts

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Summary

The synthesis of new *N*-4-trifluoromethylphenyl-*exo*-*endo*-norbornene-5,6-dicarboximide (**TFmNDI**, **2a**) and *N*-3,5-difluorophenyl-*exo*-*endo*-norbornene-5,6-dicarboximide (**DFNDI**, **2b**) was carried out. Polynorbornene dicarboximides, **3a** and **3b**, were obtained 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**), respectively. T_g's for polymers **3a** and **3b** were observed at 155°C and 142°C, respectively. Compared to polymer **3b**, polymer **3a** with the bulky trifluoromethyl group showed the highest glass transition temperature and improved mechanical properties.

Introduction

Fluorine containing polymers have attracted much attention because this kind of polymers exhibits 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-*exo*-norbornene-5,6-dicarboximide) showed a T_g of 271°C [6]. Membranes prepared from these polymers show an enhancement of the selectivity, though the permeability remains low and does not dependent on the bulkiness of side chain groups. The low gas permeability of these membranes can be explained by 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. Thus, we have already reported that gas permeability of the fluorine containing polynorbornene dicarboximide was much more higher than that of non fluorinated polynorbornenes with imide side chain groups [7]. The ROMP of norbornene derivatives with various fluorine-containing units is well established [8-11]. Furthermore, we have recently described not only the polymerization of challenging *endo*-isomers of fluorine-containing norbornene derivatives but also the structural modifications that this sort of polymers can undergo in order to exhibit desired properties for advanced applications [12, 13].

In this work, the synthesis and ROMP of new *N*-4-trifluoromethylphenyl-*exo-endo*-norbornene-5,6-dicarboximide (**TFmNDI**, **2a**) and *N*-3,5-difluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide (**DFNDI**, **2b**) 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**) are described. It is expected that the bulky imide pendant group bearing fluorine atoms in the resultant high molecular weight polymer will not only improve the thermomechanical properties but also will increase the polymer interchain distance making these materials suitable for specific gas separation applications.

Experimental Part

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. 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°C 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. FT-IR 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 using a universal column and a flow rate of 1 mL min^{-1}. X- ray diffraction measurements of **3a** and **3b** films as cast were carried out in a Siemens D-5000 diffractometer between 4 and 70 degrees 2θ, at 35 KV 25 mA, using CuK$_\alpha$ radiation (1.54 Å).

Reagents

Exo-(90%) and *endo*-(10%) 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-difluoroaniline 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.

Synthesis and Characterization of Monomer

Synthesis of N-4-trifluoromethylphenyl-exo-endo-norbornene-5,6-dicarboximide ***(TFmNDI) (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. A precipitate was filtered 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 (1.12 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. Pure exo(90%)-endo(10%) monomer **2a** (Scheme 1) was obtained after two recrystallizations from ethanol: yield = 89%, m.p. = 181-183°C.

FT-IR (KBr) = 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.

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 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, $CDCl_3$), δ (ppm) = 176.3, 137.9, 134.6, 126.1, 52.2, 47.8, 45.8, 45.5, 42.9.

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

Synthesis of N-3,5-difluorophenyl-exo-endo-norbornene-5,6-dicarboximide ***(DFNDI)*** *(****2b****).*

NDA (5 g, 30.5 mmol) was dissolved in 50 mL of dichloromethane. An amount of 3.9 g (30.2 mmol) of 3,5-difluoroaniline 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. A precipitate was filtered and dried to give 8.5 g of amic acid **1b**. The obtained amic acid **1b** (8.5 g, 29.0 mmol), anhydrous sodium acetate (1.12 g, 13.6 mmol) and acetic anhydride (12.0 g, 117 mmol) were heated at 70-80°C for 5 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 *exo*(90%)-*endo*(10%) monomer **2b** (Scheme 1) was obtained after two recrystallizations from ethanol: yield = 86%, m.p. = 154-156°C.

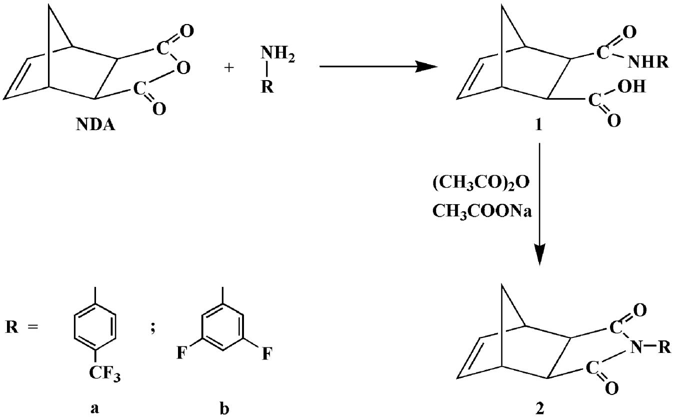
FT-IR (KBr) = 3029 (C=C-H str), 2978 (C-H asym. str.), 2945 (C-H sym. str.), 1774 (C=O), 1519 (C=C str), 1460 (C-H def), 1394 (C-N), 1195, 1169.

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 6.95-6.77 (3H, m), 6.35 (1H, s), 6.24 (1H, s), 3.39 (2H, m), 2.85 (2H, s), 1.80-1.20 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm) = 176.0, 164.2, 160.9, 137.9, 134.5, 109.9, 109.5, 104.3, 104.0, 103.7, 52.1, 47.6, 45.8, 42.9.

^{19}F NMR (300 MHz, $CDCl_3$, ref. TFA [-77ppm]) = δ (ppm) = -107.4.

Anal. Calcd. (%) for $C_{15}H_{11}O_2F_2N$ (275): C, 65.45; H, 4.0; O, 11.63; F, 13.81; N, 5.09. Found: C, 65.97; H, 4.23; N, 4.94.



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

Metathesis Polymerization of Monomer

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

*Polymerization of **2a***

Monomer **2a** (1.0 g, 3.25 mmol) and catalyst **I** ($2.68x10^{-3}$ 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 **3a** 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-trifluoromethylphenyl-*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 = 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, $CDCl_3$), δ (ppm) = 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, $CDCl_3$), δ (ppm) = 176.5, 134.8, 131.8, 130.4, 130.0, 126.4, 121.7, 50.8, 46.1.

^{19}F NMR (300MHz, $CDCl_3$, ref. TFA [-77ppm]), δ (ppm) = -67.3.

*Polymerization of **2b***

Monomer **2b** (1.0 g, 3.63 mmol) and catalyst **II** ($3.08x10^{-3}$ g, 0.0036 mmol) were stirred in 3.6 mL of 1,2-dichloroethane at 45°C for 2 h (Scheme 2). The obtained polymer **3b** 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-difluorophenyl-*exo-endo*-

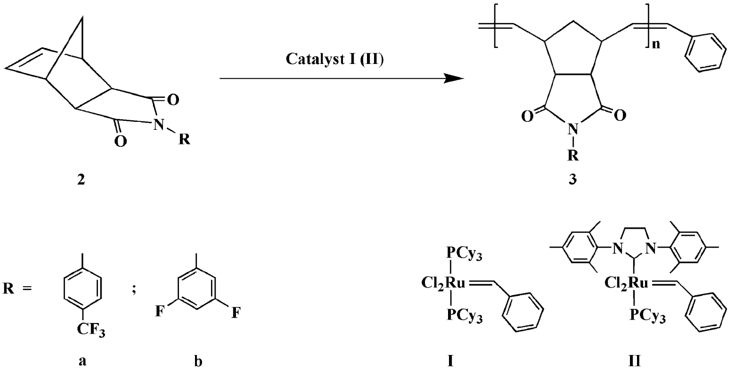
norbornene-5,6-dicarboximide) were, respectively, M_n = 239 000, M_w/M_n = 1.23, T_g = 142°C, T_d = 396°C.

FT-IR = 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}.

^1H NMR (300 MHz, $CDCl_3$), δ (ppm) = 6.95-6.81 (3H, m), 5.77 (1H, s, *trans*), 5.56 (1H, s, *cis*), 3.15 (2H, s), 2.85 (2H, s), 2.20 (1H, s), 1.69 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm) = 176.2, 164.3, 161.0, 133.6, 131.9, 109.8, 104.1, 50.7, 46.1.

^{19}F NMR (300MHz, $CDCl_3$, ref. TFA [-77ppm]), δ (ppm) = -107.4.



Scheme 2. Ring opening metathesis polymerization of monomers **2a** and **2b**.

Results and Discussion

Monomers **2a** and **2b** were prepared with high yields. 4-Trifluoromethyl aniline and 3,5-difluoroaniline reacted with **NDA** to the corresponding amic acids which were cyclized to imide using acetic anhydride as dehydrating agent (Scheme 1). ^1H, ^{13}C and ^{19}F NMR spectra and elemental analysis confirmed monomers structure and purity. The infrared spectra of monomers 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** was carried out in 1,2-dichloroethane at 45°C (Scheme 2). Table 1 summarizes the results of the polymerizations of **2a** and **2b**. The *exo-endo* monomers reacted in 2 h giving polymers with high yields (98-99%, entries 4 and 8). The results obtained by GPC analysis show that the number average molecular weights (M_n) were between 129,000 and 279,000.

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 **3a** and **3b** (entries 3, 4, 7 and 8) obtained by **II** is about M_w/M_n = 1.22-1.27 which is broader compared to polymers prepared by **I** (M_w/M_n = 1.11-1.13) due to the slower initiation of the latter catalyst [14]. Changing the pendant moiety did not affect neither the conversion of the monomer nor the stereochemistry of the double bonds in the polymer. Catalyst **I** gave polymers with predominantly *trans* configuration of the double bonds (83-84%), whereas catalyst **II** produced polymers with a mixture of *cis* and *trans* double bonds (52-53% of *cis* structure).

Table 1. Polymerization conditions of norbornene dicarboximides.

Entry	Monomer[a]	Catalyst	M/Cat[b]	Yield[c] (%)	*Cis*[d] (%)	*MW* x 10^{-5}[e]	M_n x 10^{-5}[f]	*MWD*[f]
1	2a[g]	I	1000	94	16	3.07	2.79	1.11
2	2a[g]	I	500	96	17	1.53	1.42	1.12
3	2a[g]	II	1000	98	53	3.07	2.61	1.27
4	2a[g]	II	500	99	52	1.53	1.51	1.26
5	2b	I	1000	92	17	2.75	2.53	1.13
6	2b	I	500	95	16	1.37	1.29	1.12
7	2b	II	1000	95	52	2.75	2.39	1.23
8	2b	II	500	98	52	1.37	1.35	1.22

[a] 1,2-Dichloroethane as solvent, Temperature = 45°C, Time = 2 h, Initial monomer concentration $[M_o]$ = 1 mol/L.

[b] Mole ratio of monomer to catalyst.

[c] Methanol insoluble polymer.

[d] Determined by ^{1}H NMR.

[e] Theoretical molecular weight calculated from the M/Cat ratio.

[f] GPC analysis in chloroform with polystyrene calibration standards.

[g] Initial monomer concentration $[M_o]$ = 0.7 mol/L.

Figure 1 and Figure 2 show the ^{1}H NMR spectra of (a) monomers **2a** (**2b**) and (b) polymers **3a** (**3b**) prepared by **I** and **II**, respectively. The *exo*-*endo* monomer olefinic

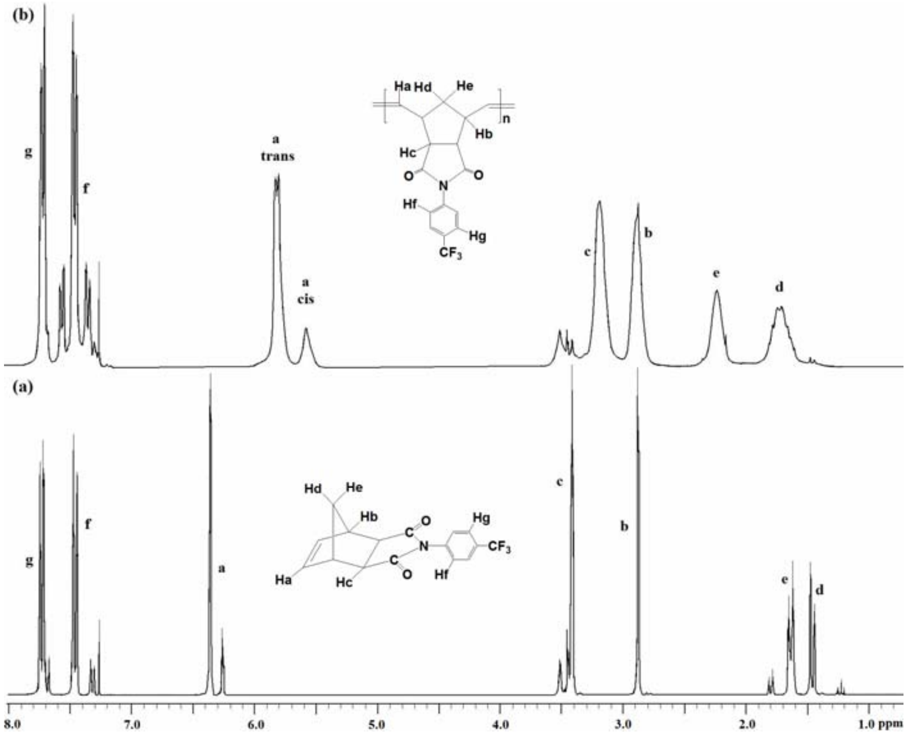


Figure 1. ^{1}H NMR spectra of a) monomer **2a** and b) polymer **3a** obtained by **I**.

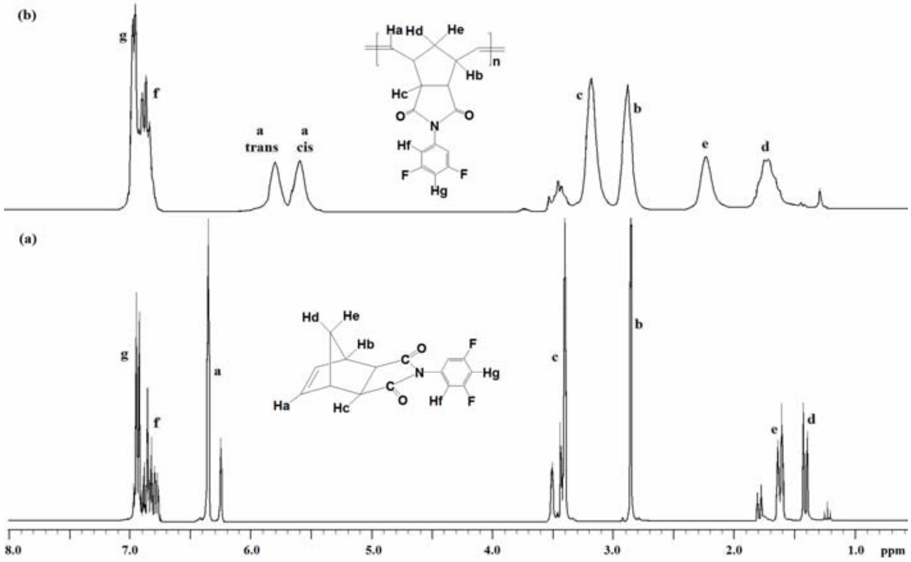


Figure 2. ^{1}H NMR spectra of a) monomer **2b** and b) polymer **3b** obtained by **II**.

signals at δ = 6.35-6.25 ppm (**2a**) and δ = 6.35-6.24 ppm (**2b**) are replaced by new signals at δ = 5.80-5.58 ppm (**3a**) and δ = 5.77-5.56 ppm (**3b**), which corresponds to the *trans* and *cis* H at the double bonds of polymers, respectively.

Thermal properties indicate that these polynorbornenes **3a** and **3b** are rigid amorphous polymers with T_g,s at 155°C and 142°C, respectively (Figure 3). The larger T_g found for polymer **3a** in comparison with polymer **3b** could be attributed to the presence of the bulky CF_3 group pending on the phenyl ring which inhibits the ability of the chains to relax. This effect has also been observed for other fluorine containing polynorbornene dicarboximides [14]. The thermal stability of the polymers was studied by TGA under N_2. The onset temperature for the decomposition of polymers **3a** and **3b** is about 402°C and 396°C, respectively.

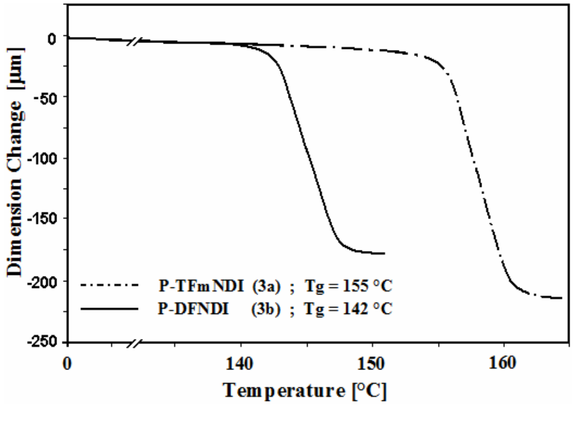


Figure 3. Thermomechanical curves of polymers **3a** and **3b**, respectively.

The stress-strain curve in tension for the films of the synthesized polymers could be observed on Figure 4. The plots shown there were cut at the maximum stress and indicate that not only the stress ($\sigma = 55.4$ MPa) but also the elastic modulus ($E = 1408$ MPa) for the sample **3a** are higher than those mechanical properties exhibited for the sample **3b** ($\sigma = 39.2$ MPa and $E = 1261$ MPa, respectively).

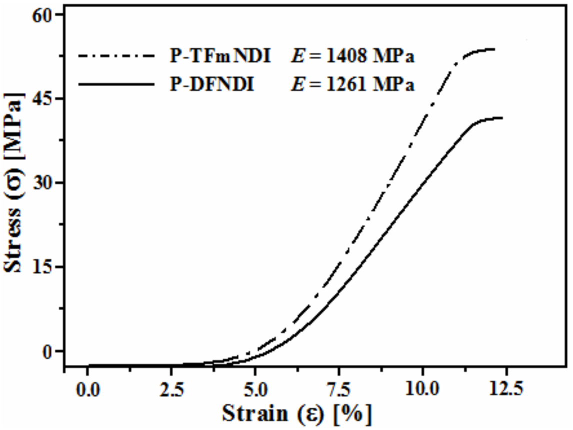


Figure 4. Stress versus strain plots of polymers **3a** and **3b**, respectively.

Figure 5 shows the x-ray diffraction pattern of the as cast **P-TFmNDI** (**3a**) film. This polymer shows a typical polynorbornene dicarboximide pattern with one broad diffraction peak with a maximum around 20° 2θ [7]. The latter indicates that the polymer as cast is amorphous since no crystallinity was detected.

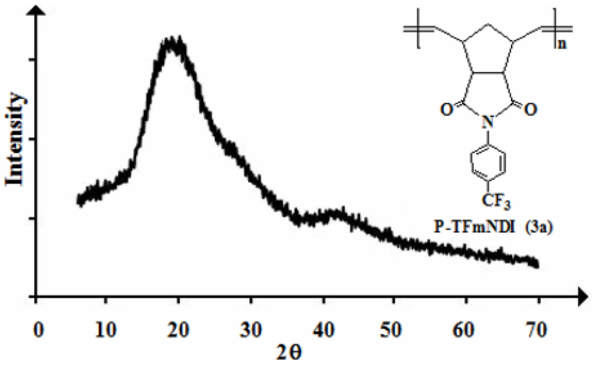


Figure 5. X-ray diffraction pattern of poly(*N*-4-trifluoromethylphenyl-*exo*-*endo*-norbornene-5,6-dicarboximide) (**3a**).

Conclusions

Exo(90%)-endo(10%) monomers of **TFmNDI** (**2a**) and **DFNDI** (**2b**) were synthesized and polymerized via ROMP using well defined ruthenium alkylidene catalysts **I** and **II**. T_g's for **P-TFmNDI** (**3a**) and **P-DFNDI** (**3b**) were observed at 155°C and 142°C, respectively. **P-TFmNDI** (**3a**) with a bulky trifluoromethyl group exhibits the highest glass transition temperature of both of the new polymers studied here (T_g = 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.

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