Polynorbornene with Pentafluorophenyl Imide Side Chain Groups: Synthesis and Sulfonation

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ABSTRACT: The mixtures of *exo-endo*-monomers and isomerically pure *endo*-monomers of *N*-pentafluorophenyl-norbornene-5,6-dicarboximide (**2a**) and *N*-phenyl-norbornene-5,6-dicarboximide (**2b**) were synthesized and polymerized *via* ring opening metathesis polymerization 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**). Ring opening metathesis polymerization of mixtures of *exo-endo*-monomers (**2a**) and (**2b**) and pure *endo*-**2b** gave the corresponding high molecular weights poly(*N*-pentafluorophenyl-norbornene-5,6-dicarboximide) (**3a**) and poly(*N*-phenyl-norbornene-5,6-dicarboximide) (**3b**). The isomerically pure *endo*-**2a** did not polymerize by **I** in these conditions, since **I** is the least active catalyst and *endo*-**2a** is the least active monomer because of the intramolecular complex formation between the Ru active center and the fluorine atom of ring-opened *endo*-**2a** on the one hand and steric hindrances caused by the pentafluorinated ring on the other. The quantitative hydrogenation of the polymer **3a**, at room temperature and 115 bar, was achieved by a Wilkinson's catalyst. The new polynorbornene bearing highly fluorinated sulfonic acid groups **(5)** was obtained by the reaction of the hydrogenated poly(*N*-pentafluorophenyl-norbornene-5,6-dicarboximide) **(4)** with sodium 4-hydroxybenzenesulfonate dihydrate. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2925–2933, 2010

KEYWORDS: fluorinated sulfonic acid polynorbornene dicarboximide; functionalization of polymers; ionomers; polynorbornene with pentafluorophenyl pendant groups; ring opening metathesis polymerization; ROMP

INTRODUCTION Fluorine containing polymers are important specialty materials because of their high thermostability, chemical inertness, and good hydrophobicity. These polymers with low intermolecular and intramolecular interactions are good candidates for membrane applications. Thus, the introduction of fluorine atoms into polynorbornene dicarboximides decreased interchain interactions between polar imide side chain groups and increased the gas permeability across them without detriment to the selectivity.[1–3] Compared with polynorbornene dicarboximides with phenyl-, adamantyl-, and cyclohexyl-side chain groups, polynorbornenes with phenylfluorine imide pendant groups exhibit much higher gas permeability.[2,4,5] Thus, it was reported that the gas permeability, diffusion, and solubility coefficients of polynorbornene dicarboximides with trifluoromethylphenyl pendant groups were up to an order of magnitude larger than those of the nonfluorinated one.[2,3]

The ring opening metathesis polymerization (ROMP) of fluorine containing norbornenes using classical metathesis catalysts is well established.[6,7] Recently, we proceeded with the synthesis and polymerizations of new norbornene derivatives with various fluorine atom units using well defined ruthenium alkylidene catalysts.[2,8,9] We recently also reported not only the synthesis but also the gas and ionic transport properties of a nonfluorinated sulfonic acid polynorbornene dicarboximide displaying ionic conductivity at low degree of hydration.[10,11] Hence, in this study we have envisioned the synthesis *via* ROMP of polymers based on *N*-pentafluorophenyl-norbornene-5,6-dicarboximide, their homogenous posthydrogenation and even further sulfonation to obtain new highly fluorinated sulfonic acid polymers. It is expected that these kinds of new polymers will exhibit good ionic properties resulting from a balanced chemical structure. On one hand, the extremely hydrophobic domains such as fluorophenyl side chain units and cyclopentane ring in the saturated hydrocarbon main chain will control the mechanical properties and proton diffusion across the membrane. On the other hand, the hydrophilic domains arising from the
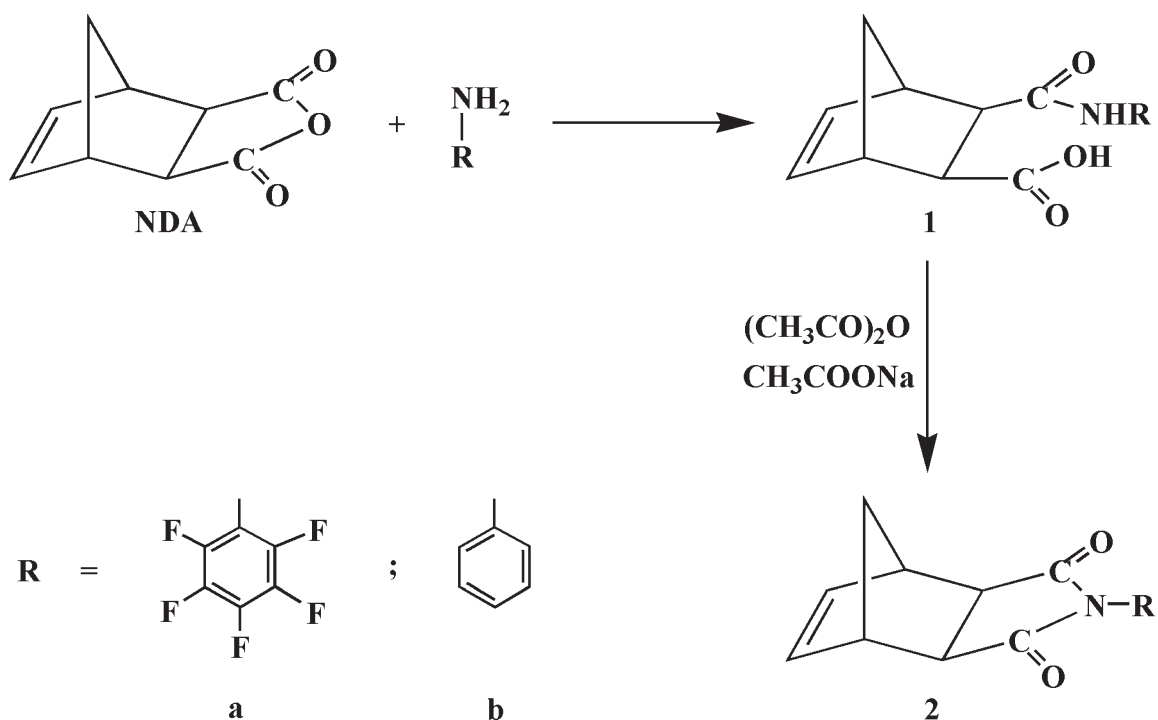
SCHEME 1 Synthesis route of monomers **2a** and **2b**, respectively.

imide functionality and polar sulfonic pendant groups will be responsible for the proton conductivity.

EXPERIMENTAL

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 deuterated chloroform (CDCl$_3$), N,N-dimethylformamide (DMF)-d_7, and dimethyl sulfoxide (DMSO)-d_6. Tetramethylsilane and trifluoroacetic acid (TFA) were used as internal standards, respectively. Glass transition temperatures, T_g, were determined in a DSC-7 Perkin–Elmer, 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, 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 Waters 2695 Alliance GPC at 35 °C in tetrahydrofuran using a universal column and a flow rate of 0.5 mL/min. Mechanical properties under tension, Young's modulus (E) and stress (σ_u), 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.

Reagents

Norbornene-5,6-dicarboxylic anhydride (NDA) was prepared *via* Diels–Alder condensation of cyclopentadiene and maleic anhydride according to literature.[10] 2,3,4,5,6-pentafluoroaniline, aniline, and sodium 4-hydroxybenzenesulfonate dihydrate were purchased from Aldrich Chemical and used without further purification. 1,2-dichloroethane, dichloromethane, p-dioxane, toluene, and N,N-dimethylacetamide were dried over anhydrous calcium chloride and distilled over CaH$_2$. Bis(tricyclohexylphosphine) benzylidene ruthenium (**IV**) dichloride (**I**), tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidene] ruthenium dichloride (**II**), and ClRh(PPh$_3$)$_3$ were purchased from Aldrich Chemical and used as received.

Synthesis and Characterization of *N*-Pentafluorophenyl-Norbornene-5,6-Dicarboximide (2a)

Monomer **2a** was synthesized by reacting 2,3,4,5,6-pentafluoroaniline with NDA to the corresponding amic acid which was cyclized to imide using acetic anhydride as dehydrating agent (Scheme 1).[12,13] NDA (5.0 g, 30.5 mmol) was dissolved in 40 mL of CH$_2$Cl$_2$. An amount of 5.58 g (30.5 mmol) of 2,3,4,5,6-pentafluoroaniline in 20 mL of CH$_2$Cl$_2$ was added dropwise to the stirred solution of NDA. 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** (10.3 g, 29.7 mmol), anhydrous sodium acetate (2.50 g, 30.47 mmol), and acetic anhydride (21.0 g, 205.7 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$_3$, and H$_2$O. Solvent was evaporated and pure monomer **2a** was obtained after
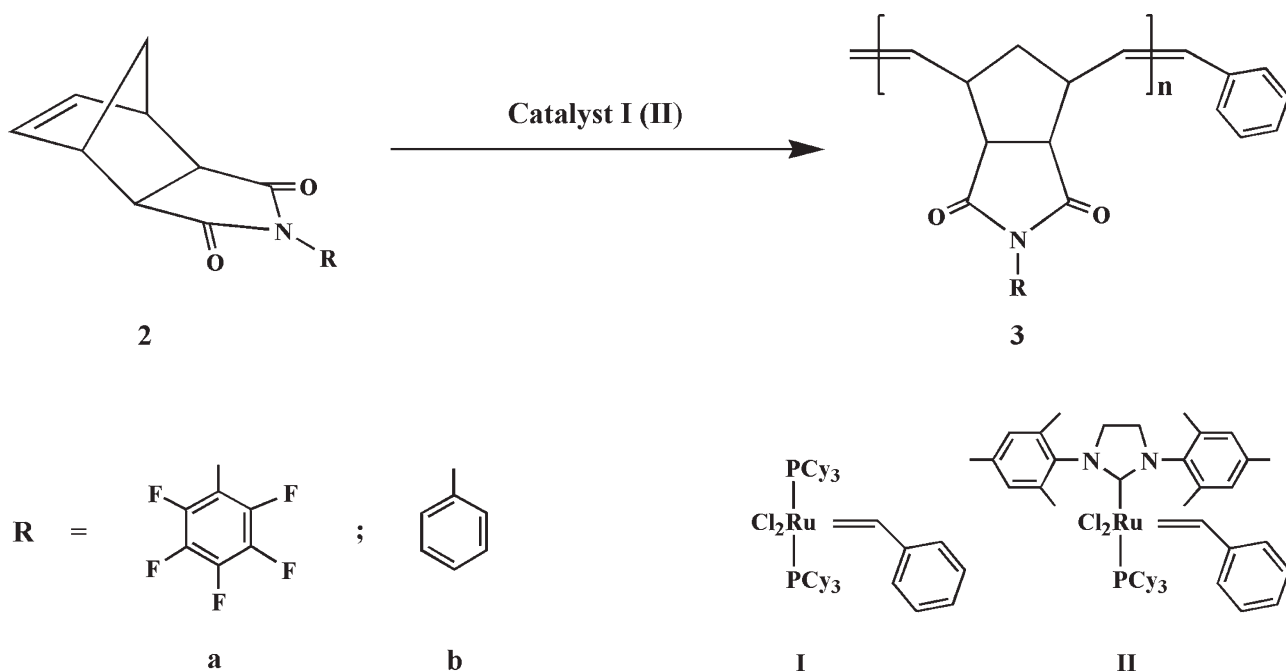
SCHEME 2 ROMP of norbornene dicarboximides **2a** and **2b**, respectively.

twice recrystallization from hexane and dried in a vacuum oven at 50 °C overnight: yield = 75%, m.p. = 112–113 °C exo(90%)–endo(10%) monomer mixture, m.p. = 128–129 °C endo(100%) monomer.

^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm) = 6.36 (1H, s), 6.25 (1H, s), 3.53 (1H, s), 3.42 (1H, s), 2.96 (2H, s), 1.70–1.54 (2H, m). ^{13}C NMR (75 MHZ, CDCl$_3$): δ (ppm) = 174.7 (C=O), 147.8–139.6 (C—F), 137.8 (C=C), 134.4 (C=C), 107.1 (C—N), 52.1, 48.4, 45.8, 45.6, 42.9. ^{19}F NMR (300 MHz, CDCl$_3$, ref. TFA [−77ppm]): δ (ppm) = −142.2, −142.4, −150.1, −150.6, −160.1, −160.4. FTIR (KBr, cm^{-1}): 3076, 2949 (C—H asym str), 2880 (C—H sym str), 1782 (C=O), 1724, 1644 (C=C str), 1519, 1356, 1299 (C—F), 1172, 1157, 984, 793.

Synthesis and Characterization of *N*-Phenyl-Norbornene-5,6-Dicarboximide) (2b)

Monomer **2b** was synthesized according to literature (Scheme 1).[13] NDA (5.0 g, 30.5 mmol) was dissolved in 50 mL of toluene. An amount of 2.8 g (30.1 mmol) of aniline in 10 mL of toluene was added dropwise to the stirred solution of NDA. The reaction was maintained at 50 °C for 3 h. A precipitate was filtered and dried to give 7.6 g (29.5 mmol) of amic acid **1b**. The amic acid obtained (7.6 g, 29.5 mmol), anhydrous sodium acetate (3.0 g, 36.0 mmol), and acetic anhydride (21.0 g, 212.0 mmol) were heated at 90 °C for 6 h and then cooled. The solid crystallized on cooling was filtered, washed several times with water and dried in a vacuum oven at 50 °C overnight. Pure monomer **2b** was obtained after twice recrystallization from toluene: yield = 81%, m.p. = 195–196 °C exo(90%)-endo(10%) monomer mixture.

^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm) = 7.49–7.25 (5H, m), 6.33 (2H, s), 6.24 (2H, s), 3.38 (2H, s), 2.84 (2H, s), 1.62–1.46 (2H, m). ^{13}C NMR (75 MHZ, CDCl$_3$): δ (ppm) = 176.8 (C=O), 137.8 (C=C), 134.4, 131.7 (C—N), 129.0, 128.4, 126.2, 47.7, 45,7, 42.8. FTIR (KBr, cm^{-1}): 3064, 2946 (C—H asym str), 2877 (C—H sym str), 1770 (C=O), 1594 (C=C str), 1454 (C—N), 1382, 1329, 1289, 1188, 975, 799.

Metathesis Polymerization of Monomers

Polymerizations were carried out in glass vials under dry nitrogen atmosphere. They 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 °C to constant weight.

Polymerization of 2a

Monomer **2a** (1.0 g, 3.04 mmol) and catalyst **I** (2.49 × 10^{-3}g, 0.0030 mmol) were stirred in 4.3 mL of 1,2-dichloroethane at 45 °C for 2 h (Scheme 2). The obtained polymer **3a** was soluble in chloroform and dichloroethane. T_g = 171 °C, T_d = 425 °C, E = 1226 MPa, σ_u = 48.7 MPa.

^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 5.78 (1H, s, *trans*), 5.56 (1H, s, *cis*), 3.28 (2H, s), 2.88 (2H, s), 2.24 (1H, s), 1.70 (1H, s). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 174.7, 147.0, 146.1, 141.0, 135.3, 133.3 (*cis*), 131.9 (*trans*), 107.1, 51.4, 46.6, 41.9. ^{19}F NMR (300 MHz, CDCl$_3$, ref. TFA [−77ppm]): δ (ppm) = −142.2, −142.5, −143.2, −150.0, −150.3, −159.8, −160.2, −160.7. FTIR (thin film, cm^{-1}): 3002, 2930 (C—H asym str), 2855 (C—H sym str), 1790 (C=O), 1725, 1647 (C=C str), 1513, 1356, 1297 (C—F), 1165, 1138, 984, 785, 767, 624.
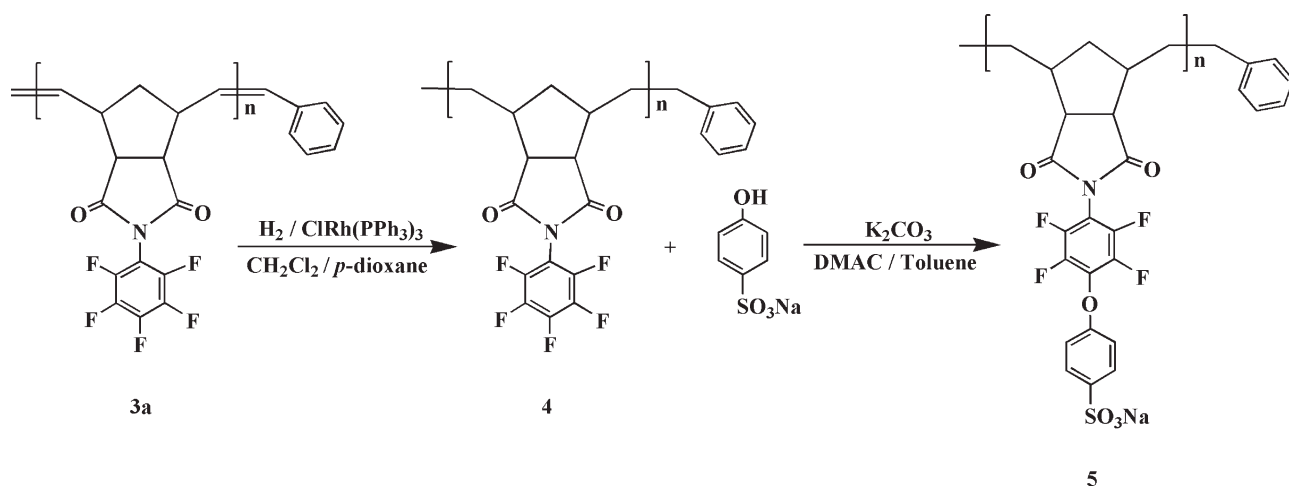
SCHEME 3 Hydrogenation of poly(*N*-pentafluorophenyl-norbornene-5,6-dicarboximide) and further sulfonation of the polymer.

Polymerization of 2b

Monomer **2b** (1.0 g, 4.18 mmol) and catalyst **II** (3.5 × 10^{-3} g, 0.0041 mmol) were stirred in 4.2 mL of 1,2-dichloroethane at 25 °C for 1.4 h (Scheme 2). The obtained polymer **3b** was soluble in chloroform and dichloroethane. T_g = 222 °C, T_d = 418 °C, E = 1560 MPa, σ_u = 57.0 MPa.

^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm) = 7.42-7.21 (5H, m), 5.78 (1H, *trans*, s), 5.54 (1H, *cis*, s), 3.49 (2H, s), 3.14–2.86 (2H, m), 2.16 (1H, s), 1.61 (1H, s). ^{13}C NMR (75 MHZ, CDCl$_3$): δ (ppm) = 177.1, 133.7 (*cis*), 131.8 (*trans*), 128.9, 126.3, 52.5, 50.9, 48.6, 46,0, 42.8, 40.5. FTIR (thin film, cm^{-1}): 3034, 2930 (C—H asym str), 2869 (C—H sym str), 1775 (C=O), 1590 (C=C str), 1457 (C—N), 1385, 1323, 1290, 1165, 980, 790.

Hydrogenation of 3a

A total of 0.5 g of **3a** was added to 60 mL of solvent (dichloromethane-*p*-dioxane 1:1) in a Schlenk tube. The catalyst (5 wt %) was previously introduced into a Parr shaker reactor. The solution was degassed and charged into the reactor under N$_2$. Then, hydrogen was added. A 99% of hydrogenation, determined by ^{1}H NMR, for **4** was achieved using Wilkinson's catalyst, ClRh(PPh$_3$)$_3$, at room temperature and 115 bar (Scheme 3). The obtained polymer **4** was soluble in chloroform and toluene. T_g = 144 °C, T_d = 448 °C, E = 1190 MPa, σ_u = 43.1 MPa.

^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 3.06, 2.31, 2.17, 1.88, 1.62, 1.25. ^{13}C NMR (75 MHZ, CDCl$_3$): δ (ppm) = 175.6 (C=O), 146.1, 144.7, 140.8, 135.8, 132.4, 107.2, 51.9, 44.6, 44.0, 42.2. ^{19}F NMR (300 MHz, CDCl$_3$, ref. TFA [−77ppm]): δ (ppm) = −142.2, −143.1, −150.2, −159.9, −160.2. FTIR (thin film, cm^{-1}): 2902 (C—H asym str), 2861 (C—H sym str), 1794 (C=O), 1720, 1502, 1460 (C—N), 1367, 1279 (C—F), 1161, 1147, 1000.

Sulfonation of 4

Hydrogenated poly(*N*-pentafluorophenyl-norbornene-5,6-dicarboximide) (**4**) (0.5 g, 1.51 mmol), sodium 4-hydroxy-benzenesulfonate dihydrate (0.70 g, 3.02 mmol), and potas-

sium carbonate (0.52 g, 3.77 mmol) were mixed in a round flask equipped with a Dean-Stark trap and stirred in 15 mL of solvent (*N,N*-dimethylacetamide-toluene 2:1) at 120 °C for 9 h (Scheme 3). Progressive precipitation overtime was observed. The product was then filtered off, washed several times with distilled water and dried in a vacuum oven at 40 °C overnight. The resulting polymer **5**, a pale-brown powder, was soluble in DMF and DMSO: yield = 94%, T_g = 228 °C, T_{d1} = 260 °C (sulfonic group loss), T_{d2} = 430 °C (main chain decomposition).

^{1}H NMR (300 MHz, DMF-d_7): δ (ppm) = 7.80 (2H, s), 7.18 (2H, s), 3.56 (2H, s), 2.73, 2.31, 1.83, 1.58, 1.91. ^{13}C NMR (75 MHZ, DMF-d_7): δ (ppm) = 175.0 (C=O), 145.5, 145.0, 140.4, 139.7, 128.2 (C—O), 115.1, 107.2, 49.0, 43.0. ^{19}F NMR (300 MHz, DMSO-d_6, ref. TFA [−77ppm]): δ (ppm) = −141.9, −143.0, −153.1. FTIR (thin film, cm^{-1}): 2926 (C—H asym str), 2860 (C—H sym str), 1787 (C=O), 1726, 1636, 1509, 1406, 1356, 1295 (C—F), 1140 (—SO$_3$H, asym str), 1132, 1039 (—SO$_3$H, sym str), 981, 833, 698, 561.

RESULTS AND DISCUSSION

Monomers **2a** and **2b** were prepared in high yields (75–81%).[12,13] 2,3,4,5,6-Pentafluoroaniline and aniline reacted with NDA to the corresponding amic acids which were cyclized to imide using acetic anhydride as dehydrating agent (Scheme 1). ^{1}H, ^{13}C, and ^{19}F NMR spectra and Elem. Anal confirmed monomers structure and purity.

The polymerizations of **2a** and **2b** were carried out in 1,2-dichloroethane using catalysts **I** and **II** (Scheme 2). Table 1 summarizes the results of the polymerizations of *exo-endo*- and *endo*- monomers. It is seen that the pure *endo*-**2a** did not polymerize by **I** (entries 6 and 7) whereas **II** led to the formation of high molecular weight polymers in high yields. The *endo*-**2b** polymerized by both catalysts (entries 9 and 10). It was shown that the reactivity difference between the *exo*- and *endo*-isomers of norbornene derivatives is primarily because of steric interactions between the propagating Ru-center and the *endo*-ring of an incoming monomer.[14]

TABLE 1 Polymerization Conditions of *N*-Pentafluorophenyl-Norbornene-5,6-Dicarboximide (**2a**) and *N*-Phenyl-Norbornene-5,6-Dicarboximide (**2b**)

Entry	Monomer	*Endo* Isomer in the Feed (%)[a]	Catalyst[b]	Temperature (°C)	Time (h)	*Cis* Content in Polymer (%)[a]	Yield (%)[c]	$M_n \times 10^{-5}$ [d]	MWD[d]
1	**2a**	25	I	45	2	16	80	1.21	1.30
2	**2a**	25	I	65	0.10	18	91	1.81	1.23
3	**2a**	25	II	45	0.66	53	96	3.07	1.62
4	**2a**	49	I	45	19	19	49	0.83	1.74
5	**2a**	49	II	45	1	51	81	1.61	1.27
6	**2a**	100	I	45	24	–	–	–	–
7	**2a**	100	I	70	108	–	–	–	–
8	**2a**	100	II	45	1	43	72	1.80	1.60
9	**2b**[e]	100	I	70	11	17	56	0.41	1.82
10	**2b**[e]	100	II	25	1.4	45	75	0.58	1.96

[a] Determined by ^{1}H NMR.
[b] Monomer/catalyst = 1000, 1,2-Dichloroethane as solvent, Initial monomer concentration $[M_0] = 0.7$ mol/L.
[c] Methanol insoluble polymer.
[d] GPC analysis in tetrahydrofuran with polystyrene calibration standards.
[e] Initial monomer concentration $[M_0] = 1.0$ mol/L.

There have been reports on the reactivity in the ROMP of *exo-endo*-isomers of norbornene derivatives with polar groups.[15] It is assumed that compared with the *exo*-monomer, where functional groups are far from the metal active center, the polar groups of the *endo*-monomer may coordinate to the metallacarbene active center inhibiting the polymerization. In the case of the *endo*-**2a** polymerization, the intramolecular reaction between the Ru-center and the fluoroaryl moiety of the monomer is possible. Thus, molecular complexes formed during the reaction of the *endo*-**2a** with the 14-electron Ru-centers of **I** and **II** were optimized using M06L functional implemented in Gaussian 09 suite of programs.[16] M06L functional was designed to deliver superior performance for organometallic systems and weak interactions.[17] 6-31G(d) Basis set was used for non metallic atoms, while for the Ru atom was used cc-pvtz basis set and Stuttgart RSC 1997 ECP.[18] The calculations show that the Ru–fluorine distances for catalysts **I** and **II** in the formed intramolecular complexes **A** and **B** are of 2.99 Å and 2.97 Å, respectively, (Fig. 1). The nonfluorinated *endo*-**2b** does not form these kinds of complexes (Ru—H distances are of 4.33 and 4.47 Å for **C** and **D**, respectively). This is more than a sum of Ru and H van-der Waals radii and clearly demonstrates Ru—F interactions for the *endo*-**2a**. The inspection of charges on Ru atoms further confirms interactions between fluorine and Ru atoms. Thus Mulliken charges on Ru atoms in **A**, **B**, **C**, and **D** complexes (Fig. 1) with the *endo*-**2a** and the *endo*-**2b** were found to be of −0.29, −0.15, −0.23, and −0.09, respectively. As seen, there is a slight but observable built up of electron density on Ru atom in fluorinated compounds revealing a transfer of electron density from fluorine to Ru-centers. In the case of an *endo*-chlorinated monomer the Cl—Ru distance in the intramolecular complex **E** (Fig. 1) is even less than for the *endo*-**2a** (2.87 Å) demonstrating a better interaction of Cl atoms with the Ru-center compared

with fluorine one. It was reported that chlorine atoms coordinated better than fluorine atoms to the Ru atom.[19] Ruthenium–fluorine interactions have been observed in Ru-alkylidene catalysts with fluorinated *N*-heterocyclic carbene ligands.[20] The intramolecular interactions between the Ru-center and carbonyl-oxygen of olefinic esters have also been studied.[20] It is important to note that ruthenium–fluorine interactions are weaker compared with Ru-carbonyl intramolecular reactions. Thus, Ru—O distances are typically 2.22–2.26 Å, compared with longer Ru—F distances.[21] On the other hand, it is generally accepted that the activity of a reactive intermediate decreases with its stability. Since, the stability of metallacarbenes decreases with the charge at a Ru-center, one can relate the reactivity of a metallacarbene with the charge at a Ru atom.[22] Thus, the Mulliken charges at Ru atoms of intramolecular complexes **A** and **B** (Fig. 1) for **I** and **II** are of −0.29 and −0.15, respectively, revealing that the metallacarbene active center of the second generation Grubbs catalyst is more active compared with this of the first generation. Experimental data demonstrated that the second generation Ru-alkylidene catalyst is more active than the first generation one.[23] Computational modeling also confirmed that the absolute activation energies of the metathesis reactions are notoriously lower for the second generation catalyst.[24] It is important to note that molecular volumes of pentafluorophenyl and phenyl groups in **2a** and **2b** were found to be of 85 and 71 Å^3, respectively. We believed that the least active catalyst **I**, the Ru–fluorine intramolecular interaction and the steric effect of the pentafluorinated ring in the *endo*-**2a** are factors which can impede the ROMP of the *endo*-**2a** using **I**. In Table 1, the results obtained by GPC analysis show that the number average molecular weights (M_n) were between 41,000 and 307,000. Furthermore, the molecular weight distribution of the polymers **3a** and **3b** (entries 3, 5, 8, and 10) obtained by **II** is about $M_w/M_n =$
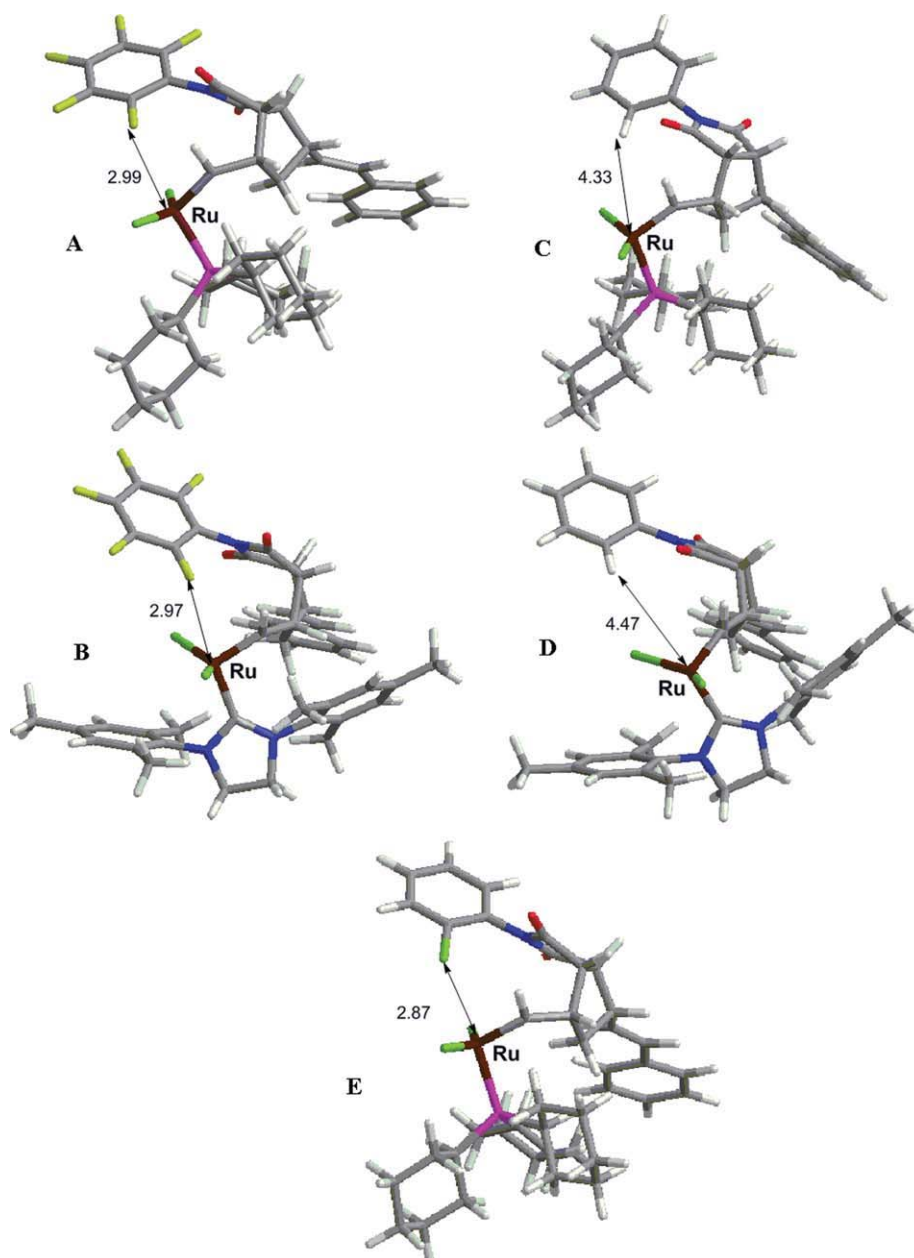
FIGURE 1 Optimized geometries of ruthenium intramolecular complexes (**A**), (**B**), (**C**), (**D**), and (**E**).

1.27–1.96 which is broader compared with polymers prepared by **I** (M_w/M_n = 1.23–1.82). Changing the pendant moiety did not affect the stereochemistry of the double bonds in the polymer. Catalyst **I** gave polymers with predominantly *trans* configuration of the double bonds (81–84%), whereas catalyst **II** produced polymers with a mixture of *cis* and *trans* double bonds (43–53% of *cis* structure).

Figure 2 shows the ^{1}H NMR spectra of (A) hydrogenated polymer **4** and (B) its unsaturated analogous polymer **3a**. The polymer olefinic signals are observed at δ = 5.78 and 5.56 ppm, which correspond 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 δ = 2.33–1.28 ppm. A 99% of hydrogenation for polymer **4** was achieved according to the methodology previously reported for this kind of polymers.[11] Stress–strain measurements in tension for the films of the synthesized polymers were carried out. The experiments were stopped at the maximum stress and indicate, on one hand, that in spite of bearing the smaller substituent, **3b** shows higher elastic modulus (E) as well as stress in tension (σ_u), 1560 MPa and 57.0 MPa, respectively, in comparison with **3a** (1226 MPa and 48.7 MPa). The latter could be attributed to the ability of polymer **3b** to chain packing which results in an increase of rigidity. On the other hand, the highest
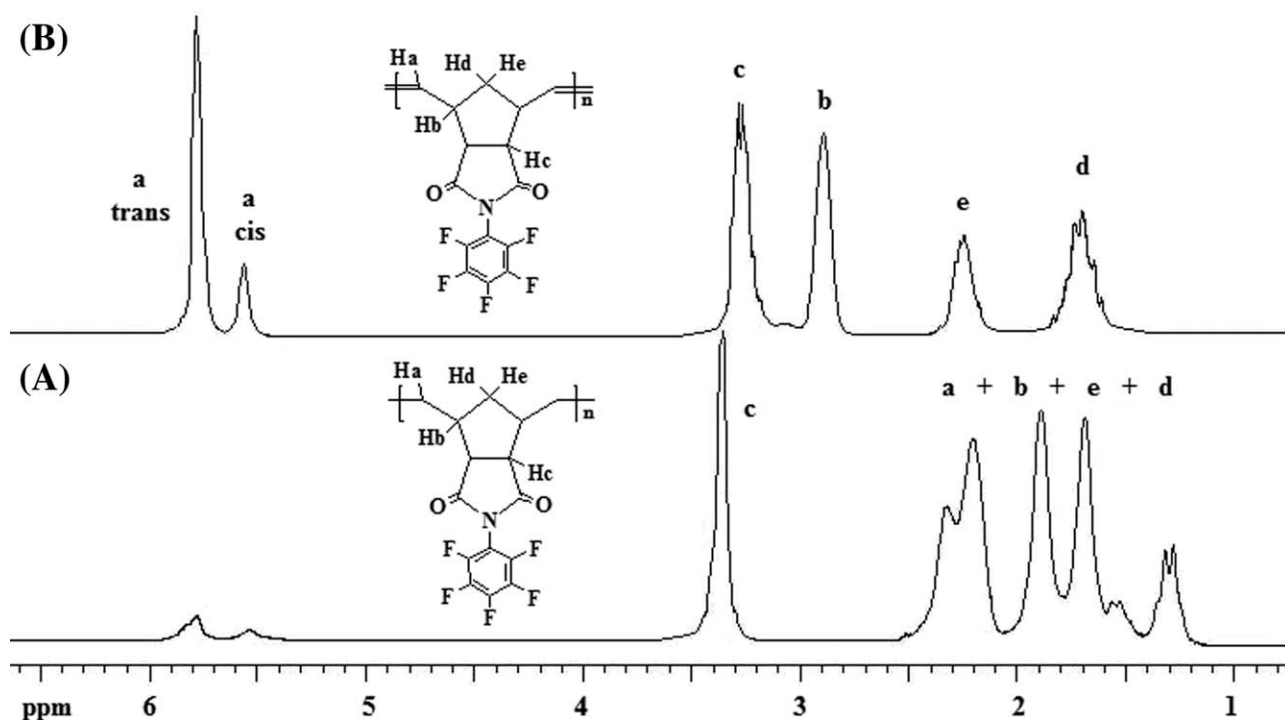
FIGURE 2 ^{1}H NMR spectra of (A) hydrogenated polymer **4** and (B) its unsaturated analogous polymer **3a**.

conformational mobility of polymer chains in the saturated backbone of polymer **4** was reflected in a lesser elastic modulus and stress in tension, 1190 MPa and 43.1 MPa, respectively. Having improved the thermo-oxidative stability of polymer **3a** by hydrogenating, the polymer reactivity towards the nucleophilic aromatic substitution in the pentafluorophenyl moiety was explored. Therefore, we reacted polymer **4** with sodium 4-hydroxybenzenesulfonate dihydrate to obtain a quantitative film forming sulfonated polymer **5**. Progressive precipitation of the ionomer overtime was observed and polymer recovery was quantitative. The ionomer was soluble in DMF and DMSO for degrees of sulfonation up to 60 mol %; however, as the degree of sulfonation was increased, the polymer solubility became poor until only DMSO was able to dissolve the fully sulfonated polymer. The substitution reaction was monitored by ^{19}F NMR spectroscopy, and the degree of sulfonation was controlled both by the nucleophilic agent amount and the time of reaction. Figure 3 shows the ^{19}F NMR of (A) nonsulfonated polymer **4**, (B) partially sulfonated polymer **5**, and (C) fully sulfonated polymer **5**. It is appreciated that as the pentafluorophenyl moiety is sulfonated, the signal corresponding to the fluorine atom in *meta* position of unsulfonated polymer **4** (A, −159.9 ppm) becomes weak and a new *meta* signal corresponding to those pentafluorophenyl moieties which have already been sulfonated become to grow (B, −154.8 ppm) until a unique *meta* signal is observed at complete sulfonation of polymer **4** (C, −153.2 ppm). At the same time, the signal corresponding to the fluorine atom in *para* position (B, −152.5 ppm) decreases until its complete disappearance

when a fully sulfonated polymer is obtained. From this analysis, we conclude that only the carbon in *para* position has undergone the nucleophilic aromatic substitution. Preliminary measurements performed in membranes of polymer **5**, equilibrated with distilled water, indicate that the protonic conductivity is slightly higher than 1.0 S m^{-1} at room temperature, comparable to that displayed by perfluorinated acidic membranes such as Nafion in the same conditions. In this regard, it is worth noting that hydrolysis stability plays an important role in the long-term ionomer performance. Sulfonated phthalic polyimides have been reported to display lesser water stability in comparison with naphthalenic sulfonated polyimides when they have been exposed in the same tough conditions, both imide structures degrade and become brittle in time mainly owing to the hydrolytic polymer chain scission.[25] Nevertheless, because the imide moiety of polymer **5** is a side chain group, this polyelectrolyte does not undergo severe degradations as those of linear polymers bearing the imide moiety in the main chain so that dramatic decreases in molecular weight as well as in dimensional stability and performance have not been observed when membranes of polymer **5** have been subjected at 80 °C in a full hydration environment up to 48 h. Furthermore, the presence of a flexible linkage such as ether bond raises the conformational mobility of polymer chains which in turn reduces the swelling stress when polymer **5** is in film form. Moreover, as the electron-withdrawing sulfonic acid groups are bonded to an aromatic ring other than the fluorine-stabilized aminophenyl ring of polymer **5**, a more basic amine moiety is obtained improving the hydrolysis stability of the
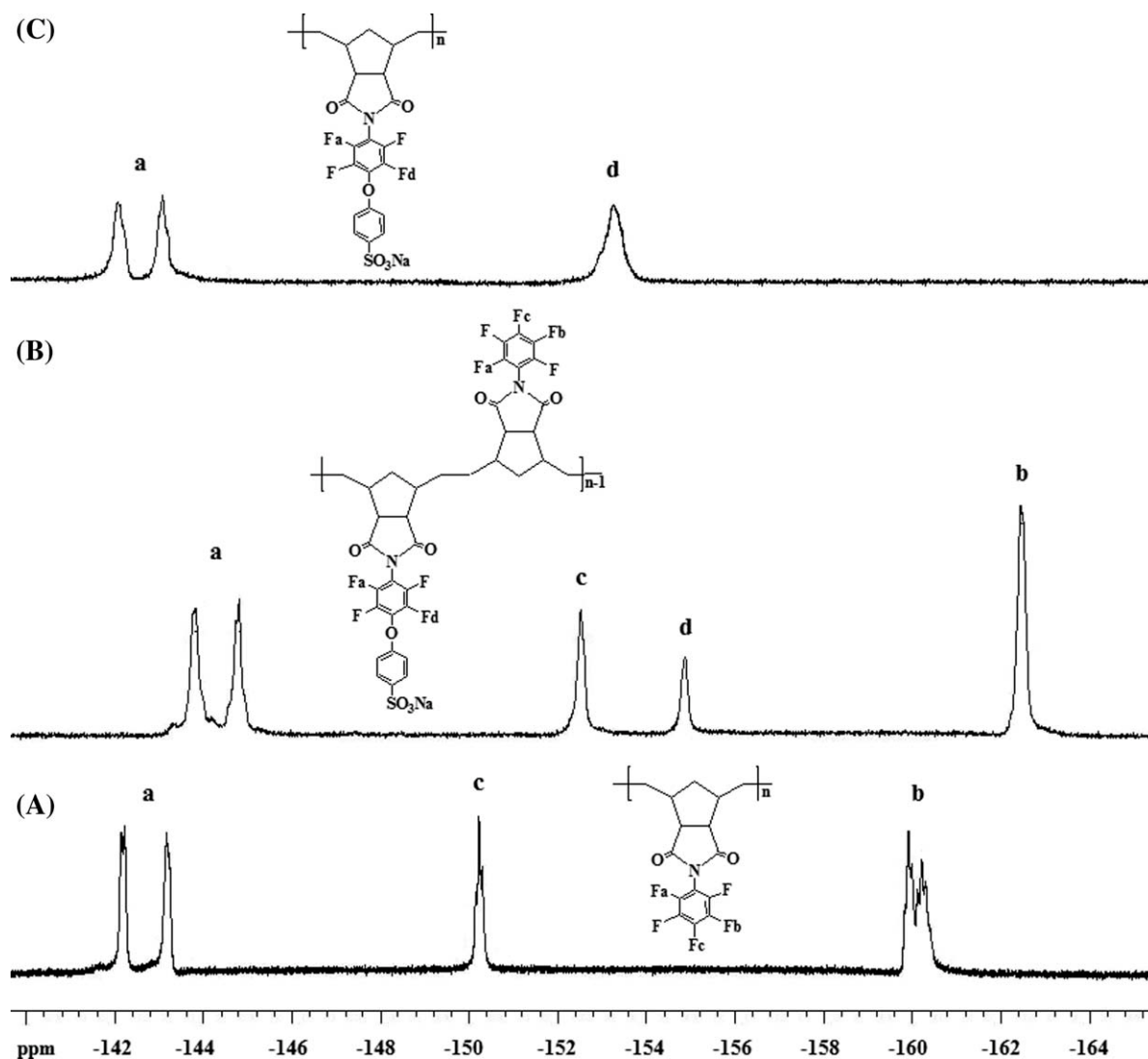
FIGURE 3 ^{19}F NMR of (A) nonsulfonated polymer **4**, (B) partially sulfonated polymer **5,** and (C) fully sulfonated polymer **5**.

imide ring. This effect of the amine basicity on the hydrolysis stability of the imide ring has also been observed in naphthalenic sulfonated polyimides synthesized *via* polycondensation reactions.[26] An extensive research concerning the ionic transport properties of this kind of ionomers is actually being carried out by our group and it will be the subject of a forthcoming article.

CONCLUSIONS

ROMP of mixtures *exo-endo*-monomers and isomerically pure *endo*-monomers of *N*-pentafluorophenyl-norbornene-5,6-dicarboximide (**2a**) and *N*-phenyl-norbornene-5,6-dicarboximide (**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**) was studied. The mixtures of *exo-endo*-monomers (**2a**), (**2b**), and pure *endo*-**2b** monomer polymerized to give the corresponding high molecular weights

poly(*N*-pentafluorophenyl-norbornene-5,6-dicarboximide) (**3a**) and poly(*N*-phenyl-norbornene-5,6-dicarboximide) (**3b**), whereas the isomerically pure *endo*-**2a** did not polymerize by **I** in these conditions. The steric effect of the pentafluorinated ring in the monomer, the intramolecular complex formation between the Ru active center and the fluorine atom of ring-opened *endo*-**2a** and, compared with **II,** the least active **I** were responsible for the ROMP inhibition of the *endo*-**2a**. The hydrogenated poly(*N*-pentafluorophenyl-norbornene-5,6-dicarboximide) (**4**) underwent a nucleophilic aromatic substitution by reacting with sodium 4-hydroxybenzenesulfonate dihydrate to give the corresponding functionalized polymer **5**. This new polymer bearing the sulfonic acid group is expected to exhibit ionic conduction features.

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