

## SYNTHESIS VIA METATHESIS OF FLUORINE CONTAINING RING OPENED POLYMERS

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### 1. Abstract

The monomers *exo-N*-pentafluorophenyl-7-oxanorbornene-5,6-dicarboximide (**1a**) and *N*-pentafluorophenyl-*exo-endo*-norbornene-5,6-dicarboximide (**1b**) were synthesized and polymerized via ring opening metathesis polymerization (ROMP) using tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolilydene][benzylidene] ruthenium dichloride to produce the corresponding polymers in high yields (92%). It was found that **Poly-1b** which bears a methylene group at the bridgehead, shows higher  $T_g$  and mechanical properties than its counterpart **Poly-1a**.

### 2. Introduction

ROMP of norbornene dicarboximides with linear aliphatic and phenyl substituents using appropriate catalysts has been reported.<sup>[1,2]</sup> Membranes prepared from early synthesized poly(norbornene dicarboximide)s exhibit not only excellent thermal and mechanical properties but also rather high gas permselectivities which make them suitable for the separation of gaseous mixtures such as hydrogen from nitrogen, hydrogen from carbon monoxide, methane from ethylene, among others.<sup>[3]</sup>

We have previously reported that the introduction of fluorine atoms into poly(norbornene dicarboximide)s considerably enhance the gas transport properties in membranes prepared from them.<sup>[4]</sup> Therefore, besides synthesizing and polymerizing *via* ROMP the monomers *exo-N*-pentafluorophenyl-7-oxanorbornene-5,6-dicarboximide (**1a**) and *N*-pentafluorophenyl-*exo-endo* norbornene-5,6-dicarboximide (**1b**) using a mesityl substituted *N*-heterocyclic carbene Ru-alkylidene catalyst, the main objective in studying this kind of polymers is its potential application as gas separation membranes.

### 3. Experimental Part

*3.1 Synthesis of  $\text{exo-N-pentafluorophenyl-7-oxanorbornene-5,6-dicarboximide}$  (**1a**).*  $\text{exo-7-oxanorbornene-5,6-dicarboxylic anhydride}$  (5.0 g, 30 mmol) was dissolved in 50 ml of  $\text{CH}_2\text{Cl}_2$ . An amount of 5.49g (30.1 mmol) of 2,3,4,5,6-pentafluoroaniline in 10 ml of  $\text{CH}_2\text{Cl}_2$  was added dropwise to the stirred solution of  $\text{exo-7-oxanorbornene-5,6-dicarboxylic anhydride}$ . 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, anhydrous sodium acetate, and acetic anhydride were heated at 70 °C for 24 h. The mixture was washed with diluted HCl and extracted into ether. The ether layer was washed with dilute HCl, saturated  $\text{NaHCO}_3$ , and  $\text{H}_2\text{O}$ . Solvent was evaporated and pure monomer **1a** was obtained after twice recrystallization from hexane and dried in a vacuum oven at 50 °C overnight.

*3.2 Synthesis of  $\text{N-pentafluorophenyl-exo-endo-norbornene-5,6-dicarboximide}$  (**1b**).* Monomer **1b** was synthesized according to literature.<sup>[5]</sup>

#### *3.3 Metathesis Polymerization of Monomers*

Polymerizations were carried out in a glass vial under a dry nitrogen atmosphere at 45 °C. After terminating the polymerization by addition of a small amount of ethyl vinyl ether, the solution was poured into an excess of methanol. The polymer was purified by precipitation in methanol from chloroform containing a few drops of 1N HCl. The obtained polymer was dried in a vacuum oven at 40 °C to constant weight.

##### *3.3.1. Polymerization of **1a**.*

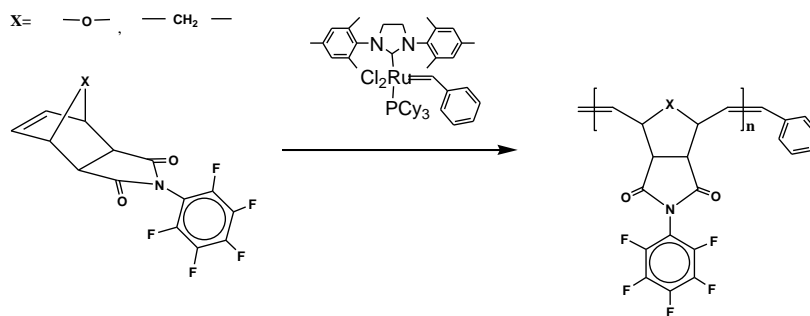
1.0 g (3.02 mmol) of monomer and 0.0024g ( $3.02 \times 10^{-3}$  mmol) of catalyst were stirred in 3.77 mL of 1,2 dichloroethane at 45 °C for 2 h. The obtained polymer was soluble in chloroform and dichloromethane, among others.

### 3.3.2. Polymerization of **1b**.

1.0 g (3.03 mmol) of monomer and 0.0025g ( $3.0 \times 10^{-3}$  mmol) of catalyst were stirred in 3.8 mL of 1,2 dichloroethane at 45 °C for 2 h. The obtained polymer was soluble in chloroform and dichloromethane, among others.

## 4. Results

Monomers **1a** and **1b** were readily prepared in high yields (86-92%). 2,3,4,5,6-Pentafluoroaniline reacted with *exo*-7-oxanorbornene-5,6-dicarboxylic anhydride and *exo-endo*-5-norbornene-2,3-dicarboxylic anhydride to the corresponding amic acids which were cyclized to imides using acetic anhydride as dehydrating agent.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra and elemental analysis confirmed monomers structures and purity. ROMP of monomers using ruthenium catalyst were carried out in 1,2 dichloroethane at 45 °C for 2 h with a monomer to catalyst ratio ( $[M]_0/[I]_0 = 1000$  and  $[M]_0 = 0.8$  mol/L. (Scheme 1)



Scheme 1. Ring Opening Metathesis Polymerization of monomers **1a** and **1b**.

The polymers were obtained in high yields (86-92%) and the results obtained by GPC indicated that the number-average molecular weights ( $M_n$ ) were between 280 000 and 300 000. The experimental number-average molecular weights were in agreement with the theoretical ones. The molecular weight distributions of the polymers were about  $M_w / M_n = 1.25$ -1.4. Mechanical properties such as tensile strength ( $\sigma_u$ ) and Young's modulus ( $E$ ) of the synthesized polymers were studied on solutions cast films. The polymers studied here showed not only much better mechanical properties but also higher  $T_g$ 's than those reported for polynorbornene (31 °C). This could be attributed to an increase in rigidity of the polynorbornene owing to the presence of the

dicarboximide with a large pendant group. In figure 1 it is shown the  $^1\text{H}$  NMR spectra of **1a** and **Poly-1a**. 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.

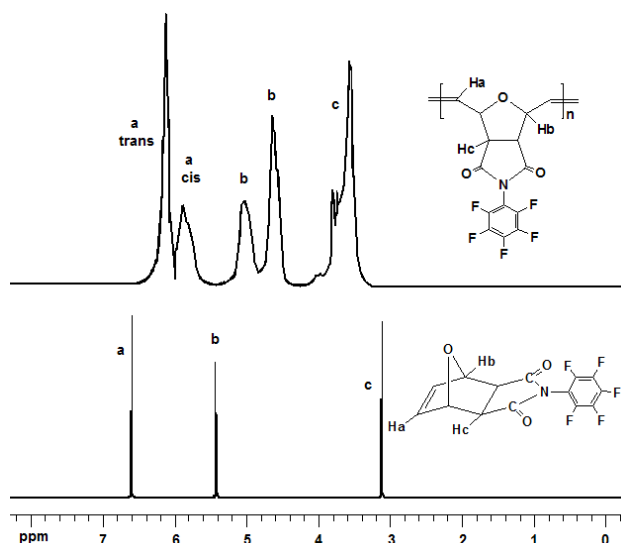


Figure 1.  $^1\text{H}$  NMR spectrum of monomer **1a** and Poly- **1a**

## 5. Conclusions

**1a** and **1b** were synthesized and polymerized *via* ROMP using a well-defined *N*-heterocyclic carbene (NHC) coordinated ruthenium alkylidene catalyst. The tensile strength ( $\sigma_u$ ) and Young's modulus ( $E$ ) of the resultant polymers bearing imide side chain groups were significantly higher than those of unsubstituted polynorbornene indicating that the imide substitution leads to restriction in the segmental motion. **Poly-1b** exhibits higher thermal and mechanical properties than those of **Poly-1a**.

## 6. References

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