Armando Pineda-Contreras, Julia V. Hernández-Madrigal*, Oscar F. Vázquez-Vuelvas and Serguei Fomine

Synthesis and ROMP of new sulfobetaine and carboxybetaine norbornene

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Abstract: The synthesis of novel norbornene based polyzwitterions via ring opening metathesis polymerization (ROMP) is present. Trifluoracetic acid (TFA) was used as a solvent to provide a homogenous medium for the polymerization reaction of sulfobetaines with the commercially available Hoveyda-Grubbs' initiator. In order to prevent the competitive complexation via carboxylate functional group of the ruthenium metal center, we carried out the controlled polymerization of ethyl protected carboxybetaines monomers.

Keywords: norbornene; polycarboxybetaines; polysulfobetaines; polyzwitterion; ROMP.

1 Introduction

Polybetaines are zwitterionic polymers containing both an anionic and a cationic group on the same monomer unit. Such materials may be divided into the three groups; polycarbobetaines, polysulfobetaines and polyphosphobetaines (1, 2). The term polybetaine denotes the presence of a permanent cationic group as quaternized ammonium. The antipolyelectrolyte effect is a distinctive solution behavior of polybetaines, the tight ion pair is separated when low molecular weight electrolyte is added (1–4). Among the applications of polyzwitterions are drag reduction (5), drilling-mud additive (6), polymers with potential application in wastewater (7, 8), nonthrombogenic biomaterial in medicine (9), antibacterial activity (10) and chelation to bind trace metals from radioactive nuclear water (11) to mention a few. Polybetaines have been synthesized either via direct polymerization of a zwitterionic monomer or zwitterionic functionalization of reactive precursor polymers and the most common approach has been the direct conventional free radical polymerization (12, 13). Recently, researchers have looked for techniques that employed direct polymerization instead the zwitterionic functionalization of reactive precursor polymer, in a controlled fashion. Because of the discovery and development of well-defined metal-carbene catalysts, among which are Ru-based complexes, nowadays, the ring opening metathesis polymerization (ROMP) is an approach which has been thoroughly studied (14, 15) and widely used in the synthesis of new well defined polymer with controlled molecular weight and narrow polydispersities (16, 17). Lately, Rankin and Lowe reported the first synthesis of the *exo*-7-oxanorbornene-based betaine monomer and their ROMP with the first-generation Grubbs' catalyst obtaining well-defined polymeric betaines (18). Other researchers have also achieved this type of synthesis to obtain novel norbornene based polycarbo- and polysulfobetaines with the Hoveyda-Grubb's catalyst as initiator, where carboxylate group was protected prior polymerization (19). We describe herein the synthesis of novel norbornene based polysulfo- and polycarbobetaines with pyridiniun group via ROMP using the third-generation Grubb's catalyst as initiator. Since carboxylates have a retardant effect on the polymerization kinetics (20, 21) we employing a protecting group method for polycarbobetaines synthesis and direct polymerization for sulfobetainic monomer. Due to low solubility of the latter, polymerization reaction was carry out in trifluoracetic acid (TFA). The monomers and polymers were characterized by NMR and FT-IR

***Corresponding author: Julia V. Hernández-Madrigal,** Facultad de Ciencias Químicas, Universidad de Colima, Km 9 Carretera Colima-Coquimatlán, Apartado Postal 29000, Coquimatlán, Colima, México, Tel.: +52-312-316-1163 (ext. 51402), Fax: +52-312-316-1163 (ext. 51401), e-mail: juliehdez@ucol.mx
Armando Pineda-Contreras and Oscar F. Vázquez-Vuelvas: Facultad de Ciencias Químicas, Universidad de Colima, Km 9 Carretera Colima-Coquimatlán, Apartado Postal 29000, Coquimatlán, Colima, México
Serguei Fomine: Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70360, CU, Coyoacán, México DF 04510, México

spectroscopies. Molecular weight and polydispersity were determined for the polymers.

2 Experimental

2.1 Techniques

^{1}H NMR (200 and 300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using a Bruker Avance III spectrometer with tetramethylsilane (TMS) as internal standard. FT-IR spectra were recorded with Varian 3100 FT-IR Excalibur Series. Elemental analysis was carried out using the Perkin Elmer 2400, Series II CHNS/O Elemental Analyzer, using cystine as the standard. Decomposition points were determined using a Mettler Toledo TGA/SDTA851. The glass transition temperatures were measured under nitrogen with a DSC StarSystem instrument, at a heating rate of 10°C/min. The samples were encapsulated in standard aluminum DSC pans in duplicate. Each sample was run twice in the temperature range between 3° and 300°C. Gas chromatography-mass spectrometry (GC-MS) analysis were performed in a Varian Saturn 2100T GC/MS mass spectrometer interfaced to a Varian 3900 gas chromatograph equipped with a VF-5ms capillary column (30 m×0.25 mm). Molecular weights and molecular weight distributions were determined with a Varian 9012 GPC instrument at 30°C in chloroform (universal column and a flow rate of 1 ml/min) using polystyrene standards.

2.2 Reagents

All solvents were distilled prior to use according to general purification procedures. Chlorobenzene was purchased from Riedel-de Haën (Toluca, Mexico) and 1,2-dichloroethane from Spectra Chemical Mfg. Corp. (NJ, USA) All other reagents were purchased from the Sigma-Aldrich (Química, Toluca, Mexico) at the highest available purity and used as received unless stated otherwise. The exo-Norbornene-5,6-dicarboxylic anhydride (**1**) was prepared accordingtoliterature(22).TheN-(3-pyridyl)-exo-norbornene-5,6-dicarboximide (**2b**), N-(4-pyridyl)-exo-norbornene-5,6-dicarboximide (**2c**) and N-(ethyl 3-pyridinium acetate bromide)-exo-norbornene-5,6-dicarboximide (**4b**) and N-(ethyl 4-pyridinium acetate bromide)-exo-norbornene-5,6-dicarboximide (**4c**) were prepared according to the procedure previously described (23).

2.3 Quaternization of norbornene derivatives

2.3.1 Synthesis of *N*-(3-pyriniumpropylsulfobetaine)-*exo*-norbornene-5,6-dicarboximide (3b)

The sufopropylbetaine derivative **3b** was prepared as follow: the dicarboximide **2b** (1.97 g, 8.2 mmol) was dissolved in 15 ml of chloroform in a 50 ml flask equipped with a magnetic stir bar, freshly distilled 1,3-propane sultone (1.10 g, 9.02 mmol) was then added to the flask in one portion. The reaction was heated at 50°C for 120 h, and a white precipitate was formed. The reaction was cooled to room temperature; the precipitate was isolated by Buchner filtration, washed several times with chloroform. The monomer **3b** was obtained as a white powder in 95% yield. m.p. 275°C (24), ^{1}H NMR (200 MHz, D_2O, 298 K) δ (ppm) 9.12, 8.91, 8.60, 8.17 (H_{arom}), 6.32 (H-C=C, s, 2H), 4.77 (H-CH-N^+, m, 2H), 3.26 (H-C-C=O, s, 2H), 3.00 (H-C-C=C, s, 2H), 2.90 (CH_2-SO_3^-, t, 2H), 2.39 (H-CH-CH_3, m, 2H), 1.47, (H-CH, d, 2H). ^{13}C NMR (75 MHz, D_2O) δ (ppm) 178.9 (C=O), 145.0, 143.7, 143.0, 133.0, 129.8 (C_{arom}), 139.0 (C=C), 61.5 (N^+-CH_2), 49.2 (CH-C=C), 47.9 (CH_2-SO_3^-), 46.7 (CH-C=O), 43.6 (CH_2), 27.2 (CH_2-CH_2-CH_2). FT-IR: 2979 (ν C-H), 1776 (ν_{as} C=O), 1712 (ν_s C=O), 1580–1505 (ν C=C, C=N_{arom}), 1383 (ν C-N), 1384 (ν_{as} S(=O)$_2$O$^-$), 1180 (ν_s S(=O)$_2$O$^-$), 781 (ν S-O-C) cm^{-1}. $C_{17}H_{18}N_2O_5S$ (330): calcd. C 61.82, H 5.45, N 8.48, S 9.69; found C 62.16, H 5.19, N 7.86, S 9.55.

2.3.2 Synthesis of *N*-(4-pyriniumpropylsulfobetaine)-*exo*-norbornene-5,6-dicarboximide (3c)

The title compound was prepared as follow: the dicarboximide **2c** (1.97 g, 8.2 mmol) was dissolved in 15 ml of THF in a 50 ml flask equipped with a magnetic stir bar, freshly distilled 1,3-propane sultone (1.10 g, 9.02 mmol) was then added to the flask in one portion. The reaction was heated at 60°C for 48 h, and a white precipitate was formed. The reaction was cooled to room temperature; the precipitate was isolated by Buchner filtration, washed several times with THF. The monomer **3c** was obtained as a white powder in 98% yield. m.p. (24) 299°C, ^{1}H NMR (200 MHz, DMSO/H_2O, 298 K) δ (ppm) 8.76, 8.07 (H_{arom}), 6.18 (H-C=C, d, 2H), 4.49 (H-CH-N^+, m, 2H), 3.15 (H-C-C=O, d, 2H), 2.84 (H-C-C=C, d, 2H), 2.67 (CH_2-SO_3^-, t, 2H), 2.22 (H-CH-CH_3, m, 2H), 1.34, (syn-H-CH, d, 1H), 1.22 (anti-H-CH, m, 1H) ppm. ^{13}C NMR (75 MHz, DMSO/H_2O) δ (ppm) 178.1 (C=O), 147.1, 139.6, 124.6 (C_{arom}), 146.5 (C=C), 61.1 (N^+-CH_2), 49.6 (CH_2-SO_3^-), 47.5 (CH-C=O), 44.3 (CH-C=C), 39.5

(CH_2), 27.7 (CH_2-CH_2-CH_2) ppm. FT-IR: 2970 (ν C-H), 1781 (ν_{as} C=O), 1723 (ν_s C=O), 1634–1512 (ν C=C, C=N_{arom}), 1359 (ν C-N), 1359 (ν_{as} S(=O)$_2$O$^-$), 1156 (ν_s S(=O)$_2$O$^-$), 740 (ν S-O-C) cm^{-1}. $C_{17}H_{18}N_2O_5S$ (330): calcd. C 61.82, H 5.45, N 8.48, S 9.69; found C 62.93, H 5.27, N 8.65, S 9.48.

2.4 Polimerization of sulfobetaine and protected carboxybetaine monomers

2.4.1 General procedure

Below is a typical procedure for the polymerization of the betaine monomeric substrates: To a flask (25 ml) equipped with a magnetic stir bar was added **3b** (1.25 g, 3.5 mmol). The flask was subsequently degassed/back-filled with N_2 three times using standard Schlenk line techniques. TFA (3.5 ml) was then added to the flask. Hoveyda-Grubbs [(4,5-dihydroIMES)Cl_2Ru=CH-*o*-OiPrC_6H_4] (11.34 mg, 18.1 μmol) catalysts was weighed into flask (10 ml capacity) under a dry nitrogen atmosphere and then anhydrous CH_2Cl_2 (3.0 ml) was added. The catalyst solution was then added through the septum via syringe to the monomer solution and the resulting mixture was stirred at room temperature for 30 min prior to being quenched with a solution consisting of CH_2Cl_2 (2 ml), ethyl vinyl ether (400 μl), and BHT (100 mg), the solution was further stirred for 30 min. The mixture was poured into large excess of acetone containing a trace of BHT to precipitate a polymeric material. The polymer was isolated by Buchner filtration. The polymer was further purified by precipitation from TFA (or DCE; 1,2-dichloroethane) to remove unreacted monomer, and then dried in vacuum oven at 40°C. All polymers were stored under nitrogen atmosphere.

2.4.2 Poly3b

The titled polymer is a white solid (0.67 g, 73%).

Fourier transfer infrared (FTIR) spectroscopy: 2966 (ν C-H), 1777 (ν_{as} C=O), 1715 (ν_s C=O), 1640, 1507 (ν C=C, C=N_{arom}), 1381 (ν C-N), 1381 (ν_{as} S(=O)$_2$O$^-$), 1174 (ν_s S(=O)$_2$O$^-$), 740 (ν S-O-C) cm^{-1}.

2.4.3 Poly3c

Polymer **Poly3c** is a white solid (1.13 g, 90%).

FTIR: 2969 (ν C-H), 1781 (ν_{as} C=O), 1717 (ν_s C=O), 1633, 1517 (ν C=C, C=N_{arom}), 1351 (ν C-N), cm^{-1}, 1351(ν_{as} S(=O)$_2$O$^-$), 1151 (ν_s S(=O)$_2$O$^-$), 740 (ν S-O-C) cm^{-1}.

2.4.4 Poly4b

The polymerization of protected monomers was carried out in the same way as sulfobetaine monomers, but methanol was used to precipitate the product instead of acetone. The polymerization proceeds at room temperature for 1 h.

The titled polymer is an orange-brown solid (0.98 g, 79%). ^{1}H NMR (400 MHz, D_2O, 298 K) δ (ppm): 9.26, 8.95, 8.85, 8.27 (H_{arom}), 5.88 (H-C=C, 2H), 5.65 (H-CH-N$^+$, 2H), 4.30 (COO-CH_2, 2H), 3.69 (H-C-C=O, 2H), 3.19 (H-C-C=C, 2H), 1.72, (H-CH, 2H), 1.29 (H-CH_2, 3H). FT-IR: 2983 (ν C-H), 1785 (ν_{as} C=O), 1717 (ν_s C=O), 1636–1513 (ν C=C, C=N_{arom}), 1349 (ν C-N), 1143 (ν_{as} C-O) cm^{-1}.

2.4.5 Poly4c

The polymerization was carried out at 50–55°C for 30 min. The [M/C] ratio was 100:1. The titled polymer is an orange-brown solid (1.03 g, 83%).

^{1}H NMR (200 MHz, DMSO, 298 K) δ (ppm): 9.21, 8.29 (H_{arom}), 5.73 (H-C=C, 2H), 5.56 (H-CH-N$^+$, 2H), 3.27 (H-C-C=O, 2H), 3.12 (H-C-C=C, 2H), 1.24, 1.60 (H-CH, 2H), 1.24 (H-CH_2, 3H). FT-IR: 2955 (ν C-H), 1778 (ν_{as} C=O), 1710 (ν_s C=O), 1637, 1505 (ν C=C, C=N_{arom}), 1373 (ν C-N), 1157 (ν_{as} C-O) cm^{-1}.

2.5 Deprotection of polycarboxybetaines

2.5.1 H-Poly4b

Poly4b (0.08 g) was dissolved in 1.6 ml of HCl 0.3 M and stirred at 80°C for 48 h. The deprotected polymer was precipitated into acetone. The polymer was dried a vacuum oven at 40°C for 12 h. The titled polymer is a brown solid (95%).

^{1}H NMR (400 MHz, TFA, 298 K) δ (ppm): 10.70 (COOH, 1H), 9.19, 8.65, 8.34, 7.94 (H_{arom}), 5.47 (H-C=C, 2H), 5.47 (H-CH-N$^+$, 2H), 3.29 (H-C-C=O, 2H), 2.94 (H-C-C=C, 2H), 1.43, (H-CH, 2H). FT-IR 3366 (ν OH), 2945 (ν C-H), 1707 (ν_{as}, ν_s C=O), 1587, 1509 (ν C=C, C=N_{arom}), 1367 (ν C-N) cm^{-1}.

2.5.2 H-Poly4c

The titled compound was prepared in the same manner as **H-Poly4b** but the mixture was stirred 24 h instead of 48 h. The titled polymer is a brown solid (90%).

^{1}H NMR (400 MHz, TFA, 298 K) δ (ppm): 10.85 (COOH, 1H), 9.19, 8.65, 8.34, 7.94 (H_{arom}), 5.40 (H-C=C, 2H), 5.14 (H-CH-N^+, 2H), 3.41 (H-C-C=O, 2H), 3.03 (H-C-C=C, 2H), 1.25, (H-CH, 2H). FT-IR 3340 (ν OH), 2941(ν C-H), 1715 (ν_{as}, ν_s C=O), 1639, 1519 (ν C=C, C=N_{arom}), 1367 (ν C-N), cm^{-1}.

3 Results and discussion

3.1 Synthesis of monomers

The goal of this research was to synthesize exclusively *exo*-norbornene derivatives since it is well know that they are more reactive in ROMP compared to *endo*-norbornene derivatives (14, 25). Moreover, it has also been reported that the presence carboxylate functional group have a retardant effect on the polymerization kinetics (21), thus protecting group approach was utilized to synthesize norbornene based polycarboxybetaines via ROMP. Monomers were prepared by a multistep procedure involving an initial Diels-Alder reaction to obtain *exo*-norbornene-5,6-dicarboxylic anhydride **1**. We have previously reported the synthesis and characterization of *exo-N*-heterocyclic norbornene dicarboxymides **2a–2c**, by reacting **1** with 2-, 3-, and 4- aminopyridines, respectively (23). In order to obtain betaine monomers, **2a–2c** were alkylated via Menshutkin reaction with ethyl-bromoacetate and with 1,3-propanesultone to yield ethyl protected carboxybetaines and sulfobetaines, respectively (Figure 1). Because of steric hindrance around the nitrogen atom in *ortho* position of aminopyridin moiety, **3a** and **4a** betaines were not obtained.

In order to synthesize zwitterionic polymers, initially we tried to polymerize compounds **2a–2c,** obtaining only the **2a** polymer (Mn=209,197; PDI=1.74). These results demonstrated that very high polymer has been obtained. However, this polymer is unable undergo a quaternization reaction. It is known that during ROMP, ruthenium should be coordinated with substrate double bond (26, 27) and there are evidence that the presence of certain functional groups like pyridines can inhibit the metathesis reaction (28). To verify this assumption we performed modeling of the complexes formed by **2a** and **2c** molecules with second-generation Hoveyda-Grubb's catalyst. We calculated the energy difference between nitrogen (pyridyl moiety)-ruthenium and double bond-ruthenium complexes. Optimized geometries were obtained using functional B3LYP, in combination with lacvp (d) basis set using JAGUAR software, version 6.5 of Schrödinger, Inc. (Figure 2) (29).

The total energies show that compound **2c** forms a more stable complex between pyridyl moiety with ruthenium, (11.8 kcal/mol), than between double bond with ruthenium, thereby inhibiting the metathesis reaction. In the case of **2a,** this difference is only 5.3 kcal/mol, allowing the complex formation between the double bound and ruthenium to further the metathesis reaction. This relatively low stability of the complex **2a** nitrogen (pyridyl moiety) with ruthenium catalyst can be related to steric factors and may be the reason why this compound is not able to quaternize.

As the ROMP cannot be accomplished with **2b** and **2c,** these monomers have been modified (Figure 1) assuming that Ru initiators are tolerant of quaternary ammonium functionality (19, 28). **3b** and **3c** were prepared by alkylsulfonation with the strained sultone, 1,3-propanesultone;

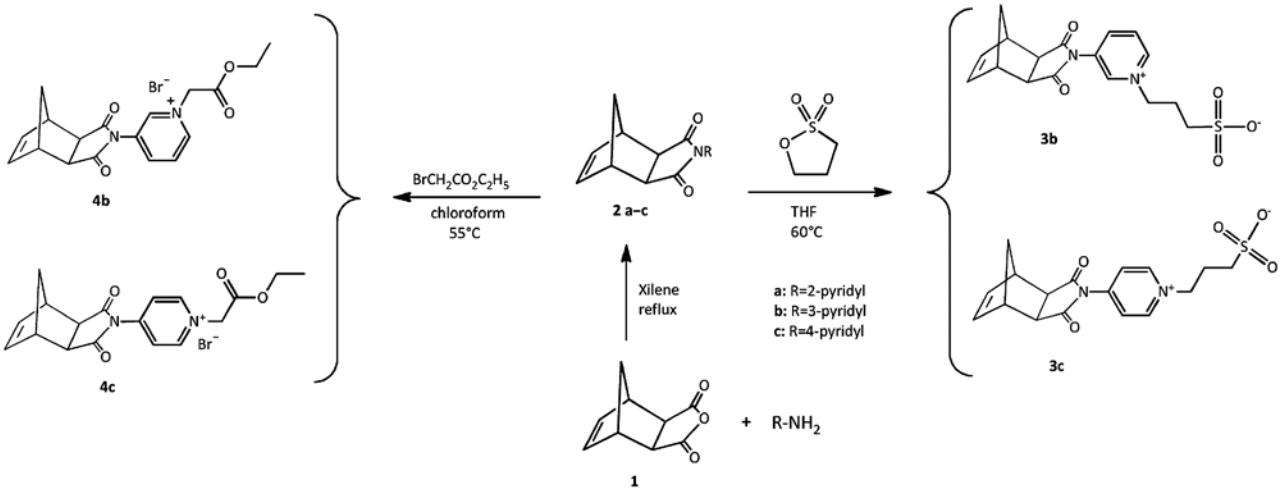

Figure 1: Synthesis of sulfobetaine-type monomers **3b** and **3c**.

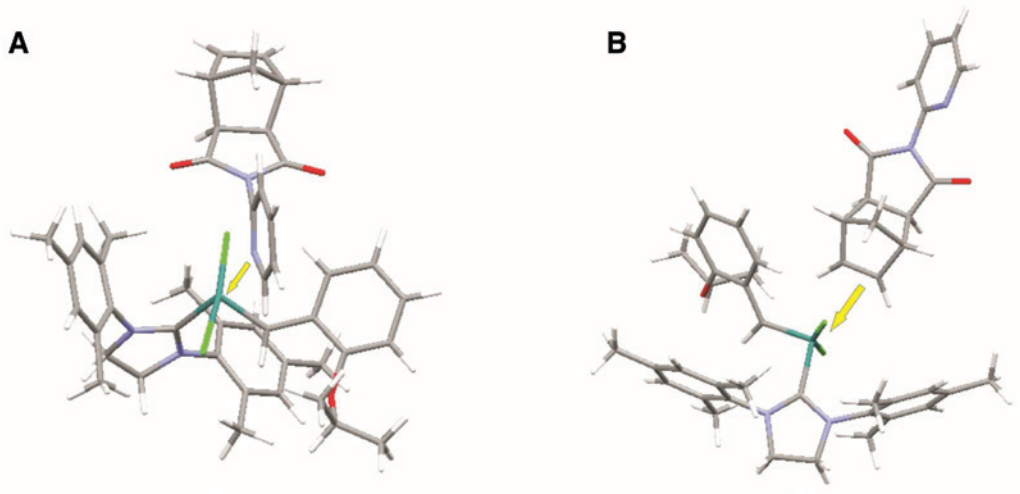

Figure 2: Structures of **2a** interacting with the H-G catalyst. (A) Nitrogen (from the aminopyridine ring)-ruthenium (catalyst), (B) double bond-ruthenium (catalyst).

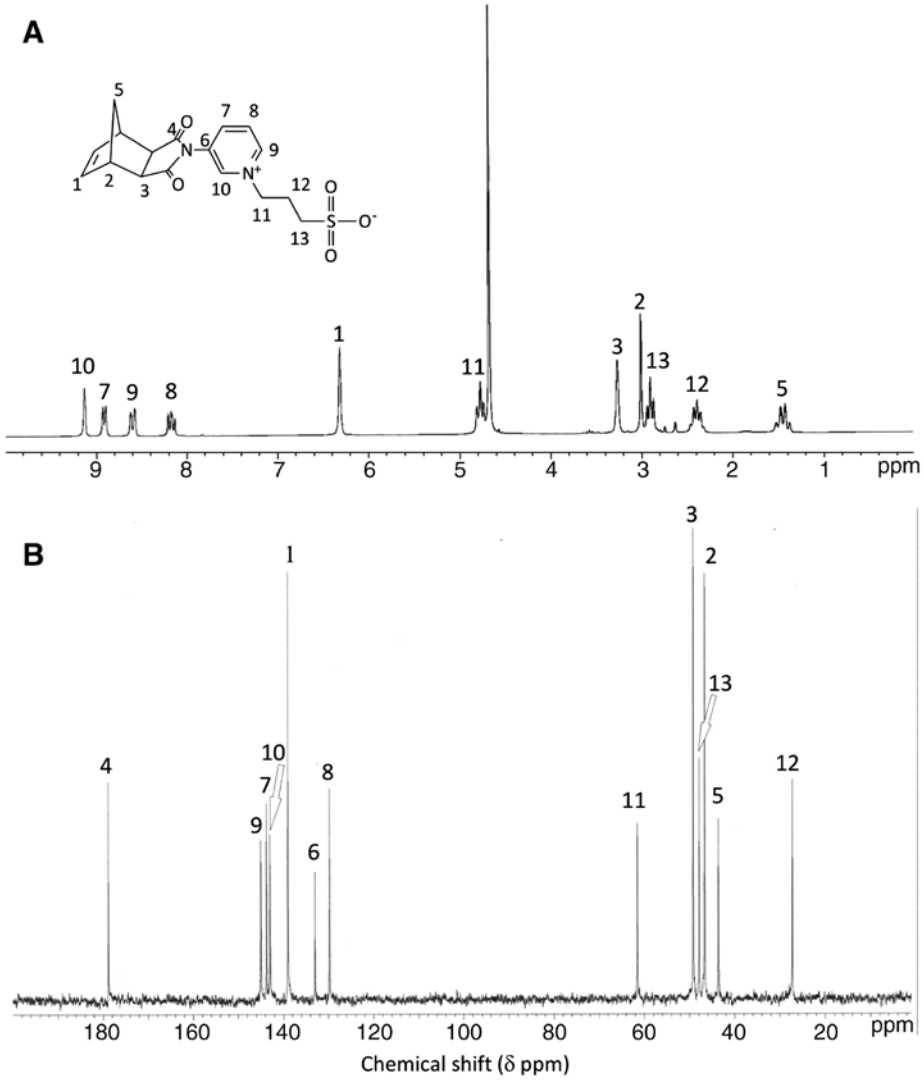

Figure 3: ^{1}H (A) and ^{13}C (B) NMR spectra of **3b** recorded in D_2O with peak assignments.

4b and **4c** were prepared via the Menshutkin reaction with ethyl-bromoacetate since the reaction with strained γ-butyrolactone did not proceed, as we reported previously (23). This route has the advantage of having polymers with 100% betaine functionality.

The FTIR spectra of **3b, 3c** and dicarboxymides precursors show, the absorption peaks for asymmetric and symmetric C=O vibrations at 1776–1781, 1712–1723, and characteristic asymmetric and symmetric $S(=O)_2O^-$ vibrations at 1384–1359, 1180–1156-cm^{-1}, respectively, confirming that the alkylsufonation reaction did proceed. ^1H and ^{13}C NMR spectra of **3b** and **3c** agree with their structures; the C resonance of carbonyl group is easily distinguished at 178 ppm as the lowest field signal. In both monomers three new signals of methylene groups from propanesultone are observed, the result of the nucleophilic substitution reaction (Figure 3). As can be seen in Table 1, the protons of the α-ammonium methylene carbon atom resonates in a lower field 4.77 ppm for **3b** and 4.49 ppm for **3c**, compared to other methylenes, showing the strong influence of the electron withdrawing group of quaternary ammonium.

Surprisingly the signal of bridge methylene of both betaines **3b** and **3c** displays now two different signals (Table 1). This could be explained by new covalent bond of pyridyl nitrogen and by the presence of sulfo group (23).

3.2 Polymer synthesis

Because of the very limited solubility of sulfobetaine monomers, generally soluble only in aqueous salt solutions and certain fluorinated alcohols as Rankin reported (30), in this work we use TFA at room temperature to polymerized **3b** and **3c** monomers (Figure 4); TFA is an excellent solvent for monomers bearing the sulfobetaine functional group (2). It has been reported that solvents with high dielectric constant lead to faster polymerizations (26). We accomplish the first time ROMP in TFA solvent, which has no apparent detrimental effect on H-G catalyst, at least on the time scale of the polymerization. The polymers were characterized by FT-IR and as expected, peaks characteristic of the imide group at ca 1775 and 1710 cm^{-1} were predominant features of the spectra. This polysulfobetaines were substantially insoluble and therefore, the molecular weight could not be determined.

On the other hand, methanol was the effective media for conducting the homogeneous polymerization of cationic monomers **4b** and **4c** with Hoveyda–Grubbs' initiator (Figure 5). Such monomers are ethyl protected carboxybetaines because the adverse effects on the ROMP kinetics.

The **4b** and **4c** polymer were characterized by ^1H NMR, confirming the structure. The chemical shifts of protons in polymers are very similar to these in monomers. It should be noted that **4b** and **4c** compounds show two different displacements H_{anti} and H_{syn} for the protons

Table 1: Chemical shifts from ^1H and ^{13}C NMR of the compounds **3b** and **3c** (ppm).

	3b[a]	3c[b]		3b[a]	3c[b]
H-1	6.36	6.18	C-1	139.0	146.5
H-2	3.00	2.84	C-2	46.7	44.3
H-3	3.26	3.15	C-3	49.2	47.5
H-5 anti	1.47	1.34	C-4	178.9	178.1
H-5 sin	1.42	1.22	C-5	43.6	39.5
H-7	8.91	8.76	C-6	133.0	147.1
H-8	8.17	8.07	C-7	143.7	124.6
H-9	8.60	H-7	C-8	129.8	139.6
H-10	9.12	H-8	C-9	145.0	C-7
H-11	4.77	4.49	C-10	143.0	C-8
H-12	2.39	2.22	C-11	61.5	61.1
H-13	2.90	2.67	C-12	27.2	27.7
			C-13	47.9	49.6

[a]D_2O, 200 MHz, [b]DMSO/D_2O, 300 MHz.

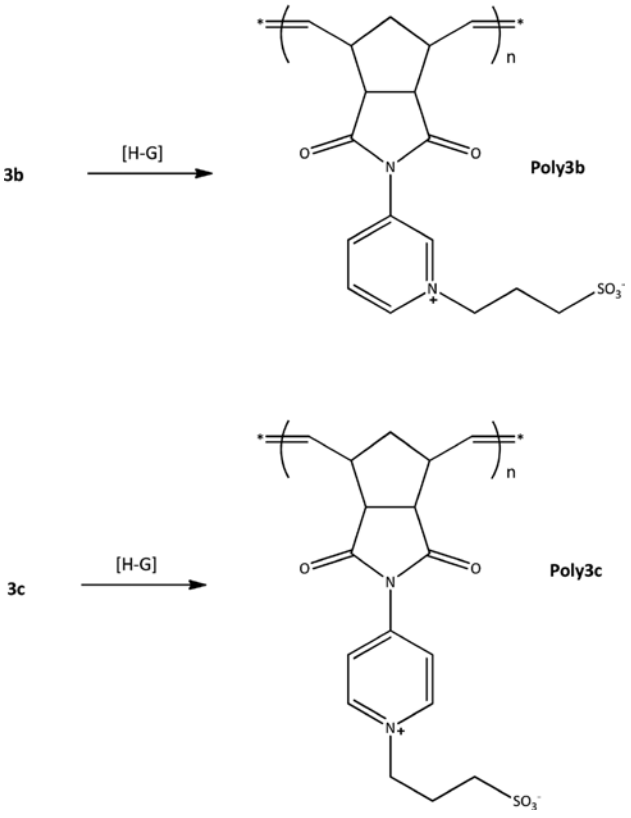

Figure 4: Repeat unit of polysulfobetaines based on norbornenes.

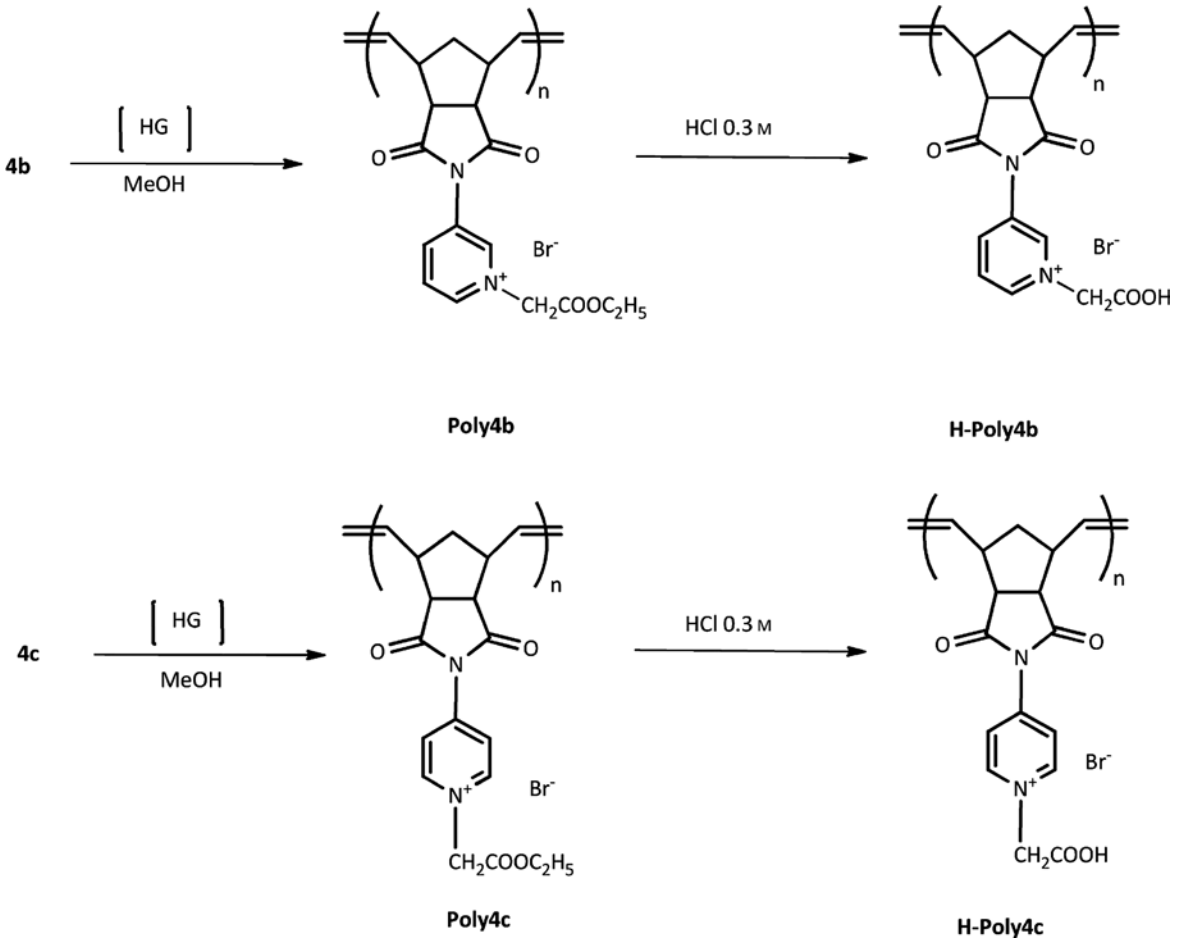

Figure 5: ROMP of **4b** and **4c** and deprotection of **Poly4b** and **Poly4c**.

of the bridging methylene group (23); in polymers Poly4b and Poly4c there are no different bridge anymore and only one signal for the methylene was observed, on account of the chemical environment being the same. The spectra show signals of ester (N^+-CH_2, O-CH_2 and CH_3), the hydrogens from the N^+-CH_2 group are found at a higher frequency due to the influence of a quaternary nitrogen and a carbonyl group (31).

The obtained polymers **Poly4b** and **Poly4c** gave narrower molecular weight distribution of the order of 2 with molecular weight in the range 13,000–19,000 Da. These results confirm that ionic functional groups ultimately affect the effectiveness of Hoveyda–Grubbs' initiator, because the molecular weight is much lower than that of the polydicarboximide **2a**.

After polymerization, the resulting homopolymer **Poly4b** and **Poly4c** were deprotected by hydrolysis of ester group to yield the corresponding **H-Poly4b** and **H-Poly4c** polycarboxybetaines. This deprotection was confirmed by ^{1}H NMR spectra, by comparing the region ca 4 and 1 ppm, where the signals of the methylene and methyl ester protons disappear in the hydrolyzed polymer.

Given that the polymers **H-Poly4b** and **H-Poly4c** are largely insoluble even in water, the molecular weights could not be determined.

4 Conclusions

The syntheses and ring opening metathesis polymerizations of two sulfobetaines monomers based on norbornene structural motif are described. TFA proved to be the suitable solvent to provide a homogenous medium for the polymerization reaction with the commercially available Hoveyda-Grubbs' initiator. The first time ROMP in TFA is reported, this media did not have adverse effect on the Ru complex, at least on the time scale of the polymerizations. On the other hand, we carried out the controlled polymerization of ethyl protected carboxybetaines monomers to prevent the competitive complexation via carboxylate functional group of the ruthenium metal center.

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