

Supplementary Material

Synthesis of Oxanorbornene based Phosphonium Polymeric Ionic Liquids (PILs) and Investigation of Their Electrical Properties

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1. Typical procedure for monomer synthesis

Synthesis of monomer has been depicted in **Figure S1**.

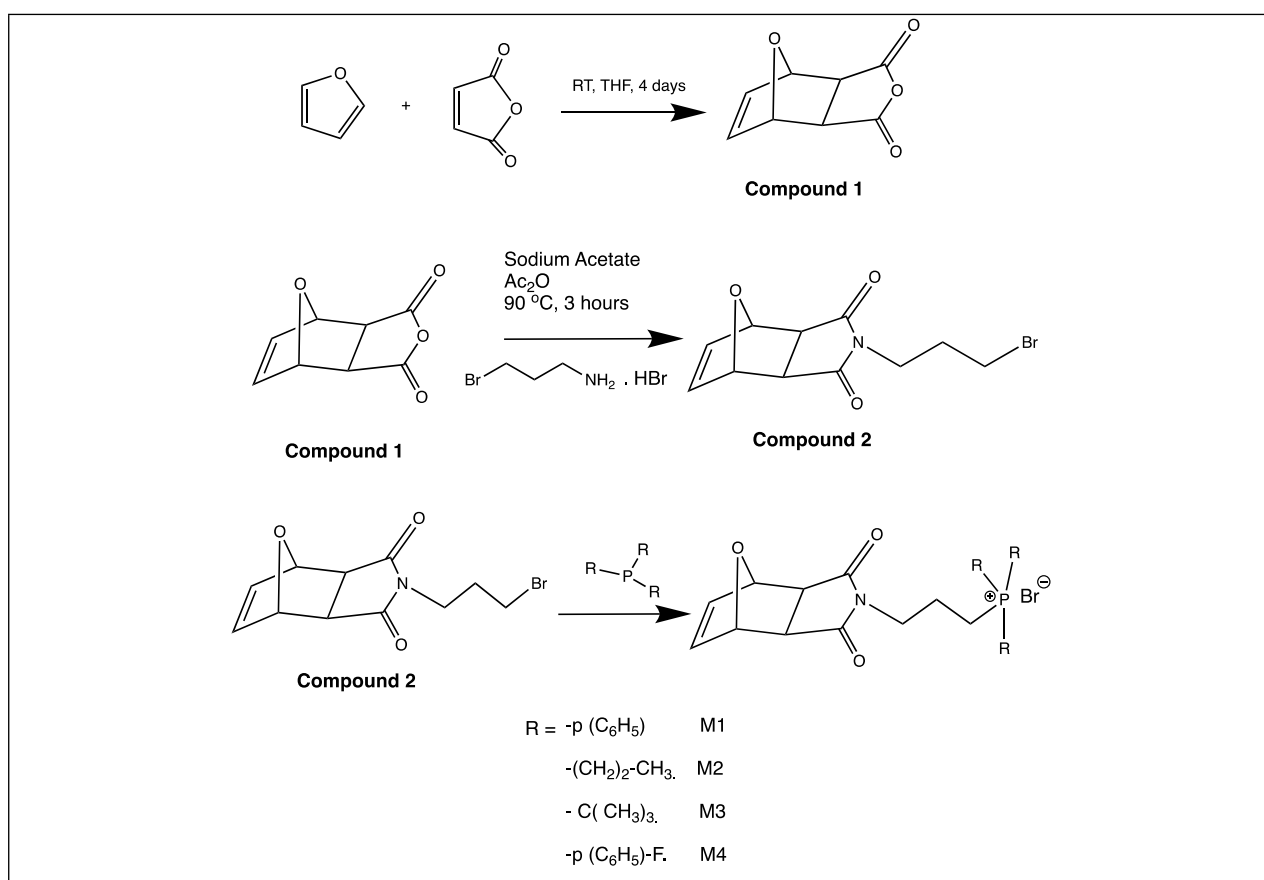


Figure S1. Monomer synthesis

Compound 1 was created according to previously published research [1].. 48 mL (660 mmol) of furan and 63 g (642 mmol) of dissolved maleic anhydride were pipette-added to the reaction liquid. After 5 minutes of mixing under nitrogen gas, the reaction was stopped, and it was kept at room temperature and in the dark for 4 days. White oxanorbornene crystals were visible in the reaction vessel after 4 days. Cleaning crystals involved washing them in cold THF. Exo-oxanorbornene (78% yield) was the end product of the Diels-Alder process in its entirety.

Compound 2 was synthesized in accordance with literature [2]. 50 mL of water were dissolved in 5.44 g, or 65 mmol, of NaHCO_3 in the reaction vessel. 65 mmol of 3-bromopropylamine hydrobromide (14.24 g) were gradually added to the solution. After adding compound 1 (10 g, 60.24 mmol), the reaction mixture was stirred for a while. The reaction was then agitated at room temperature for 30 min. It was rinsed with water and diethyl ether, then cleaned in a vacuum oven. After stirring a solution of sodium acetate (0.72 g, 8.28 mmol), acetic anhydride (16 mL), and 30% NaCl for 10 minutes at 90 °C, it was dried with MgSO_4 in the next step. When the substance was filtered, the solvent was removed using an evaporator. After being purified by column chromatography with ethyl acetate and hexane at a ratio of 1:1 (v/v), a white solid was produced (yield: 40%).

1.1 Triphenyl monomer (M1)

Compound 2 (0.5 g, 1.75 mmol) and excess triphenylphosphine (1.376 g, 5.25 mmol) were mixed in 11 mL of ethyl acetate. The reaction was carried out in a sealed vessel at 50°C for 24 hours while being stirred under nitrogen. In the reaction vessel, the quaternary phosphonium product precipitated. Ethyl acetate and THF were used to clean it. It was nitrogen dried before being kept in a desiccator. Yield 11%.

1.2 Tripropyl monomer (M2)

8 mL of THF was used to dissolve Compound 2 (0.5 g, 1.75 mmol) in a glass vial. Under nitrogen, an excessive amount of tripropylphosphine solution in THF (d: 0,801 g mol⁻¹, 97%) (1.119 mL, 0.896 mmol) was injected. The reaction was stirred at 50°C for 24 hours. The reaction vial was cooled in an ice bath after precipitation was seen to promote more precipitation. Diethyl ether and THF were combined in a ratio of 1:1 v/v to wash the product. After being nitrogen dried, it was desiccated. Yield 77%.

1.3 Tertbutyl monomer (M3))

In a glass vial, compound 2 (1 g, 3.5 mmol) was dissolved in 12 mL of THF. Nitrogen was introduced to the mixture as T-butylphosphine solution in THF (d: 0.834 g mol⁻¹) was added using a syringe. The reaction was stirred at 50°C for 24 hours. The reaction vial was cooled in an ice bath after precipitation was seen to promote more precipitation. The item was cleaned using diethyl ether. It was nitrogen dried before being kept in a desiccator. Yield 11%.

1.4 Fluorophenyl monomer (M4)

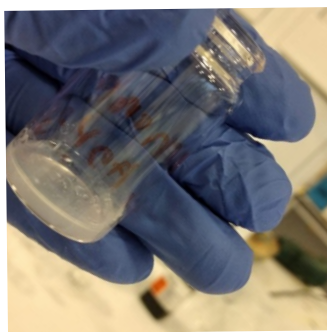
In a round bottom flask, compound 2 (0.5g, 1.75 mmol) and excess Tris(4-fluorophenyl) phosphine (1.8487 g, 5.25 mmol) were dissolved in 15 mL of ethyl acetate. The reaction was conducted for 24 hours while stirring under nitrogen at 50 °C. Diethyl ether was used to precipitate the result, and a 1:1 v/v combination of diethyl ether and THF was used to wash it. It was stored in a desiccator after being dried with nitrogen. Yield 44%.

1.5 Polymer synthesis (SM1, SM2, SM3 and SMS4) and exchange procedure

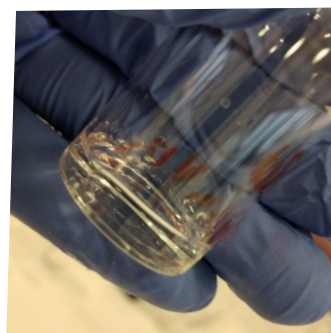
In a typical example polymerization procedure, Grubbs 3rd generation catalyst was dissolved in 0.5 mL of dichloromethane (CH₂ Cl₂), and added all at once to the strongly swirling monomer solution (in 2 mL of CH₂ Cl₂). The reaction mixture was agitated for 3 hours at ambient temperature. A further injection of 0.5 mL of 30% ethylvinyl ether (in dichloromethane) stopped the process. Polymers were precipitated and washed with either tetrahydrofuran or diethyl ether and dried under nitrogen. Then the polymers undergo anion exchange procedure. Polymers were dissolved in deuterated DMSO for NMR characterization.

2. Silver nitrate test

1 M of silver nitrate, AgNO₃ solution was freshly prepared. Small amounts of polymers were dissolved in acetone. The AgNO₃ solution was dropped into the polymer solution. The colour of the polymer solution was observed. The obtained compound was evaluated with silver nitrate, and a silver bromide precipitate was not observed, indicating the absence of bromide as depicted in **Figure S2**.



Phosphonium polymer containing bromide ion turns cloudy after addition with silver nitrate solution.



Phosphonium polymer containing trifluoro sulfonyl imides shows colorless solution after addition with silver nitrate solution.

Figure S2. Silver nitrate test.

3. TLC studies

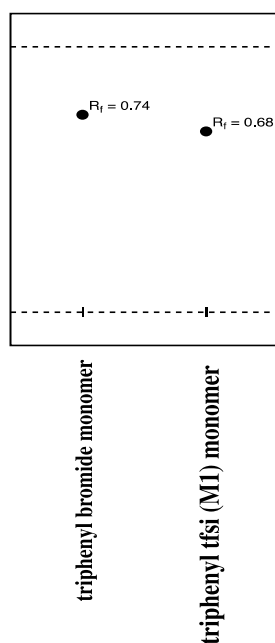


Figure S3. TLC analysis of monomer M1. 4 dichloro methane: 1 methanol ratio was used as mobile phase.

4. NMR Analysis

The monomer was dissolved in deuterated CDCl_3 . The ^1H and ^{31}P NMR were depicted in **Figure S4**.

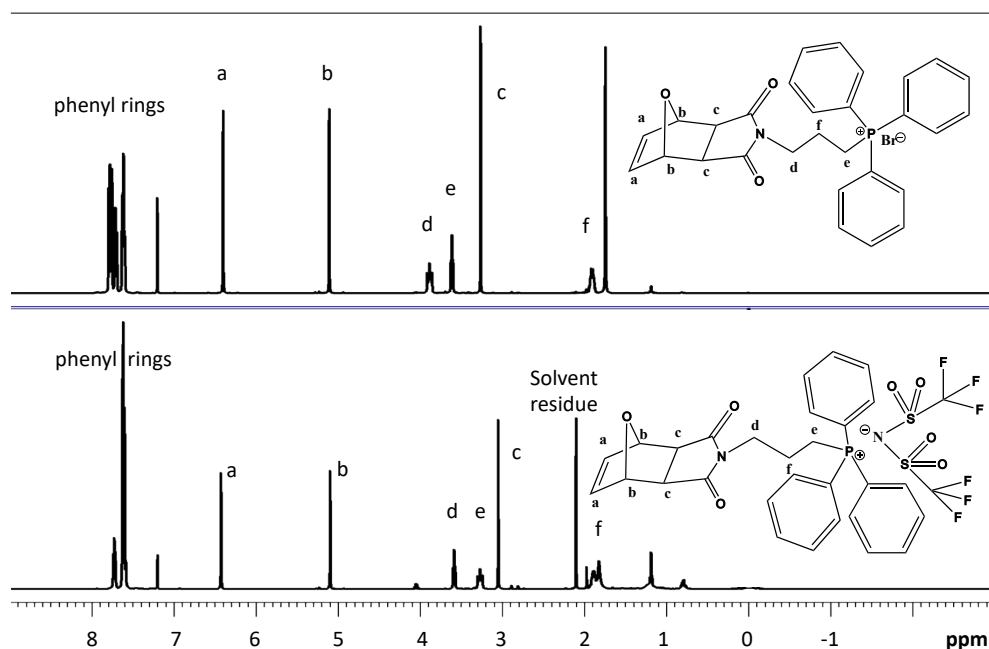


Figure S4. ^1H NMR for phosphonium oxanorbornene monomers.

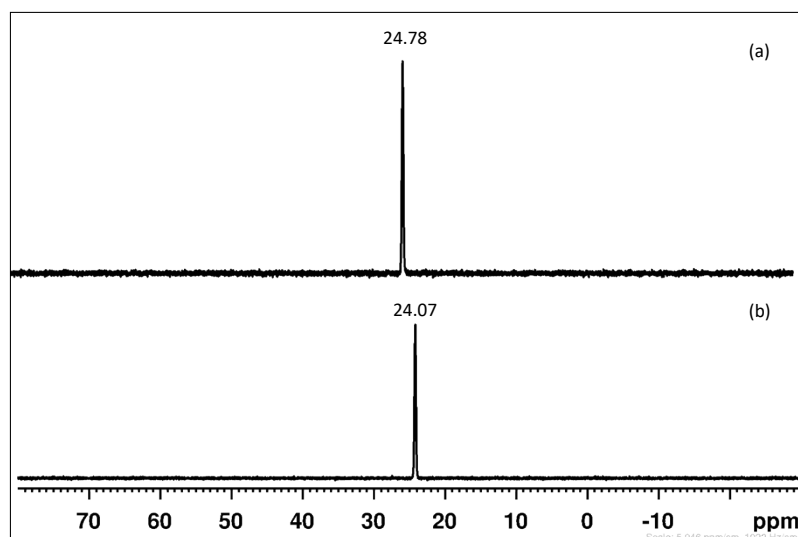


Figure S5. ^{31}P NMR spectra for a) triphenyl-Br and b) triphenyl-TFSI based oxanorbornene monomer.

5. NMR spectra for Phosphonium Polymeric Ionic Liquid

The polymer were dissolved in deuterated DMSO and undergoes ^1H and ^{31}P NMR characterization. The NMR spectra for SM2, SM3 and SM4 were provided in **Figure S6-S8**

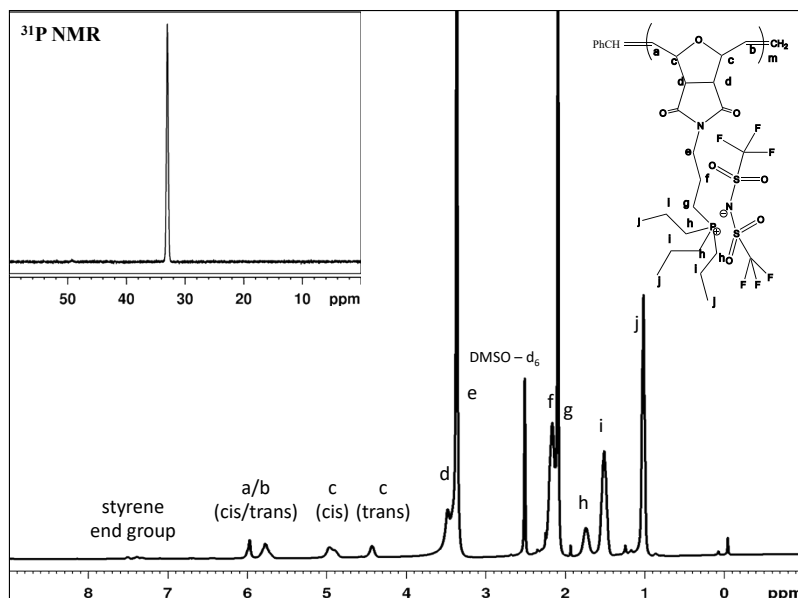


Figure S6. ^1H NMR spectrum for propyl – trifluorosulphonyl imide ion. On set is spectrum for ^{31}P NMR (**SM2**).

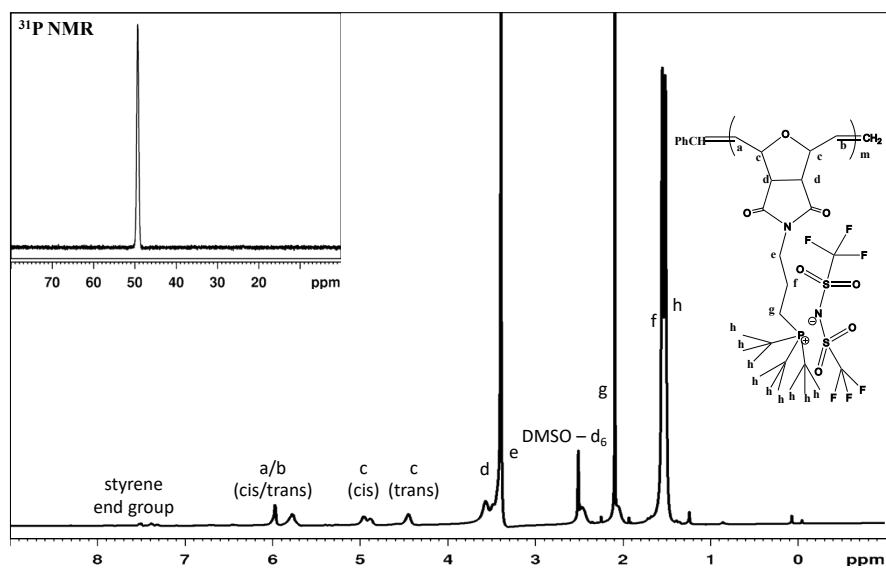


Figure S7. ^1H NMR spectrum for tertbutyl – trifluorosulphonyl imide ion. On set is spectrum for ^{31}P NMR (**SM3**).

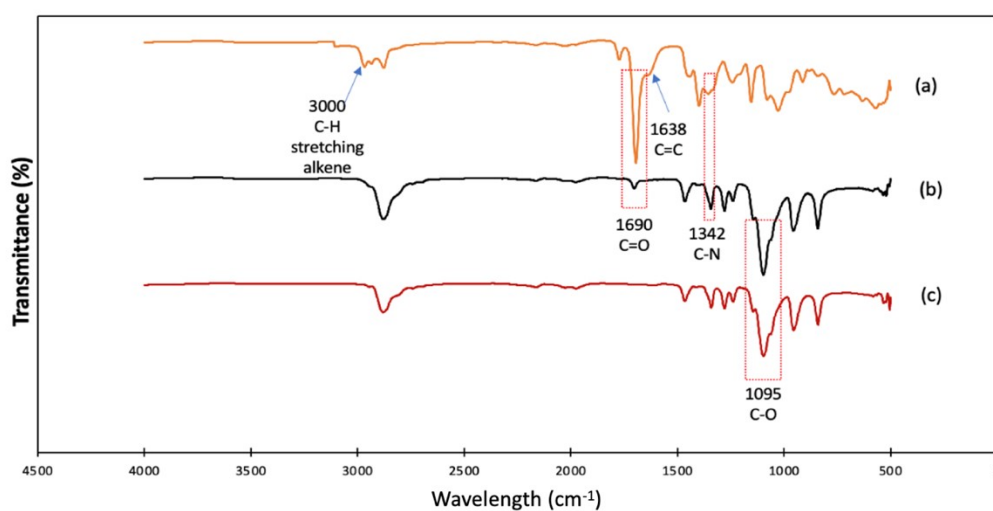


Figure S10. FTIR spectra for a) SM 2 b) PEGylated SM2 and c) Pure Polyethylene glycol dithiol (PEG dithiol).

References.

- [1] N. Ceren SÜER, T. ARASOGLU, H. CANKURTARAN, M. OKUTAN, M. GALLEI, and T. EREN, “Detection of bacteria using antimicrobial polymer derived via ring-opening metathesis (romp) pathway,” *Turkish J. Chem.*, vol. 45, no. 4, pp. 986–1003, 2021, doi: 10.3906/kim-2012-14.
- [2] N. C. Süer, C. Demir, N. A. Ünübol, Ö. Yalçın, T. Kocagöz, and T. Eren, “Antimicrobial activities of phosphonium containing polynorbornenes,” *RSC Adv.*, vol. 6, no. 89, pp. 86151–86157, 2016, doi: 10.1039/c6ra15545f.