

## Anhydrous Proton Conducting Polymer Electrolytes Based on Poly(phosphonic acid)s and Oligomeric Triazole Compounds

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### Introduction

In recent years, water-free polymer electrolyte membranes are attracting serious attention due to the possibility of the fuel cell operation at intermediate temperatures (100–200 °C). Conventional PEMs based on hydrated ionomers cannot be used in the temperature above dew point of water. But high operation temperature is essential for improving cell efficiency and reducing CO poisoning. Moreover, it is possible to simplify complex water and heat management system in fuel cells when high operation temperature and anhydrous condition are applied.

It was reported that phosphonic acid based system showed better proton conducting properties than sulfonic acid or imidazole based system under low humidity condition at intermediate temperature [1]. In this system, high degree of self-dissociation results from intrinsic amphoteric character of phosphonic acid and high mobility of protonic charge carrier are the key factors for proton conductivity. And phosphonic acid compounds are more stable against oxidation. These results reveal that phosphonic acid group is feasible for anhydrous proton conducting electrolytes. Based on this results, immobilized phosphonic acid based system was prepared by tethering of phosphonic acid to oligosiloxane [2]. Heterocycle doped polymeric system was also investigated [3,4].

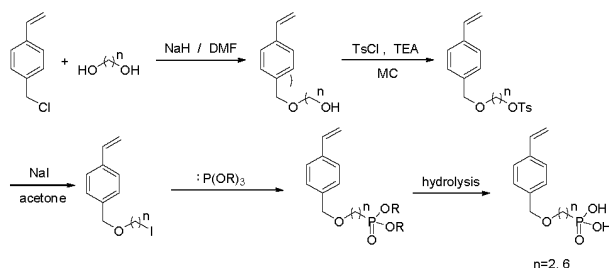
And recently, proton conduction characteristics of triazole based materials were compared with those of imidazole [5,6]. Although similar in molecular structure, triazole based materials showed better proton conductivity.

In this work, poly((4-vinylbenzyloxy)alkylphosphonic acid), styrene based polymer which have phosphonic acid group at the end of alkyl chain was synthesized. And triazole tethered cyclic siloxane was prepared. These materials were analyzed in terms of thermal stability and proton conductivity.

### Experimental

#### Synthesis

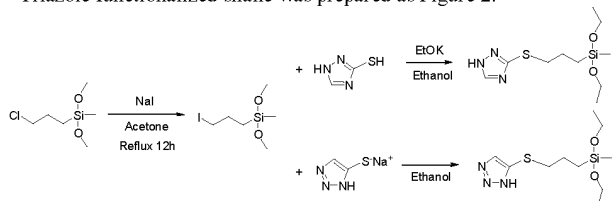
Phosphonic acid containing monomers were synthesized from 4-vinylbenzyl chloride (Aldrich) as Figure 1.



**Figure 1.** Synthesis of phosphonic acid containing monomers

Conventional radical polymerization was accomplished to prepare poly((4-vinylbenzyloxy)alkylphosphonic acid) by using AIBN as an initiator.

Triazole functionalized silane was prepared as Figure 2.



**Figure 2.** Synthesis of triazole tethered siloxane monomers.

Cyclic oligosiloxane was synthesized by sol-gel process under THF reflux for 1h in the presence of 0.2 equivalence of p-toluenesulfonic acid and 2 equivalence of water.

#### Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with a Bruker DPX-300 spectrometer at probe temperature in CDCl<sub>3</sub> and other deuterated solvent. FT-IR spectra were recorded on a JASCO FT-IR spectrometer (660 Plus equipment) with a spectral resolution of 4 cm<sup>-1</sup>.

Thermal stabilities of the synthesized materials were investigated by Thermal Gravimetric Analysis (TGA) carried out on TA instrument Q 50 with a heating rate of 10K/min under nitrogen flow.

Differential scanning calorimetry (DSC) experiments were carried out on TA instruments DSC 2910 at a heating rate of 10K/min to determine thermal transition temperature.

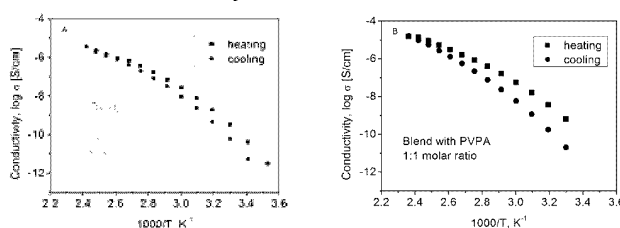
The AC conductivities of the prepared sample were measured with a impedance spectrometer in the frequency range from 10<sup>-1</sup> to 10<sup>6</sup> Hz with temperature interval of 10K.

### Results and discussion

#### Synthesis

Styrene based phosphonic acid monomers were synthesized in expectation of facile polymerization. Alkyl chain with different length were introduced into styrene moiety by simple S<sub>N</sub>2 reaction of diol compound and functional group at the chain end was successively converted. Phosphonation was accomplished by Arbuzov reaction in the presence of hydroquinone as a catalyst. Bromotrimethylsilane was used for mild hydrolysis to avoid undesirable side-product and the phosphonate compound was fully hydrolyzed to phosphonic acid at room temperature. Cyclic oligosiloxane was prepared by a known methodology.

#### Proton conductivity



**Figure 3.** Proton conductivity of (a) pure cyclic oligosiloxane tether with 1H-1,2,4-triazole and (b) Poly(vinylphosphonic acid) (PVPA) mixed material with molar ratio of 1:1

The proton conductivity of triazole tethered cyclic oligosiloxane reached  $\sim 10^{-5}$  S/cm at 140 °C under anhydrous condition. This is lower value than that of imidazole analog. However, this material showed slightly increased conductivity when blended with PVPA. The reduced conductivity during cooling cycle is thought to be resulted from the evaporation of the water.

#### Conclusions

Polymeric systems containing phosphonic acid functional group as a proton conductor and triazole functionalized cyclic siloxane were successfully synthesized. Their thermal and electrical properties for proton conducting materials showed promising results.

#### References

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