

연료전지용 Poly(styrene sulfonic acid)를 갖는 Poly(2,6-dimethyl-1,4-phenylene oxide)의 합성

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Synthesis of Poly(2,6-dimethyl-1,4-phenylene oxide) containing Poly(styrene sulfonic acid) for Fuel Cell

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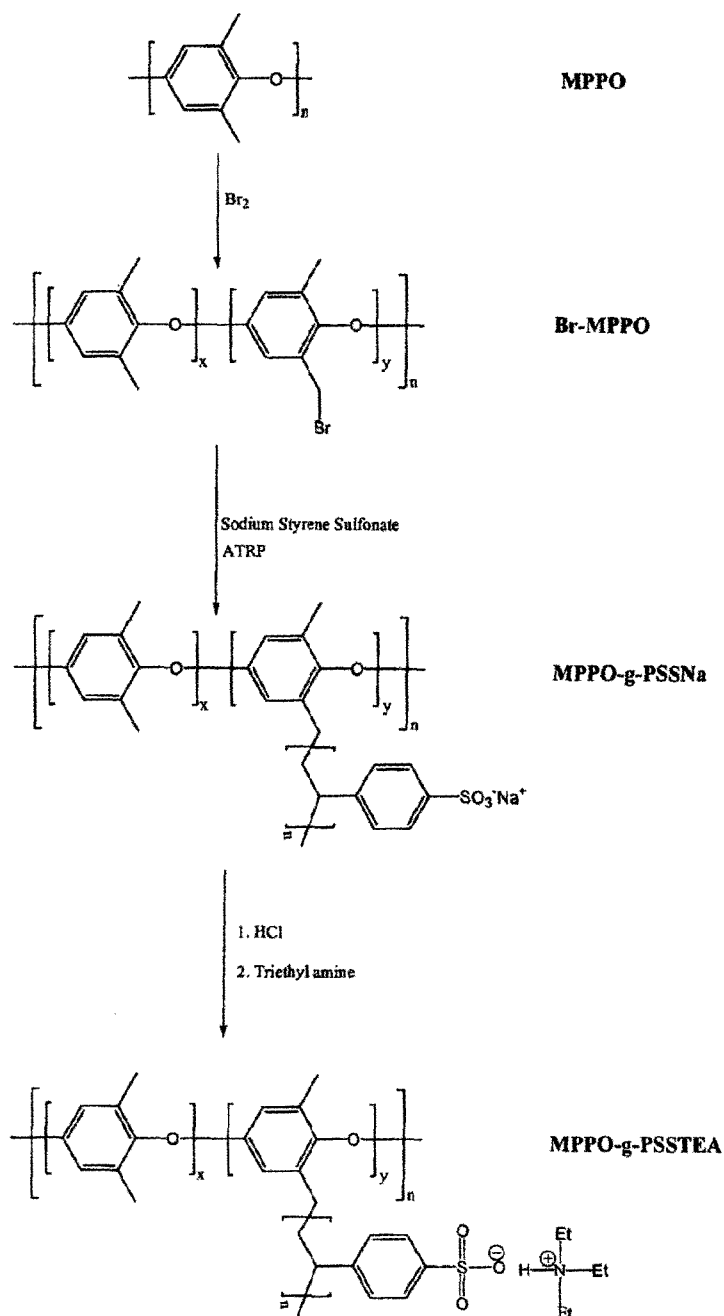
1. Introduction

The development and improvement of advanced fuel cell systems is a major topic of current research, since fuel cells are considerably more efficient than other energy converters¹. In proton exchange membrane fuel cell and direct methanol fuel cell the polymer membrane represents a key component. The membrane materials fulfill complex requirements. It has to combine electrochemical stability, workability, high ionic conductivity, low permeation of the reactants (methanol etc.), and mechanical integrity. Because of these requirements engineering plastics (EP) such as polysulfone, polyarylene, and polyimide etc. is concerned. Generally, these EPs contain cationic exchange groups such as SO_3^- group. Among sulfonic groups containing polymer Poly(styrene sulfonic acid) (PSSA) widely studied because of easy synthetic method, high conductivity etc. But PSSA is not used individually because of poor physical properties such as brittleness and relatively low Tg. So, block or graft copolymers are considered. Generally, the graft type polymers are prepared by plasma radiation on fluorine containing polymers. But this method has some defect such as control of graft chain length, and chain density. In this study we concerned to Poly(2,6-dimethyl-1,4-phenylene oxide) (MPPO) as a count block of PSSA. MPPO is a kind of EP and have good mechanical properties and thermal properties. PSSA sodium salt (PSSNa) is grafted into MPPO. The graft method is atom transfer radical polymerization (ATRP) to overcome above mentioned defect of plasma method. ATRP is a kind of living radical polymerization (LRP). So, the controlled chain architectures can be achieved via ATRP.

2. Experimental

2.1. Bromination of MPPO

Br-MPPO is synthesized by general bromination method³



Scheme 1. Synthesis of MPPO-g-PSSTEA

2.2. Synthesis of MPPO-g-PSSNa

ATRP of SSNa is proceeded by general ATRP method reported by Kim et al⁴.

2.2. Synthesis of MPPO-g-PSSTEa

A 100 mL round flask equipped with reflux condenser was charge with 1 g of MPPO-g-PSSNa and 50 mL of conc. HCl. The solution was reflux for 12 h and the polymer was filtered. The obtain polymers was dissolve in TEA/NMP solution. The solution was precipitated in ether. The percipitate is filtered and dried in vacuum.

3. Result and Discussion

Scheme 1 shows the syntetic routes of MPPO-g-PSSNa. Bromomethyl group is introduced via bromination of methyl group of MPPO for ATRP. This functional group is initing group in ATRP systems. Figure 1 shows the ¹H-NMR spectrum of Br-MPPO. The new proton peak is shown around 4.4 ppm originated from bromomethyl group (-CH₂-Br). ATRP of SSNa is perform in the prescence of Br-MPPO as a macroinitiator to synthesis of MPPO-g-PSSNa. The ATRP is controlled radical polymerization. The synthesized polymers from ATRP have controlled structures. The ATRP of SSNa is reported by Kim et al⁴. The graft copolymers synthesized via ATRP of SSNa have controlled structures. The the conversion and content of SSNa is calculated gravitative method and resulting PSSNa content is 40%. These high ionic content cause insolubility in general organic solvent such as DMAc, DMSO etc. The characterization and identification of MPPO-g-PSSNa is difficult. In figure 2, the FT-IR spectra of MPPO-g-PSSNa is shown. For more detailed study and NMR identification of synthesized polymers, the sodium is displaced to triethyl hydrogen amonimum cation. The bulky triethyl amine group is donate solubility in the NMP, and DMSO etc. For displacement of cation, sodium sulfonate group of PSSNa is protonated in conc. HCl solution. the protonated MPPO-g-PSSNa is reacted with triethyl amine to produced ionic group. In figure 2, The ¹H-NMR sapectrum is shown. The aromatic proton peak of PSSATEa is shown around 7.5 ppm and 8.7 ppm. Around 1 ppm the proton peak of methyl originated triethyl amine is shown. From these FT-IR spectrum and NMR spectrum we know the MPPO-g-PSSTEa was synthesized.

4. Summary

In this study we report novel MPPO-g-PSSNa for fuel cell membrane. The synthesized polymer has 40wt% of PSSNa. The structure of MPPO-g-PSSNa is characterized by NMR and FT-IR. The Tg of MPPO-g-PSSNa is 220 °C. The proton conductivity and methanol permeability etc. for fuel cell is will e discussed.

5. Reference

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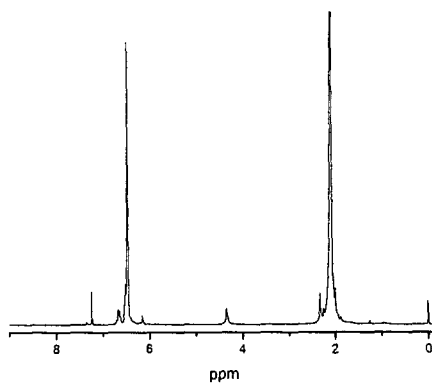


Figure 1. ¹H-NMR spectrum of Br-MPPO

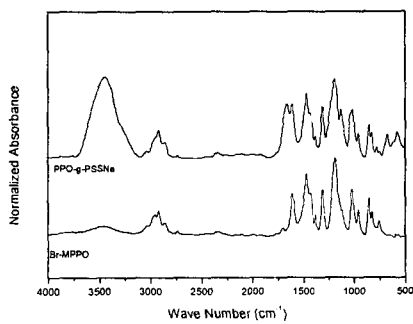


Figure 2. FT-IR spectrum of MPPO-g-PSSNa and Br-MPPO

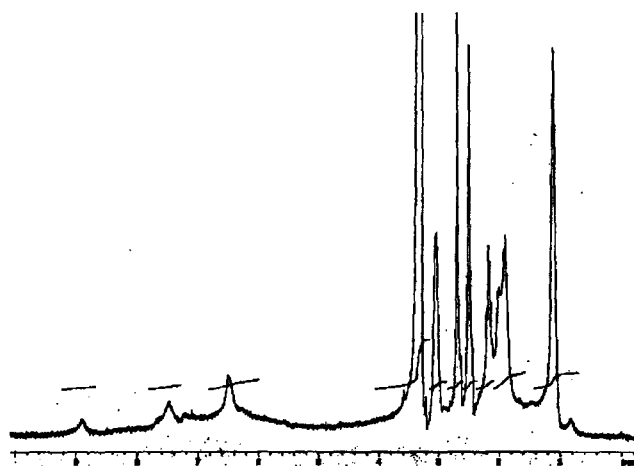


Figure 3. ¹H-NMR spectrum of MPPO-g-PSSTEAs