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Synthesis and Characterization of Phosphonium-Containing Cationic Poly(styrene) Polymers

by Kristoffer Stokes and Frederick L. Beyer

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14. ABSTRACT

Alkaline fuel cells have been proposed as a cost effective alternative energy solution due to their cheap manufacture and low operating temperatures. Their mass utilization, however, is hindered by their electrolyte material. While relatively inexpensive solid proton exchange membranes have been available for some time now, alkaline fuel cells still rely on liquid electrolyte to provide mobility to the anionic species. In this technical note, we describe an ionomeric system designed as an anion exchange membrane for these types of applications. Styrene monomer has been copolymerized with 4-vinylbenzyltrimethylphosphonium chloride to produce several statistical copolymers via reversible addition-fragmentation chain transfer (RAFT) polymerization, a controlled radical polymerization method. The synthetic approach and preliminary results are discussed, as well as future plans.

15. SUBJECT TERMS
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1. Introduction

In an effort to fully realize the value of fuel cell technology, a lot of research still needs to be performed. While proton exchange membrane (PEM) fuel cells have been at the forefront of the research for some time, the benefits of that work have been slow at producing a viable commercial solution. Due to the harsh conditions of the PEM fuel cell, some of that work has shifted to other types of fuel cells. One type, the alkaline fuel cell (AFC), has sparked particular interest within many communities as a path with a much shorter commercialization timeline. Perhaps the greatest advantage AFCs have over PEMs is the cost to manufacture (*1*). PEM fuel cell technology requires expensive platinum catalysts and specially-made perfluorinated membrane electrolytes. AFCs can use cheaper, nickel-based catalysts, but must use a liquid electrolyte for ion transport. The development of a stable, solid permselective membrane for hydroxyl ion transport in AFCs would represent a step change in technology that could drive AFCs into practical and common use for military and civilian applications alike.

2. Methods, Assumptions and Procedures

To realize a hydroxyl ion transport membrane, cationic transport sites are needed to facilitate ionic transfer. Phosphonium salts can act as a phosphorus centered cation. In this work, styrene monomers have been modified to contain cationic functional groups and copolymerized to form statistical copolymers of styrene and p-vinylbenzyltrimethylphosphonium chloride via reversible addition-fragmentation chain transfer (RAFT) polymerization. RAFT polymerization is a controlled radical polymerization technique that allows for control over the desired molecular weight distribution of synthetic polymers (*2*). This technique was used here for not only molecular weight control, but also for its functional group tolerance.

The general reaction scheme for the RAFT initiator and phosphonium containing monomer is depicted in figure 1. Synthesis of a variant of 1 has been previously reported in conjunction with phosphonium containing polymers and the synthesis modified to accommodate available materials (*3*). Compound 2 synthesis is facile with minimal purification and quantitative yields.

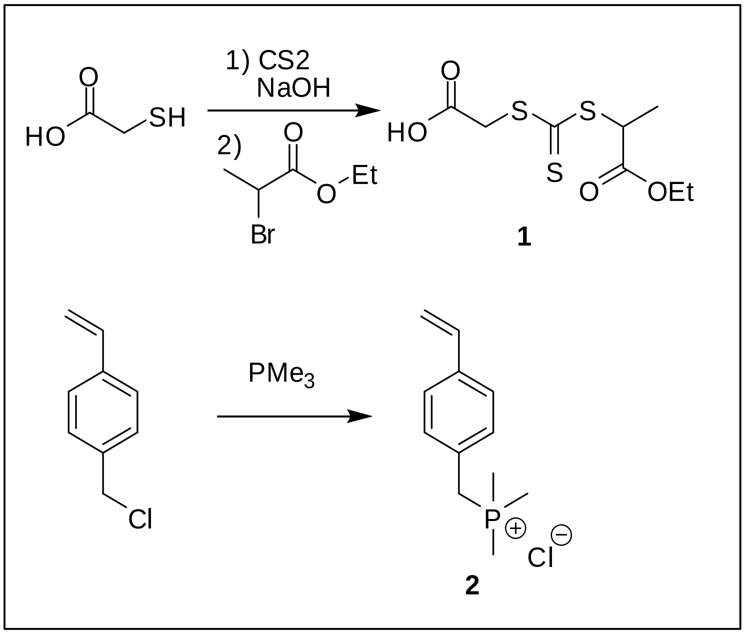

Figure 1. Synthesis of RAFT initiator (top) and synthesis of phosphonium chloride monomer (bottom).

Figure 2 schematically shows the synthesis of the copolymers P1-P5 through the polymerization of initiator 1 and monomer 2 with added styrene as a comonomer and azobisisobutyronitrile AIBN as a radical source. Polymers-designated P1-P5 correspond to a feed composition consisting of 1, 5, 10, 15, and 20 mol% compound 2, respectively. The polymers were characterized using standard characterization techniques and were determined to be within the range of 4–6k gmol^{-1}, and the polymers efficiently incorporated the phosphonium moiety. While the targeted molecular weight was much higher (30k gmol^{-1}), the polymerization was hindered by large viscosity increases. This effect was particularly noticeable at high phosphonium content in the feed. Future work will involve mitigation of these effects.

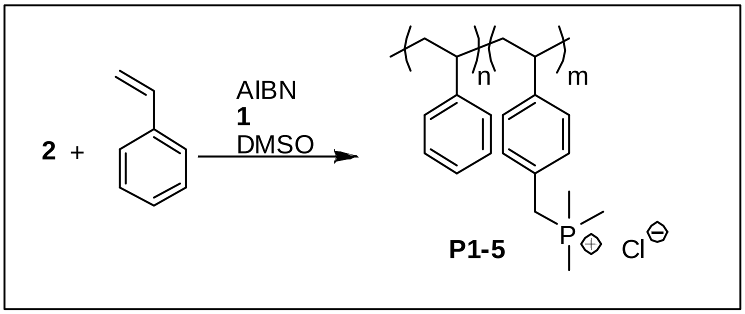

Figure 2. RAFT polymerization of poly(styrene-co-benzyltrimethylphosphoniumstyrene chloride).

Though the molecular weight is relatively low, the thermal properties are drastically altered even at low phosphonium contents. Homopolymer poly(styrene) typically has a glass transition temperature (T_g) around 100 °C; low molecular weight polymers can be even lower.

Incorporation of 1 mol% phosphonium monomer adds very little to the value of T_g because at these molecular weights, it corresponds to either zero or one phosphonium per chain. So, averaged across the bulk, there is likely to be significant amounts of homopolymer. However, raising that ionic content to 10 mol% leads to a 45 °C increase in the T_g. Figure 3 illustrates the effect of cation incorporation on the observed T_g. While the T_g does rise as a function of phosphonium content, the relationship is stronger at lower ion content. This can be attributed to the increase in the domain size and strength of ionic clusters formed. The relationship likely follows the Fox equation (*4*), but further studies need to be performed to corroborate that assertion.

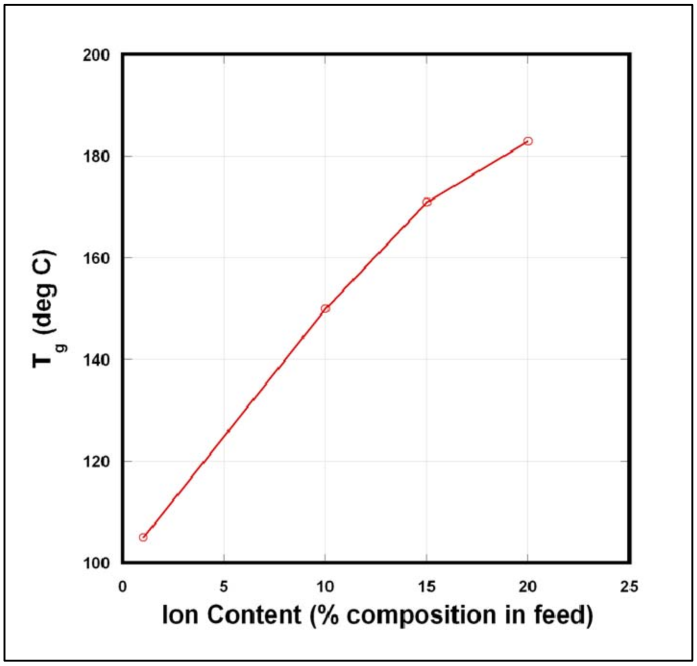

Figure 3. T_g of P1-P5 as determined by DSC of polymers P1-P5.

As fuel cells generally produce significant amounts of heat, thermogravimetric analysis (TGA) was performed on these polymers to determine their thermal stability over a temperature range. The analysis was performed under nitrogen and raised at a rate of 20 °C/ min over the range of 35-500 °C. The resulting curves depicted in figure 4 demonstrated three different transitions. The first, corresponding to water uptake, lies around 100 °C. The third is the decomposition of the hydrocarbon portion around 400 °C. Those transitions are relatively standard across the three samples. The second transition, however, is believed to be the thermal decomposition of the pendant phosphonium salt (*5*). Though the decomposition was expected, it is interesting that the decomposition temperature (T_d) was elevated in the higher ion content polymers. The T_d seems to follow similar trends to the change in T_g with ion content, so the immobile chains may hinder the decomposition reaction kinetics until they reach the polymer T_g, where the reaction can proceed unhindered. This may prove to be a useful method to stabilize the thermal decomposition under realistic fuel cell conditions; further studies are needed to confirm this mechanism.

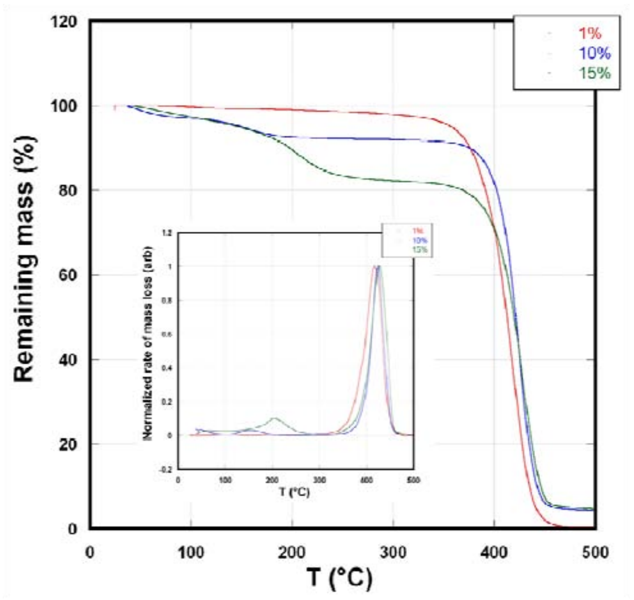

Figure 4. TGA of P1, P3, and P4. Thermal degradation of the phosphonium group can be seen before total decomposition of the styrenic portions.

3. Discussion

While the thermal properties of the phosphonium-containing poly(styrene) polymers have been tested, the morphological origin behind these properties still needs to be examined. Transmission electron microscopy (TEM) will be performed to get a visual assessment of the influence of strong cation content on the morphological self-assembly of these polymers. Additionally, small-angle X-ray scattering (SAXS) will probe the structure to determine other ordering that may not be apparent via TEM. Furthermore, while this is a random copolymer, work is currently being performed on synthesis of an analogous ion containing block copolymer system. Creation of that material may be able to help decouple the thermodynamic drivers of self assembly from the electrostatic and kinetic factors.

This research was supported in part by an appointment to the Postgraduate Research Participation Program at the U.S. Army Research Laboratory (ARL) administered by the Oak Ridge Institute of Science and Education through an interagency agreement between the U.S. Department of Energy (DOE) and ARL.

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List of Symbols, Abbreviations, and Acronyms

AFC	alkaline fuel cell
AIBN	azobisisobutyronitrile
ARL	U.S. Army Research Laboratory
DSC	differential scanning calorimetry
DOE	Department of Energy
M_n	number average molecular weight
mol	mole
PEM	proton exchange membrane
RAFT	reversible addition-fragmentation chain transfer
SAXS	small-angle X-ray scattering
T_d	decomposition temperature
T_g	glass transition temperature
TEM	transmission electron microscopy
TGA	thermogravimetric analysis

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