Synthesis and Characterization of Phosphorus Containing Poly(arylene ether)s

Daniel J. Riley

Dissertation Submitted to the Faculty of theVirginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Chemistry

Dr. James E. McGrath, Chair
Dr. Harry W. Gibson
Dr. Judy S. Riffle
Dr. David. G.I. Kingston
Dr. John G. Dillard

February 28, 1997

Blacksburg, Virginia

Keywords: Poly(arylene ether)s, Phosphorus, Degradation Analysis, Nonlinear Optics

Synthesis and Characterization of Phosphorus Containing Poly(arylene ether)s

Daniel J. Riley

(ABSTRACT)

The synthesis and characterization of phosphorus containing poly(arylene ether)s were investigated to determine the effect of phosphorus upon the thermal stability, mechanical strength, and fire resistance of thermoplastics. Phosphorus containing activated aromatic dihalides and bisphenols were synthesized in high purity. These monomers were successfully polymerized *via* nucleophilic aromatic substitution to afford high molecular weight polymers. It was determined that by incorporating the phosphine oxide moiety into the polymer backbone certain properties of the resulting poly(arylene ether)s were substantially improved, such as an increase in T_g, thermal stability in air, modulus, and char yield, compared with control poly(arylene ether sulfone)s. The high char yields obtained for these polymers in air, along with observed intumescence indicates that these materials have improved fire resistance. Preliminary cone calorimetry measurements support this conclusion.

In addition, the phosphine oxide group in the backbone was reduced to a phosphine and successfully converted to a phosphonium bromide ionomer. The resulting system was further chemically modified to ionically bond second-order nonlinear optical chromophores to the backbone of selected poly(arylene ether)s. Initial results on corona poling of cast film at low temperature produced stable second harmonic generation in these materials, indicating that they may have promise in nonlinear optical applications.

Acknowledgments

I would like to thank Professor James E. McGrath for his patience and direction throughout my education at Virginia Tech. Through his direction and leadership I have been able to expand my knowledge in many areas of polymer science. I would also like to sincerely thank the members of my committee, Dr. H. W. Gibson, Dr. J. S. Riffle, Dr. D. G.I. Kingston, and Dr. J. G. Dillard.

I would like to extend my thanks to fellow graduate students. Their advice and camaraderie, both in and out of lab eased the tension and strengthened the learning experience of graduate school. Especially worth mentioning are the contributions from the following individuals: Dr. Atilla Gungor, Dr. Duane Priddy Jr., Dr. Satya Srinivasan, Dr. Sankar Sankarapandian, Mr. Mark Muggli, Mr. Charles Tchatchoua, and Mr. Steve McCartney. I would also like to thank Kim Harich for his time, knowledge, and expertise with respect to GC-MS.

Much appreciation is due to our secretarial staff including Laurie Good, Esther Brann, Millie Ryan, and Joyce Moser.

Much thanks is due to my wife Michele for accepting my long hours in the laboratories, and for her help in assembling this thesis. Her encouragement and patience enables me to pursue my career, while at the same time enjoying a lifetime of happiness with her.

Table of Contents

List of Schemes

List of Tables

List of Figures