

**PART I: SYNTHESIS OF AROMATIC POLYKETONES VIA SOLUBLE
PRECURSORS DERIVED FROM BIS(α -AMINONITRILE)S**

**PART II: MODIFICATIONS OF EPOXY RESINS WITH FUNCTIONAL
HYPERBRANCHED POLY(ARYLENE ESTER)S**

by

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Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

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February, 1998

Blacksburg, Virginia

Keywords: Polymerization, Synthesis, Polyketones, Aminonitriles, Poly(arylene ester)s,
Modifications, Toughening, Epoxies, Functionalization, Hyperbranched

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(ABSTRACT)

Part I: This part of the dissertation describes a new approach to high molecular weight aromatic polyketones via soluble precursors derived from bis(α -aminonitrile)s. Bis(α -aminonitrile)s were easily synthesized from dialdehydes and secondary amines in very high yield by the Strecker reaction. Polymerization of bis(α -aminonitrile)s with activated dihalides using NaH as base in DMF yielded soluble, high molecular weight polyaminonitriles, which were hydrolyzed in acidic conditions to produce the corresponding polyketones. A novel approach to the synthesis of high molecular weight wholly aromatic polyketones without ether linkages or alkyl substituents in the polymeric backbones was demonstrated. These polyketones displayed excellent thermal properties and solvent resistance. A very efficient synthesis for diphenol and activated dihalide monomers containing keto groups was also developed based on α -aminonitrile chemistry. Novel activated dihalide monomers were obtained in quantitative yields. This method is suitable for any activated dihalide by reaction with 2 equivalents of 4-fluorobenzylaminonitrile and NaH, followed by hydrolysis to produce a new monomer with two more *p*-fluorobenzoyl units. For the synthesis of polyaminonitriles containing ether linkages in the polymeric backbone, only low to medium molecular weight polymers were obtained. The model studies proved that the carbanions of the aminonitriles can react with ether linkages to form more stable phenoxide anions and cause the termination of the polymerization.

Part II: Functional hyperbranched poly(arylene ester)s were synthesized by thermal polymerization of 5-acetoxyisophthalic acid or 3,5-diacetoxybenzoic acid. Carboxylic terminated hyperbranched copolyesters were also synthesized by copolymerization of 5-acetoxyisophthalic acid and 3-hydroxybenzoic acid using different molar ratios of these two monomers. Both carboxylic acid and phenolic terminated hyperbranched polyesters were functionalized with different reactive groups. The carboxyl terminated hyperbranched poly(arylene ester)s were successfully used to modify inherently brittle epoxy resins. The hyperbranched polymers were chemically incorporated into the epoxy networks using triphenylphosphine (TPP) as a catalyst and 4,4'-diaminodiphenyl sulfone (DDS) as a curing agent. The chemistry and the proper formation of crosslinked networks were confirmed by solution ^1H NMR, solid state CPMAS ^{13}C NMR, kinetic FTIR spectroscopies and gel fraction analysis. Fracture toughness was improved without sacrificing thermal properties. The fracture toughness K_{1C} values of the modified epoxies were found to be a function of the percentage loading, the molecular weights and the proportion of linear units of hyperbranched polyesters. Because the carboxylic acid terminated hyperbranched poly(arylene ester)s were immiscible with the commercially available epoxy EPON 828, the percentage loadings of hyperbranched modifiers were limited and the processibility of epoxy resins was difficult, especially at high percentage loadings of hyperbranched modifiers. These problems could be solved using phenolic terminated hyperbranched poly(arylene ester)s, which are more soluble in epoxy resins.

DEDICATION

TO

MY DEAR UNCLE

KOAY, AIK TENG

Acknowledgments

I would first like to express my sincere gratitude to Dr. Harry W. Gibson for his guidance, continued encouragement, support and patience while perusing this research.

I would also like to thank the members of my committee, Dr. Harry C. Dorn, Dr. James E. McGrath, Dr. Judy S. Riffle and Dr. James M. Tanko for their valuable suggestions and patience throughout this research. Thanks also go to professor McGrath and Professor Ward for providing thermal analysis, GPC data and the use of other equipment. Dr. Allan R. Shultz was kind enough to help me correct my thesis, his valuable help is gratefully acknowledged.

Special thanks go to Mr. Ojin Kwon and Dr. Qin Ji for their hard work and valuable help on the epoxy toughening project. Without their help, I would not have finished the second part of this dissertation. I would also like to thank students and postdocs in Dr. McGrath's and Dr. Riffle's group, especially those working on epoxy and vinyl ester areas: Drs. Sankarpandian and Shobha, Charles, Hong, Hui, Christy and others for their discussion and supply of starting materials.

I would also like to thank my friends in Dr. Gibson's group: Nori, Bill, Lesley, Donghang, Gong, Shu, Darin, Lance, Mingfei and Devdatt for their discussion and encouragement.

My dear uncle, Koay Aik Teng, who is not only a great mentor and role model, but also supported me for all my high school years, college years and post graduate education, whenever I needed it. Without his financial supports and continues encouragement, I would not have succeeded. And for my parents, even though they only had two years education and have to raise nine children, they always do their best to support me. Thank you for raising me to always believe in myself, and I did this all for you.

Finally, I would like to thank my girlfriend, Ning, for her love, support, encouragement and patience. Thank you for always being there for me!

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