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Preparation of Atomic Oxygen Resistant Polymeric Materials

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Polyphenylquinoxalines (PPQs) are an important family of high performance polymers that offer good chemical and thermal stability coupled with excellent mechanical properties.¹ These aromatic heterocyclic polymers are potentially useful as films, coatings, adhesives, and composite materials for applications that demand stability in harsh environments.

PPQs are generally synthesized by the solution polymerization of aromatic bis(*o*-diamine)s and aromatic bis(phenyl- α -diketone)s (see figure 1). The properties of the resulting polymer can vary depending on the structure of either monomer. The overall objective was to develop polymeric materials with resistance to atomic oxygen for potential space applications. PPQs are the materials of choice because of their inherent stability and the ease at which substituted versions could be synthesized.

Previous work has demonstrated that a protective silicon oxide coating applied to a polymer surface substantially decreases the erosion rate of the polymer from attack by atomic oxygen.² Polyimides containing siloxane units in the backbone have been shown by both ground-based and flight experimentation to form a protective surface coating when exposed to atomic oxygen.³ The oxygen presumably reacts preferentially with silicon to form thermodynamically stable silicon-oxygen bonds. This coating protects the underlying polymer from further erosion by atomic oxygen. However, since the siloxane unit is in the polymer backbone, cleavage of the siloxane by atomic oxygen causes a decrease in the polymer's molecular weight with a corresponding reduction in properties. If the siloxane units are attached as pendent groups their cleavage by atomic oxygen results in the polymer backbone remaining intact, thus preserving the properties of the polymer and forming a resilient silicate layer to protect the polymer (see figure 2). Recently at NASA, novel polyimides with pendent siloxane groups were prepared and exhibited superior properties to polyimides with siloxane segments in the backbone after exposure to atomic oxygen.⁴

† Our approach was to prepare PPQs with pendent siloxane groups using the appropriate chemistry and then evaluate these polymers before and after exposure to simulated atomic oxygen (Asher). Either monomer, the bis(*o*-diamine)s or the bis(α -diketone)s can be synthesized with a hydroxy group to which the siloxane chain will be attached.

Bis(3,4-diaminophenyl)methanol was prepared by the sodium borohydride reduction of 3,3',4,4'-tetraaminobenzophenone.⁵ This compound was then reacted with 1,4-bis(phenylglyoxylyl)benzene to form the PPQ as shown in figure 3. This polymer has a Tg of approximately 275°C. Reaction of this polymer with heptamethylhydrotrisiloxane in the presence of chloroplatinic acid should result in the formation of a siloxane containing PPQ. Unfortunately, the molecular weight of this polymer, as indicated by inherent viscosity, was too low to cast good films.

Preparation of a hydroxy-containing bis(α -dicarbonyl) compound is shown in figure 4. Polymerization with a tetraamine and subsequent reaction with a hydrotrisiloxane would result in a siloxane substituted PPQ (see figure 5). Work is continuing in this area and no results on this polymer are yet available.

Work to date has resulted in the preparation of several novel materials. The PPQ shown in figure 3 has been prepared and once quality film is obtained, then the siloxane derivative will be prepared. The hydroxy containing monomer, 1,4-bis(*p*-hydroxyphenylglyoxylyl)benzene, has been prepared. Reaction of this tetracarbonyl monomer with a tetraamine will result in the formation of a new PPQ. Reaction of this PPQ with the hydrosiloxane will be attempted.

Future work will involve testing of the siloxane containing PPQs with atomic oxygen (Asher), preparation of other silicon containing PPQs, and investigation of methods to simplify the synthetic path to these PPQs.

References

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b) I. Ritchie and H. B. Gjerde, *Surface and Coatings Technology*, **39/40**, 599-605 (1989).
3. J. McGrath, Virginia Polytechnic Institute and State University, unpublished results.
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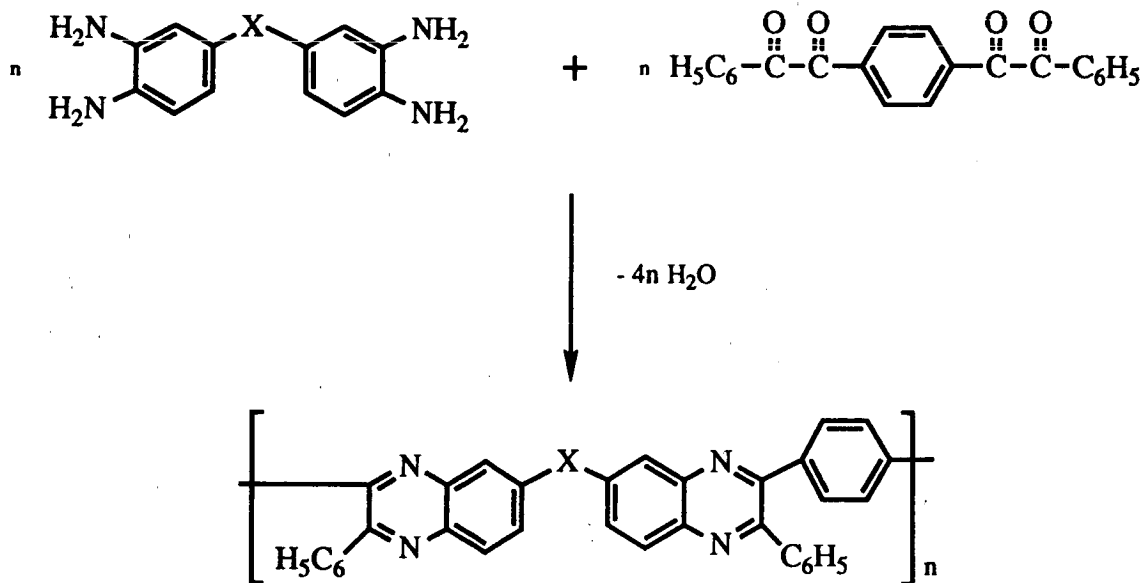


figure 1 Preparation of Polyphenylquinoxalines (PPQs)

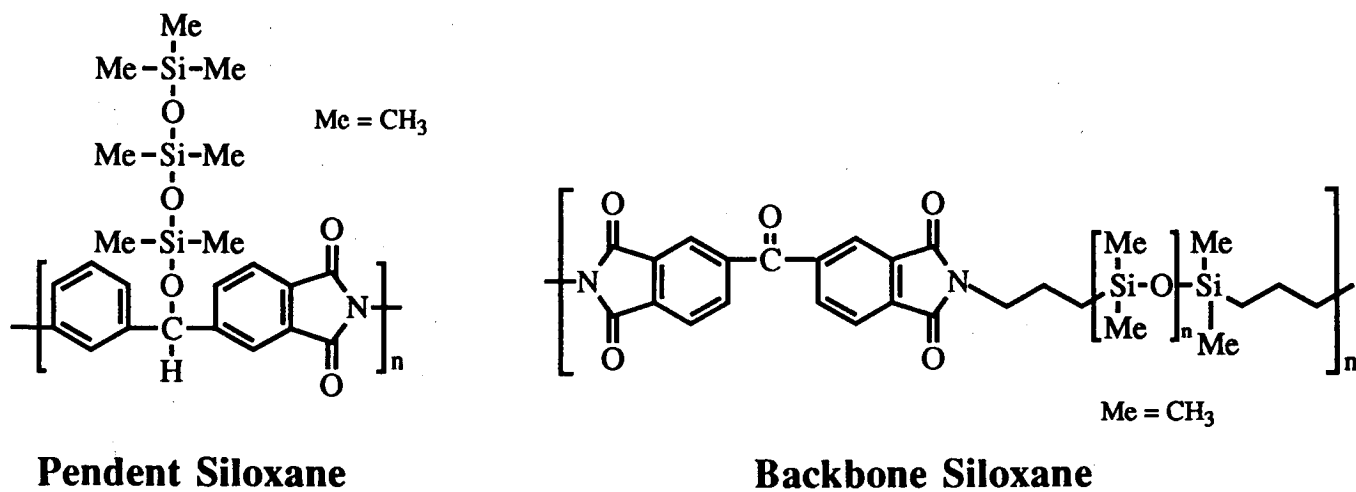
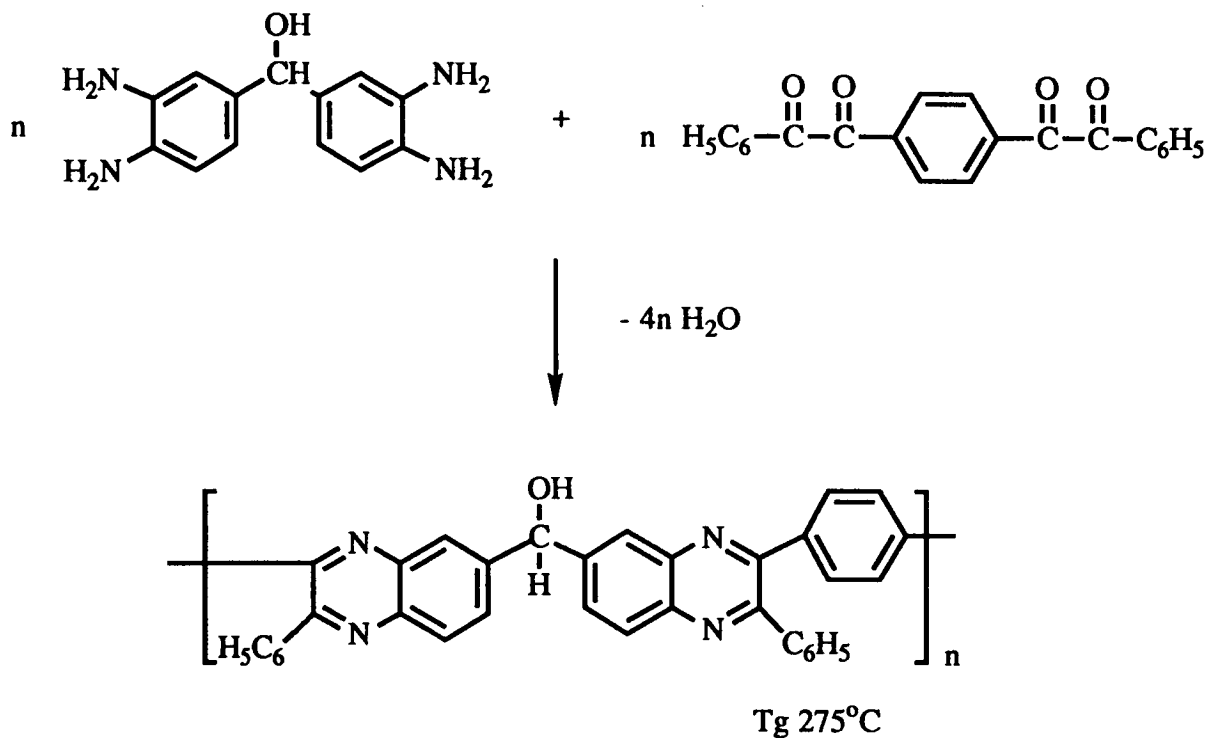
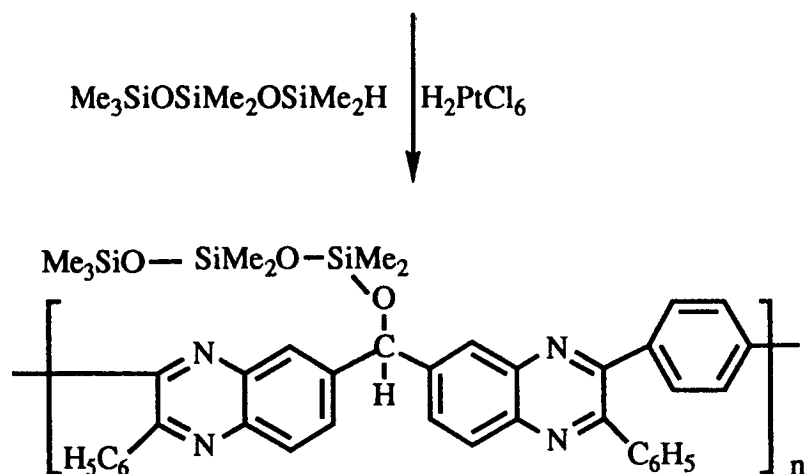


figure 2 Pendent vs Backbone Siloxane Containing Polymers

Synthesis of Hydroxy Containing PPQ



Synthesis of Siloxane Substituted PPQ



Me = CH₃

figure 3

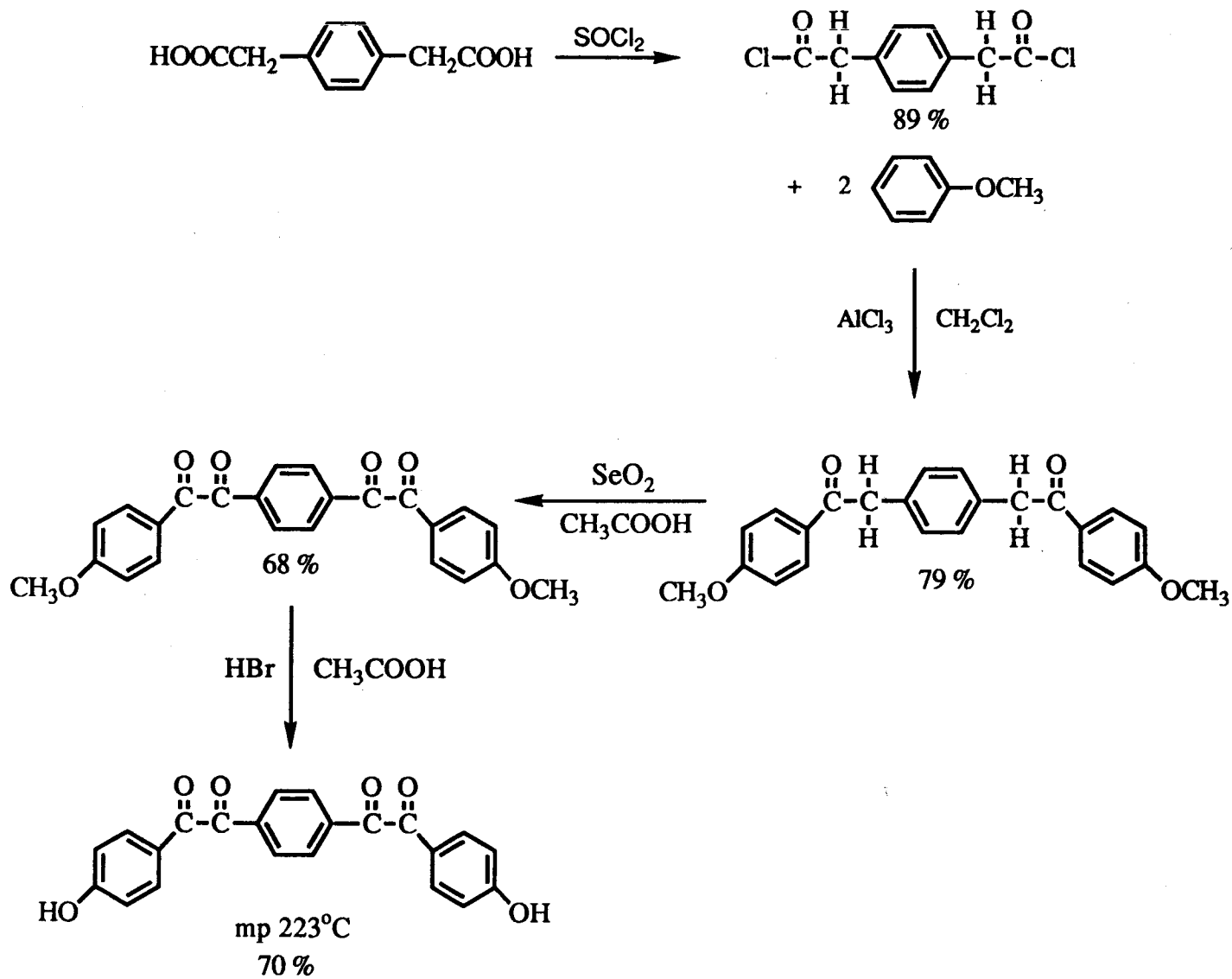
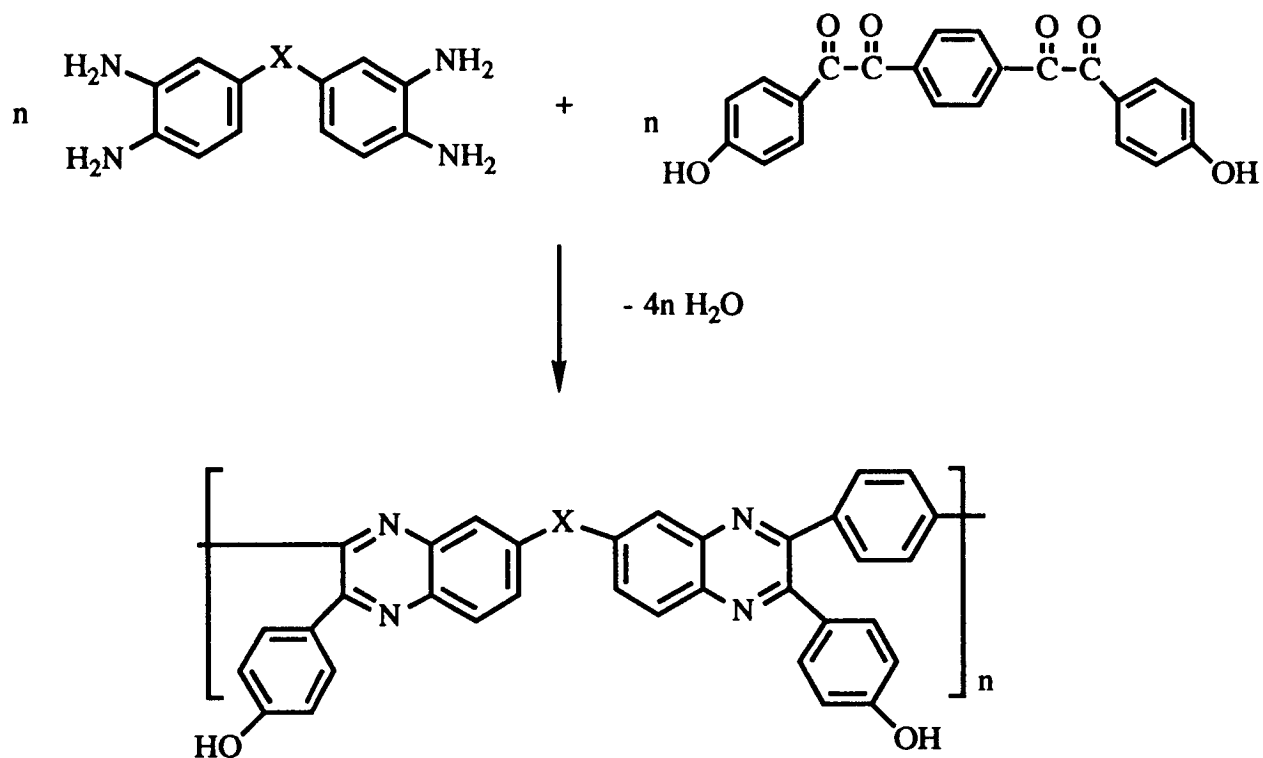


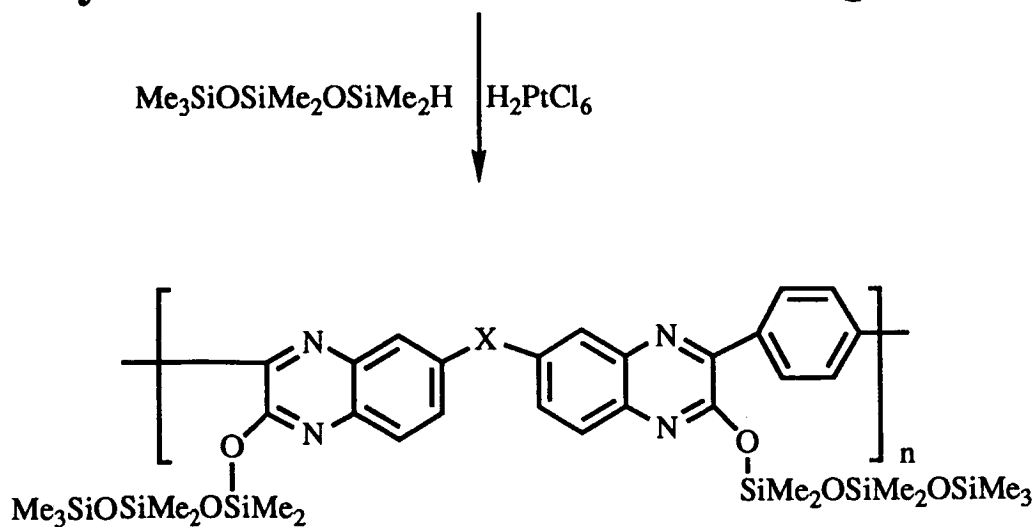
figure 4 Preparation of Dihydroxy bis(α -carbonyl) Monomer

% yields shown below each compound

Synthesis of Hydroxy Containing PPQ



Synthesis of Siloxane Substituted PPQ



Me = CH₃

figure 5