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THE PYROLYSIS OF POLY(FERROCENYLSILANES): METAL CONTAINING CERAMICS AND SMALL MOLECULES

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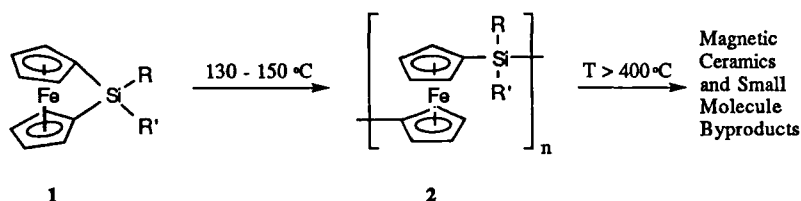
Abstract High molecular weight poly(ferrocenylsilanes) have been pyrolyzed under nitrogen, air and in vacuum to yield magnetic ceramics and interesting small molecule products. The characteristics of the materials produced in these reactions is discussed.

INTRODUCTION

Advanced ceramics represent one of the most interesting examples of modern specialty materials.¹ Polymer precursors to these products are of considerable current interest as they are easily processed into fibers or films and possess intimate atomic scale mixing. As transition metal containing solids typically display novel properties, the pyrolysis of polymers containing these elements in the polymer backbone should yield interesting ceramic materials. Poly(ferrocenylsilanes), **2**, which are derived from the thermal ring-opening polymerization of strained [1]ferrocenophanes, **1**, possess both iron and silicon in the polymer backbone.^{2,3} As part of our investigation into the preceramic characteristics of these macromolecules, they were heated under an atmosphere of static nitrogen at temperatures in excess of 400°C.⁴ This produced black, lustrous, magnetic ceramics and novel small molecule byproducts which suggest that the conversion of polymer to ceramic competes with unusual depolymerization pathways. These investigations show that ceramic properties vary with the aryl or alkyl substituent at silicon. Analysis of the ceramics has been carried out using a variety of techniques including Mössbauer spectroscopy, SEM/EDX and magnetic susceptibility measurements.

IRON, SILICON AND CARBON CONTAINING CERAMICS

Polymer pyrolyses carried out in a tube furnace under an inert atmosphere of nitrogen provided black lustrous and magnetic ceramics in yields that range from 25 to 75% depending upon reaction conditions and polymer substituent. The TGA traces for **2** ($R = \text{Me}$, $R' = \text{H}$) are in good agreement with these results and show no significant weight loss for the ceramic product from 500 to 1000°C.



Energy dispersive X-ray microanalysis (EDX) of the ceramic derived from **2** ($R = R' = \text{Me}$) indicate an approximate iron, silicon and carbon ratio of 30:17:53.⁴ A Mössbauer study carried out on the ceramic derived from the polymer, **2** ($R = \text{Me}$, $R' = \text{H}$), shows peaks which suggest that the ceramic is ferromagnetic in nature and that more than one iron environment is present.

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