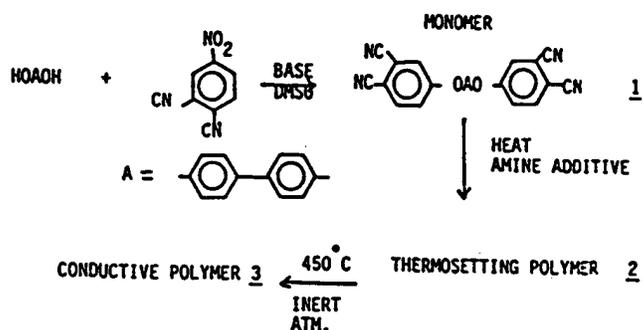


LOW TEMPERATURE MAGNETIC SUSCEPTIBILITY STUDIES
OF A PHTHALONITRILE BASED
CONDUCTIVE POLYMER

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Introduction

A doped polymeric system, such as doped polyacetylene, has a wide range of conductivity values which can be controlled by adding proton donor or electron acceptor dopants. However, most doped systems undergo conductivity changes with aging and exposure to the atmosphere. Pyropolymers have excellent conductivity stability in the atmosphere and their conductivity can be changed in a controlled manner by a precise pyrolytic procedure without the addition of external chemical dopants. Several polymers, e.g. polyacrylonitrile^{1,2}, dianil phthalonitrile resins³, and poly [N,N'-(p,p'-oxydiphenylene) pyromellitimide]^{4,5} have been shown to exhibit high conductivity upon pyrolysis. Unfortunately, polymers composed solely of these high temperature structural moieties tend to be brittle and intractable and attention has been directed toward the introduction of high temperature units and flexible linkages into the polymeric chain. Several oligomeric phthalonitriles of varying average molecular weight in which two terminal phthalonitrile units are interconnected by moieties with aromatic ether and sulphonyl linkages have been synthesized and polymerized. Of these the synthesis and polymerization of 4,4'-bis(3,4-dicyanophenoxy)-biphenyl has been reported previously by Keller⁶. This is shown in the reaction steps below:



A mixture of 4,4'-biphenol, 4-nitro-phthalonitrile, and an excess amount of anhydrous potassium carbonate was stirred overnight in dry dimethyl sulfoxide (DMSO) at room temperature to afford a quantitative yield of **1**. Monomer **1** is cured at 250-300°C in air in the presence of a minute quantity of an aromatic amine such as 4,4'-methylenedianiline. The thermosetting polymer **2** is an insulator at this stage. The polymer **2** is easily processable by melt condensation of the phthalonitrile **1** into a void-free thermosetting material. Electrically conducting components are actually fabricated to a particular shape in this initial prepolymerization step. Polymerization can be achieved under controlled conditions in one step by heating the phthalonitrile mixture above its melting point until gelation and vitrification occurs (C-stage), followed by postcuring at elevated temperatures to improve the physical properties, or stepwise to distinct stages. The latter method involves heating the polymerization mixture to a certain viscosity designated as the B-stage. Upon cooling, the B-staged prepolymer is a glassy black solid similar in appearance to obsidian which can be stored indefinitely at ambient temperature without further reaction. The prepolymer can then be remelted and heated until solidification occurs or can be pulverized and processed into any shape desired. Postcuring of **2** at elevated temperatures converts the insulating polymer into a conductor.

Conductivity at Room Temperature

The electrical conductivity of **2** and **3** is controlled by pyrolytic conditions. Between 500-900°C, the room temperature