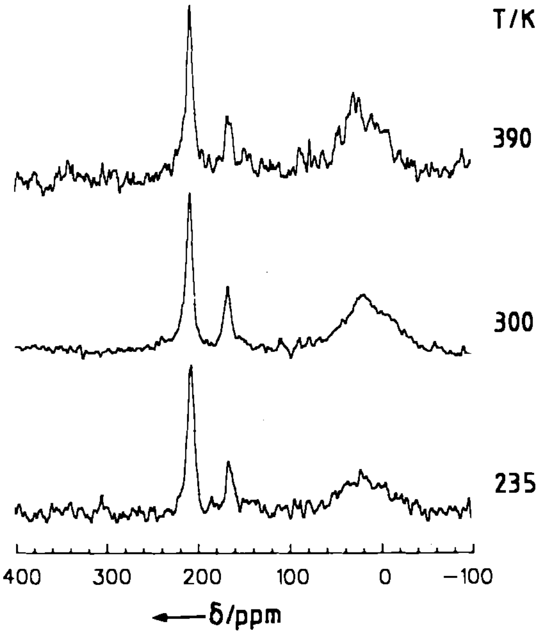

Fig. 3. ^{15}N CPMAS NMR spectra of partly oxidized $[(PcSiO)I_{1.1}]_n$ as a function of temperature. The spectra indicate slightly temperature dependent Knight-shifts of the oxidized material. Experimental conditions: 10 ms cross polarization time, 10 kHz spectral width, 52 ms acquisition time, otherwise same as Figure 2; (a) 2902 scans, (b) 15000 scans, (c) 7082 scans.

shift of the α-^{13}C spins as compared to the ^{15}N shifts needs further study.

In summary, it has been shown that structural changes of the solid state polymerization and the subsequent oxidation of ^{15}N labeled phthalocyaninatometalloxanes can be monitored by ^{15}N CPMAS NMR spectroscopy. In the oxidized state these materials are highly conductive, a fact confirmed by the observation of a ^{15}N Knight shift similar to the one observed by ^{13}C CPMAS spectroscopy. Conductive and non-conductive regions coexist and their relation can be estimated. Thus, ^{15}N CPMAS NMR spectroscopy provides interesting information on the structure and the reactions of this class of compounds.

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A New Route to Highly Conducting Polyenes

By *Henning Hopf**, *Olaf Kretschmer*,
and *Herbert Naarmann**

Dedicated to Professor Wolfgang Lüttke on the occasion of his 70th birthday

Since doped polyacetylene was shown to possess metallic conductivity in 1977 this class of organic polymers has been studied intensively.[1] The polyacetylenes used for these experiments may be prepared by various routes,[2] the polymerization of acetylene with Ziegler catalysts according to Shirakawa being a widely employed method.[3] Under certain conditions this approach provides mechanically stable polymer films which are of particular importance for the preparation of conducting material.

Regardless of the catalyst system used, it is an inherent disadvantage of this type of polymerization that ultimately a washing process will be required to remove the catalyst or its residues from the desired polymer preparation. In this communication we describe a method which avoids this pitfall and provides polyene films which form a solid layer on glass surfaces, ceramic plates, tubes etc.

Allene (propadiene) is condensed under high-vacuum into a 2 l-round bottomed flask, and after several freeze-and-pump cycles to remove residual oxygen and volatile impurities the reaction vessel is sealed (internal pressure at room temperature ca. 1000 mb). After 20 h at 460 °C (high-temperature drying oven) the inner surface of the flask is covered completely by a deep-black, shiny-film which can be removed in patches and whose electric conductivity is 10^{-8} S/cm. When this film is doped by treating it for 30 min with a saturated solution of iodine in carbon tetrachloride[4] its appearance changes to a shiny gold. After solvent removal the conductivity has increased by a factor of 10^9.

Since allene is known to isomerize to propyne at elevated temperatures[5] we also investigated the polymerization of this hydrocarbon and several other alkynes under the above conditions. The results of these experiments are summarized in Table 1.

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Table 1. High-temperature polymerization of alkynes and diynes.

monomer	electric conductivity of polymer film [a] [S/cm] undoped	doped with I_2
propyne	10^{-8}	10^{-1}
1-hexyne	10^{-9}	10^{-2}
butadiyne	10^{-8}	10
1,5-hexadiyne	10^{-6}	60

[a] Determined with the four-probe technique [4]

The reaction time of the polymerization experiments may be reduced considerably (8 h) by carrying out the above thermal processes in the presence of small amounts of various Lewis acids such as $FeCl_3$ or $MoCl_5$.

The undoped polymer films are insoluble in common solvents, possess up to 10% sp^3-hybridized carbon atoms as determined by ^{13}C NMR spectroscopy, and are more stable to air than a Shirakawa-polymer film. The oxygen-uptake of the latter amounts to 6% after 1 hour (in air, room temperature, humidity 50%) and reaches 14% after 24 hours under the same conditions. A polyene film prepared from propyne by our approach only absorbed 1.5 and 2.7% of oxygen after 1 and 24 hours respectively.

The simplicity of this new approach to conducting organic polymers makes it amenable to other highly unsaturated systems (other allenes, cumulenes, alkylacetylenes) and the results of presently performed experiments along these lines will be published in due course.

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Research News/Inorganic Materials I

Glass-Ceramics in the Scheme of Inorganic Materials

By Graham Partridge*

1. Introduction

Glass and ceramic materials have been known for several thousands of years, the technology of preparation and diversity of composition and properties increasing, perhaps relatively slowly at first, but latterly much faster leading to the advanced materials which are becoming established in todays technology and which are expected to form the backbone of developments into the 21st century.

Originally it was considered that the various materials should be classed as insulating, and were distinct in composition and properties. However, these distinctions have become very blurred at the edges, for example, conducting ceramics such as silicon carbide and the superconducting materials such as yttrium–barium–copper oxide have appeared together with semiconducting glasses of the chalcogenide type. Indeed the blurring has gone even further with the advent of such materials as amorphous metals or metallic glasses. How should these be classified—as special glasses or special metals?

A further type of material which bridges the original gap between glasses and ceramics are glass-ceramics. These are much more recent in concept and possess many of the useful properties of the earlier materials. Essentially, they help to extend the overall range of materials and provide the technologist and materials designer with more opportunities to meet the increasing technological demands of today.

The present article, intended to form part of a series describing and discussing recent developments in these materials is aimed at introducing the materials and outlining their properties and general position in the overall scheme of inorganic materials. By way of introduction it is useful to consider what is meant by the various terms used for these materials.

2. Description of the Materials

2.1. Ceramics

The definition of ceramics provided by *Kingery*; "the art and science of making and using solid articles which have as their essential component, and are composed in large part of

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