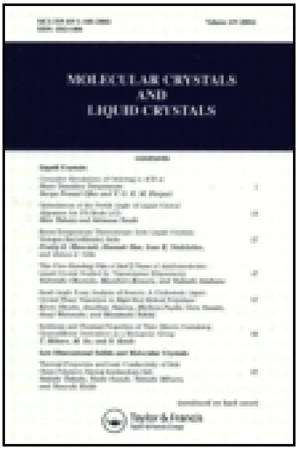

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Structure and Electric Conductivity of Vapor Deposition Products of Cyano Acetylene

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STRUCTURE AND ELECTRIC CONDUCTIVITY OF VAPOR DEPOSITION PRODUCTS OF CYANOACETYLENE

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Abstract Cyanoacetylene can be polymerized from vapor state onto an inactive surface of substrate at a temperature as low as 200°C. The structure and electric conductivity of these cyanoacetylene products have been investigated.

INTRODUCTION

The conductivity of pyrolized polyacrylonitrile has been attributed to the formation of doubly conjugated ladder structure shown in Fig.1. Similar structure is expected to be formed from cyanoacetylene as a starting monomer. Polycyanoacetylene polymerized with various catalysts have been reported.[1] The polymers are black powders and insulators. We have found that cyanoacetylene can be polymerized thermally (>200 °C)[2]. These products have metallic

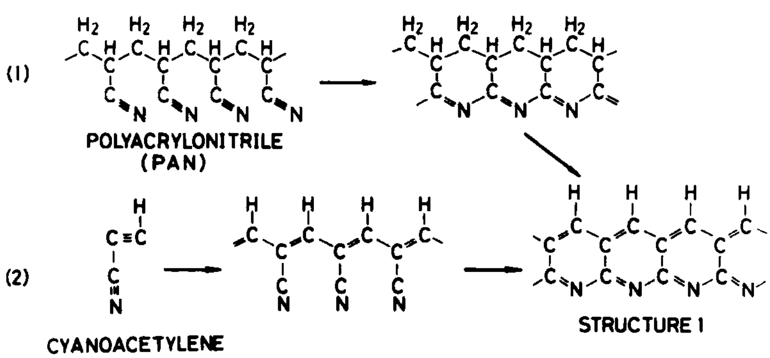

Fig.1 Synthesis of conductive polymer

lustre and conductivities higher than 10^{-2}S/cm. The present study was undertaken to investigate the structure and conductivity of the products.

EXPERIMENTAL

The polymerization was carried out using a quartz reactor heated electrically from the outside. Nitrogen gas saturated with cyano-acetylene monomer was introduced to the reactor. Cyanoacetylene was polymerized from vapor state onto the surface of substrate at temperatures from 200°C to 1000°C.

RESULTS AND DISCUSSION

SEM observation

The polymer obtained at 200°C shows black color and metallic lustre. Products obtained at temperatures above 400°C have aluminum-like metallic lustre and color. Films polymerized at lower temperatures are hygroscopic and wrinkle in the air. While, the products obtained at 1000°C are stable in the air. The growth of laminar structure can be seen at the cross section of the film obtained at 1000°C.

Elemental analysis

Results of elemental analysis of cyanoacetylene products are shown in Table 1. A hydrogen to carbon ratio of the product decreases with increasing reaction temperature. While, the decrease of nitrogen is rather slow compared with the change of the hydrogen. The reaction product at 1000°C still contains nitrogen at a concentration as high as 14wt%, which corresponds to a nitrogen to carbon ratio of 1/6.

IR and ESCA measurements

The absorption peak of mono-substituted carbon-carbon triple bond appears around 2100cm^{-1}. This peak cannot be observed for the

TABLE 1 Elemental analysis of cyanoacetylene products

Reaction temperature	Atomic ratio Carbon	Hydrogen	Nitrogen
400°C	1	0.23	0.21
700°C	1	0.09	0.17
1000°C	1	0.03	0.14
(monomer)	(1)	(0.33)	(0.33)

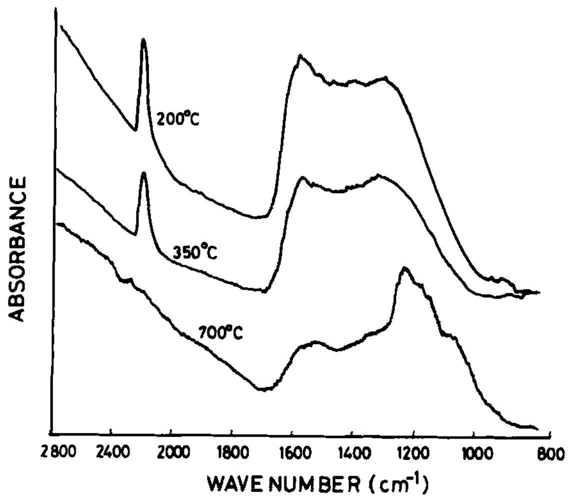

Fig.2 IR spectra of cyanoacetylene products

product obtained at a temperature as low as 200°C, as shown in Fig. 2. This fact shows that reaction first occurs by way of the carbon -carbon triple bond, but not the carbon-nitrogen triple bond. The absorption peak at 2200cm^{-1} is assigned to nitrile group. This absorption decreases with increasing temperature, and finally disappears when reaction temperature exceeds 700°C.

On the other hand, ESCA lines(N_{1s}) of all the cyanoacetylene products reveal either existance of nitrile group or the formation of naphtiridine ring. As absorption peak of nitrile group disappears in IR spectrum for the products above 700°C, naphtiridine ring is suggested to be formed in the products obtained at higher temperature (>700°C).

Conductivity

The conductivities of the products obtained at 400°C, 700°C, 1000 °C are 0.08S/cm, 91S/cm, and 1600S/cm,respectively, at room temperature. These values are extreamely higher than those of pyrolized PAN treated at the same temperature. Temperature dependence of the conductivity for the 400°C product is well explained by the variable range hopping model. While, products obtained at higher temperatures cannot be accounted for by the hopping model. This is due to the development of graphite-like structure.

CONCLUSION

We have polymerized cyanoacetylene thermally and obtained films having metallic lustre and high conductivity. It is suggested that products obtained at lower temperature are composed of polycyanoacetylene and doubly conjugated structure, and that products of higher temperature are composed of doubly conjugated structure and graphite-like structure containing some nitrogens.

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