This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 20 February 2013, At: 12:08

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH,

UK



# Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information: <a href="http://www.tandfonline.com/loi/gmcl16">http://www.tandfonline.com/loi/gmcl16</a>

# Structure and Electric Conductivity of Vapor Deposition Products of Cyano Acetylene

Kiichiro Matsumura <sup>a</sup> , Jun Tsukamoto <sup>a</sup> , Akio Takahashi <sup>a</sup> & Kazuaki Sakoda <sup>a</sup> <sup>a</sup> Pioneering R & D Laboratories, Toray Industries Inc., 3 Sonoyama, Otsu, Shiga, 520, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Kiichiro Matsumura , Jun Tsukamoto , Akio Takahashi & Kazuaki Sakoda (1985): Structure and Electric Conductivity of Vapor Deposition Products of

To link to this article: http://dx.doi.org/10.1080/00268948508074884

Cyano Acetylene, Molecular Crystals and Liquid Crystals, 121:1-4, 329-332

### PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be

independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst. 1985, Vol. 121, pp. 329-332 0026-8941/85/1214-0329/\$10.00/0 © 1985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd. Printed in the United States of America

STRUCTURE AND ELECTRIC CONDUCTIVITY OF VAPOR DEPOSITION PRODUCTS OF CYANOACETYLENE

KIICHIRO MATSUMURA, JUN TSUKAMOTO, AKIO TAKAHASHI, AND KAZUAKI SAKODA Pioneering R & D Laboratories, Toray Industries Inc., 3 Sonoyama, Otsu, Shiga, 520, Japan

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. The polymers are black powders and insulators. We have found that cyanoacetylene can be polymerized thermally (>200 °C)<sup>2</sup>. These products have metallic

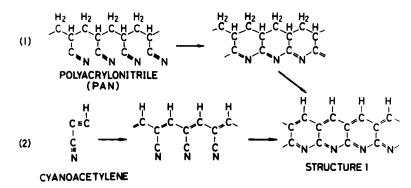


Fig.1 Synthesis of conductive polymer

lustre and conductivities higher than  $10^{-2} \, \text{S/cm}$ . 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 cyanoacetylene 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 aluminumlike 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<sup>-1</sup>. This peak cannot be observed for the

Reaction	Atomic ratio		
temperature	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)

TABLE 1 Elemental analysis of cyanoacetylene products

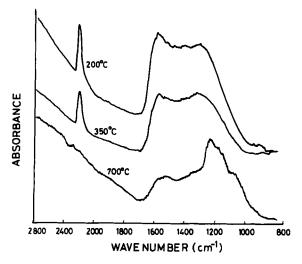


Fig. 2 IR spectra of cyanoacetylene products

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<sup>-1</sup> 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 0.085/cm, 915/cm, and 16005/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.

#### ACKNOWLEDGEMENTS

This work was performed under the management of the Research Association for the Basic Polymer Technology for synthetic metals as a part of a project on Basic Technology for Futur Industries sponsored by Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

#### REFERENCES

- 1. J. Wallach, J. manassen, <u>J. Polym. Sci.</u>, <u>Al</u>, 1983(1968).
- K. Matsumura, J. Tsukamoto, A. Takahashi, and K. Sakoda, J. Polym. Sci., Polym. Chem. Ed., (in press).