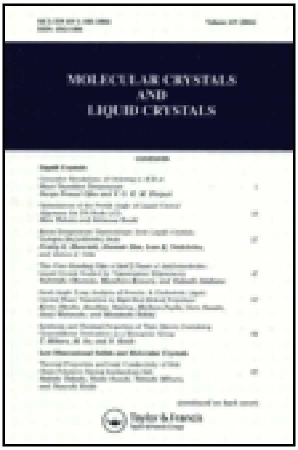
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 20 February 2013, At: 12:45
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthesis of One-Dimensional Graphite Polymer, Poly-Peri-Naphthalene, By Vapor Phase Polymerization

Mutsuaki Murakami [a] & Susumu Yoshimura [a]

[a] The Research Development Corporation of Japan, c/o Matsushita Research Institute Tokyo, Inc., Higashimita 3-10-1, Tama-ku, Kawasaki, 214, Japan

Version of record first published: 17 Oct 2011.

To cite this article: Mutsuaki Murakami & Susumu Yoshimura (1985): Synthesis of One-Dimensional Graphite Polymer, Poly-Peri-Naphthalene, By Vapor Phase Polymerization, Molecular Crystals and Liquid Crystals, 118:1, 95-102

To link to this article: http://dx.doi.org/10.1080/00268948508076194

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

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.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 95-102
0026-8941/85/1184-0095/$15.00/0
© 1985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013

SYNTHESIS OF ONE-DIMENSIONAL GRAPHITE POLYMER, POLY-PERI-NAPHTHALENE, BY VAPOR PHASE POLYMERIZATION.

MUTSUAKI MURAKAMI AND SUSUMU YOSHIMURA
The Research Development Corporation of Japan, c/o Matsushita Research Institute Tokyo, Inc., Higashimita 3-10-1, Tama-ku, Kawasaki 214, Japan.

Abstract Very fine whiskers grown via vapor phase polymerization of 3,4,9,10-perylenetetracarboxylic dianhydride have a one-dimensional graphite structure with a metallic-like electrical conductivity.

INTRODUCTION

One-dimensional graphite has been expected to have extinguished physical properties because of its unique molecular structure. Quantum mechanical calculation has recently been made with various hypothetical one-dimensional graphite polymers, such as polyacenacene,[1] polyacene,[2,3] polyphenanthrene,[4] or polynaphthalene.[5] It has been suggested that some will exhibit metallic conductivity and some will possibly have a phase with high-temperature superconductivity or ferromagnetism.[3] Although attempts have been made on the preparation of such polymers, well-defined one-dimensional graphite has not been synthesized as yet.[6,7] In this paper, we report vapor phase polymerization of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) at elevated temperatures, presenting a new approach to a successful preparation of a one-dimensional graphite polymer.

EXPERIMENTAL

A pressed pellet of PTCDA was heated in an argon or argon-hydrogen atmosphere with an infrared-radiation furnace in which the light from four quartz-made light sources was concentrated on the center of the pellet. The temperature was raised at a rate of 10°C/min to a predetermined temperature (Tp) where the pellet was heat-treated for another one hour.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013

RESULTS AND DISCUSSION

SEM Features of the Whiskers

During the experiments, growth of very fine whiskers on the pellet was encountered when Tp was higher than 520°C. It looked as if the pellet was covered with black mold of thickness less than 10 mm and quite unusual macroscopic properties were revealed by scanning electron microscopy (SEM) observation. First, almost all the whiskers grown under the same condition were of uniform size and shape with about 0.2 μm in width. (see Fig.1) Since the length of the whisker is between 1 and 10 mm, the largest ratio of the width to the length is about one to fifty thousand. This ratio is equivalent to that of five-meter long human hair. Second, as shown in Figure 2, the whisker has an essentially rectangular cross section of about 0.1 to 0.4 μm on a side. Until now many kinds of vapor-phase grown carbon fibers have been reported but all have circular cross sections. This is the first example of a rectangular fiber. Third, the angular nature of the whisker was much pronounced when grown in a hydrogen-containing inert atmosphere. Figure 3 shows the whisker grown in Ar-H_2 (3:2 in volume) at Tp= 800°C. Since the shape of the whisker differs substantially from that of benzene-derived carbon fibers [8] and the whisker grows at relatively low temperatures without any catalyst, a mechanism for the reaction and growth of this new whisker should be offered on a basis entirely different from that of ordinary carbonization reactions.

Polymerization Mechanism

The temperature at which the whisker started to grow (520°C) is just above the decomposition temperature of the PTCDA crystal (516

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013

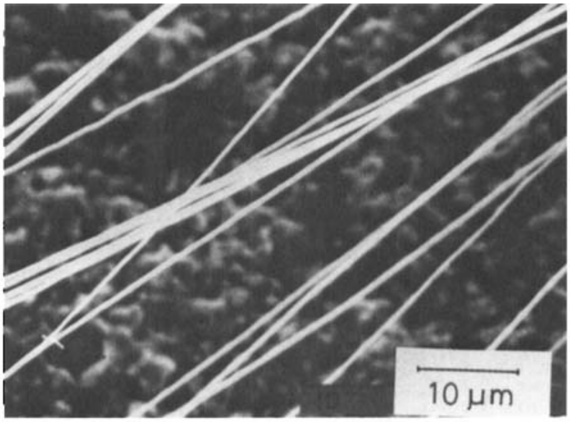


FIGURE 1 SEM picture of whisker-800.

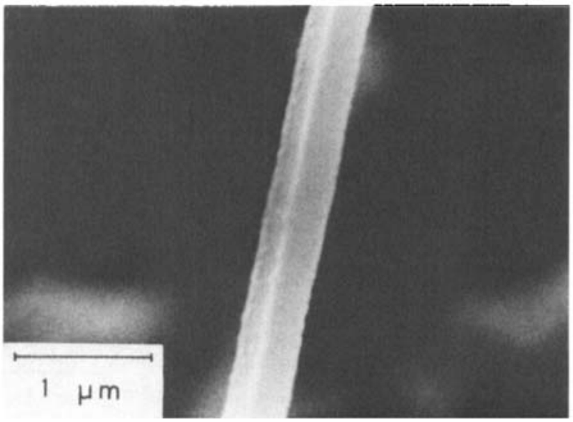


FIGURE 2 More magnified view of the whisker-800.

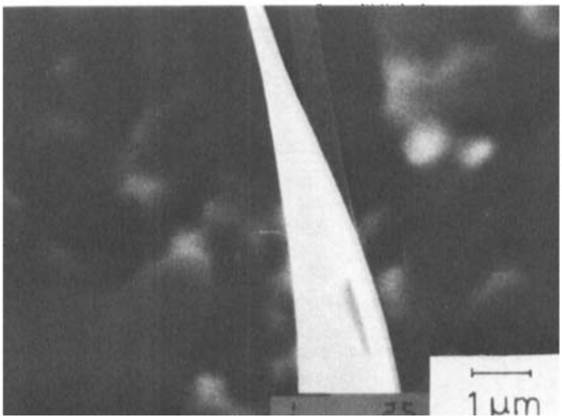


FIGURE 3 SEM picture of whisker-800 synthesized in Ar/H_2 atmosphere.

^{o}C) as evidenced from the thermogravimetric analysis. From the elemental analysis of the heat-treated PTCDA, it was found that the oxygen content of PTCDA decreased with the weight loss. For example, the content of the heat-treated PTCDA at 600^{o}C is less than 1 %. In addition, gas analysis revealed almost stoichiometric evolution of carbondioxide and monooxide gas. So that it is concluded that the scission of the dianhydride substituents in PTCDA occurs during the initial weight loss at the whiskerization temperature.

The FT-IR absorption spectra of the PTCDA whiskers synthesized at 530^{o}C and 600^{o}C in Ar are shown in Figure 4. The spectrum of PTCDA consisted of absorptions at 1774 cm^{-1}(νC=O), 1757, 1743, 1730 cm^{-1}(aromatic δ C-H, out of plane), 1594, 1538 cm^{-1}(aromatic νC=C), 1299, 1234 cm^{-1}(C-O-C), 1022 cm^{-1}($-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$), and 859, 792, 733 cm^{-1}(aromatic δ C-H, out of plane). In the spectrum of the

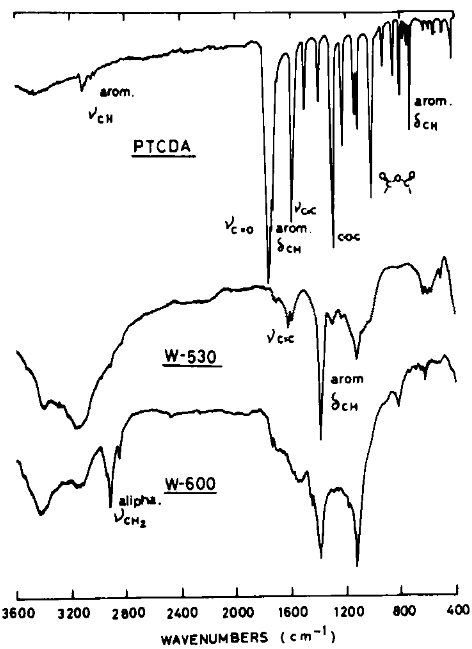


FIGURE 4 FT-IR spectra of PTCDA, Whisker-530, and -600.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013

whisker grown at 530°C, however, absorptions based on C–O–C, C=O and –C(=O)–O–C(=O)– completely disappeared and instead the absorptions at 1593 cm^{-1}(aromatic νC=C) and those due to aromatic δC–H (1400 and 1125 cm^{-1}) developed. The absorption spectrum of the whisker obtained at 600°C was almost identical with that obtained at 530°C except for absorptions at 2925 and 2854 cm^{-1}(aliphatic ν CH_2). For higher Tp, the infrared absorption spectra became broadened as in the case of conventional carbons.

The hydrogen content in the whiskers decreased with increasing Tp. For example, the contents for whiskers made at 550, 600, 800, and 1000°C were 2.9, 2.4, 0.9, and 0.4 %, respectively. Since a sufficient amount of whisker-520 has not been obtained at this stage, we cannot directly determine the hydrogen content in the whisker. However, we estimated the hydrogen content to be 3.2% by extrapolating the mentioned elemental analysis data to 520°C.

From these results, we propose a growth mechanism for the whiskers as shown in Figure 5. The decomposition is thought to

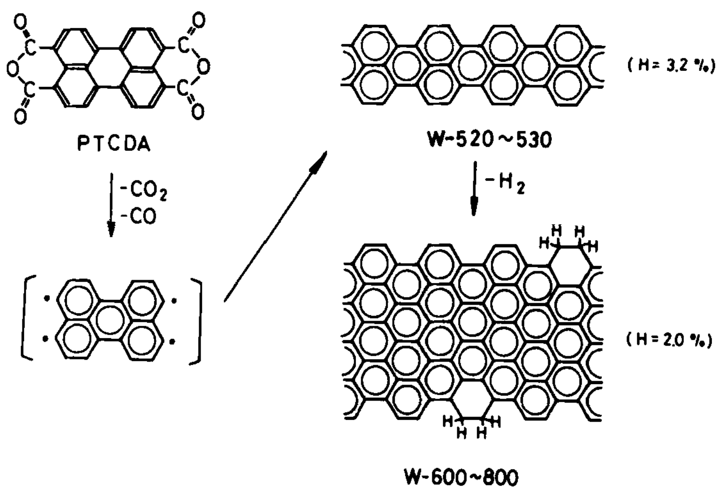


FIGURE 5 Polymerization mechanism of PTCDA.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013

have occurred at the dianhydride groups in PTCDA producing perylene-tetraradicals (II), which then polymerized to form polynaphthalene (III). The whisker had neither carboxylic nor carbonyl groups, and the theoretical hydrogen content of III, 3.2%, coincides with the estimated hydrogen content of whiskers synthesized at around 520°C. This result together with the infrared results strongly support the polynaphthalene structure. The structure of form IV in Fig. 5 is the estimated structure of whiskers heat-treated in the higher temperature range. As evidenced from the infrared spectra, a partially aliphatized graphite structure can be assumed. The theoretical hydrogen content of the structure (IV) is 2.0 %. Since the hydrogen contents of whiskers synthesized at 600 and 800°C are 2.4 and 0.9 %, respectively, they are thought to have the structure IV.

Structure of the Whiskers

From results of X-ray, XPS, TEM, and laser Raman measuerments, it was found that the structure of the whisker consisted of three phases; polynaphthalene, amorphous carbon and graphitized carbon. The whiskers which were synthesized at temperatures lower than 550°C mainly consisted of crystalline polynaphthalene. On the contrary, the whiskers synthesized between 550 and 1000°C mainly consisted of partially graphitized amorphous carbon. In the latter whiskers, a graphite like two-dimensional structure was formed as a result of degradation of the polynaphthalene structure. In a temperature range higher than 1000°C, a three-dimensional, graphite-like, layer structure gradually developed. For example, laser Raman spectrum of whisker-550 shows four absorptions at 1295 cm^{-1}(C-C stretching and CH bending mode), 1370 cm^{-1}(disorder-induced line), 1575 cm^{-1}(C=C stretching mode), and 1600 cm^{-1}(Raman-allowed graphite-like E_{2g_2} mode). This result confirms the existence of polynaphthalene structure in the whisker-550.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013

Electrical Conductivity

The room-temperature conductivities measured with the two-point method for whiskers developed in Ar at 530, 600, 800, 1000 and 1200°C were ,respectively, 0.2, 10, 200, 570 and 1100 S/cm without doping. These values are considerably larger than those of conventional carbon fibers. And the conductivities did not change after several months' aging at room-temperature.

Figure 6 shows the temperature dependence of the conductivity measured with the four-probe method for whiskers grown at various temperatures. First, it is noted that the temperature dependence of the conductivity is very small: The ratios of the room-temperature conductivity to that at 30 K for whisker-1000, 800, 600, and 530 were 1.04, 1.14, 2.68 and 5.45, respectively. The second feature is that the conductivity is completely temperature-independent at low temperatures, indicating the existence of a metallically conducting phase which is ascribed to the one-dimensional graphite structure postulated above.[9]

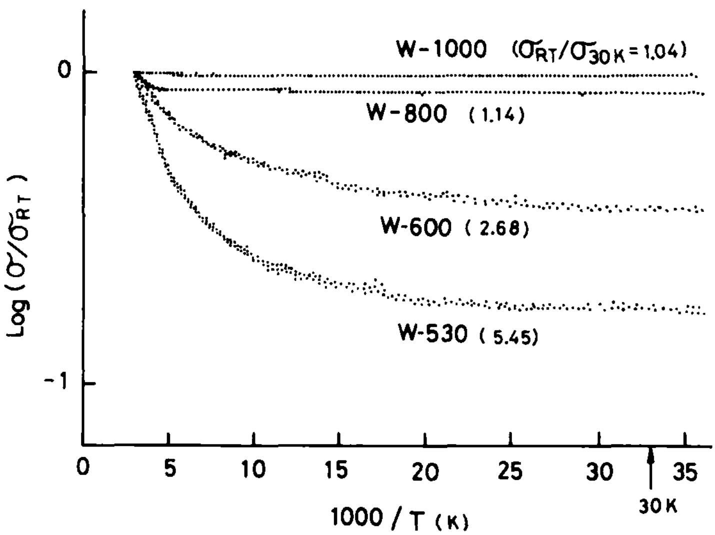


FIGURE 6 Temperature-dependence of conductivity of the whiskers

SUMMARY

The vapor phase polymerization of PTCDA yielded a well-formed one-dimensional graphite polymer which has a high electrical conductivity with metallic nature. An essential difference of the preparation process of this PTCDA whisker from that of conventional carbonaceous materials is that the molecular identity of the starting material is preserved and the graphite structure is formed without passing complete decomposition of the starting material. Some more variety of one-dimensional graphites will be synthesized with other monomers and processes which promote such reaction.

We thank Mr. H. Yasujima and Miss K. Morishita for their skillful experimental assistance, and Drs. Y. Yumoto and S. Mizogami for their keen interest in this work. Thanks are due to Prof. N. Ogata of Sophia Univ. and to Prof. S. Ohtani of Gunma Univ. for their encouragement and helpful suggestions.

REFERENCES

1 T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, Solid State Commun., 44, 823, (1982)
2 M. Kertesz and R. Hoffman, Solid State Commun., 47, 97 (1983)
3 S. Kivelson and O. L. Chapman, Phys. Rev. B, 28, 7236 (1983)
4 K. Tanaka, K. Ohzeki, S. Nankai, and T. Yamabe, J. Phys. Chem. Solids, 44, 1069 (1983)
5 K. Tanaka, K. Ueda, T. Koike and T. Yamabe, Solid State Commun., to be published.
6 M. L. Kaplan, P. H. Schmidt, C. H. Chen, and W. M. Walsh, Jr., Appl. Phys. Lett., 36, 867 (1980)
7 T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, J. Phys., Colloq. 1983 (C3, Conf. Int. Phys. Chim. Polym. Cond., 1982), 645.
8 A. Oberlin, M. Endo, and T. Koyama, J. Cryst. Growth, 32, 335 (1976)
9 M. Murakami, H. Yasujima, Y. Yumoto, S. Mizogami, and S. Yoshimura, Solid State Commun., 45, 1085 (1983)

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:45 20 February 2013