Synthesis of Poly-*peri*-naphthalene by Vapour-phase Polymerization: an Approach to a One-dimensional Graphite

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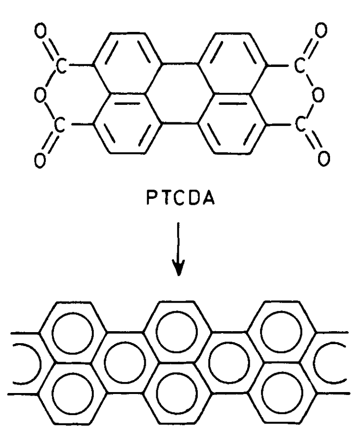
Very fine whiskers grown *via* vapour-phase polymerization of 3,4,9,10-perylenetetracarboxylic dianhydride have a poly-*peri*-naphthalene structure.

One-dimensional graphite polymer is expected to have unusual physical properties because of its unique molecular structure. Quantum mechanical calculations have been performed on various hypothetical one-dimensional graphite polymers, such as polyacene,[1] polyphenanthrene,[2,3] or polyacenacene,[4] and it has been suggested that some will exhibit metallic conductivity or even high-temperature superconductivity.[3] Although there have been attempts to prepare such polymers,[5,6] a well-defined molecular structure has not yet been obtained.

We report here vapour-phase polymerization of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) at elevated temperatures, presenting a new approach to the preparation of poly-*peri*-naphthalene.[5]

A pressed pellet (13 mm diameter and 1.5 mm thick) of PTCDA was placed in a quartz tube and heated under argon or argon–hydrogen gas flow (200 cm^3 min^{-1}) using an i.r. radiation furnace. The light from four quartz light sources on the furnace was focused on the centre of the pellet with elliptical, gold-plated reflection mirrors. The temperature was raised at a constant rate of 10 °C min^{-1} to a predetermined temperature (T_p) where the pellet was heat-treated for a further hour. Very fine whiskers, less than 10 mm in length, grew on the pellet when T_p was higher than 520 °C.



Scanning electron microscopy (SEM) indicated that the whiskers had an unusual morphology. The whiskers were flat ribbons with well-shaped rectangular cross sections of (0.1—0.2) × (0.4—4) μm^2. The angular nature of the whisker was much more pronounced when grown in a hydrogen containing argon atmosphere. Figure 1 shows an SEM picture of the whisker grown in Ar–H_2 (3 : 2 by volume) at 800 °C. Since the shape of the whisker differs substantially from that of conventional carbon fibres including benzene-derived carbon

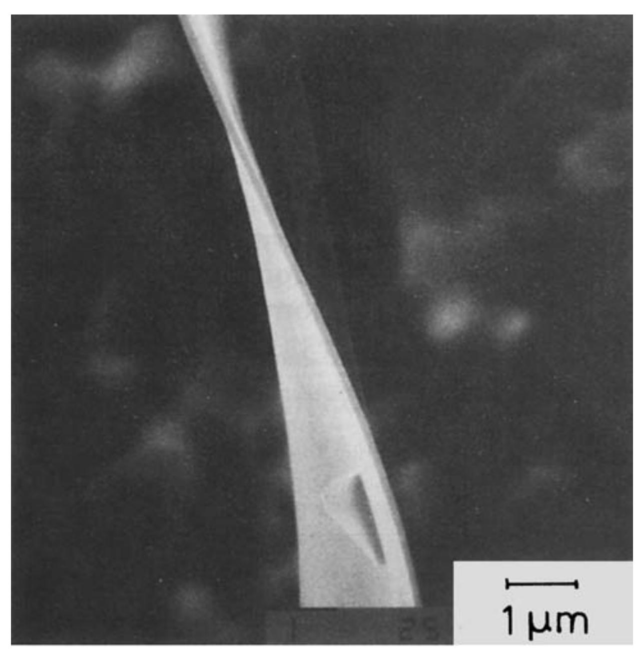


Figure 1. A SEM picture of a PTCDA whisker grown in an argon–hydrogen atmosphere at 800 °C.

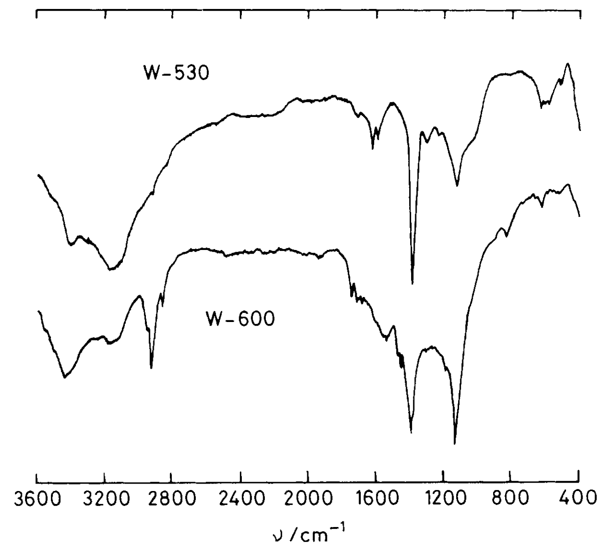


Figure 2. Fourier transform–i.r. spectra of whiskers grown at 530 °C and 600 °C in an argon atmosphere.

fibres[7] and the whisker grows at very low temperatures without a catalyst, the mechanism of reaction and growth of this new whisker will be entirely different from that of ordinary carbonization reactions.

The temperature at which the whisker started to grow (520 °C) was just above the decomposition temperature of the PTCDA (516 °C) as evidenced from thermogravimetric analysis. The decomposed products are thought to vaporise and condense to construct the whisker. SEM pictures of a whisker grown over a very short period strongly suggest vapour-phase polymerization.

I.r. spectra of the whiskers grown at 530 °C (W-530) and 600 °C (W-600) are shown in Figure 2. The spectrum of W-530 has absorptions due to aromatic $\nu_{(C=C)}$ (1593 cm^{-1}) and aromatic $\nu_{(CH)}$ (1400 and 1125 cm^{-1}) but no appreciable absorptions based on C–O–C, C=O, and –C(=O)–O–C(=O)–. The spectrum of W-600 was almost identical with that of W-530 except for absorptions at 2925 and 2854 cm^{-1} [aliphatic $\nu_{(CH_2)}$].

The hydrogen content in the whiskers decreased with increasing T_p. *E.g.*, the contents for whiskers grown at 550, 600, 800, and 1000 °C were 2.9, 2.4, 0.9, and 0.4%, respectively. Since a sufficient amount of W-520 has not been obtained at this stage, we cannot directly determine the hydrogen content of the whisker. However, we estimate the hydrogen content to be 3.2% by extrapolating the data to 520 °C, which agrees well with a calculated composition of theoretical poly-*peri*-naphthalene (C, 96.8; H, 3.2%).

From these results, we conclude that the formation of the poly-*peri*-napthalene structure is facilitated by the condensation of perylene tetraradicals. The whiskers developed at higher temperatures may have a graphitized structure with alicyclic parts as a result of hydrogenation and hydrogen migration.[8]

In summary, the vapour-phase polymerization of PTCDA yielded poly-*peri*-naphthalene condensed into very fine whiskers of unique morphology. An essential difference in 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 polyacenic structure is formed without complete decomposition of the starting material.

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References

1 T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, *Solid State Commun.*, 1982, **44**, 823.
2 M. Kertesz and R. Hoffman, *Solid State Commun.*, 1983, **47**, 97.
3 S. Kivelson and O. L. Chapman, *Phys. Rev. B*, 1983, **28**, 7236.
4 K. Tanaka, K. Ohzeki, S. Nankai, and T. Yamabe, *J. Phys. Chem. Solids*, 1983, **44**, 1069.
5 M. L. Kaplan, P. H. Schmidt, C. H. Chen, and W. M. Walsh, Jr., *Appl. Phys. Lett.*, 1980, **36**, 867.
6 T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, *J. Phys. (Paris), Colloq.*, 1983 (C3, Conf. Int. Phys. Chim. Polym. Conduct., 1982), 645.
7 A. Oberlin, M. Endo, and T. Koyama, *J. Cryst. Growth*, 1976, **32**, 335.
8 Y. D. Park, A. Oya, and S. Otani, *Fuel*, 1983, **62**, 1499.