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Z. Iqbal^a, D. M. Ivory^a, J. Marti^b, J. L. Brédas^b & R. H. Baughman^a

^a Allied Corporation, Corporate Technology, Morristown, NJ, 07960, USA

^b Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, B-5000, Namur, Belgium

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THE SYNTHESIS, PROPERTIES AND STRUCTURE OF POLY(PERI-NAPHTHALENE):
A CONDUCTING, UNDOPED ORGANIC POLYMER

Z. IQBAL[†], D.M. IVORY[†], J. MARTI[†], J.L. BRÉDAS^{††}
and R.H. BAUGHMAN[†]

[†] Allied Corporation, Corporate Technology,
Morristown, NJ 07960, USA

^{††} Laboratoire de Chimie Théorique Appliquée, Facultés
Universitaires Notre-Dame de la Paix, B-5000 Namur, Belgium.

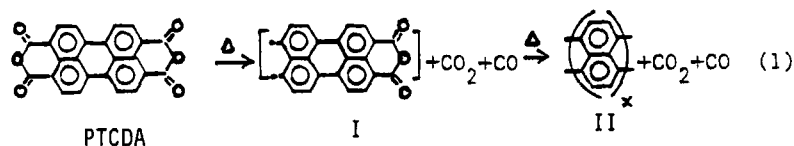
Abstract

The synthesis of ribbons of a highly conducting, undoped organic polymer by the pyrolysis of 3,4,9,10-perylene-tetracarboxylicdianhydride is described. The conductivity is not decreased upon exposure to selected donor or acceptor dopants, suggesting that the high observed conductivity is not due to a charge-transfer complex. Elemental analysis and infrared and Raman spectroscopies are consistent with structural assignment as poly(peri-naphthalene), PPN. However, observed diffraction patterns are not consistent with crystal structure derived for this polymer using model compounds. Furthermore, these patterns are quite similar to that obtained for a variety of pyrolyzed aromatic organic molecules, suggesting substantial reaction that is of a statistical nature. Quantum chemical calculations are presented for structurally ideal PPN, which suggest a small (0.3 eV) or vanishing bandgap, depending upon the precise molecular geometry and the nature of interchain coupling.

INTRODUCTION

Kaplan et al¹ were first to report that the pyrolysis of 3,4,9,10-perylenetetracarboxylicdianhydride (PTCDA, cf. eq.1) in vacuum at temperatures between 700° and 900°C yielded conducting ($\sigma_{RT} \approx 250 \text{ S cm}^{-1}$) films. Subsequent work^{2,3} established that conducting material could also be produced by electron or argon-ion beam bombardment of PTCDA. The thin films produced on pyrolysis appeared amorphous in x-ray diffraction, but did evidence electron diffraction lines. Chemical analysis of the thin films obtained by pyrolysis typically yielded 99.2% C and 0.7% H, corresponding to about $\text{C}_{10}\text{H}_{0.8}$. Hence, a partially graphitized molecular structure was suggested by the elemental analysis of the films.

We have reinvestigated the pyrolysis reaction of PTCDA with the aim of ascertaining conditions under which poly(peri-naphthalene) (PPN) could be synthesized. This might occur according to the following scheme:



Intermediate I in the above scheme is the monoanhydride di-radical. Under certain conditions, we have been able to isolate crystals of perylenedicarboxylic monoanhydride (the hydrogenated analog of diradical I). PPN will be used in the present work to denote the idealized product II as well as the reaction product obtained by the pyrolysis of PTCDA, which appears to be partially graphitized product II. We also obtain ribbons of a polymeric product which evidence a carbon/hydrogen ratio, and infrared and Raman spectroscopies consistent with PPN. However, diffraction studies suggest a crystal structure stabilized by significant reaction in more than one direction. In addition to these results, we will report quantum chemical calculations for structurally perfect PPN. Murakami and Yoshimura⁴ have independently reported at this conference the synthesis of PPN ribbons.

SYNTHESIS AND PROPERTIES:

PPN (product II, eq. 1) was prepared by the pyrolysis of PTCDA. The pyrolysis was carried out in a quartz tube (2.5 cm in diameter) containing PTCDA in a ceramic boat, which was placed inside a Lindberg furnace. The samples reported on here were prepared in a flow of either 100% Ar, 100% H₂, or a 90%-10% Ar-H₂ mixture. The starting material consisted of a pressed pellet of purified PTCDA or vapor-grown crystals of PTCDA. The temperatures in the pyrolysis zone ranged from 530° to 900°C and were maintained to within + 5°C during the course of each experiment. Pyrolysis times were typically from 1 to 24 hrs. Whisker-like crystals of PTCDA were grown under vacuum at 450°C and were also formed at the cooler end of the tube during pyrolysis. Smaller, woolly deposits were obtained at even cooler wall temperatures (~120°C), particularly when the PTCDA vapors were allowed to pass through a platinum gauze. The latter analyzed as the monoanhydride analog of PTCDA, with a crystal structure that is quite different from that of PTCDA⁵. Metallic-grey, ribbon-like growths of PPN between about 0.03 mm and a few millimeters in length grew on the surfaces of the PTCDA pellets and crystals during pyrolysis. Black, powder-like material, which gave the

same electron diffraction lines as the ribbons, was found co-mingled with the ribbons. Thin, metallic films were also deposited on the boat and walls of the quartz tubes. The properties of these films, which we believe to contain a chemically modified form of PPN, were found to be similar to that reported by Kaplan et al.¹ Pellets of PPN gave room temperature four-point probe conductivities ranging from 10^{-2} S cm⁻¹ at T_p (pyrolysis temperature) of 530°C to 15 S cm⁻¹ at a T_p of 800° and 900°C. The conductivities of PPN samples prepared at various temperatures were unchanged upon exposure to compensating agents such as NH₃ and benzoquinone, thus suggesting that the observed conductivity is intrinsic and not due to some doping process during synthesis. The C,H and O contents of representative samples are: for $T_p=530^\circ\text{C}$, C=93.5, H=3.2, O=4.1%; for $T_p=700^\circ\text{C}$, C=96.32, H=2.95 and O=0.8%; for $T_p=900^\circ\text{C}$, C=96.95, H=2.92, O<0.5%. The theoretical composition for PPN is C=96.77, H=3.23%. The chemical analysis results were independent of the carrier gas used in the synthesis. Thus, the chemical analysis for the samples prepared at 700°C and 900°C correspond closely with that of poly(peri-naphthalene) with formula (C₁₀H₄)_x. The 4.1% oxygen in the sample obtained at a T_p of 530°C remained unchanged even after the sample had been annealed at 500°C in a 10^{-2} - 10^{-3} Torr dynamic vacuum for 3 hours. This indicates that the oxygen content cannot be associated with unreacted PTCDA in the sample. Raman and x-ray diffraction analyses are also consistent with this conclusion. Infrared spectra on the annealed sample show the presence of two broad features at 1725 and 1765 cm⁻¹, attributable to C=O groups. Consistent with our conclusion above, these lines are shifted to lower frequencies compared with PTCDA and hence cannot be due to unreacted starting material. These results are consistent with bonding of the oxygen at the chain ends of short segments (corresponding to 18 naphthalene units for $T_p=530^\circ\text{C}$) of the PPN polymer.

The FTIR spectra also show three broad features located at 1570, 1385 and 1325 cm⁻¹, which are assignable to aromatic ring vibrations, and lines of medium intensity at 805 and 765 cm⁻¹, which are associated with aromatic C-H out-of-plane vibrations. The Raman spectrum shows only two features: these are located at 1594 and 1352 cm⁻¹ and correspond to the infrared lines at 1570, 1385 and 1325 cm⁻¹.

MORPHOLOGY

The ribbons were examined using both high resolution optical and electron microscope techniques. Figs. 1(A) and (B) show scanning electron micrographs of a ribbon grown at 530°C in argon. Striations on the faces are evident and in micrograph 1(B), which shows an edge-on view of the end of a ribbon, the hollow

ends of the ribbon can be seen. The transmission electron micrograph of a segment of a ribbon from the same batch Fig. 1(C) shows herring-bone striations running across the ribbon width. An electron diffraction pattern is observed with a strong 3.54 Å spacing oriented approximately orthogonal to the direction of the striations. Under higher magnification in the electron microscope, the striations resolve into layered, fiber-like bundles 1000 Å apart [Fig. 1(D)]. Similar results are obtained for ribbons grown at 900°C.

Similar whisker-like growth on the surface and an overall crystal shape unchanged from that of the precursor crystal is observed when a vapor grown crystal of PTCDA is sealed in argon in a quartz melting-point tube and pyrolyzed at 530°C for 1 hour. This suggests that the polymerization process occurs at least partially in the solid state. More detailed studies on the nature of the solid state polymerization are in progress.

STRUCTURE:

Fiber-type electron diffraction patterns were obtained from ribbons grown under different conditions. The d-spacings of the observed reflections together with those observed via x-ray diffraction on a pellet pyrolyzed at 530°C in an Ar-H₂ atmosphere are listed in Table I (the 9.9 Å line is at too long a spacing to be observed by standard electron diffraction methods). Except for the long spacing observed in x-ray diffraction, both the x-ray and electron diffraction patterns were independent of the T_p of the samples. Lines in the electron diffraction pattern are assigned as equatorial and meridional in Table I in terms of the morphology discussed earlier, where fibers were found to run approximately orthogonal to the ribbon-axis direction.

TABLE I. Summary of diffraction data

X-ray		d-spacing in Å		Electron Diffraction	
9.9	(24)††				
3.55	(100)			3.54	Et (very strong)††
2.09	(50)			2.10	M (strong)
1.72	(22)			1.80	E (weak)
1.22	(22)			1.21	M (medium)
				1.08	(weak)
				0.79	(very weak)
				0.70	(very weak)
				0.60	(very weak)

† E - equatorial or near equatorial, M - meridional or near meridional; †† Relative Intensities

Note, that the observed meridional spacing of 2.1 Å is about equal to one-half of the expected chain axis repeat of PPN (4.33 Å), which is derived from the geometry of quaterrylene. Note, however, that a reflection with about that same spacing appears for graphite and for partially graphitized hydrocarbons. Also note that, with the exception of the longest spacing, the observed diffraction lines can be tentatively indexed as harmonics of interplanar spacings at 3.5, 2.1 and 1.2 Å. Moreover, Murthy⁶ has pointed out that the x-ray diffraction patterns of PPN are very similar in line positions and relative intensities to that obtained for the pyrolysis products of a variety of aromatic hydrocarbons. The long spacing observed in the x-ray diffraction data at 9.9 Å is the molecular center-to-center separation predicted for coplanar poly-(peri-naphthalene) molecules in van der Waals contact (9.0 Å). One interpretation of these results is that poly(peri-naphthalene) chains are stacked coplanar in a layer and that the separation between each layer is about 3.55 Å.

In order to stabilize such a packing mode, some interchain crosslinking within layers would be necessary. The disappearance of the 9.9 Å line after annealing at higher temperature (~900°C), coincident with major increases in electrical conductivity, would then suggest increased interchain crosslinking (partial graphitization) so that the in-plane interchain separation is no longer observable. Consistent with these speculations, the observed diffraction lines are not consistent with molecular packing modes for PPN derived either from the dimeric structures of perylene and quaterrylene or the monomeric structure of perylene⁷.

THE BAND STRUCTURE:

The band structure of structurally ideal PPN has been computed by means of the Valence Effective Hamiltonian (VEH) technique.⁸ The VEH method has been shown to provide very good estimates for ionization potentials, bandwidths, and even bandgaps in a very large number of conjugated polymers.⁹

In the preliminary calculations reported in this paper, the PPN chain geometry has been chosen to correspond to that determined by x-ray diffraction on quaterrylene.⁷ The chain is considered to be perfectly coplanar since only very small departures from planarity are observed in quaterrylene. The solid-state ionization potential is calculated to be of the order of 4.0 eV, i.e. similar to that in polypyrrole. As expected, the highest occupied (HOMO) and lowest unoccupied (LUMO) bands are π bands. The HOMO band has a very large width of about 4.4 eV. This is about one-third smaller than in polyacetylene (PA), but one-third larger than in poly(para-phenylene).⁹

With the geometry we have used and considering isolated chains, the predicted bandgap is very small, 0.3 eV, although not vanishing. The reason for having a bandgap tending to zero in PPN can be found in a detailed analysis of the band structure.¹⁰ The LCAO coefficients for the HOMO and the LUMO are indeed anti-symmetric with respect to the mirror plane which is both parallel to the chain axis and perpendicular to the plane of the molecule. Therefore, by symmetry, the LCAO coefficients on the carbon atoms located on that mirror plane in the middle of the molecule do vanish. As a result, contributions to the HOMO and LUMO only come from the atoms on the periphery of the chain. This leads to the observation that PPN can be considered as formed by two interacting cis-polyacetylene chains. The interaction between the two cis-PA subunits in PPN provokes the splitting of the original cis-PA HOMO and LUMO bands, resulting in a much smaller band gap than in cis-PA. In this context, reduction of the bandgap to vanishing values can be expected if the actual chain geometry is such that: (i) the cis-PA subunits are closer to one another than in the geometry we have considered, thereby causing a larger splitting of the original cis-PA bands; and/or (ii) the degree of bond length alternation along the cis-PA subunits is smaller than the 0.08 Å value observed in quaterrylene.

Three-dimensional effects can also be very important in decreasing the bandgap value. A preliminary calculation indicates that the gap is reduced to zero when the chains of PPN lie on top of each other with superimposed carbon atoms and an interplanar spacing of 3.4 Å.

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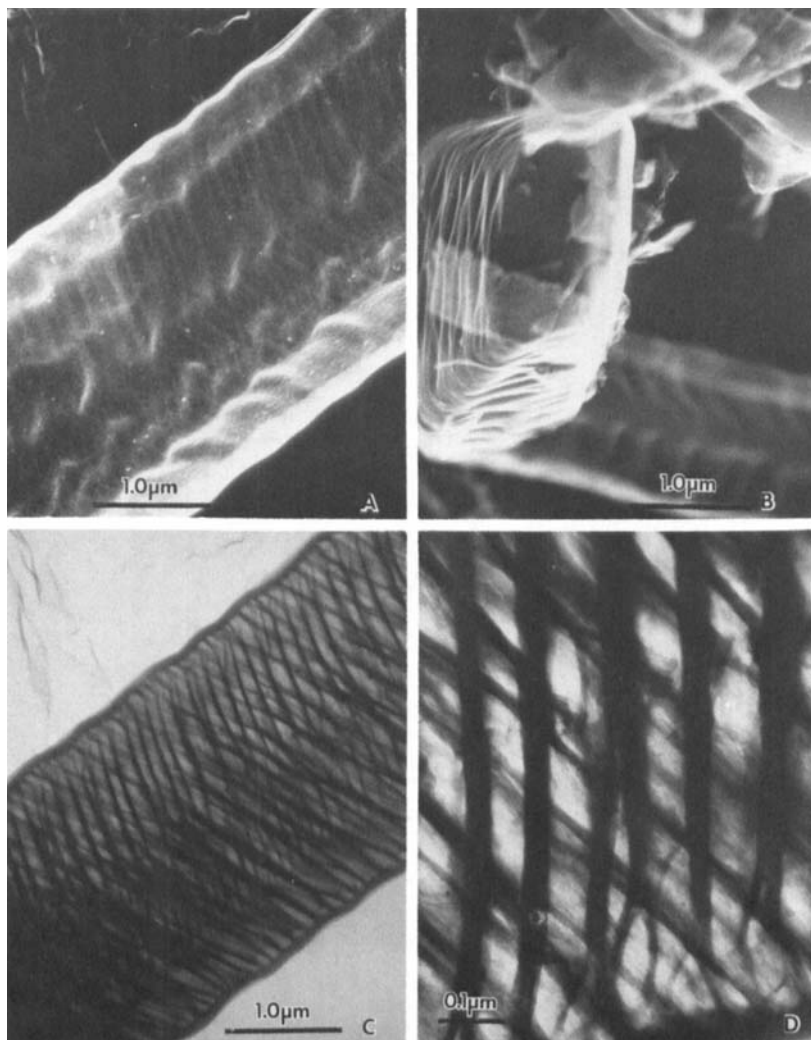


FIG. 1 See text for details