polymer reports

Morphology of poly*para*phenylene powders and pellets

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Semiconducting organic polymers have recently gained new interest since the synthesis of high quality films of polyacetylene by Ito, Shirakawa and Ikeda[1]. Observations that its conductivity can be changed many orders of magnitude by doping with acceptors and donors, led to much study[2]. Some authors have reported on other organic semiconductors, namely, polyparaphenylene[3], polypyrrole[4] and poly(paraphenylenevinylene)[5] which showed similar properties.

In our search for stable conducting materials, we have been investigating polyparaphenylene and we wish to report on the morphology of powders and pellets, showing some interesting features.

Polyparaphenylene was synthesized by the method described by Kovacic *et al.*[6]. Extensive purifications were performed on the crude polymer according to the known sequence[6]. I.r. and X-ray data have confirmed the nature of the product. Analysis performed on the purified materials gave the following contents: Non-annealed product: Cl ≃ 2%, Al ≃ 0.4%, Cu ≃ 0.1%; Annealed for 24 h at 400°C: Cl ≃ 0.8%, Al ≃ 0.2%, Cu ≃ 0.01%.

Three different series of powders were examined with a binocular microscope, namely, non-annealed powder, powder annealed for 24 h at 400°C in an oven under nitrogen flow, powder annealed for 7 days under the same conditions. All the samples showed the same morphology, an example of which is given in *Figure 1* where the powder annealed for 7 days is represented.

Pellets were made from the three series of powders under pressure (800–850 MPa) at room temperature. The surface of the pellets, observed with the microscope, demonstrated a somewhat different behaviour according to the heat treatment on the mother powder. The non-annealed powder resulted in pellets with a smooth shiny surface, but showed some darker rectangular domains randomly oriented. The 24 h annealed powder gave pellets with a rather rough surface as compared with the previous ones and also prominent rods which tended to appear. In the last series (7 days annealed powder) the pellet surface was quite rough with rods sticking out from the plane without any preferential orientation. The compacity of these pellets remained low, about half of what usually resulted even after a few hours under pressure. Their gross density was ~0.7, instead of 1.23 for the pellets made from non-annealed powder (the crystal density being estimated to 1.39 [3]). They tended to expand in thickness by a factor of 0.2 on standing and looked very loose afterwards.

The rods, seen on the surface of pellets, made from the 7 days annealed powder, were already observed in annealed as well as non-annealed powders. Their dimensions ranged from 300 to 500 μm in length and 50 to 100 μm in diameter. They were soft in the crude powder and became harder with longer heat treatment (*Figure 1*).

In order to further clarify the process leading to an enhancement in rod hardness, microhardness measurements were carried out on the pellets resulting from compaction of as-obtained heat treated powders. The results are given in *Table 1*.

A large increase in microhardness can be seen when going from regular pellets to annealed pellets and to pellets made from 7 days-annealed powder. Within these pellets the dark regions (as observed under the microscope), corresponding to the hard rods of the mother powder, presented a further increase in microhardness by a factor of 5 as compared with the former untreated pellets. These pellets could be disaggregated by solvents (alcohol or acetone) leaving dispersed rods unchanged in shape, whereas no disaggregation occurred with the

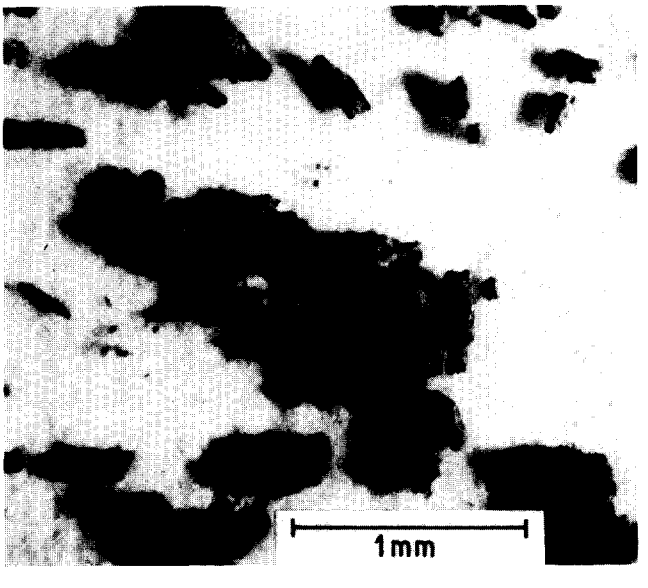

Figure 1 Powder annealed for 7 days under nitrogen at 400°C (X30): rod surrounded with micropowder

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Table 1 Results of microhardness measurements

Sample	Pellets compacted from as-obtained powder (800 MPa)	Pellets made from as obtained powder (800 MPa) then annealed at 400°C for 24 h	Pellets made from 7 days annealed powder (820 MPa)	
			Clear regions*	Dark regions*
Micro-hardness (Vickers) MH_V	600–700 MPa	≃1500 MPa	1000–1400 MPa	3000–5000 MPa

* Pellets showed definitive difference between dark regions corresponding to the hard rods seen in the mother powder and clear regions of less organized materials

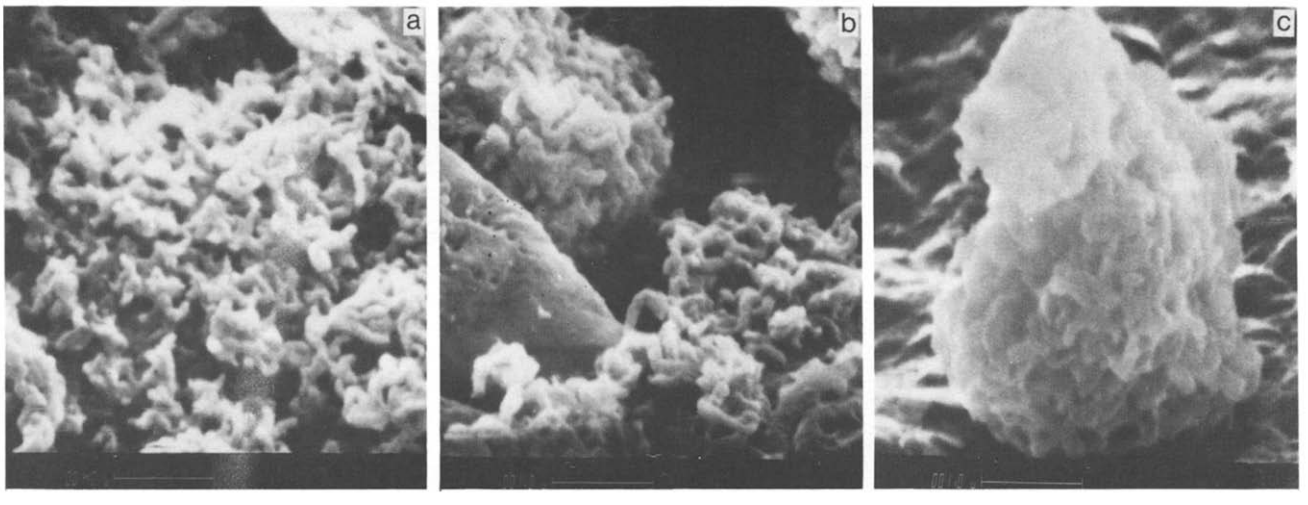

Figure 2 Scanning electron micrographs of polyparaphenylene powders (a): area with matched fibrils (X 20 000); (b): area with fibrils and globular structures (X 20 000); (c): globular structure showing the fibrils packed together (X 20 000)

pellets made from non-annealed powders.

Scanning electron micrographs were taken on the three different powders to see if any differences existed between the various samples. But the same fibrous structure was observed throughout the specimens with matched fibrils ~1000 Å in diameter (*Figures 2a* and *2b*). The rods detected in the powders presented a similar morphology suggesting no fundamental difference between the organized regions and the rest of the powders. Occasional globular structures, a few μm in diameter, as shown in *Figures 2b* and *2c*, suggested packing of fibrils with less voids in between. No difference at this level arising from the comparison of the samples, whatever their thermal history, two possibilities are left to account for the increase in rod hardness. The first is that we may be dealing with an enhancement in crystallinity, the second possibility may be in a change at the molecular level of polyparaphenylene.

Some X-ray determinations were performed on the different powders or on the pellets made from these powders. No orientation was discerned within the pellets or the rods themselves. Several conclusions may be drawn from the results appreciated in terms of half width of the strongest reflection ($\theta \simeq 9.80°$ with the diffractometer Cu $K\alpha_1$ radiation).

The crystallinity increased by annealing the powders under the conditions previously described[7] as shown in *Figure 3* where the diffractograms of crude (*Figure 3a*) and 7 days-annealed powder (*Figure 3b*) are represented. Almost no change in crystallinity appeared after compaction of this 7 days-annealed powder into a free standing pellet (820 MPa) as represented in *Figure 3c*.

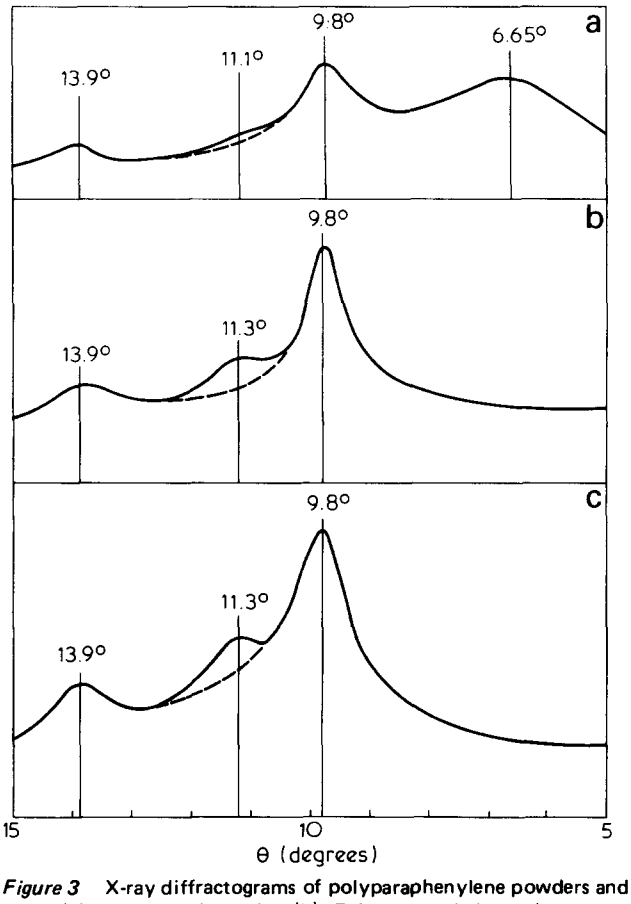

Figure 3 X-ray diffractograms of polyparaphenylene powders and pellet (a): as-obtained powder; (b): 7 days-annealed powder; (c): pellet made from 7 days-annealed powder

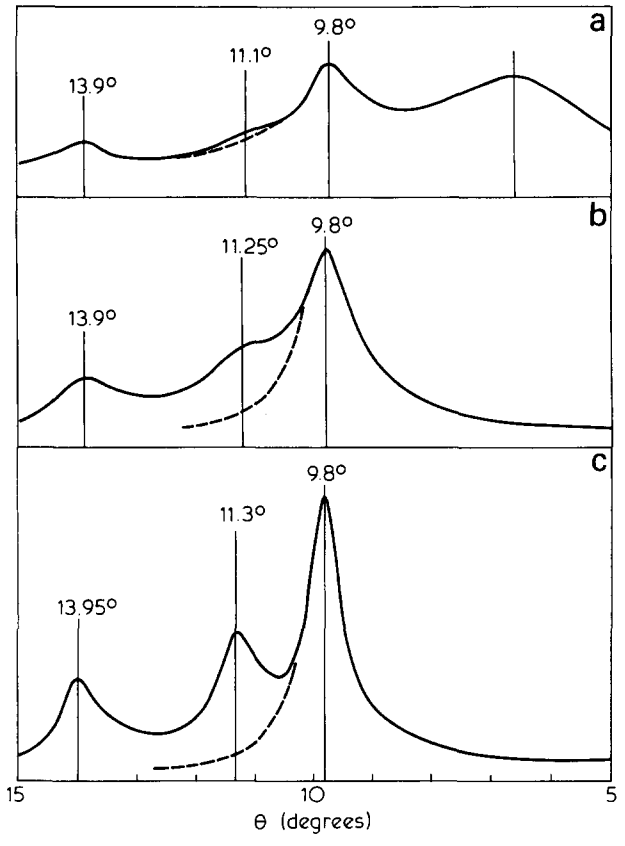

Figure 4 X-ray diffractograms of polyparaphenylene powder and pellets: (a): as-obtained powder; (b): pellet made from the as-obtained powder; (c): annealed pellet made from the as-obtained powder

The crystallinity increased as well, by compaction of the crude powder[8] into a pellet (*Figure 4b*) but annealing of this pellet enhanced the final crystallinity markedly (*Figure 4c*). These results indicate that the best sequence in terms of final crystallinity of polyparaphenylene pellets is, first, compaction of crude powder, and then annealing of pellets.

In conclusion, it seems that we are dealing with an organization at several levels within polyparaphenylene powders. All the powders show the same feature under a microscope: rods surrounded with unorganized microscopic powder. The rods are constituted by fibrils more or less matched or packed in globular structures. Thus annealing of powders does not change their morphology. But the same treatment can be correlated with an increase in microhardness which does not go along with a crystallinity enhancement since an annealed pellet made from crude powder shows higher crystallinity and lower hardness than a pellet made from annealed powder. Therefore it seems that the process of annealing leads to definitive differences between powder and pellet and we may suspect the occurrence of crosslinking in the case of powder annealing which would account for the observed enhancement in microhardness. Further work is under progress to elucidate this problem.

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REFERENCES

1 Ito, T., Shirakawa, H. and Ikeda, S. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 11
2 For a review, see: Seeger, K. and Gill, W. D. *Colloid and Polym. Sci.* 1980, **258**, 252–260; Shirakawa, H. Busseiken Dayori, 1980, **19 (6)**, 9–10
3 Shacklette, L. W., Chance, R. R., Ivory, D. M., Miller, G. G. and Baughman, R. H. *J. Synthetic Metals* 1979, **1**, 307–320
4 Kanazawa, K. K., Diaz, A. F., Geiss, R. H., Gill, W. D., Kwak, J. F., Logan, J. A., Rabolt, J. F. and Street, G. B. *J. Chem. Soc., Chem. Comm.* 1979, 854
5 Wnek, G. E., Chien, J. C. W., Karasz, F. E. and Lillya, C. P. *Polymer* 1979, **20**, 1441
6 Kovacic, P. and Kyriakis, A. *J. of Am. Chem. Soc.* 1963, **85**, 454; Kovacic, P. and Oziomek, J. *Macromol. Synth.* 1966, **2**, 23-24
7 Gale, D. M. *J. Appl. Polym. Sci.* 1978, **22**, 1955-69
8 Maurice, F. Rapport de DEA, Universitè de Paris VI, 1980