

# Equilibrium size distribution of microparacrystals in polymers

A. M. Hindeleh

Department of Physics, University of Jordan, Amman, Jordan

and R. Hosemann

Gruppe Parakristallforschung, c/o BAM, Berlin, W. Germany

(Received 30 October 1981)

On the basis of the physical meaning of the  $\alpha^*$  law, a theoretical approach to the determination of the equilibrium size distribution of microparacrystals is presented, and the findings are in excellent agreement with the experimental observation of the size distribution of microparacrystals in a real polymer, PPT fibres, recorded by high-resolution transmission electron microscopy.

**Keywords** High-resolution electron microscopy; lattice fringes; X-ray diffraction, PPT fibres;  $\alpha^*$  law; microparacrystals; paracrystalline distortion; microparacrystal equilibrium state

The theory of paracrystals introduces 18 new statistical parameters into the conventional crystallography which destroy the long range order of a crystalline lattice<sup>1-5</sup>. Refining Debye's old idea of 'a priori probability functions' in liquids<sup>6</sup>, three new a priori statistics  $H_r(x)$  ( $r=1,2,3$ ) expand the correlation function  $z(x)$  of a liquid-like distorted point lattice.  $\frown$  is the symbol of convolution (folding).

$$z(x) = \sum_{p_1=-\infty}^{+\infty} \overset{-p_1\text{-times}}{\frown} \overset{-p_2\text{-times}}{\frown} \overset{-p_3\text{-times}}{\frown} P \overset{\frown}{H_1} \overset{\frown}{H_1} \dots \overset{\frown}{H_1} \overset{\frown}{H_1} \overset{\frown}{H_2} \overset{\frown}{H_2} \dots \overset{\frown}{H_2} \overset{\frown}{H_2} \overset{\frown}{H_3} \overset{\frown}{H_3} \dots \overset{\frown}{H_3} \quad (1)$$

$$\overset{\frown}{H} \overset{\frown}{H}(x) = \int H(y)H(x-y)dy^3$$

Figure 1 shows a computer constructed two-dimensional paracrystalline lattice<sup>4</sup>. With a growing lattice the statistical fluctuations finally become so large that the construction is halted (see arrow in Figure 1). The diffraction pattern of this model shows an increase in the integral widths of the reflections proportional to the square of the order of reflection, typical of the diffraction patterns of real polymers. Figure 2 shows a plot of the integral widths  $\delta b$  of the reflections 002, 004 and 006 of a PPT fibre (PRD 49) where  $\delta b$  again increases quadratically with higher orders of reflection<sup>7</sup>. From the slope of the curve one calculates the statistical fluctuation  $g$  of netplane distances  $\bar{d}$ . The average number  $\bar{N}$  of netplane layers can be obtained from the intercept of the curve with the ordinate

$$\delta b = \frac{1}{\bar{d}} \left( \frac{1}{\bar{N}} + (\pi g h)^2 \right) \quad (2)$$

$$g = (\bar{d}^2 / \bar{d}^2 - 1)^{1/2} = 0.021;$$

$$\bar{N}_{002} = 59$$

In Figure 3,  $\sqrt{\bar{N}}$  is plotted against  $1/g$  for other microparacrystals including PRD 49.  $\sqrt{\bar{N}}$  is proportional

to  $\alpha^*/g$  and  $\alpha^*$  varies between 0.1 and 0.2 in paracrystalline materials:

$$\sqrt{\bar{N}} = \alpha^*/g \quad (3)$$

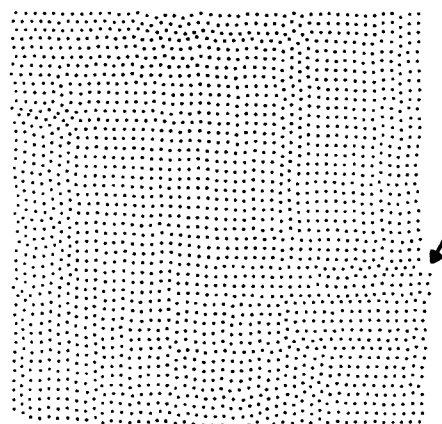


Figure 1 Computer-drawn two-dimensional paracrystal drawn by a Monte-Carlo-method with  $g = 0.02$  and  $N = 49$ , similar to  $g$  for PPT-fibres. The arrow indicates the break down of the construction

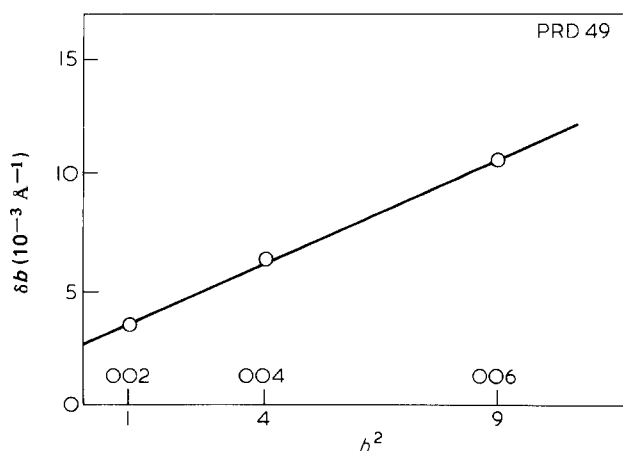


Figure 2 The  $\delta b-h^2$  plot of the reflections 002, 004 and 006 of PPT fibres of DuPont (PRD 49) with  $\bar{N}_{002} = 59$  and  $g = 0.02$

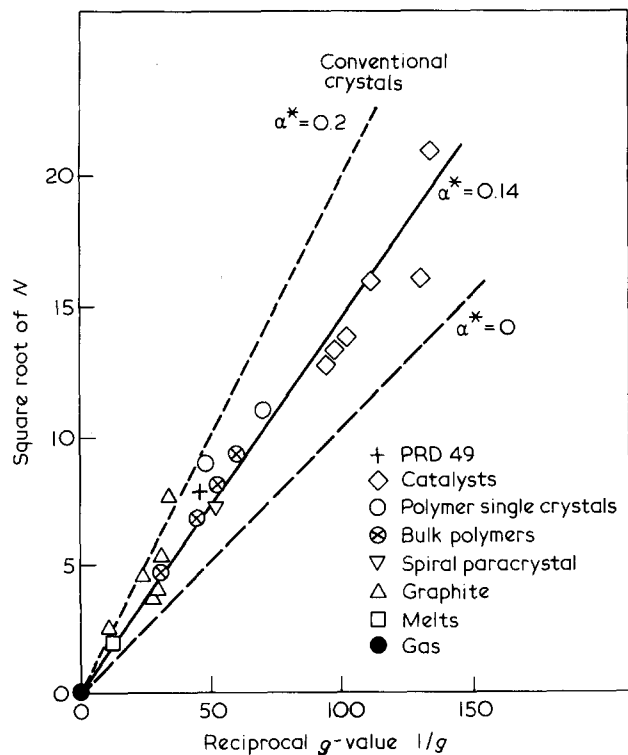


Figure 3 The  $\alpha^*$ -law, see text and equation (3)

For PRD 49,  $\alpha^* = 0.16$ . The  $\alpha^*$ -law<sup>4,8</sup> is regarded as fundamental. The synthetic paracrystal in Figure 1 also fits nicely into the assembly of natural microparacrystals (see the symbol  $\nabla$ ) and it has  $g = 0.02$  and  $N = 49$ , close to the values of PRD 49.

The physical meaning of the  $\alpha^*$ -law is that with growing microparacrystals the distortions at the boundary-netplanes reach to the extent that the binding angles of the atoms are overstrained and the netplane breaks. For PRD 49,  $\bar{N}_{002}$  along the fibre axis is about five times greater than  $\bar{N}_{110}$  or  $\bar{N}_{200}$ <sup>7,11,12</sup>. Using this idea one can calculate the number of atoms whose distance from the mean netplane exceeds a certain value  $\beta^*$ <sup>9</sup>.

Integrating over all dislocations larger than  $\beta^*$  one obtains, with the help of convolution integrals, the probability  $W(N)$  that such stopping units exist at microparacrystals with  $N$  netplanes

$$W(N) = \frac{2}{\sqrt{\pi}} \int_{\frac{1}{2}(\frac{\beta^*}{g})/\sqrt{N}}^{\infty} e^{-z^2} dz \quad (4)$$

The growing probability  $E(N)$  of an  $N$ -microparacrystal is therefore given by the following error integral:

$$E(N) = 1 - W(N) = \frac{2}{\sqrt{\pi}} \int_0^{\frac{1}{2}(\frac{\beta^*}{g})/\sqrt{N}} e^{-z^2} dz \quad (5)$$

The smaller  $g$  and  $N$  and the larger  $\beta^*$ , the higher is the probability that the netplane  $N+1$  would grow. The frequency distribution  $H(N)$  of an assembly of microparacrystals in the equilibrium state is therefore

given by

$$H(N) = E(1)E(2)E(3)\dots E(N)W(N+1) \quad (6)$$

Such statistics were calculated for the average value  $\bar{N} = 11$  and  $\bar{N} = 62$ . They are drawn in Figure 5 and approximated by Maxwellian functions with an exponent  $n = 3$  and 6. One can see that the polydispersity  $(\bar{N}^2/\bar{N} - 1)^{1/2}$  decreases with increasing  $\bar{N}$ . PPT-fibres produced by DuPont<sup>10</sup> are relatively less sensitive to the electron beam in the transmission electron microscope than other organic polymers. Dobb *et al.*<sup>11,12</sup>, at Leeds University, reported for the first time the direct imaging of the lattice fringes in PPT fibres and demonstrated that the lattices of the (110) and (002) netplanes are in the form of an array of almost parallel fringes, but in rare cases slightly curved lattices were observed (see Figure 4). Dobb *et al.*<sup>12</sup> also reported a statistical distribution of the microparacrystal size obtained by counting the lattice fringes from the (110) netplanes of 500 microparacrystals. These lattices of PRD 49 fibre ranged between 4 and 24 fringes with  $\bar{N} = 12$  corresponding to an average microparacrystal size  $\bar{D}$  of 5.4 nm. The size distribution of microparacrystals obtained from two samples of PPT fibres<sup>12</sup> which have  $\bar{N} = 12$  is drawn in Figure 5. It agrees well with the predictions shown in our theoretical curve for  $\bar{N} = 11$ .

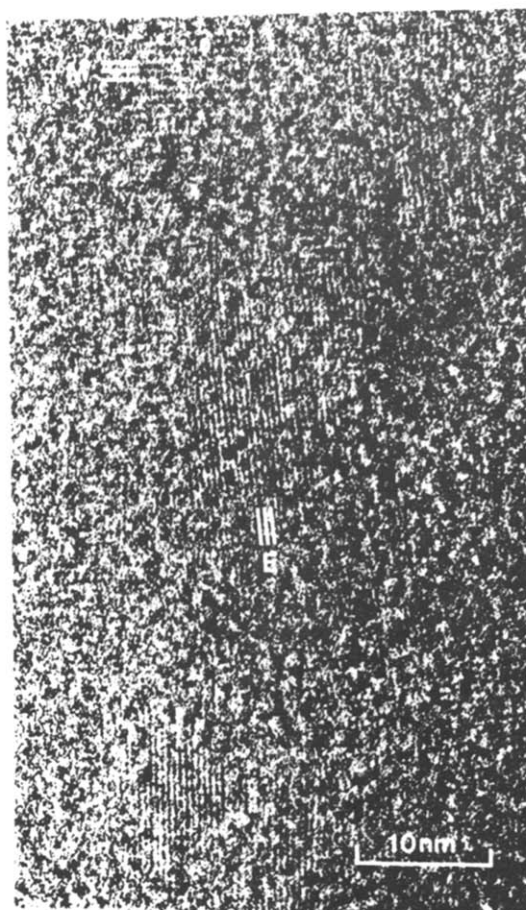


Figure 4 Transmission electron diagram of DuPont-fibres PRD 49

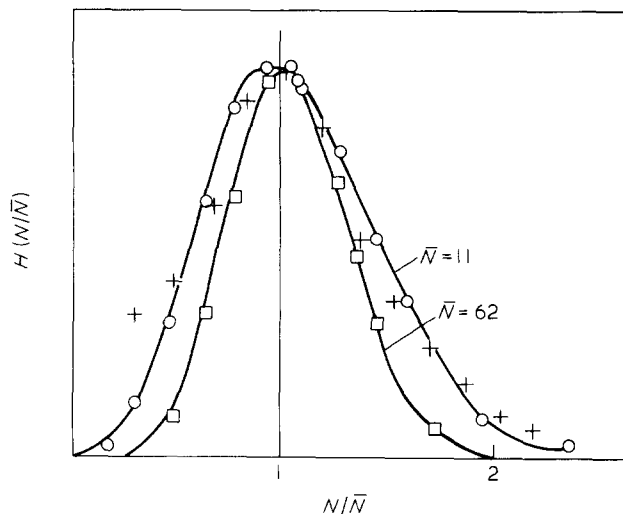


Figure 5 Theoretically calculated frequency distribution  $H(N/\bar{N})$  of microparacrystals in equilibrium for two values of  $\bar{N}$  ( $\circ\circ$ ,  $\square\square$ ), approximation by Maxwellian functions (—) and the size distribution of the microparacrystals of PPT-fibres with  $\bar{N}_{110} = 12$  ( $++$ )

### Acknowledgement

One of us (A.M.H.) thanks the DAAD of the Federal Republic of Germany for the Fellowship obtained during 1981.

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## E.p.r. studies on poly(paraphenylene)s synthesized by two different routes

G. Froyer and F. Maurice

CNET, Centre Lannion B, ROC/TIC — B.P. 40 — 22301 Lannion, France

and P. Bernier

Groupe de Dynamique des Phases Condensées\*, USTL, Place Eugène Bataillon — 34060 Montpellier, France

and P. McAndrew

Department of Chemistry, University of Pennsylvania, Philadelphia PA 19104, USA

(Received 16 February 1982)

Polyphenylene has been prepared using two different polymerization procedures. We show that, if the two materials are very similar from a structural point of view, their magnetic properties as seen by e.p.r. are very different. We show that the existence of unpaired spins in one of these polymers is correlated with structural defects which are probably created during the polymerization process.

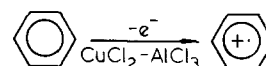
**Keywords** Polyphenylene; electron paramagnetic resonance; structural defects; magnetic behaviour

Much of the work performed on conducting and semiconducting organic polymers has been focused on polyacetylene in the last few years<sup>1</sup>. Only a small amount of work has been concentrated on the polyphenylene (PPP) system<sup>2</sup>. Shacklette *et al.* have made some structural determinations<sup>3</sup> on a PPP polymer prepared by the Kovacic method<sup>4</sup> (see below). Ivory *et al.* observed that the conductivity of this material could be raised by more than twelve orders of magnitude upon doping with the electron acceptor  $\text{AsF}_5$ <sup>5</sup>. While it was recognized that the d.c. conductivity of the undoped system was very sensitive to any thermal or chemical treatment<sup>6</sup>, investigations of the magnetic properties have shown the presence in these materials very stable radicals yielding singlet e.p.r. spectra with a  $g$ -value close to 2.0023 and linewidths of the order of 5 Gauss<sup>7</sup>. It has been suggested

that these radicals could be associated with structural defects due to an imperfect polymerization<sup>8,9</sup>. In this communication we want to show that the same PPP polymer synthesized, using two different techniques, yields two very different types of magnetic behaviour.

The polyphenylenes were synthesized using the methods described by Kovacic *et al.*<sup>4</sup> and by Yamamoto *et al.*<sup>10</sup>.

The Kovacic method involves an oxidative cationic polymerization of benzene in the presence of  $\text{CuCl}_2$  and  $\text{AlCl}_3$ . In this reaction, the initiation step would be the loss of an electron from the  $\pi$  cloud of benzene *via*  $\text{CuCl}_2$  or a  $\text{CuCl}_2\text{-AlCl}_3$  complex, leading to



\* Laboratoire associé au CNRS