

## Reminiscences on the discovery of chain folded single crystals<sup>☆</sup>

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My own journey to the discovery of polymer single crystals and the underlying chain folding has followed a convoluted path that I shall try to convey in this article. The twists and turns on the way may be of interest both scientifically and anecdotally in their own right, but in addition, I hope that they also provide an instructive example of how new insights are and can be obtained.

I entered the polymer field in 1948 while in industry (ICI, Manchester). My assignment was the study of crystallization in aid of quality control of nylon moldings and in service of potential applications of the then new poly(ethylene terephthalate). At that time the crystallinity of a polymer was envisaged in terms of the fringed micelle concept. According to this concept the crystals, responsible for the observed X-ray reflections, arose through localized parallelization of chain portions in an otherwise random overall chain entanglement. These crystal regions were regarded to be too small even to be seen by imaging techniques. The formation of single crystals, as conventionally identified through crystallographic facets, was deemed to be impossible in view of the restricted organizational capability of the entangled chains in their amorphous state, whether in melts or solutions. In the course of my work on crystallization, at this stage by dilatometry, I happened to look at some of the samples under the polarizing microscope. So I became aware of the fascinatingly beautiful world of spherulites. Here, clearly, were strikingly distinct organizations on the microscopic scale seemingly in contradiction with the total featurelessness implied by the fringed micellar view of polymers. Little notice was taken of such spherulites at the time, and such as there was tried to reconcile them by visualizing some ad hoc spherically symmetrical arrangement of fringed micellar entities.

I, however, became so fascinated by these spherulites that I simply could not leave matters at that. Looking for their origin I soon recognized that they resulted from the fanning growth of entities which could be identified morphologically with the aid of the electron microscope (primitive as it was at the time), and in special cases also the optical microscope [1,2]. This is in close analogy with spherulites in simple organic and inorganic substances. In fact, from the morphological and optical viewpoints there was nothing that distinguished the spherulites of polymers from any other spherulites. All this greatly strengthened my conviction, that in common with all other spherulite forming substances there must exist a basic underlying single crystal also in polymers. As it emerged eventually, this turned out to be so, nevertheless with a major and totally unexpected difference, as I shall indicate shortly.

At this stage another development attracted my attention, namely the recognition of discrete X-ray reflections at small angles (SAX) reported from several other laboratories. These reflections signaled the existence of some more or less periodically arranged structure elements in the range of a few 100 Å, basically unrelated to the crystal structure and affected by crystallization conditions. I believed that there had to be a connection between such SAX effects and the fine structure, which I was just beginning to glimpse by imaging techniques. As the size range of the structure elements indicated by the SAX effects was within the resolution of the transmission electron microscope (TEM) even of that time, I believed that the way ahead was to follow up this suggested correlation by establishing it first qualitatively with quantitative confirmation to follow. In addition, I became aware of the capability of the electron microscope to produce diffraction patterns from preselected image areas through the same electrons which are forming the image (something self-evident today, but then hardly recognized, let alone applied). By that time, 1954, my future plan became clearly set: a combined attack on polymer crystallization by the TEM (including its selected area diffraction application) and SAX techniques. This would be backed all along by optical microscopy combining its polarizing optical and the then newly arising phase contrast potential capable of imaging very thin objects, so as to link up optical and electron microscopy (something that, again, was totally

<sup>☆</sup> This manuscript was brought to me during the Thanksgiving week of 1998, the last visit of Professor Andrew Keller to Akron. During his visit, we discussed the possibility of the publication of this manuscript in *Polymer*. After he returned to Bristol, I had several communications with him regarding this manuscript. Unfortunately, this process was interrupted due to his sudden death. I believe that it is very proper to publish this manuscript, as it is the last manuscript he prepared, in this Special Issue to memorialize his great contribution to polymer science.—Stephen Z.D. Cheng

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missing at the time: electron microscopy was then largely a world of its own unrelated to anything else). As it emerged, to be described below, it was the confluence of the investigation of such different phenomena, as revealed by different techniques, which has led to the basic discoveries, and in fact was needed to achieve them. When it all suddenly “clicked” it was the highlight of my scientific career. Yet this “clicking into place” occurred quite differently from what I originally envisaged.

Not surprisingly, to pursue my plans I needed an academic environment. In fact more than that, a forward-looking receptiveness that pointed beyond the conceptual horizons of those days. For example, the combined use of different structure techniques for a single, specific purpose, as I wanted to use them, is obvious today but was not so at the time. Then, each expert cultivated his own specialty to perfection, and a compromise between breadth and depth, as my approach entailed, was largely disdained. My acceptance at Bristol University and in the Physics Department (by training I was a chemist) and my own choosing of Bristol (as far as I had any choice) has to be seen in this perspective. This proved to be decisive, not least because the Bristol Physics Department, one of the leading places in basic physics, did not refrain from “stooping as low” as to embrace a subject so down to earth as polymers, something totally unprecedented at the time. The person responsible for it and to whom my subsequent progress owes so much was Professor (later Sir) Charles Frank (a more detailed and anecdotal account of the ‘discovery’ of single crystals is explicitly dedicated to him, see Ref. [3]).

So at Bristol I had the advantage of an unparalleled high level of basic physical science (for a polymer chemist) and a uniquely stimulating intellectual atmosphere. But there was a price to pay. First, there was nobody who knew anything about polymers, and in that respect I was quite alone. Also, with no means to travel and because, unknown as I was then, nobody came to me, I was totally cut off from the polymer community. As it turned out this was a blessing in disguise, because when the novel results kept coming I did not have to face the obstacle of preconceptions, as indeed it has happened to a contemporary elsewhere [3]. As long as the science was sound there was nobody to tell me that “this just cannot be”; on the contrary if it seemed interesting I was encouraged. Secondly, while I got the green light for all I planned to do, the facilities available were either nonexistent or hardly useable for my purpose. It seemed to be there on paper (otherwise I would not have accepted) but either geared to some other individual’s requirement or not in working order (most seniors in the Department were theoreticians not depending on every day practicalities), and there were no funds to buy much, if anything. The single item for which the resources sufficed (and that only after some lapse of time) was an optical microscope that I specifically chose for my combined requirements. It is still the most suitable one and in use in Bristol (and, as far as I know, an exact counterpart of it in Bell Laboratories where I

purchased it for the same purpose when invited as a visiting scientist there a few years later). I built an X-ray generator myself (with some help) from discarded Army–Navy junk from the war. With no oil sealed high-tension terminal (too expensive to buy), it was enveloped in permanent corona discharge. Lead for screening was too expensive as well, so we kept the photographic films elsewhere (otherwise they would have gone black on storage) while we (my first research student, Tony O’Connor, and myself) shared the same largish room both as office and laboratory, also doing other experiments there. Similarly, I built the Kratky SAX camera myself (fortunately just announced by Kratky) from the only rust-free and dimensionally stable piece of steel I could obtain (as a present from a metallurgist acquaintance in Los Angeles), but honed flat and tested interferometrically in an advanced optical workshop of a colleague (a combination of the extremely primitive with the ultimate sophistication where it really mattered). To reduce air scatter I wrapped the whole camera in a polyethylene balloon (available in another part of the department known for their renowned cosmic ray research) and filled it with hydrogen, without any respect for the sparks of the corona discharge which were lapping at it. Topping it all, there was no hood available and the fumes of boiling solvents, including benzene, tetrachloroethylene, etc. were filling the room serving both as laboratory and office. There was an open-duct drain system (as in Roman Pompeii) and when pouring the waste down the sink (there was nowhere else to dispose of it, except by pouring out the window from the fourth floor which I also did sometimes) the solvent fumes became nearly uniformly distributed throughout the whole building. Yet I survived to tell the tale.

On the scientific plane there was yet a serious hurdle, but with a fortunate circumstance to follow, the scene for success was set. The hurdle was my inability to obtain electron diffraction patterns from anything polymeric under the electron microscope. Our microscope was old, even by the standards of the day, and poorly maintained. Even so it did produce diffraction patterns, say of mica, but not of polymers. The cause of course was the now well-known damage by the electron beam, which destroyed the diffraction patterns as soon as I switched on the beam in accordance with the operating instructions. The way I found this out is a story in itself with some personal anecdotes, but there is no space here to elaborate upon this. Suffice to say that in the absence of a sufficient condenser control on that instrument I was forced to use unsaturated filament current to save my specimens (see, e.g. Ref. [4]). Much later, after the success, Professor Ruska, the inventor of the electron microscope, was surprised that I got any image at all; by coherence considerations I should not have had any, but luckily I did not know that at the time, so I succeeded. Having overcome this hurdle, the fortunate circumstance referred to above was the advent of stereoregular polymers, and at that time linear polyethylene in particular which paved the way to the recognition of well defined crystals.

It is now time to turn to the actual subject of my investigations. Following some preliminary works of mine while still in industry I was precipitating crystallizing polymers from solution. First I looked at the precipitating particles by TEM to see what they are. For this they had to be thin enough to reveal anything, a serious limitation. Aware of the danger of artifacts I made special efforts to ensure that what I was seeing was representative of the preparation as a whole. Of this I was assured when I established an overlap with what could be seen over representative sample areas using the optical microscope with the aid of phase contrast, which enabled the viewing of the thin sample feature required for TEM. After that, I recorded the electron diffraction patterns of selected entities, first to ensure that they indeed consisted of the polymer intended for examination and then to establish the crystallographic orientation within. Finally, I collected macroscopic samples from the precipitate for X-ray examination, SAX in particular, for establishing the intended correlation enunciated above.

At first the materials I looked at in this way were nylons. As to the present day these give essentially fibrous entities. Although by later knowledge these are manifestations of lamellae containing all the features of chain folding [4], they were clearly not the ideal model substances for establishing the basic phenomenon itself. The latter came about by using linear polyethylene, in my case the Philips product Marlex. I shall never forget when I had the first glimpse of the perfectly regular faceted lozenge shape crystals. Here were true single crystals at last! But were they from a polymer? After all, crystals of short paraffins look the same! Also, and chiefly, the all vital electron diffraction pattern revealed that the chains were perpendicular to the lamellar surfaces, just as in paraffins, inconceivable—so it seemed at first—for a long chain polymer. It is well to remember that Till, who has the priority of seeing these crystals first [5], left the whole matter inconclusive at that stage (Fischer's often quoted paper on the same subject [6], while of great importance for seeing lamellae also in surface replicas of melt cast films, left the same question mark). I struggled for the best part of a year to ensure that what I saw was representative of a polymer. Phase contrast optical microscopy, while helpful, did not fully assure me because of the large, thick, structurally unspecifiable lumps comprising most of the material within the field of view. Hence, I resorted to increasingly higher dilutions until I was satisfied that the lamellae I was seeing were representative of the polymer itself—and not only of a short chain paraffinic fraction (from a later viewpoint this was a totally unnecessary worry; those thick lumps in the usual solutions turned out to consist of lamellae as well but in a collapsed multilayer configuration).

The next crucial point was interpretation. How could the chains be perfectly perpendicular to the surfaces of lamellae the thickness of which was only a small fraction of the average chain length (the lamellar thickness was 10–20 nm, as could be readily determined from the shadow

length in the TEM images of obliquely metal coated preparations)? In this dilemma I even considered the possibility that the chains break up into ~10 nm segments on crystallization, and in as far as subsequent MW determination (which was viscosity at the time) shows that it is still a polymer, these fragments somehow link up again on dissolution. Even without any polymer expert to advise me to the contrary, after some reading, I abandoned such ideas by my own judgement. Hence in my mind there remained no other possibility but that the chains fold up at regular intervals so that the reentrant straight stems can still constitute the crystal lattice (note that I did not say *adjacent reentry* and *regular fold portion* at that stage, the subject of much controversy later, although it is fair to say that it seems to be implied as a plausible, even if not strictly necessary consequence, on which I am not retracting even now).

The idea of chain folded crystals seemed so outlandish that at first I could hardly believe it myself, and I hesitated coming out with the idea in the open. Then, quite unexpectedly I found support for it from elsewhere. I was reading about basics of electron diffraction in the book "Electron Diffraction" by Pinsker, where amongst the examples quoted there was a single entry on polymers. It was on guttapercha thin films (no electron microscope and selected area involved) where the chains were found to be perpendicular to the film surface. This was noted by a casual remark from Pinsker, "of course in polymer crystals the chains are folded" (or something like that—I am quoting from memory). The work referred to was by Storks [7] (virtually unknown in the polymer field) dating from 1938 and published in such an *obscure* source as the *Journal of the American Chemical Society* so that it has remained totally unnoticed except by an outsider such as Pinsker. It was Saturday afternoon, so the University Library was closed. In my impatience I rushed to the City Library where, surprisingly, I found the journal and the article in it. It seemed convincing. Storks saw no crystals as such and measured the overall film thickness by interferometry before reaching his conclusion. His only doubt was that it might have degraded, a possibility with guttapercha in the form of a thin film, which he had no means to check (in fact, later when I eventually met him, he told me that to minimize this possibility, he did the interferometry virtually in the dark). From that moment on, my own mind was set and the definitive first publication followed [8]. Here I add that I always gratefully acknowledged Storks' precedent and I was rewarded by the ensuing amicability when fate brought us together in 1990 at Bell Laboratories by which time Ken Storks was in a different field.

Is chain folding true, does it really exist? These were thoughts that were going through my mind in those days. To my great delight assurances in the affirmative followed at every step. These were grand days when new vistas were opening up and everything seemed to fall in place. This only happens when one hits the nail right on the head. To give one example: sectorization. Even simple doodling with

pencil on paper shows that the chains are likely to fold up along the side (prism) faces as a lamella grows. This would mean that what appears to be a single crystal should be composed of as many sectors as there are prism faces distinguished by the fold plane direction. Can this fantasy be true? I can hardly describe my delight when such sectors within the crystals were directly seen [9]. (The first in fact was through the phase contrast optical microscope on a slide that had been previously placed on a temperature gradient bar. Here, in a narrow temperature interval one sector type became distinct by melting, or transforming otherwise, before the rest of the crystal.) An a priori prediction arising from the newly postulated model of chain folding here verified!

The next salient step was the correlation with SAX. As already mentioned, for this we used the coherent mats as formed by the sedimentation of the suspended single crystals that had precipitated from solution. On examination by the usual wide angle X-ray diffraction technique it turned out that such mats, in the first preparations at least, were oriented. This was in accordance with the lamellae predominantly lying horizontally, i.e. the lamellar normals, hence also the straight chain direction (*c*-axis) being perpendicular to the plain of the macroscopic mat. The same preparations imaged by the appropriate camera gave highly distinct reflections at small angles, and this in at least four orders (no doubt Bragg reflections!). The reflections were sharply arced, the orientation corresponding to that of the lamellar normals and the Bragg spacing to that of the lamellar thickness as previously assessed by TEM. This was undoubtedly my greatest moment. The hitherto mysterious SAX reflections were fully accounted for; they were found to be due to stacked (chain folded) lamellae previously identified by direct imaging. Conversely, the lamellae have acquired an X-ray fingerprint, which being on a macroscopic aggregate can now serve as providing a representative measure of the lamellar thickness [10]!

All the above was on solution crystallized preparations. Can it also apply to crystallization from the melt? At this stage I made one step in this direction. I still had melt crystallized samples from my industrial past where the spherulites were not allowed to develop into spheres, as usual, but the underlying crystallizing entities were confined to grow all in parallel directions, i.e. the macroscopic sample (here a filament) had the texture of a spherulite radius. It turned out that such samples (they happened to be nylons) displayed distinct sharply oriented SAX reflections with plain normals perpendicular to the filament axis

(hence also to the inferred spherulites radius). I added this finding to Ref. [10] (a never referred to paper, of which I am nevertheless very proud), suggesting that going by the new interpretation of SAX reflections, as acquired from solution prepared samples, melt grown spherulites also consist of lamellae with the lamellar normals perpendicular to the spherulite radius. In fact in the same paper I went even further: I invoked residual chain folded lamellar fragments, with folded stems parallel to the draw direction as being responsible for SAX patterns in drawn fibers. At that time nobody took this extrapolation to the melt crystallized bulk, not to speak of drawn fibers, seriously; in fact I was, by some authorities, rebuked for going too far. It took another decade or more till all this became verified by which time its first source was forgotten. Nevertheless, I have had the satisfaction of having been proven right.

To end with, the story as told above may merit some reflection. The “discovery”, to use this pretentious term, was clearly not just a single fortunate incident. It should have become apparent from the above that it was preceded by much well considered planning—involving both much effort and risk taking—and was backed by years of accumulated personal experience. On the other hand, chance also played an essential part in it: without fortunate coincidences all the planning would have been fruitless. In fact the main events just did not happen according to plan and the outcome was not as foreseen. Nevertheless, without the prior planning and associated awareness those chances may not have arisen, or if they had, they may not have been recognized nor utilized. It is this interweaving of the purposeful and coincidental, the rational and the intangible, which makes scientific research such an exciting experience, both intellectually and emotionally, something the above story has intended to convey.

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