V STRUCTURE OF FIBERS

A comparison of the physical properties of large, bulky objects with those of fibers made of the same polymer discloses surprisingly large differences: moduli, breaking stress, elongation at break. On the other hand, it has been said that the great majority of fiber formation processes is connected with some extent of cold drawing. It is known also that cold drawing introduces orientation into morphology of the drawn material. It results then that fibers must have an oriented structure.

Looking at the problem from still another point of view, we have to accept that though fibers are made so to develop certain properties, we may control the properties only indirectly. The process of fiber formation results in the creation of objects with a certain structure. The structure, in turn, is responsible for a set of properties. Consequently, the better an understanding of fiber structure and its formation we possess, the easier it will be to relate it to physical properties which we want to impart to the produced fibers.

V.1 Spun Fibers

One may rightfully expect that the process of cold drawing, and its effects, must depend on the state of polymer the process of cold drawing starts with. Nonetheless, the question goes further back to the question of the condition, or state, of the polymer which was extruded under the action of shear. Later, the material is extended with a tractional force, and crystallized to some extent. A question may then arise: What is the result of all these changes?

Polymer science has not given us the answers we would like to have. There is, however, a number of observations and different notions common in the circles of fiber makers. Many of these notions are correct and helpful, but there are also some which are outright wrong. And here we must overcome one very popular, more or less intuitive, but incorrect notion.

Often it is believed that the amorphous polymer has molecules oriented due to the action of shear and extension. Careful investigations of the problem were conducted over many years and some portion of them was published.[1] Similar investigations, though using different techniques, led to the same conclusions.[2,3] The result of these investigations is: the common fiber forming polymers consisting of flexible chain molecules are not oriented by the perturbations of extrusion, or the orientation does not survive the relaxation taking place in the die swell, and extension definitely does not introduce any measurable orientation of the melt. This is quite clearly visible in figure V.1. A meaningful orientation starts to develop at the end of crystallization, perhaps with a slight overlap, and is the result of the onset of the cold drawing.

The X-ray diffractograms presented in figure V.1 were obtained during fiber formation (on line) from polypropylene of molecular mass of 450, 000. The polymer was extruded through a spinnerette of hole diameter 0.381 mm and aspect ratio of $l/d = 7$. In case A the polymer was extruded under shear rate of $\dot{\gamma} = 5000\ s^{-1}$.

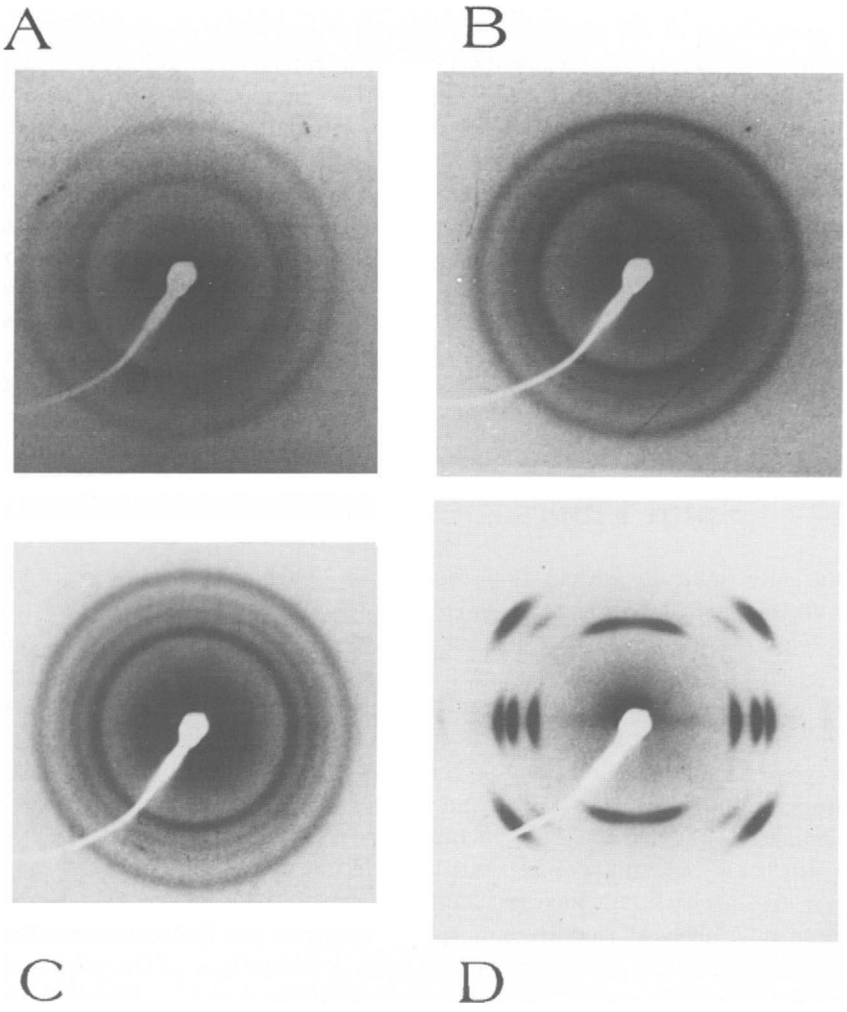

Figure V.1: *X-ray diffractograms obtained during fiber formation (on line) from polypropylene. Explanation in text. After Z. K. Walczak*[31]

Total melt extension (melt draw) between the spinnerette and the take-up roller amounted to $\lambda = 21\times$ at a modest take-up velocity of 50 m/min. Diffractogram A was obtained at the end of the crystallization range, and it represents 42 % of crystallinity and no signs of orientation. The quench intensity was adjusted so that the end of crystallization zone was within few centimeters from the take-up rollers. Diffractogram B was obtained also at the end of the crystallization zone, which, as a result of more intensive quench, was some distance upwards from the take-up rollers. Polymer, extrusion, melt extension, and take-up velocity were the same as in case A. The diffractogram B indicates $\alpha = 51$ % of crystallinity and crystalline orientation is immeasurable. The diffractogram C represents another process, with the extrusion of the same polymer intensified to $\dot{\gamma} = 7500\ s^{-1}$ shear rate. The quench was as in case B, take-up velocity was 110 m/min, which amounted to the extension of $\lambda = 40\times$. The diffractogram was obtained at the end of crystallization zone, crystallinity was $\alpha = 52\ \%$ and orientation is immeasurable. Diffractogram D was obtained from the same process as diffractogram B, except very close to the take-up roller, far below the end of crystallization. During the travel from the end of crystallization (case B) to the take-up substantial orientation was developed, crystallinity determined by density was $\alpha = 52\ \%$.

What is affected, and particularly strongly, by shear, is the number of entanglements and their "strength".[4] This effect depends strongly also on molecular mass, or better, on the degree of polymerization, of the polymer involved.

As the investigations mentioned in section IV.4.c show, the creep retardation function and the retardation time depend to a quite marked degree on the magnitude of the drawing force. This means that something in the melt morphology is changing. A serious investigation, as difficult as it may be, of these phenomena and their relationships is needed. At present, details of the changes involved are not known, leave alone their quantification. With the currently available facts one may only speculate.

The strongest entanglements, the deepest reaching loops, seem to be responsible for formation of crystallization nuclei. The number of such long stems is normally so small that it escapes all applicable analytical techniques. By X-ray analysis of fibers collected at the point where the crystallization process just ends, one may sometimes detect traces of orientation, but the traces are so small that they cannot be quantified. Similarly, determination of birefringence on fibers collected from a moving spinline, with so called "cutting traps", showed only traces of orientation at the point where the crystallization process goes to its completion. For example, polypropylene spun at speeds close to 5000 m/min gave a birefringence of maximum 0.0010.

For the time being, we must leave the subject just with a short statement: depending on processing conditions, some important changes are introduced to the melt morphology. The changes are important to the future crystallization process. The nucleation rate may increase faster than the growth ability, and this has an impact on morphology of the crystals. However, the changes in the morphology of the melt prior to crystallization appear to be much stronger rather than numerous; they themselves escape the analytical techniques, only the effects are detectable.

Figure V.2 shows a transmission electron micrograph of polyethylene lamellar crystals growing epitaxially on the long "fibers" created through a baguette shearing of the solution to crystallize. Figure V.2A shows the general topography and interpenetration of the lamellae. Figure V.2B shows the same specimen at a higher magnification; here the interlamellar tie molecules along some longer range connections are clearly visible. .

The long "threads" are, most probably, the result of extention, due to flow, of

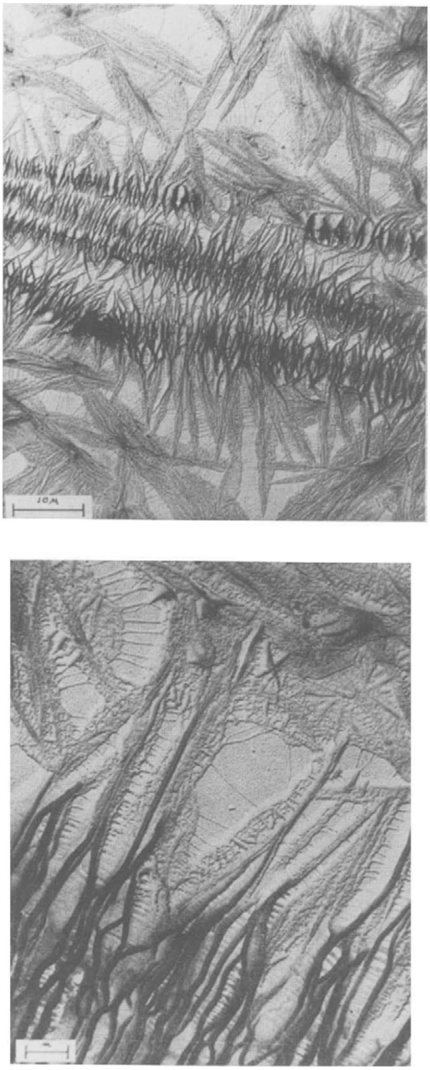

Figure V.2: *Transmission electron micrograph of row nucleated polyethylene crystals. Top: general view of morphology and interpenetration of various lamellae. Bottom: higher magnification than above showing interlamellar tie molecules and some longer range connections. Reproduced from R. C. Novak and R. B. Williamson*[5] *by permission of the copyrights owner, John Wiley & Sons, Inc.*

very strong, deeply nested entanglements. Most likely, these are loops formed at points far from molecule ends of both molecules involved. In a flow field, such long strands may also bundle together and in this way achieve the critical minimum size of a nucleus. Here it is easy to see that the size of the nucleus is rather the size of its surface; length is then exchangeable with diameter. Once the process starts, normal, folded chain crystallization proceeds. It has been claimed lately[85] that the "shish" modus of crystallization is "autocatalytic". One shish initiated by strain may propagate further into unstrained areas. As the data presented in figures 4.29 through 4.31 of section IV.5 show, under influence of forces of fiber formation, the process of nucleation is substantially faster than the process of crystal growth. One may suppose also that it is faster than the possible propagation of shishes.

If the crystallization rate is high, large crystals are formed; if the process is slow, small crystallites along a and b-crystalline axes are formed. The true reason for this fact is unknown, though it may well be related to the discrepancy between the rates of nucleation and growth. Mainly the stored elastic energy seems to be responsible for the nucleation. What constitutes the limiting factor for the rate of crystal growth is yet unclear. The size of the crystallites (mosaic blocks) appears to be the result of competition between the velocity of flow and crystal growth. If the flow is faster, the growth may be disturbed, more imperfect alignments incorporated, larger g - factor results, and mosaic blocks formed are smaller. Nevertheless, though probable, this is a conjecture only

There are several theories claiming that certain preorder exists in polymer melts. Perhaps the furthest developed and most popular of these theories is the *meander model* developed by W. R. Pechhold and co-workers.[6–10] The model assumes the existence of more or less regular folds with dimensions similar to those present in crystals. The folds are less regular than in crystals. Besides them, there exist some *superfolds* which consist of parallel aligned chains spanning over a distance larger than one fold. Such superfolds may span from one meander cluster to another and, in effect, they may play a role similar to the entanglements, as assumed in the free coil theory, though they are anchored in the structure rather than in the conformation.

This author believes that in reality, noncrystalline melts consist of both elements, free coiled and clustered molecules. The ratio probably depends on the character of the polymer, on chain rigidity. The liquid crystals may serve as an extreme example where no, or almost no, coils exist.

Some of the entanglements, or the superfolds, due to their character or due to the flow forces, may not be able to develop into raw nuclei. Nevertheless, they form connections between different crystalline lamellae; they are responsible for the formation of *tie molecules.*

Barham and Keller[11] used synchrotron X-ray radiation to investigate *in situ* crystallization of polyethylene. The authors found that initially, polymer crystallized in very thin lamellae. Later, the lamellae thickened in steps to double, triple, or quadruple the length of the initial folds. Such a dramatic refolding was more frequent at a higher crystallization temperature. Later, after the dramatic refolding, the lamellae thickened logarithmically with time, similarly as they do in annealing. The stepwise refolding led to the formation of tie molecules between lamellae.

E. W. Fischer and co-workers,[12] using neutron scattering, confirmed the existence of the tie molecules and developed a method to determine the average number of clusters per one molecule, the radius of gyration of the centers of stems belonging to one cluster, and the radius of gyration of the centers of clusters in respect to the center of molecule. From these, one may calculate the average number of tie molecules.

It has been anticipated[13] that in a flow field, such long structures as the epitaxially growing lamellae cannot remain intact: they must bend back or break off, thereby disorienting themselves. Such effects have been shown quite convincingly by electron microscopic investigations conducted by G. Kanig.[14] Bending back and breaking of the long lamellae has been shown to take place in the initial stages of cold deformation. Similar events are equally, or even more likely, when some still noncrystalline polymer flows by the crystalline *kebabs*. One must accept that even in extensional flow, some structural elements pass by other elements and thus are subject to some shearing forces, which are strong to the point of possible chain scission, leave alone other deformations.

The crystalline lamellae of the majority of polymers do not form flat surfaces – they are mostly roof or hollow pyramid shaped.[15,16] This results from the fact that the majority of polymers crystallize in the lattices of low symmetry, where the c - crystallographic axis is not normal to the remaining axes, a and b.[17] This together with other kinds of irregularities and defects may contribute to the deformability of lamellae.

In the case of fiber formation from the melt, crystallization proceeds during more or less rapid cooling. This causes the lamellae to become gradually thinner as they are further removed from the nucleus; the long period depends on growth temperature. The interlamellar spaces become occupied by crystallizing amorphous material, or are penetrated by the thin lamellae originating from other nuclei.[18]

Although the long strands which form the *row nuclei* are undoubtedly oriented parallel to the flow direction, their number is far too small to be detectable as orientation. The epitaxially growing lamellae close to the row nucleus have probably chain folds parallel to the nucleus, the chain folds more remote from the nucleus change their alignment, sometimes drastically. If a crystal ***shish-kebab*** grows very large lamellae, then the dimensions normal to the c - crystallographic axis may be the largest. Flow of such "overgrown" lamellae may force an orientation of the c - crystallographic axis normal to the flow direction, to the fiber axis. It is not an exception that a certain amount of transversely oriented crystallites is found even in extensively drawn fibers; sometimes it is called "γ - orientation".

Investigation of a noncrystalline material is still difficult. The tools to do the investigation directly are few, quantification of the indirect results is difficult. This causes our knowledge of spun fibers prior to crystallization to be very sketchy, full of conjectures. One thing, however, is certain: the conditions of formation, temperature profile, shear in capillary, and extension profile play a very important role. It goes without special underlining that the polymer properties are also responsible for how the material reacts to the treatment.

V.2 Cold Drawing

The structure of undrawn fiber may be imagined to be similar to the *shish-kebab* shown in figure V.2. In reality, this should be taken as one of the main elements of the structure; nature gives here an almost infinite number of "mixed" situations. It is important how densely such *shish-kebabs* are packed together, the degree of the lamellae interpenetration, it is how deeply they intrude into their neighbors, how much of the still noncrystalline material is present and how is it distributed between the crystalline elements; all these are important. There are many researchers who agree to such a scheme.[19,20]

The structural changes taking place in neck drawing were studied in great detail by Kasai and Kakudo.[21] They found that starting from the yield point, or at the yield point according to a newer report,[74] all the way through the natural draw ratio, a process of destruction of the crystalline lamellae takes place. Kasai and Kakudo have confirmed that the lamellae break down into mosaic blocks, as earlier described by Hosemann and co-workers[22–25] and others.[26–28] The discontinuous break down of lamellae appears to be the reason for the formation of the neck. These authors also find that the deformation along the fiber axis changes gradually from the symmetric small angle X-ray scattering (SAXS) patterns to the four-point diagrams. While close to the specimen surface in the necking area, the diagrams become asymmetric, but past the necking area they assume the four-point pattern equal to that in the center of the specimen.[21]

There were quite conflicting reports by different authors regarding the degree of crystallinity and the magnitude of long period. Some authors claimed that crystallinity upon cold drawing goes up, some insisted that it goes down. Similar lack of agreement regarded long period.

From the perspective of time, it appears that all of the above cases may be true, depending on the structure of the undrawn fiber and on the process conditions. First of all, the drawing process is highly exothermal and temperature control may be difficult, particularly at high drawing rates and/or thick specimens. Whether total crystallinity goes up would obviously depend on the availability of a noncrystalline material.

If the temperature inside the neck increases a little, then the long period may grow due to some annealing effect. If the temperature increases significantly, then some portion of the crystals may melt and recrystallize. The necking area is very small, so the material will crystallize back after leaving the neck area, where cooling may be intensive, and in such a way the long period may decrease. Another mechanism for growth of long period may be similar to the mechanism of annealing: longitudinal translation along the chain axis.[50,51]

It has been published[74] recently that remelting, if at all possible, may take place only in the necking (at yield point), and it may be caused by stress, not necessarily by elevated temperature. In the remelting process, mainly imperfect crystals are involved.

The lamellae of a *shish-kebab* disintegrate into the mosaic blocks by forces transmitted through the tie molecules. Some molecules are involved in two blocks, providing connections between the blocks originating from the same lamella. During the lamella break-down, these chains either unfold or break; they may also change their length due to translation motion along the chain axis, similarly as in annealing.[52] The last process seems to be slower and thereby less frequent. Several different mechanisms were suggested for the unfolding of chains from the crystal blocks.[26,29–30] The mechanism proposed by Kobayashi[29] seems to require significantly more force than might be available in an average drawing process. The mechanism proposed by Peterlin[26] requires far reaching recrystallization, or reorganization, of the block structure; it may take place to some extent, particularly when drawing is conducted at relatively high temperature.

The boundaries between the different blocks of one lamella represent a weak spot. X-rays do not see them as crystalline. It is entirely logical then that the destruction of the lamellae takes place along the weak spots. Based on the above, the principal scheme for change of lamellar morphology into fibrillar has been proposed as depicted in Figure V.3.[13,31]

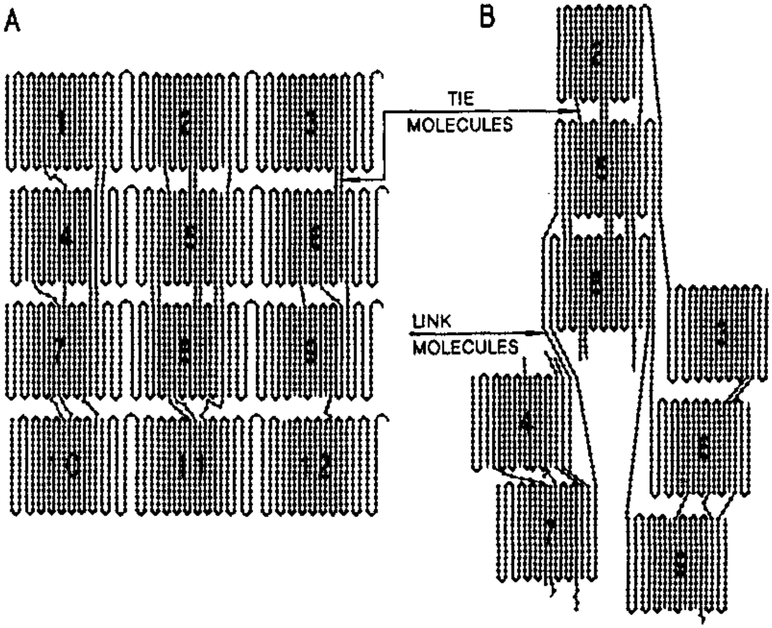

Figure V.3: *Schematic representation of the transformation from lamellar into fibrillar morphology as a result of cold drawing.*[13,31]

A strain imposed on a stack of crystal lamellae initially causes stretching of the tie molecules, which corresponds to the first, pre-yield part of the force-strain curve. Further stretching leads to tearing out of the mosaic blocks from their original places, leading to the initial abrupt discontinuous change in fiber diameter (neck). The process of disintegration of a mat seems to start at the peak of the yield in the force-strain curve and proceeds throughout the entire natural draw ratio.

Since the tie molecules do not have equal length, the connected blocks cannot have exactly parallel fold planes. This causes a certain degree of unavoidable residual disorientation,[46] not to speak of various crystal defects – some of which may even assume the complexity of a knot.[47] The unequal length of the tie molecule may lead to occasional breaks of these ties.

When the drawing continues past the natural draw ratio, the slope of force-strain curve increases markedly. This increase is related to the further unfolding of the outer layers of the blocks. The unwound polymer, termed *link molecules*,[13,31] forms a kind of sheath around the core consisting of a "column" of blocks. The link molecules provide a long range connection both intrablocks and interblocks, simultaneously forming a layer defining the individual fibrils, a layer which thickens with increasing draw ratio.[32] The important difference between the tie and link molecules is that the tie molecules seem to have constant length, if recrystallization or translation are not involved, while link molecules have a length dependent on the draw ratio, and later thermal and strain history. Existence of the extended chain links in layers with some organization of hexagonal type has been confirmed by Z. Bartczak and co-workers.[75] The reported[76] peculiar longitudinal "voids" in etched polypropylene fiber cross sections may well be assumed to be the non-crystalline link molecules that have been etched away. The only problem with this interpretation may cause the high degree of axial dimensional regularity, as well as the lateral regular arrangement.

It is necessary to stress that the outer perimeter of a mosaic block has a larger concentration of lattice defects. Once it is removed from the mat, one should take into consideration an edge effect: the molecules are not held in place from all four sides. All this permits us to infer that it takes much less force to remove a polymer chain from the outside of a block rather than from the inside. The latter would more likely lead to a chain break. Existence of *destructible micro-paracrystals* has been proved[72] and will be discussed in section V.7.

It has been determined that neck drawing results in some chain breaks, but the number of ruptured bonds in high density polyethylene drawn at room temperature amounts only to 10^{-3} to 10^{-2} of one percent of the total number of chain carbon atoms. Increase of drawing temperature causes a decrease of bond ruptures, which may indicate also that some portion of the breaks is due to frictional forces involved in the drawing process.[52] In place of the ruptured bonds new chain ends are formed, from double bonds to various carbonyl groups, if the drawing is conducted in presence of oxygen, and this is usually the case.[45] Since the number of broken bonds is small, the effect on the average molecular mass is not very important and possibly correctable. The foreign characteristic groups are more detrimental to crystallization, and perhaps to certain chemical properties.

As the number of ruptured bonds is approximately steady over draw ratio up to seven, at higher strains the number of ruptures increases very sharply. As such a high draw ratio is limited mainly to extension and formation of link molecules, one may easily infer that some of these molecules break.[45]

The breakdown of lamellae is not necessarily uniform, it may proceed in a staircase fashion[30] or along other not very regular patterns. With increasing draw ratio, the regularity of the formed fibrils increases to become quite regular, as may be seen in figures V.4 and V.5.[33,34] Figures V.6 and V.7[33,34] show the connections between the fibrils - particularly figure V.6 shows more details. Some of the connections may have a crystalline form themselves[36,37]. Figure V.8 shows that the fibrillar nature of a fiber extends over the entire cross section of a fiber.

The fibrils shown in figures V.4 to V.8 have diameters of the order of 2000 Å, and they may be composed of microfibrils of the type suggested in figure V.3. Such a bundling of fibrils has been reported by Bonart and Hosemann.[23] In fibers drawn to low draw ratios, *protofibrils* with diameters of the order of 6000 to 7000 Å have been found.[53] How the fibrils become gradually smaller is not clear; it appears that the division of protofibrils is similar to the breakdown of lamellae. Some tendency toward fibril splitting may be seen in figure V.6.

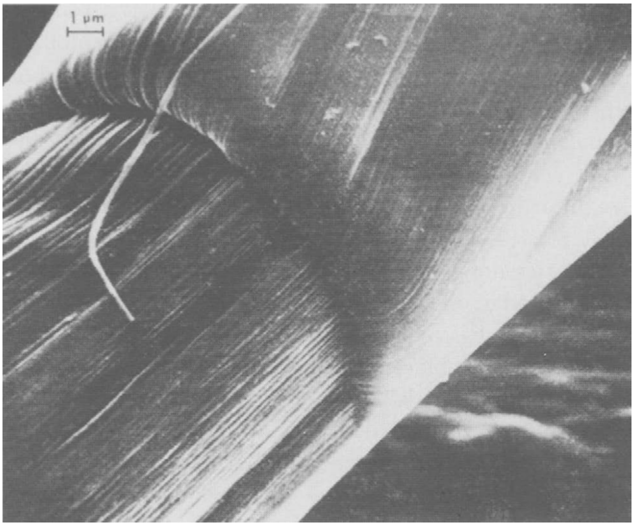

Figure V.4: *Scanning electron micrograph of skin peeled polyester fiber. Reproduced by courtesy of H. R. Billica.*[34]

Some of the interfibrillar connections may well assume intermediate phases. Hosemann's paracrystals cover the entire range from crystalline to noncrystalline, and the intermediate phases have been detected in fibers.[41]

The unfolding of molecules from the mosaic blocks may be seen as a decrease of the volume of crystalline material. Such a decrease of crystallinity was detected only at higher draw ratios.[32,44] This may be seen as an indication that the folds

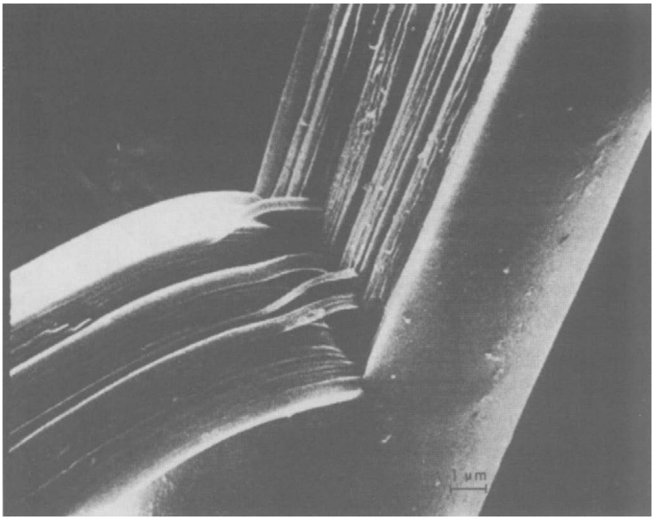

Figure V.5: *Scanning electron micrograph of a chord peeled polyester fiber. Reproduced by courtesy of H. R. Billica.*[34]

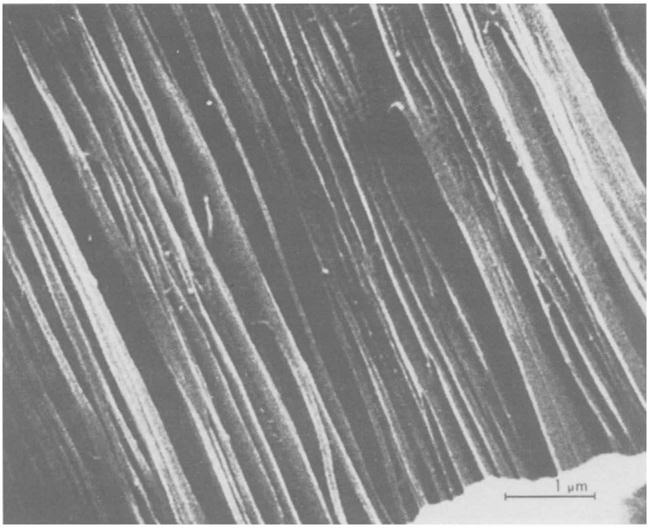

Figure V.6: *Stereoscan micrograph showing microfibrils and interconnections between them. Reproduced by courtesy of H. R. Billica.*[34]

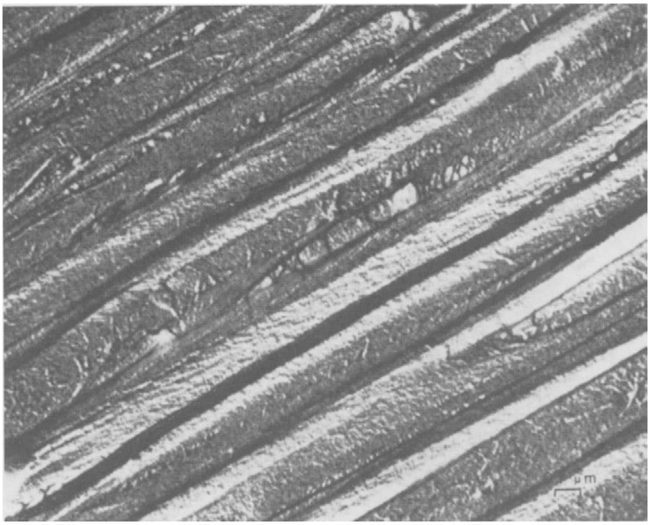

Figure V.7: *Micrograph of fibrils at higher magnification which shows more interfibrillar connections and voids. Reproduced by courtesy of H. R. Billica.*[34]

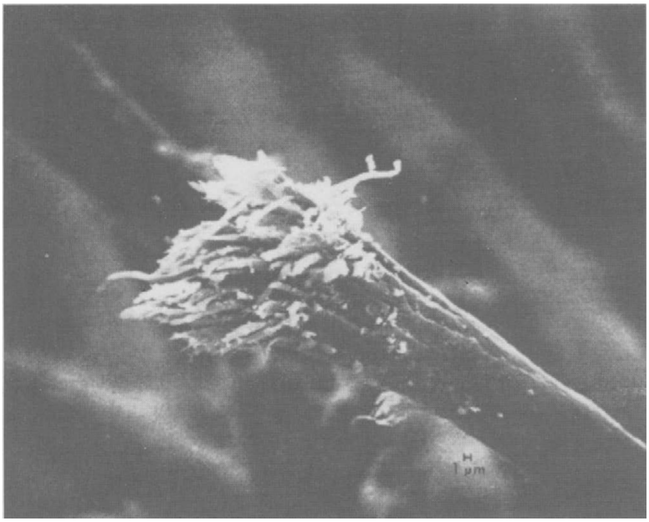

Figure V.8: *Micrograph of a fiber break which shows the fibrillar nature throughout the fiber cross section. Reproduced by courtesy of H. R. Billica.*[34]

unwound in drawing are not necessarily seen as crystalline by X-rays. More extensive drawing strips the block perimeter to a more perfect crystalline form,[41–43] but at the same time it produces more link molecules which are noncrystalline.

A structure similar to that proposed in figure V.3[13,31] has been suggested later by Prevorsek and co-workers.[35] Such a structure is strongly confirmed by the work of Billica and co-workers,[33,34] and others.[36,37]

Rolf Hosemann[38] has published a kind of "catalog" of different possibilities of structural arrangements in fiber; it is reproduced in figure V.9. These correspond primarily to the inner side of the fibrils – to their core.

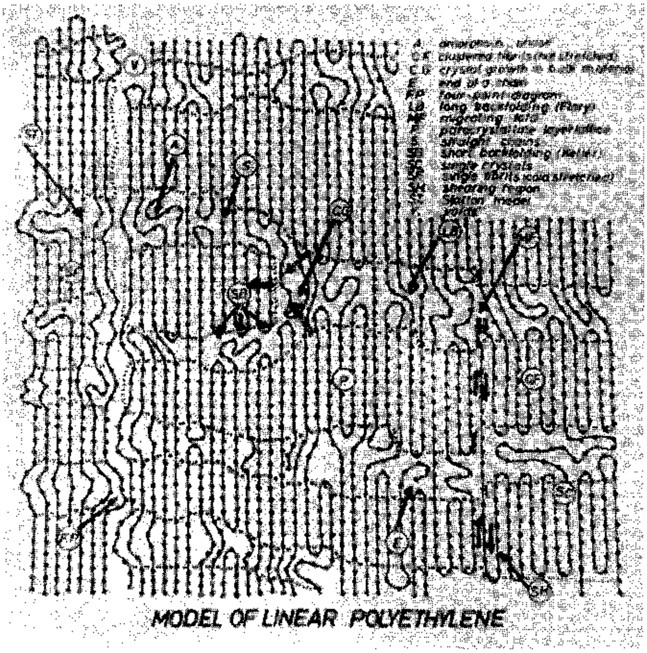

Figure V.9: *Schematic model of various crystalline structures which may be found in a drawn fiber as given by R. Hosemann.*[38] *Reproduced with permission of copyrights holder, Elsevier Science Publ.*

The investigations by Pinaud and co-workers[49] show that the orientation of amorphous material depends mainly on the crystalline orientation and morphology. This suggests that the amorphous chains are embedded in the crystalline elements. As it transpires from the presented picture of fiber structure, the crystalline forms serve as anchors for the amorphous chains, which are the main load bearing part of the structure.

As an additional argument for the above suggested fiber structure may serve the fact that if an undrawn fiber contains spherulites with radial arrangement, as it happens occasionally in slow formation processes, neck drawing is very difficult and no significant strength of fibers is obtainable.[40]

As every scheme is a simplification, one should remember not to vitrify it. The nature of various polymers and their crystallization habits, as well as the entire set of processing conditions have their say in the final outcome of a process in terms of a specific structure and further in terms of the properties. And this truism cannot be overemphasized, it is a matter of producing fibers with a desired set of properties, and it is a matter of process reproducibility.

When the drawing force is removed, a post-draw relaxation takes place. This is probably due to relaxation of the tie and link molecules. Considering the geometry, and particularly the length of the connections, the link molecules seem to bear more responsibility for the shrinkage. Being highly stretched, and thereby forced into "uncomfortable" positions, the ability of the links to crystallize in the new locations decreases with the increasing draw ratio and tension experienced by the link molecules. Upon removal of force, the link molecules relax and seek more "comfortable" positions.

It is well known that a fiber does stabilize. If drawing is divided into several stages, care must be taken that the fiber is not given the chance to relax.[48] If the fiber does relax, then only a limited amount of drawing will be possible in the next stage.

Considering the above presented fibrillar structure of drawn fibers one may conclude that the strength of fibers is dictated primarily by tie molecules and link molecules. As the number of the tie molecules in the drawing process is essentially constant, with the exception of occasional breaks or a major recrystallization, the number of link molecules increases with increasing draw ratio, especially above the natural draw ratio.

V.3 Drawing Performance

Some noncrystalline polymers may also be drawn with neck formation. It is assumed that in noncrystalline polymer, the molecular clusters play the role which the mosaic blocks play in crystalline polymers – knots of a net in which amorphous chains serve as the strings. This leads to the obvious conclusion that the neck drawing may be performed over the entire range of crystallinity starting from zero, or close to it, to as high as it may go. Nevertheless, the actual degree of crystallinity in the undrawn fibers has its significance.

Besides the total amount of crystallinity, one needs to consider the size of crystallites. As results from the studies of crystallization in polymer flow, the size of crystallites depends on the crystallization rate. Low rate of crystallization favors small crystallite size. The size of crystallites is also affected by the shear the polymer experienced during extrusion. High shear rates invariably lead to smaller size of crystallites. For example, increase of shear rate from 250 s^{-1} to 1250 s^{-1} causes a decrease of crystallite size from 90 $\AA$ down to 70 $\AA$. The influence of capillary length appears to be much more complicated.[1]

The significance of the crystallite size is rather obvious; drawing force requirement, number of link molecules, potential size of fibrils are related to the size of mosaic blocks. The fiber properties are affected by the crystallite size more stronger than the drawing performance is influenced.

Capuccio and co-workers[54] studied extensively the fiber formation from polypropylene. The authors found a relationship between the degree of crystallinity in fiber before neck drawing and the maximum of tenacity obtainable, as presented in figure V.10. Though the range of crystallinity before drawing appears unusually wide, both on the high and on the low side of the bracket, the general trend and conclusion are very much in line with the findings of many researchers and regarding many polymers.

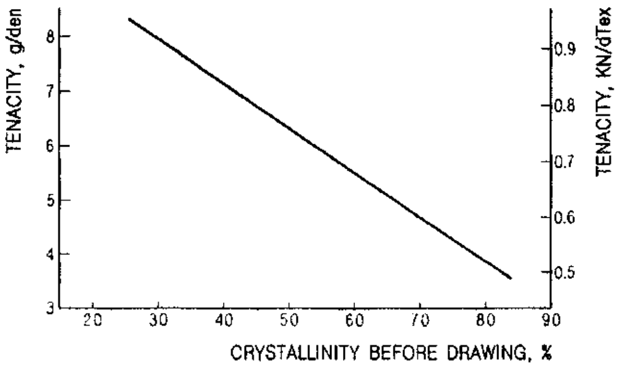

Figure V.10: *Maximum of obtainable fiber tenacity in relation to the degree of crystallinity existing in fiber before neck drawing. After V. Capuccio and co-workers.*[54]

Considering what was said above about the fiber structure, the results in figure V.10 are by no means surprising. It is certainly energetically easier to unwind molecular coils, rather than unfold long periods from a crystal block. Furthermore, larger number of the noncrystalline chains per fiber cross section may be obtained, and this means higher tenacity. Last, though not least, drawing of fibers with less crystallinity requires substantially less force. This makes the drawing process less vulnerable to fiber breaks, and in the end may lead to higher maximum draw ratio.

The amount of crystallinity alone does not mean everything. The degree of "preorientation" of the crystals before drawing is also important. Figure V.11[1] presents the influence of a small difference in crystalline orientation in undrawn fiber on drawing performance. Drawing force, for the same strain, increases substantially with increasing orientation. The resulting fiber tenacity is somewhat higher for more preoriented fibers, but only at low draw ratios; later the benefit disappears. Break elongation for fibers obtained from more preoriented filaments is lower, the modulus is higher. Closer analysis of these results, which are otherwise quite common, may indicate that the changes in the fiber are such that one may assume that the preorientation and the neck drawing are additive. To some extent this is true, but fiber properties loose on the additivity. The increase of the drawing force required is much larger than a simple additivity might justify, and in effect this may often limit the practical maximum draw ratio.

The experiments presented in figure V.11 indicate also the problem of structure

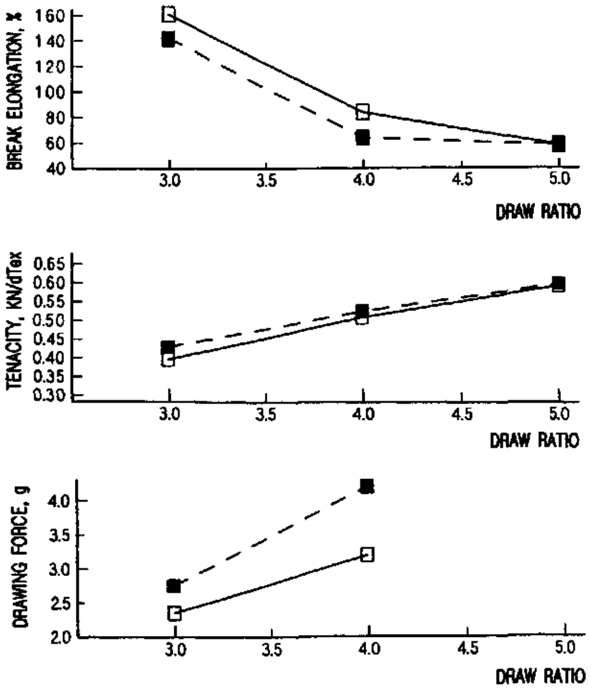

Figure V.11: *Comparison between the property build-up versus draw ratio for somewhat higher (filled squares) and somewhat lower (open squares) orientation in undrawn fibers. After Z. K. Walczak.*[1]

settling. The time span from the point where the neck drawing was initiated (end of the crystallization in the quench zone) to the drawing zone (for in-line drawing) was sufficient to start some structure settling, as is evident from the large increase in the drawing force requirement. True, the process was slow, maximum drawing speed 750 m/min, but still the time involved was short. Similar conclusions regarding structure setting (ageing) may be drawn from the work of L. C. E. Struik on ageing.[73]

Often multiple zone annealing is applied in order to increase fiber strength, especially for the so called "high strength" fibers. Such operations should be conducted so that the drawing temperature is gradually increased in subsequent zones. The temperature increase "softens" the structure, reducing the force requirement which normally increases with the draw ratio. Also, increasing the temperature helps to ease the problem of structure setting, as some finite time must pass between the drawing zones.

The influence of temperature on neck drawing has been discussed in section IV.6. Here, it is necessary to add that temperature also has an influence on crystallinity. The magnitude and direction of such an influence is also greatly dependent on the type and amount of crystallinity before drawing. Excessive drawing temperature may cause partial, or even more extensive, melting and subsequent recrystallization. It may determine whether crystallinity will increase or decrease, and how much. High drawing temperature is also a matter of the thermal response and thermal stability of the fibers, as directed by the final size of crystalline long period and on the degree of relaxation of the link molecules. These matters are highly interrelated and it is impossible to describe them in very concrete terms. Every case must be separately analyzed and conducted accordingly.

V.4 Structure - Properties Relations

The discovery of fibrillar structure of fibers and the notion of link molecules, which hold a fibril together and at the same time separate it from its neighbors, led to the first model of fiber structure capable of explaining the majority of fiber properties. And so, one of the important questions, the loss of transverse properties accompanying every gain of tensional properties becomes easy to understand. With increasing stretch, the layer of principally noncrystalline chains surrounding a fibril grows in thickness and the individual polymer chains become more taut. Both of the states contribute to the lowering of the interfibrillar cohesion.

Another property which was impossible to explain with the earlier models of fiber structure was the large elongation to break in some fibers. It is highly improbable that tie molecules might accommodate fifty or sixty per cent of elongation. It is much more probable that upon application of force some of the periferal lamellae unfold further into the link molecules. It is thinkable that some of the folds on the mosaic blocks boundaries being poorly fit and subject to an edge effect may stay within the mosaic block with very little of energetic benefit. Such an unfolding may be energetically comparable to the uncoiling of rubber molecules. Such a hypothesis may explain the large strains, and the somewhat sluggish and incomplete recovery upon release of stress. It is thinkable that certain of the new environments acquired due to a strain may be energetically equivalent, or even better than at the starting point, before the extension.

High elongations may be encountered with fibers of a modest draw ratio. When a draw ratio is high, the periferal folds are stripped from the mosaic blocks to such an extent that there are no more imperfect, weakly held folds to succumb to the relatively low force available.

D. Hofmann and E. Schultz[55] conducted a very meticulous study of the crystalline and amorphous chain structure of high modulus polyethylene fibers. This work leaves essentially no doubt that *"The axial Young's modulus of smooth fibrillar samples is a function of the content of these taut tie molecule segments and the crystallinity of the samples. ... a high degree of crystalline orientation is the necessary but not a sufficient condition for obtaining high modulus specimen."*[55] The structure of some natural fibers, like silk or spider silk, is also of relatively low crystallinity, with very small and rather well oriented crystals. The strength depends on the amorphous chains which are anchored in the small crystals. High molecular mass ($> 300,000$) strongly contributes to the strength.[79 & ref.] Thus, there is no discrepancy in the principles of the fiber structure, be it natural or synthetic.

Some of the recently propagated theories suggest[52] that the forces involved in neck drawing are sufficient to pull out chains from a crystal; the shearing forces involved, particularly with non-polar polymers, are not prohibitively high. These theories may explain the elongation, though it would be much more difficult to explain eighty, or so, percent of the observable strain recovery. It seems highly unlikely for the chains to go back, to re-enter deep into the crystal. The size of the hysteresis loops does not agree with the notion that molecules are pulled out, and stay out of a crystal.

In a significant paper, N. S. Murthy and co-workers[78] present the results of small angle X-ray scattering (SAXS) with synchrotron radiation on a series of poly(ethylene terephthalate) fibers. An expanded data evaluation system, besides the standard long period, gave other quantities: diameter of lamella stack, interfibrillar spacing (including layers of link molecules and voids), length of lamellar stacks (few lamellae), length of fibrils, angle of the tilt of the lamella fold surface. The fibers investigated had various amounts of crystallinity and different degree of predraw orientation. The work confirms everything that was said above. The additional new information gained is that a small diameter of fibrils favors higher tensile strength. One might expect that a finer diameter of fibrils leads to a larger number of structural elements which must result in more uniform load distribution, and this gives higher strength. Also, the authors find that neck drawing results in the creation of voids, with numbers increasing with the increasing draw ratio; this has been observed before. However, significant elongated voids may be formed in the interfibrillar areas. Some of these voids may extend on distances comparable to the length of fibrils. Such voids may strongly affect the transverse strength of the fibers.

N. S. Murthy and co-workers[78] stress the difficulties with correlation of the fiber properties with fiber structure. In this multifaceted relationship, every element of the structure plays its role, none may be omitted, be it regarding the crystalline or the amorphous phase. Such a multivariable system is difficult from the experimental point of view, and equally so from the interpretation side.

The hypothesis of unfolding and refolding is very well compatible with the thermal response of fiber, with annealing. If the degree of shrinkage is small, it is mostly by way of shrinkage of the tie molecules connecting different blocks within a microfibril; they may participate in an improvement of the crystalline lattice, such shrinkage is irreversible. If shrinkage is more extensive, it is mostly through shrinkage of the intercrystalline link molecules, through a parallel shift of the fibrils.[35] Naturally, this is true in case of the fibers with the structure as already described. In case of fibers with predominantly extended chains, so called *high strength*, or *high modulus*, or *ultrahigh modulus and/or strength*, the mechanism of thermal shrinkage may be different.

V.5 High Strength Fibers

In the late sixties, so called *high performance fibers* came on the market. The intensive work on space exploration demanded new materials, new fibers for technical purposes and for some very specialized apparel were needed. As an answer to these challenges, *Nomex* and *Kevlar* were brought onto the world market.

High performance fibers are usually made of polymers with rigid chains. As a rule, the chain rigidity is obtained from monomers containing ring, or even condensed rings, structures. Most of these polymers have very high melting points, often higher than their thermal stability. Thus, fiber formation is mainly done from solutions, even though the only practical solvents may be as obnoxious as concentrated sulphuric acid. The more common of the polymers involved are: poly(p - phenylene-terephthalamide) (PPTA), poly(p - benzamide) (PBA), poly(aryl - ether - ether - ketone) (PEEK), poly(ethylene - naphthalene - 2,6 - dicarboxylate), poly(hydroxybenzoic acid - co - hydroxynaphthoic acid), and many others.

Shearing forces orient the polymers with rigid molecules only little, or not at all, but the rigid molecules are strongly oriented in extensional flow, even a weak one.[56,57,77] In effect, the fibers, even if the formation conditions prevent crystallization, possess a high degree of orientation. If such a noncrystalline fiber is heated above the glass transition temperature, the crystallization process starts and the developing structure is oriented and fibrillar.[58]

The highly fibrillar nature causes the fibers to easily defibrillate on action of normal forces, not to speak of fracture. The internal structure of the fibrils resembles the structure of "ordinary" fibers: lattice with paracrystalline lattice distortions of different degree (g-factor), and microparacrystals (mosaic blocks) of sizes comparable to those in the flexible chain polymers, except that the longitudinal size along the c-axis is substantially larger.[59] The fibrils have a diameter on the order of 600 nm. Naturally, the fibrils consist of paracrystalline blocks and are not, as some authors have implied, a result of the splitting of a fiber built of a single monocrystal. The fibrils really are the elements of the fiber structure. Some individual chains, or bundles of them, are built-in in two neighboring fibrils and provide interfibrillar links. They represent also the element of lower orientation.[36]

The individual fibrils, obtained from splitting a fiber, show a high degree of flexibility, quite contrary to the properties of the whole fiber. Some polymers produce *pleated* fibrils; that is, the fibrils have a *zig-zag* form, parallel to the fiber axis. The zig-zagging is inclined to the fiber axis by about 5°. One zig-zag extends for some five to six hundred nanometers. Such pleated structures are easily detectable by optical microscope due to periodic change of refractive index.[36 & ref.]

Some of the high performance fibers show a skin-core effect which is due to the somewhat better orientation of the fibrils on the fiber surface and close to it. Inside the fiber, the parallelization of the fibrils with the fiber axis may be not quite so perfect.[36]

Generally, some of the lattice defects help the final fiber properties. Less perfect structure may be less inclined to defibrillation. Often, to further improve the fiber properties along this line, small amounts of comonomers are polymerized. This is to reduce the perfection of the crystalline structure.

The chain rigidity of the many kinds of polymers varies significantly. Following this difference, the effect of processing on the structure and fiber properties also varies within very wide brackets.

Once the fibrillar structure of fibers was learned, and particularly after the fibrillar nature of the high performance polymers was explored, a great deal of effort was invested into obtaining strong fibers from ordinary flexible coil polymers. The great majority of the efforts originated in university research centers. This is understandable since the market for high performance fibers is small, prices are very high, competition is vigorous and profits rather low. The main goal of the research efforts was directed toward obtaining fibrillar structure with a minimum, or preferably with no chain folded crystals, or even something approaching extended chain crystals.

From a number of different techniques[60], the more successful seem to be only solid state extrusion and formation by gel-extrusion, and so called *ultra drawing.*

Research efforts on ultra drawing very recently have brought interesting results regarding the mechanism of extensive drawing[80 & ref.] (see also section IV.6.a). It has been shown that the translational movement of polymer chain within the crystals is the crucial mechanism here. In terms of structure, the model, in principle, does not deviate much from the model given in figure V.3. Besides the unwinding of the noncrystalline chains and stripping of the less than perfect aligned chains on the perimeters of the mosaic blocks and formation of the link molecules, the tie molecules extend at the expense of the lateral dimensions of the mosaic blocks. Ultimately this may lead to bundles of extended molecules which are crystalline in some segments and with a lesser degree of order in the other segments. The fibrillar nature becomes less and less defined. The difference between the chain morphology in the interfibrillar areas and within the gradually thinning fibrils decreases. The ultradrawing, usually considered for $\lambda \geq 15$, is possible only for ductile crystals, it is for crystals showing $\alpha_c \geq 10^3/s$.[80]

V.6 Fibers from Block Copolymers

Commercially much more important are the fibers made from block copolymers, primarily from polyurethanes. Both the apparel and technical fibers industries have interest in the elastic materials.

The polymers in question here consist of alternating blocks of "hard" and "soft" nature. "Hard" means here a moiety either of high glass transition temperature, *e.g.* polystyrene, or strongly polar segment, particularly with hydrogen bonding capability, *e.g.* urethane groups, or segments capable of a crystalline lattice formation. The "soft" segment is usually a flexible chain of rubbery nature, like poly(butadiene), poly(isoprene), poly(oxymethylene), poly(adipic lactone), and other similar. The two segments are incompatible, and this is not difficult to accomplish, as list of the compatible polymers is very short.

Incompatibility of the segments causes phase separation, and this is the *clue* of the matter. The material consists of two phases of different properties. The "hard" phase usually provides the strong anchors for the "soft" phase, which is responsible for the high rubbery stretch. In such a way we obtain highly elastic fibers, and so far this is about the only area of application for the block copolymers. The wealth of the different material properties this group of copolymers offers permits us to believe that a number of new, different fibers with marvelous properties will appear on the market.

The majority of the block copolymers is thermoplastic, though polyurethanes represent a borderline case. Despite the thermoplasticity, this group of polymers ought to be formed into fibers from solution; this is a matter of facilitating the phase separation. The morphology depends very strongly on the volume ratio of the two phases and on the sequence distribution along the copolymer chain. For example, the most "rubbery" materials are tri-blocks of H - S - H sequence, polyurethanes usually have alternating urethane (H) and soft segment. The elastic nature increases with the volume ratio of the soft segments, as well as with their length. Naturally, the degree of flexibility of the soft segment chains has a cardinal significance.

Separation of the phases proceeds according to the principle of achieving a maximum of separation at a minimum of the separating surface; this is just a matter of thermodynamics. The noncrystallizable blocks may agglomerate into spheres, or lamellae, or cylindrical forms. The crystallizable segments may form all kinds of crystalline morphological structures: spherulitic, lamellar.[61] Low temperature, high viscosity prevent the material from reaching the low energy goal. Processing of the materials from solution is the answer to the problem.

The proper selection of the solvent to use is not without great significance. The final selection of the most advantageous solvent is a matter of experimenting, and this is nothing new in the area of fiber formation from solution.

It is quite obvious that elastic fibers cannot be subject to cold drawing. For this reason it is even more important to provide for such process conditions which lead to the proper morphological organization at the moment of formation. There is little that can be done later. That "little" may be annealing which improves phase separation and perhaps coalesces some small, more dispersed areas.[61]

Extrusion of block copolymer melts is difficult. Even polymers of relatively low molecular mass, like elastomeric polyesters or polyamides, often show plug type flow in capillaries during melt extrusion.[62] Despite this, the flow through capillaries may have significant influence on the material properties, and the influence appears to be rather erratic.[63] In general, it is known that the large forces involved in extrusion through capillary brutalize the phase separation and it is a rule that comforting of a material gives better results.

V.7 Hard Elastic Fibers

In 1965, Celanese Corporation of America was granted a Belgian patent related to the invention of polyoxymethylene fibers of $2g/den$ tenacity and up to 250% of break elongation accompanied with a high recovery – 92% from 50% extension.[64] One year later a U.S. Patent was issued to DuPont De Nemours and Co. for similar fibers made of polypropylene and showing elongations at break up to 700%, but not quite as good a recovery as the previous work.[65] In both of the cases, the fibers were highly crystalline. Later it was shown that the so called *hard elastic fibers* may be obtained from practically any semicrystalline polymer, like nylon 6, poly(4-methyl pentene-1), poly(pivalolactone).

The initial publications, mostly patents, on the subject gave rather involved descriptions of the operational process variables leading to the hard elastic fibers. Work on the structure associated with such elastic fibers followed for some fifteen years, some of the highest caliber researchers became involved in it. From today's perspective, the results of all the investigations may be summarized as in figure V.12.

The elastic fiber structure consists primarily of crystalline mats which grow epitaxially on a small number of row nuclei. Besides being limited in number, most of the row nuclei are also limited in their length. The number of fibrils in an elastic fiber is very small, and preferably consisting of strongly distorted *destructible micro- paracrystals* of a small size along the a and b-crystalline axes.[66–70] There should be a rather small number of tie molecules involving an equally small fraction of the paracrystalline mosaic blocks of which the mats are built.

On extension, large segments of the lamellae bend and tilt, thereby increasing the interlamellar distance on portions of their surface. For this reason, the number of interlamellar connections needs to be small. The separation of the lamellae produces voids, which leads to an increase of the specimen volume on extension. Such volume increase has no place in the extension of rubbers or polyurethanes. During the investigation of the hard elastic fibers, the existence of the destructible micro-paracrystals has been determined. Up to twelve per cent of their volume could decrease on extension; this decrease means that the folds were transformed into link molecules. The unfolding is reversible, on cessation of strain the chains are folded back into their previous, or similar, positions.[70,72]

If in retrospect one analyzes the process conditions leading to the hard elastic fibers, particularly with the recent results obtained on crystallization in flowing polymer (section IV.5), it is easy to realize that all the precautions led toward the limiting of the rate of nucleation. If the process of nucleation is faster than the crystal growth, then increases the number of row nuclei which extend over larger distance and connect many lamellae in th *shish-kebob* fashion. Also, based on the work of Barham and Keller[11], one may suppose that under such process conditions the number of double or triple folds – *ergo* – tie molecules, would be drastically smaller.

In thermodynamic terms, the energy elasticity plays a role only below the yield

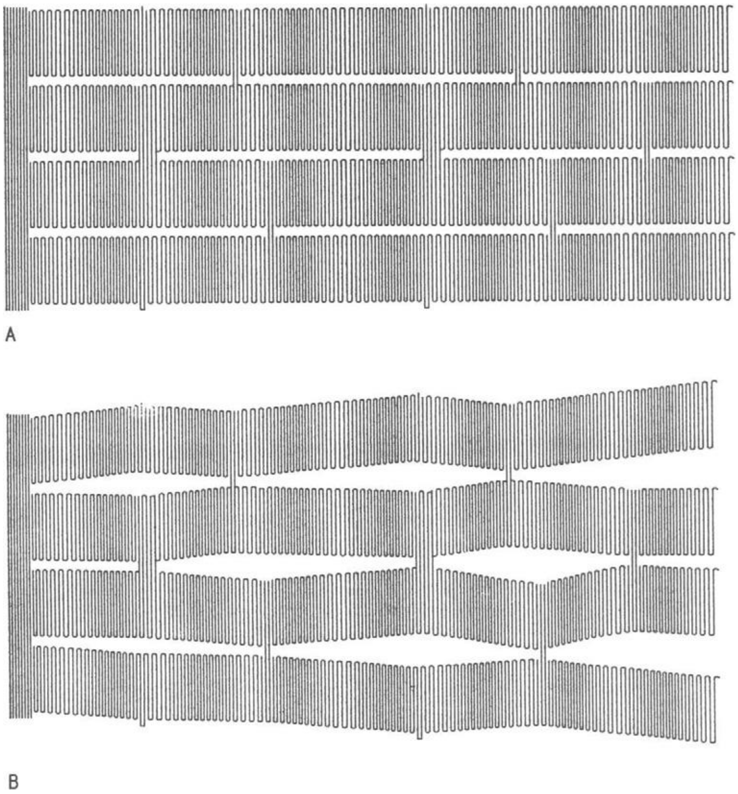

Figure V.12: *Schematic representation of the structure of hard elastic fibers: A - relaxed, B - strained.*

point, that is, below some five per cent of elongation. Above the yield point, the free energy increases with the increasing strain due to growth of inner surfaces. Entropy effects are classified as having a minor effect. The retractive force connected with generation of the link molecules on extension is mainly determined by the surface tension of the newly created surfaces.[70]

The hard elastic fibers did not make any great commercial career. The reason for this is simple: with the level of technical skills in the industry at the time of discovery of these fibers it was difficult to assure sufficient reproducibility of the processes. And last, though not least, the properties are insufficient to compete with polyurethane fibers. Recovery after extension in hard elastic fibers is relatively good, but that is relatively to the hard fibers, not to the elastic fibers.[71] And this is the key property of interest.

Why are we discussing here the hard elastic fibers? To show the wealth of possible structures obtainable from crystallizable polymers. If to connect the possibilities of development various structures with the sound ways of process manipulation, new sets of properties may be generated. Consequently, one may treat this information merely as stepping stones to technology expansion to newer groups of polymers, perhaps to new formation methods. The work on the structure of hard elastic fibers brought many solutions to the problems concerning also the "regular", the "conventional" fibers, mass produced for the apparel industry, as well as for the more exotic applications.

V.8 References

1. Z. K. Walczak, *J. Appl. Polymer Sci.*, **17 (1973)**, 177. 1
2. H. Sasano, T. Kawai, *Makromol. Chem.*, **184 (1983)**, 217.
3. P. J. Hendra, M. A. Taylor, and H. A. Willis, *J. Polymer Sci, Pt. C., Polymer Letters*, **24 (1986)**, 83.
4. J. D. Tanzer, B. Crist, and W. W. Graessley, *J. Polymer Sci., Pt. B, Polymer Phys.*, **27 (1989)**, 859, 875.
5. R. B. Williamson and R. C. Novak, *J. Polymer Sci., Polymer Letters*, **5 (1967)**, 147.
6. W. R. Pechhold, *Colloid Polymer Sci.*, **258 (1980)**, 269.
7. W. R. Pechhold and H. P. Grossmann, *Faraday Discuss. Chem. Soc,*, **68 (1979)**, 58.
8. W. R. Pechhold, T. Gross, and H. P. Grossmann, *Colloid Polymer Sci.*, **260 (1982)**, 378.
9. W. R. Pechhold, *Polymer Bull.*, **7 (1982)**, 615.
10. W. R. Pechhold, *Makromol. Chem. Suppl.*, **6 (1984)**, 163.
11. P. J. Barham and A. Keller, *J. Polymer Sci., Pt. B, Polymer Phys.*, **27 (1989)**, 1029.
12. E. W. Fischer, K. Hahn, J. Kugler, U. Struth, R. Born, and A. Stamm, *J. Polymer Sci., Polymer Phys. Ed.*, **22 (1984)**, 1491.
13. Z. K. Walczak: *Formation of Synthetic Fibers*, Gordon and Breach, London - New York, 1977, p. 131.
14. G. Kanig, *Progr. Col. Polymer Sci.*, **57 (1975)**, 176. 14.
15. R. Bonart and R. Hosemann, *Makromol. Chem.*, **34 (1960)**, 105.
16. R. Bonart, *Kolloid - Z.*, **194 (1964)**, 97; **211 (1966)**, 14.
17. I. G. Voigt - Martin, E. W. Fischer, and L. Mandelkern, *J. Polymer Sci., Polymer Phus. Ed.*, **18 (1980)**, 2347.
18. G. R. Strobl, M. J. Schneider, and I. G. Voigt - Martin, *J. Polymer Sci., Polymer Phys. Ed.*, **18 (1980)**, 1361.
19. F. J. Padden and H. D. Keith, *J. Appl. Polymer Sci.*, **37 (1966)**, 51.
20. K. Katayama, T. Amano, and K. Nakamura, *Kolloid - Z.*, **226 (1968)**, 125.
21. N. Kasai and M. Kakudo, *J. Polymer Sci., Pt. A*, **2 (1964)**, 1955.
22. R. Hosemann, *Polymer*, **3 (1962)**, 349.
23. R. Bonart and R. Hosemann, *Kolloid - Z.*, **186 (1962)**, 16.
24. R. Hosemann, W. Wilke, and F. J. Balta - Calleja, *Acta Cryst.*, **21 (1966)**, 118.

25. R. Hosemann, K. Lemm, A. Schönfeld, and W. Wilke, *Kolloid - Z.*, **216-217 (1967)**, 103.
26. A. Peterlin, *J. Polymer Sci., Pt. C*, **No 9 (1965)**, 61. 26.
27. I. L. Hay and A. Keller, *Kolloid - Z.*, **204 (1965)**, 43.
28. A. Peterlin and K. Sakaoku, *J. Appl. Phys.*, **38 (1967)**, 4152.
29. K. Kobayashi *cit. in* P. H. Gail, *Polymer Single Crystals*, Interscience Publ., New York, 1963.
30. T. Matsumoto, T. Kawai, and H. Maeda, *Makromol. Chem.*, **107 (1967)**, 250.
31. Z. K. Walczak, *unpublished paper*, 1969.
32. K. Fujimoto, K. Iohara, S. Oswaki, and Y. Murase, *J. Appl, Polymer Sci.*, **42 (1991)**, 1509.
33. R. D. van Veld, G. Morris, H. R. Billica, *J. Appl. Polymer Sci.*, **12 (1968)**, 2709.
34. H. R. Billica, paper presented at *Meeting of The Society of Rheology*, Knoxville, Tennessee, October, 1971; *Private communications*, 1970 - 1972. 34.
35. D. C. Prevorsek, G. A. Tirpak, P. J. Harget, and A. C. Reimschuessel, *J. Macromol. Sci., - Phys.*, **B9 (1974)**, 733.
36. M. Panar, P. Avakian, R. C. Blumke, K. H. Gardner, T. D. Gierke, and H. H. Yang, *J. Polymer Sci., Polymer Phys. Ed.*, **21 (1983)**, 1955.
37. J. M. Brady and E. L. Thomas, *Polymer*, **30 (1989)**, 1615.
38. R. Hosemann, *Polymer*, **3 (1962)**, 349.
39. M. Aboulfaraj, C. G'Sell, B. Ulrich, and A. Dahoun, *Polymer*, **36 (1995)**, 731.
40. W. Chen, Y. Fu, B. Wunderlich, and J. Cheng, *J. Polymer Sci., Pt. B, Polymer Phys.*, **32 (1994)**, 2661.
41. W. Glenz, A. Peterlin, and W. Wilke, *J. Polymer Sci., Pt. A-2*, **9 (1971)**, 1243.
42. S. Nagaou, *J. Macromol. Sci. - Phys.*, **B10 (1974)**, 115.
43. J. Petermann and H. Gleiter, *J. Polymer Sci., Phys.*, **10 (1972)**, 2333; **1 (1973)**, 359.
44. T. Tagawa, T. Tabuchi, M. Kashima, and K. Kobayashi, *J, Macromo. Sci. - Phys.*, **B10 (1974)**, 331.
45. C. L. Hammond, P. J. Hendra, B. G. Lator, W. F. Maddams, and H. A. Willis, *Polymer*, **29 (1988)**, 49 *and ref. cited.*
46. K. Prasad, D. T. Grubb, *J. Polymer Sci., Pt. B, Polymer Phys.*, **28 (1990)**, 2199.
47. D. L. Tzou, K. Schmidt - Rohr, and H. W. Spiess, *Polymer*, **35 (1994)**, 4728.
48. A. O. Baranov and E. V. Prut, *J. Appl. Polymer Sci.*, **P44 (1992)**, 1557.
49. F. Pinaud, J. P. Jarry, Ph. Sergot, and L. Monnerie, *Polymer*, **23 (1982)**, 1575.
50. A. Peterlin, *J. Polymer Sci., Pt. B*, **2(1963)**, 279. 50
51. J. D. Hoffman, *S. P. E. Trans.*, **4 (1964)**, 315.
52. H. H. Kausch and C. J. G. Plummer, *Polymer*, **35 (1994)**, 3848.
53. Z. K. Walczak, *previously unpublished results*, 1992.
54. V. Capuccio, A. Coen, F. Bertinotti, and W. Conti, *Chim. e Ind. (Milano)*, **44 (1962)**, 463.
55. D. Hofmann and E. Schultz, *Polymer*, **30 (1989)**, 1964. 55.
56. D. E. Turek and G. P. Simon, *Polymer*, **34 (1993)**, 2750; 2763.

57. P. Maïssa, A. Ten Bosch, and P. Sixou, *J. Polymer Sci., Polymer Letters Ed.*, **21 (1983)**, 757.

58. D. J. Blundell, A. Mahendrasingam, D. McKerron, A. Turner, R. Rule, R. J. Oldman, and W. Fuller, *Polymer*, **35 (1994)**, 3875.

59. A. M. Hindeleh, R. Hosemann, G. Hinricksen, and H. Springer, *Polymer Comm.*, **31 (1990)**, 205.

60. T. Ohta, *Polymer Eng. Sci.*, **23 (1983)**, 697.

61. M. Dröscher, U. Bandara, and F. G. Schmidt, *Makromol. Chem., Suppl.*, **6 (1984)**, 107.

62. Z. K. Walczak, *previously unpublished results*, 1983.

63. J.-M. Charrier and R. J. P. Ranchoux, *Polymer Eng. Sci.*, **11 (1971)**, 381. 63.

64. *Belgian Pat.* **No 650,890 (Jan., 1965)** to Celanese Corporation of America.

65. A. J. Herrman, U. S. Pat. No 3,256,258 (June, 1966) to Du Pont De Nemours and Co., Inc.

66. R. Hosemann, J. Laboda-Čačković, and H. Čačković, *J. Polymer Sci., Polymer Symp.*, **42 (1973)**, 563.

67. E. Ferracini, A. Ferrero, J. Laboda-Čačković, R. Hosemann, and H. Čačković, *J. Macromol. Sci., Phys.*, **B10 (1974)**, 97. 67.

68. R. Hosemann, J. Laboda-Čačković, and H. Čačković, *Colloid Polymer Sci.*, **254 (1976)**, 782.

69. G. S. Y. Yeh, R. Hosemann, J. Laboda-Čačković, and H. Čačković, *Polymer*, **17 (1976)**, 309.

70. J. Laboda-Čačković, H. Čačković, and R. Hosemann, *J. Macromol. Sci., Phys.*, **b16 (1979)**, 127.

71. S. L. Cannon, G. B. McKenna, W. O. Statton, *J. Polymer Sci., Nacromol. Rev.*, **11 (1976)**, 209.

72. R. Hosemann, *Makromol. Chem. Suppl.*, **1 (1975)**, 559. 72.

73. L. C. E. Struik, *Polymer*, **30 (1989)**, 799, 815.

74. B. K. Annis, J. Strizak, G. D. Wignall, R. G. Alamo, and L. Mandelkern, *Polymer*, **37 (1996)**, 137.

75. Z. Bartczak, A. Gałęski, A. S. Argon, and R. E. Cohen, *Polymer*, **37 (1996)**, 2113.

76. M. I. Aabo El Maaty, D. C. Basset, R. H. Olley, M. G. Dobb, J. G. Tomkam and I. – C. Wang, *Polymer*, **37 (1996)**, 213.

77. W. A. Kernick III and N. J. Wagner, *Macromolecules*, **32 (1999)**, 1159.

78. N. S. Murthy, D. T. Grubb, K. Zero, C. J. Nelson, and G. Chen, *J. Appl. Polymer Sci.*, **70 (1998)**, 2527.

79. D. T. Grubb and L. W. Jelinski, *Macromolecules*, **30 (1997)**, 2860.

80. W. G. Hu and K. Schmidt - Rohr, *Acta Polym.*, **50 (1999)**, 271.

81. I. F. Govaert and P. J. Lemstra, *Coll. Polymer Sci.*, **270 (1992)**, 455.

82. R. H. Boyd, *Polymer*, **26 (1988)**, 323.

83. S. Bensason, J. Minick, A. Moet, S. Chum, A. Hiltner, and E. Baer, *J. Polymer Sci., Part B, Polymer Phys.*, **34 (1996)**, 1301.

84. W. T. Mead and R. S. Porter, *J. Polymer Sci., Polymer Symp.*, **63 (1978)**, 289.

85. I. Liberwirth, J. Loos, J. Petermann, A. Keller, *J. Polymer Sci., Pt. B, Polymer Phys.*, **38 (2000)**, 1183.