Strain-Induced Crystallization

II. Subsequent Fibrillar-to-Lamellar Transformation*

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Part II discusses numerous examples of a morphological fibrillar-to-lamellar transformation that has reportedly been observed in stretched polymers upon additional thermal treatment (or TIC). Stretched polymers containing initially a typical fibrillar morphology for either crystallites in cold-drawn polymers, crystallites induced by stretching, or simply non-crystalline fibrils can yield a more or less lamellar morphology after the thermally-induced transformation. There is no evidence of extended-chain crystals present in either the original fibrils or the transformed lamellae; however, the extent of the transformation is strongly dictated by the annealing conditions and the stretch ratios, and therefore the local strains on tie molecules between the crystallites. Of particular interest is the observation of lamellar formation in conjunction with decreasing stress (or increasing length) during TIC under strain. This is in conflict with the generally expected stress increase if chain folding is presumed to occur during formation of lamellae. Consequently, it leads to the conclusion that lamellae form from *prefolded* structures during TIC. In the light of this surprising conclusion, available evidence on the presence of structure or non-Gaussian chain segments in the amorphous state is also cited. Included are the most recent neutron scattering results from concentrated solutions of polystyrene.

In Part I (1) the morphology of strain-induced crystallization (SIC) was discussed. It was pointed out that whenever direct experimental evidence can be obtained, the morphology is characteristically fibrillar, regardless of the applied strains and regardless of whether or not the polymer is stretched in the melt, the glass, or the solution state. The fibrils consist of strain-induced crystallites, with limited longitudinal and lateral dimensions of the order of 100 Å, about the same as that of the characteristic fibril diameter.

Part II discusses a very important fibrillar-to-lamellar morphological transformation that has been reported to occur *upon further thermal treatment* of the stretched polymer, regardless of whether or not the original fibrils contain crystallites. The transformation can be either irreversible or reversible with temperature, depending upon whether the stretched polymer is thermally treated above or below its original stretching temperature. In particular, we wish to point out the following: (a) the tendency towards lamellar transformation depends greatly on the annealing conditions (free vs restrained)

and the applied strains, and therefore the local strains on tie molecules between the strain-induced (and/or the thermally-induced) crystallites, (b) the extent of transformation, its resultant morphology and its relation to the so-called "row" morphology, (c) the absence of extended-chain line nuclei in the transformed lamellae, and (d) the formation of oriented chain-folded lamellae during stress decay.

The following examples of fibrillar-to-lamellar transformation are taken primarily from our comprehensive studies of cold-drawn polyethylene (2), partially strain-crystallized polyethylene terephthalate (PETP) (3), and cold-stretched, but not yet crystallized, isotactic polystyrene (IPS) (4), as well as strain-crystallized and not yet strain-crystallized natural rubber in the melt (5). Emphasis will be on the structure of the transformed lamellae and its relation to the structure of the fibrils that are originally present in a wide variety of oriented systems.

A very well-known example of fibrillar-to-lamellar transformation occurs in crystallized polymers after cold drawing and annealing at high temperatures. *Figure 1*
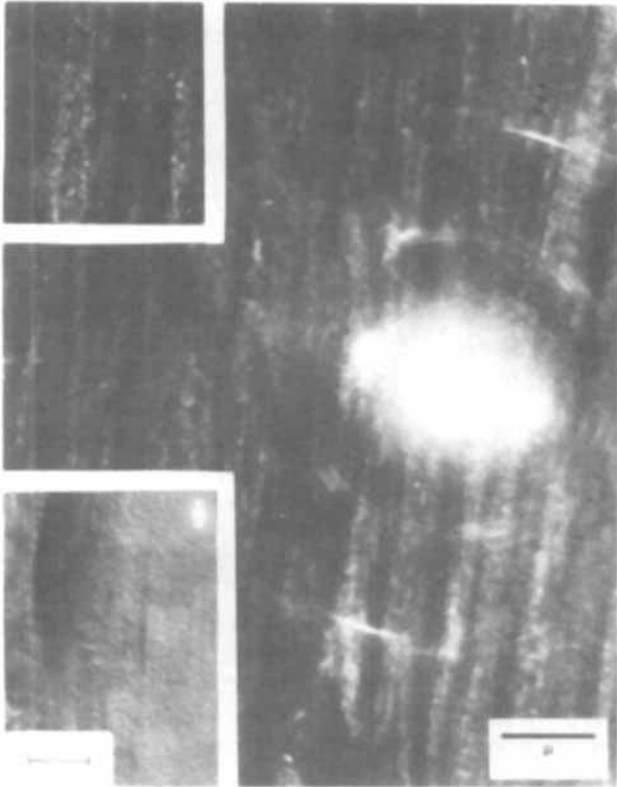
Fig. 1. Dark field electron micrograph of a highly drawn thin film of polyethylene; upper left insert shows a more destructive region (2); lower left insert shows the lamellar structure after annealing at 127°C for about 20 hrs.

(lower insert) shows an example of the lamellar morphology that is typical of cold-drawn polyethylene after annealing for sufficient lengths of time between 100 and 130°C. The structure of unannealed cold-drawn polyethylene is now well established and shown to be essentially fibrillar, consisting of 100 Å size microparacrystallites running more or less parallel to the stretch direction. The microparacrystallites contain partially folded chains and are tied to one another by numerous tie molecules. It may be of interest to note that the structure of highly drawn polymers was at one time a subject of much controversy and often thought (6) to consist of extended-chain crystals produced by the unfolding of previously chain-folded crystals. The extended-chain hypothesis was not entirely ruled out until the most unquestionable, albeit experimentally more difficult, dark field diffraction microscopy technique was applied to show the limiting extents of coherent scattering regions along the stretch- or c-axis. Examples of dark field electron micrographs are shown in Fig. 1 in order to demonstrate the limited dimensions of crystallites. Annealing at high temperatures results (7) in lateral alignment of neighboring microparacrystallites, partial lateral melting and/or epitaxial recrystallization so that the original fibrillar morphology finally disappears and is permanently replaced by an apparent lamellar type "row" morphology, with thicker crystals, but again limited to about 100 Å. This is one example where well-oriented lamellae have been established to form without requiring any extended-chain crystals as

backbones in order to account for their excellent c-axis orientation parallel to the stretch direction.

PETP AND IPS STRETCHED IN THE GLASSY STATE

A similar fibrillar-to-lamellar transformation that is also thermally irreversible occurs in stretched glassy polymers upon annealing to above their T_g's, regardless of whether the original drawn polymer is partially "crystallized" (e.g., to a smectic order in the case of PETP (3)) or not (e.g., IPS or plasticized IPS (4)) by the straining process. The results cited below refer to PETP (3) and IPS (4) and show, in particular, how the resultant morphology depends on the annealing condition (restrained vs unrestrained) and on the applied strain.

Figure 2 shows a pair of electron micrographs obtained from annealed thin films of PETP. The one on the left was annealed for 15 mins at 260°C (~5°C below Tm) in a restrained state, and the one on the right was annealed for 15 mins at 253°C in an unrestrained state while lying freely on a glass substrate. Both films were originally stretched to 500 percent in the glassy state and had a particulate "fibrillar" morphology with an essentially frozen-in c-axis orientation. After annealing, the particulate fibrillar morphology seems to have disappeared entirely and was replaced by a more or less "lamellar", again very particulate, morphology. However, there are apparent differences between the two lamellar morphologies. In the one annealed in the unrestrained or free state (Fig. 2, right), the lamellae appear to be slightly tilted and clearly much more pronounced and wider than those seen in the film which has been annealed in the restrained state (Fig. 2, left). These differences appear to be rather similar to those noted by Keller and Machin (8) between the so-called low stress lamellar morphology and the high stress lamellar morphology in polyethylenes, and to those noted by Yeh and Lambert (4) between the low strain (low stress) lamellar morphology and the high strain (high stress), but much
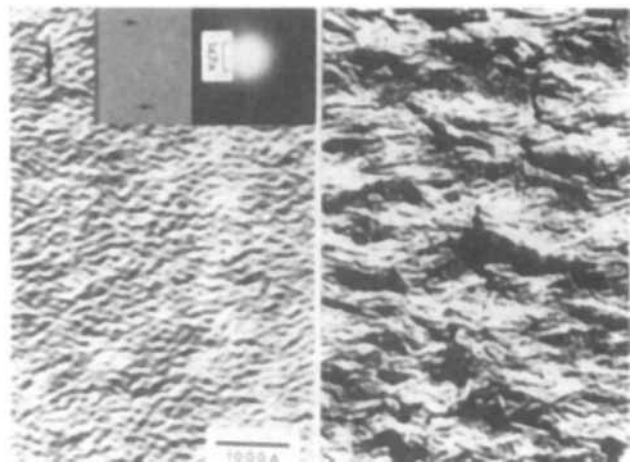

Fig. 2. PETP stretched to 500 percent at 65°C after annealing at 260°C in the restrained state (left) and at 253°C in the unrestrained state (right). The insert shows a small angle electron diffraction picture with a 147 Å periodicity, which agrees well with the lamellar periodicity seen in the electron micrograph (3).

less pronounced, lamellar morphology in IPS that developed *after annealing*.

Examples of our results on IPS annealed in the *re-strained* state are given in *Figs. 3* and *4*. Before annealing, all the stretched thin films had a more or less fibrillar, but not yet crystallized, morphology with varying degrees of orientation according to their gold decorated patterns as well as their diffraction patterns. After annealing, the transformed morphology is distinctly more lamellar in the low strain samples than in the high strain samples. For the 100 percent applied strain samples, the fibrillar-to-lamellar transformation seems essentially "complete" as judged from three different preparations (*Fig. 3*). Whereas the morphological transformation does not even seem to have started for the 600 percent applied strain sample (bottom, *Fig. 4*) since its fibrillar morphology remains almost the same as the original, a phase transformation must have taken place as indicated by its corresponding highly crystalline diffraction pattern.

From the above discussion on the changes in observed morphology with residual strain or with applied
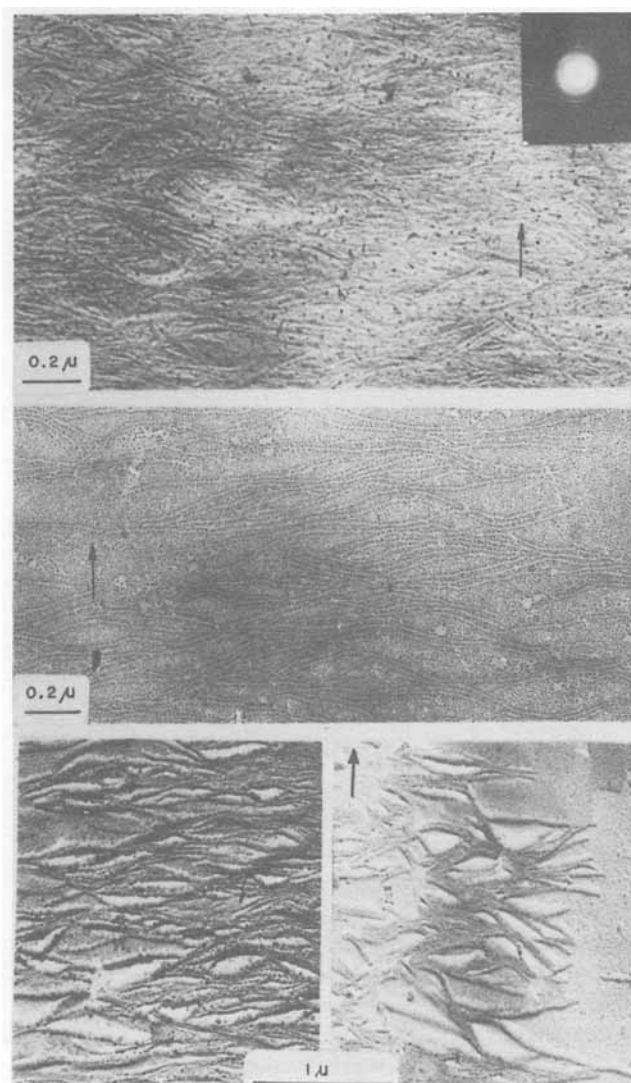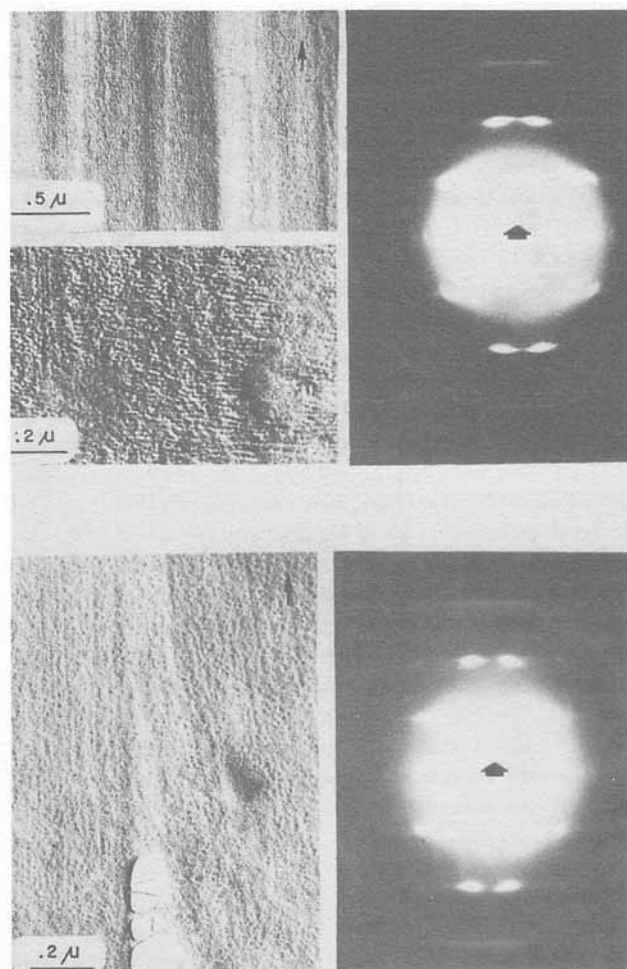

Fig. 4. Plasticized IPS stretched to 500 percent and annealed at 125°C (top) and 600 percent and annealed at 175°C (bottom)(4).

strain in stretched PETP and IPS, we can conclude that the morphology of stretched polymer does depend markedly on strain (or stress), but only after thermal treatment or *after TIC*. This is quite different from the statement often made in the literature that the morphology of SIC depends markedly on applied strain, changing from lamellae at low strains to fibrillar at high strains. The initial morphology of SIC is always fibrillar, as discussed in Part I (1), regardless of applied strains.

Another important observation is the established (3, 4) absence of extended-chain line nuclei within the transformed morphology that are essential, according to Keller and Machin's model, for the epitaxial growth and therefore the observation of oriented lamellae. How, then, can we account for the orientation of observed lamellae and its dependency on applied strain? We believe the answer lies in our finding of the fibrillar-to-lamellar transformation, especially the observed dependency of the extent of transformation on strain during TIC. The observed dependency suggests that the extent of morphological transformation is primarily controlled by the *degree of restraints* on the crystallizing units *by the tie molecules* between them. If it is substantial, e.g., in highly strained samples, the crystallizing units are prevented from lateral packing with one another, i.e., from transforming to a lamellar morphol-

Fig. 3. IPS stretched to 100 percent and annealed at 175°C, Pt-shadowed (top), Au-decorated (middle), and solvent etched (bottom) (4).

ogy that has a lower total surface free energy. At intermediate levels partial transformation may take place. Consequently, fibrils and transformed lamellae may be seen mixed in with one another in an apparently unrelated manner as, for example, seen in the 500 percent strained sample shown in *Fig. 4*, top. Furthermore, the lamellae in these more highly strained samples tend to remain adhered to one another after solvent etching, unlike those seen in the low strain sample (*Fig. 3*, bottom) where the lamellae are attached to one another at only a few places along the fold surfaces—again reflecting the important role played by the tie molecules on the final morphology after TIC.

A third important observation in these studies lies in the observed increase in axial length whenever samples are annealed to crystallize (TIC) in the *restrained* state, especially at high strains. For example, as much as a 10 percent increase in axial length was reported after annealing bulk stretched PETP (3). The usual explanation for such length increases during crystallization under strain is the formation of extended-chain crystals. However, as mentioned earlier, we have no experimental evidence for extended-chain crystals in these annealed samples. Instead, a fibrillar-to-lamellar morphological transformation was noted to be taking place during the axial length increase. Since the transformed lamellae have all the indications of chain-folded conformation as judged from Au-decoration, solvent etching and small-angle X-ray scattering, etc. (3, 4), it seems that there exists an apparent conflict between the morphological observation of chain-folded lamellae and the observation of macroscopic length increases, during lamellar formation, especially if the presence of extended-chain crystals is ruled out entirely based on our experimental evidence. Furthermore, the observed axial length increases are not simply restricted to these preparations upon heating. It is also found in bulk stretched natural rubber (as much as 4-10 percent after complete stress relaxation (9) at constant strain, and in bulk stretched polyethylene at constant load (10), both upon *cooling* and during formation of lamellae (see below).

NATURAL RUBBER STRETCHED IN THE MOLTEN STATE

All the fibrillar-to-lamellar morphological transformations discussed earlier occur upon heating in annealed polymers which have been cold-stretched either from the crystalline or non-crystalline glassy state and are essentially irreversible with temperature. A thermally reversible fibrillar-to-lamellar transformation has also been reported in strain-crystallized natural rubber (cis-polyisoprene) (5, 11) and gutta percha (trans-polyisoprene) (12, 13) upon additional cooling of the polymer in the strained state. We shall use some of the results obtained on natural rubber to show additional aspects of the transformation process.

Figure 5 shows the transformed lamellae in *unstained* 700 percent strained natural rubber thin films. The strained samples were first cooled to liquid N_2 temperatures and then examined in an electron microscope cold stage. The lamellae are seen perpendicularly oriented to
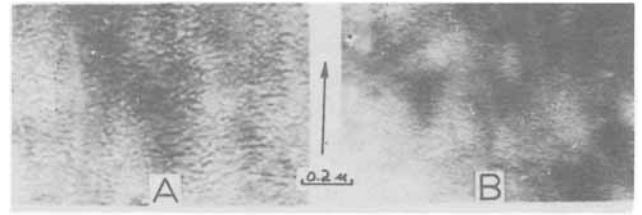

Fig. 5. Natural rubber unstained 700 percent stretched thin films after cooling for 4 hrs at −28°C (A) and after quenching in liquid N_2 (B) (5).

the stretch direction. Although these lamellae are not so well resolved in unstained thin films, their presence confirms the chain-folded lamellae that were established many years ago (14) on cleavage-freeze-fractured surfaces from bulk stretched crosslinked natural rubber after freezing at liquid N_2 temperatures. The most surprising finding was that the fibrillar crystals originally present throughout such 700 percent strain-crystallized samples (see Fig. 1, Part I) are no longer detectable after cooling to low temperatures.

These two findings, namely the apparent disappearance of fibrillar crystals and the appearance of chain-folded lamellae at low temperatures for highly stretched natural rubber, have led to a series of comprehensive studies on natural rubber (and on gutta percha), including the use of various electron microscopy (OsO_4 staining, ·dark field, Au-decoration, etc.), X-ray (small angle and wide angle), and stress relaxation experiments (9). The stress relaxation experiments were carried out not only to confirm the reported continuous stress decay in strain-crystallized natural rubber upon cooling but also to compare the kinetics of stress relaxation with the kinetics of the morphological transformation. Since the results from all of these experiments have been detailed and discussed elsewhere (5, 9, 11), the examples cited below are aimed at pointing out the following: (a) lamellar formation occurs at all strains between 100 and 700 percent during stress decay at low temperature, (b) there is an absence of extended-chain crystals within transformed lamellae, (c) the morphological transformation rate is about the same as the stress relaxation rate, (d) the strain-induced crystallites become unstable upon temperature or stress decrease, and (e) lamellae disappear and strain-induced fibrils reappear upon heating back to near room temperature.

Figure 6 demonstrates the presence of oriented lamellae in a 100 percent stretched, previously uncrystallized sample (left) and a 700 percent strain-crystallized sample (right). Both samples were stained at −28°C after cooling to −28°C for extensive periods of time to develop the lamellar morphology at constant strains. Their presence has been established (11) by the appearance of meridional discrete maxima (corresponding to a 135 Å periodicity) in small-angle X-ray patterns that were obtained from bulk crosslinked samples prepared under similar conditions. The fibrils dotted with 50-150 Å size crystallites that were originally present throughout the as-strained 700 percent sample (shown in the insert) appear to have disappeared entirely upon cooling the highly strained sample. Nor were any extended-chain
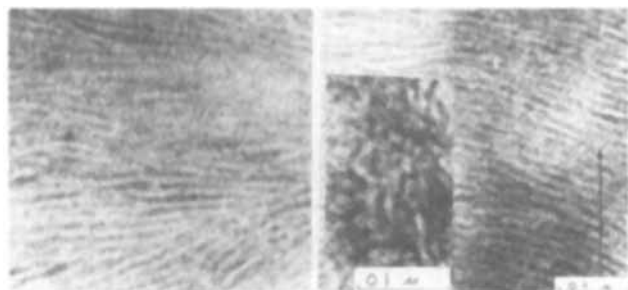
Fig. 6. Stretched natural rubber after cooling to −28°C for a time sufficient to develop the lamellae; 100 percent strain (left) and 700 percent strain (right) (5). Insert shows the fibrillar morphology of the 700 percent strained sample at room temperature.

crystals detected by dark field electron microscopy within any of these very thin film samples, regardless of whether or not they were initially strain-crystallized. This gives another established example of how well-oriented lamellae can be formed in stretched polymer without requiring any extended-chain line nuclei.

Figure 7 shows the disappearance of fibrils and the gradual appearance of lamellae as a function of time at −28°C for the 700 percent strained specimens. About 1 minute (*Fig. 7A*) after quenching to −28°C, the disappearance of some of the SIC crystallites can already be detected. After 3 mins (*Fig. 7B*), 200-400 Å wide, 134 Å thick lamellae are formed and mixed in with some of the fibril remnants at various places. After about 20 mins, or at about the same time the stress has relaxed to half of its original value at −25°C (9), the transformation to a lamellar morphology can be seen to be essentially completed (*Fig. 7C*). Longer times do not show any more substantial morphological changes. Similar changes were observed at +2°C, but the complete transformation took more than 20 hrs, about the same length of time the axial stress was observed to decay to half its initial value (9). Crystal growth along the stretch or fibrillar axis as expected from Flory's model (15) was not observed in any of our kinetic studies during TIC. In fact, there appears to be a crystal thickness decrease along the c-axis from 50-150 Å SIC crystallites at room temperature to 55 Å thick crystalline lamellar core at −28°C.

Upon reheating to room temperature the lamellae "breakup", partially melt, recrystallize and repack into thicker lamellae until reaching about +16°C, beyond which the lamellae disappear and the original fibrillar
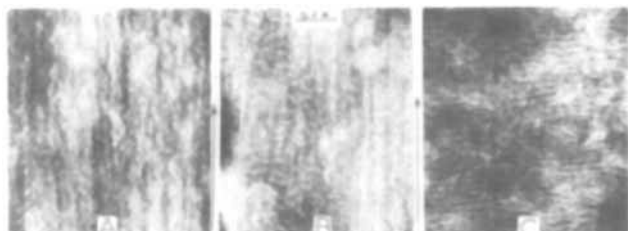

Fig. 7. Natural rubber stretched to 700 percent at room temperature after cooling to −28°C for 1 min (A), 3 mins (B), and 20 mins (C) (5).

morphology returns, which again contains 50-150 Å size strain-crystallized crystallites (5).

An explanation for the reversible morphological transformation has been given in references (5, 9). It is sufficient to note that the tie molecules again play an important role here, namely, the strain (transmitted mainly through the tie molecules) which initially brings about the formation of strain-induced crystallites is reduced upon temperature decrease, thereby creating a situation in which the strain-induced crystallites can become unstable and probably "pseudo-melt" as quickly as they crystallize, i.e., within a fraction of a second, after which recrystallization with a new fold period can take place at the low temperature in the oriented state. Upon temperature increase, annealing to a new fold period corresponding to the annealing temperature will take place (7); the strain will also gradually return due to thermoelasticity and will eventually result in the return of SIC crystallites. However, there is an obvious difference between these tie molecules that are primarily responsible for the generation of strain-induced crystallites and those present in cold-stretched polymers as mere ties. On the other hand, their number is expected to be very limited between successive SIC crystallites within any given fibril as judged by the restricted crystal growth along the fibrils upon cooling.

ORIGIN OF ORIENTED KEBAB TYPE MORPHOLOGY

The thermal reversibility of fibrillar-to-lamellar transformation in natural rubber described above is not a unique phenomenon for natural rubber alone; it has also been observed in transpolyisoprene (12, 13). The finding has not only contributed to a much better understanding of lamellar formation in stretched polymers at low temperature, but also to the understanding of two other very important classical problems, namely, annealing phenomena (7) and the thermal reversibility of long period (16). Although there are still some questions which can be raised concerning some of the finer details of morphological changes with temperature, crystallinity and molecular weight, etc., we can conclude, based on the extensive experimental evidence showing the transformation from a fibrillar to a lamellar morphology upon additional TIC, the following: (a) the mechanism for the formation of the so-called shish-kebab or simply kebab morphology is very much different from that proposed by Keller and Machin (8), (b) the mechanism for SIC is most likely not deducible from studies which have been subjected to additional TIC, and (c) no extended-chain, strain-induced nuclei exist within the lamellae either after or before (1) the fibrillar-lamellar transformation.

A few comments on the first conclusion are perhaps called for here, since Keller and Machin had proposed their 2-step row nucleation model based heavily on the evidence provided by Andrews (17) on natural rubber. As pointed out briefly in Part I (1), Andrews' study was very limited and contained several misinterpretations due to lack of data from concurrent bulk studies (e.g., replica and small-angle X-ray) and from time studies.

Consequently, Andrews missed some very important aspects of morphology of strain-crystallized natural rubber, including the all-important fibrillar-to-lamellar transformation and therefore the unexpected transformation that can occur in a highly stretched sample from a fully SIC fibrillar morphology to a fully lamellar morphology with a distinct small angle X-ray long period (11) upon TIC at low temperatures after long times. Therefore, Andrews' erroneous conclusion that only fibrillar nuclei, but no lamellae, can form in highly strained natural rubber (which he attributed to lack of space between fibrils for subsequent growth of lamellae) fits in well with Keller and Machin's 2-step line nucleation and chain-folded growth model, since a suppression of chain-folded lamellar growth will lead to a suppression in stress rise at constant strain according to their model. No stress rise is indeed observed in natural rubber at high or at low strains upon cooling (9, 18). However, since we have now established lamellar formation in stretched natural rubber upon cooling under both high strains *and* low strains, we can safely rule out the applicability of Keller and Machin's model to natural rubber as well.

The origin of oriented kebab type lamellae is shown to stem from a fibrillar-to-lamellar transformation. The formation of lamellae from fibrils is essentially induced by temperature changes. Its driving force is in the lowering of total surface free energy by means of lateral alignment of crystallites (or crystallizing or recrystallizing units) in neighboring fibrils, regardless of whether or not the original fibrils consist of crystallites brought about by plastic deformation of crystallized polymers, or crystallites brought about by SIC in the rubbery state, or smectic crystallites brought about by SIC in the glassy state, or simply of "aligned chain segments" brought about by stretching in the melt or the glass. The restraints to transformation are primarily the tie molecules between the little 100 Å crystallites. The extent of lamellar formation is therefore strongly dictated by annealing conditions, applied strains and possibly molecular weight, degree of crystallinity and crosslinking, etc. Consequently, the mechanism for the formation of the so-called "shish kebab" morphology is found to be very different from that envisioned by Keller and Machin; it occurs through a fibrillar-to-lamellar or a shish-to-kebab transformation.

LAMELLAR FORMATION DURING STRESS DECREASE

Another major, and an even more surprising, conclusion is the establishment of lamellar formation during stress decay in natural rubber upon cooling or during axial length increase in PETP upon heating. As pointed out in the Introduction of Part I (1), thermally-induced lamellar formation must also be occurring in polyethylene as well, during the time (20-60 min) the length was still noted to increase after completion of fast SIC (< 1 sec.). A new question arises. How can we account for this very general phenomenon of stress relaxation during formation of chain-folded lamellae? If molecular chain-folding is occurring from either a ran-

dom or an oriented amorphous mass of molecules, it must lead to a stress rise, as already pointed out by Judge and Stein (19) and by Keller and Machin (8). It seems that the only possible way out of this apparent dilemma is if " prefolds" were already there associated with either the crystallites, SIC crystallites or "non-crystallites" in the oriented fibrils. Lamellar formation can then initiate without stress rise by lateral alignment of crystallites or crystallizing structures, leading to an axial stress decay during the formation of c-axis oriented lamellae due to the increase in conformational freedom given to the remaining attached non-crystallized chain segments along the stretch direction (9).

Au-decoration experiments (5) tend to support the suggested presence of folds in SIC crystallites (e.g., in natural rubber), which may also explain why upon cooling crystal growth does not continue along the expected path of oriented aligned chain segments or along the fibrils, but instead occurs perpendicular to it. For cold-drawn polyethylene, there is ample evidence that folds exist in the original undeformed lamellae and in micro-paracrystallites produced after plastic deformation. Direct evidence for presence of folded structures in stretched but not yet crystallized polymers is rare. Cold stretched PETP shows small angle diffuse maxima (3), suggesting the presence of folds. The presence of distinct nodular structures on the surface of cold stretched thin films gives another indication that partial fold-backs occur at the nodular boundaries, which is the same argument we had used earlier to postulate chain-folds at the nodular boundaries in unstretched polymer melt or glass (20, 21).

Other evidence for fold-backs is found in dilute solutions of polyethylene and polystyrene from NMR (22, 23). More recently coherent neutron scattering experiments (24, 25) on semi-dilute concentrations of deuterated atactic polystyrene in carbon disulfide also give results that cannot fit a random-coil hypothesis at a local scale; it is highly dominated by excluded volume effects. Unfortunately, none of the small angle neutron scattering (SANS) experiments, including the earlier ones on bulk polystyrene or on polystyrenes at theta conditions (26), can reveal what the molecular chain conformation is at the local level. This was indeed carefully pointed out by the original authors in their final paragraph (26), which we quote, "This (SANS) result might seem to be in contradiction to the observations of glassy (or according to us, also melt) polymers which have shown what has been called supermolecular structures, i.e. the existence of domains of different densities. This conflict does not in fact occur; these domains can exist as long as they do not interfere with the statistical properties (statistical dimensions) of each molecular chain."

ACKNOWLEDGMENT

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