Studies of the Development of Fibrillar Structure in Nylon 6

The writers have been examining the production of trilobal nylon 6 filaments mimicking certain commercial production techniques in a laboratory setup. In the course of this work, we have observed some rather special fiber properties that appear to depend upon the quenching conditions to which the fiber is subjected after it emerges from the spinneret prior to its take-up preceding any drawing treatments. The quenching conditions that were introduced involve maintaining the temperature of the molten filament while it moves through the first 5 cm of filament line after emerging from the spinneret followed by quenching in enhanced turbulence, which, it is hoped, provided a rapid chill at the surfaces of the fiber. Subsequently, the as-produced filaments, which approximated a commercial carpet yarn, with an appropriate trilobal geometry were subjected to tensile testing and a tensile factor, or a figure of merit, determined for the tensile quality of the fiber in the form of an index, which was originally due to Rosenthal[1] and describes the tenacity-elongation exchange relationship. The factor we use is the product of the breaking tenacity and the square root of the numerical value of the elongation expressed as a percentage. Nominally, the commercial products and the process that we were studying produced values of the order of 35–38 in this index. The delayed quenching processes tended to produce filaments that gave tensile figures of merit in excess of 40 (42 in one particular quenching configuration). The yarn product with this higher property was subjected to a closer examination, and the work reported in this letter followed.

Small lengths of the filaments were sectioned and examined longitudinally in a thermal microscope at heating rates of 10°C/min until very close to the terminal melting. After the disappearance of the primary birefringence of these filaments, lines of residual birefringence were observed in the tips of the lobes of the trilobal filament, which persisted for several degrees above the normal melting point; namely, 216–220°C. Further, in nonpolarized light, optical examination of the melting sections revealed that the tips of the lobes tended to extend beyond the shrunken surfaces of the cut ends, suggesting a thermally more stable element in the tips than in the body of the trilobal yarn. A similar kind of stability was observed earlier by one of the writers[2] in polyethylene filaments that had been extruded just above the conditions for melt fracture. When short sections of these filaments were examined near the melting point in a thermal microscope, the central portions of the filaments retained their original cut lengths but the body pulled back into a more or less equilateral "glob" around the central spike, which persisted to relatively higher temperatures.

The presence of these thermally stable (extended) regions in extruded products can be taken as evidence of a fibrous crystalline content that is characteristically desirable in the production of high-performance fibers by the melt extrusion process. As an example, line nuclei observed originally by Whitley[3,4] in the chips of a high-molecular-weight polyethylene can be maintained through a low-temperature melt extrusion. The fiber so produced resulted in a filament that, when subjected to a certain degree of drawing after extrusion and annealing under restraint, produced a tensile modulus filament that was substantially above the conventional modulus observed for such polyethylenes. The modulus observed was approximately 670 g/denier, approximately one-third of the ultimate theoretical modulus, or half of the highest modulus observed to date for linear polyethylene of comparable molecular weight extruded under special conditions to give high-performance characteristics.[5]

It became interesting to examine the nylon 6 filaments containing the fibrous structures in the tips of the lobes in differential scanning calorimetry using a Perkin-Elmer DSC-II. Results of this examination yield an endotherm typically of the type shown in the solid curve of Figure 1. The lower temperature region of this endotherm is of some interest in that the heat evolution commences at approximately the glass temperature, as noted many years ago by Gordon,[6] and exhibits a maximum that ranges from a high of about 125°C to lower values between 60 and 80°C, depending on the conditions of the filament extrusion. This region is followed by a high-tempera-
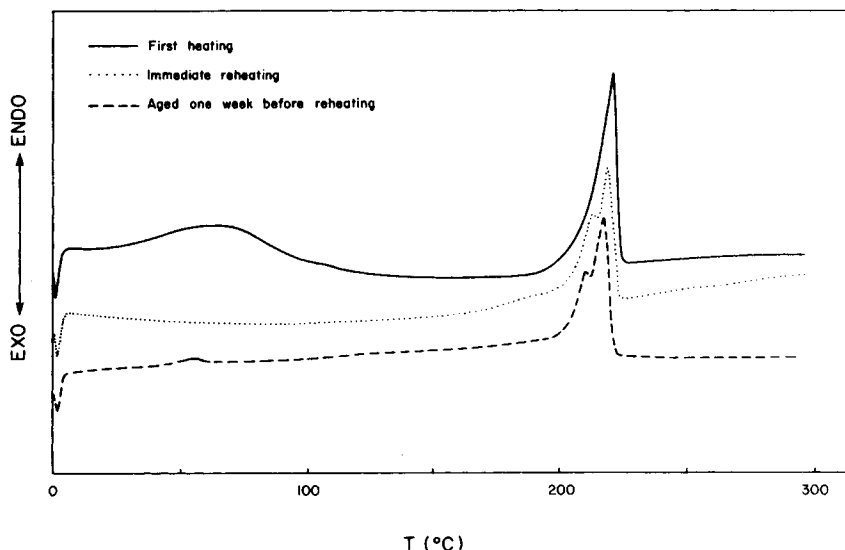
Fig. 1. DSC II thermograms of the high tensile factor nylon 6 filaments (scanning rate, 10°C/min).

ture endotherm reflecting the primary crystalline melting point. The higher temperature region of the endotherm contains a substantial asymmetry, and the peak is often rather jagged and irregular. In all cases, the endotherm cuts off sharply at temperatures somewhat above 200°C for the nylon 6 filaments referred to above. On reheating the sample immediately after the first heating cycle followed by cooling and recrystallization, the lower temperature region of the endotherm is removed in accordance with the observations of Jeziorny,[7] and the higher temperature region of the endotherm tends to develop more structure, as shown in the dotted curve of Figure 1. The dashed curve corresponding to the solid curve in Figure 1 was obtained upon rerunning the endotherm after melting and aging the specimen for a period of about 1 week. From these endotherms, it is clear that the lower temperature region of the endotherm tends to reappear after prolonged aging following the initial melting and recrystallization upon cooling. This is essentially the result disclosed by Jeziorny.[7] Inasmuch as Jeziorny suggests that the lower temperature endotherm is related, at least in part, to the presence of "tie" molecules and bridging structures between fibrous elements within a filament, it became interesting to attempt to model in a shaped object from nylon 6 a macrostructure that would be rich in fibrous content.

Accordingly, 20% solutions of nylon 6 were prepared in metacresol at room temperature and small drops placed on microscope slides that were then covered with a second slide and the two sheared apart to produce a highly distorted smear of polymer solution on the slide surface. This smear was allowed to dry at room temperature under two conditions: (1) quiescent air above the smear, and (2) a transverse airflow obtained by placing the slide in a chemical fume hood and dropping the door down to within a short distance from the hood floor. The latter case gave a highly directed flow over the film, more or less parallel to the slide surface. This resulted in extracting the metacresol more rapidly from the polymer, leaving a solid film behind. In the former case, the films were allowed to stand quiescently in the laboratory air and dried overnight. The DSC results of these two films are shown in Figure 2, in which the dashed curve represents the former case and the solid curve the latter. The structure of the endotherm was enhanced in the case of the film that was dried in transverse airflow.

On reheating of the film that was dried in the transverse airflow, immediately after the first heating cycle followed by cooling and recrystallization, the initial lower temperature broad endotherm is removed and the lower temperature region of the bimodal endotherm continues to be reduced, as shown in Figure 3. Note in the case of both solid curves of Figure 2 and Figure 3 that the higher temperature endotherm tends to remain sharp and the peak temperature varies by only 3°C.
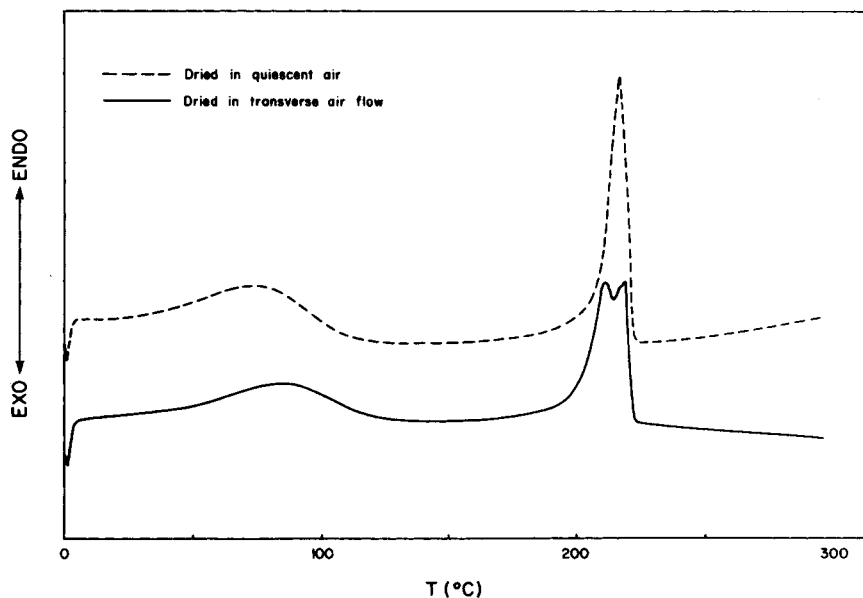
Fig. 2.   DSC II thermograms of the sheared nylon 6 films dried in the quiescent air and transverse airflow (scanning rate, 10°C/min).
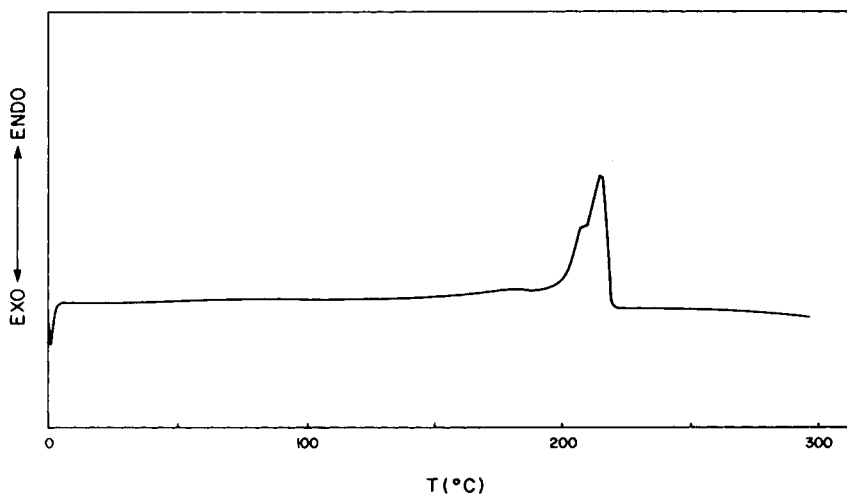

Fig. 3.   DSC II thermogram obtained after immediate reheating of the sheared nylon 6 film dried in the transverse airflow (scanning rate, 10°C/min).

It is tempting to interpret the second peak as associated with the more extended form of crystallization since from optical microscopy one knows that there is a substantial amount of fibrillar crystal in the films. If the films are formed by casting freshly prepared solutions with only simple fluid spreading and then dried in the transverse airflow, the high-temperature endotherm region appears as shown in Figure 4 (compare with Fig. 2). Figure 4 reflects the general suppression of the lower temperature endotherm; the bimodal endotherms seem to collapse into one broad, somewhat irregular endotherm with a low-temperature tail. Also, note that the peak temperature from this endotherm is about 3°C lower than the higher temperature seen in Figure 2.
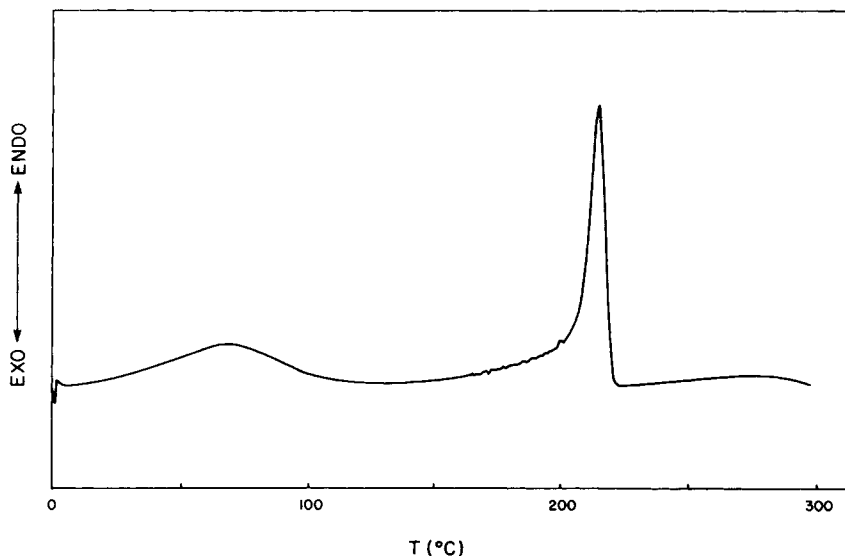
Fig. 4.   DSC II thermogram of the cast nylon 6 film dried in the transverse airflow (scanning rate, 10°C/min).

The low-temperature portion of the endotherms for those films derived from the sheared solutions strongly suggests that the polymeric material, which began to be loosened at the glass temperature, undergoes a restoration of configurational randomness that has in some way been removed. It is tempting to conjecture that this loss in randomness is the result of a certain portion of the molecular structure having collapsed into a loose, more or less unoriented network as the solidification process is first initiated.[8] This may result in the formation of small tactoidal structures oriented in various directions. When the shearing is applied to the solution, apparently this network is rearranged with a substantial amount of the initial structure lying parallel to the direction of distortion of the fluid field. As solidification proceeds, this distortion becomes the locus for elements of crystallization leading to the formation of line nuclei. The ultimate evidence for this can be seen in the partially crystallized film when viewed in the polarizing microscope.

Recent studies[9,10] show important details concerning the fiber precursor-phase separation and the development of oriented crystallization processes that occur particularly for growth from solution. It seems that the rheological phenomena of structure formation as a result of shearing are related to fiber formation in crystallizable polymers. Rietveld and McHugh[9] show fibers become crystalline via the growth of oriented crystallites, not via amorphous orientation followed by crystallization. The precursor phase can be viewed as a network structure, containing a high density of trapped entanglements that act as effective cross-links transmitting stress from the surrounding flowing solution.

As the solidification process proceeds, nuclei form in regions apart from the network structure. The network structure appears to exist in all solutions but with greater probability and intensity in the more concentrated solutions. The subsequent shearing of this quasi-structure in the solution gives rise to visible polarizing effects showing a strong orientational bias for molecules located within linear regions displaced one from another. There is little or no evidence of macroscopic polarization in directions other than that of the shearing of flowing direction in the fluid prior to solidification. Upon solidification, one finds well-developed line nuclei and structures, reminiscent of shish kebabs, in the crystallization product of dilute polyethylene systems subjected to prior extensive shear at elevated temperatures.[11]

Many of the features of the nylon 6 endotherms described above were observed by Artunc and Egbers.[12] They found that stretching assists the development of the bimodal characteristic of the higher temperature endotherm, at the same time suppressing the lower temperature region. Also, they were able to suppress the lower temperature endotherm by reducing the rate of scanning in the DSC; that is, the lower temperature endotherm was enhanced by scanning rapidly. The

general character of our endotherms and of those presented earlier by Artunc and Egbers seem to be in rather good agreement, even after semiquantitative comparison. We hope to expand this comparison in subsequent communications.

The higher temperature region of the endotherms on rerunning after the first melting is significant in two respects. (1) The initial low heat evolution that precedes the basic burst of heat indicates real structure and must have meaning. (2) The complex peak is generally resolved into two peaks closely spaced, suggesting the presence of two possibly separate phases in the microstructure.

When these films are observed through the optical microscope as they are slowly solidified, one sees a series of rather interesting structures. First, while the smear is still primarily liquid, if one analyzes the image under polarized light with a quarter-wave plate, bluish streaks in the direction of the deformation appear within the fluid. These streaks represent regions of birefringence, suggesting that the molecules have been extended along this region with their axes parallel to the general direction of the deformation. As the solidification process continues, the streaks gradually transform into collections of small bits of crystals that are similarly oriented, ultimately becoming embedded in a general maze of crystals, which completes the solidification process. The three stages of these advances are depicted in Figure 5.

Microscopic observations of the sheared film, together with DSC endotherms, allow a qualitative understanding of the endotherms in terms of the microstructural or morphological character of the specimens. In turn, we can infer from the endotherms derived from the extruded filaments that perhaps similar morphological structures are involved in this case. With this inference, we see the possibility of the production of synthetic filaments with elongated structures from relatively low molecular weight nylon 6, which should, if adequately concentrated in a macrofilament, lead to the development of enhanced properties that are popularly termed "high performance."

This inference is a bit surprising in view of the fact that most high-performance fiber properties, such as those observed in polyethylene by Smook and Pennings,[13] have always involved the use of extra high molecular weight polymer. The nylon 6 we have used has a relatively conventional molecular weight typical of commercial textile polymer. The presence of entanglements normally thought to be essential to providing the resistance required for the development of elongated structures in polyethylene are less probable in the case of the nylon 6 we have used. However, there is an extensive amount of hydrogen bonding in this polymer, and it is conceivable that lateral constraints introduced by such bonding can provide a stabilizing influence for the development of elongated line structures within the morphology.

The work of Smook and Pennings[13] on polyethylene suggests that the low-temperature region of the endotherm can be eliminated by appropriate hot drawing of the filament after its initial formation. If the draw ratios are sufficiently high, the low-temperature peak is eliminated from the endotherm. The higher peak of the endotherm doublet is thought to represent the extended chain structure or linear crystalline structure, and the lower region represents the melting of lamellar overgrowth usually present in the shape of shish kebabs. In the work of those authors, the shish kebab structure was clearly evident in the initial filament formation, which was derived from Pennings' gel extrusion technique.[10] In the case of the filaments made by us from nylon 6, there is no such clear observation. The birefringent regions that persist upon melting of the trilobal filaments suggest elongated molecular structures, but the resolution is insufficient to develop the presence of true shish kebabs. The suggestion of Smook and Pennings is indeed tempting in that, upon further drawing of such crystals, it is possible to remove the lamellar content and produce a smooth, more nearly fully extended fibrous crystal. This suggests that, in addition to quenching to produce these structures, an afterdrawing process will have to be used to remove the lamellar crystalline content of the morphology as produced by quenching.

Kunugi et al. have enhanced the extended chain structure of nylon 6 by a multistep zone-annealing method.[14] The modulus they observed was approximately one-tenth of the ultimate, theoretical modulus.

Kyotani has prepared nylon 6 crystals grown from stirred 1,2,6-hexanetriol solution.[15] The DSC curve of the samples of the crystals grown suspended in stirred solutions revealed double or triple peaks in the high-temperature endotherms. He interpreted his multiple peaks as resulting in part from the crystals that formed during cooling the solution to room temperature, following the isothermal crystallization. Pennings et al.[16] have similarly studied the solidification of nylon 6 in quiescent solutions of 1,4-butanediol at elevated temperatures. The resulting crystals
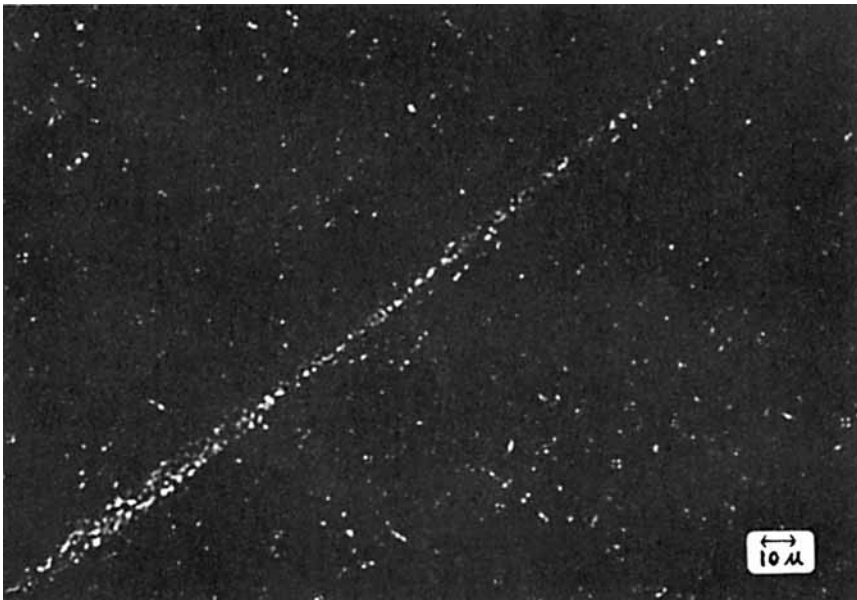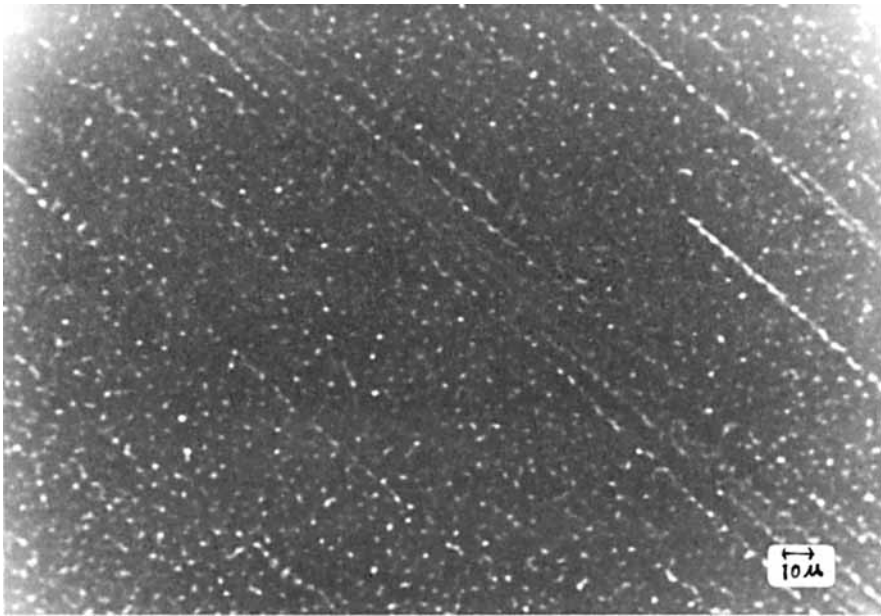
Fig. 5.   (a) Optical microscope view of initial stages of orientation developed in solution (×250, analyzed polarized white light). (b) Optical microscope view of initially thinner section of fluid than Figure 5a (about 30 min after shearing). (c) Field of b after becoming substantially dry (1 h after initiation of crystallization).

were elongated ribbons that in some cases resembled shish kebabs. In the case of crystals grown in high-temperature solutions, with and without deformation, the α axis of the nylon 6 unit cell of the α structure was oriented perpendicular to the long axis of the crystal. This was demonstrated by electron diffraction results in selected cases.

Fig. 5. *(Continued from the previous page.)*

Although the DSC II results obtained for crystals formed dynamically at high temperatures from a 1,2,6-hexanetriol are similar to those shown in Figure 2, we think they represent essentially different types of order. Our fibrous elements exhibit typical c-axis birefringence in those cases in which we can resolve the color of the relevant deformed region. The effects are always seen in either 100% polymer or drying solutions containing at least 20% polymer, the latter at room temperature.

Our high-temperature endothermic region has a distinct "tail" around the 209°C region. Kyotani related this region to evidence of a transversely oriented crystal structure that he thought to be rich in folded chain components. Our highest temperature peak is relatively sharp, suggesting a possibly more extended structure.

The endotherms shown in Figures 1 through 4 all indicate a maximum temperature of about 220°C, whereas fully developed extended chain crystals of nylon 6 yield[17] a much higher peak of greater than 240°C. The latter was obtained with added pressure during a high-temperature annealing, which promoted chain cleavage that tended to remove folded polymer from within the ordered regions. Our best structures, melting at the lower temperatures, surely retain substantial orientation imperfection. The higher temperature region of the DSC endotherms from nylon 6 do, however, offer promise of following the development of fibrous structure. It may thus be possible to recognize the development, in filaments of moderate molecular weight nylon 6, the potential for enhancement of the modulus and tenacity using the DSC as a guide indication of microstructure. Thus one may enhance the fibrillar content of a fiber by an appropriate stretching treatment of the molten polymer followed by quenching under highly controlled temperature conditions prior to further drawing and annealing.

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