

Influence of Shearing History on Polymer Properties. III.

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Synopsis

As a continuation of the investigation of the effects of shearing history on the subsequent properties of polypropylene, the changes of crystalline structure induced by differences in shearing history were examined. It was found that even extremely high shear in a capillary does not increase the crystal orientation in the extrudate. Such orientation is increased by either extremely high rates of extension of the molten extrudate or by slight plastic deformation occurring in the solidified extrudate as a result of imposed stress. The size of crystallites was found to decrease with increasing shear rate experienced by the polymer prior to the crystallization process. A possible explanation for these changes in polymer properties related to shearing history is proposed as an extension of the cluster flow theory of Busse. This explanation takes into account the size of the ball-like clusters, their internal structure, as well as the type, number, and length of the intercluster connections. The changes induced in a polymer by shearing are of technologic importance in connection with both melt flow characteristics and solid-state properties subsequently developed.

INTRODUCTION

In the previous parts of this series,¹ it was shown that although the molecular weight and degree of polydispersity are the main factors determining the melt flow properties of a polymer, the shearing which the polymer experiences may also affect the melt flow properties significantly. Both the intensity of shearing and the flow pattern influence the properties of polymer, as shown by the effects of differences in capillary length and entrance geometry. In part II of this series an incompatible polymeric additive was used as tracer, which showed that within the range of shear rates investigated, flow in the capillary was of the telescopic type. The supermolecular structure of the melt and the changes caused by shearing were assumed to be responsible for the variations in the melt flow properties observed, since no changes in the molecular weight or molecular weight distribution were detected.

It has been proposed by Busse^{2,3} that the principal unit of the supermolecular structure of noncrystalline polymers (and molten polymers) is a "ball" of coiled molecules. This idea has been supported by several other

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authors.³⁻⁵ The internal structure of these balls would depend on the extent of molecular entanglement or interpenetration, as well as the number, length, and type of ties between balls. This complexity suggests many possible conformations for the polymer molecules. Assuming that the globules of the polymeric tracer as used in part II and the molecular ball-like clusters behave similarly, despite the large difference in dimensions, it was supposed that the size of the molecular clusters would decrease with increasing shearing intensity (shear rate) and duration of shear (capillary length). A similar effect is caused by traction in the molten state, but plastic deformation (neck drawing) gives different effects.¹ It is not known whether the actual decrease in size of the molecular clusters results in the generation of new smaller balls, or whether the molecules are simply unwound and remain in the extended conformation. If the latter is true, a large orientation effect should be observed in highly sheared samples. If the interconnected molecular clusters align themselves in the direction of flow, the tie molecules would be expected to cause some, though perhaps less, orientation effect. As far as this author was able to ascertain, no systematic investigation of this problem has been published. The opinions expressed in the literature are, in fact, quite different in explaining the orientation effect caused by shearing or traction of the melt.⁶⁻⁹ Exploration of some aspects of this problem was undertaken in this study in connection with studies related to the effects of shearing on flow properties of polymer melt.

EXPERIMENTS AND DISCUSSION OF RESULTS

A sample of polypropylene fluff (sample F¹) which had never been exposed to any mechanical work at elevated temperatures was used in this study. In the experiments described earlier,¹ the polymer was subjected to shearing in an Instron capillary rheometer at various rates of shear using capillaries of 0.5-mm diameter and different aspect ratios (L/D ratios). X-Ray diffraction patterns of the control polymer (sample F) and of some of the extrudate strands were obtained with a flat plate camera. Figure 1 presents four of the diffractograms which cover the whole range of shearing conditions studied. Sample F is the control (not extruded), and samples F₁ and F₂ represent extrudates obtained from a capillary with an aspect ratio of 3 at shear rates of 250 and 1250 sec⁻¹, respectively. Extrudate F₃ was obtained at a shear rate of 1250 sec⁻¹ from a capillary with an aspect ratio of 20. None of the diffractograms revealed any traces of orientation by visual examination or by photodensitometer tracing of the film.

These polymer extrudates were free to relax in the die swell zone immediately upon emerging from the capillary exit. The orientation induced in the capillary could have vanished during this relaxation process. To determine if this had actually happened, the following experiment was performed. Polymer was extruded at a very high shear rate 9500 sec⁻¹ through the capillaries of a spinnerette with an L/D ratio of 9 and was subjected to various degrees of extension while being air quenched. Cross-flow cooling air

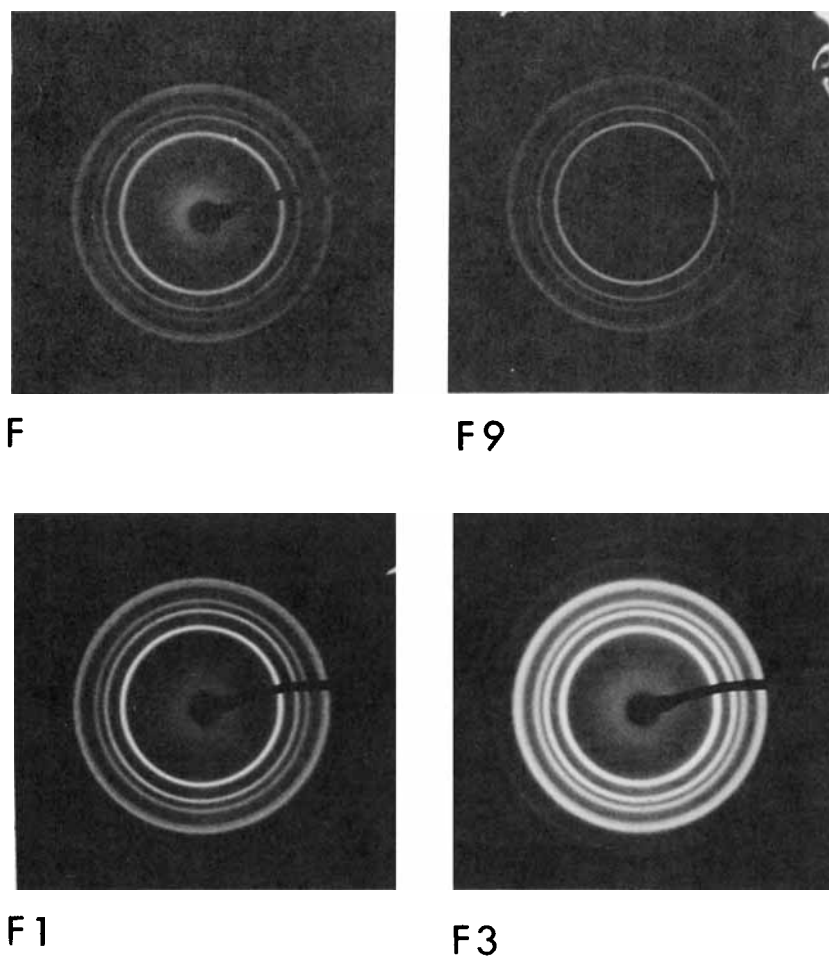


Fig. 1. X-Ray diffractograms showing lack of preferential crystalline orientation: (F) "as polymerized" sample; (F1) sample sheared in capillary with aspect ratio of 3 at 253 sec^{-1} shear rate; (F3) sample sheared in capillary with aspect ratio of 3 at 1250 sec^{-1} shear rate; (F9) sample sheared in capillary with aspect ratio of 20 at 1250 sec^{-1} shear rate.

was used for easier velocity profile control. Two different profiles of air velocity (Fig. 2) provided different rates of cooling, referred to subsequently as "warm" and "cold." The temperature of the cooling air was 39°C , and the velocity level was kept low since only 14 filaments were being extruded and no extreme cooling rates were intended. The melt temperature was 240°C . Take-up speeds were 100, 150, 250, and 350 m/min at both air flow intensities. The change of filament take-up speed certainly must have influenced the cooling rate, but the actual filament temperature profiles were not determined in these experiments. The data obtained in these experiments are shown in Table I. Figure 3 shows the x-ray diffraction patterns obtained for all of the samples generated.

TABLE I
Experimental Conditions and Filament Properties

Quench	Sample	Take-up Speed, m/min	Degree of melt Extension ^a	Filament density, g/cm ³
Warm	A	100	28	0.8986
Warm	B	150	42	0.8995
Warm	C	250	71	0.9010
Warm	D	350	99	0.9015
Cold	a	100	28	0.8995
Cold	b	150	42	0.9006
Cold	c	250	71	0.9001
Cold	d	350	99	0.9020

^a Ratio of take-up speed to calculated linear velocity of the polymer in the point of maximum bulge diameter, sometimes described as "melt draw ratio."

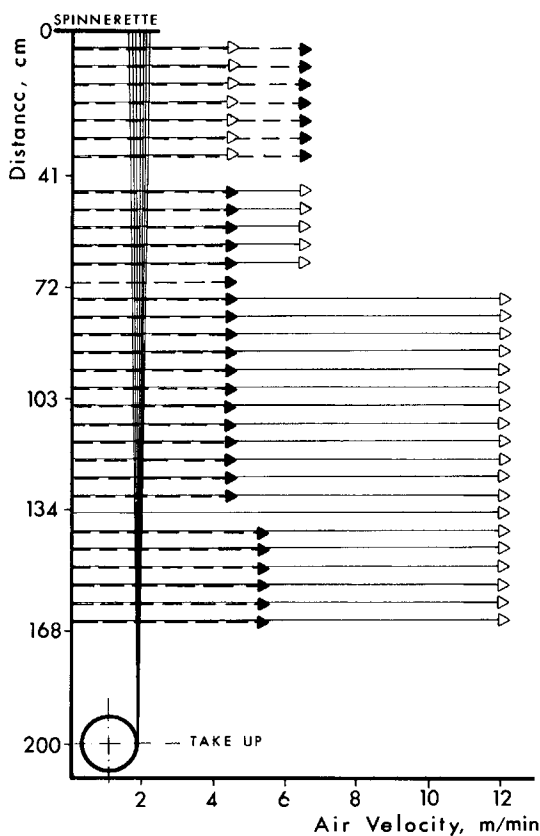


Fig. 2. Fiber quenching conditions: (→) warm; (⇨) cold.

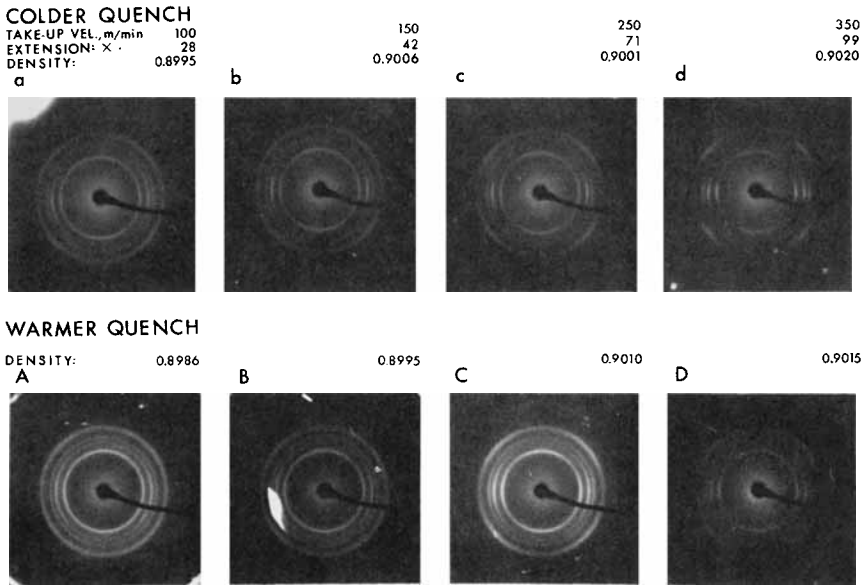


Fig. 3. X-Ray diffractograms of filaments extruded under high shear rate and melt drawn from 28 to 99 times at two different quench intensities. Detailed identification given in Table I and in text.

The die swell, or the ratio of the bulge diameter to the capillary diameter, was 2.47, representing about a sixfold contraction in extrudate length. The lowest degree of extension applied to the filaments was 28, so the extension could perhaps have caused some orientation even beyond that which may have been lost in the die swell. The filaments were extruded at 9500 sec^{-1} shear rate so that any shear orientation effect would be strong enough to be observed. As shown in Figure 3A, only traces of crystal orientation were detected. On the other hand, an increase in cooling intensity with all other conditions remaining unchanged (Fig. 3a) increased crystal orientation appreciably. The level of crystallinity remained essentially unchanged. Although there was some increase in density with increasing take-up speed (Table I), the extreme densities translated into per cent of crystallinity represented a range of only 57 to 61.5. Thus, the differences in overall crystallinity were too small to be considered as responsible for the changes in orientation.

With increasing degree of melt extension, the orientation effect was increased, but the orientation of the less intensely cooled filaments remained lower over the entire range investigated. From these data, it is impossible to predict if there might be a temperature profile which would completely prevent orientation, irrespective of the degree of melt extension and the degree of crystallinity. This possibility is suggested by the observation that in other experiments with polypropylene melts extended 40 to 50 times, x-ray diagrams similar to Figure 3A were obtained. The fact that variations in temperature had little effect on orientation is not surprising,

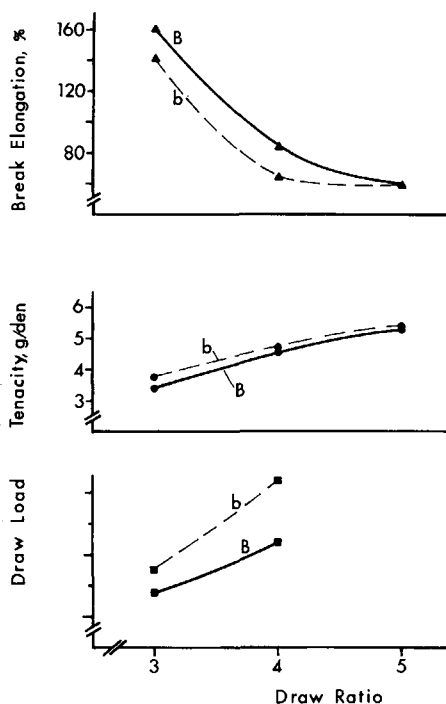


Fig. 4. Comparison between the property build-up vs. draw ratio for polymers with higher (b) and lower (B) predraw orientation.

particularly since the differences in the filament quench conditions investigated here were not very large.

Samples B and b were neck drawn at draw ratios of 3, 4, and 5 at 120°C to determine the properties of the filaments in relation to the degree of orientation. Mechanical properties of the drawn fibers and the load necessary for drawing are shown in Figure 4. An analysis of these results shows that the filaments with higher initial orientation behaved as if they had been already partially neck drawn. The force required to draw the more highly oriented fiber at a draw ratio of 3.0 was as high as that required to draw the less oriented fiber at a draw ratio of 3.5. The tenacity of the more highly preoriented fiber drawn at a draw ratio of 3.0 was as high as the other fiber after drawing at a draw ratio of about 3.3. The corresponding comparison of the breaking elongation of these filaments showed that they were equivalent at draw ratios of 3.0 and 3.2, respectively. The brief analysis suggests that the orientation induced while extending a polymer melt is mainly a result of slight plastic deformation which takes place while the filaments remain under stress below the temperature of solidification rather than from true melt drawing or shearing. Other features of the crystalline structure may also be affected, and this causes certain fiber properties to change with melt draw ratio for other reasons.

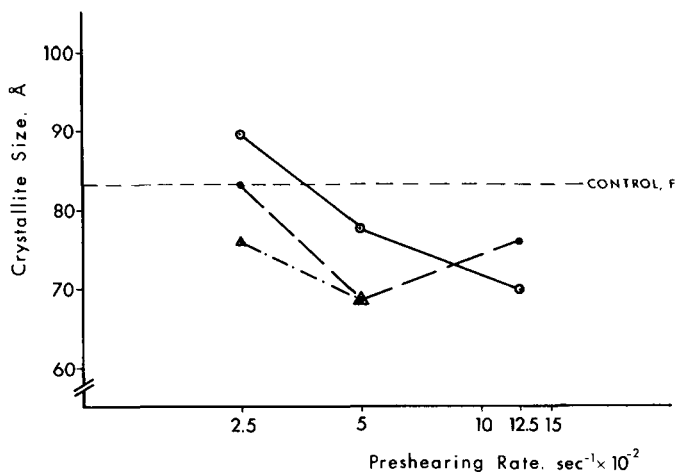


Fig. 5. Relation between apparent crystallite size and rate of preshearing, F series of samples: full circles, capillary with aspect ratio of 20; open circles, capillary with aspect ratio of 3; open triangles, capillary with aspect ratio of 9.

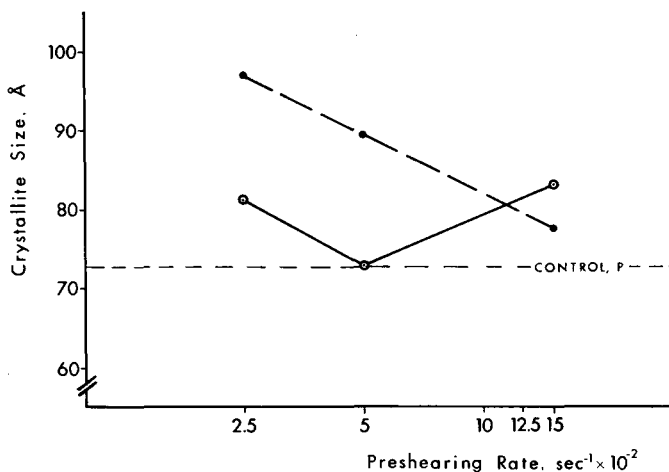


Fig. 6. Changes of apparent crystallite size in relation to the rate of preshearing, P series of samples: full circles, capillary with aspect ratio of 20; open circles, capillary with aspect ratio of 3.

The diffractograms of samples which were presheared at different shear rates and in different capillaries¹ revealed another interesting feature. The apparent crystallite size, measured from line broadening,¹⁰ decreased with increasing shear rate of preextrusion. The capillary length also had some effect, but this was difficult to define. The results of these experiments are presented in Figures 5 and 6. Despite some irregularities, there seems to be a relationship between crystallite size and shear rate in the capillary. The samples obtained at different extrusion conditions differed in diameter and had, therefore, experienced a different rate of cooling.

Thus, the crystals were not developed at exactly the same temperature conditions. At higher shear rates, the diameter of the extrudate was larger and the rate of cooling was slower. Larger crystallite sizes are usually associated with higher crystallization temperatures. Therefore, if the crystallization temperature had been the determining factor, crystallite size would have increased rather than decreased with increasing shear rate as observed in these experiments (Figs. 5 and 6).

The crystallite size measured from x-ray line broadening represents the size of mosaic blocks within single crystals or fibrils.^{11,12} Hosemann and co-workers established that the size of mosaic blocks is related to the degree of lattice distortions.¹² There are two possible explanations for the influence of mechanical shearing on the size of mosaic blocks. The size of the mosaic blocks may be related to the size of the molecular clusters. Such an explanation would require the polymer to crystallize within the molecular clusters which then join together to form a mat of a single crystal. Figures 5 and 6 are very similar to Figure 3 in part II of this series,¹ which shows the change of tracer particle size with shear rate, and this seems to support this explanation. A similar way of polymer crystallization has also been recently postulated by Yeh and Lambert.¹⁶ As an alternative explanation, the shear experienced by the polymer may have a large influence on the number of molecular entanglements which survive the process of crystallization and then cause a corresponding number of lattice distortions in the solidified polymer.

Irrespective of which of these explanations is more nearly correct, there is one observation which should be stressed. Figure 6 shows that the crystallite size in the sheared samples was larger than in the control. This observation suggests that the thermal treatment the polymer experienced prior and during extrusion caused either an increase in the size of molecular clusters or a decrease in the number of molecular entanglements. Thus, the thermal treatment has an effect opposite to the effects of shearing. The data presented in Figure 5 also seem to confirm this.

CONCLUSIONS

The results of these studies show that shear in a capillary does not cause orientation of polymer molecules in the extrudate. Traction (melt drawing) also does not seem to cause orientation of polymer molecules in the melt, except at very high extension rates. The orientation effects observed in these studies and in certain other studies reported in the literature^{9,14} seem to originate from slight plastic deformation taking place in the freshly solidified extrudate. One possible mechanism for explaining this behavior is the cluster type of flow proposed by Busse.^{2,3} The melt flow properties of a polymer of a certain molecular weight vary somewhat with the change of supermolecular structure. A ball-like molecular cluster seems to be the main element of this structure, although in addition it may be assumed that the internal structure of the balls (e.g., density and strength of the molecular entanglements) together with the number, size,

and length of the connections existing between the clusters also plays a significant role. In general, the size of the molecular clusters decreases with increasing shear intensity, but the decrease of the average cluster volume seems to result in an increase in the number of smaller clusters, rather than in unwinding and extending the molecules. The flow pattern of the interconnected clusters does not seem to cause orientation of the cluster ties parallel to the direction of flow. However, the orientation of molecules within the tie strands may be considerable.

Shear nucleation of polymer crystallization^{3,13,17} is believed to take place in the intercluster ties. Such a concept appears to be in agreement with the row type of nucleation suggested by other authors and with the absence of simultaneous development of preferential orientation reported in this work. The network of the intercluster ties seems to be also related to the shearing history, as indicated by the increase of the traction stress requirement with increase of shear rate in the capillary, as reported in part I of this series.¹

The changes introduced in the supermolecular structure of a polymer melt by shearing persist and may be reflected in the solid state as changes in some features of the crystalline structure. Changes in physical properties would be expected to accompany these changes in solid state morphology. Indeed, small crystals are associated with high tensile strength and modulus.¹⁵ Therefore, application of high shear in a process such as melt spinning should help develop such properties.

References

1. Z. K. Walczak, *J. Appl. Polym. Sci.*, **17**, 153 (1973); *ibid.*, **17**, 169 (1973).
2. W. F. Busse, *J. Polym. Sci.*, **A2**, **5**, 1261 (1967).
3. R. B. Williamson and W. F. Busse, *J. Appl. Phys.*, **38**, 4187 (1967).
4. G. S. Y. Yeh and P. H. Geil, *J. Macromol. Sci. (Phys)*, **B1**, 235 (1967).
5. V. A. Kargin, The Structure of Polymers in the Amorphous State, presented at IUPAC Symposium on Macromolecular Chemistry, Toronto, 1968.
6. A. Peterlin, in *Man-Made Fibers*, Vol. 1, H. F. Mark, S. M. Atlas, E. Cernia, Eds. Interscience, New York, 1967.
7. T. Manabe and M. Hiram, *A.C.S. Polymer Preprints*, **7** (No. 2), 876 (1966).
8. R. J. Samuels, *A.C.S. Polymer Preprints*, **7**, (No. 2), 870 (1966).
9. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, **2**, 14 (1959); A. Ziabicki, *ibid.*, **2**, 24 (1959); A. Ziabicki and K. Kedzierska, *ibid.*, **6**, 111, 361 (1962).
10. A. Guinier, *X-Ray Diffraction*, W. H. Freeman, San Francisco/London, 1963, pp. 124, 135 and 143.
11. R. Hosemann, W. Wilke, and F. J. Baltá-Calleja, *Acta Crystallogr.*, **21**, 118 (1966)
12. R. Hosemann, K. Lemm, A. Schönfeld, and W. Wilke, *Kolloid Z.*, **216-217**, 103 (1967).
13. A. K. van der Vegt and P. P. A. Smit, *Soc. Chem. Ind. (London) Monogr.* No. 26, 1967, p. 313.
14. K. Katayama, T. Amano, and K. Nakamura, *Kolloid Z.*, **226**, 125 (1968).
15. R. Bonart, *Kolloid Z.*, **210**, 16 (1966).
16. G. S. Y. Yeh and S. L. Lambert, *J. Appl. Phys.*, **42**, 4614 (1971).
17. Z. K. Walczak, *Formation of Synthetic Fibers*, Gordon & Breach, London/New York, in press.

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