Studies on the Orientation Phenomena by Fiber Formation from Polymer Melts.   IV. Effect of Molecular Structure on Orientation. Polyethylene and Polystyrene

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INTRODUCTION

It was shown in the preceding paper[1] that the general relationships of the process of orientation macromolecules by fiber formation from molten polymers are valid for various condensation polymers. All the formerly investigated polymers were typical fiber-forming materials, consisting of strongly polar, linear, not very long macromolecules. In the molten state all these polymers were viscous liquids with short retardation times and no evident elasticity. We felt it was important and interesting to extend these investigations to other polymers, which, though not typical fiber forming, in the molten state can be drawn into fibers. The present paper involves the results obtained from high-pressure polyethylenes and atactic polystyrenes and general conclusions concerning the effect of molecular structure on the process of orientation.

EXPERIMENTAL

Spinning apparatus, spinning conditions, and methods of examining the fibers are described in the previous papers.[1,2]

The polymers investigated were two high-pressure polyethylenes and two atactic polystyrenes. The characteristics of these materials are given in the Table I.

All these polymers evidently differ from the typical fiber-forming polyamides, polyurethane, and polyester treated in the preceding work. The average molecular weight of the polyethylenes and polystyrenes is higher than that of polycondensation polymers. The rheological behavior of molten polymers is more complex: there are as a rule long

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retardation times and strongly expressed elements of elasticity. In the case of molten polymeric hydrocarbons treated in this paper we are no longer dealing with viscous liquids, but with viscoelastic or elastoplastic bodies. Polyethylene, though possessing no polar groups, is a rapid crystallizing polymer; on the contrary atactic polystyrene is entirely amorphous.

RESULTS AND DISCUSSION

Preliminary experiments carried out on polyethylene L showed that this polymer in the molten state, at temperatures up to 300°C., has too long a retardation time for being rapidly drawn into fibers. Over the take-up velocity $V_E = 20$ m./min. at deformation ratio $S = 4$ the polymer stream broke. Fibers obtained by "gravitational spinning" were crystalline and had a slight positive birefringence.

Spinning Conditions and Fiber Birefringence

The *effect of deformation ratio* $S = V_E/V_0$ at constant take-up velocity V_E and fiber diameter ϕ_E was investigated, as in the previous work, by means of varying the spinneret orifice diameter ϕ_0. For low birefringent polystyrene PS3 no influence of S could be observed within the range of scattering of experimental data. The results for polyethylene T (PE) and polystyrene BW (PS-BW) are presented in Figure 1. Within a wide range of S (10–1000) there may be observed a slight but evident increase of birefringence. This effect distinguishes the polymeric hydrocarbons from polycondensation polymers, for which no substantial effect of deformation ratio was found.

The effect of deformation ratio is a deviation from the postulated mechanism of orientation, and

TABLE I
Characteristics of Polymers

Polymer	Commercial name, manufacturer	Symbol	Chain unit	Vis. av. mol. wt.	Melt flow index	Spinning melt temp., °C.	Rheol. behavior of melt at spinning temp.
High-pressure polyethylene L	Lupolen H (BASF, Ludwigshafen)		$[CH_2\text{---}CH_2]$	50,000	2.2	290	Elastoplastic body with long re-tardation time. $\eta_a = 10^4 P$
High-pressure polyethylene T	Tenite polyethylene 811A (Eastman Chem. Products, Kingsport, Tenn.)	PE	$[CH_2\text{---}CH_2]$	18,000	20	275	Elastoplastic body with long re-tardation time. $\eta_a = 10^3 P$
Atactic polystyrene BW	Polystyrol BW (VEB Bunawerke Schkopau, G.D.R.)	PS-BW	$[CH_2\text{---}CH]$	170,000	—	277	Viscoelastic liquid. $\eta_a = 6 \times 10^3 P$
Atactic polystyrene PS3	Dow Resin PS3 (Dow Chemical Co., Midland, Mich.)	PS-3	$[CH_2\text{---}CH]$	35,000	—	195	Viscoelastic liquid. $\eta_a = 10^3 P$

was expected for another mechanism: the extension of net structures (rubber, swollen gels). Therefore it should be suggested that also in the case of . molten polyhydrocarbons we are dealing with some net structures. From the molecular point of view such structures may be expected in long-chain polymers, somewhat branched (polyethylene), and doubtless tangled. An independent evidence of existing network structures and confirmation of this concept is rheological behavior: observed long retardation times and elasticity of melts. It is suggested that the elements of net structure are
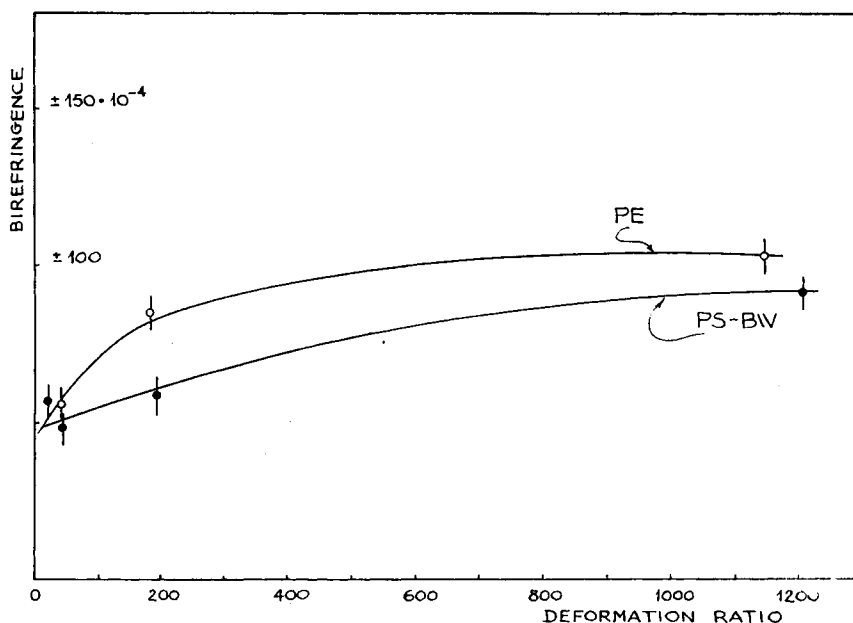

Fig. 1. Fiber birefringence vs. deformation ratio $S = V_E/V_0$ for polyethylene T (PE) and polystyrene BW (PS-BW).
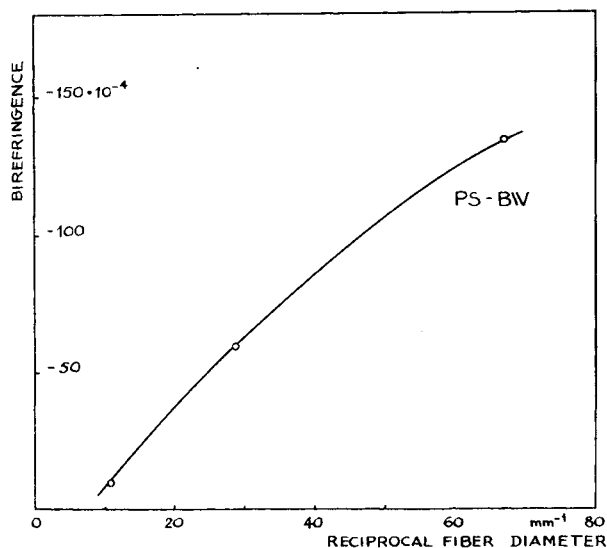
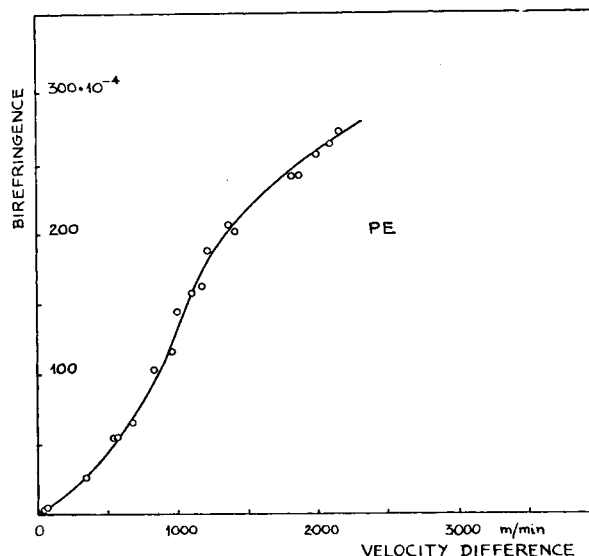Fig. 2. Fiber birefringence vs. reciprocal fiber diameter for polystyrene BW.

Fig. 4. Fiber birefringence vs. velocity difference $(V_E - V_0)$ at constant flow intensity W = const. for polyethylene T.
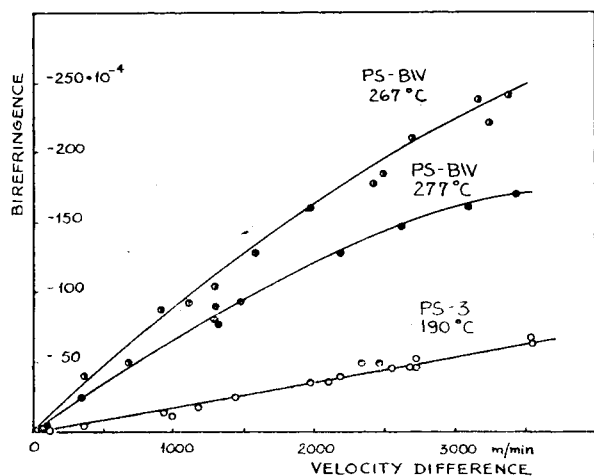

Fig. 3. Fiber birefringence vs. velocity difference $(V_E - V_0)$ at constant flow intensity W = const. for polystyrene BW (PS-BW) and polystyrene PS3 (PS-3). Spinning temperatures indicated.

responsible for the observed effect of deformation ratio on fiber orientation.

The *effect of cooling rate* was, as in the previous experiments,[1,2] investigated by varying the fiber diameter ϕ_E at constant take-up velocity V_E and deformation ratio S. The reciprocal fiber diameter ϕ_E^{-1} (directly related to heat transfer) was used as a comparative measure of cooling rate.

In the case of polyethylene T a notable decrease 'of fiber diameter (and increase of cooling rate) led to an immediate breakage of polymer stream. The retardation time, short enough for deformation at low cooling rates (thick fibers, ϕ_E = 0.05–0.10

mm.) became too long when cooling rate increased. This polymer should, therefore, be regarded as one of considerably limited spinnability.

For both polystyrenes, fiber birefringence is a monotonically increasing function of reciprocal fiber diameter ϕ_E^{-1} (Fig. 2).

The relations between birefringence and *velocity difference* $(V_E - V_0)$ (or mean velocity gradient) were determined, as for polycondensation polymers, at constant flow intensity, initial velocity, and spinning way length:

$$W = 3 \text{ g./min.}; \quad V_0 = 15 \text{ m./min.}; \quad L = 4.5 \text{ m.}$$

The results are presented in Figures 3–4.

The characteristics Δn vs. $(V_E - V_0)$ are monotonically increasing curves; the curve for polyethylene, however, evidently differs from those for polystyrenes. In polyethylene we observe an S-shaped curve as for polyamides,[1] but steeper and without a saturation within the range of velocities examined. It should be noted that an exceeding of this range in the direction of higher velocities led to an immediate breakage, as in the case of varying fiber diameter. This is a further evidence for the limited spinnability of polyethylene. For polystyrenes the characteristics Δn vs. $(V_E - V_0)$ are linear or slightly convex. The initial slope of these curves is greater for polymer of higher molecular weight (PS-BW), and for the same polymer greater for the lower spinning temperature. Both effects are in good agreement with our theory of orientation, which involves relaxation phenomena. Doubtless

an increase of molecular weight as well as a decrease of disorientation rate (due to the lowering of initial melt temperature) should lead to higher degrees of macromolecular orientation.

Spinning Stress and Birefringence

The relations spinning stress–velocity difference are similar to those found for polycondensation polymers. The curves increase monotonically, are concave, and the values of σ are of the same order of magnitude as in previously investigated polymers (10^6–10^8 dynes/sq. cm.). It is evident and completely comprehensible that the stress curve for low molecular polystyrene PS-3 is placed below the one for high molecular polystyrene PS-BW (Fig. 5).

The characteristics Δn vs. σ (Fig. 6) calculated from the corresponding relations Δn vs. $(V_E - V_0)$ and σ vs. $(V_E - V_0)$ are no longer similar to those observed in polycondensation polymers.[1]

For polyethylene T we observe a steep S-shaped curve with a point of inflection about $\sigma = 4.10^7$ dynes/sq. cm. For both polystyrenes we have convex curves, passing through the origin of coordinate system. The comparison of results for low and high molecular polystyrenes leads to the conclusion that the molecular weight of polymer affects the orientation immediately, not only through an influence on the viscosity and stress

needed to deform. It may be regarded also as an evidence for our mechanism of orientation.

The discussion of the molecular significance of the above results is now very difficult. In the case of condensation polymers we treated polymer melt as a viscous liquid. For such a rheological model the Δn vs. σ characteristic had a simple physical sense and led us to draw some conclusions about the rigidity of flowing structural units. However such a simplified assumption is no longer admissible when we are dealing with polyethylene or polystyrene, which are much more complex rheological systems involving elasticity. The curves Δn vs. σ do not reflect here the orientational behavior of flowing macromolecules alone, but are affected also by rheological factors.[3]

X-Ray Examination

In the Figures 7–9 are shown x-ray patterns of polyethylene fibers obtained by low-speed, high-speed melt-spinning and cold-drawing followed by heat treatment.

It is evident that all the fibers are crystalline. In the case of high-speed spun fiber (Fig. 8), we observe several distinct and sharp arcs—a characteristic pattern of oriented crystalline polymer. It should be noted that the interference spots in that pattern are more sharp than those in the pattern of cold-drawn fiber (Fig. 9). This fact is evidence for
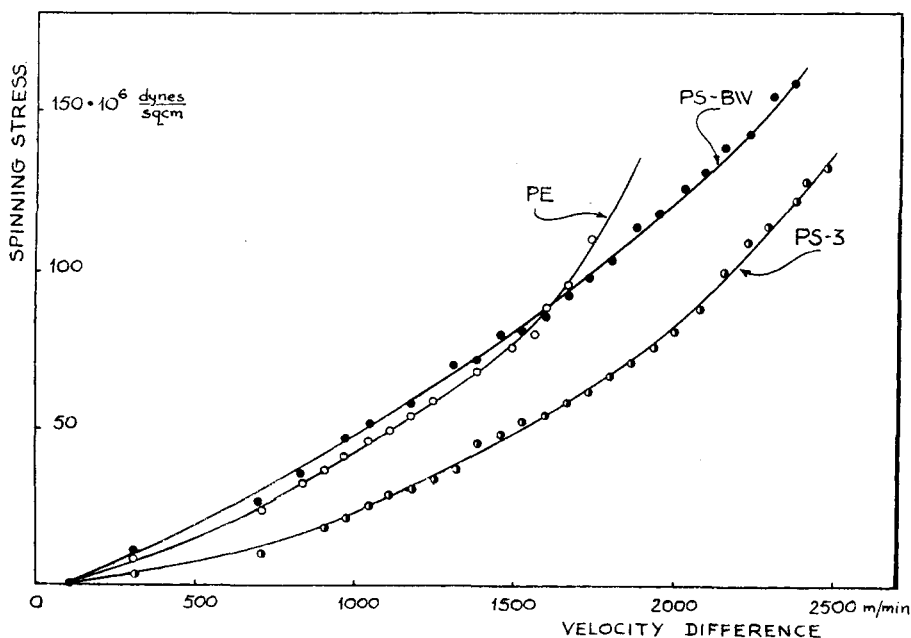
Fig. 5. Spinning stress vs. velocity difference $(V_E - V_0)$ at constant flow intensity W-const. for polyethylene T (PE), polystyrene BW (PS-BW) and polystyrene PS3 (PS-3).
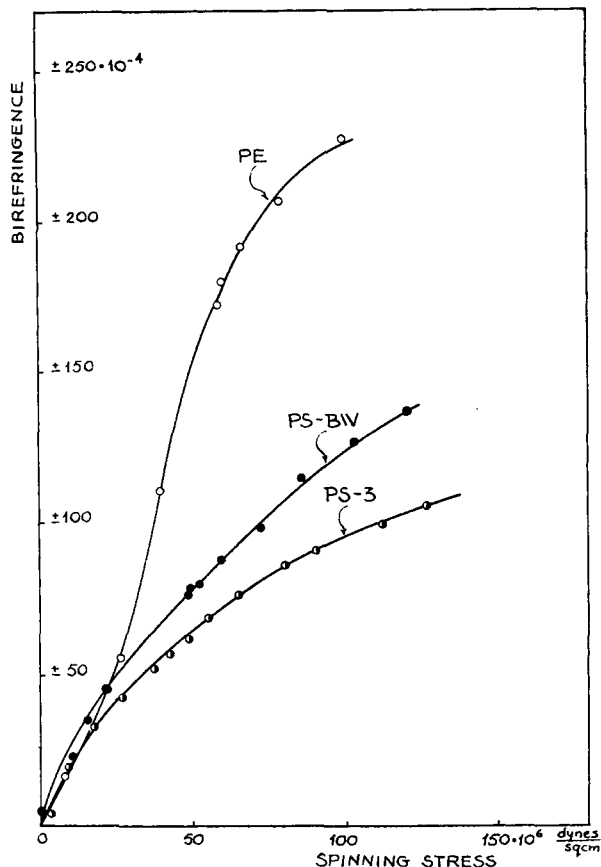
Fig. 6. Fiber birefringence vs. spinning stress for polyethylene T (PE), polystyrene BW (PS-BW) and polystyrene PS3 (PS-3).

a more complete crystal lattice in the melt-spun sample.

In the diffraction patterns of atactic polystyrenes (Figs. 10–11), there are evident two diffuse rings corresponding to the mean distances $d = 8.7$–8.9 A. and $d = 4.6$–4.8 A. The diffuse character of the x-ray patterns shows that polystyrenes are amorphous.

Comparison of the x-ray results obtained for melt-spun fibers from various polymers (cf. results of this and the preceding paper[1]) leads to the conclusion that polymers behave in a different way when melt-spun into fibers. Some of them give amorphous fibers with axially oriented, but noncrystalline structures; others give mesomorphous or crystalline fibers. Formerly it was supposed that in the process of melt-spinning macromolecules orient in structural modification similar to the arrangement in the molten state, i.e., amorphous or mesomorphous. The more extensive experimental material however needs a more general explanation.

It should be mentioned that during fiber formation two structural processes proceed simultaneously and not independently one of another: the crystallization, and orientation along the fiber axis. The course of crystallization and the resulting degree of crystallinity are affected first of all by thermal conditions. The effect of orientation on crystallization is an additional influence. Orientation, on the other hand, is strongly affected both by spinning conditions alone (velocity field, thermal relaxation) and crystallization.

When, under the given spinning conditions, the crystallization rate is great as compared with the rate of orientation, the structural elements that undergo orientation are previously formed crystallites. In polymers, which form strong intermolecular bonds (e.g., H bonds), the macromolecules in the melt join together; these aggregates, and not individual macromolecules, undergo orientation. In both cases fibers result with ordered structures (crystalline, mesomorphous) and orientation proceeds in a system of rather rigid structural elements. Such a behavior is suggested to occur in polyamides, polyurethane, and rapidly crystallizing polyethylene.

When the crystallization rate is considerably smaller than the rate of orientation, the macromolecules do orient along the fiber axis but do not form any crystalline regions. Fibers spun from such polymers consist of amorphous though axially oriented material (polyethylene terephthalate, polystyrene). In this case orientation is supposed to proceed in a system of individual, coiled, and tangled soft chains.

The differences between the relative crystalline and orientation rates seem to be closely connected with fiber texture as well as responsible (together with rheological factors) for the shape of dynamo-optical characteristics Δn vs. σ.

CONCLUSIONS

The results of investigations carried out on polymers with different molecular structure give evidence for the general character of the proposed mechanism of orientation.[1,2] This mechanism (a simultaneous action of velocity field and thermal relaxation) is valid not only for viscous melts of typical fiber-forming, condensation polymers, but also in principle for viscoelastic and elastoplastic melts of polyhydrocarbons; in the latter case there is, however, a slight deviation from the expected relation birefringence–deformation ratio, which sug-
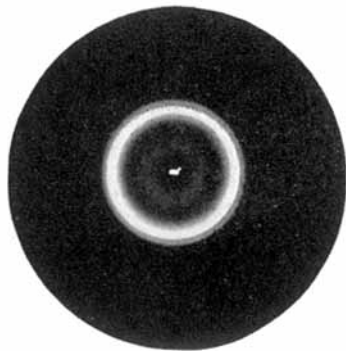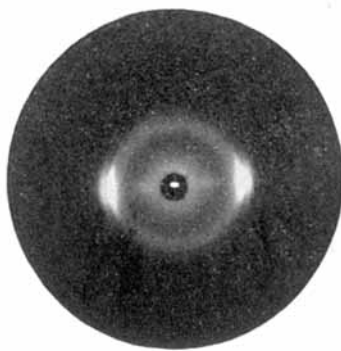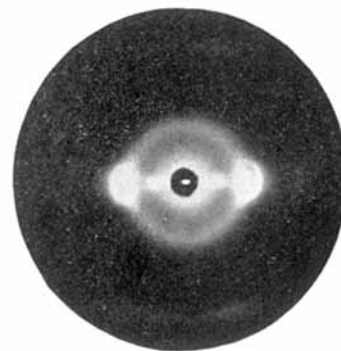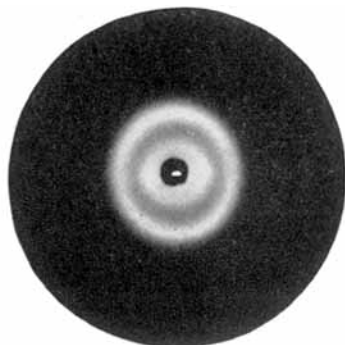
Fig. 7.   Fig. 8.   Fig. 9.

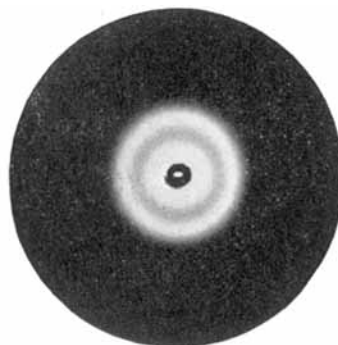Fig. 10.   Fig. 11.

Figs. 7–9. X-ray patterns of fibers from polyethylene T. CuK$_\alpha$ radiation, specimen–film distance $D = 30$ mm., fiber axes vertical. Fig. 7. Low-speed melt-spun. Fig. 8. High-speed melt-spun. Fig. 9. Cold-drawn and heat-treated (100°C., 1 hr.).

Figs. 10–11. X-ray patterns of high-speed melt-spun fibers from atactic polystyrenes. CuK$_\alpha$ radiation, specimen–film distance $D = 30$ mm., fiber axes vertical. Fig. 10. Polystyrene BW. Fig. 11. Polystyrene PS3.

gests a participation of another mechanism: deformation of a network.[2]

The formation of polymer texture in the melt-spun fiber is determined by two simultaneous and mutually bound processes: crystallization, and orientation along the fiber axis. As a result of experimental investigations carried out on various polymers it is suggested that the relative rate of these two processes determines, under given spinning conditions, fiber texture and the way in which the orientation is produced.

The shape of dynamo-optical characteristic Δn vs. σ (fiber birefringence vs. spinning stress) is determined by the manner of orientation as well as by rheological properties of polymer.

The orientation phenomena as observed in fiber formation are suggested to be a regular part of behavior of viscous and viscoelastic polymer melts.

References

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2. Ziabicki, A., and K. Kędzierska, *ibid.*, **2**, 14 (1959).

3. Ziabicki, A., *Thesis*, Tódź, 1959, unpublished.

Synopsis

The effect of spinning conditions on fiber birefringence and spinning stress has been studied on high-pressure polyethylene and two atactic polystyrenes. The general character of the relations observed is similar to that found for polycondensation polymers, but some deviations concerning the effect of deformation ratio have been noted. The x-ray patterns of the obtained fibers have been presented and discussed. A general interpretation of the observed structural phenomena in the molten linear polymers, based upon the relative crystallization and orientation rates has been given.

Résumé

L'effet des conditions de filature sur la biréfrengence de la fibre et l'effet de la tension de filature ont été étudiés en utilisant du polyéthylène haute pression et deux polystyrènes atactiques. Le caractère général des relations

observées est semblable à celui des polymères de poly-condensation, mais on note quelques différences en connection avec le degré de déformation. Les diagrammes des raies des fibres obtenues sont présentés et discutés. Une interprétation générale des phénomènes structurels observés dans les polymères linéaires fondus est donnée. Cette interprétation est basée sur les vitesses relatives de cristallisation et orientation.

Zusammenfassung

Der Einfluss der Spinnbedingungen auf die Faserdoppelbrechung und die Spinnspannungen wurde unter Verwend-ung eines Hochdrukpolyäthylens und zweier ataktischer Polystyrole untersucht. Der allgemeine Charakter der beobachteten Beziehungen ist ähnlich wie bei Polykon-densationspolymeren, es wurden jedoch einige Unterschiede im Zussammenhang mit dem Einfluss des Deformations-verhältnisses festgestellt. Das Röntgendiagramm der erhaltenen Fasern wurde angegeben und diskutiert. Es wird eine allgemeine Deutung der beobachteten Strukturphänom-ene in den geschmolzenen linearen Polymeren gegeben, die auf den relativen Kristallisations-und Orientierungsgesch-windigkeiten beruht.