

Studies on the Orientation Phenomena by Fiber Formation from Polymer Melts. III. Effect of Structure on Orientation. Condensation Polymers

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INTRODUCTION

In two former papers,^{1,2} the phenomena of macromolecular orientation as observed in the melt-spinning process have been investigated for polycapronamide, and have been theoretically discussed. It was the purpose of the following studies to obtain more extensive experimental material and to prove the effects, described for one polyamide, on various fiber-forming polymers. This paper discusses the experimental data on a few polycondensation polymers: polyamides, copolyamides, polyurethane, and polyester. Some polymeric hydrocarbons will be treated in another paper.

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EXPERIMENTAL

The spinning apparatus, spinning conditions, details of birefringence, and x-ray examinations were described in the first paper.¹

Spinning stress (the ratio of take-up force, measured on a free-running fiber just above the take-up device, to the fiber cross-section) was determined with the aid of an electronic tensiometer (Tensoron). Because of the considerably higher sensitivity and accuracy of this apparatus, the measurements previously obtained with the aid of a more primitive spring tensiometer (Kovo)¹ are not fully consistent with the present ones.

The characteristics of the investigated polymers are given in the Table I. All the materials investi-

TABLE I
Characteristics of Polymers

Polymer	Commercial name, manufacturer	Symbol	Chain unit	Visc. av. mol. wt.	Optical m. p., °C.	Spinning temp., °C.
Polycapronamide (Nylon 6)	Steelon (GZWS, Poland)	N6	$-\text{[NH(CH}_2)_5\text{CO]}-$	20,000	220-222	275
Polyhexamethylene adipamide (Nylon 6.6)	Nylon (ICI Ltd., London)	N6.6	$-\text{[NH(CH}_2)_6\text{NHCO(CH}_2)_4\text{CO]}-$	12,000	266-269	297
Polyundecanamide (Nylon 11)	Rilsan (Soc. Organico, Paris)	N11	$-\text{[NH(CH}_2)_{10}\text{CO]}-$	16,000	190-192	230
Polyurethane 64	Durethan U_6 (Bayer AG, Leverkusen)	PU64	$[\text{NH(CH}_2)_6\text{NHCO.O(CH}_2)_4\text{O.CO}]$	15,000	181-182	245
Polyethylene terephthalate	Lab. product	PET	$-\text{[CO} \langle \text{C}_6\text{H}_4 \rangle \text{CO.O(CH}_2)_2\text{O]}-$	15,000	259-260	278
Copolyamide I (66:6 = 2:1)	"	CoI	—	21,000	228-230	274
Copolyamide II (66:6 = 1:1)	"	CoII	—	21,000	190-194	250
C-Methylated copolyamide (C-Me6:6 = 1:2) mixt. of isomers	"	MeCo	—	17,500	180-182	250

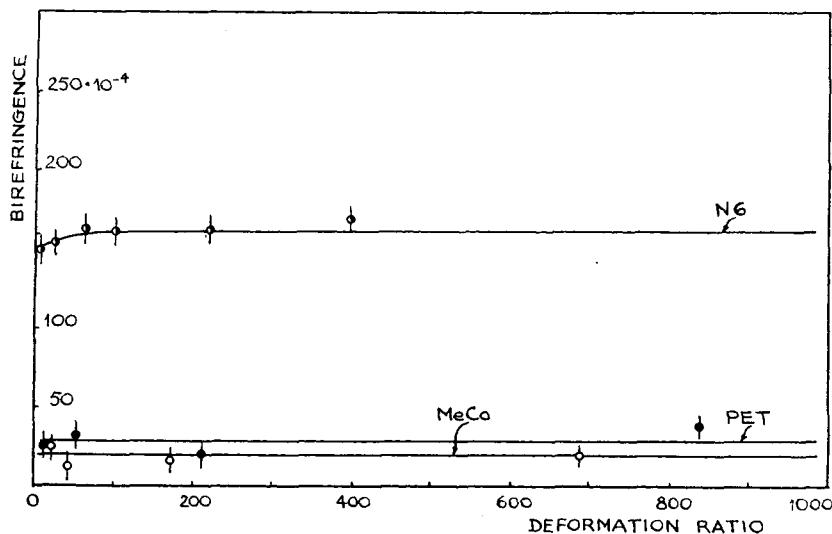


Fig. 1. Fiber birefringence vs. deformation ratio $S = V_E/V_0$ for polycapronamide (N6), polyethylene terephthalate (PET) and *C*-methylated copolyamide (MeCo).

gated in this work were linear, heterochain, rather low molecular weight polymers or copolymers with strongly polar chemical groups. These polymers form, as a rule low-viscous melts (1000–2000 poises in the spinning temperature) with relatively short relaxation times. They are all typical fiber-forming and crystallizable polymers.

RESULTS AND DISCUSSION

Spinning Conditions and Fiber Birefringence

The birefringence of fibers, as in the former work, was used as a comparative measure of the mean degree of axial orientation. In the preliminary investigations on polycapronamide¹ it was found that birefringence practically does not depend on the deformation ratio $S = V_E/V_0$, when fiber diameter ϕ_E and take-up velocity V_E are held constant. The main factors determining the degree of orientation for polycapronamide were: velocity gradient $G = dV/dl$ and relaxation phenomena, first of all the cooling rate.

The comparative measurements carried out on other polymers do not show any evident effect of deformation ratio S on the fiber birefringence. Within a wide range of S the birefringence remains practically constant. Results for methylated copolyamide (MeCo), and polyethylene terephthalate (PET) as compared with polycapronamide (N6) are shown in Figure 1.

The effect of cooling rate, realized through the varying of fiber diameter ϕ_E , was investigated on the same polymers. A decrease of flow intensity

W at constant initial (V_0) and take-up (V_E) velocities leads to a decrease of fiber diameter and to an increase of cooling rate, while the deformation ratio $S = V_E/V_0$ and the mean velocity gradient $G_m = (V_E - V_0)/L$ remain constant. As a comparative measure of cooling rate a reciprocal fiber diameter ϕ^{-1} was used. The physical significance of this quantity and its relation to heat transfer are clearly evident: ϕ_E^{-1} is proportional to the ratio of fiber surface (surface of cooling) to fiber volume.

(Such an expression seems to be more simple and correct than the "cooling rate criterion Z " introduced in the first paper.¹)

Fiber birefringence vs. reciprocal fiber diameter has been plotted in Figure 2. It may be seen from

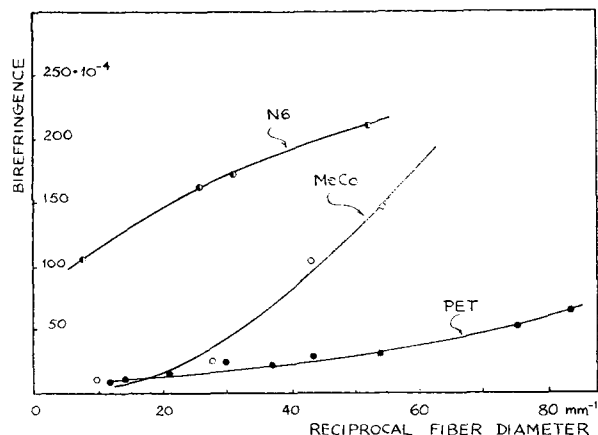


Fig. 2. Fiber birefringence vs. reciprocal fiber diameter ϕ_E^{-1} for polycapronamide (N6), polyethylene terephthalate (PET) and *C*-methylated copolyamide (MeCo).

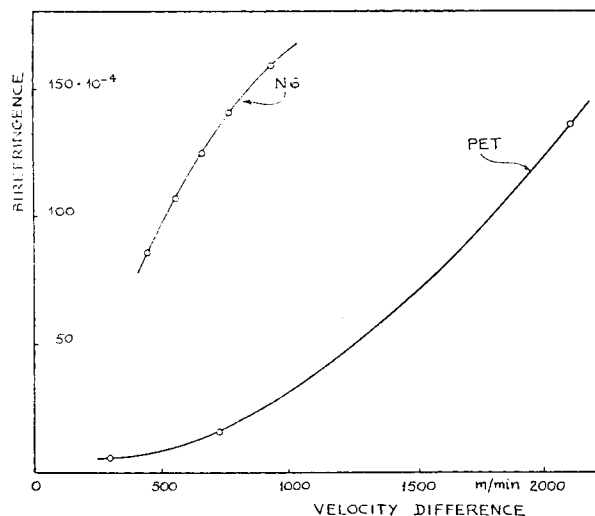


Fig. 3. Fiber birefringence vs. velocity difference ($V_E - V_0$) at constant fiber diameter $\phi_E = \text{const.}$ for polycapronamide (N6) and polyethylene terephthalate (PET).

the diagram that, for all the investigated polymers, birefringence more or less steeply increases with ϕ_E^{-1} . Such a behavior is quite consistent with the assumed mechanism of orientation.^{1,2}

The effect of velocity gradient seems to be the most interesting one. It has already been pointed out that in the spinning process the mean velocity gradient cannot be varied independently of the cooling rate.¹ It has been found for polycapronamide that birefringence increases with velocity gradient when fiber diameter is held constant (slight decrease of cooling rate) as well as when

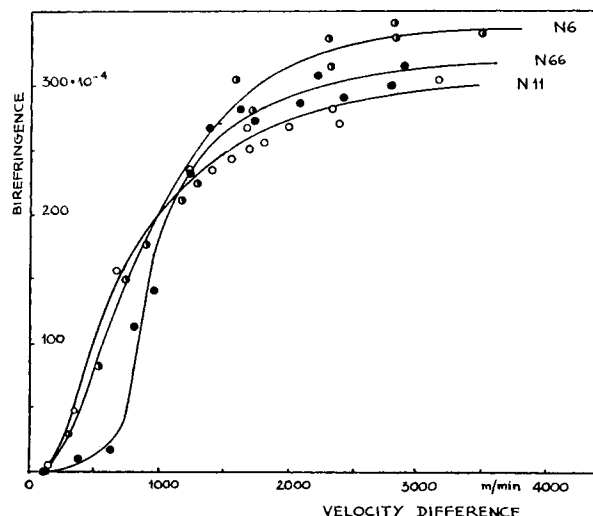


Fig. 4. Fiber birefringence vs. velocity difference ($V_E - V_0$) at constant flow intensity $W = \text{const.}$ for polycapronamide (N6), polyundecanamide (N11), and polyhexamethyl adipamide (N6.6).

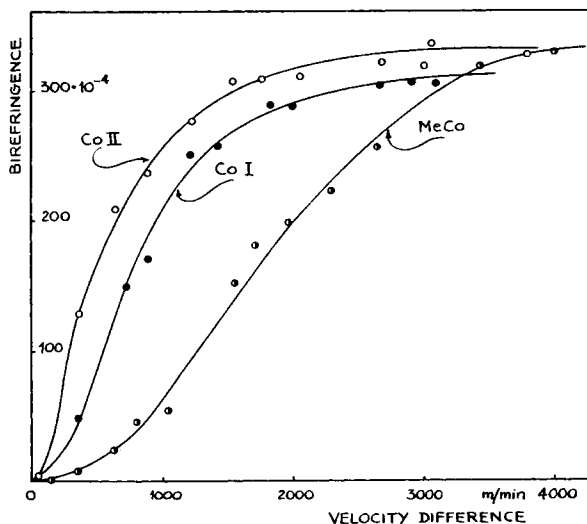


Fig. 5. Fiber birefringence vs. velocity difference ($V_E - V_0$) at constant flow intensity $W = \text{const.}$ for copolyamides (CoI, CoII) and *C*-methylated copolyamide (MeCo).

the flow intensity is constant (fiber diameter decreases, cooling rate increases).

In Figure 3, are presented the birefringence-velocity difference curves at constant fiber diameter for polycapronamide (N6) and polyethylene terephthalate (PET).^{*} In both cases there may be observed a monotonic increase of birefringence. There is, however, a difference between the two polymers. The curve for polyamide is convex, that for polyester concave. This difference, more evident in another series of experiments (Figs. 4 and 6) will be treated below.

The relations birefringence-velocity difference at constant flow intensity W (hence, decreasing fiber diameter and increasing cooling rate) were investigated for all polymers named in Table I under comparative conditions:

$$W = 3 \text{ g./min.}; V_0 = 30 \text{ m./min.}; L = 4.5 \text{ m.}$$

The results are presented in Figures 4-6.

From these results it is evident that, in every polymer, birefringence increases monotonically with velocity difference. The curves for various polyamides (N6, N11, N6.6) and for modified polyamides (CoI, CoII, MeCo)—see Figures 4 and 5—are S-shaped and tend to definite limits. So also is the curve for polyurethane (Fig. 6). The characteristic for polyester has quite a different form. It is a concave, rapidly increasing curve with no signs of saturation within the investigated range of

* The velocity difference ($V_E - V_0$) at the constant spinning way length, L , is used as a measure of the mean velocity gradient G , while $G_m = (V_E - V_0)/L$.

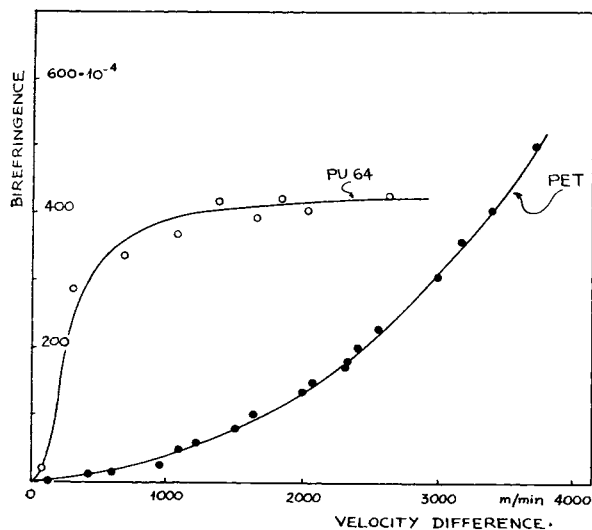


Fig. 6. Fiber birefringence vs. velocity difference ($V_E - V_0$) at constant flow intensity $W = \text{const.}$ for polyurethane 64 (PU64) and polyethylene terephthalate (PET).

velocities (Fig. 6). The possible explanation of this difference will be given in a later section of this paper.

Generally, it may be said, that the above results agree well with the postulated mechanism of orientation. For all investigated polymers the degree of orientation practically does not depend on the deformation ratio, and is determined by the velocity gradient (velocity difference) and the relaxa-

tion phenomena (cooling rate). The postulated mechanism of orientation—a simultaneous action of velocity field and thermal relaxation (disorientation)—seems to be proved as a general mechanism for typical fiber-forming polymer melts. The origin of different behaviors of polyamides, copolyamides, and polyurethane on one hand, and polyester on the other is now an open question. For this purpose some further experiments comprising spinning stress measurements and x-ray examination have been carried out.

Spinning Stress and Birefringence

It was shown in the previous papers that spinning stress, i.e., the ratio of take-up force to area of fiber cross-section, is affected by the same parameters and in a similar way as birefringence. A more extensive treatment of this problem has been published in separate papers.³

The variation of fiber birefringence with velocity difference (or velocity gradient) as observed in Figures 4–6 results from two equally directed effects: an increase of mean velocity gradient alone and an increase of cooling rate accompanying a decrease in fiber diameter. Therefore the shape of Δn vs. ($V_E - V_0$) curve does not reflect just the dynamic behavior of macromolecules or other flowing units in the velocity field, but involves also variation in viscosity and of the diffusion (dis-

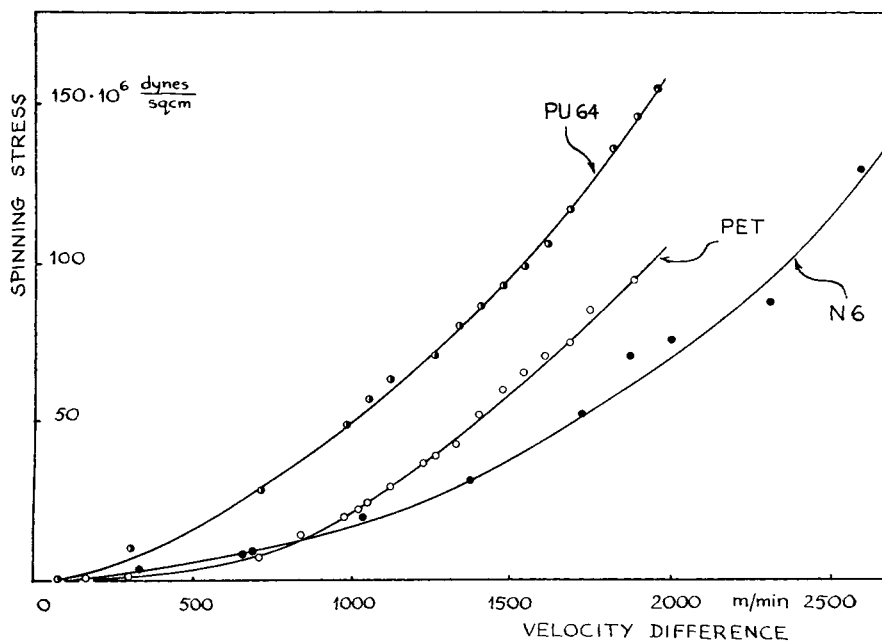


Fig. 7. Spinning stress vs. velocity difference at constant flow intensity for polycapronamide (N6), polyethylene terephthalate (PET), and polyurethane 64 (PU64).

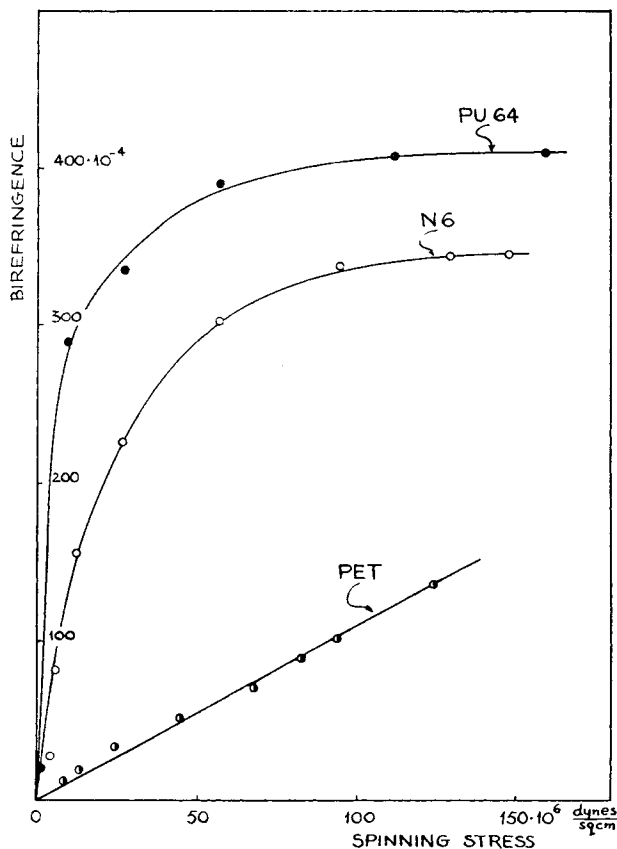


Fig. 8. Fiber birefringence vs. spinning stress for polycapronamide (N6), polyethylene terephthalate (PET), and polyurethane 64 (PU64).

orientation) rate constant D with cooling rate. This difficulty in the interpretation of results may be, at least partially, evaded by a consideration of relations birefringence–spinning stress instead of birefringence–velocity difference (or velocity gradient) treated previously. Spinning stress may be in the first approximation taken as proportional to velocity gradient G and Trouton viscosity λ or the reciprocal diffusion rate constant D :

$$\sigma \sim G/DkT$$

where σ = spinning stress and k = the Boltzmann constant.

Since the temperature variation in the experiments may be assumed to be independent of polymer structure, the characteristics Δn vs. σ seem to be more competent for a discussion of molecular effects than Δn vs. $(V_E - V_0)$.

In Figure 7 are given the spinning stress–velocity difference relations for three polymers. A combination of these data with the corresponding

relations birefringence–velocity difference led to the characteristics Δn vs. σ presented in Figure 8.

For all the polymers investigated the spinning stress curves are concave. The stress increases more rapidly than linearly with velocity difference, probably because of the simultaneously increasing viscosity (increasing cooling rate, structural effects).

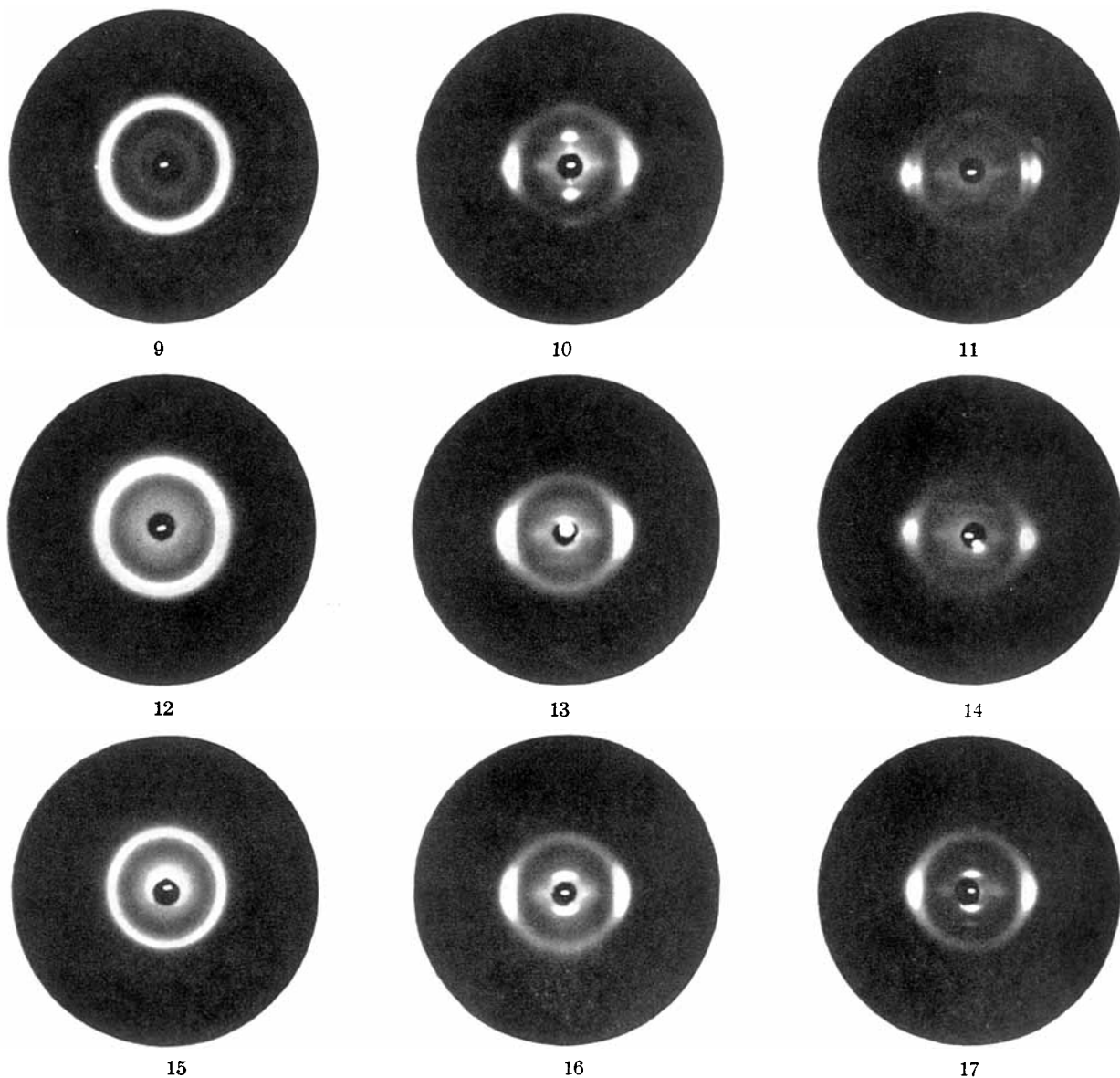
The relations Δn vs. σ for polycapronamide (N6) and polyurethane (PU64) are convex curves increasing with evident saturation. On the contrary, the characteristic for polyethylene terephthalate (PET) is linear.

The analogous relations in the theory of streaming birefringence in polymer solutions, Δn vs. $\alpha = G/D$, are connected with the character of flowing particles or macromolecules. Rigid, nondeformable particles show, as a rule, convex Δn – α curves with saturation as connected with pure orientation effects. On the other hand, soft, statistically coiled macromolecular chains not only orient in the velocity field, but also extend, uncoil, and straighten. The result of such a behavior is a linear or even concave characteristic Δn – α . Considering our problem as an analogy to streaming orientation² and the Δn – α characteristics as similar to Δn – α , it may be suggested that, in the case of molten polyamides and polyurethane, we have to do with some rigid structural elements that undergo orientation in the velocity field. In the case of polyethylene terephthalate we should have softer units, extending and orienting in the process of fiber formation. This assumption is justified by consideration of the chemical structure of these polymers as well as by the results of x-ray investigations described below.

X-Ray Examination

In Figures 9–20 x-ray patterns of various polyamide and polyurethane fibers obtained by low- and high-speed melt spinning are given and compared with diffraction patterns of fibers submitted to cold-drawing. X-ray patterns of high-speed spun copolyamide fibers are shown in Figures 21–23. Those of polyethylene terephthalate fibers are given in Figures 24–27.

It is evident from the figures that in polyamides, copolyamides, and polyurethane the orientation of macromolecules during fiber formation proceeded in ordered structures. In polycapronamide the structural modification produced by melt-spinning evidently differs from that obtained by cold-drawing; however, both are ordered structures.⁴ In other polyamides and polyurethane the melt-

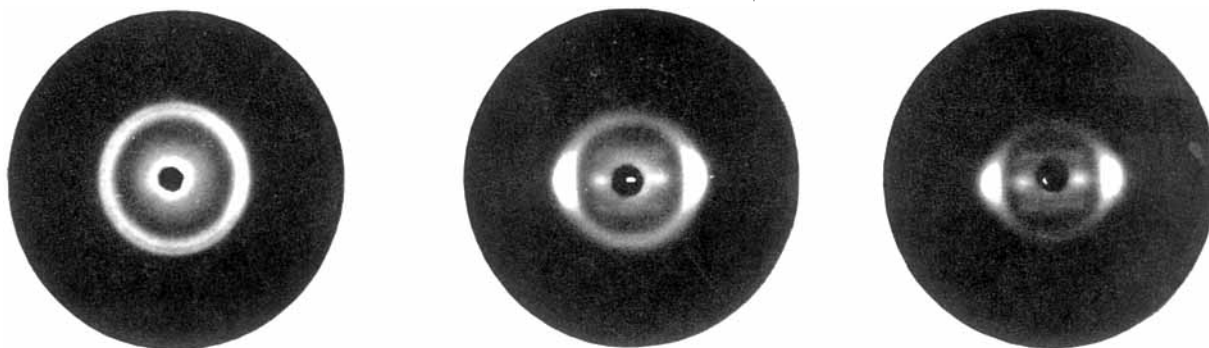


Figs. 9-17. X-ray patterns of polyamide fibers. $\text{Cu } K_{\alpha}$ radiation, specimen-film distance $D = 30$ mm., fiber axes vertical. Fig. 9. N6 low-speed melt-spun. Fig. 10. N6 high-speed melt-spun. Fig. 11. N6 cold-drawn and heat-treated. Fig. 12. N6.6 low-speed melt-spun. Fig. 13. N6.6 high-speed melt-spun. Fig. 14. N6.6 cold-drawn. Fig. 15. N11 low-speed melt-spun. Fig. 16. N11 high-speed melt-spun. Fig. 17. N11 cold-drawn.

spun fibers are partially crystalline, like the cold-drawn. The diffraction spots for the melt-spun fibers may be less sharp and intense than those for the cold-drawn and heat-treated fibers, but an ordered state always exists. The same may be said about the copolyamides spun at high take-up velocities (Figs. 21-23). The x-ray patterns show definite, though somewhat diffuse, interference arcs. The diffuse character of x-ray patterns is particularly evident in the case of C-methylated poly-

amide (MeCo); see Figure 23. It is quite obvious that copolymerization and introduction of side groups into the polymer chain leads to a decrease of chain symmetry and lowers the degree of macromolecular order; in the case of methylated polyamide it is evident in the decrease of melting point as well (cf. Table I).

It should be emphasized that polyamides and polyurethane cannot be obtained in an entirely amorphous state as a result of supercooling. This

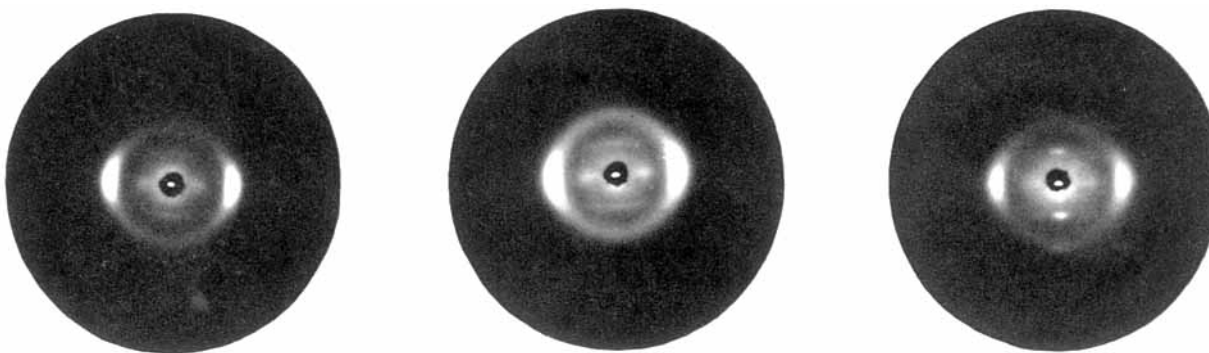


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Figs. 18-20. X-ray patterns of polyurethane fibers. $\text{CuK}\alpha$ radiation, specimen-film distance $D = 30$ mm., fiber axes vertical. Fig. 18. Low-speed melt-spun. Fig. 19. High-speed melt-spun. Fig. 20. Cold-drawn.



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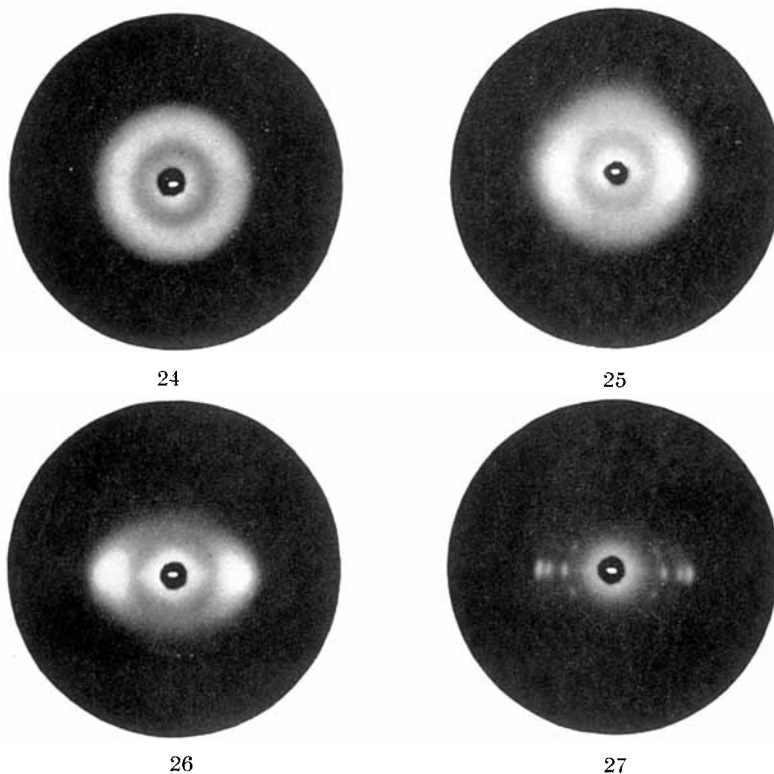
Figs. 21-23. X-ray patterns of high-speed melt-spun fibers of modified polyamides. $\text{Cu K}\alpha$ radiation, specimen-film distance $D=30$ mm., fiber axes vertical. Fig. 21. Copolyamide I (CoI). Fig. 22. Copolyamide II (CoII). Fig. 23. *C*-Methylated copolyamide (MeCo).

property has its origin probably in the molecular structure. All these polymers form hydrogen bonds between the individual chains. The H bonds $\text{CO} \dots \text{HN}$ are so strong that, even in the molten state, there is a high probability of occurrence of associates and small ordered regions. It may be now suggested that these H bonds and associates related to them are responsible for the observed orientation behavior. Orientation in the flowing molten polymer does not comprise individual macromolecules, but some aggregates or associates bound with H bridges; hence the orientation proceeds here in a system of relatively rigid elements instead of soft, coiled chains and the birefringence-spinning stress characteristics are convex, saturation curves.

Quite a different behavior may be expected in polyethylene terephthalate. From the x-ray patterns it may be seen that the melt-spun fibers are entirely amorphous. There are no distinct rings or spots evident on the diffraction patterns,

only a very diffuse halo, in the strongly oriented specimen somewhat densified on the equator (Figs. 24, 25). Cold-drawing also does not produce any evident crystallization (Fig. 26). The normal pattern of a crystalline fiber can be obtained only after an annealing of drawn fiber under tension (Fig. 27).

This behavior becomes understood when we take into consideration that polyethylene terephthalate does not form any strong H bonds as do polyamides and polyurethane. As a consequence no aggregates or associates are expected to exist in the molten polymer. The crystallization rate is also considerably lower than in the case of polyamides. So we have a right to assume that the orientation in the molten polyester proceeds in a system of individual, coiled and tangled macromolecular chains. The orientation in such a system involves not only a rotation but also an uncoiling and extending of chains; hence a linear birefringence-spinning stress characteristic (Fig. 8) different



Figs. 24–27. X-ray patterns of polyethylene terephthalate fibers. Cu K_{α} radiation, specimen–film distance $D = 30$ mm., fiber axes vertical. Fig. 24. Low-speed melt-spun. Fig. 25. High-speed melt-spun. Fig. 26. Cold-drawn. Fig. 27. Cold-drawn and heat-treated under tension.

from the saturation curves found for polyamides and polyurethanes.

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References

1. Ziabicki, A., and K. Kędzierska, *J. Appl. Polymer Sci.*, **2**, 14 (1959).
2. Ziabicki, A., *ibid.*, **2**, 24 (1959).
3. Ziabicki, A., *Kolloid Z.*, **175**, 14 (1961); *Chemia Stosowana*, in press.
4. Ziabicki, A., *Kolloid Z.*, **167**, 132 (1959).

Synopsis

The principal regularities of molecular orientation occurring by fiber formation from polymer melts have been proved for several polyamides, copolyamides, polyurethane, and polyester. It has been found for these polymers, as for the formerly investigated polycapronamide, that fiber birefringence (used as a comparative measure of the mean degree of macromolecular orientation) practically does not depend on the deformation ratio $S = V_E/V_0$, and monotonically increases with velocity difference ($V_E - V_0$) and reciprocal fiber diameter ϕ_E^{-1} (measure of cooling rate). Hence the general character of the postulated mechanism of orientation, simultaneous action of velocity field and

thermal relaxation, seems to be proved for the typical fiber-forming polymers. The differences between the shapes of characteristics birefringence–velocity difference, birefringence–spinning stress, and between the x-ray patterns of polyamides and polyester have been interpreted in terms of molecular structure and occurrence of H bonds.

Résumé

On a vérifié les régularités principales de l'orientation moléculaire, qui se réalisent lors de la formation de fibres à partir de polymère fondu, dans le cas de différents polyamides, copolyamides, polyuréthanes et polyesters. On a trouvé pour ces polymères comme pour la polycapronamide étudié précédemment que la biréfringence des fibres (utilisée comme mesure comparative du degré moyen d'orientation moléculaire) ne dépend pratiquement pas du rapport de déformation $S = V_E/V_0$, et qu'elle augmente régulièrement avec la différence de vitesse $V_E - V_0$ et l'inverse du diamètre de la fibre (une mesure de la vitesse de refroidissement). Donc le caractère général du mécanisme d'orientation supposé (action simultanée du champ de vitesse et de la relaxation thermique) semble avoir été démontré dans le cas de polymères typiques formant des fibres. Les différences entre les formes au départ des caractéristiques (la différence de biréfringence—vitesse et de biréfringence—tension de filage) et les diagrammes aux rayons-X des polyamides et polyesters ont été interprétées sur la base de la structure moléculaire et la présence de liaisons-hydrogène.

Zusammenfassung

Es wurden die Hauptregelmässigkeiten in der molekularen Orientierung bei der Faserbildung aus Polymerschmelzen an einigen Polyamiden, Copolyamiden, Polyurethan und Polyester untersucht. Für diese Polymeren wurde, wie für das früher untersuchte Polycapronamid, gefunden, dass die Faserdoppelsbrechung (als relatives Mass für den mittleren makromolekularen Orientierungsgrad verwendet) praktisch vom Deformationsverhältnis $S = V_E/V_o$ unabhängig ist und monoton mit der Geschwindigkeitsdifferenz $V_E - V_o$ und dem reziproken Faserdurchmesser ϕ_E^{-1} , einem Mass der

Kühlgeschwindigkeit, ansteigt. Damit scheint der allgemeine Charakter des vorgeschlagenen Orientierungsmechanismus—gleichzeitige Wirkung des Geschwindigkeitsfeldes und thermische Relaxation—für typische faserbildende Polymere gesichert zu sein. Die Unterschiede in der Form der Charakteristika—Doppelbrechung—Geschwindigkeit, Doppelbrechung—Spinnspannung und zwischen den Röntgenogrammen der Polyamide und Polyester—wurden auf Grund der Molekülstruktur und durch Auftreten von H-Bindungen gedeutet.

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