

Polyamides and Polyesters with Improved Mechanical Properties

STOYKO FAKIROV, MICHAIL EVSTATIEV,* and JEROLD M. SCHULTZ¹

Laboratory on Structure and Properties of Polymers, University of Sofia, 1126 Sofia, Bulgaria, and
¹Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

SYNOPSIS

An attempt is made to establish the most proper initial structure for the obtaining of highly drawn (at room temperature) nylons and polyesters. It is found that neither the completely crystalline structure nor the fully amorphous one but a low-crystallinity, very imperfect structure (with a large number of small crystallites) is the most suitable one. Through ultraquenching of nylon 6 and PBT melts, and storage at ambient conditions, draw ratios of 7 and 8, respectively, are achieved. Subsequent annealing results in the obtaining of doubly higher values of the elasticity modulus and tensile stress. By means of WAXS, SAXS, IR spectroscopy, and DSC measurements the obtained structure is characterized. The highly drawn and annealed samples show a strongly reduced concentration of chain folds and a lack of long spacing.

INTRODUCTION

In the search of new materials unexpected opportunities are offered nowadays by polymeric substances. In some cases their properties not only surpass those of natural materials (e.g., tensile strength of metallic fibers) but polymers could be obtained with "tailored" properties.¹ A very attractive field in this respect is the preparation of high performance materials, particularly those distinguished by high strength and high modulus values. It is already generally recognized² that for the realization of such systems at least three requirements should be fulfilled: (i) extended polymer chains with maximal orientation; (ii) molecular weight as high as possible, and (iii) perfect crystallites. Several approaches have been described to the obtaining of high performance polymer materials³:

- (a) spinning from gels of ultrahigh molecular weight polymers (e.g., polyethylene),
- (b) processing from the liquid crystalline state in melts (thermotropic systems, e.g., co-

polyesters of poly-(ethylene terephthalate) and *p*-hydroxybenzoic acid),

- (c) processing from the liquid crystalline state in solutions (liotropic systems, e.g., Kevlar),
- (d) special techniques for solid state drawing or extrusion.

In the last case one applies cold or hot drawing,³⁻⁷ solid state extrusion,^{3,5,8-12} zone drawing, fast spinning,¹³⁻¹⁵ and zone annealing.¹⁶⁻²²

Obtaining a highly oriented macromolecular system with perfectly parallel chains is related to a basic question: what is the most favourable initial state of the polymer—completely amorphous, maximally crystalline, or a semicrystalline one? According to Peterlin, a highly oriented system can be obtained only by starting from highly crystalline polymers, at least in the case of polyethylene.⁵ It has been established, however, that polyethylene with very low crystallinity, obtained by rapid cooling, exhibits a drawability higher by an order of magnitude as compared to that of the maximally crystalline polymer.²³ The amorphous state seems more appropriate for drawing and orientation in the case of polymers with low chain flexibility. This assumption is checked in the present study.

* To whom correspondence should be addressed.

EXPERIMENTAL

In order to obtain samples with as low crystallinity as possible (or completely amorphous ones) a technique for ultraquenching was developed.

The facilities for ultraquenching of polymer melts are similar to those used in the production of glassy metals. A schematic presentation is given in Figure 1. In some cases the melt was thermally treated in order to destroy the crystallization centers.^{24,25} The extruded strips (4–6 mm wide and 0.08–0.12 mm thick, depending on the roll-to-roll distance and extrusion rate) were immediately subjected to ultraquenching (the die-to-rolls distance was kept as small as possible) and tested with or without additional treatment. In some cases the samples were stored under ambient conditions and thereafter mechanical and thermal treatments were carried out, followed by static mechanical tests. Drawing and testing were performed at room temperatures on Instron or Zwick machines at a cross-head speed of 5 mm/min.

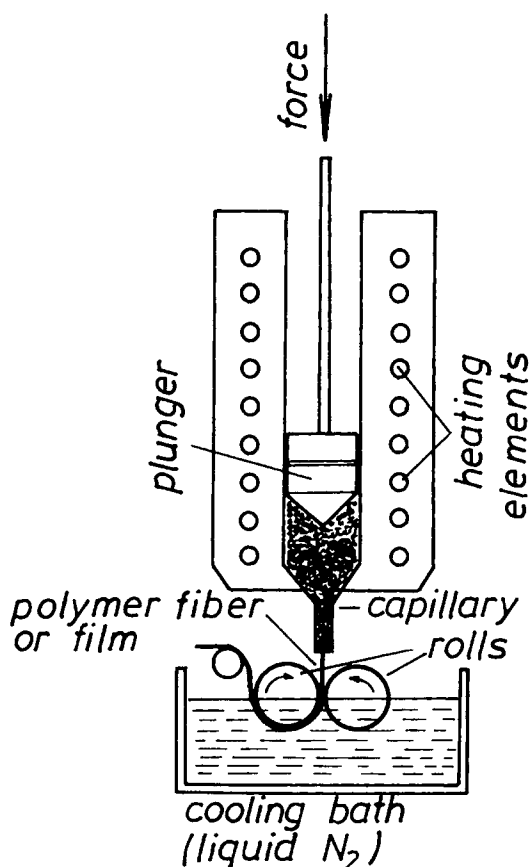


Figure 1 Scheme of the facility for ultraquenching of polymer melts.

In general, drawing of the ultraquenched samples was carried out to the maximal achievable degree. Annealing was carried out in a vacuum oven (40 mbar) for 6 h, the drawn samples being always with fixed ends.

X-ray studies (SAXS and WAXS) were performed on a Siemens Kristalloflex instrument with Cu K_{α} radiation. The thermal behavior and degree of crystallinity, w_c , of the samples were checked on a Mettler DSC apparatus TA 3000 at a scanning rate of 20°C/min in N_2 atmosphere. IR measurements were performed on a Perkin-Elmer 383 spectrophotometer.

The polymers studied were commercial ones. Chips of nylon 6 and poly(butylene terephthalate) (PBT) (kindly supplied by E. I. Du Pont de Nemours and Co., Wilmington, DE) as well as films (both products of Hoechst, FRG) were used for the preparation of the samples.

RESULTS AND DISCUSSION

The data of static mechanical tests of commercial and ultraquenched nylon 6 and PBT films stored for 10 months are summarized in Table I.

The first conclusion drawn from these results²⁶ is that the mechanical properties of commercial and ultraquenched (stored) samples are almost the same, except for their drawability. The samples prepared according to our technique have $\lambda = 7.0$ (nylon 6) and $\lambda = 8.0$ (PBT) against $\lambda = 4.0$ and 4.5, respectively, for the commercial materials [Table I (A), (B), samples nos. 2 and 3]. At the maximum draw ratio ($\lambda = 7$ –8) the tensile strength σ_b and the elasticity modulus E double their values for both polymers subjected to ultraquenching, the elongation at break, ϵ_b , being in the same time reduced by three times [compare samples 2 and 3, Table I (A), (B)].

After thermal treatment at 120°C for 6 h of the drawn samples, the observed relationships are preserved in general—only the modulus increases, reaching its maximum value [compare samples 4 and 5, Table I (A), (B)]. Taking into account that the E -values of the starting materials [samples no. 1, Table I (A), (B)] are of the same order of magnitude (ca. 1 GPa), it should be pointed out that drawing and subsequent annealing at 120°C of the commercial samples lead only to twice higher values of E [Table I (A), (B), samples nos. 1 and 4] while a drastic increase of E is observed with the ultraquenched samples—by six times for nylon 6 and by five times for PBT [compare samples nos. 1 and 5, Table I (A), (B)].

Table I Effect of Thermal and Mechanical Treatment on the Properties of Commercial and Ultraquenched (Stored for 6 Months) Films of Nylon 6 (A) and PBT (B)^a

Sample No.	Drawn at 22°C λ (after relaxation)	Annealed for 6 h at T_a (°C)	Commercial Samples			Ultraquenched Stored Samples		
			σ_b (MPa)	E (GPa)	ϵ_b (%)	σ_b (MPa)	E (GPa)	ϵ_b (%)
(A) Nylon 6								
1	—	—	118	0.9	340	148	0.7	620
2	4.0	—	120	1.2	42	—	—	—
3	7.0	—	—	—	—	310	2.1	36
4	4.0	120	180	1.5	20	—	—	—
5	7.0	120	—	—	—	396	4.4	19
6	4.0	210	190	1.4	29	—	—	—
7	7.0	210	—	—	—	448	2.4	27
(B) PBT								
1	—	—	136	1.1	380	156	1.1	740
2	4.5	—	230	1.4	22	—	—	—
3	8.0	—	—	—	—	470	3.0	26
4	4.5	120	250	1.8	17	—	—	—
5	8.0	120	—	—	—	530	5.4	16
6	4.5	210	300	1.6	36	—	—	—
7	8.0	210	—	—	—	615	3.4	32

^a λ —draw ratio (after relaxation (i.e., the sample under stress was kept at the achieved strain for 20 min)); σ_b = tensile strength; E = elasticity modulus; ϵ_b = relative elongation at break.

Thermal treatment at a higher temperature (210°C) of the same duration (6 h) causes a slight increase of σ_b (ca. 10% for the ultraquenched samples) and a significant decrease of E (down to two times, again for the ultraquenched samples) [Table I (A), (B), samples nos. 6 and 7]. Thus, the obtained values for the stress at break are the highest possible ones—448 MPa for nylon 6 and 615 MPa for PBT (Table I).

Considering the fact that both types of materials—commercial and ultraquenched ones—have undergone the same thermal treatment, the observed strong increase in the elasticity modulus can be attributed only to the better orientation due to the enhanced drawability at room temperature ($\lambda = 7-8$), which, by the way, is not observed with the as quenched samples (the maximal draw ratio achieved is of about 3–3.5²⁷).

Coming back to the basic question—what should be the starting polymer structure in order to achieve maximum orientation—one has to recall the existence of numerous reports on the poor drawability of amorphous polymers (due to the large number of entanglements).^{28–32} The results of a previous study of ours support to some extent this conclusion if one

compares the drawability of the as quenched samples²⁷ ($\lambda = 3-3.5$) to that of the quenched and stored ones [Table I (A)]. The commercial samples have higher crystallinity [w_c (DSC) = 0.28] than those subjected to ultraquenching and storage [w_c (DSC) = 0.23], the second value being much higher than the actual one due to additional crystallization in the calorimeter, hence the actual difference in w_c is much greater.³³ This conclusion is supported by the WAXS patterns of the starting (commercial and ultraquenched) PBT films presented in Figures 2A, 2B (samples a) as well as by the fact that a clearly expressed glass transition can be observed only in the thermograms of the ultraquenched PBT samples²⁶; T_g cannot be registered in samples with increased crystallinity (achieved by annealing or observed in commercial ones). Another proof of the lower crystallinity of the stored ultraquenched samples is the appearance of double melting peaks in the case of PBT (Table II, sample 1). It is well known and proved, precisely in the case of PET and PBT that the multi-peak phenomenon is connected with recrystallization (including additional crystallization) during scanning in the calorimeter. For this reason the values of w_c (DSC) are

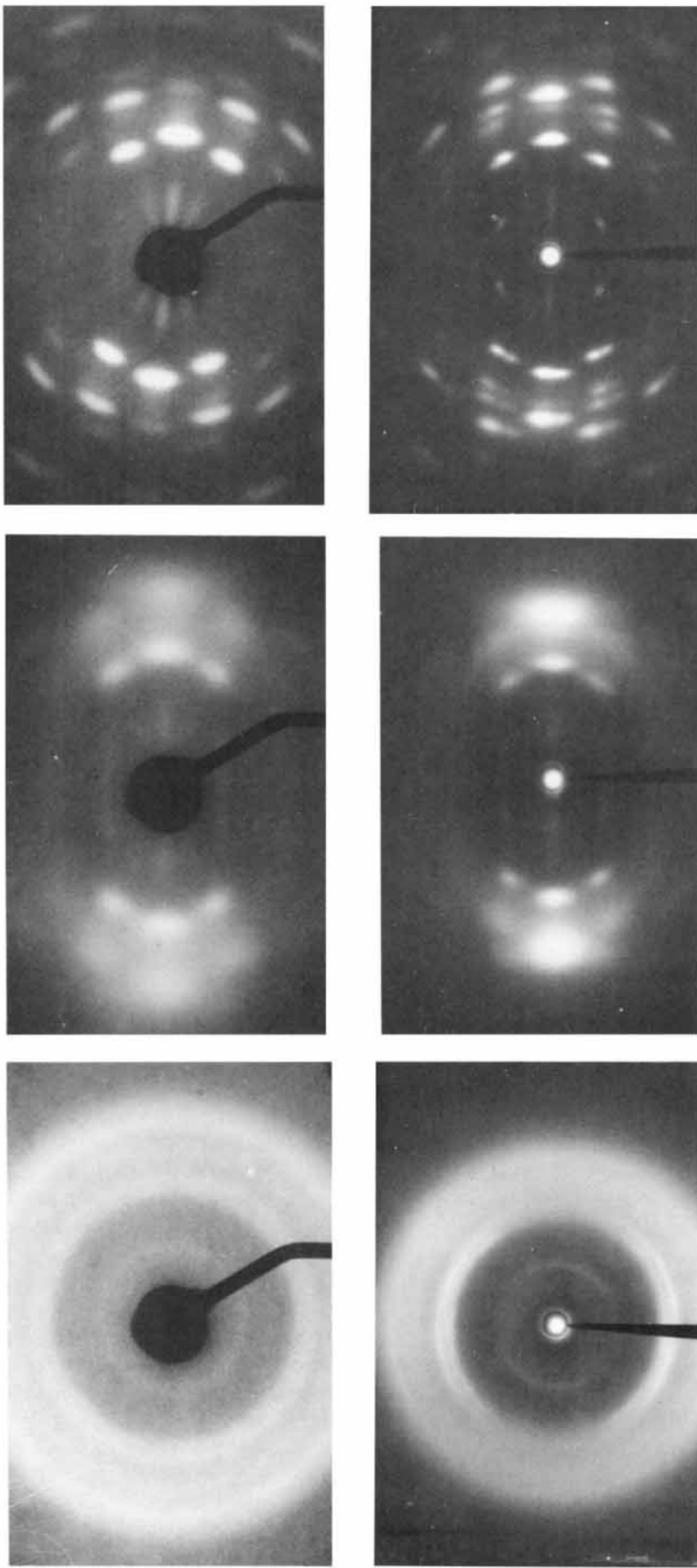


Figure 2 WAXS patterns of commercial (top) and ultraquenched stored (bottom) and ultraquenched stored (bottom) films of PBT undergone additional treatments as follows: (top) commercial: (a) untreated, (b) drawn ($\lambda = 4.5$), (c) drawn ($\lambda = 8$); (bottom) ultraquenched and stored: (a) untreated, (b) drawn ($\lambda = 8$), (c) drawn ($\lambda = 8$) and annealed at 210°C for 6 h.

Table II Effect of Mechanical and Thermal Treatment on the Properties of Commercial and Ultraquenched (Stored for 10 Months) Films of PBT (for $\Delta H^\circ = 144.5 \text{ kJ/kg}^{34}$)

Sample No.	Draw Ratio at 22°C (λ)	T_a (for 6 h) (°C)	Commercial Samples			Ultraquenched Stored Samples			
			T_m (°C)	w_c (DSC)	L (Å)	T'_m (°C)	T''_m (°C)	w_c (DSC)	L (Å)
1	Starting	—	224	0.28	96	115	225	0.23	—
2	4.5	—	226	0.43	106	—	—	—	—
3	8	—	—	—	—	118	226	0.42	—
4	4.5	120	227	0.40	118	—	—	—	—
5	8	120	—	—	—	160	226	0.41	—
6	4.5	210	226	0.44	123	—	—	—	—
7	8	210	—	—	—	225	229	0.43	122

always higher than the actual ones and this trend is the stronger, the lower the initial crystallinity is.³³

If drawing is enhanced by higher crystallinity, one should expect higher draw ratios for the commercial samples [Table I (A), (B), samples no. 1]; just the opposite situation is actually observed. Comparison with the data discussed in²⁴ leads to the following assumption: the most favorable structure for the achievement of high orientation is that characterized by a large number of small crystallites (i.e., by an imperfect crystalline phase) [Fig. 2 (B), sample a].

Ultraquenching of the polymer melt, particularly after thermal treatment above the melting temperature, creates an almost amorphous or slightly crystalline structure. Subsequent storage at room temperature preserves this structure or causes additional crystallization under very unfavorable conditions (close to T_g). Thus, the crystalline phase should consist of a large number of small and imperfect crystallites (Fig. 2).

Another characteristic feature of this imperfect structure is the lack of large, spatially well defined regions, differing substantially in their electron densities (i.e., crystalline and amorphous regions). Otherwise one should expect a long spacing in the SAXS curves presented in Figure 3. It is seen that such a scattering maximum is typical of commercial samples only [Fig. 3(A)]. The lack of a maximum in the SAXS curves of the unannealed ultraquenched samples of PBT [Fig. 3(B), (a), (b)] demonstrates the very small density difference between the amorphous and crystalline regions and hence the imperfection of the crystalline phase visualized by the WAXS patterns, also [Fig. 2(B), (a), (b)].

The WAXS patterns (Fig. 2) provide information also about the orientation of the ultraquenched and commercial materials. The starting materials differ in their degree of orientation which is much higher

in the case of ultraquenching [Fig. 2(B), (a)]. This difference is preserved after cold drawing [Figs. 2(A), (b) and 2(B), (b)], leading to a more perfect structure after annealing [Fig. 2(B), (c)].

It can be concluded, on the basis of the results obtained, that in contrast to polymers distinguished by a very high chain flexibility (e.g., polyethylene)

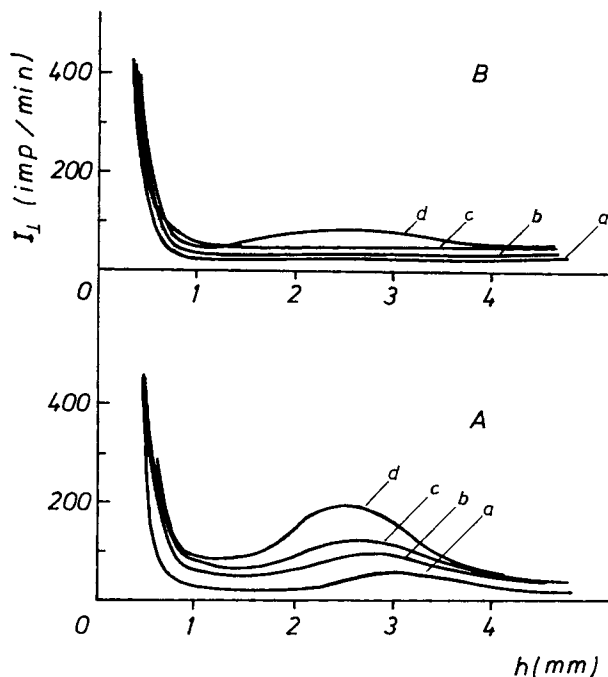


Figure 3 SAXS curves of commercial (A) and ultraquenched stored (B) films of PBT undergone additional treatments as follows: (A) commercial: (a) untreated, (b) drawn ($\lambda = 4.5$), (c) drawn ($\lambda = 4.5$) and annealed at 120°C for 6 h, (d) drawn ($\lambda = 4.5$) and annealed at 210°C for 6 h; (B) (ultraquenched and stored): (a) untreated, (b) drawn ($\lambda = 8$), (c) drawn ($\lambda = 8$) and annealed at 120°C for 6 h, (d) drawn ($\lambda = 8$) and annealed at 210°C for 6 h.

where as perfect as possible crystalline structure is the most favourable one for the achievement of high orientation,^{3,7} the situation with polymers characterized by reduced chain flexibility (polyesters and polyamides) seems to be rather different.

Just the opposite case, when the system is as amorphous as possible, is also not the most appropriate one.²⁷⁻³² The highest draw ratio at room temperature ($\lambda = 8$) was achieved with polymers characterized by a semicrystalline, very imperfect structure (Fig. 2). Consequently, for the preparation of highly oriented polyesters and nylons (resulting further in high-strength and high-modulus fibers), one has to start from a disordered polymer, the amorphous matrix of which embeds a large number of small crystallites. Such a structure can be created by ultraquenching of a polymer melt in the shape of thin films or fibers.

Another peculiarity of the ultraquenched samples is their lower concentration of chain-folds in crystallites, as compared to commercial ones. It is well known^{22,26,35} that the IR-spectral band at 988 cm^{-1} in the case of PBT (and PET) is assigned to chain folding in the crystallites.

The IR spectra of films of both types of samples are shown in Figure 4. It is seen that annealing of drawn commercial samples results in a strong increase of the band at 988 cm^{-1} [Fig. 4(A), (c)] which is not observed with ultraquenched samples [Fig. 4(B), (c)]. Further, unlike commercial samples [Fig. 4(A), (c)], the higher draw ratio of ultraquenched ones ($\lambda = 8$ against $\lambda = 4.5$) destroy drastically the chain folds.

In the same table are summarized the data of calorimetric and SAXS measurements. The appearance of a melting peak at much lower temperatures (T'_m) for the ultraquenched samples is an indication of their lower and much less perfect crystallinity, as revealed also by the SAXS patterns (Fig. 2).

As expected, the long spacing L of the commercial samples increases after drawing and annealing (Table II). On the contrary, no long spacing can be observed with ultraquenched samples [Fig. 3(B)] except for $T_a = 210^\circ\text{C}$. This weak maximum corresponds to $L = 122\text{ \AA}$ (i.e., the value is the same as that of the respective commercial sample). On the basis of this equality it can be assumed that the weak maxima [Fig. 3(B), (d)] are caused by very small amounts of crystallites formed at high temperature from chain residues which did not crystallize earlier. This assumption is supported also by the WAXS patterns [Fig. 2(B), (c)] showing a very perfect crystalline structure (at least more perfect than that of commercial samples [Fig. 2(A), (c)]

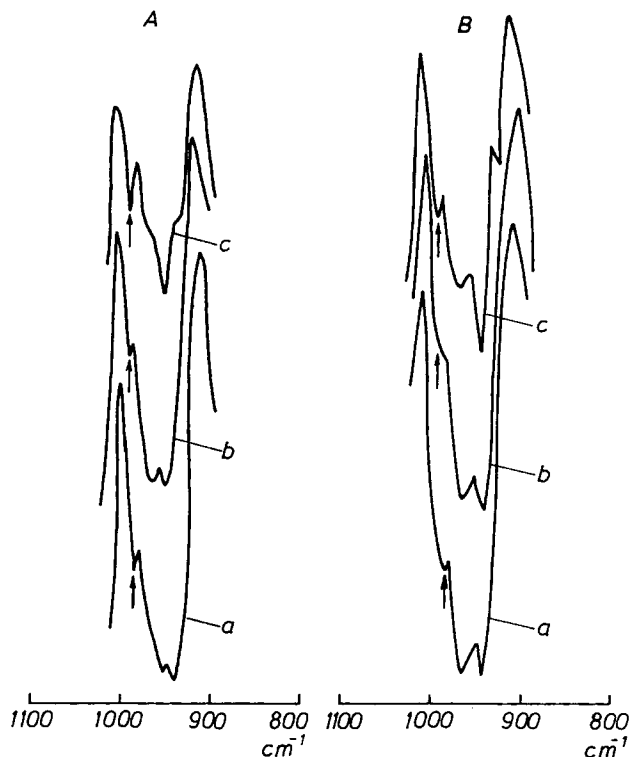


Figure 4 IR spectra of commercial (A) and ultraquenched stored (B) films of PBT undergone additional treatments as follows: (A) commercial: (a) untreated, (b) drawn ($\lambda = 4.5$), (c) drawn ($\lambda = 4.5$) and annealed at 210°C for 6 h; (B) (ultraquenched and stored): (a) untreated, (b) drawn ($\lambda = 8$), (c) drawn ($\lambda = 8$) and annealed at 210°C for 6 h.

which exhibits strong SAXS maxima [Fig. 3(A)]. Comparison of both types of X-ray measurement, WAXS [Fig. 2(A), (c)], and SAXS [Fig. 3(B), (d)], leads to the conclusion that the crystallites causing the WAXS pattern are not involved in the SAXS (i.e., they are not regularly distributed along the fiber axis of the highly oriented material).

Finally, it should be stressed that having at disposal polymers with maximal chain orientation, additional steps are necessary for the achievement of a perfect final structure and a molecular weight as high as possible. In the case of linear polycondensates, an easy and convenient way to increase the molecular weight is offered by the additional solid state condensation (postcondensation).^{36,37} In addition to the rise in molecular weight, solid state processes (particularly the exchange reactions) contribute to the formation of a more perfect structure through elimination of defects of various types (entanglements, crossing point, chain ends, etc.).³⁸ It should be pointed out that these favourable

chemical changes occur simultaneously with ones during thermal treatment of the polycondensates. By a proper combination of cold drawing (after ultraquenching) and thermal treatment, it is possible to improve drastically the mechanical properties of polyamides and polyesters—their tensile strength can be increased by 2–3 times and the modulus—up to 5 times.³⁹ It should be noted, however, that the reported strength and modulus values^{26,38,39} are much lower than those typical of ultrahigh-strength and ultrahigh-modulus polymers (e.g., those obtained from the liquid crystalline state³). This could be explained by differences in the chemical compositions, sample thickness, or measurement conditions (drawing rate, load, deformation range for modulus evaluations, etc.). Nevertheless, the main purpose of the present paper is to demonstrate some useful and interesting approaches to the realization of the final goal—preparation of high performance polycondensates.

The authors gratefully acknowledge the NSF support, Grant No. Int. 8520639. M. Evstatiev appreciates the hospitality of the Department of Chemical Engineering at the University of Delaware where this work was carried out.

REFERENCES

1. *Opportunities in Chemistry*, National Academy Press, Washington, DC, 1985.
2. K. Suzuki, H. Fujimori, and K. Hashimoto, in *Amorphous Metals*, K. Hashimoto, Ed., Moscow Metallurgia, 1987 (in Russian).
3. *Ultra High Modulus Polymers*, A. Cifferi and I. M. Ward, Eds., Appl. Sci. Publ., London, 1979.
4. *The Strength and Stiffness of Polymers*, A. E. Zachariades and R. S. Porter, Eds., Dekker, New York and Basel, 1983.
5. T. Pakula and E. W. Fischer, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1705 (1981).
6. G. Cappacio, T. A. Crompton, and I. M. Ward, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1641 (1976).
7. A. Peterlin, *Coll. Polym. Sci.*, **265**, 357 (1987).
8. K. Imada, T. Yamamoto, K. Shigematsu, and M. Takayanagi, *J. Mater. Sci.*, **6**, 357 (1971).
9. J. B. Sahary, B. Parsons, and I. M. Ward, *J. Mater. Sci.*, **20**, 348 (1985).
10. L. Fischer and W. Ruland, *Coll. Polym. Sci.*, **201**, 717 (1983).
11. C. A. Davies, *Polym. Eng. Sci.*, **9**, 14 (1974).
12. K. Yamada and M. Takayanagi, *J. Appl. Polym. Sci.*, **27**, 2091 (1982).
13. E. Liska, *Kolloid Z. Z. Polym.*, **251**, 1028 (1973).
14. H. Brody, *J. Macromol. Sci. Phys.*, **B22**, 19 (1983).
15. J. Petermann and R. M. Gohil, *J. Mater. Sci.*, **14**, 2260 (1979).
16. T. Kunugi, A. Suzuki, and M. Hashimoto, *J. Appl. Polym. Sci.*, **26**, 213 (1981).
17. T. Kunugi, A. Suzuki, and M. Hashimoto, *J. Appl. Polym. Sci.*, **26**, 1951 (1981).
18. T. Kunugi, I. Akiyama, and M. Hashimoto, *Polymer*, **23**, 1193 (1982).
19. T. Kunugi, I. Akiyama, and M. Hashimoto, *Polymer*, **23**, 1199 (1982).
20. T. Kunugi, I. Aoki, and M. Hashimoto, *Kobunshi Ronbunshu*, **38**, 301 (1981).
21. T. Kunugi, T. Ito, M. Hashimoto, and M. Ooishi, *J. Appl. Polym. Sci.*, **28**, 179 (1983).
22. T. Kunugi, Ch. Tchirose, and A. Suzuki, *J. Appl. Polym. Sci.*, **31**, 429 (1986).
23. J. P. Bell and J. H. Dumbleton, *J. Polym. Sci., A-2*, **7**, 1033 (1969).
24. N. Avramova, I. Avramov, and S. Fakirov, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 311 (1984).
25. N. Avramova and S. Fakirov, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 761 (1986).
26. M. Evstatiev, Ph.D. thesis, Sofia University, 1988.
27. S. Fakirov, N. Avramova, M. Evstatiev, Proceedings of the 2nd Dresden Polymer Discussion, March 28–April 1, 1989, Dresden, GDR.
28. A. S. Argon and M. M. Salama, *Mater. Sci. Eng.*, **23**, 219 (1976).
29. P. Smith, R. R. Matheson, Jr., and P. A. Irvine, *Polymer*, **21**, 1091 (1984).
30. F. De Candia, R. Gennaro, and V. Vittoria, *Makromol. Chem.*, **175**, 2983 (1974).
31. R. E. Lyon, R. J. Farris, and W. J. Mac Knight, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 329 (1983).
32. G. S. Y. Yeh and P. H. Geil, *J. Macromol. Sci.*, **B1**, 235, 351 (1967).
33. S. Fakirov, *Structure and Properties of Polymers*, Sofia Press, Sofia, 1985.
34. V. P. Privalko, *Properties of Block Polymers*, Naukova Dumka, Kiev, 1984 (in Russian).
35. M. Evstatiev, I. Seganov, and S. Fakirov, *Acta Polym.*, **39**, 192 (1988).
36. S. Fakirov, in *Solid State Behavior of Polyesters and Polyamides*, J. M. Schultz and S. Fakirov, Eds., Prentice-Hall, New York, 1990.
37. S. Fakirov, *Polycondensation Polymers and Solid State Reactions*, Nauka i Izkustvo, Sofia, 1989 (in Bulgarian).
38. S. Fakirov and M. Evstatiev, 8 Güstrower Hochschultage 25. Jahrestagung der Forschungsgemeinschaft "Organische Festkörper" der DDR, June 1988, Güstrow, GDR.
39. S. Fakirov and M. Evstatiev, 32nd UPAC International Symposium on Macromolecules (Macro '88), August 1988, Kyoto, Japan.

Received April 24, 1989

Accepted February 26, 1990