

## **Effect of monomeric unit length on crystallinity and Young's modulus for highly oriented fibers**

**N. Okui and T. Sakai**

Department of Textile and Polymeric Materials, Tokyo Institute of Technology,  
Ookayama, Meguroku, Tokyo, 152 Japan

### SUMMARY

Crystallinity and Young's modulus for ultra-drawn fibers in relation to the crystallographic monomeric unit length ( $d$ ) are studied. Unique relationships with the logarithm of  $d$  are found in the ultimate crystallinity and the ultimate Young's modulus. For producing ultra-high modulus fibers from flexible or rigid polymers, the shorter the unit length is better or the higher the thermal characteristic temperature such as glass transition temperature is preferred.

### INTRODUCTION

Productions of high modulus and high tenacity fibers from commercially available flexible polymers and from rigid polymers have been attractive for the last decade. For example, ultra-high Young's modulus fibers with 130-330 GPa have been produced by wet-spinning of rigid polymers such as poly(*p*-phenylene benzobisthiazole) (PBT) [1], poly(*p*-phenylene bebzamide) (PBA) [2] and poly(*p*-phenylene terephthalamide) (PPTA) [3]. These rigid polymers are expected to form a perfectly aligned structure along the fiber axis. In addition, ultra-drawing of an ultra-high molecular weight polyethylene has also yielded the Young's modulus as high as 200-220 GPa [4,5]. This experimental achievement is very close to the crystal Young's modulus in the chain axis direction (the intrinsic Young's modulus). Ultra-high Young's modulus fibers have been also attained in ultra-drawn poly(oxymethylene) (POM) [6,7] and poly(propylene) (PP) [8,9], but not in other flexible common polymers such as poly(ethylene terephthalate) (PET) [10,11] and nylon-6 (N6) [12,13]. In fact, maximum moduli achieved experimentally (the ultimate axial moduli) for PET and N6 are nearly 10-20 % of the intrinsic values. Here, the ultra-high modulus PE, PP and POM have appreciably high crystallinities, but the crystallinities of ultra-drawn PET and N6 are considerably low. The low crystallinity may result in the low modulus. The former three polymers have smaller monomeric units than those for the later two polymers. These results indicate that the crystallinity for the flexible polymers may depend on a polymer chemical structure, that is, a monomeric unit length. So, this paper is focused on crystallinity and Young's modulus for ultra-drawn fibers in relation to the repeating unit length.

### REPEATING UNIT EFFECT ON CRYSTALLINITY

There is a good example for the repeating unit length effect on crystallinity. Crystallinity of lamellar crystal depends on the ratio of the

number of monomeric units associated with crystalline and chain folded regions. PE lamella with ca. 100 Å thickness may be constructed with ca. 70 monomeric units in crystalline stem and with at least 5 units or more in folded region. Thus, the crystallinity yields as high as 80-90 %. On the other hand, nylon-12 (N12) with the long repeating unit length will form lamellar crystals with ca. 100 Å thickness associated with 4-5 units in the stem and with at least 1 unit or more in the fold. So, the crystallinity of the N12 is 65-80 %.

It may be thought that the unit length effect will become more pronounced on crystallization under molecular orientation. The crystallization rate is considered to be astonishingly high. In fact, for the ultra-high speed melt spinning of PET [14], the crystallization is accomplished within a millisecond in the spinline, which is millions times faster than that under non-oriented state. The crystallization rate is governed by the diffusion control process, and so the increase in filament temperature caused by the heat of crystallization can accelerate the crystallization rate, and this gives rise to a dramatic increase in crystallinity in the spinline. On the other hand, when cold drawn fibers with high molecular orientation are annealed, a slow crystallization (secondary crystallization) occurs after a rapid crystallization. The rapid crystallization derives from predetermined oriented nucleation and proceeds along the oriented molecular axis. The subsequent slow crystallization strongly depends on molecular diffusion.

It is assumed that a bundle of the highly aligned molecules, which are laterally well ordered but translational shifts along the chain, is performed before crystallization. Crystallization of the molecules in the bundle will be affected by molecular motion in the chain axis direction. The molecular motion will be influenced significantly by the length of crystallographic repeating unit ( $d$ ). That is, the longer the unit length, the unit length translation parallel to the chain axis needs the longer distances to generate a crystalline packing finding a set of nearest lattice points. This relation can be illustrated as seen in figure 1. If partial chain

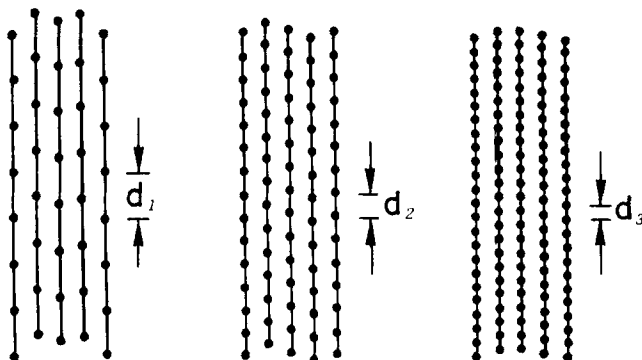


Figure 1. Schematic illustration of a bundle of the highly aligned molecules, which are laterally well ordered but translational shifts along the chain, the longer the unit length ( $d_1 > d_2 > d_3$ ), the unit length translation parallel to the chain axis needs the longer distances to generate a crystalline packing finding a set of nearest lattice points.

translation along the fiber axis is possible, each successive step translation will form laxed molecular defects in the fibers as shown in figure 2. In other words, the crystallinity is proportional to the frequency of finding the repeating units in the lateral directions occupying geometrically equivalent positions with respect to the fiber axis. So, this probability (crystallinity) can be expressed as a function of the unit length such as  $\ln(d)$ . The  $d$  is identical to the fiber identity period,  $C$ , for a polymer with a planer conformation. In a polymer with a helical conformation ( $u/t$ ), each successive step involving the rotation by  $360^\circ/u$  and the translation of  $C/u$  in the screw axis can generate the lattice points and hence the  $d$  is employed with the value of  $C/u$ , where  $u$  and  $t$  are the number of monomeric units in the  $C$  and that of turns of the helix, respectively.

#### ULTIMATE CRYSTALLINITY

Several methods such as high-pressure extrusion [15,16,17], die-drawing [18], zone-drawing [19,20] or annealing [8,10,12,21], drawing of solution grown crystals (SGC-drawing) [5,9,22], gel-drawing [4,23], microwave heating drawing (MH-drawing) [6,11] and high-speed melt-spinning (HSM-spinning) [14, 22-26] have been used to produce high modulus and high tenacity fibers from commercially available flexible polymers. Maximum crystallinities achieved experimentally (the ultimate crystallinities) in several polymers are listed in table 1. PE, PP and POM containing the relatively short unit length show the crystallinities as high as 70-95 %. But for polymers with the long unit length, that is, N12 and PEET (poly(ester/ether); (poly(ethylene-1,2-diphenoxyethane-*p,p'*-dicarboxylate))), the crystallinities do not exceed above 50 %. All of their crystalline orientation, however, are almost perfect. A unique relationship is found between the ultimate crystallinity and the logarithm of  $d$  as seen in figure 3, although data are scattered. It suggests that the unit length plays a significant role in the crystallinity for highly oriented fibers.

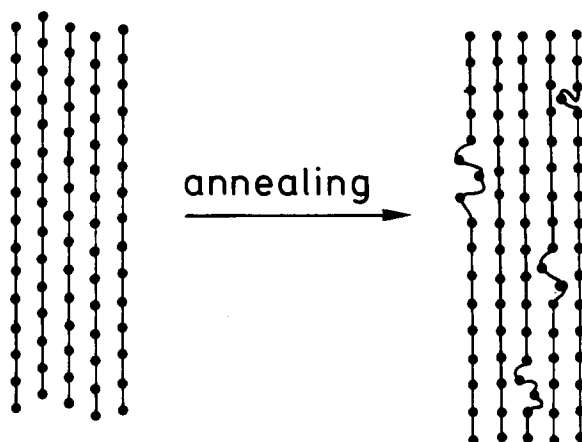


Figure 2. Schematic illustration of the unit length translation parallel to the fiber axis on annealing and each successive step translation will form laxed molecular defects.

Table 1. Maximum crystallinities  $X_c$  and Maximum Young's moduli  $E$  achieved by several experimental methods, and the ratio of  $E$  to the axial crystal modulus  $E_c$  and together with the crystallographic repeating unit length  $d$ , which is the ratio of the fiber identity period  $C$  to the number of monomeric unit  $u$  in the  $C$ .

Polymer	$d$ (Å)	Method	$X_c$ (%)	$E$ (GPa)	$E/E_c$ (%)	ref.
PE	1.27	SGC-drawing	92	220	93-65	5
POM	1.93	M.H.drawing	95	60	63-40	6
PP	2.17	SGC-drawing	85	34	81-69	9
PVA	2.52	SGC-drawing	78	60	24-21	22
N6	8.6	Zone-annealing	50	17	10- 7	12
		Dry-spinning	--	19	11- 8	13
PEEK	10.0	Zone-annealing	35	13	19	21
PET	10.76	Zone-annealing	60	19	18-16	10
N11	15.0	Coextrusion	44	5	---	17
N12	16.0	H.S.M-spinning	43	3	---	26
N66	17.2	H.S.M-spinning	41	4	2	24
PEET	18.64	H.S.M-spinning	49	19	16	25
PBA	6.48	Wet-spinning	--	156	96-78	2
PBT	12.4	Wet-spinning	--	330	89	1
PPTA	12.9	Wet-spinning	--	130	72-66	3

X-ray wide-angle pattern of N12 fibers obtained by melt-spinning above 6,000m/min shows the higher order of reflection on meridian but not on equator [26]. This pattern suggests a simple hexagonal packing of axially staggered periodic cylinders, that is, just like a rod-like molecular packing suggesting one dimensional para-crystalline structure. Similar x-ray patterns are observed in high-speed melt-spun PEET fibers [25,27] and also in wet-spun fibers of rigid polymers such as PBT [1,28,29] and PBA [2]. For example, the crystallinity of wet-spun PBT fibers is considered to be only two-dimensional [28,29], that is, the chains while parallelly, closely and regularly packed lack longitudinal register.

Annealing the hexagonal N12 at 160°C still remains in the hexagonal pattern. This indicates that large translational shifts along the chain axis do not take place to generate a three dimensional crystalline packing at that temperature. On the other hand, a true crystalline order will be achievable on annealing polymers with the short unit length such as PE, since the small shifts are enough to generate the true crystalline packings, as seen in figure 1 and 2. The axial shifts are not favorable for producing high modulus fibers despite increasing in crystallinity, because of formations of laxed molecular defects as noted previous section.

#### ULTIMATE MODULUS

In any case, molecular orientation plays a significant role in production of high modulus fibers. In particular, taut tie molecules and fraction of intercrystalline bridges are responsible for large increase in Young's modulus. Role of amorphous orientation in crystalline polymers is not well understood, however, the unique relation is found that the reciprocal of amorphous birefringence is directly proportional to that of draw ratio squared [20]. This relation suggests that the orientation of amorphous

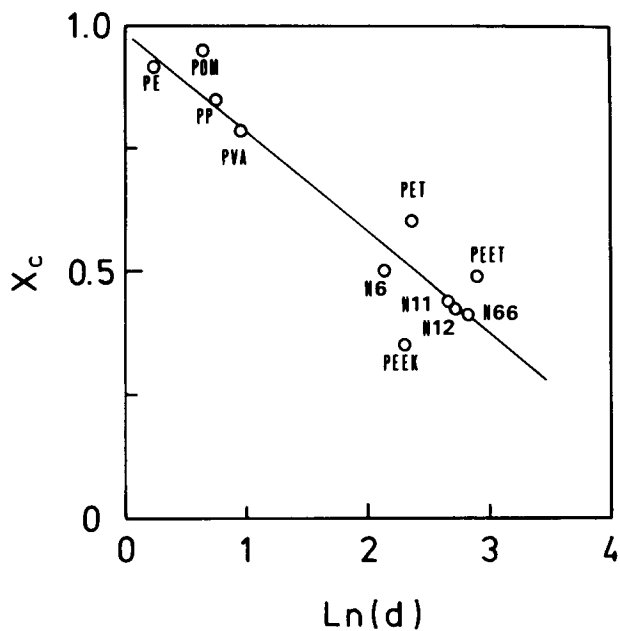


Figure 3. Relationship between the ultimate crystallinity  $X_c$  and logarithm of the repeating unit length.

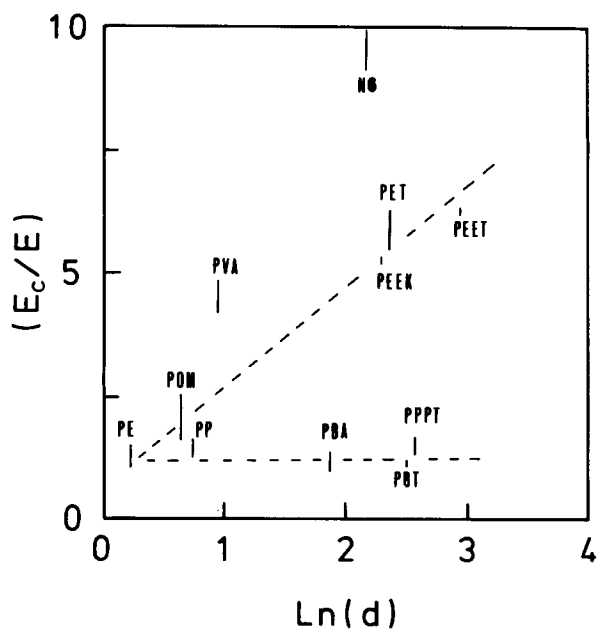


Figure 4. Relationship between the ratio of the axial crystal modulus  $E_c$  to the ultimate Young's modulus  $E$  and the logarithm of the unit length.

regions may be governed by an affine deformation of a Gaussian network. In addition, crystalline blocks will become increasingly linked with inter-crystalline bridges as the draw ratio increases. Such bridges are responsible for stabilizing the amorphous molecules in the oriented state [20] and also for exhibiting the ultra-high modulus. In other words, the higher the crystallinity, the fiber will be constructed with many linked crystal blocks and consequently the fiber modulus approaches the intrinsic value. Thus, the Young's modulus of the fibers will depend on the crystallinity.

For depicting a general behavior of the ultimate Young's modulus, the modulus ( $E$ ) is divided by the axial crystal modulus ( $E_c$ ) reported in the literature [30-34]. However, several different values of the  $E_c$  are reported in each polymer, and so they cause variations in the ratio of  $E/E_c$  as seen in table 1. It is assumed that the parallel mechanical model is applicable to the ultimate modulus, that is, the reciprocal of ultimate Young's modulus is proportional to the crystallinity ( $X_c$ ) by the equation.

$$E_c/E = X_c + X_a \cdot E_c/E_a \quad \dots (1)$$

where  $E_a$  is the amorphous Young's modulus and  $X_a = (1 - X_c)$ . Figure 4 shows the relationship between  $E_c/E$  and the  $\ln(d)$ . Two straight lines are observed: one is a group for the flexible polymers and the other is for the rigid polymers. In the rigid polymers, the unit length may not be important for exhibiting the ultra-high modulus. Rigid polymers may have comparatively high temperature characteristics such as high thermal stability and high glass transition temperature, which is responsible for maintaining the chains in the highly oriented states at room temperature. The effect of high glass transition temperature is also found in the flexible polymers. In PEEK (poly(ether/ether/ketone); poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene)), the modulus locates fairly well on the line in figure 4, whereas the crystallinity deviates from the line in figure 3. Melting temperature and glass transition temperature of PEEK are 334°C and 143°C, respectively. These high thermal characteristics may stabilize the molecules in the oriented state.

On the other hand, for the flexible polymers, the ultimate modulus strongly depends on the unit length, in analogy with the case in crystallinity. This suggests that the crystallinity plays a dominant role in performing the ultra-high modulus fibers. However, the moduli for poly(vinyl alcohol) (PVA), nylon-6 and nylon-66 (N66) deviate largely from the line based on the other flexible polymers. In contrast with these low moduli, the crystallinities yield proper values predicted from the dependence on the unit length as seen in figure 3. All three polymers contain high proportions of hydrogen bonds. Such strong cohesive forces between molecules may prevent ultra-drawing of the polymers, while they give rise to the proper crystallinities as predicted from the unit length dependence.

### CONCLUSION

Crystallographic unit length strongly affects on the crystallinity and the Young's modulus for highly oriented fibers. For producing ultra-high modulus fibers from flexible or rigid polymers, the shorter the unit length is better or the higher the thermal characteristics such as high glass transition temperature is preferred.

Note: A part of the present study was reported at 2nd SPSJ, International Polymer Conference 1986 August 18-21 at Tokyo, Japan.

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