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

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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 benzamide) (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 (NI2) 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 NI2 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 (d₁ > d₂ > d₃), 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.