

Effects of molecular weight on the drawing and the draw efficiency of nylon-6

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Abstract

Tensile drawing was carried out on nylon-6 films of different viscosity average molecular weights ($M_v = 77$ and 440×10^3) and crystalline forms (α - and γ -forms). The effects of M_v on the deformation behavior and the draw efficiency were discussed on the basis of the stress/strain curves recorded upon hot drawing, and wide-angle and small-angle X-ray diffraction, birefringence and tensile properties for the draw ratio (DR) series. The draw stress at a given strain and the fracture stress upon hot drawing were both higher for the higher M_v than for the low M_v , in either the α - or the γ -form sample. For a given M_v , the draw stress was lower for the γ -form than one with the α -form and the fracture stress was independent of the crystal forms, leading the former crystalline form to have a higher drawability than the latter, as previously reported. The M_v and the crystal form of predrawn samples had no effect on the crystalline chain orientation function (f_c) measured as a function of DR. In contrast, the draw efficiency evaluated from the amorphous chain orientation function (f_a) vs. DR and the tensile modulus and strength vs. DR was significantly higher for the higher M_v than for the low M_v . These drawing characteristics were discussed in terms of the entanglement effect and the deformability of the two crystal forms. The maximum achieved tensile modulus of 7.7 GPa and a strength of 760 MPa were thus obtained by the straight tensile drawing of the higher M_v sample that was initially a γ -form. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon-6; Molecular weight; Deformation

1. Introduction

Nylon-6 is a family of thermoplastics with a high crystal modulus along the molecular chains (165 GPa) [1] and with strong intermolecular interactions, which result in a higher melting temperature around 220°C. Thus, extensive work have been done to increase the tensile properties of nylon-6, particularly in the form of drawn fibers and films. The comparison of tensile modulus vs. draw ratio (DR) data [2–9] revealed that the draw efficiency of nylon-6 was greatly affected by the draw technique, predrawn morphology, and molecular weight. However, the reason for the difference of draw efficiency has not yet been fully understood. We found that the efficiency of draw in the crystalline regions was greatly affected by the initial morphology [10]. That is, the efficiency was higher for the predrawn films with well developed intercrystalline network structure than for the film composed of an aggregate of solution grown-crystals which had a minimum number of intervening tie chains and chain entanglements. The results were quite different from

those observed in polyethylene. In case of polyethylene, the chain extension and orientation by solid-state deformation can be achieved for a single crystal mat which has a minimum entanglement network [11,12]. This is due to an extremely low level of interchain interactions, which lead to the crystal deformation through slippage along the various crystallographic planes. Hu and Schmidt–Rohr report that the thermally activated chain translation through the crystallites in the α_c -relaxation is the fundamental microscopic process that permits solid-state ultradrawing of polyethylene [13]. These results suggest that the efficient transmission of an extensional stress on draw within a sample must be considered for the solid-state deformation of the semicrystalline polymers with strong interchain interactions showing no α_c -relaxation. There may be two possible routes to increase the efficiency of transmission of stress on draw. The first is to increase the entanglement density in the pre-drawn films. However, a high entanglement density may lead to low ductility [14] and enhance a structural heterogeneity in the drawn samples which results in the lower tensile properties. For a given low entanglement state, the number of entanglements per chain increases with increasing the chain length,

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Table 1
Observed density and weight percent crystallinity of the original and reduced films

Sample	$M_w = 74,000$		$M_w = 440,000$	
	Density (g/cm ³)	Crystallinity (%)	Density (g/cm ³)	Crystallinity (%)
Original	1.142	41.9	1.140	40.6
Reduced	1.135	70.0	1.135	70.0

which may increase the efficiency of draw. This is the second route.

In this work, the effect of molecular weight of nylon-6 on the efficiency of chain extension and orientation during deformation was studied. It was found that the efficiency increased with increasing molecular weight, with this tendency being more prominent in the noncrystalline regions than in the crystalline regions, similar to the case of poly(ethylene terephthalate) [15].

2. Experimental

2.1. Sample preparation

A high molecular weight nylon-6 was obtained by anionic polymerization of ϵ -caprolactam according to the method reported by Ueda et al. [16]. Nylon-6 with the intrinsic viscosities (IV) of 2.8 ($M_v = 77,000$) and 7.7 dl/g ($M_v = 440,000$) were prepared by controlling the amount of initiator. The IV was determined at 30°C by using a sulfic acid as a solvent. As-polymerized nylon-6 was purified by using formic acid as a solvent and a mixture of water and acetone (9/1, v/v) as a coagulant. About 2 wt% polymer solution was prepared by dissolving the purified nylon-6 into a mixture of hexafluoro-2-propnol and dichloromethane (50/50, v/v), followed by casting of the polymer solution onto a glass plate at room temperature. The solution cast films with the thickness of ~ 0.1 mm were obtained by evaporation of solvent under reduced pressure at room temperature. The crystals developed in the as-cast films were a monoclinic α -form. The crystalline form was converted to the γ -form by a chemical treatment [17]. For this, the as-cast film was immersed in an iodine–potassium iodide aqueous solution for 72 h at room temperature. The aqueous solution was composed of 39 g of iodine, 47 g of potassium iodide and 300 cc of distilled water. The iodine was washed out from the film by keeping it in an 0.13 mol/l sodium thiosulfate solution for 120 h at room temperature. After the wash treatments, no trace of iodine was detected in the films by elemental analysis.

Tensile drawing was carried out on the films with different molecular weights and different crystalline forms at constant temperatures in the range of 120–200°C and constant cross-head speeds corresponding to an initial strain rate of 20/min.

2.2. Measurements

Wide-angle (WAXD) and small-angle (SAXS) X-ray scattering measurements were carried out on a Rigaku RU-200 diffraction unit with a Ni-filtered Cu-K α radiation generated at 50 kV and 150 mA.

Sample densities were determined at 30°C in a density gradient column with an accuracy of ± 0.001 g/cm³, using mixtures of *n*-heptane and carbon tetrachloride. The volume percent crystallinity (X_c) was calculated from the observed density on the basis of a two-phase model. The crystalline densities were taken to be 1.24 [18] and 1.16 g/cm³ [17] for the α - and γ -crystals, respectively. The amorphous density was taken to be 1.08 g/cm³ [19].

The birefringence (Δn) was measured by a polarizing optical microscope equipped with a Berek compensator. The orientation function of the non-crystalline phase (f_a) was determined by the combination of orientation function of the crystalline phase (f_c), Δn and X_c using the equation:

$$\Delta n = X_c \Delta n_c f_c + (1 - X_c) \Delta n_a f_a \quad (1)$$

where Δn_c and Δn_a are the intrinsic birefringences of the crystal and amorphous phases, 0.0780 and 0.0689 [20], respectively.

3. Results and discussion

3.1. Predrawn morphology

In Table 1, the observed densities and weight percent crystallinities (X_c) are shown for the original film and its chemically treated (reduced) one. By the chemical treatment, the observed density decreased, but the X_c increased from 41 to 70%, reflecting the transformation of the initial α -form to γ -form at the lower crystal density (1.24 vs. 1.16 g/cm³). The X_c of reduced sample is considerably higher than that reported by Chuah and Porter [7]. This is reasonable because the X_c determined by them was for nylon-6-l complex, but our sample (reduced) involved no iodine molecule. It is reported that the X_c of nylon-6-l complex is considerably lower than the pure nylon-6 [10].

An effect of molecular weight on the observed densities were less. In general, different molecular weights will affect the chain arrangement, density and crystallization rate. In this work, all predrawn films were prepared by casting of dilute polymer solutions (~ 2 wt%). Thus, it is assumed that

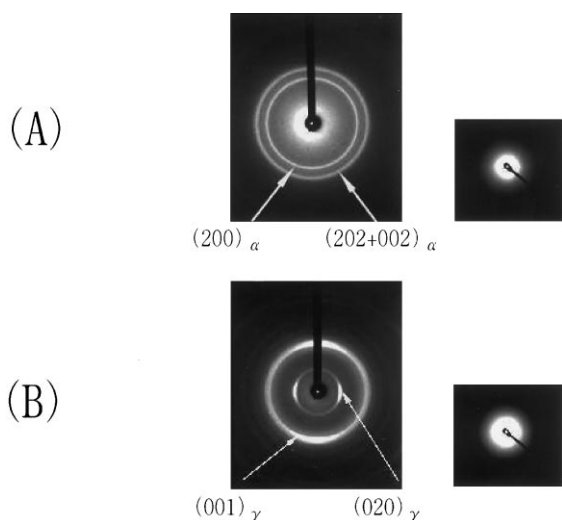


Fig. 1. WAXD and SAXS photographs of the original film (A) and reduced film (B).

all predrawn films have a comparable and low entanglement density, leading to the production of predrawn films with comparable densities.

Fig. 1 shows WAXD and SAXS photographs of the original film with M_v of 74,000 and its reduced one. These photographs were obtained with the incident X-ray beam parallel to the film surfaces. For the original film, the WAXD pattern showed that the crystals were predominantly in the α -form with random chain orientation. In the SAXS patterns, the intensity maxima were not observed.

In the WAXD pattern of the reduced film, the reflections from γ -crystals were clearly seen, which showed slightly anisotropic orientation of the crystals. The reason for the

formation of the anisotropic arrangement of the crystals by the chemical treatment of the initially randomly oriented α -form crystals is not clear. Similar to the case of original film, the intensity maxima were not observed in the SAXS profile. The missing intensity maxima in the SAXS profiles of the original and reduced samples might be due to a large fluctuation in the lamellar thickness. That is, the structure of nylon-6 cannot be described by a simple two-phase model consisting of crystalline and amorphous phases. Murthy and coworkers suggested [21,22] that the amorphous phase could have varying degrees of disorder, just as the crystalline phase could have varying degrees of order.

X-ray measurements were carried out also for the films of the higher molecular weight ($M_v = 440,000$). However, no effect of molecular weight was observed in the diffraction profiles.

In order to evaluate the structural differences in non-crystalline regions of the original and reduced films, dynamic mechanical measurements were carried out on these films. Fig. 2 shows the temperature dependence of storage (E') and loss (E'') moduli for the original and the reduced films of $M_v = 74,000$. After the chemical treatment, the α -dispersion peak, corresponding to the onset of micro-Brownian motions in non-crystalline regions [23], shifted to a higher temperature and the drop of E' around the α -dispersion became less prominent. These results indicate that the non-crystalline segments in the reduced film are highly strained compared with those in the original α -form film. On the basis of infra-red results of nylon-6, Murthy and coworkers report [22] that the IR spectra of the γ and the amorphous phases are very similar to each other, and very different from that of the α -phase, suggesting that the γ and the amorphous chains possess very similar conformations. This suggests that the structure of non-crystalline regions of reduced sample is not a completely amorphous, but has some degrees of order, which might constrain the molecular motions of non-crystalline segments.

3.2. Deformation behavior

Fig. 3 shows nominal stress/strain curves of films with different crystalline forms and molecular weights. The curves were obtained at 180°C and at a constant cross-head speed corresponding to the initial strain rate of 20/min. As was shown in Table 1, the X_c for reduced films were higher than for original films. Nevertheless, for a given molecular weight, the draw stress at a given strain, during drawing, for the film with α -crystals (original film) was higher than that for the film with γ -crystals (reduced film). Thus, the results indicate that the stress on draw of nylon-6 crystals is significantly higher for α -crystals than for γ -crystals. This means that the shear deformation resistance is higher for α -crystals than for γ -crystals, which is ascribed to the difference of interchain interactions. Since the distance between the adjacent amidic groups, where hydrogen bondings are formed, is longer for γ -crystals

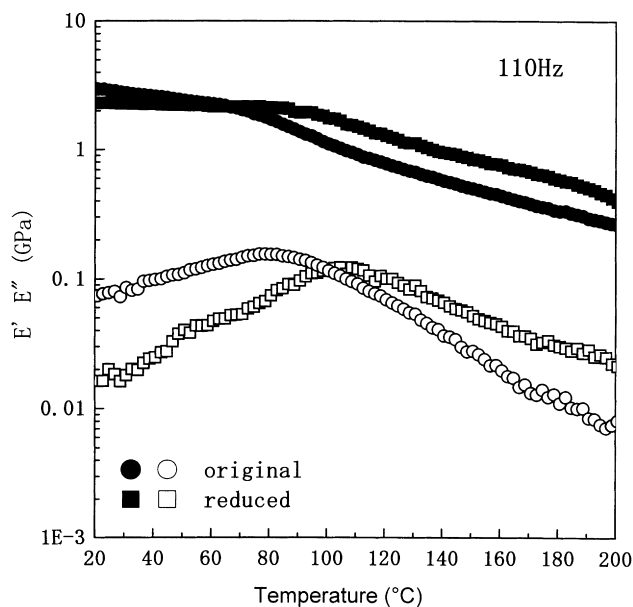


Fig. 2. Temperature dependence of dynamic storage (E') and loss (E'') moduli for the original and reduced films at 110 Hz.

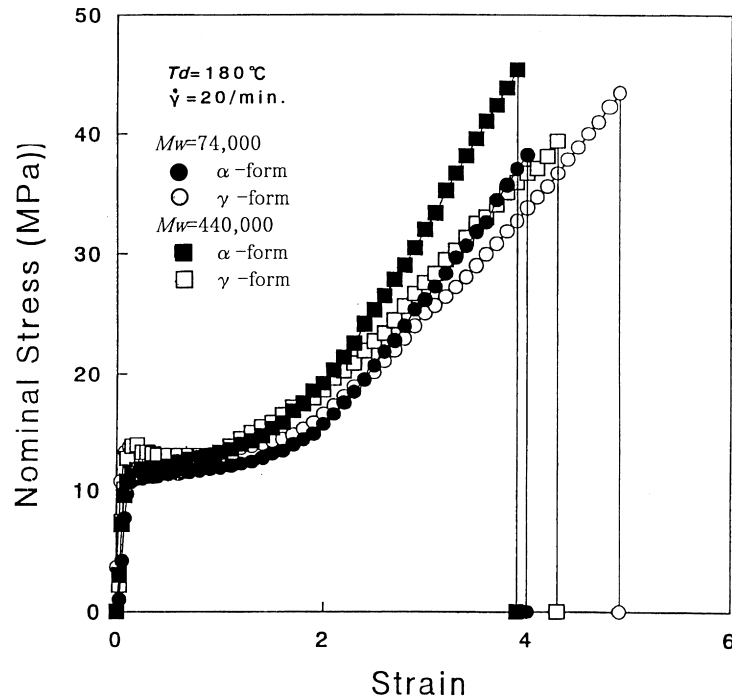


Fig. 3. Nominal stress/strain curves of films with different molecular weights and crystalline forms at 180°C and at a strain rate of 20 min⁻¹.

than for α -crystals [17,18,24,25]. The ductility of a polymer is primarily determined by the competition between the shear deformation resistance and the tensile strength of the sample. As will be shown later, the tensile strength at

a given DR for drawn sample was not affected by the crystalline form of the predrawn films. Therefore, for a given molecular weight, the ductility is higher for the predrawn films with γ -crystals than for α -crystals.

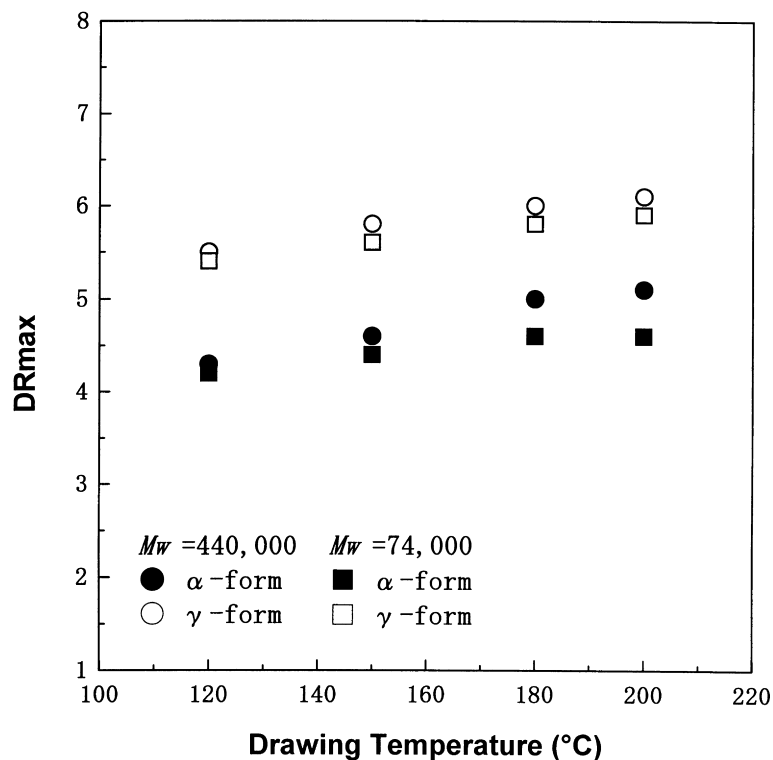


Fig. 4. The maximum achieved draw ratio (DR_{max}) as a function of draw temperature (T_d).

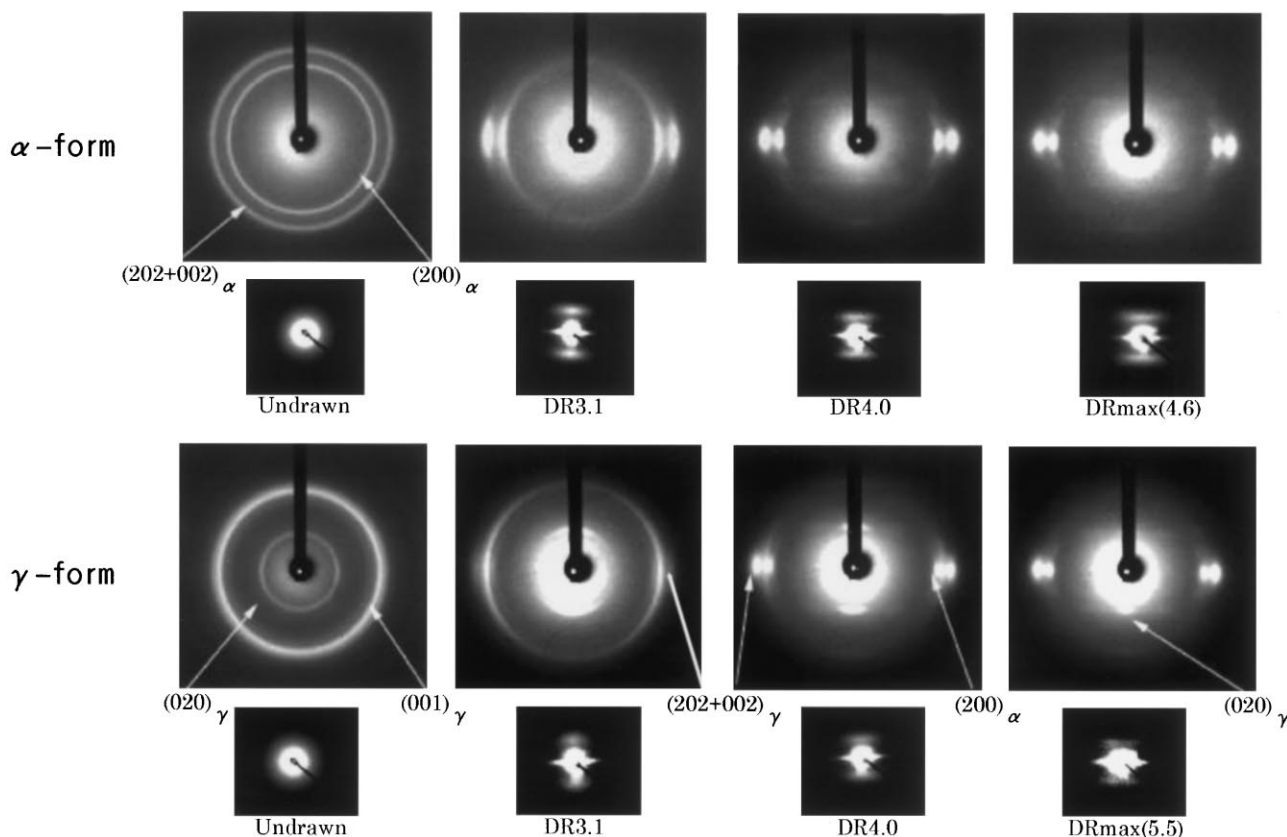


Fig. 5. WAXD and SAXS photographs of predrawn films with high molecular weight and their drawn samples with different draw ratios obtained at $T_d = 180^\circ\text{C}$.

For a given crystalline form and at a given strain, the stress on draw was higher for the higher molecular weight. As was shown, the predrawn films of different molecular weights were prepared from the polymer solutions with the same concentrations by a solution casting technique. Thus, it is assumed that all the predrawn films have a comparable entanglement density. In this case, the number of entanglements per-chain should increase with increasing the chain length, leading to the increase of stress on draw with increasing molecular weight.

In Fig. 4, the maximum achieved draw ratio (DR_{\max}) is plotted against draw temperature (T_d) for various predrawn films. It can be seen that the DR_{\max} does not depend on the sample M_v and is primarily determined by the crystalline form of the predrawn film. This is due to the high ductility of γ -crystals compared with α -crystals, as discussed above. For a given crystalline form, no molecular weight dependence on the DR_{\max} is reasonable since all the predrawn films have a similar entanglement density. The minimum draw ratio necessary for full chain extension between entanglement points from random coil is a function of entanglement density.

It is well known that the ductility of a polymer sharply increases above the temperature of crystalline relaxation [13,26]. However, nylon-6 has no such a relaxation [23]. The fact that the DR_{\max} increased only slightly with T_d

suggests that molecular motions in nylon-6 crystals are severely restricted even near the melting temperature.

3.3. Structural changes upon drawing

Fig. 5 shows WAXD and SAXS photographs of the predrawn films of a high molecular weight ($M_v = 440,000$) and its drawn samples obtained at $T_d = 180^\circ\text{C}$. The diffraction profiles for both predrawn films of the high molecular weight are qualitatively similar to those for low molecular weight films (see Fig. 1). For the predrawn films with α -crystals, the uniform rings in WAXD transformed to arcs which varied depending on the draw ratio. Both the $(200)_\alpha$ and $(202 + 002)_\alpha$ reflection maxima from α -crystals stayed on the equator and the azimuthal intensity distribution became narrower with increasing DR. The SAXS intensity maxima on the meridian became evident at a low DR of 3.1. As will be shown later, such structural changes with DR were accompanied by the increase of the tensile modulus along the draw direction. Thus, the SAXS profiles suggest that with increasing the DR, the fibrillar structure develops [27] without noticeable change in the long period (~ 10.5 nm). Murthy and coworkers report [28] the changes in the fibrillar and the lamellar structure in nylon-6 fibers resulting from drawing and annealing. A detailed analysis of small-angle X-ray

Table 2
Crystal orientation function of drawn samples with draw ratio of 4.0

	$(0\ 14\ 0)_\alpha$	$(0\ 2\ 0)_\gamma$
$M_w = 74,000$ (γ -form)	0.959	0.922
$M_w = 440,000$ (γ -form)	0.958	0.926

scattering patterns revealed the existence of fibrils of 1000–3000 Å length, which is larger than the length of the lamellar stack. In this work, however, direct information on the fibril structure was not obtained by our X-ray measurements.

At a low DR of 3.1 for the drawing of a predrawn film with γ -crystals, the WAXD intensity maxima from α -crystals appeared on the equator, but there still remained a strong $(001)_\gamma$ reflection from γ -crystals. At a higher DR, the reflection maxima on the equator from α -crystals became strong with narrow azimuthal intensity distribution. The reflection intensity from γ -crystals still existed on both meridian $(020)_\gamma$ and equator $(001)_\gamma$ even at the highest DR of 5.5. This means that some of γ -crystals could not be deformed even at the highest deformation ratio achieved in this work. The long period along the fiber axis of the drawn films, calculated from the SAXS intensity maximum, was simply related to the T_d , independent of the DR and the crystalline form of the pre-drawn films, as was described in a previous report [10].

As discussed, oriented α -crystals were generated by the stress-induced crystallization during drawing of the predrawn films with γ -crystals. However, a significant amount of oriented γ -crystals coexisted in these drawn films. Table 2 compares the chain orientation functions (f_c) of the α - and γ -form crystals coexisted in the samples drawn to a DR of 4.0 at $T_d = 180^\circ\text{C}$. The f_c s of the α - and γ -form crystals were calculated from the azimuthal intensity distribution of the $(0\ 14\ 0)_\alpha$ and $(020)_\gamma$ reflections, respectively, assuming fiber symmetry. It is noted that the f_c of neither α -nor γ -form was affected by the sample M_w , and it is higher for the α -form than for the γ -form ($f_c = 0.959$ vs. 0.922 – 0.926). This suggests that the draw stress was not uniformly distributed within a sample. The oriented γ -crystals were likely produced by the deformation of the initial γ -crystals under a lower stress. Fig. 6 shows the $(020)_\gamma$ reflection

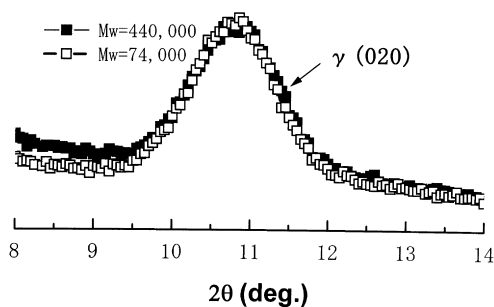


Fig. 6. Meridional diffraction intensities from $(020)_\gamma$ plane of γ -crystals for drawn samples with draw ratio of 4.0.

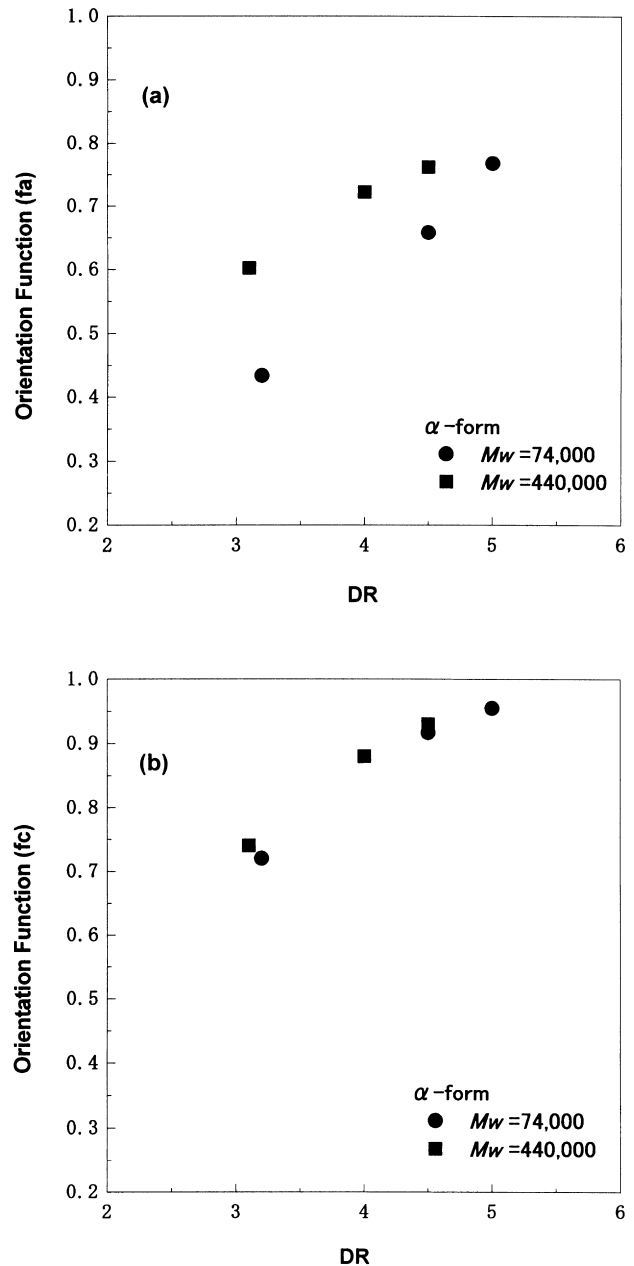


Fig. 7. Orientation function of non-crystalline (f_a) (a) and crystalline (f_c) (b) phases as a function of draw ratio.

tion on the meridian, recorded by a symmetrical transmission method, for the DR 4.0 samples of $\sim 50\ \mu\text{m}$ thickness prepared from a high and a low M_w nylon 6. The two samples showed comparable intensities, suggesting that M_w had no effect on the amount of oriented γ -crystals coexisted with α -crystals in the drawn sample. These facts show that the efficiency of draw in crystalline regions, as evaluated from the f_c values and the amounts of γ -form crystals, was not affected by the sample M_w .

An effect of molecular weight on the efficiency of draw in non-crystalline regions was evaluated from the birefringence data. For this, the draw ratio series prepared from

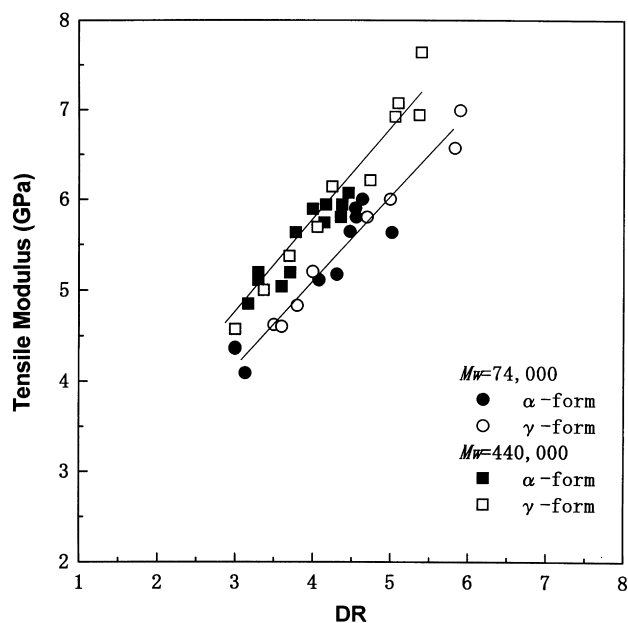


Fig. 8. Tensile modulus as a function of draw ratio for drawn samples obtained at $T_d = 180^\circ\text{C}$.

the predrawn films containing only α -crystals were used because the drawn samples consisted of only α -crystals, allowing the amorphous chain orientation function (f_a) to be calculated. In Fig. 7, the f_a is plotted as a function of DR for the drawing of two molecular weights. As stated in the Experimental section, the f_a was determined by the combination of the observed birefringence, density, and Herman–Stein crystalline chain orientation function, f_c , obtained from an azimuthal scan of the $(0140)_\alpha$ reflection. The f_c values are also plotted in Fig. 7. The f_c increased steadily with DR and reached $f_c = 0.970$ at the highest DR of 5.0, independent of the molecular weights. The f_a also increased with DR. It should be noted that the f_a value at a given DR is significantly higher for the higher M_v than for the low M_v . The number of entanglements per molecular chain may increase with increasing the molecular weight for the samples prepared at comparable condition. Further, all entanglements exist in non-crystalline regions. The disentanglement and chain slippage during deformation might be suppressed for longer chains with increased number of entanglements, leading to the increase of draw efficiency in the non-crystalline regions. Indeed, Smith et al. [14] found that chain slippage occurred to a much greater extent in a low molecular weight than in a high molecular weight polyethylene. We have also observed a similar behavior in poly(ethylene terephthalate) [15] and poly(ethylene 2,6-naphthalate) [29].

3.4. Relation between tensile properties and structure

In Figs. 8 and 9, the tensile modulus and strength, respectively, are plotted as a function of DR for the drawn samples

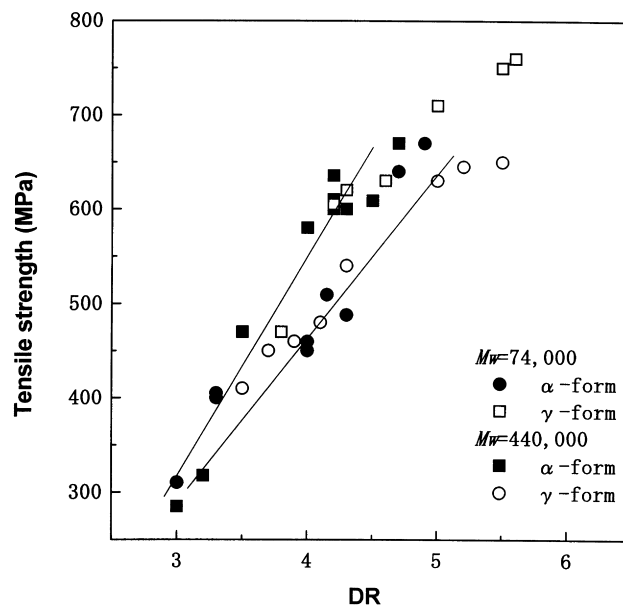


Fig. 9. Tensile strength as a function of draw ratio for drawn samples obtained at $T_d = 180^\circ\text{C}$.

obtained at $T_d = 180^\circ\text{C}$ from various predrawn films. At a given draw ratio, both the tensile modulus and the strength were higher for the higher M_v than for the low M_v samples. Such higher tensile properties for the higher M_v samples are ascribed to the increased efficiency of the draw in the non-crystalline regions, as discussed above.

The highest achieved modulus was only 7.7 GPa, which is as low as 4% of the α -crystal modulus of nylon-6 along the chain direction [1]. The orientation function of amorphous phase reached around 0.8 by the tensile drawing at 180°C . However, the increase of sample crystallinity by the drawing was quite small and X_c was $\sim 47\%$ at the highest achieved DR of 5.0 for the drawing of predrawn films with α -crystals. This fact suggests that the chain extension and orientation in the non-crystalline phase were not high enough to promote the strain induced crystallization and/or the crystallization rate was too slow during drawing under the conditions utilized in this work. In order to confirm these assumptions, annealing of the drawn samples was carried out at 190°C for 1 h under a constant stress of 150 MPa, followed by a rapid cooling to room temperature. The results are shown in Table 3. The coexistence of γ -crystals with α -crystals in the drawn samples from predrawn films with γ -crystals made it difficult to determine the X_c of drawn samples. However, the diffraction intensities from γ -crystals in the drawn samples almost disappeared upon annealing. Thus, the X_c of annealed drawn samples could be determined, assuming that all crystals in the drawn samples were α -form. After the annealing under a constant stress, the DR and X_c showed small increases of 7–13 and 13%, respectively. However, the tensile modulus showed a remarkable increase of 36–47%. Under the annealing

Table 3
Characteristics of drawn samples before and after annealing

Sample		DR	Δn	X_c (%)	Modulus (GPa)
Original	Before-annealing	4.4	0.062	47.0	5.8
	After-annealing	4.7	0.067	53.0	7.9
Reduced	Before-annealing	5.3	–	–	6.8
	After-annealing	6.0	0.070	55.0	10.0

conditions mentioned above, highly oriented non-crystalline segments might be able to crystallize without relaxation, leading to the large increase of tensile modulus. The density of highly oriented non-crystalline phase is larger than that of completely amorphous phase. Thus, the increase of X_c by the crystallization was small. These results support our second assumption mentioned above.

4. Conclusion

Two nylon-6 samples of different M_v were tensile drawn at 120–200°C. The following conclusions were derived based on the observations of drawing characteristics and the structure and properties of drawn samples.

1. Under a comparable entanglement density, the stress on draw at a given strain increased with increasing the chain length due to the increased number of entanglements per chain. However, the macroscopic deformability was not affected by the chain length of nylon-6.
2. The macroscopic deformability was not significantly affected by drawing temperature but improved by the introduction of γ -crystals in the pre-drawn films.
3. The efficiency of draw in the noncrystalline regions increased with increasing the molecular weight. However, the efficiency in the crystalline regions was independent of the molecular weight.
4. The maximum tensile modulus of 7.7 GPa and strength of 760 MPa were achieved by drawing the higher M_v sample composed initially of γ -form crystals. Upon annealing in the vicinity of melting temperature under a constant stress, the modulus increased by 36–47%.

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