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# Ultradrawing of ultrahigh molecular weight polyethylene reactor powders prepared by highly active catalyst system

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## Abstract

Drawability of ultrahigh molecular weight polyethylene (UHMW-PE) reactor powders, prepared by using a highly active Ziegler type catalyst, has been studied as functions of catalyst activity, polymerization temperature, monomer pressure and sample molecular weight. Compacted powder films of UHMW-PE, prepared in a 1000-fold range of polymerization rates, were drawn by a two-stage technique; i.e. the initial solid-state coextrusion at 110°C followed by tensile drawing at 135°C, some 5°C below the melting point. It was found that an appropriate range of molecular weights ($M_v = 1.6$–$3.0 \times 10^6$) existed for achieving a high draw. The UHMW-PE prepared even at a high polymerization rate of 43,600 (g of PE)/(mmol of transition metal,h) could be drawn to draw ratios (DR) over 50, producing tapes with tensile modulus and strength over 100 and 1.0 GPa, respectively. This level of catalyst activity is sufficient for the modern industrial production of UHMW-PE. The reduction of polymerization rate, by lowering monomer pressure and polymerization temperature, produced UHMW-PE with improved ductility. Furthermore, at the same polymerization rate, the ductility of reactor powder was improved more significantly by lowering the former parameter than the latter, reflecting the characteristic effect of each of these polymerization variables on the morphology formation during polymerization. Thus, the reactor powders prepared at 40–60°C and monomer pressure of 1 atm could be drawn to DR's of 100–125. Such highly drawn products exhibited tensile moduli and strength up to 144 and 1.6 GPa, respectively. © 2001 Published by Elsevier Science Ltd.

*Keywords*: Ultrahigh molecular weight polyethylene reactor powders; Drawability; Highly active catalyst

## 1. Introduction

It is well-known that ultrahigh modulus and strength polyethylene materials can be produced by ultradrawing of ultrahigh molecular weight polyethylene (UHMW-PE) from gel [1–3] and single crystal morphologies [4,5]. However, once they are molten, they quickly loose the excellent ductility [6], since the arrangement of chain-folded stems are disturbed and/or the number of entanglements of polymer chains increases in a molten state. A recent review [7] on the tensile modulus increase on uniaxial drawing of high density polyethylene with various molecular weights and initial morphologies shows that almost all moduli versus draw ratio (DR) data from different sources can be expressed by the same curve. The gel-spinning technology has been an industrial process to produce ultradrawn UHMW-PE with high mechanical performance [8]. This technology involves dissolution of the polymer in some solvents for untanglement of the polymer chains, followed by gelation crystallization and drawing. Thus, the gel-spinning technology requires much solvent for the limitation of polymer solubility in solvents and the solvent recovery during processing.

Recently, new techniques of solvent free routes have been proposed for the production of high modulus/strength UHMW-PE. Porter and co-workers [9,10] have demonstrated that UHMW-PE reactor powder could effectively be drawn by solid-state extrusion [9] and coextrusion [10]. Smith et al. [11,12] introduced a technique based on tensile drawing of virgin (i.e. as-polymerized) UHMW-PE films, which were prepared by depositing a vanadium catalyst system on a glass slide, followed by polymerization of ethylene at relatively low temperatures. They [13] also investigated tensile drawing of compacted films of reactor powders prepared at relatively low polymerization rates. The highly drawn films exhibited tensile moduli of 80–125 GPa,

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depending on the polymerization conditions of reactor powders. They state that the modern, highly active catalysts may result in the reactor powder having poor processing and drawing characteristics.

Kanamoto et al. [4,14] have proposed a two-stage drawing technique, which consists of the initial solid-state coextrusion to a low DR, followed by tensile drawing at controlled temperatures and rates. They have shown that a single crystal mat of UHMW-PE has been ultradrawn to DRs ≤400, producing extremely chain-extended and oriented films with tensile moduli ≤220 GPa, approaching the theoretical maximum value reported for the perfect crystal of polyethylene (235–300 GPa) [15,16]. Furthermore, they [17,18] have applied the two-stage processing technique to several UHMW-PE reactor powders of commercial grades. It has been shown that Hercules Hifax 1900 grade could be ultradrawn to DR ≤ 80, and the resultant drawn tapes showed tensile moduli of ≤135 GPa. However, most of other grades of commercial reactor powders, such as a Hostalen GUR 415 grade, exhibited poor drawability. The remarkable difference in the ductility of samples is likely related to the initial powder morphologies that were formed during polymerization [12,19–23].

Porter and co-workers [24] have reported that the UHMW-PE reactor powders synthesized in a slurry phase were highly drawable by the two-stage technique. On the other hand, the powders obtained in a gas phase were not highly drawable. In contrast to the prediction by Smith et al. [11,12], they found that a higher molecular weight UHMW-PE prepared at the highest polymerization temperature of 80°C showed the highest drawability up to DR of ~100, producing films with tensile moduli ≤75 GPa.

The purpose of this paper is to study on the preparation of high modulus and strength tapes by the two-stage drawing technique of UHMW-PE reactor powders prepared by using our highly active Ziegler catalyst, having an activity sufficiently high for industrial production. More specifically, the effects of polymerization rate, temperature, ethylene pressure and sample viscosity-average molecular weight ($M_v$) on the drawability of reactor powder and the resultant tensile properties of drawn products have been discussed.

## 2. Experimental

### 2.1. Samples

Reactor powders of UHMW-PE were obtained by the polymerization of ethylene using a highly active Ziegler catalyst in hexane solvent in the temperature range of 20–90°C, and at ethylene pressures of 1–11 atm. In some cases, the $M_v$ of UHMW-PE was controlled by adding a small amount of hydrogen gas. After polymerization, the polyethylene was filtered and dried, without eliminating the catalyst residue. The $M_v$ was calculated from the inherent viscosity in decalin at 135°C.

### 2.2. Drawing

The dried powder was compression molded into a sheet at 130° and 120 atm. The sheet was cut into strips with a width of 5 mm and a length of 60 mm. The strip was drawn by a two-stage method. For the first-stage drawing, a strip was sandwiched between split billet halves of high density polyethylene, and the assembly was coextruded at 110°C through a conical brass die having an entrance angle of 20°and at a rate of ~1 cm/min to a low extrusion draw ratio (EDR) of 5. For the second stage, the extrudate was cut into four pieces, and these pieces were simultaneously tensile-drawn at a constant cross-head speed of 5 cm/min at 135°C in an air oven until two pieces broke. The maximum draw ratio ($DR_{max}$) after two-stage drawing is defined by multiplying the initial EDR by the second-stage tensile DR.

### 2.3. Characterization

Ultradrawn tapes were characterized by the tensile modulus and strength measured at room temperature and at strain rates of $10^{-3}$ and $10^{-2} s^{-1}$, respectively. The melting characteristics of reactor powders were determined on a Seiko Denshi DSC-20 differential scanning calorimeter (DSC) at a heating rate of 5°C/min. The melting peak temperature ($T_m$) and heat of fusion ($\Delta H_f$) were calibrated with an indium standard.

## 3. Results and discussion

### 3.1. Effect of molecular weight on drawability

UHMW-PE reactor powders having various molecular weights can be prepared by changing the polymerization conditions, such as polymerization temperature ($T_{poly}$), polymerization pressure ($P_{poly}$) and concentration of hydrogen as a chain transfer agent. As a preliminary study on the effect of molecular weight of UHMW-PE on drawability, polymerization of ethylene was carried out by changing the $T_{poly}$ from 20 to 90°C at a constant $P_{poly}$ of 11 atm and without hydrogen. The reactor powders having a $M_v$ range of $1.6–8.1 \times 10^6$ were obtained, as shown in Table 1 with their $T_m$ and $\Delta H_f$ determined by DSC. The $M_v$ decreased with increasing the $T_{poly}$.

Each reactor powder was compressed into a sheet below the ambient melting point and was drawn by a two-stage method under the standard conditions; i.e. the initial coextrusion at 110°C and an EDR of 5, followed by tensile drawing at 135°C. Fig. 1 shows the relationship between the $M_v$ of the reactor powders and the $DR_{max}$. The reactor powders having $M_v$ in the range of $1.6–3.0 \times 10^6$ could be drawn to $DR_{max}$ over 50. For the samples with higher $M_v$ exceeding $3.0 \times 10^6$, which were prepared by polymerization at 20–60°C, the $DR_{max}$ decreased considerably with increasing $M_v$ for the standard draw condition of the two-stage method. It should be noted, however, that such

Table 1
Effects of polymerization conditions on the polymerization rate ($R_{poly}$), melting temperature ($T_m$) and heat of fusion ($\Delta H_f$), maximum achieved draw ratio ($DR_{max}$), and tensile modulus ($E$) and strength ($\sigma$) of the resultant drawn tapes

| Sample | $T_{poly}$ (°C) | $P_{poly}$ (atm) | $H_2$ (mol%) | $R_{poly}$[a] | $M_v \times 10^{-6}$ | $T_m$ (°C) | $\Delta H_f$ (J/g) | $DR_{max}$ | $E$ (GPa) | $\sigma$ (GPa) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 20 | 11 | 0 | 400 | 8.1 | 142.1 | 200 | 14 | 26 | 0.4 |
| 2 | 40 | 11 | 0 | 3700 | 5.3 | 141.9 | 197 | 18 | 43 | 0.6 |
| 3 | 60 | 11 | 0 | 15,000 | 3.6 | 141.4 | 201 | 32 | 73 | 0.6 |
| 4 | 65 | 11 | 0 | 24,000 | 3.2 | 142.0 | 211 | 31 | 76 | 0.9 |
| 5 | 70 | 11 | 0 | 31,600 | 2.5 | 141.0 | 193 | 50 | 93 | 1.2 |
| 6 | 75 | 11 | 0 | 42,000 | 2.6 | 141.6 | 205 | 55 | 98 | 1.0 |
| 7 | 80 | 11 | 0 | 43,600 | 2.0 | 140.1 | 195 | 51 | 93 | 1.1 |
| 8 | 90 | 11 | 0 | 39,700 | 1.6 | 139.9 | 201 | 54 | 78 | 0.9 |
| 9 | 20 | 11 | 5 | 110 | 2.6 | 140.9 | 197 | 73 | 112 | 1.0 |
| 10 | 40 | 11 | 1 | 4900 | 2.7 | 141.4 | 201 | 62 | 114 | 1.2 |
| 11 | 60 | 11 | 0.5 | 18,600 | 2.6 | 141.3 | 196 | 50 | 91 | 1.1 |

[a] Polymerization rate in gPE/mmolTM h.

samples with higher $M_v$ could be drawn up to a higher DR by drawing at higher temperatures. For example, the $DR_{max}$ of the sample having a $M_v$ of $5.3 \times 10^6$ reached to a $DR_{max}$ of 80, when the second-stage tensile drawing was made at 155°C, although the efficiency of draw, as evaluated by the modulus versus DR, slightly decreased at such a high temperature.

Table 1 and Fig. 1 also show $DR_{max}$ of the reactor powders having $M_v$ in the range of $1.6–3.0 \times 10^6$ controlled by the addition of hydrogen at $T_{poly}$ of 20, 40 and 60°C. These samples could be drawn to higher $DR_{max}$ than that of the samples prepared at $T_{poly}$ of 70–90°C without hydrogen but having the same range of $M_v$. The difference is probably caused by differences of the polymerization rate ($R_{poly}$); i.e. the $R_{poly}$ of the former samples are lower than that of the latter ones.

The results described above suggests the existence of an optimum range of $M_v$ to achieve ultradraw for two-stage drawing of UHMW-PE reactor powders prepared by the present highly active catalyst system. However, it should be remembered that the $M_v$ of the samples was controlled by changing the $T_{poly}$ and the concentration of hydrogen. The ductility of UHMW-PE, on the one hand, is known to depend dramatically on the morphology [1,6,25,26] and $M_v$ of samples [25,26]. On the other hand, the morphology of reactor powder is determined by the crystallization during polymerization, which is controlled by the polymerization conditions such as $T_{poly}$, $P_{poly}$, concentration of hydrogen and polymerization rate. Thus, it is not clear whether the ductility of reactor powders examined above is directly related to the $M_v$ alone or is affected also by other polymerization parameters. Therefore, the effect of each of these parameters on the ductility of reactor powder has been studied as discussed below.

### 3.2. *Effect of polymerization rate on drawability*

The influence of $R_{poly}$ on drawability was studied by changing the $T_{poly}$ and $P_{poly}$. To eliminate the effect of $M_v$ on the ductility, the $M_v$ of samples examined here was controlled, by the addition of a small amount of hydrogen, to be in the range of $1.6–3.0 \times 10^6$, which was appropriate for the two-stage drawing conditions as described above. The polymerization conditions and the drawability of UHMW-PE are shown in Table 2. The $R_{poly}$, which was represented as the yield (g) of UHMW-PE per 1 mmol of transition metal (TM) on the catalyst per 1 h, increased with increasing the polymerization temperature and pressure.

Fig. 2 shows $DR_{max}$ as a function of $R_{poly}$; the data of samples having $M_v$ in the range of $1.6–3.0 \times 10^6$ were selected from Tables 1 and 2 and were plotted. The reactor powder obtained at the very high $R_{poly}$ of more than 10,000 gPE/mmolTM h, even at 43,600 gPE/mmolTM h for $T_{poly}$ of 80°C, could be drawn to $DR_{max}$ over 50. Such highly drawn tapes showed tensile moduli of 80–100 GPa. The $DR_{max}$ increased steadily from 50 to 70 with the decrease of the $R_{poly}$ from 43,600 to

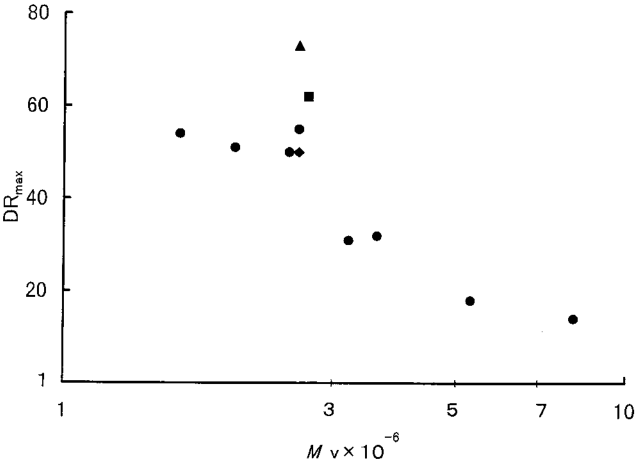

Fig. 1. Effect of molecular weight, $M_v$, on the maximum achieved draw ratio, $DR_{max}$. (●) — $T_{poly}$ = 20–90°C, $P_{poly}$ = 11 atm, $H_2$ = 0 mol%; (▲) — $T_{poly}$ = 20°C, $P_{poly}$ = 11 atm, $H_2$ = 5 mol%; (■) — $T_{poly}$ = 40°C, $P_{poly}$ = 11 atm, $H_2$ = 1 mol%; (◆) — $T_{poly}$ = 60°C, $P_{poly}$ = 11 atm, $H_2$ = 0.5 mol%.

Table 2
Effects of polymerization temperature ($T_{poly}$) and monomer pressure ($P_{poly}$) on the melting characteristics, drawability, and tensile properties of the resultant drawn tapes for UHMW-PE reactor powders having a molecular weight ($M_v$) range $1.6–3.0 \times 10^6$

| Sample | $T_{poly}$ (°C) | $P_{poly}$ (atm) | $H_2$ (mol%) | $R_{poly}$[a] | $M_v \times 10^{-6}$ | $T_m$ (°C) | $\Delta H_f$ (J/g) | $DR_{max}$ | $E$ (GPa) | $\sigma$ (GPa) |
|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 20 | 6 | 5 | 300 | 2.2 | 140.5 | 202 | 78 | 114 | 0.9 |
| 13 | 20 | 2 | 8 | 90 | 2.4 | 140.4 | 202 | 63 | 104 | 1.1 |
| 14 | 20 | 1 | 8 | 40 | 2.5 | 140.5 | 199 | 86 | 111 | 0.9 |
| 15 | 40 | 6 | 3 | 1300 | 2.6 | 141.0 | 202 | 65 | 107 | 0.9 |
| 16 | 40 | 2 | 3 | 240 | 1.7 | 140.2 | 205 | 57 | 84 | 0.7 |
| 17 | 40 | 1 | 0 | 170 | 2.8 | 141.6 | 207 | 108 | 144 | 1.3 |
| 18 | 60 | 6 | 0 | 6500 | 2.8 | 141.0 | 199 | 51 | 92 | 1.3 |
| 19 | 60 | 2 | 0 | 490 | 2.0 | 140.7 | 217 | 72 | 114 | 1.2 |
| 20 | 60 | 1 | 0 | 160 | 2.3 | 140.6 | 208 | 124 | 139 | 1.6 |

[a] Polymerization rate in gPE/mmolTM h.

200 gPE/mmolTM h, and then more rapidly from $DR_{max}$ of 70 to 124 in the $R_{poly}$ range of 200–50 gPE/mmolTM h. The resultant tensile modulus and strength of a drawn tape of $DR_{max}$ 124 reached 139 and 1.6 GPa, respectively.

Smith et al. [13] investigated straight tensile drawing of reactor powders prepared by vanadium catalysts at low $R_{poly}$ corresponding to 30–2000 gPE/mmolTM h calculated from their data. They found that the reduction in $R_{poly}$ to 30–300 gPE/mmolTM h by lowering $T_{poly}$ and $P_{poly}$ resulted in a drastically enhanced $DR_{max}$ over 40. They also state that the development of modern catalysts has mostly been towards a more active (high yield, at relatively high temperature) system, which result in UHMW-PE with poor processability and drawability. However, the reactor powders obtained by using our highly active catalyst were ultradrawable, in spite of the 100–1000 times higher $R_{poly}$ than that of Smith's catalyst system. The difference between their results and ours may be related to the nature of the catalyst systems and the drawing techniques. The highly active catalyst with $R_{poly}$ of more than 10,000 gPE/mmolTM h can be available for the industrial production of UHMW-PE by a non-deashing process: namely it is not necessary to eliminate the catalyst residue from the polymer in the production system of polyethylene.

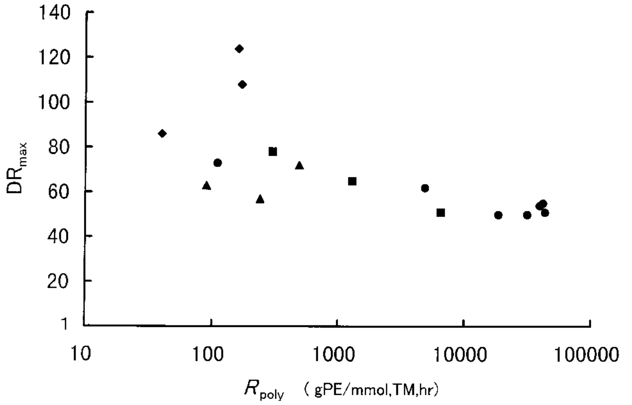

Fig. 2. Effect of polymerization rate on the drawability. (●) — $T_{poly} = 20–90°C$, $P_{poly} = 11$ atm, $H_2 = 0–5$ mol%; (■) — $T_{poly} = 20–60°C$, $P_{poly} = 6$ atm, $H_2 = 0–5$ mol%; (▲) — $T_{poly} = 20–60°C$, $P_{poly} = 2$ atm, $H_2 = 0–8$ mol%; (◆) — $T_{poly} = 20–60°C$, $P_{poly} = 1$ atm, $H_2 = 0–8$ mol%.

## 3.3. Effects of polymerization temperature and pressure on drawability

As shown in Fig. 2, $DR_{max}$ increased slowly with decreasing $R_{poly}$, which depends on both the $T_{poly}$ and the $P_{poly}$. Therefore, the effect of each of these parameters on drawability has been studied separately. The $M_v$ of samples were controlled to be $1.6–3.0 \times 10^6$ to minimize the effect of $M_v$ on the ductility.

Fig. 3 shows schematic representations of the $R_{poly}$ and $DR_{max}$ as functions of $T_{poly}$ and $P_{poly}$ for the reactor powders. The white poles indicate $R_{poly}$ and the black ones show $DR_{max}$ of the reactor powders prepared at each temperature and ethylene pressure. At $T_{poly}$ of 80°C and at $P_{poly}$ of 11 atm (abbreviated as $T/P = 80/11$, indicating $T_{poly} = 80°C$ and $P_{poly} = 11$ atm), the $R_{poly}$ was 43,600 gPE/mmolTM h. The rate decreases steadily with the decrease of $T_{poly}$ and $P_{poly}$ and at $T/P = 20/1$, the $R_{poly}$ decreased to 40 gPE/mmolTM h.

The ductility of reactor powder was fairly complexly affected by $T_{poly}$ and $P_{poly}$. At the highest $P_{poly}$ of 11 atm examined in this work, the $DR_{max}$ increased slightly from 50 to 70 with decreasing $T_{poly}$ from 80 to 20°C. At the lowest $P_{poly}$ of 1 atm, however, an opposite effect was observed; i.e. the $DR_{max}$ increased with increasing $T_{poly}$. Drawability was also significantly affected by $P_{poly}$. At a $T_{poly}$ of 60°C, the $DR_{max}$ increased sharply from 50 to 124 with decreasing $P_{poly}$ from 11 to 1 atm. Therefore, it was concluded that reducing $P_{poly}$ for the preparation of reactor powder had more beneficial effect on the drawability of compression-molded sheets, for the present catalyst system. As a result, the $DR_{max}$ of the reactor powder prepared under the polymerization condition of $T/P = 60/1$ was much higher than that prepared at $T/P = 20/11$ ($DR_{max} =$ 124 versus 73), though the whole $R_{poly}$ under the two conditions were comparable. The marked difference in $DR_{max}$ between the two samples is likely related to the initial

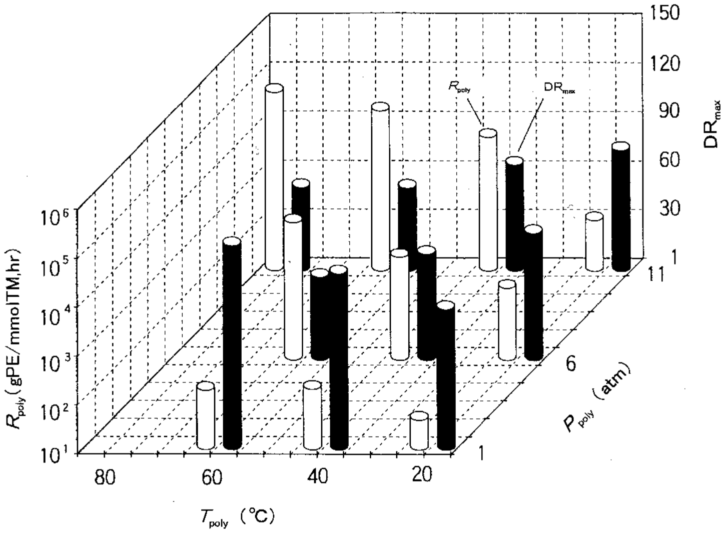

Fig. 3. Effects of polymerization temperature and pressure on the polymerization rate drawability. White poles represent polymerization rates ($R_{poly}$), and black poles show the maximum achievable draw ratios of the reactor powder ($DR_{max}$).

powder morphology [23] that was formed during polymerization. It is interesting to remember that Smith et al. [11–13] state that a highly drawable UHMW-PE reactor powder is produced at lower $T_{poly}$s. In contrast, Porter and co-workers [24] report that the drawability was higher for the sample prepared at a higher $T_{poly}$. These apparently opposite effects of $T_{poly}$ on the ductility of UHMW-PE powders can be well explained, if we take the effect of $P_{poly}$ into account, as discussed above.

One of the significant differences between the polymerization conditions of $T/P = 60/1$ and 20/11 was the concentration of ethylene in the solvent during polymerization. The ethylene concentration of the former was approximately 1/70 of the latter, as estimated by gas/liquid equilibrium. Further, at a higher $T_{poly}$ of 60°C, the number of active sites per unit area of the catalyst surface might be larger and they were distributed more densely than at a lower $T_{poly}$ of 20°C. These features, combined with the fact that the overall polymerization rates were comparable for the two conditions, suggest that the growth rate of a polymer chain at a catalyst site was slower for $T/P = 60/1$ than for $T/P = 20/11$. In a previous paper [23], we found that the crystal thickness along the chain direction in these reactor powders increased with $T_{poly}$ from 19.0 nm at 20°C to 22.5 nm at 60°C. This suggests that the crystallization occurred near $T_{poly}$, after the segmental length of a growing chain had reached to a certain value during polymerization, and that the critical segment length at a higher $T_{poly}$ of 60°C was likely to be longer than at a lower $T_{poly}$ of 20°C. Such a crystallization mode, combined with a slower chain growth-rate at $T_{poly} = 60$°C, suggests that the time required for a growing chain reaching the critical value might be significantly longer at $T_{poly} = 60$°C than at 20°C. Thus, the crystallization of a growing chain likely had proceeded significantly slower for $T/P = 60/1$ than for $T/P = 20/11$, resulting in a less entangled reactor powder for the former condition.

## 4. Mechanical properties and characterization

Fig. 4 shows the tensile modus as a function of $DR_{max}$ for all drawn tapes from compression-molded sheets of UHMW-PE, which were prepared in the wide range of $T_{poly}$ (20–80°C) and $P_{poly}$ (1–11 atm). This graph shows that the polymerization conditions do not affect the efficiency of tensile drawing, and the tensile modulus increased rapidly with $DR_{max}$ up to 144 GPa at $DR_{max}$ 108. The tensile strength at break, which we believe to be regarded as a

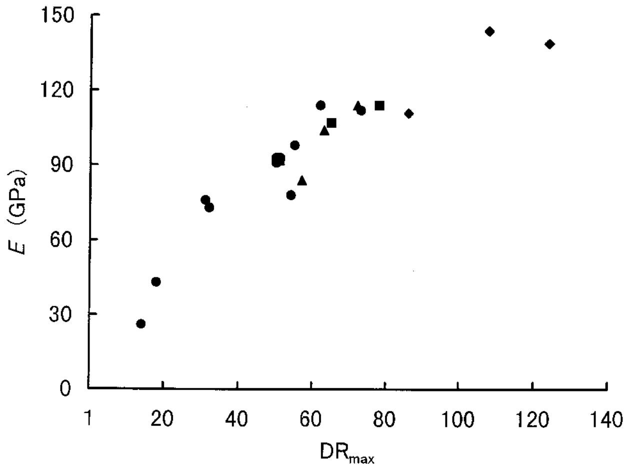

Fig. 4. Tensile modulus as a function of draw ratio. (●) — $T_{poly} =$ 20–90°C, $P_{poly} = 11$ atm, $H_2 =$ 0–5 mol%; (■) — $T_{poly} =$ 20–60°C, $P_{poly} = 6$ atm, $H_2 =$ 0–5 mol%; (▲) — $T_{poly} =$ 20–60°C, $P_{poly} = 2$ atm, $H_2 =$ 0–8 mol%; ( (◆) — $T_{poly} =$ 20–60°C, $P_{poly} = 1$ atm, $H_2 =$ 0–8 mol%.

minimum value for the highly oriented, high modulus and high strength tape, was 0.7–1.6 GPa in the $DR_{max}$ range of 50–124, as shown in Tables 1 and 2.

We examined the melting characteristics of reactor powders by DSC. The melting temperatures and enthalpies of fusion were found to be in the range of 140–142°C and 190–220 J/g, respectively, for all the reactor powders prepared in the wide range of $T_{poly}$ (20–80°C) and $P_{poly}$ (1–11 atm), as shown in Tables 1 and 2. No distinct correlation was found between these thermal properties and the drawability. The high $T_m$ of UHMW-PE reactor powders, 140–142°C, which are close to the $T_m$ of a chain-extended polyethylene crystal [27], has been shown to be due to the rapid reorganization of the initial crystals during DSC heating scans, as revealed by the significant depression of $T_m$ by cross-linking the amorphous regions with electron beam [28] and by fuming nitric acid etching [23]. Indeed, Raman longitudinal acoustic mode [29] and wide-angle X-ray diffraction [23] studies of reactor powders revealed that the crystallite size along the chain direction was 19–30 nm depending on the $T_{poly}$ of 20–90°C. The melt-crystallized UHMW-PE samples, which are believed to be highly entangled [1,6,30], exhibit $T_m$ of 134–135°C, suggesting no occurrence of significant structural reorganization during DSC heating scan. Therefore, the rapid reorganization during heating of these reactor powders is likely ascribed to their specific morphology with less entanglements, formed during polymerization.

## 5. Conclusions

The effects of polymerization variables on ultradrawing of UHMW-PE reactor powders, prepared by our highly active Ziegler catalyst system, have been studied in detail, and the following conclusions were obtained.

The reactor powders prepared at high polymerization rates of more than 10,000 gPE/mmolTM h, even at 43,600 gPE/mmolTM h ($T_{poly} = 80$°C and $P_{poly} =$ 11 atm), which is sufficient for the modern industrial production, could be ultradrawn by means of the solid state two-stage drawing technique. The resultant tensile moduli and strength of drawn products from such samples reached nearly 100 and 1.0 GPa, respectively.

The preparation of high modulus and high strength UHMW-PE materials by a solid-state two-stage drawing technique is affected by the kind of catalyst, polymerization conditions and molecular weight. The optimum range of $M_v$ for achieving a high draw, and hence high tensile properties, was found to be $M_v = 1.6\text{–}3.0 \times 10^6$ for our highly active catalyst system.

The reduction in ethylene pressure for the production of reactor powder gave an extremely beneficial effect on the ductility of compression-molded sheets; i.e. at $T_{poly} =$ 40–60°C and $P_{poly} = 1$ atm, the maximum DR reached 108–124 and the resultant tensile modulus and strength of drawn tapes were 139–144 GPa and 1.3–1.6 GPa, respectively.

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