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## Ultradrawing of High-Molecular-Weight Polyethylene Cast from Solution. II. Influence of Initial Polymer Concentration

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## **Synopsis**

Ultradrawing of films of high-molecular-weight polyethylene ( $\overline{M}_w=1.5\times10^6$ ) produced by gelation crystallization from solution is discussed. The influence of the initial polymer volume fraction ( $\phi$ ) on the maximum draw ratio ( $\lambda_{\max}$ ) of the dried films is examined in the temperature region from 90–130°C. The results can be described very well by the relation  $\lambda_{\max}=\lambda_{\max}^1\phi^{-1/2}$ , where  $\lambda_{\max}^1$  is the (temperature-dependent) maximum draw ratio of the melt-crystallized film. An attempt is made to discuss the marked influence of the initial polymer volume fraction on  $\lambda_{\max}$  in terms of the deformation of a network with entanglements acting as semipermanent crosslinks.

#### INTRODUCTION

In the past decade ultradrawing (i.e., drawing to ratios of 20–40) of polyethylene has been employed successfully to produce structures with Young's moduli up to 70 GPa, which compares with moduli of glass and aluminum.<sup>1–3</sup> In view of improved creep properties and tensile strength, it would be of significance to orient high-molecular-weight polyethylene by elongation to similar high draw ratios. It is known, however, that melt-crystallized polyethylene with a molecular weight  $(\overline{M}_w)$  exceeding  $10^6$  cannot be drawn effectively to ratios higher than about 5–10.<sup>4,5</sup>

In previous papers we reported a drastically enhanced effective drawability of continuous structures of high molecular weight polyethylene which were obtained by spinning<sup>6–8</sup> or casting<sup>9</sup> from semidilute solutions, in comparison with melt-crystallized material. For example, fibers of polyethylene having a molecular weight  $\overline{M}_w$  of  $1.5 \times 10^6$  spun from a 2% w/w solution in decalin could readily be elongated to a draw ratio of 30 at a temperature of 120°C and at a strain rate of about 1 sec<sup>-1</sup>. This phenomenon of increased effective drawability enabled the production of filaments of polyethylene with high strength (3 GPa) and high modulus (100 GPa).

The origin of the enhanced drawability of high molecular weight polyethylene that is spun or cast from semidilute solutions was qualitatively discussed in Paper I of this series.<sup>9</sup> The discussion was essentially based on the well-known concept of entanglements in polymer melts and concentrated solutions (see, e.g., ref. 10).

In this approach the macromolecules are thought to form a transient network with entanglements acting as friction centers or nonlocalized junctions. It was argued that a high entanglement density impedes large deformation of solidified high-molecular-weight polymers, and that by a reduction of the number of entanglements, for example through crystallization from solution, their drawability could be improved.

The molecular weight between entanglements in the undiluted polymer melt is usually denoted  $M_e$ . In a solution with a polymer concentration c exceeding the value for onset of coil-overlap the molecular weight between entanglements  $(M_e)_{\text{soln}}$  is given approximately by

$$(M_e)_{\text{soln}} = (\rho/c)M_e = M_e/\phi \tag{1}$$

where  $\rho$  refers to the bulk density of the polymer and  $\phi$  is the polymer volume fraction.<sup>11</sup> Equation (1) shows that  $(M_e)_{\text{soln}}$  is inversely proportional, and hence the number of entanglements is proportional, to the volume fraction of the polymer.

In our efforts to explain the improved effective drawability of solution spun or cast high molecular weight polyethylene, we then argued that upon quenching of the polymer solution, the macromolecular network having a relatively low entanglement density was, at least partially, fixed by the formation of a polymeric gel. It was suggested that removal of solvent from the gel did not change this favorable intermolecular topology essentially.

It follows from the arguments presented that the initial polymer volume fraction should influence the drawability of solution cast or spun high-molecular-weight polyethylene markedly, and in a systematic manner. The aim of the present study was to examine the relation between the maximum draw ratio and the initial polymer concentration.

#### **EXPERIMENTAL**

High-molecular-weight polyethylene Hostalen GUR with  $\overline{M}_n=2\times 10^5$  and  $\overline{M}_w=1.5\times 10^6$  was used. The polymer was stabilized with 0.5% w/w of the antioxidant di-t-butyl-p-cresol. The solvent was decalin (decahydronaphthalene) from J. T. Baker Chemicals.

Films of the more concentrated solutions (exceeding 2% v/v of the polymer) were prepared by heating well-blended polyethylene–solvent mixtures at 160°C for 45 min, and subsequent compression molding at the same temperature. Less concentrated solutions were also prepared at 160°C, and then cast to form a film. In both methods the homogenized polymer solutions were solidified by quenching to room temperature, upon which gel films were generated.<sup>9</sup> The solvent was allowed to evaporate at ambient conditions from the polyethylene gels.

Dumb-bell shaped specimens with a length of 20 mm and a width of 2 mm were cut from the dried films. The hot-drawing behavior of the various samples was studied in the way described previously, using an Instron tensile tester equipped with a temperature-programmed oven. The drawing experiments were performed at a constant cross-head speed of 100 mm/min, unless indicated otherwise.

The draw ratios were determined in the usual way by measuring the dis-

placement of ink marks placed 1 mm apart on the specimens prior to drawing.

Densities were measured employing the frequently used flotation method.

#### RESULTS

#### **Characteristics of Films**

Table I shows the characteristics of the various films of high molecular weight polyethylene. The initial polymer volume fraction in the solutions from which the films were prepared, was calculated assuming equal densities of polyethylene and decalin at the dissolution temperature ( $160^{\circ}$ C).

The manner of solvent removal from the solidified polyethylene solutions affected the apparent densities of the films. For example, extraction of decalin immediately after the films were quenched to room temperature occasionally resulted in an overall density of a dried film as low as 500 kg/m³ (calculated from the weight and the volume), owing to high porosity. The density of the polyethylene constituting the porous structure, however, was found to be in the range 930–970 kg/m³. Compression at room temperature of the highly porous material produced a semitransparent film with an overall density equal to the density of the polymer, within experimental error. If the solvent was allowed to evaporate from the cast or compression-molded films, as in the present study, the apparent density was quite in accord with that of the polyethylene. It was established quantitatively that the method of solvent removal, as well as compression of the porous films, did not affect the hot-drawing behavior.

## **Influence of Initial Polymer Concentration**

Casting of the 0.1% v/v polyethylene solution did not result in the formation of a coherent gel, but rather loose agglomerates of single crystals were generated. This observation can readily be explained by the fact that the polymer concentration of 0.1% v/v only slightly exceeds that for onset of coil overlap, which is roughly given by  $[\eta]c \approx 1$ . Here  $[\eta]$  is the intrinsic viscosity of the polymer, and c is the polymer concentration in g/dl. This critical concentration for the present polyethylene sample, having an intrinsic viscosity of 14.5 dl/g, is approximately 0.07% v/v. Macroscopic gels may be generated from such dilute solutions by, e.g., mechanical  $^{12,13}$  or ultrasonic  $^{14}$  agitation, but these modes of gel formation

TABLE I Characteristics of Polyethylene Films

Initial polyethylene volume fraction, $\phi$	Thickness (mm)	Density (kg/m <sup>3</sup> )
1.00	0.16	936
0.14	0.12	950
0.10	0.15	953
0.08	0.16	948
0.02	0.11	945
0.01	0.15	955
0.005	0.06	970
0.001	•••	

do not fall within the scope of this study. By drying of the quenched 0.1% v/v polyethylene solution, a brittle film was obtained, much like a mat of single crystals. Although this film could be hot drawn by hand, as was reported for single-crystal mats,  $^{15-17}$  it was not particularly suitable for machine drawing, and the film was therefore excluded from the present study.

Quenching of all other polyethylene solutions resulted in the formation of homogeneous, coherent polyethylene gel films. Nominal stress—strain curves recorded at 120°C at a cross-head speed of 100 mm/min for the various dried gel films are presented in Figure 1. These curves virtually reflect the hot-drawing process. It is seen in Figure 1 that the initial polyethylene concentration had a marked influence on the drawing behavior, indeed. The rate of strain hardening (i.e., the slope of the stress—strain curve) rapidly decreased with decreasing concentration. In fact, at polyethylene volume fractions below 0.01 this slope was negative, which, of course, gave rise to an unstable deformation process (curve G). In this case each local fluctuation in strain leads to catastrophic failure of the specimen.

It is interesting to note that drawing of the film cast from the 1% v/v solution required a nearly constant nominal stress. A similar stress–strain curve was reported earlier for hot drawing of single-crystal mats<sup>16</sup> and of the optimal melt-crystallized sample of lower-molecular-weight polyethylene that allowed large deformations.<sup>18</sup>

Figure 1 shows that the  $\epsilon_b$  strain at break at 120°C, and accordingly, the maximum draw ratio ( $\lambda_{max} = \epsilon_b + 1$ ), strongly increased with decreasing initial polyethylene concentration. In Figure 2,  $\lambda_{max}$  is plotted against  $\phi$ . For the sake of clarity, the latter quantity is plotted on a logarithmic scale in this graph, and even on this scale a severe upswing of the maximum draw ratio at low initial polymer volume fractions is exhibited.

At a given polyethylene concentration the "maximum" draw ratio depends, of course, on the drawing temperature, 8,19 cross-head speed, 9 and, most likely,

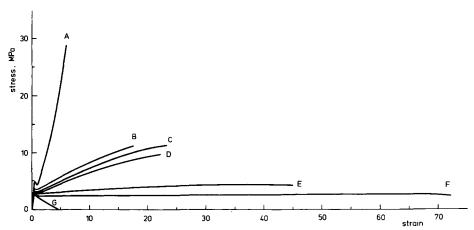


Fig. 1. Nominal stress/strain curves recorded at 120°C and at 100 mm/min cross-head speed for various films of high-molecular-weight polyethylene ( $\overline{M}_w = 1.5 \times 10^6$ ). Initial polymer volume fraction (for explanation, see text): (A) 1.00; (B) 0.14; (C) 0.10; (D) 0.08; (E) 0.02; (F) 0.01; (G) 0.005.

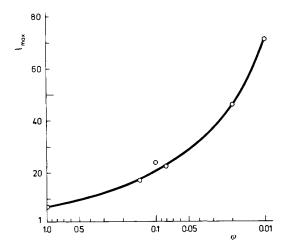


Fig. 2. Maximum draw ratio vs. initial polyethylene volume fraction.

on the gelation conditions of the films (see the Discussion section). In the present study the latter variable was eliminated as much as possible by maintaining a standard solidification procedure.

## Influence of Cross-Head Speed

In preliminary experiments it was found that the drawing stress depended markedly on the cross-head speed, which is typical for plastic deformation.<sup>20</sup> The strain at break, and therefore the maximum draw ratio, decreased only slightly with increasing cross-head speed.

It should be noted that our drawing experiments were performed at constant cross-head speed S, as is customary, rather than at a constant strain rate, which from a deformation kinetics point of view would be more appropriate. Accordingly, our specimen length L varied with time t as

$$L = L_0 + St \tag{2}$$

where  $L_0$  is the initial length. Denoting the true strain  $\ln \lambda$  by  $\gamma$ , the strain rate  $\dot{\gamma}$  is given by

$$\dot{\gamma} = S/L = S/L_0 \lambda \tag{3}$$

Equation (3) shows that  $\dot{\gamma}$  varies linearly with  $\lambda^{-1}$ .

It follows from this relation and the results presented in Figure 2 that the strain rate at fracture was lower by a factor of about 10 for the film cast from the 1% v/v polyethylene solution than for the melt-crystallized sample. Increasing the cross-head speed S by a factor of 10, which caused an increase of the strain rate by one decade, only reduced  $\lambda_{\rm max}$  by less than 10%, which is within the overall experimental error. Therefore, it seems justified to compare values of  $\lambda_{\rm max}$  for the various films, despite the fact that these results were obtained at different strain rates.

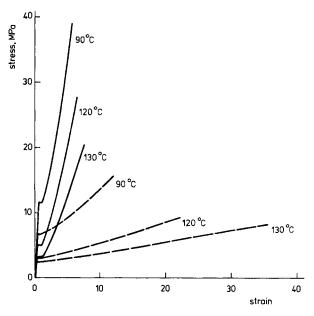


Fig. 3. Nominal stress/strain curves recorded at the indicated temperatures for melt-crystallized high-molecular-weight polyethylene (---) and for the identical polymer sample "gelled" from an 8% v/v solution in decalin and subsequently freed from solvent (---).

## **Influence of Drawing Temperature**

The influence of temperature on the deformation behavior of polymers is known to be significant. It is therefore pertinent to include the drawing temperature as a variable in this study. At temperatures below 70°C none of the samples could be drawn to a draw ratio exceeding 6.

Typical stress-strain curves for the melt-crystallized film and for the film obtained from the 8% v/v solution, recorded at 90, 120, and 130°C (where drawing of this polyethylene sample was shown to be effective),8 are presented in Figure 3. As is known, 19 a marked increase of the elongation at break, and hence of the maximum draw ratio, is seen with increasing drawing temperature. The drawing stress, by contrast, was found to decrease at higher temperatures.

The maximum draw ratios calculated from the stress/strain curves for the various films are given in Table II.

TABLE II Maximum Draw Ratio of Polyethylene Films

Initial polyethylene	Maximum draw ratio, $\lambda_{max}$		
volume fraction, $\phi$	90°C	120°C	130°C
1.00	5.5	6.9	9.4
0.14	12	17	28
0.10	14	24	32
0.08	13	23	36
0.02	27	46	62
0.01	36	72	a

<sup>&</sup>lt;sup>a</sup> Unstable draw. Films of polyethylene with  $\overline{M}_w = 3.5 \times 10^6$ , cast from a 1% v/v solution, could be drawn to  $\lambda_{\text{max}} = 110$  at 130°C.

#### **DISCUSSION**

## Influence of Initial Polymer Volume Fraction

The results presented here indicate a strong correlation between the maximum draw ratio  $\lambda_{max}$  of high-molecular-weight polyethylene obtained from solution, and the initial polymer volume fraction  $\phi$ . In this discussion an attempt will be made to put the relation between  $\lambda_{max}$  and  $\phi$  on a semiquantitative basis.

The deformation behavior of semicrystalline polymers usually is discussed in terms of the deformation of a three-dimensional network with entanglements and crystallites acting as physical crosslinks (cf. ref. 4). At first we will focus solely on the role of the entanglements, and deliberately ignore the contribution of the crystallites. This may seem rather premature, or even doubtful; but various arguments and experimental facts will be presented later to support this approach. Moreover, we assume that the major portion of the entanglements was trapped in the solidification process, and act as permanent crosslinks on the time scale of the drawing experiment. These assumptions will also be discussed below.

According to the classical theories of rubber elasticity,<sup>21</sup> the maximum draw ratio of a permanent network varies with the number  $N_c$  of statistical chain segments between crosslinks as

$$\lambda_{\text{max}} = (N_c)^{1/2} \tag{4}$$

The assumption that the majority of the entanglements trapped in the polymeric solid will act as permanent crosslinks gives

$$N_c \approx N_e$$
 (5)

Here  $N_e$  is the number of statistical chain segments between entanglements, which equals  $M_e/m_s$ ,  $m_s$  being the molecular weight of a statistical chain segment, which for polyethylene has a value of about  $140.2^2$  Substitution of eq. (5) in eq. (4) and introduction of the concentration dependence of  $M_e$ , given by eq. (1), finally yields

$$\lambda_{\text{max}} = (N_e/\phi)^{1/2} \tag{6}$$

or

$$\lambda_{\max} = \lambda_{\max}^1 \, \phi^{-1/2} \tag{7}$$

Here  $\lambda_{\max}^1$  is  $\lambda_{\max}$  at  $\phi = 1$ , and equals  $(N_e)^{1/2}$ .

The molecular weight between entanglements in a polyethylene melt is stated to be about 1900.<sup>23</sup> Thus, the number of statistical chain segments  $N_e$  between entanglements is 13.6, which leads to  $\lambda_{\text{max}}^1 = 3.7$ .

In Figure 4 the maximum draw ratios obtained at 90, 120, and 130°C for the various films of high-molecular-weight polyethylene are plotted against the square root of the inverse polymer volume fraction, i.e.,  $\lambda_{\rm max}$  vs.  $\phi^{-1/2}$ . It is seen in Figure 4 that the linear interdependence of these two quantities, as suggested by relation (6), holds surprisingly well at all drawing temperatures. The slopes of the curves in Figure 4, which equal  $\lambda_{\rm max}^1$ , are listed in Table III. The calculated value of  $\lambda_{\rm max}^1$  of 3.7 is in excellent accord with the experimental value of 3.8, found in drawing at 90°C (see Table III). The positive temperature dependence of  $\lambda_{\rm max}^1$  will be discussed in a succeeding paragraph. In fact, the calculated value

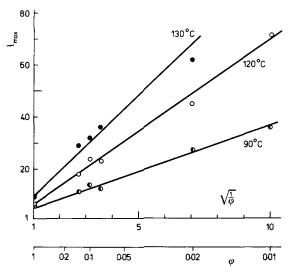


Fig. 4. Maximum draw ratio vs. (initial polymer volume fraction) $^{-1/2}$  at the indicated temperatures.

of 3.7 will be looked upon as a lower bound, which will be approached if all restrictive assumptions are met.

## **Entanglement Trapping**

One of the primary assumptions made in the previous subsection was that all entanglements were trapped during the solidification procedure. Therefore, some consideration should first be given to the influence of the solidification conditions on entanglement trapping. Although the topic of disentangling through crystallization by "reeling in" is still a matter of controversy,<sup>24</sup> it now seems well established that under favorable solidification conditions this phenomenon definitely occurs. Slow cooling, low molecular weight of the polymer sample, and crystallization from dilute solution are known to promote reeling in, ultimately yielding perfect single crystals. In particular, specimens produced under these conditions contain highly disentangled molecules, and one may expect that these samples will exhibit excellent drawability. Indeed, polyethylene single crystals have been drawn to very high draw ratios.<sup>2,15–17</sup> The problems encountered in drawing mats of single crystals may be explained by the large number of grain boundaries and cracks, rather than entanglements, causing fracture upon drawing of these macroscopic structures.

In the present study all films were solidified by rapid quenching to room

TABLE III Values of Slopes in Figure 4 [ $\lambda_{max}^{1}$  in eq. (7)]

	$\lambda_{ ext{max}}^1$
Calculated	3.7
Experimental at 90°C	3.8
Experimental at 120°C	7.2
Experimental at 130°C	9.7

temperature, in order to eliminate as much as possible the reeling-in effect mentioned above, and to reveal solely the influence of the initial polyethylene volume fraction. In view of the high molecular weight of the polymer sample used and the solidification method applied, it seems that we indeed may exclude disentangling through reeling in of the solution-cast (or "gelled") films. The observed linear interdependence of  $\lambda_{\rm max}$  and  $\phi^{-1/2}$  supports this remark, since any reeling in would cause a positive departure from this relationship.

#### Chain Slippage

At this point we will discuss the assumption that the majority of the entanglements trapped in the polymeric solids act as permanent crosslinks. First we will use an indirect demonstration. If disentanglement through chain slippage, and subsequent formation of new entanglements, were the predominant feature in the drawing process, as in the deformation of a polymer melt, drawing would not cause the significant chain orientation and enhancement of the mechanical properties evidenced by many experiments. Moreover, chain slippage would occur to a much larger extent in low than in high-molecular-weight polyethylene. As a matter of fact, the effectiveness of drawing in polyethylene, which is usually indicated by the slope of the Young's modulus/draw ratio curve, depends only moderately on the molecular weight of the polymer sample below a certain temperature. This is reflected by the "universal" modulus/draw ratio curve at a drawing temperature of 75°C for various lower-molecular-weight polyethylenes,<sup>4</sup> and, for example, our results obtained with a very high molecular weight specimen at various temperatures.<sup>6,8</sup> In view of these observations, it does not seem likely that disentanglement through chain slippage primarily governs the maximum draw ratio on the time scale of our drawing experiments. Finally, the very close agreement between the experimental value of  $\lambda_{max}^1$  of 3.8 (at 90°C) and the calculated one of 3.7, assuming no slippage of entanglements, points to the same conclusion.

This may be true for very high-molecular-weight materials and at relatively low drawing temperatures (well below the melting point); but at more elevated temperatures the chance of slippage increases owing to higher chain mobility. This effect, however, is merely reflected in an increase in the value of  $\lambda_{\rm max}^1$  (see Table III), rather than in departure from the linear relationship between  $\lambda_{\rm max}$  and  $\phi^{-1/2}$ , which is of prime interest here.

## Influence of Crystallites

A major objection that can be made to the approach presented here is that the role of the crystallites in the polymeric solid has been ignored in the description of the drawing behavior. It should be noted that our drawing experiments could be performed successfully only at temperatures exceeding ca. 70°C. In fact, at lower temperatures we observed no marked influence, or sometimes a negative effect, of the initial polymer volume fraction on  $\lambda_{\text{max}}$ . This minimum temperature of about 70°C is found on the upper flank of the so-called  $\alpha_c$  dispersion, e.g., in dynamic mechanical measurements at low frequency. This  $\alpha_c$ -relaxation range is commonly attributed to movement of polyethylene chains through the crystalline lattice,  $^{25}$  which allows of large deformations. In fact, ultradrawing

of polyethylene can be carried out primarily near or above this  $\alpha_c$ -relaxation range. Also in drawing polyethylene single crystals a minimum temperature of about 80°C was observed, above which the crystals became pliable. From this fact, taken together with the experimental observation that in ultradrawn samples virtually no trace of the crystallites initially present could be found, it seems quite doubtful that the polymer crystals act as rigid bodies or permanent junctions in the deformation process in the temperature range of interest. Rather, they yield and contribute to a very high viscosity of the material, and thus affect the relaxation times of the macromolecules. In this way the crystallites may influence the stability or semipermanent nature of the trapped entanglements.

Of course, at temperatures well below the  $\alpha_c$ -relaxation range, and at low strain, the contribution of the crystals is significant, and in a network description of the drawing process they should be taken into account, as was recently demonstrated by Kilian.<sup>26</sup>

#### **General Picture**

The trapped entanglement approach presented so far may be illustrated graphically by Figure 5. Here we depict schematically the influence of the variables, such as molecular weight, entanglement slippage, solidification conditions, and initial polymer concentration, on the drawability of polyethylene at temperatures well below the melting point, but exceeding ca. 70°C.

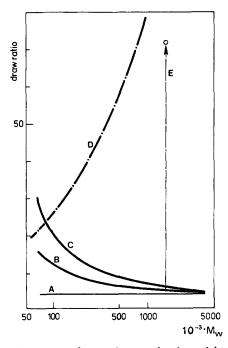


Fig. 5. Schematic plot of maximum draw ratio vs. molecular weight of polyethylene. (A)  $\lambda_{\rm max} = (N_e)^{1/2} = 3.7$ ; all entanglements trapped; no slippage. (B) All entanglements trapped; slippage predominantly near chain ends. (C) Partial disentanglement upon solidification. (D)  $\lambda_{\rm max} \propto M^{0.5}$  for isolated chain. (E) Partial disentanglement through crystallization from solution.

For melt-crystallized samples in which all entanglements existing in the liquid phase are trapped in the solid by fast quenching, the maximum draw ratio should be independent of the molecular weight (since  $M_e$  does not depend on molecular weight), if no entanglement slippage occurs (curve A), and should be 3.7.

Slippage of chain ends through trapped entanglements of melt-quenched samples is reflected in curve B. This effect will be more important at low molecular weights.

Disentanglement through reeling in may occur at lower solidification rates, and this phenomenon is progressively favored at lower molecular weights. Consequently, the maximum draw ratio of slowly cooled samples will increase at low molecular weights (curve C), provided that a certain minimum molecular weight is exceeded.<sup>5</sup>

Naturally the respective curves in Figure 5 depend markedly on the drawing temperature, but this effect will not be dealt with here.

Curves B and C illustrate the general tendency for  $\lambda_{max}$  to decrease with increasing molecular weight, which, in fact, is well documented in the literature (cf. ref. 4). This is, of course, completely in contrast with expectations based on the maximum (and ultimate effective) draw ratio of a single chain. Obviously,  $\lambda_{max}$  for an isolated chain will vary roughly with the molecular weight as

$$\lambda_{\text{max}} \propto M^{0.5} \tag{8}$$

as schematically represented by curve D in Figure 5. From this severe discrepancy between the molecular weight dependence of  $\lambda_{max}$  of a single chain and the experimentally observed relation we must once more conclude that the structure of the polymeric solid state primarily determines the drawability, a point which has previously been emphasized by Capaccio and Ward<sup>1</sup> and Barham and Keller,<sup>2</sup> among others.

Disentanglement through crystallization from solution, finally, causes a profound increase of  $\lambda_{max}$ , proportional to  $\phi^{-1/2}$ , as is shown in this study for quenched solutions of high-molecular-weight polyethylene (curve E). If lower rates of solidification were employed, additional disentanglement through reeling in would have occurred, resulting in a positive deviation from the linear relation eq. (7).

A final remark should be made about a correlation that was made previously by other authors between the maximum draw ratio of polyethylene structures, both of single crystals <sup>15</sup> and spherulitic material, <sup>27</sup> and the lamellar thickness l of the crystals constituting the polymer solid. It was suggested <sup>27</sup> that  $\lambda_{\text{max}}$  should vary with l as

$$\lambda_{\text{max}} \propto l/\delta$$
 (9)

where  $\delta$  is the separation between adjacent chains in the crystalline lattice. Preliminary small-angle x-ray and differential scanning calorimetric measurements on our melt-crystallized sample and the film cast from the 2% v/v solution showed that the lamellar thickness in these specimens was of the same order of magnitude. Hence eq. (9) can by no means account for the difference in  $\lambda_{\text{max}}$ , e.g., by a factor of ca. 7 at a drawing temperature of 120°C, observed for these two samples. We conclude therefore that the lamellar thickness of polyethylene crystals is not the factor that governs the maximum draw ratio of macroscopic structures of polyethylene, although it may apply to single crystals.

Summarizing this discussion, we arrive at the conclusion that the number of entanglements trapped in solid polyethylene is one of the dominant features influencing draw at temperatures exceeding about 70°C. It should be noted that the significance of entanglements in extension of polyethylene was stressed previously by Porter et al.<sup>28</sup> in a study on extrusion of single crystals, and by Capaccio et al.<sup>4</sup> Despite the fact that the maximum draw ratio is an extremely difficult parameter to tackle—it depends on molecular weight, drawing conditions, solidification procedure, and moreover, fracture, which determines  $\lambda_{\text{max}}$ , is a statistical, time-dependent phenomenon—the number of trapped entanglements seems to underlie the ultimate effect of these variables.

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