Macromolecules **1996,** *29,* 5326−5331

A Latent Entanglement Model: Effects of Irregularities of the Crystallite Surface on Polymer Draw

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Received November 6, 1995; Revised Manuscript Received May 1, 1996⊗

ABSTRACT: In a previous study on the drawing of polyethylene nascent reactor powders, the maximum achievable uniaxial draw ratio, DR, was found to be strongly dependent on prior synthesis conditions. Samples synthesized at 85 °C by a slurry process had the highest ductility. Synthesis at lower temperatures (60 and 30 °C) led to samples of lower DR. The highest achievable ductility is believed to correspond to the lowest entanglement density, but simple models suggest that lower synthesis temperatures should produce fewer entanglements. However, low crystallization temperatures lead to irregular fold surfaces, and these irregularities or defects can convert into entanglements when folded chain segments are drawn out of the crystals into more extended conformations. We have called these defects "latent entanglements". This concept can explain experimental data on the structure and drawability of certain classes of nascent reactor powders and can prove helpful to the goal of tailoring ductility by control of synthesis.

Introduction

The concept of entanglement[1,2] is involved in several molecular models used to interpret chain dynamics and the drawing behavior of polymers. Macromolecules in the noncrystalline state are assumed to form a transient network, with entanglements acting as friction centers or temporary junctions.[3−5] The macroscopic draw of high polymers is influenced by the extension of this entangled network. According to this hypothesis, draw provides extension and parallel alignment of the polymer chains. In these conditions, the macroscopic tensile deformation of the fiber is mostly transferred, at the molecular level, to the deformation of stiff covalent bonds and bond angles along the chain backbone. Thus, the elastic modulus of the fiber can be increased to values approaching the theoretical limit for such deformations.[6]

Entanglements therefore constitute a major obstacle for the achievement of a high extension and a uniform chain alignment. Thus, several efforts have been directed to the development of methods capable of removing entanglement constraints of networks. Solvent addition can increase chain mobility and favor disentanglement of chain segments in a system under draw.[7] As such, gel-spinning techniques are currently employed in the draw of high and ultrahigh molecular weight polyethylene (HMWPE). However, this method presents several inconveniences related to the long dissolution times required by high molecular weight polymers and to the additional stages for subsequent solvent removal after draw.

The solid-state draw of reactor powders provides an alternate and successful processing route. This is because nascent reactor powders may inherently have low degrees of entanglements, since crystallization of chain segments immediately after synthesis can reduce the chances for entanglement[3,8,9] and favor more extended chain conformations.[10] Draw of reactor powders below the melting point can preserve such a low nascent degree of entanglements,[11] leading to high degrees of extension and consequently to high values of the tensile moduli.

This study is part of a general effort to understand the dependence of the ductilities of reactor powders on the synthesis conditions. In the preceding papers,[12−18] HMWPE reactor powders synthesized in different conditions have been tested by different techniques to relate their mechanical, structural, and thermal properties to synthesis conditions. Results obtained by these methods have been discussed and correlated with both the ductility and synthesis parameters. These relationships have been interpreted on the basis of the molecular models for draw proposed by several authors.[19−26] The above-mentioned hypothesis, that draw is controlled by the degree of entanglement of the system, has been substantially confirmed.[18] Nonetheless, the important point concerning the relationship between synthesis conditions and the nascent degree of entanglements has not been completely clarified. Simple models have been proposed to describe the effects of changes in synthesis parameters upon the molecular mechanisms involved in entanglement formation.[27,28] However, conclusions from these models are in contrast with some experimental results.[12] In this study a novel molecular model, that of the latent entanglement, is presented to fill this gap. The model focuses on entanglements that are not in the amorphous phase but are latent in the crystal folds.[29] This approach seems able to provide a unified interpretation of the different aspects of the solid-state drawing of nascent reactor powders which were unresolved in preceding works.[16,18]

Experimental Section

HMWPE samples were synthesized by Union Carbide Corp., using Ziegler−Natta heterogeneous catalysis, by either a slurry or gas-phase process. Relevant data for the molecular, thermal, and structural characterization of the reactor powders have been published.[12−17] Samples have been classified by

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.

Table 1. Polyethylene Characterization

sample identification	$\bar{M}_v \times 10^{-6}$ [a]	cryst. in %, DSC[b]	α_b in %, Raman[c]	TDR (135 °C)[d]	tensile modulus [GPa]
Sl30-02.9	2.86	65.2	11	15	
Sl30-05.9	5.95	67.2		9	
Sl30-12.4	12.4	66.8	18	6	
Sl30-14.9	14.9	65.8		24	
Sl60-01.6	1.57	63.6		8	
Sl85-00.3	0.30	69.4		50	49
Sl85-00.9	0.93	70.2			
Sl85-01.0	0.96	67.8	10	90	62
Sl85-02.0	2.00	67.6		85	57
Sl85-04.8	4.80	67.8	5	98	75
Gp30-01.9	1.93	62.4	19	7	
Gp85-00.2	0.16	63.2		19	
Gp85-01.0	0.96	64.7	14	22	
Gp85-01.2	1.16	63.0		9	

[a] Molecular weight viscosity average. [b] Percent crystallinity computed by DSC enthalpies of melting. [c] Relative amount of the interfacial region (%). [d] Total draw ratio (TDR) is the extrusion draw ratio (EDR) multiplied by the final tensile draw ratio.

synthesis process type, synthesis temperature, T_{synth}, and molecular weight according to the following pattern:

SStt-mm.m

where SS is the synthesis type, tt the synthesis temperature, and mm.m the molecular weight. Thus Sl30-02.9 stands for a sample synthesized by a slurry process at 30 °C, having a molecular weight, $\bar{M}_v$, equal to 2.9×10^6. Percent crystallinities of nascent reactor powders were estimated by differential scanning calorimetry (DSC)[13] as the ratio of the enthalpies of melting, ΔH_m, to the enthalpy of fusion of pure crystalline PE, ΔH°_m (=69.2 cal/g[30]). Raman spectroscopy on nascent reactor powders provided relative estimates of the amounts of polymer chain segments in the crystalline and amorphous phases and in the interfacial region.[15] Such values of the relative interphase content, α_b, are reported in Table 1. Reactor powder ductilities have been evaluated by uniaxial solid-state draw.[12] Strips cut from compressed powder specimen plates were inserted between the halves of a cylindrical split billet of high-density polyethylene and coextruded through a bronze conical die of 20° entrance angle. The extruded fiber was then drawn in free space to the maximum achievable extension. Values of the maximum total draw ratio (TDR) were obtained as the product of the draw ratios in the two steps.

Results and Discussion

Data reported in Table 1 show that a defined relationship exists between synthesis conditions and ductility: for both synthesis processes, gas-phase or slurry, ductility increases as T_{synth} was increased from 30 to 85 °C. Moreover, samples synthesized by a slurry process at 85 °C display the highest TDR. In the present work attempts to account for such correlations have focused on the evaluation of structural parameters more directly related to the amount of trapped entanglements in the nascent systems. [The term "*trapped entanglement*" or "*nascent entanglement*" is used in the present work to indicate the strong interactions at the crossover points between different chain segments, stemming from the trapping of these disordered conformations in the intercrystalline regions during crystallization on synthesis (see Figure 1). This term is used in contrast to other types of entanglements which may develop as a consequence of drawing, such as those in crystal defects.]

On crystallization, large volume-demanding defects, like entanglements or knots, cannot be accommodated in the crystals. Entanglements should involve rather long chain segments removed from the crystalline portions (Figure 1). Thus, higher nascent crystallinities should correlate with lower degrees of entanglements and with higher drawabilities. This relation has been confirmed for samples synthesized between 30 and 95 °C,[16,31] but, as reported in Table 1, it proved highly sensitive to small changes in nascent percent crystallinity: changes of less than 1% led to a 10-fold increase in TDR.[16] Thus, a question arises on what are the actual changes in the number and structure of the entanglements, which correspond to such a small increase in nascent crystallinity and to the large increase in drawability.

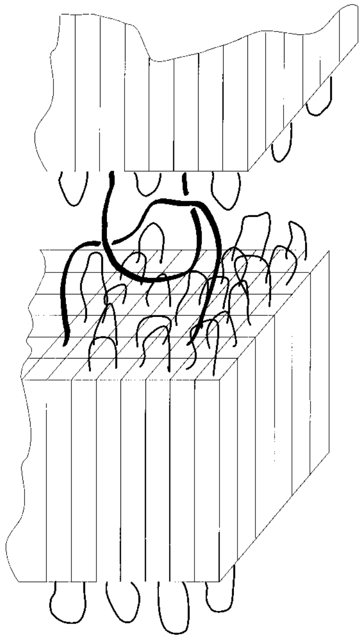

Figure 1. Trapped entanglement (thicker lines) in the intercrystalline region.

According to structural investigations on semicrystalline polymers,[32] the interphase represents a disordered anisotropic phase, located in a transition zone between crystalline and amorphous regions. Stretched chain segments related to entanglements are presumed to concentrate in the interphase.[32] Thus, its relative amount can provide an estimate of the degree of entanglements of the nascent reactor powders. Table 1 shows that drawability decreases as the relative amount of the interphase, α_b, is increased. However, small changes in α_b correspond to major changes of TDR.[15]

A simple and effective model has been proposed to correlate changes in synthesis conditions with different amounts of entanglements.[27,28] According to Wunderlich, supercooling enhances the crystallization rate and simultaneously reduces the polymerization rate.[27] Then, crystallization on synthesis at high undercooling leaves shorter times for the growing chain segments to hang loose before being absorbed on the crystal surface. Thus, the probability of entanglement formation is reduced. In contrast, at higher synthesis temperatures, polymerization and crystallization become practically independent processes. Effects of annealing and (for slurry synthesis) of partial solubilization of growing chain segments become more important. Polymer segments spend longer times in the molten state, and chances to form entanglements increase. Data on the synthesis of HMWPE confirm that the transition temperature between these two regimes lies in the interval 70−100 °C and that <70 °C higher nascent

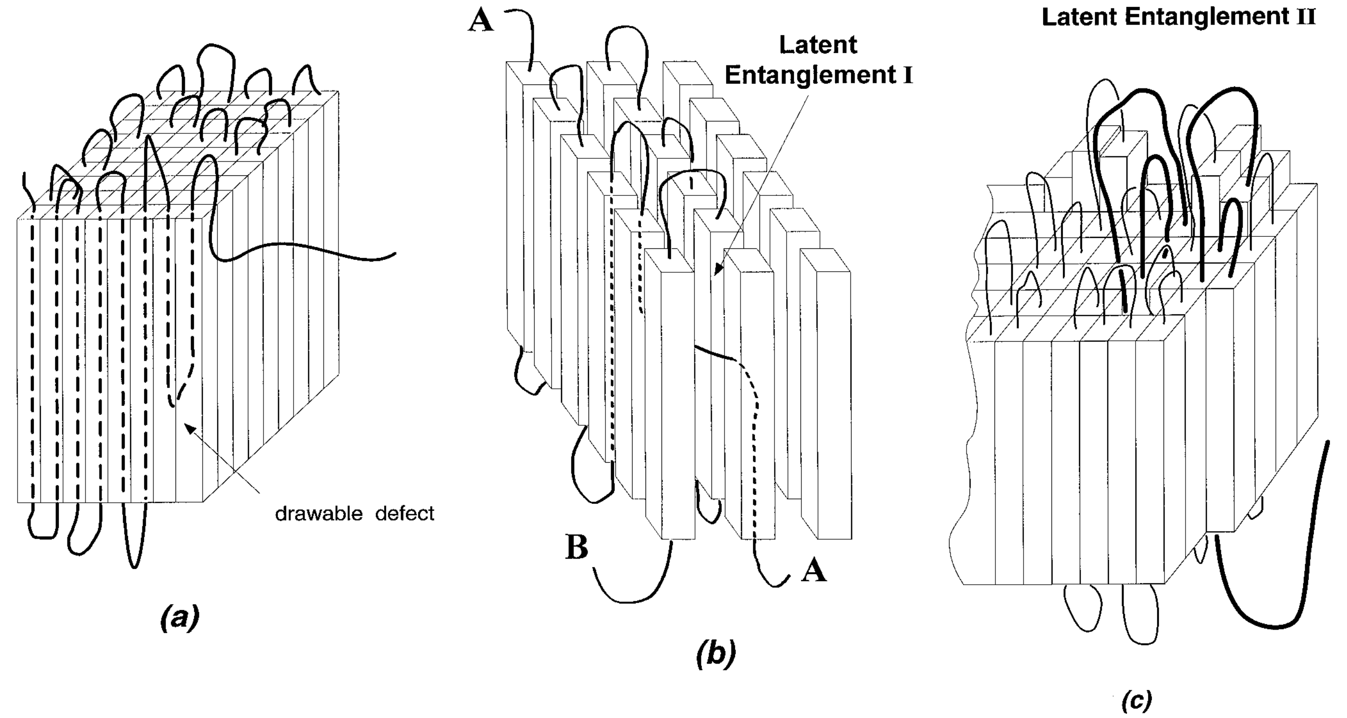

Figure 2. (a) Noncritical, drawable defect. (b) Possible arrangement of a latent entanglement inside the crystal. On unfolding chain A, the line defects in the first two crystal layers can develop an entanglement with chain B. (c) Possible arrangement of a latent entanglement (thick line) in the fold surface. Pulling this chain out of the crystal surface develops an entanglement.

crystallinities are usually obtained.[28] Thus, according to this model, samples synthesized below this temperature should have lower degrees of nascent entanglements. Experimental confirmations for this model have been reported,[28] in particular with samples synthesized <0 °C.[10,31] In contrast, samples investigated in this work display the opposite trend: as reported in Table 1, ductility increases as T_{synth} is increased from 30 to 85 °C.

Attempts to explain these discrepancies have led to the hypothesis that, for the set of synthesis conditions investigated in this work, reactor powder ductility is not uniquely controlled by the amount of entanglements trapped in the intercrystalline regions. Likely, other types of nascent chain arrangements will also influence drawability.

1. Latent Entanglement Model: Effects of Crystallite Structure on Drawability. This work focuses on evaluating the relationships between ductility and defects in the core and in the fold surface of nascent crystallites (in this context the term "defect", when referred to the fold surface, indicates a chain arrangement different from adjacent reentry). Crystallite defective boundaries, where permanent noncrystallizable defects (entangled fold-loop) are anchored, have been recognized as a major controlling factor for the plastic deformation of semicrystalline polymers.[33,34] However, in this work, the concept of defective boundaries has been extended to defects in the fold surface produced by crystallization. It has been proposed that the maximum draw ratio in HMWPE is achieved when the unfolding of all clusters of adjacent reentered stems is completed.[35] Thus particular attention has been devoted to defects arising from nonadjacent reentry. These defects can be regarded as the potential loci of entanglements; *viz.*, they will convert into entanglements when the involved chain segments are drawn out of the crystals into more extended conformations. Referring to the drawing process, defects may be classified into three categories:

(i) Noncritical or Drawable Defects. Folds which do not reach out to the fold surface of the crystalline lamellae are examples of this defect. They do not hinder unfolding and chain extension (see Figure 2a).

(ii) Latent or Draw-Induced Entanglements. This type of defect stems from the crossing of two chain segments, such as in the Flory switchboard model. Defects of this kind are rather localized and do not necessarily imply high disorder. They may also be hosted inside the crystallites, resulting in crystallographic line defects. As reported in Figure 2b, unfolding chain A leads to an intersection with chain B which can develop an entanglement. Chain crossing may more frequently be in disordered fold surfaces of crystal lamellae. If the reentry positions of two close but independent chain segments are such that the folds intersect, like in the "leapfrog model",[36] a latent entanglement is produced (see the thicker lines in Figure 2c). On drawing, when the chain with the lower fold is pulled out of the crystal, it will pull out also the upper fold. Interactions between the two chain segments give rise to an actual entanglement.

(iii) Fully Developed Entanglements (the Thicker Lines in Figure 1). They can be considered a kind of dead-end limit for draw. Chain slippage may be so hindered that fibers may break even at low draw ratios. Unfolding chains beyond these defects would be practically impossible, since they can have the strength of a chemical bond. Defects of this kind will be preferentially located in noncrystalline regions (trapped entanglements).

Considering how these types of defects, reported in Figures 1 and 2a–c, can affect sample ductility, one must observe that these arrangements involve different numbers of chain segments. Defects of type i (Figure 2a) can be considered single-segment defects, because only one chain segment at a time must be unfolded and pulled out of the crystal for draw to proceed. Similarly, the defect in Figure 2b, type ii, is a dual-segment defect since, on unfolding chain A beyond the crossing point with chain B, two segments at a time must be pulled out of the crystal. The defect in Figure 2c, type ii, is a multiple-segment defect since at least three or more segments (perhaps even a whole crystalline block) are simultaneously involved in the unfolding. Finally, the entanglement (iii) in Figure 1 can be resolved only by unfolding a large number of chain segments, from two different crystallites. Thus, drawing difficulties must increase on passing from defects of type i to ii and then to type iii, because more cooperative and simultaneous motions of different chain segments are required to unfold the corresponding defect.

The correlation among crystallinity, interphase amount, and drawability may now be better understood. Structures like that reported in Figure 2c can be considered defects in the fold surface. Their effect should be mostly related to some displacement of close chain segments from their crystallographic position, which should likely not extend deeply into the crystallite core. The other type of latent entanglement in Figure 2b is just a combination of two crystallographic line defects, which can be accommodated without great losses of crystal coherency. Thus, both types of latent entanglements are associated with rather small degrees of crystallographic disorder. One can conclude that higher amounts of latent entanglements can reside in the samples of lower ductility with only a small decrease of the nascent crystallinity. Similarly, the interphase thickness should not be strongly affected by increases in latent entanglements. Most of the fold surface defects are localized, involving close reentry positions. The amounts of loose loops, which can provide more significant increases in the interphase thickness, are not prominent,[36,37] so that the energetic stability of the crystallite fold surface can be preserved.

Different amounts of latent entanglements should lead to significant differences in the structure of drawn samples. In fact, as chains are extracted from the crystals, structures of the type reported in Figure 2c will progressively strain the surrounding chain segments. Moreover, a latent entanglement, hindering the stepwise unfolding of the surrounding segments, can force the extraction of a whole crystalline block. This same latent entanglement will then become a new tie between two different crystalline blocks. It can be concluded that more latent entanglements will increase both the stress on the interphase and the number of taut tie molecules in drawn samples.[18]

2. Formation of Latent Entanglements: Effects of Synthesis Conditions on the Crystallization Dynamics. The latent entanglement concept and the molecular models in Figure 2b,c can provide the additional relationships required to fill the gap between data and theories concerning both the draw process and the crystallization dynamics on synthesis. Hoffman's variable cluster model of chain folding[37] specifically accounts for a significant increase in the type of chain arrangements reported in Figure 2b,c as crystallization temperature is reduced, approaching this range of his regime II and regime III dynamics. In fact, irregularities in the folding direction are increased by crystallization in regime II.[37] This may also lead to increases in defects reported in Figure 2b.

The way crystallization in regime III affects reactor powder ductilities may be understood by recalling that this regime is characterized by fast absorption of chain segments on the crystal surface. In these conditions the growth surface becomes irregular with clusters of absorbed chain stems. The probability of nonadjacent chain reentry is higher,[37] and situations like the sketch in Figure 2c are more frequent. In its simplest form, this kind of chain arrangement, leading to a latent entanglement, can be described, in Hoffman's formalism, as the combination of a "tight fold" plus a "next near fold".[38] Moreover, the known direct relationship between tortuosity of chain loops and entanglement density[39,40] suggests that the number of trapped entanglements (Figure 1) can also increase, if the disorder of the fold surface is increased. Such chain arrangements are reported for some models for polymer crystals (viz., the fringed-micelle and the switchboard models), which are compatible with significant numbers of loose loops. Disorder in the crystallite fold surfaces actually increases as the crystallization temperature is lowered, forcing the system toward regime III,[37] yet, according to the "gambler's ruin" statistical model, it cannot pass a critical limit to avoid destruction of the crystalline lamella.[41] Thus, synthesis at low temperatures may lead to crystallization in regime II or III: the number of nascent entanglements is kept low,[27,28,31] but latent entanglements are increased and may well become the controlling factor for sample ductility.

Crystallization in Hoffman's regimes II and III agrees with several features of the mentioned Wunderlich's crystallization–polymerization model.[27] As confirmed by experiments on melt-crystallized PE[42,43] at high undercoolings the growth rate of chain-folded crystallites is no longer compatible with the reeling-in of chain segments from the melt. Reeling-in must be replaced by a different reptation process to account for the observed significant changes in the diffusion rate of chain segments with temperature. In Hoffman's words, "Regime II → Regime III transition ... represents the temperature where steady-state reptation just begins to be replaced by reptation of slack".[37] The same mechanism seems also valid for crystallization on synthesis at low temperatures. Especially for samples synthesized at 30 °C, reptation of slack must dominate the chain dynamics to allow the crystallizing system to keep pace with the polymerization process. Moreover, it can be suggested that the uncoupling of the crystallization and polymerization processes, which has been observed in the interval 70–100 °C,[28] may correspond to the transition from regime III to regime II as T_{synth} is increased from 30 to 85 °C.

A case must be mentioned where latent entanglements do not seem to control ductility. Experiments on reactor powders synthesized between −7 and −40 °C[10,31] show that (a) chain-extended crystals can actually be obtained directly on synthesis and that (b) lower synthesis temperatures correspond to higher ductilities. These results have been explained by the close packing of catalyst particles on the support, which can lead to the lateral impingement of growing polymeric globules.[44] Extensive transcrystallization can result in chain-extended crystals and highly compacted polymer globules, which prevent further diffusion of monomer to the active catalyst site. Both synthesis and crystallization can be slowed and the amount of latent entanglements can be significantly reduced. Thus, synthesis between −7 and −40 °C provides correlations with sample ductilities which agree with Wunderlich's model for crystallization on synthesis at low temperatures.

Another question which can limit the general validity of the latent entanglement model arises from the temperature limit for the transition from regime II to regime III, T_{II-III}, in the crystallization of PE from the melt. Literature results[37,42] place this transition between 119 and 123 °C, a value which is much higher than the present synthesis temperatures range, 30−85 °C. Moreover, the fact that molecular weight is changing during crystallization on synthesis does not account for a large displacement of T_{II-III}. Fatou *et al.*[42] showed that the T_{II-III} of PE increases from 119 to 120.5 °C, viz., only by 1.5 °C, when $\bar{M}_w$ is increased from 10^4 to 10^6. Possible explanations for the depression of the T_{II-III} transition point are based on mass- and heat-transfer effects. First the *n*-paraffin used to obtain the monomeric solution in the slurry process can partially desolve the growing chain segments, as long as their molecular weights do not exceed the solubility limit. The dynamics of the crystallization of PE remain substantially the same for both melt and solution crystallization,[45] yet transition temperatures in solutions are systematically lower than those in melt crystallization. Thus, depression of the T_{II-III} transition in the slurry process can be explained by the partial involvement of the solvent into the crystallization process. A second reason for the T_{II-III} depression can be found in the exothermicity of the synthesis reaction. Polymer particles surrounding the active catalyst sites can give rise to thermal insulation. Heat transfer is likely insufficient to dissipate the heat of polymerization.[13] In this case the T_{II-III} shift to lower temperatures would only be apparent, stemming from an incorrect estimate of the crystallization temperature. The actual crystallization temperature of an as-synthesized polymer segment would be higher than the temperature of the synthesis bath. According to this hypothesis, T_{II-III} may be closer to the value obtained in melt crystallization.

Conclusions

Trapped entanglements, that is “entanglements existing in the liquid phase, ... trapped in the solid by fast quenching”,[5] are currently considered to be the limiting factor for PE drawability,[3,10] since they can hinder the unfolding and the alignment of chain segments in the crystallites under draw. Wunderlich’s model of crystallization on synthesis relates the amount of trapped entanglements to the synthesis temperature. For low T_{synth} the model provides the correct relationships with ductilities of reactor powders.[10,31] However, previous results obtained on the samples in Table 1[13−16] showed that the entanglements trapped in the fold surface do not completely explain the large differences in sample ductilities and their dependence on T_{synth}. Small changes in the nascent parameters, which seem more directly related to trapped entanglements, such as crystallinity and interphase content, are associated with large changes in drawability. These results suggest that, in addition to trapped entanglements, other chain arrangements may further reduce ductilities.

Attention was then focused on the crystalline component of the reactor powders. Both theoretical models for draw[19−24] and experimental results[33−35] lead to the conclusion that the process of extracting polymeric segments from the nascent chain-folded crystallites controls the transformation of the nascent morphologies into the final chain-extended crystals.[25,26] Defects in the crystallite core and in the crystal fold surface, like those reported in Figure 2b,c, can be regarded as sources of potential or latent entanglements. At the beginning of the drawing process their effect is likely negligible, but, as soon as crystallite unfolding is started, such crossings of chain segments can give rise to an actual gridlock at the crystal fold surfaces. Thus, at higher draw ratios, these defects transform into active entanglements, reducing sample ductility, hence, the definition of latent entanglements given to these types of chain rearrangements on draw.

The latent entanglement concept provides also an explanation of the experimental relationship between synthesis conditions and drawability. According to Hoffman’s model,[37] crystallization at high undercoolings increases fold-surface irregularities. Assuming that the decrease of synthesis temperature from 85 to 30 °C moves crystallization conditions toward regime II and III, the corresponding increase of the number of latent entanglements (Figure 2b,c) may explain the decrease of powder ductilities reported in Table 1. Such a correlation seems able to provide a common explanation for the experimental trends obtained for TDRs, nascent crystallinities, and interphase content of the reactor powders and the corresponding coextruded fibers.[16,18]

Wunderlich’s principles of crystallization on synthesis provide the correct relationship between synthesis conditions and drawability as long as trapped entanglements control crystallite unfolding. Accordingly, low numbers of trapped entanglements and regular fold surfaces are both required to increase ductility. Several kinds of polymeric systems can approach these conditions. However, crystallization from dilute solutions, slightly below the equilibrium dissolution temperature, provides the best experimental conditions matching these requirements. The extremely high draw ratios (>250) obtained with single-crystal mats of PE[46] strongly confirm the validity of these criteria. Nascent reactor powders come next. Lower degrees of nascent entanglements[3,10] obtained by crystallizing directly on synthesis provide good levels of draw, which become higher if synthesis conditions favor more ordered crystals and lower amounts of latent entanglements. Thus, crystallization dynamics on synthesis become the key factor for the drawabilities of nascent reactor powders. Controlling this factor can open the way to the tailoring of ductilities directly by synthesis.

Acknowledgment. This work was partially supported by CNR, Progetto Strategico “Tecnologie Innovative” and by Ministero per l’Università e la Ricerca Scientifica e Tecnologica (MURST). Thanks are also due to MRSEC at the University of Massachusetts for use of its facilities.

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MA951653G