Tensile drawing behaviour of ethylene/ α-olefin copolymers: influence of the co-unit concentration

R. Seguela and F. Rietsch
Laboratoire de Structure et Propriétés de l'Etat Solide, L.A. 234, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cédex, France
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The tensile drawing study of a series of ethylene/1-butene copolymers having similar molecular weights and various concentrations of co-units shows that the strain hardening effect and the maximum achievable draw ratio are very sensitive to the degree of crystallinity. The strain hardening becomes more pronounced and the ultimate draw ratio is reduced drastically as the crystallinity decreases. A model is proposed to account for these phenomena on topological grounds connected with the presence of the co-units, a prime rôle being attributed to the entanglement density. It is suggested that, during the crystallization, the well known trend of rejection of the co-units out of the crystals hinders the chain folding process and the concomitant reeling-in motion of the chains dangling in the melt. The disentanglement of the deeply interspersed coils is thus progressively hampered as the co-unit content increases, and the remaining entanglement density in the solid copolymers must grown in parallel. A limiting situation is, however, expected, the characteristic entanglement density of which is equal to that prevailing in the melt.

(Keywords: ethylene copolymers; tensile drawing; strain hardening; crystallinity; molecular topology; entanglement density)

INTRODUCTION

The physical properties of ethylene/α-olefin copolymers – the so-called linear low density polyethylene (LLDPE) – are well known to be very sensitive to the nature and concentration of the comonomer units (see refs. 1–4 and the comprehensive reviews therein). It is obvious that the short branches due to the co-units disturb the crystallization mechanism of the methylene chains and modify the structural and thermodynamic characteristics of the crystallized copolymers to variable extents, with respect to linear high density polyethylene (HDPE). The thickness of the crystalline lamellae, crystallinity and melting point are more notably affected.

Ethylene/α-olefin copolymers have also been reported to behave quite differently from HDPE with regard to the mechanical properties. The stiffness and tensile strength decrease with increasing branch content[5]. Furthermore, the presence of short branches, even at low concentrations, leads to an enhancement of the strain hardening effect during the tensile drawing and reduces the maximum achievable draw ratio[6–9]. On the other hand, ethylene copolymers exhibit improved impact strength[5] and stress-cracking resistance[10,11] in comparison with HDPE. The tear strength and puncture resistance of copolymer blown films are also remarkable[12], while drawn fibres display an excellent resistance to creep[13].

Very few explanations have been given for these surprising properties, which deserve more exhaustive investigation. In two previous papers concerned with the drawing behaviour of LLDPE, we studied the effect of the drawing conditions on the maximum achievable draw ratio[9] and the changes of physical properties accompanying the plastic deformation[14].

The present work deals with the influence of crystallinity or short branch content on the drawing behaviour of a series of ethylene/1-butene copolymers having nearly equal molecular weights. A model is given to account for the effects observed on the strain hardening and the maximum achievable draw ratio on topological grounds, in relation to the crystallization mechanism. This study is complementary to the previous work of Capaccio and Ward[8], which set forth an explanation for the effect of short branches on the drawing behaviour of ethylene copolymers in terms of molecular mobility.

EXPERIMENTAL

Six linear polyethylenes having roughly similar molecular weights and different densities (i.e. different crystallinities) have been supplied by C.d.F. Chimie. The polymers contain various concentrations of 1-butene comonomer units, which control the density.

The molecular and physical characteristics of the samples are shown in *Table 1*. The weight- and number-average molecular weights, $\bar{M}_w$ and $\bar{M}_n$, were determined from gel permeation chromatography (g.p.c.) measurements made by the C.d.F. Chimie Research Centre. The values of the co-unit contents were estimated from the densities according to a relation previously established between these two parameters in the particular case of ethylene/1-butene copolymers[5,15]. Density and calorimetry data were obtained by using the procedures described elsewhere[14]. The melting temperature, T_f^{max}, was determined at the peak of the differential scanning calorimetry (d.s.c.) melting endotherm of every sample recorded at a heating rate of 10°C/min. The crystallization temperature, T_{cr}^{max}, was taken at the peak of the d.s.c. exotherm recorded at a cooling rate of 5°C/min.

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Table 1 Molecular and physical characteristics of the polyethylenes studied

Samples	Manufacturer trade name	$\bar{M}_w \times 10^3$	$\bar{M}_n \times 10^3$	Co-unit content (mole %)	T_f^{max} (°C)	T_{cr}^{max} (°C)	Density (g/cm^3)	Crystallinity (wt%) from density	from d.s.c
PE-1	Chemische Werke Hüls, Vestolen	135	15	virtually nil	137	118	0.960	75	73
PE-2	Solvay, Eltex	157	30	0.6	132	116	0.950	69	66
PE-3	Phillips, Manolene	178	19	1.1	129	114	0.943	65	62
PE-4	C.d.F. Chimie, Lotrex	136	31	2.5	124	107	0.930	55	53
PE-5	C.d.F. Chimie, Lotrex	140	29	5	122	106	0.919	48	43
PE-6	C.d.F. Chimie, Lotrex	146	27	8	120	102	0.913	44	38

The original polymer pellets were milled before being compression moulded into sheets about 1.7 mm thick at 190°C. The polymer sheets were allowed to relax in the press in the molten state for a period of 10 min before cooling at about 15°C/min.

The drawing experiments were made at a cross-head speed of 50 mm/min by means of an Instron Tensile Testing Machine provided with an environmental chamber, with use of dumbbell-shaped samples cut out from the sheets. For polymers PE-3 to PE-6, the test pieces had gauge length and width of 24 mm and 5 mm, respectively. For the polymers PE-1 and PE-2, which can be drawn more than 20-fold, test pieces of 16 mm and 4 mm in gauge length and width, respectively, were used to allow a one-stage drawing within the limited height of the environmental chamber.

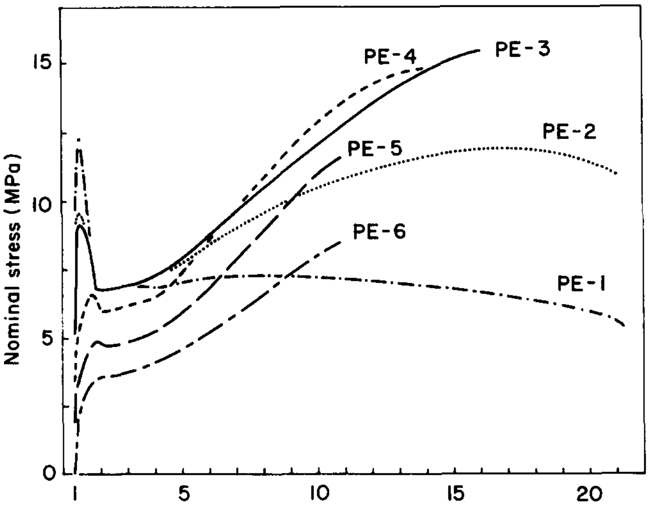

Figure 1 Nominal stress–strain curves at $T_d = 80°C$ of the polymers PE-1 to PE-6

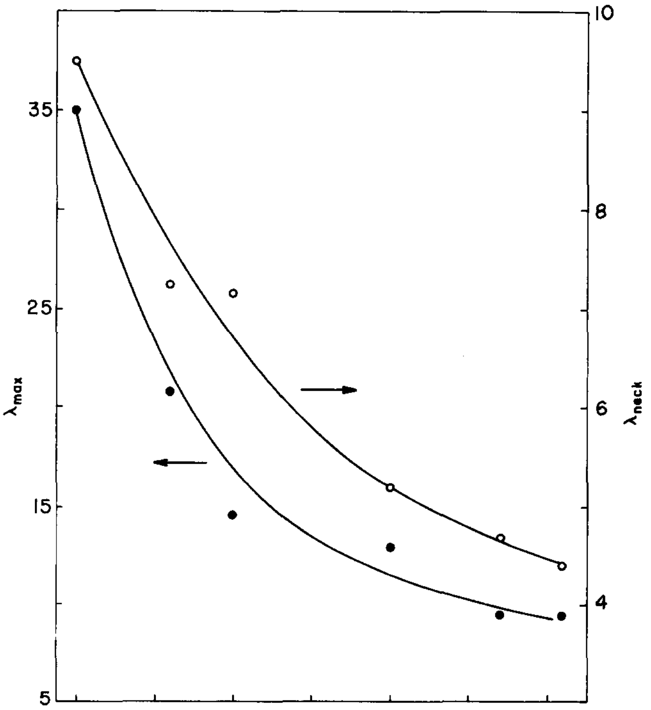

Figure 2 Curves showing the variation of the draw ratio in the neck, λ_{neck}, and the maximum achievable draw ratio, λ_{max}, as a function of the crystallinity assessed from the densities

RESULTS

To begin with, it is worth mentioning that the choice of a series of copolymers having the same type of co-unit and nearly equal molecular weights was made to eliminate all effects other than the specific ones due to the co-unit content. *Table 1* shows that the grading of the six polyethylenes PE-1 to PE-6 according to their crystallinities assessed from density is absolutely corroborated by the d.s.c. data. Besides, along with crystallinity, the melting and crystallization temperatures of the polymers are directly controlled by the co-unit content.

The tensile drawing behaviour of the six polymers is shown in *Figure 1* through the nominal stress–strain curves recorded at the drawing temperature $T_d = 80°C$ (we have previously shown that this temperature leads to the highest draw ratio for LLDPE[9]). At low strains, it can be seen that the yield stress decreases with the degree of crystallinity as a result of the lower thickness and perfection of the crystalline lamellae, which exhibit a weaker resistance to the onset of plastic deformation. Along with this, the drop of stress from the yield point to the draw plateau is drastically reduced, indicating a broadening of the neck profile while the draw ratio in the incipient neck decreases steadily as indicated in *Figure 2*.

At large strains, the situation is quite different. The strain hardening effect increases gradually with the decrease of crystallinity, from PE-1 to PE-4, then seems to become stable from PE-4 to PE-6. On the other hand, the ultimate draw ratio decreases monotonically with the degree of crystallinity of the polymers, as shown in *Figure 2*. These observations give a clear indication that the extension of a molecular network is involved in the drawing process at large strains, in parallel with the plastic deformation of the crystalline phase. It seems, moreover, that this contribution is gradually enhanced in the order of polymers of decreasing crystallinity.

We have reported in *Figure 3* the deformation profiles measured just before rupture along samples of the polymers PE-1 and PE-2 drawn at $T_d = 80°C$. This Figure shows that the vanishing of the strain hardening effect observed in *Figure 1* for PE-1 is accompanied by a loss of the deformation homogeneity.

The effect of the temperature on the drawing behaviour of the polymers PE-1, PE-2 and PE-4 is shown in *Figures 4*, *5* and *6*, respectively. For the most crystalline sample, PE-1 (*Figure 4*), the highest even draw ratio is obtained at the temperature $T_d = 60°C$, which corresponds to the maximum of the α-relaxation process in the crystal[16]. Above 60°C, the strain hardening disappears and the deformation in the necked region increases continuously as the neck propagates. This causes an early rupture of the sample before the completion of the neck propagation, the local deformation being very high in the region where the neck was initiated. For PE-2 (*Figure 5*), which is slightly less crystalline than PE-1, the maximum draw ratio is also reached for $T_d = 60°C$. However, the strain hardening effect persists up to $T_d = 120°C$, and the deformation remains nearly homogeneous at this temperature. The persistence of the strain hardening is yet more evident for PE-4 (*Figure 6*) and the deformation is quite homogeneous in the whole range of temperature investigated. This is all the more remarkable as PE-4 is more than 60% melted at $T_d = 120°C$, whereas PE-2 and PE-1 have just lost, respectively, about 16% and 10% of their original crystallinity, as can be judged from the d.s.c. curves reported in *Figure 7*. So, disregarding the temperature shift due to the heating rate during the d.s.c. experiments, the residual crystal content of the three samples at $T_d = 120°C$ can be roughly estimated at 0.20, 0.55 and 0.68 for PE-4, PE-2 and PE-1, respectively.

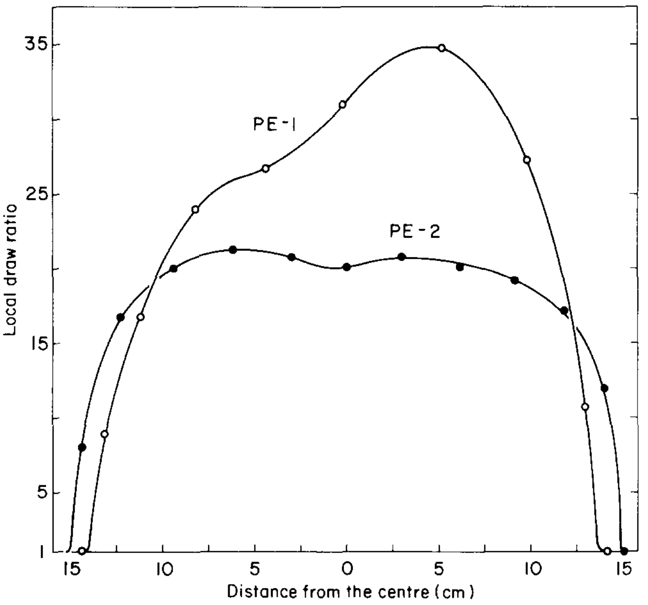

Figure 3 Longitudinal deformation profiles before rupture for the polymers PE-1 and PE-2 drawn at $T_d = 80°C$

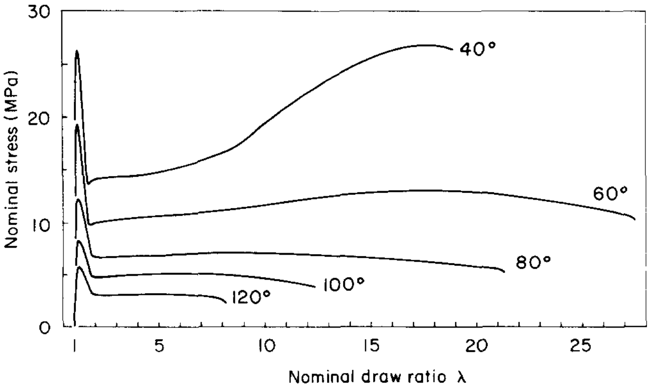

Figure 4 Nominal stress–strain curves of the polymer PE-1 for different draw temperatures (°C)

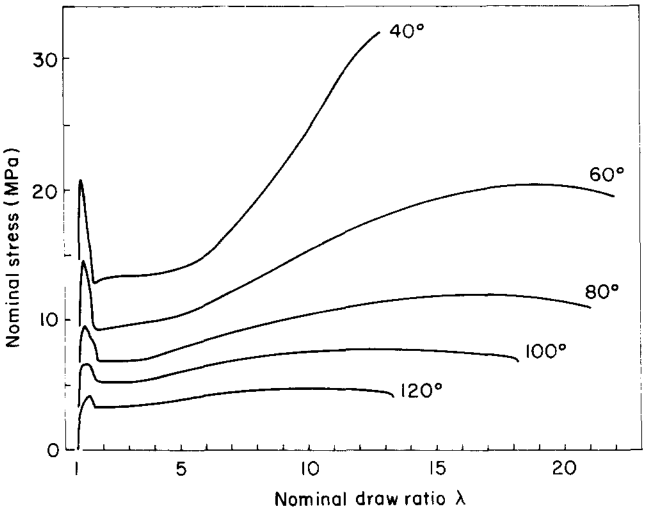

Figure 5 Nominal stress–strain curves of the polymer PE-2 for different draw temperatures (°C)

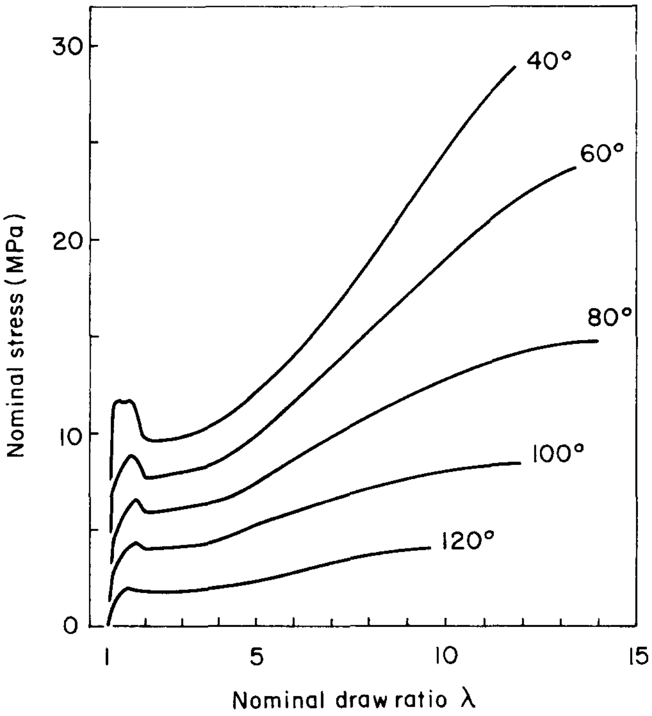

Figure 6 Nominal stress–strain curves of the polymer PE-4 for different draw temperatures (°C)

The effect of the temperature rise emphasizes the contribution of the molecular network extension in the drawing mechanism at large strains, with respect to the plastic deformation of the crystalline phase. The former conclusion that this contribution depends on the crystallinity level of the copolymers is confirmed. It suggests, therefore, that the molecular topology of the copolymers is also closely related to the crystal content.

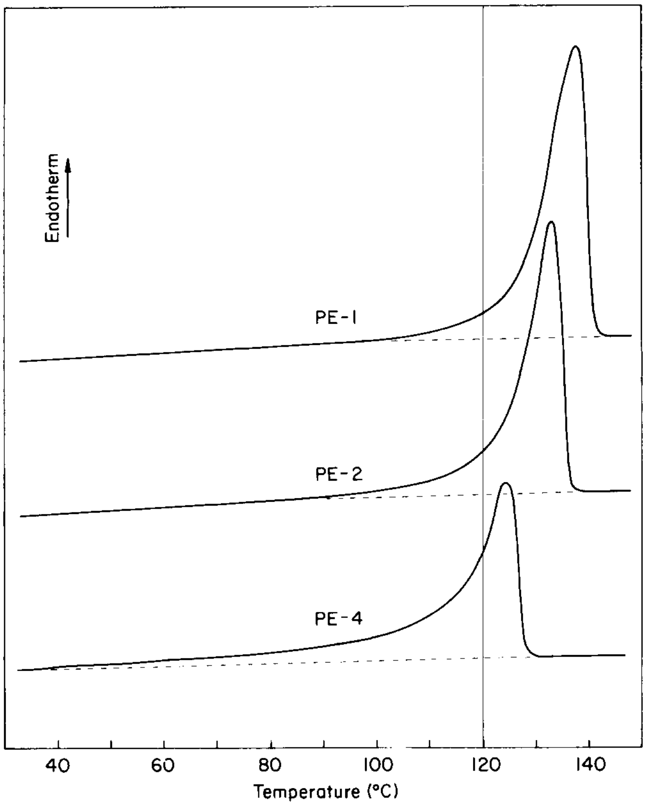

Figure 7 D.s.c. melting curves of the polymers PE-1, PE-2 and PE-4

DISCUSSION

Origin of strain hardening

Several authors[17-20] have successfully endeavoured to approach, from a theoretical standpoint, the drawing behaviour of semi-crystalline polymers at large strains by assigning the strain hardening effect to the extension of a physically crosslinked molecular network composed of tightly entangled chains. Ward *et al.*[21,22] have pointed out that the most favourable morphological and topological situation for drawing is achieved by regular lamellae having the minimum interconnections required to maintain a coherent network.

The most salient feature in the drawing behaviour of the ethylene copolymers studied in this work is the analogy between the incidence of the crystallinity or co-unit content and the effect of molecular weight[23-25] or crosslinking[26,27] already observed for homopolyethylene. As a matter of fact, the increase of co-unit content (i.e. decrease of crystallinity) leads to an amplification of the strain hardening and reduces the maximum achievable draw ratio (*Figure 1*), as does the increase of molecular weight or crosslinking rate for homopolyethylene.

Capaccio and Ward[8] have previously noticed such a similarity and have concluded that short branches reduce the chain mobility in the copolymers in comparison with homopolyethylene, so that molecular disentanglement is prevented during drawing. However, if the reduction of the chain mobility was the main factor responsible for the limitation of the copolymer drawability, one could expect a significant improvement of the maximum achievable draw ratio by raising the drawing temperature close to the melting point or by lowering the strain rate. But, as we have already shown[9], the drawing of a LLDPE with an average molecular weight $\bar{M}_w \simeq 1.6 \times 10^5$ at a temperature $T_d > 80$°C or at a strain rate $\dot{\varepsilon} < 10^{-2}\ s^{-1}$ results in an opposite effect to the one anticipated above. Besides, this seems to hold true also for HDPE of similar molecular weight[28-30].

It is suggested, therefore, that it is more likely that the restrictive influence of the co-units on the drawing behaviour of ethylene/α-olefin copolymers is founded on a topological effect than on a dynamical one, although molecular dynamics must certainly have a part to play. This hypothesis is very well supported by the recent results from Smith *et al.*[31,32] showing that the decrease of the entanglement density in an ultra-high molecular weight polyethylene, provided by means of a crystallization procedure in solution, give rise to a considerable lessening of the strain hardening effect with a corresponding spectacular increase of the maximum achievable draw ratio. It is worth mentioning that this can change from $\lambda_{max} = 6$ for the melt crystallized sample to $\lambda_{max} = 72$ for the film cast from a 1% solution[32].

Influence of the co-units on the topology

It is most generally admitted that ethyl and longer side groups are preferentially expelled from the crystal lattice of ethylene/α-olefin copolymers[1-4]. We have recently discussed[33] the origin of this phenomenon in terms of steric interactions, by considering the bulkiness of the side groups compared with the volume of the vacancies afforded through thermodynamically stable conformational defects in which the side groups may be accommodated.

Starting from that point, it is obvious that the relegation of the side groups out of the crystal seriously disturbs the crystallization mechanism, which involves a *reeling-in* process of the linear chains from the entangled melt onto the growing surface of the crystal (see ref. 34a, b, c and f). The natural propensity of the chains to fold back with regular adjacent re-entry[34a,35,36] is therefore likely to turn into a tendency of random re-entry. This situation is depicted in *Figure 8*, which takes into account that, for crystallization of polyethylene from the melt, chain folding occurs within (200) planes[36] while crystal growth proceeds parallel to the [010] direction[37]. When the

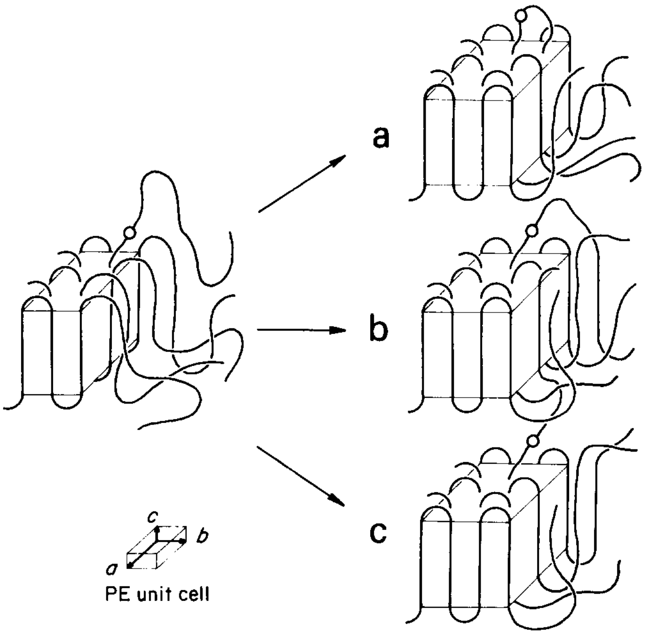

Figure 8 Schematic crystallization routes open to a chain after the interruption of the adjacent re-entry folding process due to an uncrystallizable co-unit (see text for details)

deposition of a chain onto a growing surface is interrupted by the presence of a cumbersome uncrystallized co-unit, three different crystallization options are available to the chain:

(1) to fold back on itself after making a more or less loose loop that relegates the co-unit within the amorphous layer, in the case when no other chain has been deposited in the adjacent crystallization site during the time required for the rearrangement of the former chain into a conformation more favourable to continue crystallizing (*Figure 8a*);

(2) to take on the crystallization again in a non-adjacent site of the same growing lamella, if another chain has taken the adjacent site during the time of the conformational rearrangement (*Figure 8b*);

(3) to transverse the amorphous layer and settle down onto the growth surface of the neighbouring lamella, giving rise to an intercrystalline tie molecule (*Figure 8c*).

These three eventualities occur at the expense of the regular tight folds, as the co-unit content increases in the copolymers. They contribute to break off the reeling-in motion, owing to which the chains are allowed to disentangle. Thus ethylene/1-butene copolymers are expected to contain more entanglements after crystallization from the melt as the co-unit content increases, in agreement with the changes in strain hardening and ultimate draw ratio observed in *Figure 1*.

The above interpretation is supported by the fact that ethylene/propylene copolymers, the only ones among ethylene/α-olefin copolymers that do not undergo the phenomenon of co-unit rejection[2,4], exhibit a mechanical behaviour close to that of homopolyethylene[8].

It is worth noting that the ultimate draw ratio seems to be no more sensitive to the co-unit content for the most branched copolymers, PE-5 and PE-6, in agreement with previous results of Popli and Mandelkern[7]. Within the framework of the interpretation given above for the tensile drawing behaviour of ethylene copolymers, this phenomenon can be explained by the fact that there is more than one co-unit per chain fold in the crystal, i.e. about 5 co-units per stem for sample PE-5 according to the average long period estimated from the melting point and the crystal content[9]. On account of this result, it is indeed easily understandable that the chain folding process during the crystallization of the copolymers PE-5 and PE-6 is likely to be disturbed at every stem emerging from the crystal, so that the *reeling-in* effect will be quite frozen and the disentanglement could no longer occur. The resulting topology for these two copolymers will be that of the 'solidification model'[34d], otherwise called 'switchboard model'[34e], which assumes the retention of the copious chain intertwining that prevails in the liquid state.

Of course, the last conclusion deserves to be confirmed by comparison of the experimental value of the maximum achievable draw ratio for the copolymers PE-5 and PE-6 with the theoretical value that could be assessed from the relation $\lambda_{\max} = N_c^{1/2}$ applicable to the extension of polymer networks, considering that the average chain length between entanglements, N_c, expressed in a number of statistical segments, is that which exists in the melt. Unfortunately no value for N_c is available in the literature for ethylene/1-butene copolymers. For homopolyethylene, the values of N_c collected from a great number of various sources[38] exhibit a very large scatter, which does not allow a reasonable determination of the maximum draw ratio theoretically achievable in the assumption of no disentanglement during crystallization.

The changes in molecular topology related to the presence of short branches in ethylene copolymers are not only expected to influence the drawing behaviour at large strains but also the plastic deformation at low and moderate strains. As already mentioned in the preceding section, the draw ratio in the neck is strongly reduced as the copolymer crystallinity decreases (*Figure 2*). Moreover, the shape of the stress–strain curves of the copolymers at the yield point (*Figures 4*, *5* and *6*) exhibit salient details revealing a modification in the yielding mechanism as a function of the crystallinity, for a given temperature. All these features let us foresee some additional effects of the peculiar topology of ethylene copolymers, which seems, in the circumstances, to impede the fibrillar transformation associated with the necking. Indeed, the mechanism of the lamellar crystal fragmentation precursory of the fibrillar transformation is liable to be influenced by the chain topology on the lamella surfaces. In this connection, further investigations are in progress concerning the yielding behaviour of the copolymers studied in the present work.

CONCLUSIONS

The enhancement of the strain hardening effect and the drastic reduction of the maximum achievable draw ratio of ethylene/1-butene copolymers suggest that the entanglement density increases with increasing co-unit content. The presence of the co-units seems to have an overiding influence on the molecular topology of the copolymers after crystallization from the melt. A satisfactory interpretation is provided by the model of the random chain re-entry at the surface of the crystalline lamellae, which takes place at the expense of the regular adjacent re-entry folding as the branching rate increases. This interpretation assumes that the relegation of the co-units within the amorphous phase breaks off the *reeling-in* motion of the chains during the crystallization from the melt and precludes chain disentanglement. Then, the greater the co-unit content is, the higher the remaining entanglement density after crystallization of the copolymers. A limiting situation is, however, expected, and actually observed, for the case where the entanglement density is conserved throughout the duration of the crystallization, the maximum achievable draw ratio being in that case no more sensitive to the co-unit content.

Mandelkern[39] emphasized recently that crystallinity and mechanical properties of semicrystalline polymers are both controlled by the molecular topology of the solid materials, which depend primarily on the molecular weight. Here, ethylene/1-butene copolymers prove to be an excellent illustration of Mandelkern's statement thanks to the effect of the co-unit concentration.

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