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Phenomenological aspects of the double yield of polyethylene and related copolymers under tensile loading

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The double yield point is shown to be a common feature to polyethylene and ethylene copolymers, regardless of the crystallinity level. Particular attention has been paid to the influence of draw temperature and strain rate which unambiguously indicate a combination of two thermally activated rate processes. Various thermal treatments have been investigated in order to check the influence of the crystal thickness distribution and the chain topology on the yield behaviour. Isothermal crystallization at high temperature is shown to have little effect compared with variations of crystallinity, temperature and strain rate in the case of compression-moulded samples. On the other hand, a strong effect has been observed in the case of solution crystallization which is well known to affect the chain-folding topology. The results are fairly consistent with the previous proposal by Takayanagi that (1) two processes govern the plastic deformation of the crystalline lamellae in semi-crystalline polymers, and (2) these processes are closely related to the viscoelastic relaxations in the crystal. The crystalline lamellae may deform plastically through sliding of crystalline blocks (brittle process) and/or homogeneous shear (ductile process). In order to account for the dependency of the brittle-to-ductile transition on the copolymer structure and crystallization method, a molecular model is put forward on the basis of the chain topology concepts borrowed from our former investigations on the tensile drawing and the melting behaviour of ethylene copolymers.

1. Introduction

The plastic deformation in polymers at small strains has been the subject of numerous investigations dealing with the modelling of the process [1–5]. The Eyring formalization [6] for thermally activated rate processes has been the most largely used model for studying the yield mechanism of glassy as well as semi-crystalline polymers. However, behind this formalization lies two different approaches to polymer plasticity. One of these theories relies on the classical framework of solid-state physics, owing to the obvious phenomenological analogy with plasticity of non-polymeric materials. It relies on the hypothesis that the nucleation of dislocation-like defects takes place at the early stage of the anelastic deformation. The yield point or stress threshold for the plastic flow results from the onset of propagation of such defects after the build up of a sufficient stock. The second approach assumes that plastic deformation is accommodated through molecular relaxation processes involving co-operative motions of several segments of the macromolecular chains. In this case, the yield point corresponds to the stress level at which the plastic flow rate is equal to the applied strain rate. The main difference with the former theory is that the basic processes of the plastic flow already exist in the material in a latent form prior to deformation. It is worth mentioning that the first approach is more likely valid at very low temperature when only short-scale elementary processes are allowed to accommodate plastic deformation, while the second one is more appropriate at high temperatures when various segmental motions can be activated cooperatively under stress [3].

Semi-crystalline polymers have received much less attention than glassy polymers in regard to the study of the yield process because of the problem of separating the crystalline and amorphous contributions to both stress and strain. Investigations in this field have been mainly devoted to polyethylene with particular efforts to characterize the elementary processes of the yield phenomenon [7–10] and to establish constitutive equations for the plastic flow [11, 12].

Some authors [13–17] have treated the yielding phenomenon in semi-crystalline polymers by analogy with melting, on energetics grounds. Indeed, the mechanical work provided to the crystallites by the applied stress should overcome the molecular interactions that hold the chains in crystallographic register, just as heat does in the melting process. Moreover, a strong clue supporting this hypothesis is that the fibrillar long period of materials drawn up to the natural draw ratio only depends on the draw temperature. This approach proved to be fairly successful, despite the fact that it neglects the contribution from the amorphous chain portions connecting the crystalline stems. Ichihara and Iida [17] have further developed this thermodynamic approach by taking into account the conformational contribution of the amorphous chains to the melting process.

Using the plastic deformation model based on the nucleation and propagation of dislocation-like defects that has been developed for glassy polymers, Porzucek *et al.* [18, 19] have studied the compressive yield behaviour of polypropylene and its blends with polyethylene below room temperature, assuming that the crystal is much more compliant than the glassy amorphous phase. The evolution with temperature of the thermal activation parameters of the deformation disclosed well-defined transitions which have been ascribed to the activation of the various molecular mobilities of the components. On the other hand, it has been shown by several authors [20–22] that the tensile yielding of polyethylene above the glass transition in a wide range of crystallinities can be fairly well accounted for by a simple quantitative model based on the nucleation of screw dislocations in the crystalline phase. In fact, the role of dislocations in polymer crystal plasticity was pointed out long ago by Predecki and Statton [23, 24], but these authors emphasized that dislocations alone could not account for the macroscopic plasticity. A contribution from the amorphous chains should be expected because of the extension of the chain folds that bridge the planes involved in a shear process. Attempts have been made to account for this effect through the so-called internal stress that operates in the plastic flow, in addition to the effective flow stress [25–28]

Much work has been carried out, on the other hand, on the structural aspects of plasticity in crystalline polymers. Diffraction methods and electron microscopy have been widely applied to scrutinize the elementary processes of deformation, notably in polyethylene single crystals (see, for instance, [29] and references cited therein). Evidence of a predominant (1 0 0) [0 0 1] slip process has been invariably provided, together with twinning and phase transformation effects. Bartczak and co-workers [30–32] have recently published an extensive study of the elementary deformation processes in highly textured bulk-crystallized high-density polyethylene under various mechanical testings, which corroborates the predominant activation of (1 0 0) [0 0 1] slip. However, generally little information has been obtained concerning the contribution of the amorphous phase.

The yielding of glassy as well as semi-crystalline polymers usually gives rise to a single yield point. However, several studies dealing with polyethylene have disclosed a singularity in the shape of the stress–strain curves about the yield point in the case of uniaxial compression [7], simple shear [33] or tensile loading [34]. This peculiar feature that consists of a hump in the vicinity of the upper yield point, raised no comment until Popli and Mandelkern [35] reported well-resolved double yield points for low crystallinity ethylene copolymers and branched polyethylenes under tensile testing at room temperature. These authors suggested that the broad distribution of the crystalline lamella thickness of the materials could be responsible for their rather odd yield behaviour. In fact, ethylene copolymers are well known to have a heterogeneous distribution of the co-units along the chains [36–38] which entails a spreading of the length distribution of the ethylene sequences eligible for crystallization and this has the direct effect of widening the crystal thickness distribution [39–41]. Nevertheless, it is doubtful that a broad crystal thickness distribution could lead to a well-resolved double yield point; a broad yield point would rather be expected. Moreover, it is unlikely that deeply interconnected crystals of various thicknesses might be allowed to yield independently from each other, to give rise to distinct yield points.

More recently, Gupta *et al.* [42] have suggested that the occurrence of a double yield point in a low-density ethylene–octene random copolymer is indicative of an association of the co-units that become dissociated during the second step of the yield. This is rather unlikely, in view of the fact that co-units with side branches bulkier than ethyl groups are preferentially excluded from the crystal [43]. On the other hand, when analysing the tensile and compressive yielding of several ethylene–hexene random copolymers, Brooks *et al.* [44] have shown that the capability of recovery of the deformation within 3 days is much greater in the range of the first yield point than in the range of the second one. This led the authors to model the yield mechanism as a parallel association of two non-linear Maxwell elements.

The above contradictory interpretations show that this problem deserves to be investigated more extensively. The fact that a double yield point has been also observed in the case of polyamide 6, carefully dried under vacuum [45], indicates that this phenomenon might be a general feature of semi-crystalline polymers. Therefore, in continuation of a previous tensile drawing study on a series of ethylene/butene copolymers [34], we have studied the plastic deformation of these materials at low strains. In a preliminary work [46] we have shown that a medium-density copolymer which displays a single sharp yield point at room temperature, can exhibit a very well-resolved double yield maximum at higher temperature, this latter being dependent on the strain rate. The lower the strain rate, the lower is the temperature at which the double yield point occurs. This has been interpreted as evidence that the phenomenon arises from the combination of two thermally activated rate processes having different activation parameters.

The present work was concerned with a series of ethylene–butene copolymers having similar molecular weights and spanning the range of crystal weight fraction $0.30 < \alpha_c < 0.75$. Compression-moulded and thermally treated samples have been investigated, together with dried gels recovered from solution, in order to probe the effects of crystallinity, crystallite-size distribution and chain macroconformation.

2. Experimental procedure

The seven polymers studied were supplied by the Norsolor Research Center, Mazingarbe, France. Their characteristics are given in Table I. The characterization methods have been described elsewhere [22, 34]. The samples were compression moulded into sheets from the bulk at 190 °C and cooled to room temperature at about 40 °C min^{-1}. Solution-crystallized sample was prepared from a decalin solution of copolymer PE-4 at 160 °C by means of an injection-moulding device. The mould was quenched into water at room temperature in order to produce a fast crystallization of the polymer solution. The self-supporting swollen gel that resulted from the crystallization was subsequently dried, according to a procedure previously described [47].

The drawing experiments were carried out using dumb-bell-shaped samples of gauge length 25 mm and width 5 mm, that were cut out from 1.5 mm thick sheets with a cutting punch. The samples were kept in the oven of the Instron tensile testing machine at the temperature of the drawing experiment for 10 min prior to the drawing. The nominal strain and nominal stress are defined as the ratio of the draw force to the initial cross-section of the sample and the ratio of the crosshead displacement to the initial gauge length of the sample, respectively. The nominal strain rate is the ratio of the crosshead speed to the initial gauge length of the sample.

Thermal analyses have been performed on a Perkin–Elmer DSC-7-Delta apparatus at a scanning rate of 10 °C min^{-1}. The sample weight was in the range 5–10 mg. The melting of indium and zinc samples was used to calibrate the temperature and the heat-flow scales at the same heating rate. The weight fraction crystallinity was assessed from the equation

$$X_c = \Delta H_f / \Delta H_f^\circ \qquad (1)$$

where ΔH_f is the enthalpy of fusion of the sample and $\Delta H_f^\circ = 290$ J g^{-1} is the enthalpy of fusion of a perfect infinite crystal of polyethylene at its thermal equilibrium melting point $T_f^\circ = 140$ °C [48].

The viscoelastic behaviour of the materials was investigated on a Toyo Baldwin Rheovibron Model DDVIIB, using rectangular strips 50 mm long, 4 mm wide and 0.2 mm thick. The measurements were achieved at a constant frequency of 11 Hz as a function of temperature, the heating being controlled at a constant rate of 2 °C min^{-1} after cooling the sample chamber to − 60 °C. The data were corrected for the clamping effect of the sample ends, according to the manufacturer's standard technique involving measurements of infinitely short samples as a function of temperature [28].

3. Results and discussion

3.1. Temperature and strain-rate dependence

Fig. 1 shows the nominal stress–strain curves as a function of draw temperature of the polymers PE-1, PE-2, PE-4 and PE-5. Every copolymer exhibits a single yield point, Y_1, at low temperature but as temperature increases a second yield point, Y_2, gradually develops beyond Y_1 before becoming predominant at high temperature. However, it should be mentioned that homopolymer PE-1 still gives a broad hump on the large-strain side of the first yield maximum at 120 °C, i.e. close to the melting temperature. This point will be discussed further. Notwithstanding this fact, the results of Fig. 1, together with the previous ones dealing with a medium-density copolymer (PE-3 in Table I) clearly show that the double yield point is a general feature of ethylene copolymers over a wide range of crystallinities.

The strain rate is as important as the temperature in the phenomenon. Fig. 2 shows that, whatever the copolymer, the second yield point can become predominant over the first one as a result of a two decade drop in the strain rate. In addition, for a given range of strain rate, namely $3.5 \times 10^{-2}\,\mathrm{s}^{-1} < \dot{\varepsilon} < 3.5 \times 10^{-4}\,\mathrm{s}^{-1}$, the temperature at which the change of deformation regime takes place, is strongly dependent on the crystallinity of the materials.

These equivalent effects of strain rate and temperature provide strong evidence that two thermally activated rate processes are involved in the plastic deformation of the crystalline lamellae, irrespective of the crystallinity of the copolymers.

Fig. 3 shows photographs of the neck profiles of polymers PE-2 and PE-5 for various draw temperatures and strain rates. The change in the geometry of the neck shoulder which turns from sharply cut to diffuse with increasing temperature (Fig. 3a and b) clearly corroborates the change in the deformation regime disclosed in Fig. 1. In addition, a comparison of the neck profiles of PE-2 and PE-5 shows that the lower the crystallinity of the materials, the lower is the temperature at which the change from sharp neck to diffuse neck occurs. In addition, in a way analogous to the increase of temperature, a decrease in strain rate in the drawing of PE-2 (Fig. 3c) is accompanied by a broadening of the neck shoulder, which confirms the change of deformation regime. As already reported by Vincent [49] and G'Sell [50] but without comment, such geometrical effects are additional evidence of the temperature–strain rate equivalence in the activation of plasticity. These results firmly support our previous

TABLE I Weight average, $\bar{M}_w$, and number average, $\bar{M}_n$, molar weights, density, ρ, melting enthalpy, ΔH_f, weight fraction crystallinity, X_c, and total ethyl group concentration, E, of the materials studied

Materials	$\bar{M}_w(\times 10^{-3})$	$\bar{M}_n(\times 10^{-3})$	ρ(g cm^{-3})	ΔH_f (J g^{-1})	X_c (%)	$E_{(\mathrm{ethyl/CH_2 in\%})}$
PE-1	130	15	0.960	215	74	Virtually nil
PE-2	157	30	0.950	200	69	0.4
PE-3	178	19	0.943	180	62	0.70
PE-4	136	31	0.932	159	55	1.35
PE-5	140	29	0.922	135	46	2.25
PE-6	146	27	0.910	102	35	3.80
PE-7	148	35	0.900	93	32	6.5

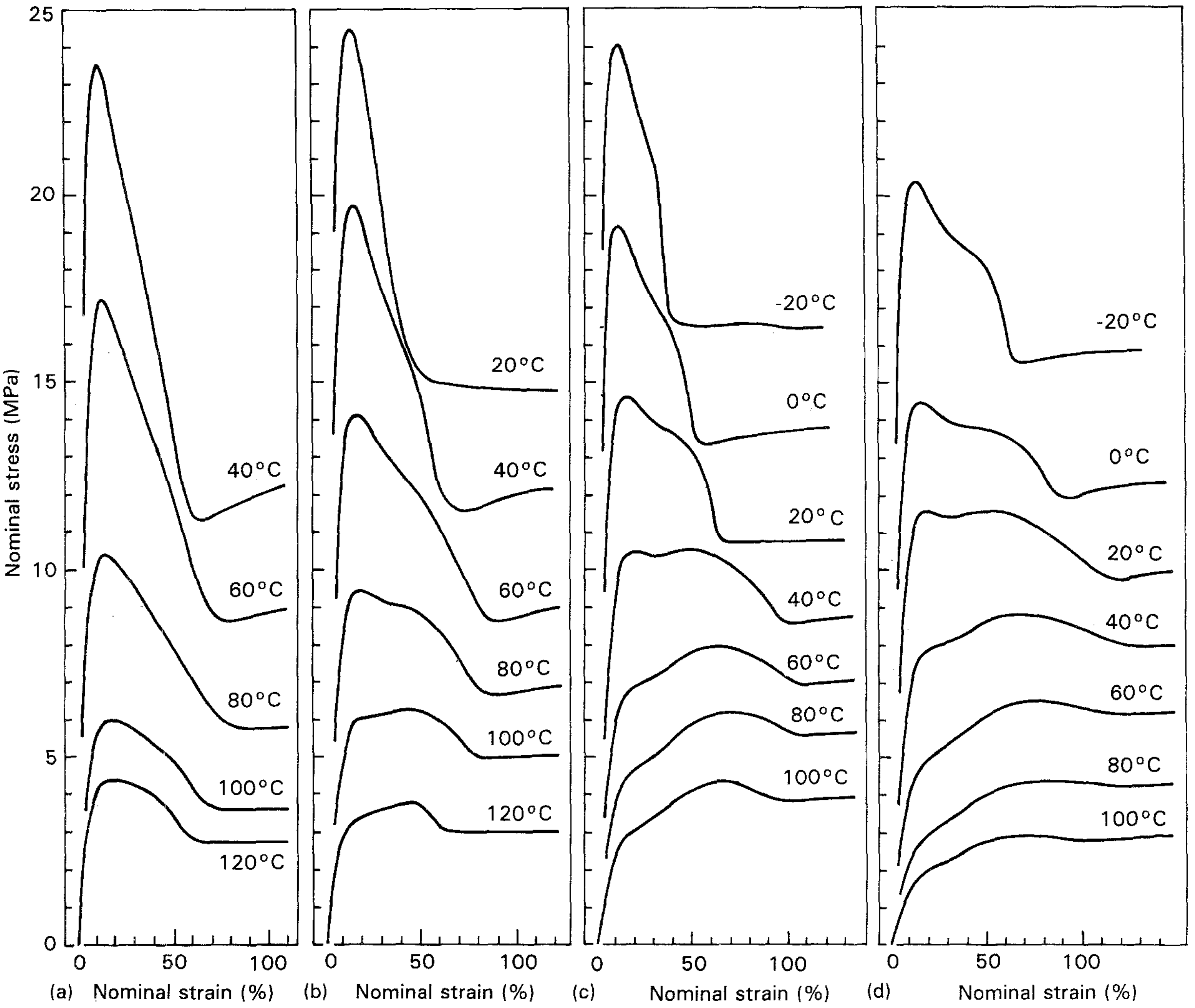

Figure 1 Nominal stress–strain curves of the polymers (a) PE-1, (b) PE-2, (c) PE-4 and (d) PE-5 as a function of draw temperature, for a constant nominal strain rate $\dot{\varepsilon} = 3.5\times10^{-2}\ \mathrm{s}^{-1}$.

conclusion [46] that the plastic deformation of the crystalline lamellae involves two mechanisms that operate preferentially at low temperature and high strain rates (Y_1) and at high temperature and low strain rates (Y_2).

3.2. Influence of the crystallite thickness distribution

The hypothesis put forward by Popli and Mandelkern [35] that the double yield phenomenon could arise from the crystallite thickness distribution deserved some experimental support. The differential scanning calorimetry (DSC) melting curves of Fig. 4 show that the low crystallinity copolymers indeed have a broad crystal thickness distribution as indicated by the low-temperature melting tail. In order to gain a better insight into the phenomenon, a sample of PE-4 was provided with a clear-cut bimodal crystallite population by isothermal crystallization for 3 days at 122 °C followed by slow cooling to room temperature. The efficiency of the thermal treatment is demonstrated in the DSC melting curve of Fig. 5a which exhibits two melting endotherms of nearly equal areas. The optical micrograph of Fig. 6 shows two distinct types of crystalline structures. The large lanceolated single crystals, aggregated into axialite-like structures, which melt in the range 118–135 °C have been formed during the high-temperature isothermal crystallization [51, 52]. The small spherolites which melt in the range 68–118 °C have grown during the subsequent slow cooling to room temperature. According to Hoffman *et al.*'s theory [51] of polymer crystallization, these two different structures are relevant to a change of crystallization regime in the two stages of thermal treament, in connection with the change of crystallization temperature. The stress–strain curves of sample PE-4 thermally treated following the procedure described above, are reported in Fig. 7a. Irrespective of the double crystal population, but depending on the temperature, either a single yield point or a double yield point may occur, as is the case for the compression-moulded PE-4 sample (see Fig. 1c). The yield stress level is, however, different for the two types of sample, under the same testing conditions, because of the major influence of the average crystal thickness in the temperature range where plasticity is governed by the thermally activated nucleation of dislocations [22].

The occurrence of a single yield point for a sample having a double crystal population is evidence that the two kinds of crystal cannot yield individually. Indeed, shear bands are generally a few micrometres wide and extend over dimensions much larger than the spherulite size [53], so that any shear band that develops in

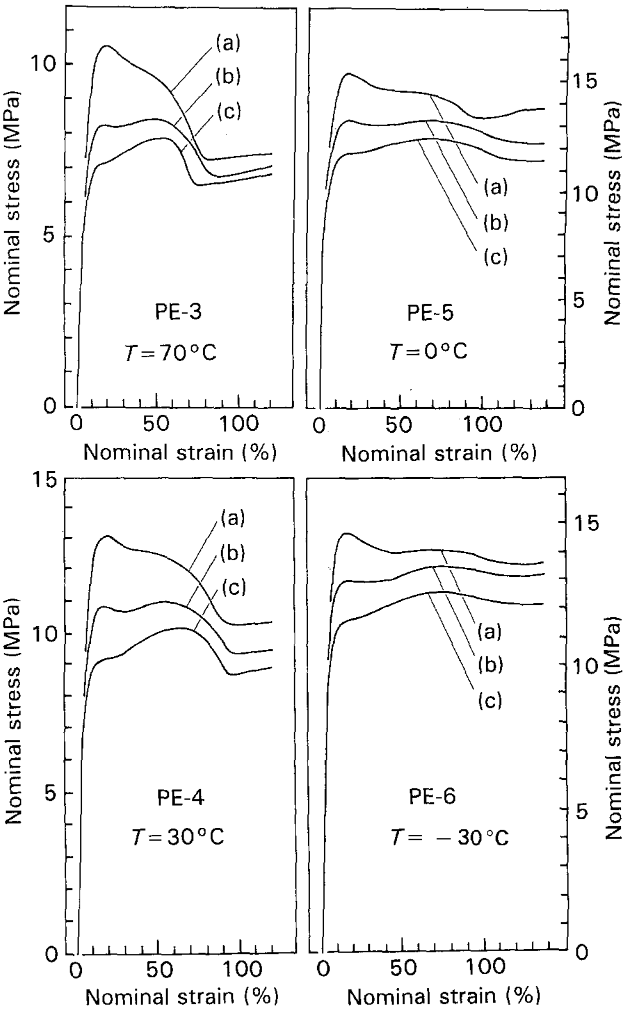

Figure 2 Nominal stress–strain curves of the polymers PE-3, PE-4, PE-5 and PE-6 at the nominal strain rates (a) $\dot{\varepsilon} = 3.5\times10^{-2}$ s^{-1}, (b) $\dot{\varepsilon} = 3.5\times10^{-3}$ s^{-1}, (c) $\dot{\varepsilon} = 3.5\times10^{-4}$ s^{-1}. For each polymer, the draw temperature is chosen such that the predominant yield point turns from Y_1 to Y_2 with decreasing strain rate.

the isothermally crystallized PE-4 should simultaneously involve both kinds of crystalline structures.

In summary, this experiment shows conspicuously that the crystallite thickness distribution is not the main factor of the double yield point phenomenon, although it may affect the conditions for its appearance.

3.3. Influence of solution crystallization

Crystallization from solution is a simple route to modify the average crystal thickness and the chain topology with relatively little change of the crystallinity level. Fig. 7b shows the stress–strain curves of a dried gel from the medium-density copolymer PE-4 recovered from a 50% decalin solution. Comparison of the curves of Figs 7b and 1c shows that the predominance of the Y_1 yield process of PE-4 is extended to higher temperatures in the case of the dried gel. The DSC melting curve of Fig. 5b shows that there is no major change in the broadness of the crystal thickness distribution of the dried gel with respect to the compression-moulded PE-4 (Fig. 4). However, the significant increase of the melting point at peak, namely 130 °C compared with 123 °C, is relevant to the improvement of the regular chain folding in the dried gel as judged from the reduction of the surface free energy [54].

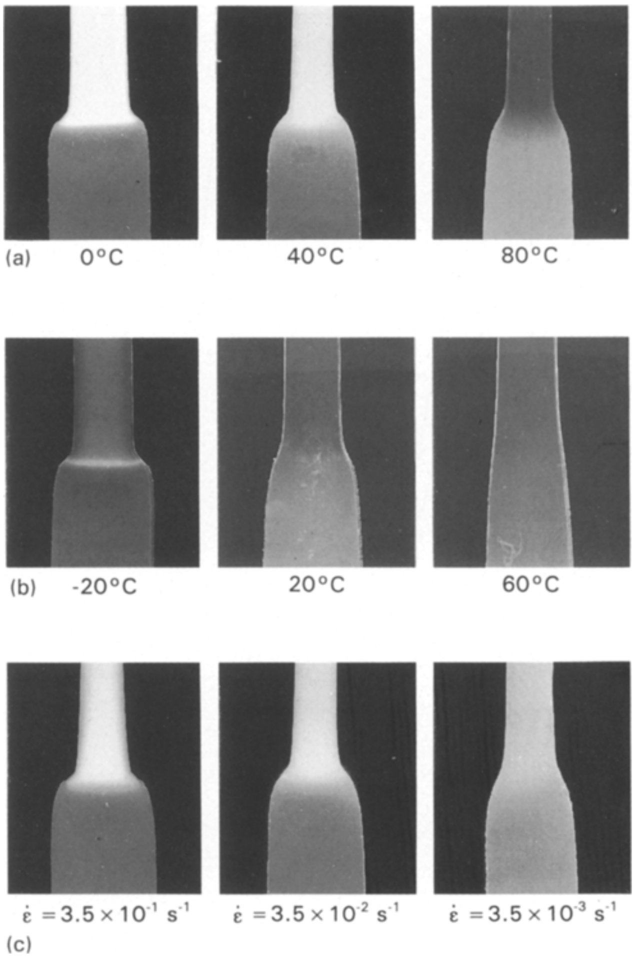

Figure 3 Neck profiles of the polymers (a) PE-2 and (b) PE-5 at various temperatures, for a constant nominal strain rate $\dot{\varepsilon} = 3.5\times10^{-2}$ s^{-1}, and (c) of the polymer PE-2 at various nominal strain rates, for a constant draw temperature $T = 40$ °C.

This mechanical comparison is in perfect agreement with a previous study [47] concerned with the drawing of dried gels from a low-density copolymer close to PE-6 in which we reported striking changes of the yield behaviour as a function of concentration: the higher the dilution of the initial solution, the stronger was the first yield point, for the same drawing conditions below 60 °C.

3.4. Viscoelastic behaviour

In all the cases investigated in the present study, the strain rate affects the shape of the yield point in an asymmetrical fashion very similar to the frequency effect on the loss modulus of polyethylene at the α relaxation in the crystal. The analysis of Takayanagi and co-workers [55–57] for the latter phenomenon is that the crystalline viscoelastic relaxation involves two overlapping processes with different activation energies. Fig. 8 depicts schematically the variations with temperature and frequency of the two contributions to the loss modulus at the α relaxation. From the above-mentioned analogy, we suspected that the elementary

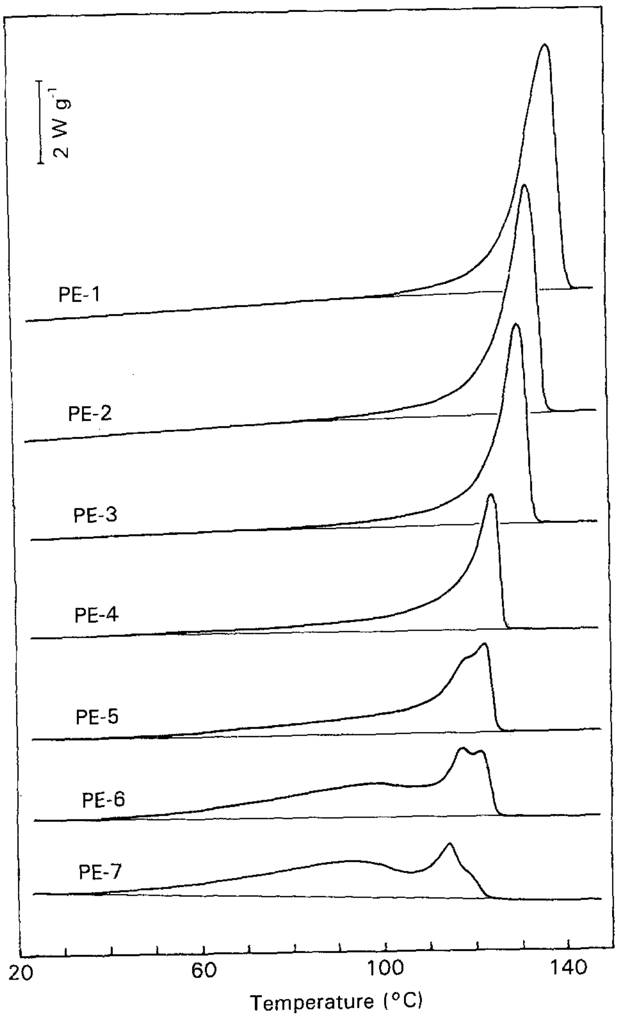

Figure 4 DSC heating curves of the compression-moulded polymers (for PE-6 and PE-7 the sensitivity of the heat flow scale is twice that indicated).

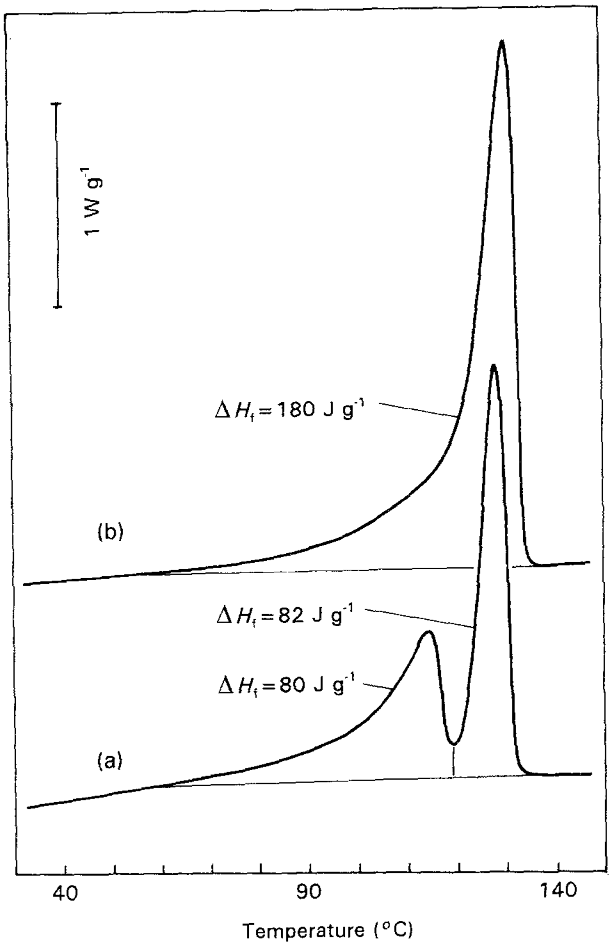

Figure 5 DSC heating curves of the polymer PE-4 (a) isothermally crystallized at 122 °C and subsequently cooled down to room temperature, and (b) crystallized from a 50% decalin solution and subsequently dried.

mechanisms of plasticity relied on viscoelastic precursors. This idea is supported by previous studies on glassy polymers [3] and also on high-density polyethylene [9] which disclosed changes of deformation regime in the curves of the variation of temperature with yield stress. The activation energies of the various regimes determined from the Eyring formalization fitted fairly well the activation energies of the viscoelastic relaxations characteristic of the molecular mobilities of the polymers, indicating a close relationship between the plastic elementary processes and the viscoelastic ones.

According to Takayanagi, the origin of the viscoelastic relaxation processes in the crystal is connected with the mosaic structure of the crystalline lamellae which consists in crystallographically incoherent blocks: the α_1 and α_2 relaxations which are, respectively, active in the low- and high-temperature sides of the loss-modulus peak have been ascribed to the sliding motion of the mosaic blocks past each other and to the homogeneous shear of these blocks. It is worth noting that despite some conflicting conclusions among the literature reports (see, for instance, the discussion in [3], Ch. 8), many authors agree with this model [58–61]. Therefore, the Y_1 and Y_2 yield processes could be quite logically associated with the relaxations α_1 and α_2, respectively. Two main facts support this. First, several investigations concerned with the microstructural aspects of the plastic deformation in semi-crystalline polymers have disclosed the occurrence of two mechanisms [7, 29, 62, 63]. In fact, the slip along planes parallel to the chain axis, which is the main process of plastic deformation in polymeric crystals, may entail either heterogeneous shear or homogeneous shear of the crystalline lamellae, otherwise coarse slip or fine slip [29]. Second, the

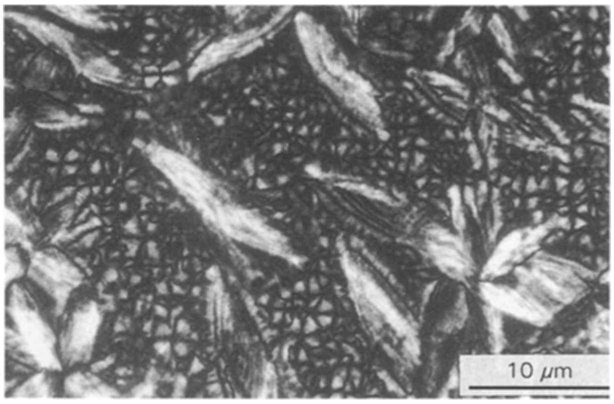

Figure 6 Optical micrograph of polymer PE-4 isothermally crystallized at 122 °C and subsequently cooled to room temperature.

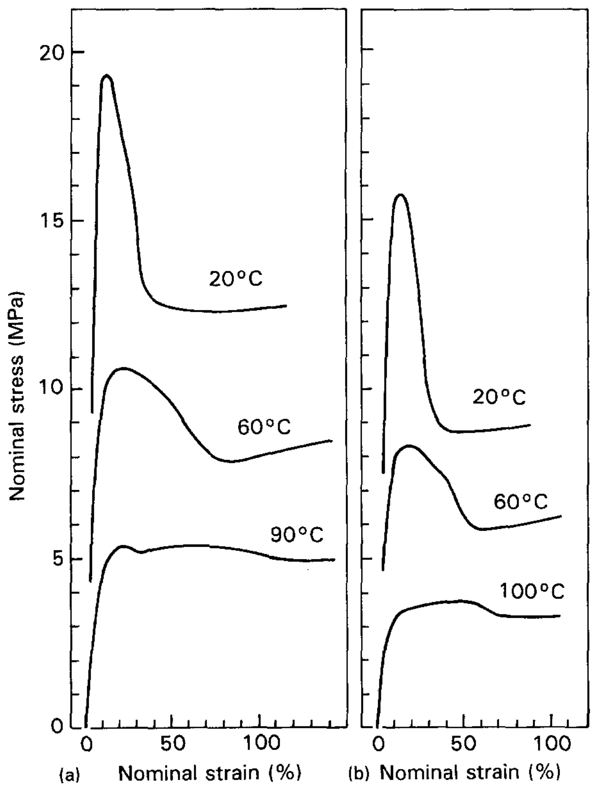

Figure 7 Nominal stress–strain curves as a function of temperature of the polymer PE-4 (a) isothermally crystallized at 122 °C, and (b) crystallized from solution (nominal strain rate $\dot{\varepsilon} = 3.5 \times 10^{-2}\ \mathrm{s}^{-1}$).

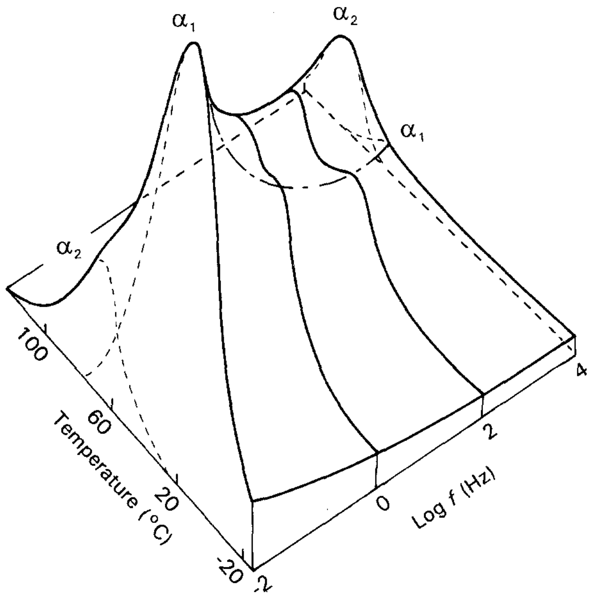

Figure 8 Schematic mapping of the loss modulus variations as a function of temperature and frequency for linear homopolyethylene after Takayanagi (reprinted from [56] with permission of Marcel Dekker Inc.).

loss modulus versus temperature curves for the various copolymers display a severe lowering of the amplitude of the α peak with decreasing crystallinity, as can be seen in Fig. 9, but also a strong shift of this peak towards lower temperatures. This latter phenomenon is well-known to issue from the reduced crystallite thickness [55, 64]. However, an unsuspected consequence of this shift is that, for a given temperature above room temperature, the α_2 relaxation which is mainly active on the high-temperature side of the α maximum, becomes gradually more active than the α_1 relaxation for the copolymers of lower crystallinity. This perfectly parallels the predominance of the Y_2 yielding process at lower temperatures for the low-crystallinity copolymers than for the high-crystallinity ones (see Fig. 1).

3.5. Brittle-to-ductile transition

The dependence of the double yield point on temperature is not consistent with the assumption that plastic yielding is simply analogous to a melting process. Moreover, the morphology is obviously not the main factor that governs the occurrence of a double yield point. Indeed, our results are contradictory with an effect of crystallite-size distribution which assumes that crystallites of various thickness or perfection could yield at different strains. In fact, if the above statement was true, one should associate the first yield point with the larger and more perfect crystals, in view of the fact that, for given temperature and strain-rate conditions, it becomes more predominant as the crystallinity and melting point of the copolymers become higher. However, increasing the draw temperature for a given copolymer has the reverse effect to the above conclusion because the second yield point becomes more important as the less-perfect crystals gradually melt. The DSC melting curves of Fig. 4 show notably that copolymers PE-4 to PE-7 are deprived of a substantial fraction of their more defective crystals for the draw temperatures above 80 °C. Therefore, the well-developed second yield point of PE-4 and PE-5 (Fig. 1c and d) cannot be ascribed to a specific mechanical response of small imperfect crystals. From Peterlin's model [65, 66], which depicts macroscopic necking as a result of an accumulation of micronecking processes in the individual lamellae, the build up of a sharp neck could be ascribed to a local avalanche of microscopic and highly heterogeneous deformation events, i.e. the sliding of crystal blocks which is a process of brittle nature, while the development of a diffuse neck should originate from a gradual propagation of a homogeneous process, i.e. the shearing of the crystal blocks which is a ductile process. In this instance, the results of Figs 1–3 indicate that increasing the temperature or lowering the strain rate promote the homogeneous deformation regime. The particular case of PE-1 (Fig. 1a), which only displays a predominent Y_1 yield point, is consistent with X-ray diffraction data from Peterlin and Meinel [62] showing that the sliding of unsheared blocks persists up to temperatures close to the melting point for highly crystalline homopolyethylene.

A particular feature of Fig. 3 is that the samples whiten in the necked region when the Y_1 process is largely predominant, indicating that this process leads to fragmentation of the crystallites with a concomitant microvoid formation. However, when the Y_2 process enters into action, even without being predominant, whitening no longer appears. This phenomenon clearly discloses the brittle and ductile natures of the Y_1 and Y_2 processes, respectively. They are to be related

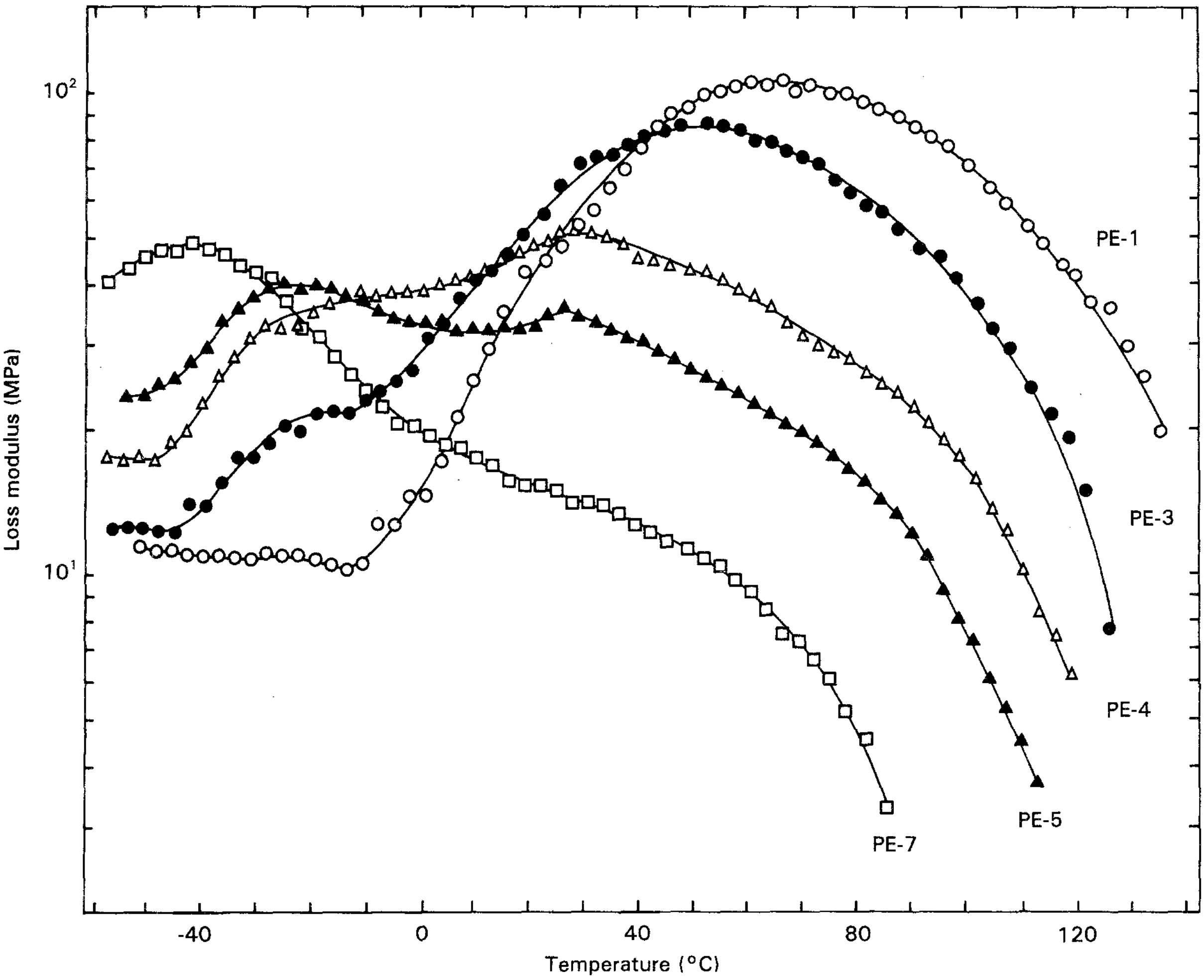

Figure 9 Loss modulus versus temperature variation curves for the polymers studied at a frequency of 11 Hz (the data for PE-2 and PE-6 are not shown for the sake of clarity).

to the crazing and shear banding that can contribute cooperatively in semi-crystalline polymers above the glass transition temperature [53].

We have discussed the yielding behaviour with regard to the structure level of the crystallites only. It has been pointed out by Schultz [67] that among structure-level effects, the spherulite effects are not clear because of the concomitant variations of crystallinity and crystallite thickness with the spherulite size. In addition, it seems that the more conspicuous effects of spherulite size appear at temperatures near the glass transition temperature, T_g, of the amorphous phase, as is typically exemplified by polypropylene at room temperature. We believe that, owing to the glassy state of the inter-lamellar amorphous phase at temperatures close to T_g, the spherulites behave as hard entities surrounded by defective regions which constitute a mechanical discontinuity and thereby offer a preferred way to crack propagation. However, for temperatures well above T_g, as is the case in the present study, the crystalline lamellae become hard entities embedded in a rubber matrix, so that their intrinsic behaviour becomes more important in comparison with the whole spherulites. This is perfectly supported by the unique relationship between the yield stress and the crystal thickness for polyethylene above room temperature [20–22].

The question remains, why does the temperature range of predominance of each of the two plastic deformation regimes change in relation with crystallinity? A strong modification of the chain topology, otherwise chain macroconformation, may account for this change.

3.6. Topological model

We have already suggested from mechanical [28, 34] and thermodynamic [54] studies of ethylene–butene copolymers that the rejection of the butene co-units in the amorphous phase is likely to disturb the chain-folding process during the crystallization step. The regular chain-folding macroconformation that should prevail in homopolyethylene may turn into random chain folding or fringed micelle macroconformation in co-unit-rich copolymers. It is noteworthy that Hoffman's theory of crystallization of linear polymers predicts a change of crystallization regime with decreasing crystallization temperature that involves an upset of the chain topology [68–70]. At very low undercoolings, crystal growth takes place through regular chain folding with adjacent re-entry, thanks to a high probability for tertiary nucleation of a new crystalline stem involving two surfaces of deposition only available at the position adjacent to the preceding stem. At high undercoolings, random chain folding is more likely to occur owing to a high probability for secondary nucleation of a new stem using a single surface of deposition at any place on the crystal growth front. Then, considering that the copolymers crystallize as nearly pure orthorhombic polyethylene and that the crystallization temperature of the copolymers decreases significantly with increasing co-unit content, as shown on the DSC cooling curves of Fig. 10, additional support is provided to our previous conclusion on the changes in the chain topology, from mechanical testing.

Fig. 11 shows how the chain topology must change as a function of co-unit concentration, or crystallinity, for the melt-crystallized copolymers. In the case of random chain-folded crystals, the dislocations that convey the plastic deformation at a molecular level through the crystals are not allowed to glide over large distances because of the deeply intertwined chain folds that bridge all types of $(hk0)$ slip planes and distribute the load homogeneously on the crystal surface. Climbing of dislocations at low temperatures or thermal nucleation of new dislocations at high temperatures should thus favour homogeneous shear. On the other hand, regular chain-folded crystals are particularly suited to an easy glide of the dislocations along the folding planes. The defective boundaries in the mosaic structure are privileged regions where the sliding of crystal blocks can operate at a lower energy cost than homogeneous shear. Therefore, low-crystallinity copolymers will be more prone to homogeneous shear with diffuse necking than high-crystallinity copolymers.

The yielding behaviour of the dried gels may be perfectly accounted for in the scheme of the topological incidence discussed above. In fact, crystallization from solution improves regular chain folding [54] in the copolymers in the same way as does the reduction of the co-unit content, as depicted in Fig. 11. Therefore, the more diluted is the solution prior to crystallization, the greater is the capability of sliding of crystal blocks in the dried gels. This is in agreement with the growing predominance of the brittle Y_1 yield process over the ductile Y_2 process in the dried gels compared with the melt-crystallized homologues.

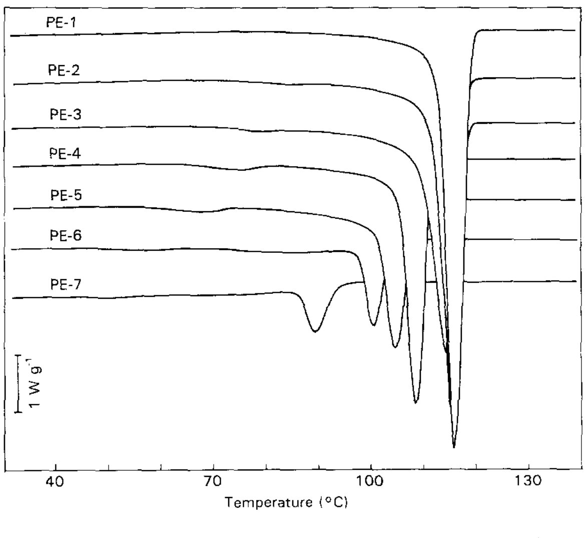

Figure 10 DSC cooling curves of the polymers from the melt.

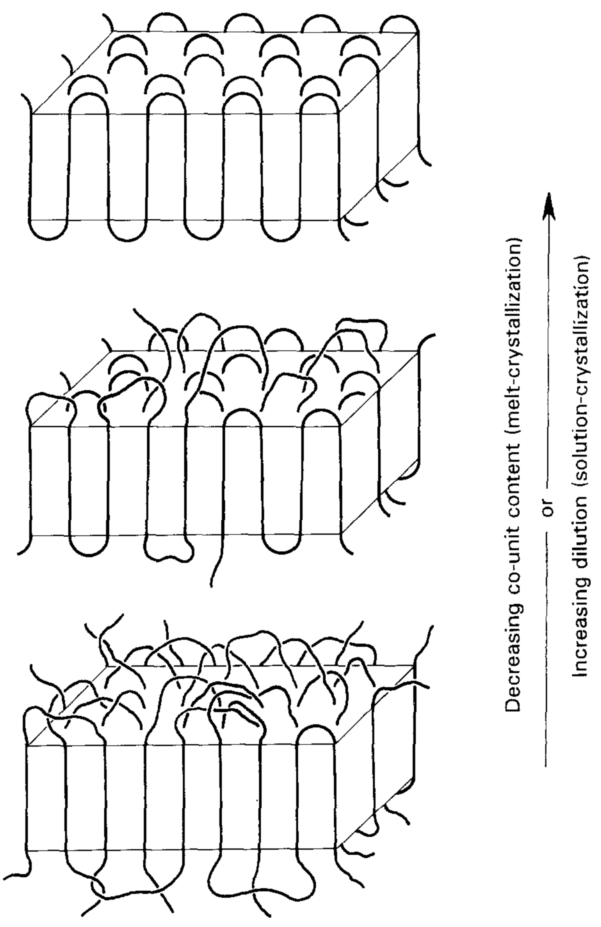

Figure 11 Molecular model showing the changes of the chain-folding topology as a function of the co-unit concentration in the melt-crystallized polymers and as a function of dilution for the solution-crystallized polymers.

It should be pointed out that the improvement of regular chain folding that parallels the increase of crystallinity for the melt-crystallized copolymers is accompanied by a decrease of the entanglement density, as judged from the variation of the maximum extensibility of the materials [28]. The reason is that random chain folding results from crystallization without profound rearrangement of the chains from the melt, the entanglements being segregated in the amorphous phase (see the bottom part of Fig. 11). Regular chain folding, on the contrary, builds up together with a reeling motion of the chains during crystallization which entails disentanglement of the chains from the melt [68–70]. The brittle yield process that prevails for the high-crystallinity copolymers crystallized from the melt is thus to be related to a lower entanglement density than for the low-density copolymers, in concomitance with the more regular chain-folding macroconformation, because entanglements are likely to improve the homogeneity of the stress distribution over the crystalline lamellae by transferring the load from chain to chain.

The situation is the same for the solution-crystallized materials. In addition to the improvement of the regular chain folding, dilution involves chain disentanglement prior to crystallization [47], and this entails a greater propensity towards brittle yield.

4. Conclusion

Evidence has been given that two thermally activated regimes of deformation take place during the tensile drawing of polyethylene and related copolymers. It is suspected that this is a general behaviour of semi-crystalline polymers. The elementary processes of the plastic deformation are associated with the molecular mobilities that give rise to the viscoelastic relaxations in connection with the mosaic block structure of the crystalline lamellae.

The modifications of the macromolecular topology as a function of the co-unit concentration in the melt-crystallized materials and as a function of dilution in the solution-crystallized samples is shown to be responsible for the change of plastic behaviour. The chain-folding macroconformation, together with the entanglement density, play a prime role in the brittle or ductile yield of the crystalline lamellae.

Further work is in progress to investigate the thermal activation of the two processes through the determination of the true stress–true strain curves of the materials under various drawing conditions.

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