JOURNAL OF MATERIALS SCIENCE **33** (1998) 1801–1807

Plastic deformation of polyethylene and ethylene copolymers

Part II *Heterogeneous crystal slip and strain-induced phase change*

R. SÉGUÉLA, S. ELKOUN, V. GAUCHER-MIRI
Laboratoire "Structure et Propriétés de l'Etat Solide", Unité de Recherche associée au CNRS 234, Université des Sciences et Technologies de Lille, Bâtiment C6, 59655 Villeneuve d'Ascq Cédex, France

The plastic behaviour of polyethylene and ethylene copolymers is studied under uniaxial tensile testing with particular attention to the development of plastic instability. Heterogeneous crystal slip is suggested to take place when homogeneous crystal slip either is not allowed at the temperature and strain rate of the experiment or is exhausted owing to extension of the chain folds. The chain unfolding concomitant to the fragmentation of the crystalline lamellae is suspected to have a low strain hardening that is responsible for the phenomenon. Partial screw dislocations with a shorter Burgers vector than in the case of homogeneous slip are proposed to become operative because of the activation of 90° chain twists in the crystalline stems. Dissociation of dislocations into partials involves stacking faults in the orthorhombic structure that may turn into monoclinic structure through a martensitic-like transformation. Crystal slip is likely to concentrate in these faulty regions owing to the reduced molecular interactions and lower density. Two types of correspondence of the transformed monoclinic phase with the parent orthorhombic structure are observed. The modification of the chain-folding macroconformation as a function of the crystallinity of the materials is suspected to influence the transformation shear mode. © *1998 Chapman & Hall*

1. Introduction

Semicrystalline flexible chain polymers exhibit a high ductility above the temperature of the glass transition [1, 2]. However, plastic instability is commonly encountered under tensile or shear deformation modes [3–6]. This phenomenon is prejudicial for the processing of semicrystalline polymers by drawing means. It relies on the shape of the true-stress–true strain curve of the material. Indeed, the occurrence of plastic instability (also called necking) is governed by the Considère criterion that involves the strain-hardening coefficient [7–9]. It is well known to occur in ductile crystalline materials such as metals; however, the main difference with polymers is that a strong strain hardening builds up at large strains because of chain unfolding. Thereby, the deformation in the necked region turns out to be stabilized and neck propagation takes place.

In previous studies dealing with polyethylene and related copolymers we have shown that, depending on the temperature and strain rate conditions, as well as on the crystallinity, plastic instability upon tensile drawing may appear or not [10, 11]. We have recently proposed a deformation model involving the competition of homogeneous and heterogeneous slip processes in the crystalline lamellae [11]. Homogeneous crystal slip was associated with the occurrence of a macroscopically homogeneous plastic deformation. Heterogeneous crystal slip (otherwise known as localized slip) was proposed to be responsible for the macroscopically heterogeneous plastic deformation, i.e., plastic instability. Because of a greater thermal activation of the homogeneous slip compared with the heterogeneous slip, a transition from heterogeneous to homogeneous macroscopic deformation was predicted from the model as a result of increasing temperature or decreasing strain rate.

Homogeneous crystal slip has been discussed in detail in an accompanying paper [12]. The present paper deals with the mechanism of localized slip from which plastic instability arises. The kinetics of dislocation nucleation and propagation are emphasized in relation to temperature and strain rate.

2. Experimental procedure

The three ethylene–butene copolymers labelled A, B and C are described in Part I of this series [12]. They have the following crystal weight fractions: 0.67, 0.55 and 0.35, respectively.

The mechanical study has been carried out in tensile mode using a video-monitored optical extensometer. The true stress and true strain measurements have been carried out following a procedure described elsewhere [13].

The wide-angle X-ray scattering (WAXS) experiments have been recorded in photographic mode, as previously reported [10].

3. Heterogeneous crystal slip model

It is generally accepted that the fibrillar transformation that occur at high strains in semicrystalline polymers involves fragmentation of the crystalline lamellae into crystal blocks which rearrange into fibrils parallel to the draw direction [14, 15]. No attempt has been made to model the mechanism of the obviously heterogeneous slip mode of deformation (otherwise known as coarse slip [16] or block sliding [14]) that leads to the lamella fragmentation. The reason may be that the physical origin of the sliding process of blocks from the crystalline lamellae is still obscure. Galeski *et al.* [17] suggested from a plane-strain stretching analysis that the balance between the interface stretching resistance and the plastic shear resistance of the crystalline and amorphous layers is likely to result in the pinching off and subsequent break-up of the crystalline lamellae. However, the above researchers have neither proposed a molecular mechanism for the lamellae breakup nor defined the experimental conditions for its occurrence.

3.1. Stacking-fault slip

In our previous approach to modelling the plastic behaviour of polyethylene and related copolymers [11], the defective boundaries of the crystal blocks in the mosaic structure of the crystalline lamellae were assumed to be the locus of heterogeneous slip because of the presence of growth dislocations that can compensate for the deficiency of thermal nucleation of dislocations at low temperatures or high strain rates. Indeed, homogeneous plastic deformation that has been ascribed to the activation of homogeneous crystal slip gradually gives place to plastic instability as the deformation temperature is decreased below the α crystalline relaxation.

According to Hosemann *et al.* [18] who have put forward the concept of mosaic block structure for polymer crystals, arrays of growth dislocations create defective interfaces of the kind shown in Fig. 1a. Such dislocation arrays may be generated by the introduction of interstitial chain ends in the crystals [19] owing to the build-up of chain kinks. The Hosemann *et al.* model suggests that block boundaries are composed of broad dislocations of the Peierls type which look more like stacking faults than like pure dislocations [20]. In the case of copolymers, partial inclusion of the co-unit side groups at interstitial positions in the crystal is liable to play an analogous defect-initiating role owing to the similar ability for chain kink promotion [21].

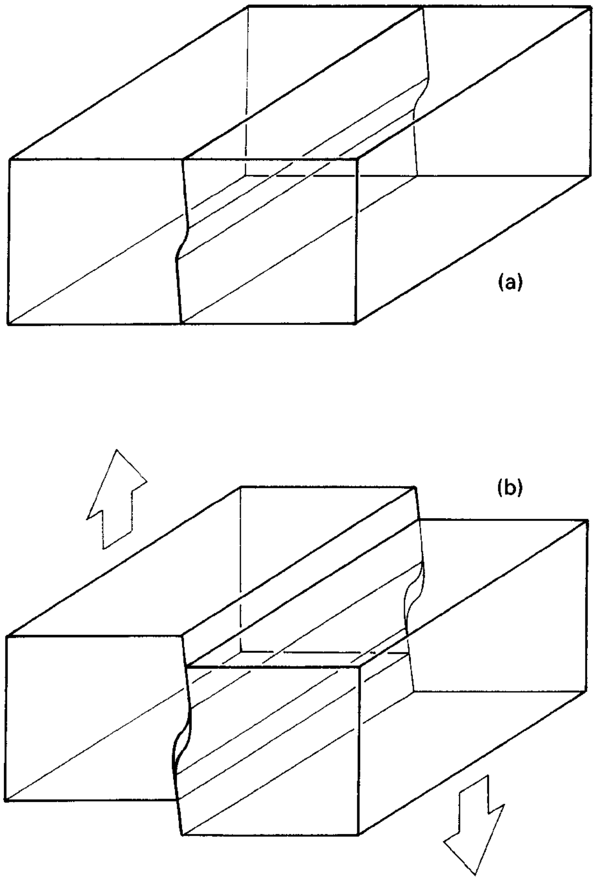

Figure 1 Defective block boundary in the mosaic structure of a crystalline lamella: (a) prior to slip; (b) at the onset of slip.

The sliding of crystal blocks via the defective boundaries of the mosaic block structure, according to Fig. 1b, is typically a heterogeneous slip phenomenon that was originally proposed by Takayanagi and Kajiyama [22]. It is suspected to occur only at low temperatures when thermal nucleation of dislocations is prohibited. As soon as the blocks are shifted, the mismatch of the uneven glide surfaces entails a very low drag stress. This sudden drop in the crystal strength entails stress concentrations on the chain folds that bridge the glide plane. This results in chain unfolding accompanied by crystal micronecking. Transfer of the very high local strain to the neighbouring crystallites gives rise to the macroscopic necking through multiplication of micronecks [23] accompanied by low strain hardening.

In an approach of the yield behaviour of glassy polymer, Escaig [24] proposed a mechanism of slip of corrugated surfaces owing to the lack of crystallographic planes in the amorphous state which is responsible for the generation of many molecular misfits within a shear interface. This model was obtained from that previously proposed by Friedel [25] for the plasticity of metallic glasses at low temperatures, and which assumes a major activity of stacking faults over dislocations. Indeed, it is well known that stacking faults are preferred loci for heterogeneous slip in metallic glasses [20] and close-packed crystalline metals as well [26].

In the model of corrugated surface slip, the tensile flow stress for trailing the stacking fault, according to

Fig. 1b, is given by the following relation [24]:

$$\sigma_y \approx \mu\left(\frac{h}{d}\right)^2 \approx \frac{\gamma}{d} \qquad (1)$$

where μ is the shear modulus of the stacking-fault planes, h is the height of the stacking fault normal to the shear interface, d is the length of the defect in the shear direction and γ is the free energy per unit area of the stacking-fault interface.

From this approach, an estimation can be made of the flow stress for the heterogeneous crystal slip provided that the various parameters in Equation 1 are known. Although the stacking faults undoubtedly lie in various planes of the $(h\,k\,0)$ type, one ought to take into consideration the $(0\,1\,0)$ planes which cut the crystal lamellae through their shorter dimension and should therefore provide the main contribution to the heterogeneous slip. From the length of the 2g1 chain kinks that most probably compose the defective interfaces of the crystal blocks, a value $d \approx 1.0 \pm 0.2$ nm corresponding to eight methylene units [27], can be assessed for the extent of the stacking fault in the direction of the chain axis. The value of the stacking-fault height can be approximated to the transverse distortion of the planar chain segments adjacent to each 2g1 kink [27], i.e., $h \approx 0.07 \pm 0.01$ nm. Then, owing to the variation with temperature in the $(0\,1\,0)$ shear modulus [28], the following equation can be derived for the flow stress of the heterogeneous slip process:

$$\sigma_y(\text{MPa}) \approx 21.6 - 2.85 \times 10^{-2}T + 1.96 \times 10^{-5}T^2 \qquad (2)$$

For comparison, a value of the stacking-fault interface free energy can be assumed from the surface free energy of the side faces of the lamellar crystals since the same kinds of $(h\,k\,0)$ crystallographic planes containing the chain stems and therefore having similar van der Waals interactions are involved in both situations. From an analogous point of view, Balta-Calleja *et al.* [29] have previously proposed to account for the plastic work of crystal lamella fragmentation in polyethylene upon indentation by taking into account the free energy increase for the formation of new crystal side surfaces. Considering the value $\gamma \approx 1.5 \times 10^{-2}\,\text{J m}^{-2}$ reported from the study of the crystallization kinetic of melt and solution-crystallized linear polyethylene [30], a tensile flow stress of 15 MPa can be assessed from Equation 1. In spite of the assumptions and approximations of the model, this latter value is identical with that predicted from Equation 2, at room temperature.

3.2. Dislocation dissociation

Although very useful to account for both the mechanical and the structural aspects of the deformation of polyethylenes in the viscoelastic strain range [31–33], the mosaic block structure of the crystalline lamellae is rather an assumption than experimentally shown. The existence of the dislocation-like boundaries that is the keystone of the mosaic block structure has been seriously questioned [34, 35]. An alternative for the origin of localized slip comes from the kinetic restriction to dislocation nucleation. In this connection, the two contributions by Li [20] and Argon [36] pointing out the kinetic aspects of the occurrence of plastic instability through localized slip are worth mentioning. In the previous paper dealing with homogeneous slip [12], we emphasized that decreasing the temperature below that of the crystalline relaxation is likely to slow down both the rate of homogeneous nucleation of the dislocations and the dislocation motion in the crystal.

It is obvious that the dislocation velocity is directly related to the mobility of the 180° chain twist which is the molecular process of the $c/2$ screw dislocation motion. The macroscopic strain rate available through homogeneous crystal slip may therefore become lower than the applied strain rate when the temperature is decreased. In order to overcome this inability of the material to afford a sufficiently high strain rate through homogeneous nucleation of screw dislocations having a $c/2$ Burgers vector, partial dislocations with a shorter Burgers vector may be activated. This is achievable because of 90° chain twists involving a $c/4$ chain translation, such a chain twist having a free energy barrier very close to that of the 180° twist [37]. The benefit is that two $c/4$ partials provide an overall $c/2$ translation at a velocity that a $c/2$ screw dislocation could not afford.

A schematic picture for the dissociation of the screw dislocations is sketched in Fig. 2. The foreground of the picture represents the propagation of two partial screw dislocations after dissociation from a perfect screw dislocation that moves owing to the generation of 180° chain twists involving a $c/2$ translation of the chain stem [12]. The background of the picture shows the resulting situation after exit of the partials from the crystal. The net elementary slip is analogous to that of the single perfect dislocation. However, such partials build up a stacking fault. Fig. 3 shows the top view of the crystal structure about the locus of the dislocation dissociation according to the mechanism proposed above. The 90° twist and the concomitant

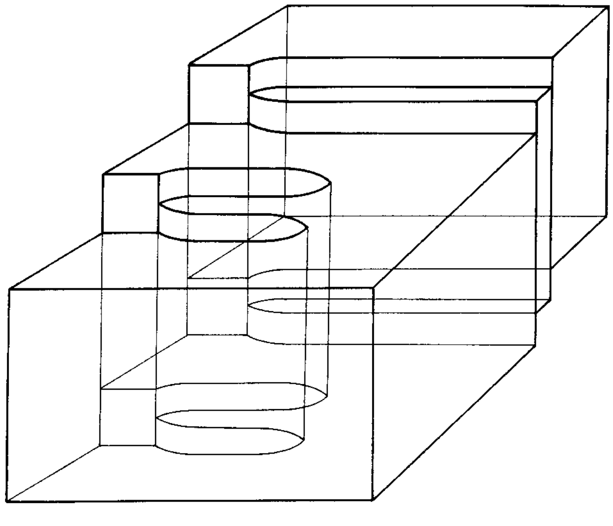

Figure 2 Schematic mechanism of dissociation of a screw dislocation into partials.

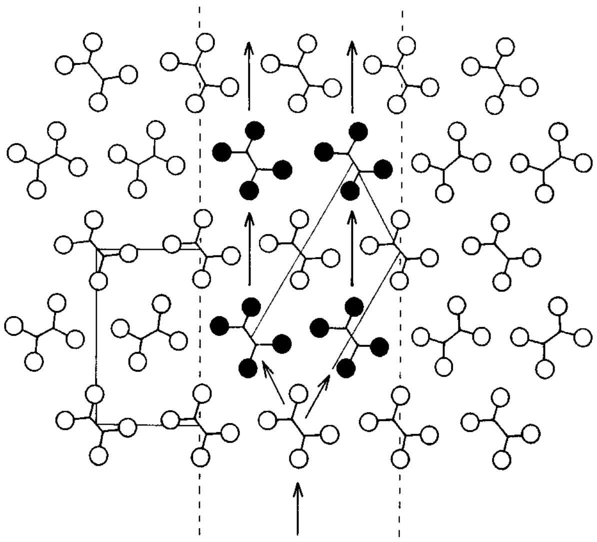

Figure 3 Top view of an orthorhombic polyethylene crystal lattice about the locus of dissociation of a screw dislocation. The black molecules have undergone a 90° rotation; the arrows indicate the slip direction of the partials in their glide plane; the broken lines show the limits of the stacking fault.

$c/4$ translation put the chains lying in the two slip planes of the partials out of the orthorhombic crystallographic register. The stacking fault that remains between the slip planes of the two partials displays a monclinic-like arrangement of the chains since all of them have their backbone plane parallel. Considering that further partials will preferentially nucleate close to the former faulty regions, in order to avoid creation of new defective interfaces and owing to the excess volume in the fault, one may reasonably expect a widening of the stacking fault. Then a martensitic-like phase change is able to occur owing to a coherent transverse crystal shear after the piling up of a sequence of stacking faults, the excess free energy of the fault being the driving force to the process.

Most of the studies dealing with the monoclinic structure of polyethylene agree to ascribe its origin to a martensitic-like transformation involving a coherent transverse shear process [38–41]. However, no molecular mechanism has been proposed for the phase change, notably to account for the rotation of the chain standing at the centre of the orthorhombic unit cell. This rotation can in no way be achieved in a coherent manner. The present model accounts for the rotation of the chains through a step-by-step process, so that the coherent component of the phase transformation is only concerned with the transverse shear process. In addition, our proposal agrees with several studies suggesting the occurrence of the monoclinic structure from a regular sequence of stacking faults [19, 38, 42]. Frank *et al.* [38] and Burney and Groves [43] have also pointed out that phase transformation takes place on the planes undergoing the more intense slip, which is generally parallel to the chain axis.

In a recent paper, Butler *et al.* [44] reported that the onset of the monoclinic structure is concomitant with the phenomenon of cavitation. This is perfectly consistent with our scheme for the phase change pathway since we have already shown that cavitation occurs at the onset of the plastic instability [10], which is itself the consequence of heterogeneous crystal slip.

Stacking faults arising from dislocation dissociation are preferred loci for localized slip owing to their excess volume. So, in the proposed dissociation scheme, localized slip appears as a direct consequence of the kinetic hindrance to homogeneous slip, and the phase change can be viewed as a corollary of the process that plays the role of a probe for its occurrence. The model of corrugated surface slip of Section 3.1 perfectly fits this peculiar stacking-fault scheme. Also, the surface energies computed by Geary and Bacon [45] for this kind of stacking fault in orthorhombic polyethylene fall in the range $(1.0\text{–}1.7)\times 10^{-2}\,\mathrm{J\,m^{-2}}$, which is in excellent agreement with the value $\gamma \approx 1.5\times 10^{-2}\,\mathrm{J\,m^{-2}}$ taken in Section 3.1.

4. Results and discussion

4.1. Stress–strain behaviour

The true stress–true strain curves of copolymer A that have been reported in the previous paper [12] show that plastic instability may occur either at the onset of the plastic flow, namely, at $T_{\mathrm{d}} = 20\,^{\circ}\mathrm{C}$, or after a homogeneous plastic deformation stage, giving rise to a second yield point at $T_{\mathrm{d}} = 80\,^{\circ}\mathrm{C}$. The first situation is when homogeneous crystal slip is prohibited for dislocation kinetic reasons, as discussed previously. Additional evidence for this is given in Fig. 4 which shows the effect of strain rate on the yield behaviour of copolymer B. For a constant draw temperature $T_{\mathrm{d}} = 20\,^{\circ}\mathrm{C}$, two yield points occur at a cross-head speed of $0.05\,\mathrm{mm\,min^{-1}}$, as indicated by the arrows. However, increasing the cross-head speed makes the stage of homogeneous plastic deformation gradually disappear. The second case of occurrence of plastic instability results from the exhaustion of homogeneous crystal slip due to the chain fold extension. In this case, heterogeneous slip proceeds at a strain level that depends little on the copolymer and on the drawing conditions. For instance, Fig. 5 shows the occurrence of a second yield point at the strain $\varepsilon \approx 0.8$ for copolymer B at $T_{\mathrm{d}} = 40\,^{\circ}\mathrm{C}$ for a cross-head speed of

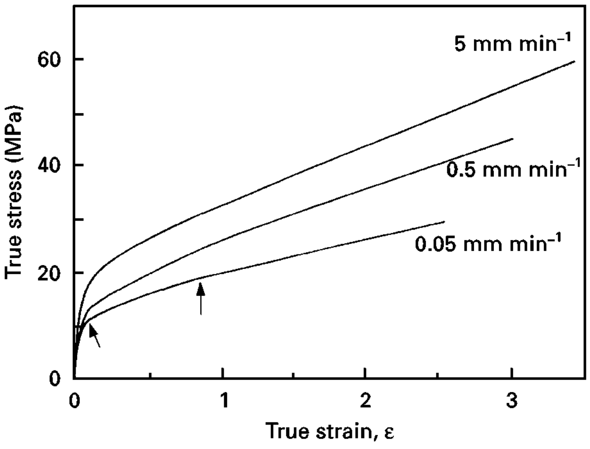

Figure 4 True stress–true strain curves of copolymer B at $T_{\mathrm{d}} = 20\,^{\circ}\mathrm{C}$ for three cross-head speeds.

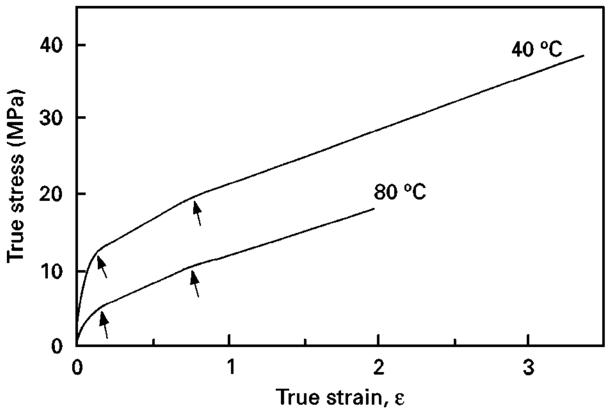

Figure 5 True stress–true strain curves of copolymer B at $T_d = 40\,^{\circ}\mathrm{C}$ for a cross-head speed of $5\,\mathrm{mm\,min^{-1}}$ and at $T_d = 80\,^{\circ}\mathrm{C}$ for a cross-head speed of $0.05\,\mathrm{mm\,min^{-1}}$.

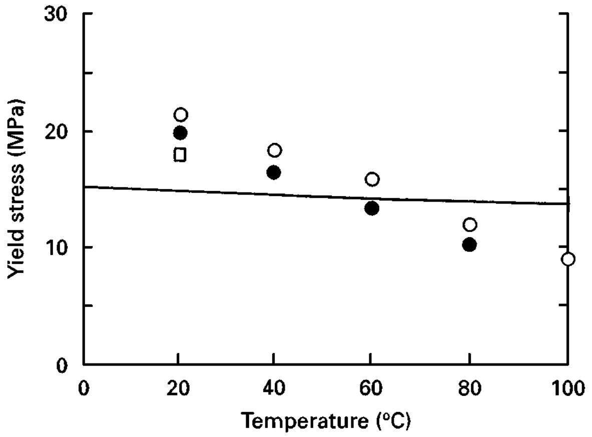

Figure 6 Yield stress versus temperature for the plastic instability for the three copolymers compared with the predicted curve for heterogeneous crystal slip according to Equation 2. (○), copolymer A; (●), copolymer B; (□), copolymer C.

$5\,\mathrm{mm\,min^{-1}}$, and also at $T_d = 80^{\circ}\mathrm{C}$ for a cross-head speed of $0.05\,\mathrm{mm\,min^{-1}}$. This suggests a topological origin for the limit to the homogeneous slip and supports the assumption of strain hardening due to a network effect [11].

Fig. 6 shows the variation with temperature in the true yield stress data for the plastic instability of the three copolymers compared with the theoretical prediction for heterogeneous crystal slip. The fitting is not so good because the model is only a first approximation. The temperature dependence is somewhat stronger for the experimental data, but the order of magnitude of the predicted yield stress is quite good. The more important fact is that the experimental yield stress is not sensitive to the crystallinity of the copolymer, over the whole temperature range. This is one of the main characteristics of the proposed model for the heterogeneous crystal slip to be crystallinity independent, compared with the homogeneous slip [12], in addition to its lower temperature dependence.

4.2. Stress-induced phase change

The WAXS patterns of copolymers A and C at the early stage of plastic deformation are reported in Fig. 7. The two copolymers display the same orientational trend, i.e., quick rotation of the *a* axis in the equatorial plane and of the *b* axis in a preferred diagonal direction, indicating that the same kinds of slip plane are activated. However, the stress-induced phase change that is revealed by the appearance of the innermost (0 0 1) reflection of the monoclinic crystalline modification provides evidence of significant differences in the deformation routes of the two copolymers. In the case of copolymer A, the WAXS patterns in Fig. 7a and b show a clear coincidence of the $(0\,0\,1)_{\mathrm{mono}}$ reflection with the $(1\,1\,0)_{\mathrm{ortho}}$ reflection, for strains $\varepsilon = 1.0$ and $\varepsilon = 2.0$. In contrast, the WAXS patterns in Fig. 7c and d show a coincidence of the $(0\,0\,1)_{\mathrm{mono}}$ reflection with the $(2\,0\,0)_{\mathrm{ortho}}$ reflection for copolymer B at the strains $\varepsilon = 0.4$ and $\varepsilon = 1.6$, respectively. According to Seto *et al.* [39], three types of correspondence of the transformed monoclinic form with the parent orthorhombic form may be predicted, as shown in Fig. 8. The case of copolymer A corresponds to type 1 transformation which is the most favourable owing to the least chain rearrangement. The case of copolymer C corresponds to type 3 transformation, which is energetically much less favourable than the other two types and has never been reported previously.

It is worth mentioning that the lower strain values for the patterns recorded from copolymer C do not mean that the phase change occurs at an earlier stage of plastic deformation, compared with copolymer A which has been claimed to be very prone to localized crystal slip. This is just relevant to a better trend of copolymer C for preferred orientation of the chain axis oblique to the draw direction. Indeed, the greater amount or rubbery amorphous phase allows faster rotation, and therefore orientation, of the crystals towards the direction of maximum resolved shear stress on the preferred slip system. This latter turns out to be (0 1 0)[0 0 1], according to the orientational trend of the *a* and *b* axes [10], despite the fact that (1 0 0)[0 0 1] should be more favourable owing to a lower critical shear stress [16]. The reason lies in the fact that, owing to the large extent of the crystal lamellae in the *b*-axis direction, the (0 1 0)[0 0 1] slip through the width of the lamellae is easier to activate than longitudinal (1 0 0) [0 0 1] slip. This conclusion, from experimental observations, which gives a prime role to the crystal shape in the build-up of the preferred active crystal slip is somewhat different from that of Galeski *et al.* [17] who concluded that the activation of the energetically more favourable crystal slip governs the processes of crystal rotation.

4.3. Chain topology

Considering that the orientational trend of the orthorhombic lattice is roughly the same for the two copoloymers A and C, it is doubtful whether the main slip system could be different. So we suspect that the chain-folding topology plays a part in the mode of coincidence of the two crystal lattices, during the course of the phase change that we suspect to be thermodynamically driven (see Section 3.2). Indeed, it

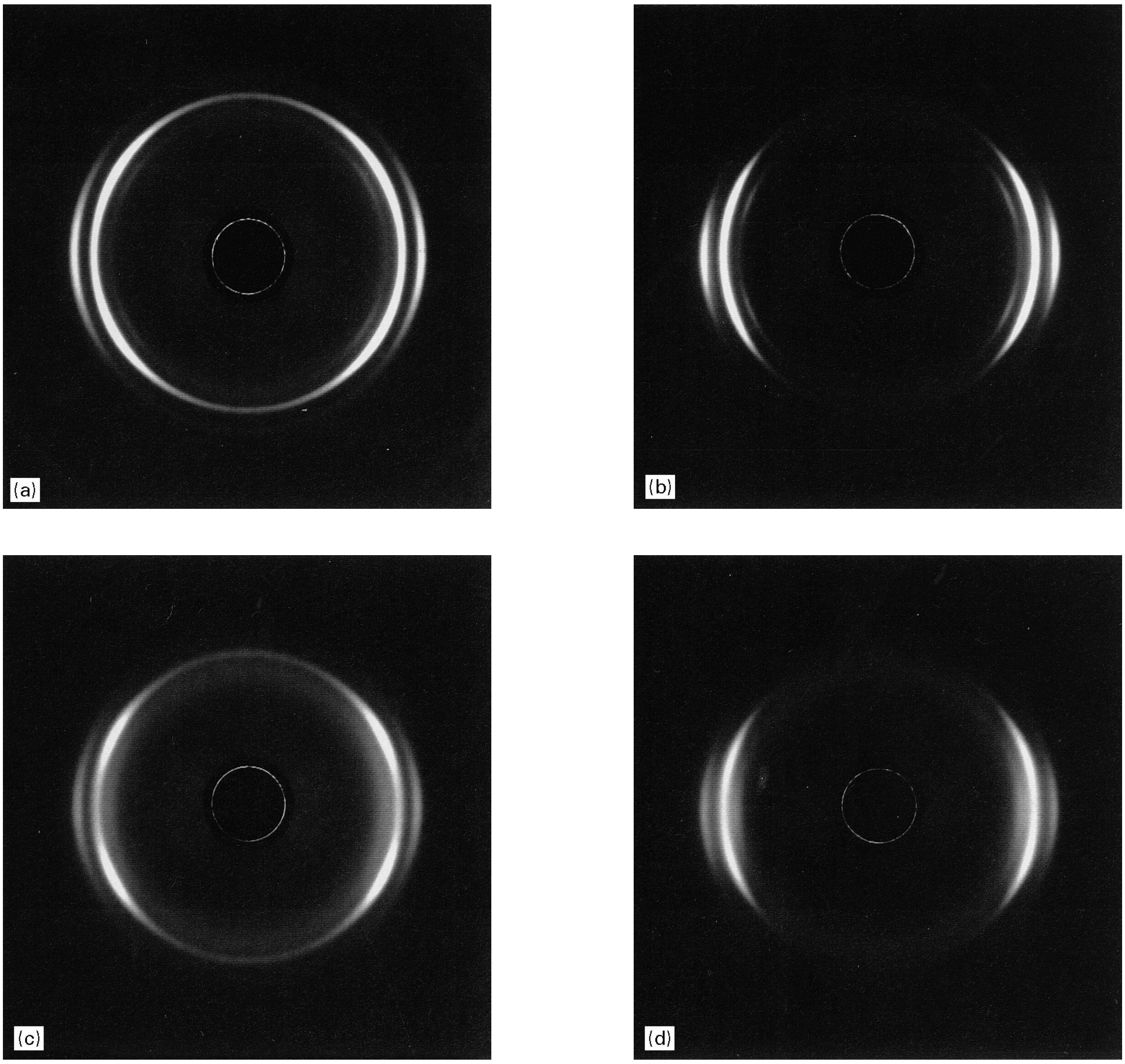

Figure 7 WAXS patterns for various true strains at $T_d = 20\,^\circ C$: (a) copolymer A, $\varepsilon = 1.0$; (b) copolymer A, $\varepsilon = 2.0$; (c) copolymer C, $\varepsilon = 0.4$; (d) copolymer C, $\varepsilon = 1.6$.

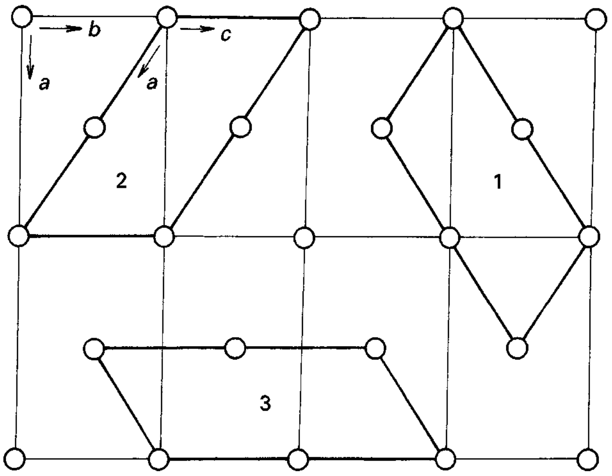

Figure 8 Three types of correspondence of the orthorhombic and monoclinic crystal lattices of polyethylene in the basal plane after Seto *et al.* [39]. The open circles indicate the chain positions irrespective of the orientation of the backbone plane.

has been experimentally demonstrated by Allan and Bevis [40] that the orientation of the principal stress with respect to the chain-folding planes in polyethylene single crystals may influence the coherent shear mechanism of the martensitic transformation. Thereupon, considering that the chain topology in ethylene copolymers changes from a regular chain-folded macroconformation to a fringed-micelle macroconformation, as their ability for crystallization decreases with increasing co-unit concentration [46, 47], different types of coherent shear can be expected for the two copolymers. On the one hand, for the regular chain-folded macroconformation that should take place along the (2 0 0) planes [48] in the case of high-crystallinity copolymer A, (3 1 0) transverse slip involving the least chain displacement [39] can operate without building up significant surface stresses since it is almost parallel to the main folding planes (see Fig. 3). This would involve a type 1 transformation (Fig. 8) which is consistent with the correspondence of the $(0\,0\,1)_{\text{mono}}$ and $(1\,1\,0)_{\text{ortho}}$ reflections observed above. On the other hand, for the fringed-micelle macroconformation that is likely to prevail in the melt-crystallized low-density copolymer C, any kind of transverse slip that is able to bring about a coherent shear of the orthorhombic crystal lattice will build up surface stresses parallel to the slip direction. The operative slip system will therefore be the system involving the least stresses, but no definite crystal slip can be proposed to account for the phase transformation of type 3 that occurs in copolymer C.

5. Concluding remarks

The heterogeneous plastic deformation of ethylene copolymers is described in the framework of a heterogeneous crystal slip process due to hindrance to the nucleation of screw dislocations. The two main obstacles are the kinetic restrictions due to thermal activation and the exhaustion due to chain-fold extension. The final stage of the heterogeneous crystal slip is the crystal block separation which results in the fibrillar transformation. The unfolding of the chains that bridge the two blocks about the localized slip region involves low strain hardening compared with that due to the chain fold extension accompanying the homogeneous crystal slip. Competition with homogeneous slip comes, on the one hand, from the strain-hardening behaviour and, on the other hand, from the different dependences on temperature and crystal thickness of the yield stress associated with the two models.

A mechanism of dissociation of screw dislocations into partials is proposed when the thermally activated rate of nucleation and propagation cannot fit the applied strain rate. The stacking fault that builds up in the orthorhombic crystal lattice, between the partials, is likely to turn into the monoclinic lattice because of coherent transverse shear. The different ways of correspondence of the two crystal lattices in high crystallinity and low-crystallinity copolymers are tentatively ascribed to the difference in the chain folding topology.

Acknowledgements

The authors would like to acknowledge Professor B. Escaig for helpful discussions on the mechanics of dislocations and for encouragement in the achievement of this work.

References

1. H. OHTA, *Polym. Engng Sci.* **23** (1983) 697.
2. P. J. LEMSTRA and R. KIRSCHBAUM, *Polymer* **26** (1985) 1372.
3. G. MEINEL and A. PETERLIN, *J. Polym. Sci., Polym. Phys. Edn* **9** (1971) 67.
4. C. G'SELL, N. A. ALY-HELAL and J. J. JONAS, *J. Mater. Sci.* **18** (1983) 1731.
5. C. G'SELL, S. BONI and S. SHRIVASTAVA, *ibid.* **18** (1983) 903.
6. Z. BARTCZAK, A. S. ARGON and R. E. COHEN, *Polymer* **35** (1994) 3427.
7. P. I. VINCENT, *ibid.* **1** (1960) 7.
8. C. G'SELL, A. MARQUEZ-LUCERO, P. GILORMINI and J. J. JONAS, *Acta Metall.* **33** (1985) 759.
9. I. M. WARD, "Mechanical Properties of Solid Polymers" (Wiley–Interscience, New York, 1985) Chap. 11.
10. V. GAUCHER-MIRI, P. FRANÇOIS and R. SÉGUÉLA, *J. Polym. Sci., Polym. Phys. Edn* **34** (1996) 1113.
11. V. GAUCHER-MIRI and R. SÉGUÉLA, *Macromolecules* **30** (1997) 1158.
12. R. SÉGUÉLA, V. GAUCHER-MIRI and S. ELKOUN, *J. Mater. Sci.* **33** (1997) 1273.
13. P. FRANÇOIS, V. GAUCHER and R. SÉGUÉLA, *J. Phys., Condens. Matter* **6** (1994) 8959.
14. A. PETERLIN, *Colloid Polym. Sci.* **265** (1987) 265.
15. J. SCHULTZ, "Polymer Materials Science" (Prentice-Hall Englewood Cliffs, NJ, 1974) pp. 499–501.
16. P. B. BOWDEN and R. J. YOUNG, *J. Mater. Sci.* **9** (1974) 2034.
17. A. GALESKI, Z. BARTCZAK, A. S. ARGON and R. E. COHEN, *Macromolecules* **25** (1992) 5705.
18. R. HOSEMANN, W. WILKE and F.- J. BALTA-CALLEJA, *Acta Crystallogr.* **21** (1966) 118.
19. P. PREDECKI and W. O. STATTON, *J. Appl. Phys.* **38** (1967) 4140.
20. J. C. M. LI, "Metallic Glasses" (American Society for Metals, Metals Park, OH, 1978) Chap. 9.
21. M. HEINK, K.- D. HÄBERLE and W. WILKE, *Colloid Polym. Sci.* **269** (1991) 675.
22. M. TAKAYANAGI and T. KAJIYAMA, *J. Macromol. Sci. Phys.* **138** (1973) 1.
23. A. PETERLIN, *Colloid Polym. Sci.* **253** (1975) 809.
24. B. ESCAIG, *Polym. Engng Sci.* **24** (1984) 737.
25. J. FRIEDEL, in "Alliages et métaux amorphes" , 21 ème Colloque de Métallurgie (Institut National des Sciences et Techniques Nucléaires, Saclay, Gif-sur-Yvette) pp. 59–96.
26. A. H. COTTRELL, "The Mechanical Properties of Matter" (Wiley, New York, 1964) pp. 264–302.
27. B. WUNDERLICH, "Macromolecular Physics: Crystal Structure, Morphology, Defects", Vol. 1 (Academic Press, New York, 1973) Chap. 4.
28. R. L. Mc CULLOUGH and J. M. PETERSON, *J. Appl. Phys.* **44** (1973) 1224.
29. F. J. BALTA-CALLEJA, J. MARTINEZ SALAZAR, H. CACKOVIC and J. LOBODA-CACKOVIC, *J. Mater. Sci.* **16** (1981) 739.
30. J. D. HOFFMAN, G. T. DAVIS and J. I. LAURITZEN Jr, in "Treatise on Solid State Chemistry: Crystalline and Non-crystaline Solids", Vol. 3, edited by N. B. Hannay (Plenum, New York, 1976) Chap. 7.
31. T. KAJIYAMA, T. OKADA, A. SAKODA and M. TAKAYANAGI, *J. Macromol. Sci., Phys. B* **7** (1973) 583.
32. A. TANAKA, E. P. CHANG, B. DELF, I. KIMURA and R. S. STEIN, *J. Polym. Sci., Polym. Phys. Edn* **11** (1973) 1891.
33. S. SUEHIRO, T. YAMADA, H. INAGAKI, T. KYU, S. NOMURA and H. KAWAI, *ibid.* **17** (1979) 763.
34. E. L. THOMAS, S. SASS and E. J. KRAMER, *ibid.* **12** (1974) 1015.
35. I. R. HARRISON, A. KELLER, D. M. SADLER and E. L. THOMAS, *Polymer* **17** (1976) 737.
36. A. S. ARGON, "Inhomogeneity of Plastic Deformation" (American Society for Metals, Metals Park, OH, 1973) pp. 161–189.
37. D. H. RENEKER and J. MAZUR, *Polymer* **24** (1983) 1387.
38. F. C. FRANK, A. KELLER and A. O'CONNOR, *Phil. Mag.* **3** (1958) 64.
39. T. SETO, T. HARA and K. TANAKA, *Jpn. J. Appl. Phys.* **7** (1968) 31.
40. P. ALLAN and M. BEVIS, *Proc. R. Soc. A* **341** (1974) 75.
41. R. J. YOUNG and P. B. BOWDEN, *Phil. Mag.* **29** (1974) 1061.
42. V. F. HOLLAND, *J. Appl. Phys.* **35** (1964) 3235.
43. S. G. BURNEY and G. W. GROVES, *J. Mater. Sci.* **13** (1978) 639.
44. M. F. BUTLER, A. M. DONALD, W. BRAS, G. R. MANT, G. E. DERBYSHIRE and A. J. RYAN, *Macromolecules* **28** (1995) 6383.
45. N. A. GEARY and D. J. BACON, *J. Mater. Sci.* **18** (1983) 864.
46. R. SÉGUÉLA and F. RIETSCH, *ibid.* **23** (1988) 415.
47. O. DARRAS and R. SÉGUÉLA, *Polymer* **34** (1993) 2946.
48. B. WUNDERLICH, "Macromolecular Physics: Crystal Structure, Morphology, Defects", Vol. 1 (Academic Press, New York, 1973) Chap. 3.

Received 6 January
and accepted 30 July 1997