Phase partitioning of the chain defects in ethylene–butene copolymers in the framework of the crystalline chain kink model

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The distribution of the co-units between the crystalline and amorphous phases in a series of five ethylene–1-butene copolymers has been studied by means of X-ray diffraction measurements in the framework of Balta-Calleja's model for the crystalline insertion of structural chain defects. This model assumes that the side groups are accommodated at interstitial positions within the crystalline phase owing to 2g1 kinks of the main chain. The defect concentration in the crystalline phase of solution-crystallized samples is shown to be fairly insensitive to the solution concentration. Besides, the determination of the crystalline and amorphous chain defect concentrations in the melt-crystallized copolymers, together with the study of their melting behaviour, allowed us to draw the ethylene-rich side of the poly(ethylene-*co*-butene) phase diagram for normal pressure crystallization. The self-consistency of the present data and the favourable comparison with recent ^{13}C n.m.r. spectroscopic measurements give support to the interstitial kink model. In addition, our results clearly indicate that the solubility of the butene co-units in the crystal is governed by thermodynamic equilibrium.

(Keywords: ethylene–butene copolymers; crystalline defects; chain kink)

INTRODUCTION

The problem of determining the co-unit partitioning in crystalline copolymers has often been tackled by removing the non-crystallizable co-units from the solid materials by an acidic-oxidation treatment which preferentially dissolves the amorphous phase[1–7]. Indeed, spectroscopic measurements of the copolymer composition before and after the acidic treatment give the overall and crystalline co-unit concentrations, respectively, in the raw material. However, it has been shown that the acidic attack can remove co-units from inside the crystals. This has been taken as evidence that co-units included in the crystalline phase form amorphous defects, but this makes the data irrelevant as concerns the true values of the crystalline and amorphous concentrations of the co-units.

Wide-angle X-ray diffraction has proved to be very sensitive to slight crystallographic changes due to structural or conformational chain defects. Many experiments performed on ethylene copolymers have shown lattice expansion effects that have been unanimously ascribed to the partial inclusion of the co-unit side branch in the crystal[8–16]. Because bulky side branches have a lower effect on the average unit cell expansion than methyl, hydroxyl or carbonyl groups, it has also been concluded that the degree of co-unit inclusion decreases with the side branch bulkiness (see for instance ref. 13 and references cited therein). However, the lack of information about the intrinsic distortion introduced by a side branch within the unit cell has prevented any attempt to determine the rate of inclusion of the co-units within the crystalline phase.

Balta-Calleja and co-workers[15,16] have proposed a model of 2g1 kinks involving *gtg'* conformational defects of the main chain to account for the crystalline inclusion of any kind of structural chain defects, in the case of polyethylene and related copolymers. This assumption is based on the fact that a *gtg'* conformational defect is accompanied by an expansion of the polyethylene crystal unit cell which allows interstitial inclusion of a side group dangling from the main chain. Besides, the 2g1 kinks are by far the most thermodynamically stable conformational defects of a methylene chain.

We have discussed the steric implications of this structural model in a previous paper[17] and have pointed out that short side branches, such as methyl groups, are likely to enter the polyethylene crystal lattice at interstitial positions afforded through 2g1 kinks of the main chain giving rise to isomorphism, according to the current terminology[13]. However, bulkier groups should be either rejected in the amorphous phase or eventually accommodated in the crystal at substitutional positions[18] involving much less probable chain jogs. Ethyl side groups are at the boundary between isomorphism and pure polyethylene crystal phase formation.

One of the major interests of this model relies on the knowledge of the intrinsic value of the unit cell expansion due to an isolated 2g1 kink. Indeed, previous calculations

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of the more stable arrangement of the neighbouring chains about a kinked chain have been performed by Pechhold and co-workers[19,20] from the values of the elastic constants in a polyethylene crystal lattice. This is a fundamental point of Balta-Calleja's model, which makes it possible to determine the concentration of the structural chain defects included in the crystalline phase of ethylene-based polymers.

The present work is concerned with a series of five ethylene–1-butene copolymers and a homopolymer crystallized from the melt or from decalin solutions of various concentrations. The assessment of the co-unit concentrations in the crystalline phase and consequently in the amorphous phase gives the co-unit partitioning as a function of the copolymer overall co-unit concentration. Combining these results with melting temperature data obtained from scanning calorimetry measurements allowed us to draw the ethylene-rich side of the poly(ethylene-*co*-butene) phase diagram.

THE CHAIN KINK MODEL

The 2g1 chain kink model proposed by Balta-Calleja and co-workers[15,16] to account for the inclusion of structural chain defects in the crystalline phase of polyethylenes and related polymers is sketched in *Figure 1*. The two methylene groups in the centre of the unit cell are in a *trans* conformation, which is not in crystallographic register with respect to the surrounding chains because of the two *gauche* conformations of the *gtg'* sequence characteristic of the kink. The model is borrowed from previous studies by Pechhold and co-workers[19,20] which showed that such a conformational defect enforces a unit cell expansion $\Delta V \approx 60$ Å^3, i.e. about 2.6 times the volume occupied by a methylene unit in the crystal[21]. This is intuitively large enough to accommodate methyl or ethyl groups at interstitial positions in the crystal. In this connection, it is worth mentioning that in the case of ethylene–vinyl chloride copolymers the chlorine side groups, which have a van der Waals volume close to that of a methyl group, have been shown to cause a conformational disturbance over two carbon atoms of the main chain in the crystal[22], which is perfectly consistent with a 2g1 kink.

It is obvious that side branches larger than ethyl groups cannot fit the place afforded through a 2g1 kink and should prefer substitutional positions that do not involve unit cell expansion[17,23]. Experimental support for this assumption is provided by Vonk[12] for ethylene–vinyl acetate and ethylene–acrylic copolymers, and by Cutler *et al.*[5] and Balta-Calleja and Hoseman[24] in the case of high-pressure branched polyethylene. The model is, however, perfectly suitable for ethylene–1-butene copolymers, with which the present work is concerned.

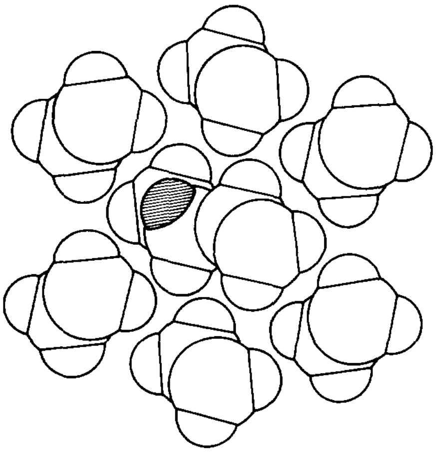

Figure 1 Sketch of a 2g1 kink in a polyethylene crystal lattice. The shaded proton shows the position at which a side group can be accommodated as an interstitial crystalline defect

The concentration of chain defects included in the crystal, ε_c, expressed as the number of ethyl side groups per methylene group of the main chain in the crystal, is given by the relation[15,16]:

$$\varepsilon_c = \frac{V - V_0}{4\Delta V} \qquad (1)$$

where V and V_0 are the average unit cell volumes of the sample and of a linear polyethylene having no structural chain defects, respectively, and the number 4 represents the number of methylene groups in the unit cell. The reference unit cell volume, V_0, should be that of a crystal having a concentration of kinks in thermodynamic equilibrium in order that the calculations based on relation (1) only account for the concentration of kinks due to side branch inclusion in the copolymer crystals. The average concentration of structural chain defects which remain in the amorphous phase, ε_a, is given by:

$$\varepsilon_a = \frac{\varepsilon - \phi_c \varepsilon_c}{1 - \phi_c} \qquad (2)$$

where ε is the overall structural defect concentration in the polymer, i.e. the total number of ethyl side groups per methylene unit in the main chain, and ϕ_c is the volume fraction crystallinity. The latter can be derived from the weight fraction crystallinity, X_c, through the following equation

$$\phi_c = X_c \rho / \rho_c \qquad (3)$$

ρ_c and ρ being the crystalline and the overall densities of the material, respectively. The crystalline density is assessed from:

$$\rho_c = \frac{4(M_{CH_2} + \varepsilon_c M_{C_2H_5})}{V N_a} \qquad (4)$$

where N_a is the Avogadro number, 4 represents the number of methylene groups in the unit cell, M_{CH_2} and $M_{C_2H_5}$ are the molar weights of a methylene group and an ethyl group, respectively.

EXPERIMENTAL

Sample characterization and preparation

The six polymers studied were a homopolyethylene (PE-1) and five ethylene–1-butene copolymers (PE-2–PE-6) having nearly equal molar weights but various concentrations of co-units. *Table 1* shows the molecular characteristics of the polymers determined previously[25]. The physical characteristics given in *Table 1* refer to the as-moulded polymers. For the purpose of mechanical investigations performed in parallel, the materials were cast into sheets 2 mm thick by means of an injection-moulding device described elsewhere[26]. The molten polymers, as well as the decalin solutions of various concentrations, were moulded at temperatures between 190 and 150°C, depending on the melting temperature

Table 1 Weight-average, M_w, and number-average, M_n, molar weights, density, ρ, melting enthalpy, ΔH_f, and total ethyl group concentration, ε, of the polymers studied

Sample	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	ρ (g cm^{-3})	ΔH_f (J g^{-1})	ε(ethyl/CH$_2$, %)
PE-1	135	15	0.9600 (0.9770)[a]	215 (246)[a]	virtually nil
PE-2	157	30	0.9500	200	0.4_0
PE-3	178	19	0.9430	180	0.7_0
PE-4	136	31	0.9315	159	1.3_5
PE-5	140	29	0.9220	125	2.2_5
PE-6	146	27	0.9100	102	3.8_0

[a] Density and melting enthalpy values for the isothermally crystallized PE-1 sample

and the dilution of the polymers. The materials were crystallized by plunging the mould into water at room temperature. The cooling rate in the mould was about −40°C min^{-1}. In the moulding of polymer solutions, the swollen gels resulting from the crystallization were dried under vacuum at room temperature for 3 days after extraction of the solvent for 24 h in a methanol bath.

X-ray diffraction

The wide-angle X-ray scattering experiments in transmission were performed photographically on a flat film goniometer, using the nickel-filtered CuKα radiation of a Siemens X-ray tube operated at 20 mA and 40 kV. A graphite powder was used as an internal reference for calibrating the X-ray diffraction patterns. As suggested by Preedy[14], the powder was deposited onto the surface of the samples in order to avoid nucleation effects during crystallization within the bulk samples, the crystal spacing calculations being subsequently corrected for the thickness of the samples. The relatively large thickness of the sample slices cut from the cast sheets, about 0.8 mm, was chosen in order to reduce the influence of the plastic defects introduced by the cutting operation. The characteristic spacing of the graphite reference, $d_{(002)} = 3.374_7$ Å, was determined from a very thin powder layer using a high resolution goniometer having an angular resolution of 0.5′. The diffraction patterns of the samples were scanned with an Enraf-Nonius microdensitometer giving a spacing measurement accuracy of 5×10^{-4} Å. The volume of the orthorhombic unit cell was assessed from the (110) and (200) spacings, assuming a constant value $c = 2.54_6$ Å for the crystallographic parameter parallel to the chain axis[13]. Indeed, despite some disagreements between literature data, the c parameter is affected very little by defect inclusion[27]. The equilibrium volume of the unit cell, V_0, was determined from sample PE-1 isothermally crystallized at 125°C. This polymer contains virtually no side branches, so that its unit cell volume only takes into account the 2gl kinks at equilibrium in the crystal.

Thermal behaviour

Differential scanning calorimetry (d.s.c.) measurements were performed on a Perkin–Elmer DSC-7 Delta apparatus. The temperature and the heat flow scales were calibrated from the melting of high purity indium and zinc samples. The weight of the samples was about 5 mg. A 10°C min^{-1} scanning rate proved to be fast enough to avoid recrystallization effects during the heating scan and slow enough to reduce the melting delay due to thermal inertia[28]. The crystal weight fraction of the samples, X_c, was determined from the ratio of the melting enthalpy of the samples to that of a perfect and infinitely large polyethylene crystal, $\Delta H_f^\circ = 290$ J g^{-1}, at the equilibrium temperature of fusion $T_f^\circ = 140$°C[29]. The baseline under the melting endotherm was drawn linearly between the onset and the end of the melting process, as shown in the d.s.c. curves of *Figure 2*. The accuracy of the measurements is about 5 J g^{-1}. It is worth noting that the broadening of the melting endotherm, notably of the main melting peak which exhibits two maxima in the case of sample PE-6, is due to a well-known chemical heterogeneity of the copolymers that involves a broad crystal thickness distribution[30,31]. Thereby, when a single maximum does not appear clearly, the temperature of the most abundant crystal family is taken at the middle of the main melting peak. The temperature of the end of melting is taken at the intersection of the baseline with the tangent to the d.s.c. signal drop of the melting endotherm.

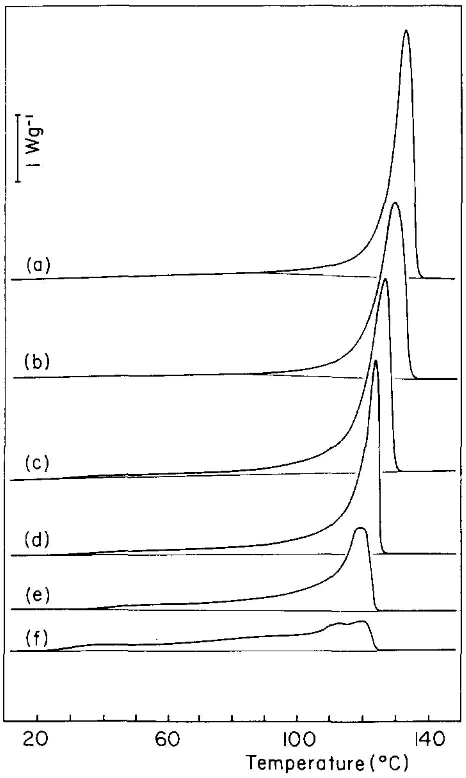

Figure 2 D.s.c. melting curves of the six melt-crystallized polymers: (a) PE-1, (b) PE-2, (c) PE-3, (d) PE-4, (e) PE-5 and (f) PE-6

Density measurements

The densities of the materials were determined at 23°C by the flotation technique in a water–isopropanol gradient column made according to the ASTM method D1505-68[21]. Calibration was made with 10 hollow glass beads having a density accuracy of 10^{-4}.

RESULTS

Determination of ε_c and ε_a

Figure 3 shows the unit cell volume of the six polymers as a function of the co-unit content. The steady increase of the unit cell volume is indicative of an increasing solubility of the butene co-units in the crystalline phase of the polymers with the increasing overall concentration of co-units. The fair linearity of the relationship suggests that an equilibrium partitioning of the defects between the crystalline and amorphous phases sets in during the crystallization stage. The crystalline and amorphous concentrations of the co-units, ε_c and ε_a calculated from Balta-Calleja's model according to equation (1) and (2) respectively, are reported in *Table 2*. The much lower values of ε_c compared with ε_a are in full agreement with conclusions drawn from previous work, that ethyl side groups have very little propensity to be accommodated within the crystalline phase of polyethylene (see, for instance, ref. 17 and references cited therein). Besides, the nearly constant ratio $k=\varepsilon_c/\varepsilon_a \approx 0.10$ perfectly supports the previous conclusion of a partitioning of the defects under thermodynamic equilibrium conditions:

$$\text{amorphous defects} \overset{k}{\leftrightarrow} \text{crystalline defects}$$

In the expression of the equilibrium constant, k, the concentrations of the co-unit species can stand for their activities because of the high dilution among the ethylene units.

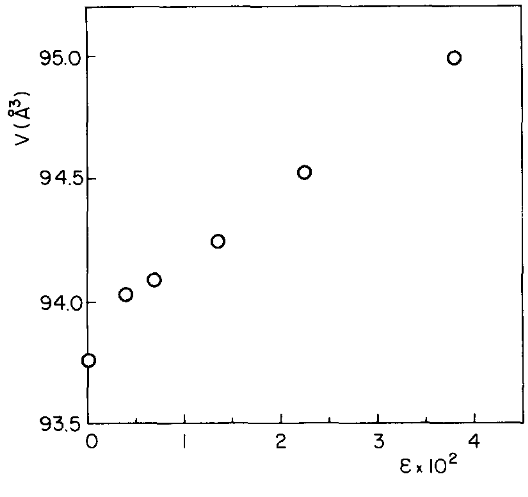

Figure 3 Unit cell volume, V, of the melt-crystallized copolymers as a function of the total ethyl branch concentration per methylene group, ε

Table 2 Crystalline and amorphous defect concentrations, ε_c and ε_a, in the melt-crystallized copolymers

Sample	ε_c (defects/CH$_2$, %)	ε_a (defects/CH$_2$, %)
PE-2	$0.11 \pm 0.01_5$	1.04 ± 0.22
PE-3	$0.13 \pm 0.01_5$	1.62 ± 0.28
PE-4	$0.20 \pm 0.02_0$	2.76 ± 0.50
PE-5	$0.31 \pm 0.02_5$	3.71 ± 0.60
PE-6	$0.51 \pm 0.02_5$	5.56 ± 0.83

Table 3 Crystal defect concentration in the solution-crystallized samples

Polymer	Polymer weight fraction	ε_c (defects/CH$_2$, %)
PE-2	0.20	0.15
	0.50	0.11
	0.70	0.13
	1.00	0.11
PE-6	0.20	0.45
	0.50	0.52
	0.70	0.55
	1.00	0.51

It is worth mentioning that ρ_c values computed from equation (4) for the determination of ε_a are fairly independent of the crystalline defect concentration. The values that fall in the range 1.005–0.991 g cm^{-3} are in fair agreement with the literature data reported for the crystalline density of linear polyethylene[32], indicating that the volume expansion is roughly balanced by the weight increase due to the defect inclusion. In other words, an ethyl group perfectly fits the place afforded through the 2g1 kink and therefore brings additional consistency to the model.

Table 3 shows the ε_c values determined for dried gels of the copolymers PE-2 and PE-6 prepared from decalin solutions as a function of the initial concentration prior to crystallization. The near-invariance of ε_c strongly suggests that the co-unit phase partitioning in a given copolymer depends very little on the crystallization conditions and therefore provides additional support to the conclusion that the partitioning process obeys a thermodynamic equilibrium.

Phase diagram

The poly(ethylene-*co*-butene) phase diagram can be drawn from the knowledge of ε_c and ε_a in consideration of the fact that the ε_c value determined for every copolymer from the peak position of both the (110) and (200) X-ray diffraction rings is concerned with the most abundant crystal population in the crystalline defect distribution. Thus, the corresponding melting point is that of the most abundant crystal population, i.e. the peak temperature of the melting endotherm. The (ε_c, T_f^{peak}) points characteristic of the five copolymers are representative of the solidus line of the phase diagram, while the (ε_a, T_f^{peak}) points determine the liquidus line. Besides, the determination of the temperature of the end of the melting endotherm, T_f^{end}, for the six polymers under investigation, including the PE-1 homopolyethylene, provides additional points for the phase diagram. Since T_f^{end} is the melting temperature of the last crystals (i.e. the thermally more stable ones) for every polymer, the structural chain defect concentration of the corresponding liquid is $\varepsilon_a = \varepsilon$. Therefore, the six ($\varepsilon$, T_f^{end}) points should fall on the liquidus line of the phase diagram. *Figure 4* shows the ethylene-rich side of the eutectic-like poly(ethylene-*co*-butene) phase diagram that can be drawn from the data of the five copolymers and the homopolymer, in the present experimental conditions, i.e. crystallization of the polymers from the melt by cooling at about -40°C min^{-1} and d.s.c. measurements at a heating rate of 10°C min^{-1}. The mole fraction of butene co-units $X_B = 2\varepsilon$ has been used on the abscissa.

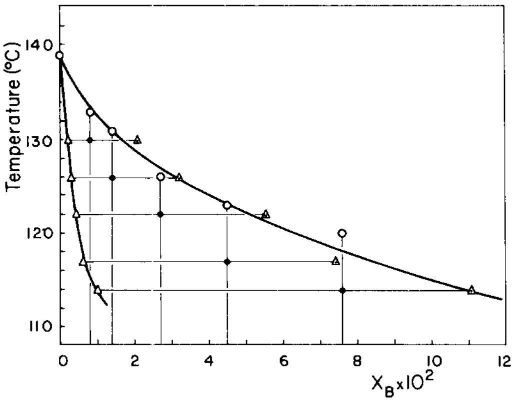

Figure 4 Ethylene-rich side of the poly(ethylene-*co*-butene) phase diagram: solid (Δ) and liquid (▲) in equilibrium at the peak melting temperature for every copolymer; final melting point (○) of the last crystals in equilibrium with a liquid having the chain defect concentration of the overall material ($X_B = 2\varepsilon$ is the butene mole fraction)

DISCUSSION

The good consistency of the (ε, T_f^{end}) and (ε_a, T_f^{peak}) data for the six polymers, which determine the liquidus line of the phase diagram, strongly supports the 2gl kink model of Balta-Calleja for the interstitial inclusion of ethyl branches in the crystal lattice of ethylene–butene copolymers. This kink model, which assumes a *gtg'* conformational defect of the main chain, relies on the high probability that one of the two C–C bonds adjacent to the side group takes a *gauche* conformation because of steric effects, the second *gauche* conformation of the kink being required by the necessity for the distorted chain to set itself back in a parallel position with respect to the neighbouring chains in the crystal[17,19]. If no experimental conclusion can be inferred concerning the substitutional insertion of ethyl groups, it can be pointed out that this process is certainly much less probable than the interstitial one because, despite the reduced local stresses, it requires cooperative contributions of jog defects in the form of deformation lines[12]. This situation is much less favourable than isolated kink defects, on both thermodynamic and statistical grounds.

Howard and Crist[27] have suggested, from X-ray diffraction experiments, that the unit cell expansion with increasing branch content in ethylene–butene copolymers is due mainly to limitation of crystal thickness coupled with surface stresses. However, VanderHart and coworkers[33,34] have recently shown, from ^{13}C n.m.r. spectroscopic measurements on two ethylene–butene random copolymers having 0.54 and 3.4 mol% of butene units (weight fraction crystallinity 0.76 and 0.41, respectively), that the crystalline chain defect concentration is about one-tenth the overall chain defect concentration. This result is in excellent agreement with the present data from the five copolymers, and provides additional support to the assumption of an interstitial inclusion of ethyl side groups, which is the basis of the chain kink model.

The nearly constant value of the ratio $\varepsilon_c/\varepsilon_a$ for the melt-crystallized copolymers, and the near-invariance of ε_c for the dried gels of a given copolymer at various concentrations of the initial solutions, are clear indications that an equilibrium solubility of the chain defects in the crystalline phase has been reached. This is in perfect agreement with previous results from X-ray diffraction[10,34] and ^{13}C n.m.r. spectroscopy[35,36], which indicate that the relative level of branches incorporated into the crystalline phase is independent of the crystallization conditions in the case of methyl and ethyl side groups. Besides, the self-consistent phase diagram drawn from the data of five copolymers and the homopolymer is evidence that the butene units are distributed in the solid and liquid phases under thermodynamic equilibrium conditions during the crystallization stage. It is worth noting that several authors[9,34,37] have previously concluded that methyl branches enter the crystal lattice under equilibrium conditions, while longer branches constitute non-equilibrium crystalline defects. From differential thermal analysis, Bodily and Wunderlich[38] concluded that only very small side groups, such as chlorine, carbonyl and hydroxyl groups, are capable of forming point defects in solid solution with polyethylene. These authors suggested that even methyl branches form non-equilibrium amorphous defects in the crystal. However, the recent solid-state ^{13}C n.m.r. spectroscopic study of Perez and VanderHart[39] strongly suggests that methyl branches do form crystalline defects. It seems that a similar situation even holds for ethyl side groups included in the crystal, although the n.m.r. analysis is much less obvious than for methyls[34]. We believe that the conclusions for a non-equilibrium solubility of the co-units in the crystal are somewhat erroneous because they only rely on the lower capability of accommodation of the bulky side branches compared with the small ones. Indeed, it is well known that binary blends of metals[40], as well as organic compounds such as paraffins[29], exhibit various degrees of mutual solubility in the crystalline state depending on the compatibility of the two species in terms of size, crystalline lattice and specific interactions.

This point has been discussed on theoretical grounds by Wunderlich[41] in a review of the various models that have been proposed to predict the melting behaviour of crystallizable copolymers at thermodynamic equilibrium, for both pure eutectic crystals and mixed crystal solid solutions. The problem of co-crystallization has been tackled by introducing an excess free enthalpy for the incorporation of the comonomer in the crystal lattice of the major component[42,43]. The equilibrium concentration of defects in the crystalline phase, $X_{\mathrm{B,cr}}$, is thus given by the relation:

$$X_{\mathrm{B,cr}} = \frac{(1-X_{\mathrm{A}})\,\mathrm{e}^{-E/RT_{\mathrm{f}}}}{X_{\mathrm{A}}+(1-X_{\mathrm{A}})\,\mathrm{e}^{-E/RT_{\mathrm{f}}}} \tag{5}$$

and the equilibrium temperature of fusion of the copolymer, T_f obeys the equation:

$$1/T_{\mathrm{f}} - 1/T_{\mathrm{f}}^{\circ} = -(R/\Delta H_{\mathrm{f}}^{\circ})\ln[X_{\mathrm{A}} + (1+X_{\mathrm{A}})\,\mathrm{e}^{-E/RT_{\mathrm{f}}}] \tag{6}$$

where T_f° is the equilibrium temperature of fusion of the corresponding homopolymer, X_A is the overall mole fraction of the major component A in the copolymer, E is the excess defect energy, R is the gas constant and ΔH_f° is the enthalpy of fusion of the homopolymer per monomer unit. The solidus line of the phase diagram of *Figure 4* can be fairly well described by relation (5), assuming $E = 8 \pm 2\,\mathrm{kJ\,mol^{-1}}$. This value is significantly higher than those reported for copolymers of L- and DL-lactides and for copolymers of tetrafluoroethylene and hexafluoropropylene[43], but it is relevant to the low solubility of the butene units in the polyethylene crystal lattice and is consistent with our previous conclusion that ethyl groups are hardly accommodated within 2gl kinks[17]. However, using the value for the excess defect energy estimates above, the melting point variation with composition that can be predicted from equation (6) falls well above the experimental liquidus line of the phase diagram. This strong inconsistency is due to the fact that equation (6) holds for infinitely thick crystals, according to the Flory model for the melting of random copolymers with no mixed crystal formation, which has been extended to the case of copolymers forming solid solutions[41]. The present copolymers, which have been crystallized at normal pressure either from the melt or from solution, have finite crystal thicknesses[28] that involve a depression of the melting point with respect to infinitely thick crystals. It is worth mentioning that crystallization at elevated pressure, which is the usual way to obtain chain-extended crystals (otherwise infinitely thick crystals), is likely to bias the equilibrium solubility of the co-units in the crystal because the process enforces the inclusion of the co-units in the crystal at a concentration level equal to the overall co-unit concentration in the copolymer. So, on the one hand, this method cannot provide a phase diagram at thermodynamic equilibrium and, on the other hand, the model is not suited for partial solubility[41].

The very small influence of the crystallization conditions on the solubility of the butene units in the polyethylene crystal lattice of ethylene–butene copolymers is the main factor leading to our conclusion that the phenomenon obeys (or nearly obeys) a thermodynamic equilibrium. This contrasts strongly with the well known crystallization kinetics effects that occur at the scale of the lamellar morphology. The reason may be that the forward and backward rates of inclusion of a chain defect in the crystal, which rule the equilibrium, depend not only on the crystallization rate but also on the molecular mobility in the melt, namely the velocity at which a defect can be pulled from the growth surface to the fold surface along with the stem to which it is attached prior to crystallizing. In this connection, Hoffman *et al.*[44] have pointed out that, except for high supercoolings, the reeling velocity of polyethylene chains from the melt is high compared with the crystallization rate. Under these circumstances, the defect partitioning is allowed to reach equilibrium before substrate completion. In a study dealing with ethylene–vinyl chloride copolymers, Roe and Gieniewski[45] have shown that the amount of chlorine atoms trapped in the crystalline phase depends on the crystallization rate, indicating that the segmental relaxation time scale required for rejection of the co-units is comparable to the crystal growth time scale. This is not in disagreement with the conclusion of the preceding paragraph, but it means that non-equilibrium solid solutions may be formed under drastic crystallization conditions in the case of copolymers with small side branches which exhibit a high solubility in the crystal.

CONCLUSION

The present work shows that the phase partitioning of the co-units in ethylene random copolymers crystallized at normal pressure is governed by thermodynamic equilibrium between the crystal and the amorphous phase, provided that the crystallization rate is not too fast. However, the limit of the solubility of the co-units in the crystal is strongly dependent on the bulkiness of the side group.

The 2gl kink model is perfectly suitable to account for the volume effect of the side group on the solubility of the co-unit in the crystal. As previously pointed out, methyl or smaller side groups can be easily accommodated at the interstitial positions afforded through such kinks. Larger side groups may only enter the crystal at substitutional positions, which are much less probable than interstitial positions on thermodynamic grounds, hence they are preferentially excluded from the crystal. Ethyl side groups just fit the excess volume of the 2gl kink so that the solubility behaviour of ethylene–butene copolymers is intermediate between copolymers that are prone to isomorphism and those that give rise to a pure polyethylene crystal lattice.

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