Surface free energy of the chain-folding crystal faces of ethylene–butene random copolymers

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The determination of the surface free energy of the chain-folding faces of crystals of ethylene–butene random copolymer is performed by fitting the most probable value of the crystal thickness distribution with the average crystal thickness assessed from small-angle X-ray scattering. The surface free energy is the adjustable parameter in the equation of the crystal thickness distribution derived from the Thomson–Gibbs relation for the melting of lamellar crystals of finite thickness. On the one hand, the steady increase of the surface free energy of bulk-crystallized copolymers with increasing co-unit concentration is relevant to a growing disorder in the amorphous overlayer of the lamellar crystals. On the other hand, the decrease of the surface free energy with increasing dilution for a given copolymer crystallized from decalin solutions is an indication of an improved regular chain folding. Both conclusions support previous studies dealing with the mechanical behaviour of ethylene–butene copolymers in relation to co-unit concentration and crystallization conditions.

(Keywords: ethylene copolymers; surface free energy; crystal thickness; chain topology; melting point)

INTRODUCTION

In preceding papers[1,2], we reported the tensile drawing behaviour of ethylene–butene copolymers in relation to the co-unit concentration. The decrease of the drawability together with the reinforcement of the strain-hardening effect with increasing co-unit concentration, i.e. with decreasing crystallinity, was taken as evidence of hindrance to the chain unfolding process. It was stressed that the exclusion of the butene co-units from the crystalline phase is likely to disturb the natural propensity of linear polyethylene chains for regular chain folding and to turn it into random chain folding. This conclusion was in perfect agreement with previous[3–5] reports, which stated that structural chain defects such as branches, co-units or stereo-irregularities can generate fringed-micelle macroconformations at the expense of regular chain-folded macroconformations. However, little experimental support has been provided for this statement.

More recently[6], we reported investigations on solution-crystallized samples of a low-density copolymer that showed significant improvement of drawability and reduction of strain hardening with increasing dilution. This effect was attributed to the build-up of regular chain-folded macroconformations, which result from an easier crystallization mechanism of long-chain molecules in solution. In order to gain a better insight into the real conformational changes involved by modifying the crystallization conditions, we have performed surface free-energy determinations on the ethylene–butene copolymers previously studied, investigating melt-crystallized as well as solution-crystallized samples. Indeed, surface free energy of chain folding in polymer crystals is directly connected with the degree of disorder in the amorphous overlayer[7,8]. So, a growing disorder in the amorphous phase of copolymers due to increasing concentration of non-crystallizable co-units is expected to increase the surface free energy of the crystals grown from the melt. On the other hand, the improvement of regular chain folding with increasing dilution, for a given copolymer crystallized from solution, should reduce the surface free energy of the crystals.

The method involves the determination of the crystal thickness distribution from the melting curve obtained by differential scanning calorimetry (d.s.c.)[9–11], using the Thomson–Gibbs relation for the melting temperature of finite-dimension polymer crystals. As an adjustable parameter, the surface free energy of the chain-folding faces of the crystals was assessed by fitting the most probable crystal thickness of the distribution with the value of the average crystal thickness obtained from the small-angle X-ray scattering (SAXS) long period. According to a similar analysis, Mandelkern and co-workers[12] have reported a slight trend of increasing surface free energy with increasing co-unit content in ethylene copolymers. They also reported a decrease of the surface free energy for single-crystal mats of copolymers grown from dilute solution compared with the bulk-crystallized ones. The present work is an extension to melt-crystallized copolymers covering a wide range of co-unit concentrations and to solution-crystallized copolymers prepared from a wide range of solution concentrations.

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EXPERIMENTAL

The materials under investigation are a series of four ethylene/1-butene copolymers containing various concentrations of co-units. *Table 1* shows the characteristics of these materials. The co-unit concentrations were assessed from the densities of the melt-crystallized samples according to a calibration curve established from literature data[13,14]. The densities were determined in a water–isopropanol gradient column at 23°C. The samples were crystallized by quenching into cold water from the melt or from decalin solution at 160°C. The gels thus formed were dried according to a method described elsewhere[6].

The thermograms were recorded on a Perkin–Elmer DSC-7 analyser using samples of about 5 mg. The temperature and the heat flow scales were calibrated at every heating rate using the melting of high-purity indium and zinc samples. The heating rate of 10°C min^{-1} was chosen as a good compromise between sufficiently high signal and reduced melting delay. This scanning rate also proved to be fast enough to prevent melting–recrystallization effects. Evidence for this is provided from *Figure 1*, which shows the d.s.c. traces, at various heating rates, of a dried gel of copolymer D crystallized from a 0.30 polymer weight fraction solution.

Table 1 Physical characteristics of the polymers

Polymer	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	Density ($\mathrm{g\,cm^{-3}}$)	Co-unit content (mol%)	X_c	L_c (nm)
A	157	30	0.9455	1.2	0.67	17.5
B	136	31	0.9315	2.7	0.55	11.5
C	140	29	0.9220	4.5	0.48	10.5
D	146	27	0.9100	7.6	0.35	10.0

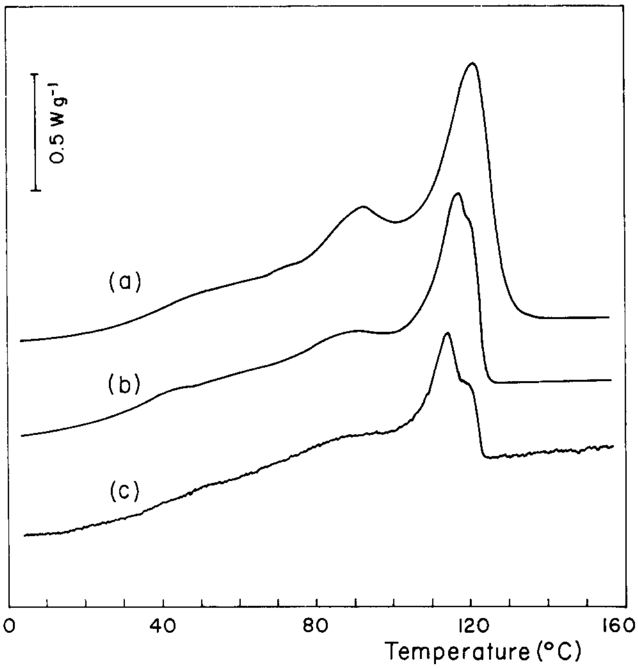

Figure 1 D.s.c. melting curves of a dried gel of copolymer D crystallized from a 0.30 polymer weight fraction solution for various values of the scanning rate (*SR*): (a) $SR = 40$°C min^{-1}, (b) $SR = 10$°C min^{-1} and (c) $SR = 2.5$°C min^{-1}. The heat flow scale bar relates to (b); the sensitivity is 2.5 times lower in (a) and 2.5 times greater in (c)

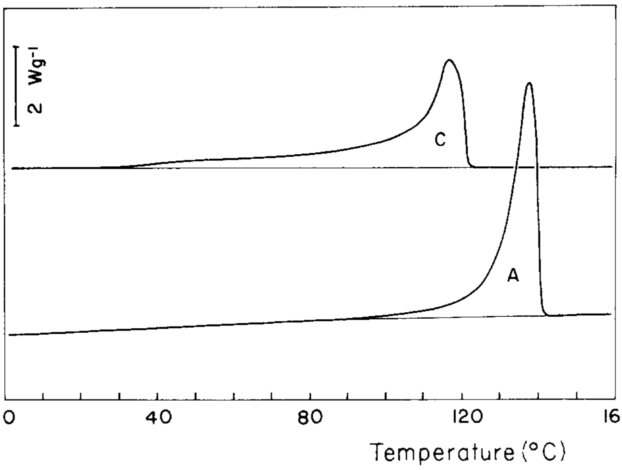

Figure 2 D.s.c. melting curves of the melt-crystallized copolymers A and C

The slight differences in the three d.s.c. traces indicate that a minor melting–recrystallization effect may possibly occur in the low-temperature melting tail, during the heating scan at low scanning rate. This reorganization is indeed of very little importance compared with what can be observed for single-crystal mats[15]. Besides, the slight upward shift and the broadening of the main melting peak are indicative of the thermal inertia of the sample at high scanning rate.

The crystal weight fractions, X_c, have been determined from the ratio of the melting enthalpy of the samples to that of a perfect and infinite polyethylene crystal, $\Delta H_f^\circ = 290\ \mathrm{J\,g^{-1}}$ at the equilibrium temperature of fusion $T_f^\circ = 140$°C. The baseline under the melting endotherm was drawn linearly between the onset and the end of the melting process. The onset of melting, which is highly dependent on the crystallinity of the polymers was determined at the first signs of deviation of the d.s.c. curve from the baseline as indicated in *Figure 2*. No account was taken of the temperature dependence of the melting enthalpy. Indeed, this latter is depressed by about 10% between the thermodynamic melting temperature and room temperature[16], but very little crystalline material is concerned with such a phenomenon.

RESULTS AND DISCUSSION

Determination of the surface free energy

Attempts have been made to assess the crystal thickness distribution from d.s.c. experiments using the Thomson–Gibbs equation and assuming a constant surface free energy for the chain-folding faces of the lamellar crystals[9–11]. Indeed, the general form for the Thomson–Gibbs equation in the case of square crystalline platelets is[17,18]:

$$T_f = T_f^\circ\left(1 - \frac{2\sigma_e}{\Delta H_f^\circ \rho_c L_c} - \frac{2\sigma_s}{\Delta H_f^\circ \rho_c D_c}\right) \qquad (1)$$

where T_f° is the temperature of fusion of an infinite crystal, σ_e and σ_s are the surface free energies per unit area of chain-folding faces and lateral faces, respectively, ΔH_f° is the enthalpy of fusion per unit mass of an infinite crystal, ρ_c is the crystalline density, and L_c and D_c are the thickness and the lateral dimension of the crystals, respectively. In the case of polyethylene the various parameters of equation (1) have the following values: $T_f^\circ = 140°\mathrm{C}$ (see next section), $\Delta H_f^\circ = 290\ \mathrm{J\,g^{-1}}$ (ref. 16) and $\rho_c = 0.997\ \mathrm{g\,cm^{-3}}$ (ref. 19) at room temperature.

It is generally assumed that the crystalline lamellae are much more large than thick, so that equation (1) is often used in its simplified form:

$$T_f = T_f^\circ\left(1 - \frac{2\sigma_e}{\Delta H_f^\circ \rho_c L_c}\right) \tag{2}$$

Alberola *et al.*[11] have shown that the crystal thickness distribution can thus be expressed by the following relation:

$$\frac{1}{M}\frac{\mathrm{d}M}{\mathrm{d}L_c} = \frac{(\mathrm{d}E/\mathrm{d}T)(T_f^\circ - T)^2}{2\sigma_e T_f^\circ} \tag{3}$$

where dM is the mass of crystals having a thickness between L_c and $L_c + \mathrm{d}L_c$ that melt between T and $T + \mathrm{d}T$ with an energy absorption dE.

Instead of assuming a constant surface free energy of the chain-folding faces of the lamellar crystals, equation (3) can be used to estimate the true value of σ_e by fitting the L_c value at the maximum of the distribution curve to the most probable crystal thickness given by small-angle X-ray scattering:

$$L_c = L(\rho/\rho_c)X_c \tag{4}$$

where L is the SAXS intercrystalline long period and ρ the density of the sample.

Melting point of ethylene–butene random copolymers

Studying ethylene–butene copolymers, Mandelkern and co-workers[12] suggested using the T_f° value predicted from Flory's theory of crystallization of random copolymers[20]. This theory only holds for non-crystallizable co-unit copolymers such as ethylene–butene copolymers that exhibit very little propensity to isomorphism. It assumes that crystallizable sequences behave like small molecules so that, at the equilibrium melting point, their chemical potential is the same in the crystal and in the melt. Reference has often been made to this model, but little experimental work has been done to check its relevance. Martuscelli and Pracella[21] have reported thermal and structural data on two ethylene–butene copolymers having 2.2 and 7.3 mol% of co-units. From the plot of melting point at peak as a function of the long period and using relation (2), they derived T_f° values for infinite crystals significantly greater than the values predicted from Flory's theory. Namely, for the copolymer having 7.3 mol% of co-units, an extrapolated value $T_f^\circ = 134°\mathrm{C}$ has been reported compared with a predicted value $T_f^\circ = 127°\mathrm{C}$. However, considering that the Thomsom–Gibbs relation involves the crystal thickness instead of the long period, the data from Martuscelli and Pracella have been replotted in *Figure 3* as a function of the crystal thickness computed from relation (4). Because of the lack of density data, the volume fractions, $\Phi_c = (\rho/\rho_c)X_c$, have been assessed from the crystal weight fractions, X_c, obtained from the melting enthalpy data using the following equation:

$$\Phi_c = \rho_a X_c[\rho_c(1 - X_c) + \rho_a X_c]^{-1} \tag{5}$$

with $\rho_a = 0.855\ \mathrm{cm^{-3}}$ (ref. 19). *Figure 3* provides a value $T_f^\circ = 138°\mathrm{C}$ for the 7.3% butene copolymer, which is greater than the value determined by Martuscelli and Pracella and very close to that of homopolyethylene.

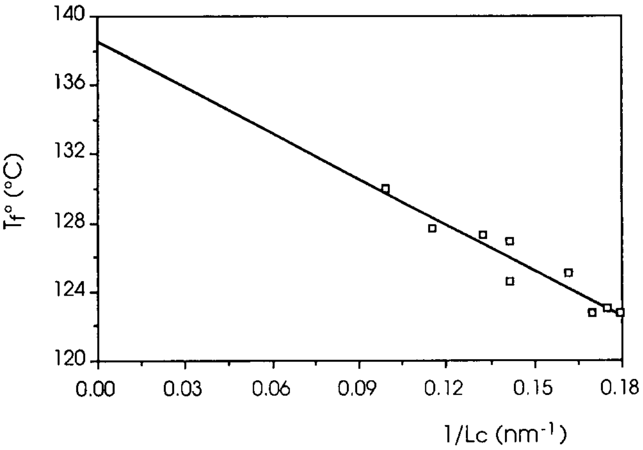

Figure 3 Melting temperature variation as a function of crystal thickness for an ethylene–butene copolymer containing 7.3 mol% of co-units (data from Martuscelli and Pracella[21])

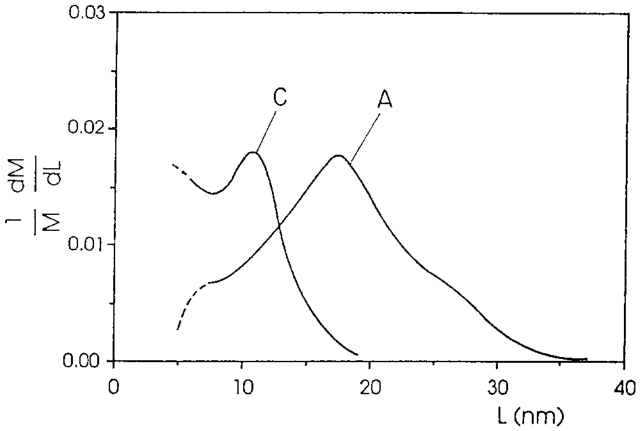

Figure 4 Distribution curves of the crystalline lamellae thickness for the melt-crystallized copolymers A and C (the vertical scale is expanded 10 times in the case of copolymer C)

It is obvious that ethylene–butene copolymers are far from obeying Flory's model and it is therefore quite reasonable to use the value $T_f^\circ = 140°\mathrm{C}$ of homopolyethylene for the calculations of the crystal thickness distributions in our four copolymers.

Melt-crystallized copolymers

Figure 4 shows the distribution curves of crystal thickness for the melt-crystallized copolymers A and C. The low-crystal-thickness side of the distributions cannot be drawn reasonably with the assumption of a constant surface free energy because of the well known effect of segregation of the more co-unit-rich chains[22–24], which crystallize into highly defective crystals having very low melting temperature and higher surface free energy than the average material. This effect is expected to be particularly strong for the low-crystallinity copolymers, which exhibit a very broad low-temperature melting tail in the d.s.c. thermograms[6]. The values of the surface free energy determined by the fitting procedure for each of the four copolymers crystallized from the melt are plotted in *Figure 5* as a function of the co-unit content, using the X_c and L_c values of *Table 1*. The steady increase of σ_e with the butene concentration is an indication of increasing disorder in the amorphous overlayer. This is in perfect agreement with our previous conclusions from mechanical

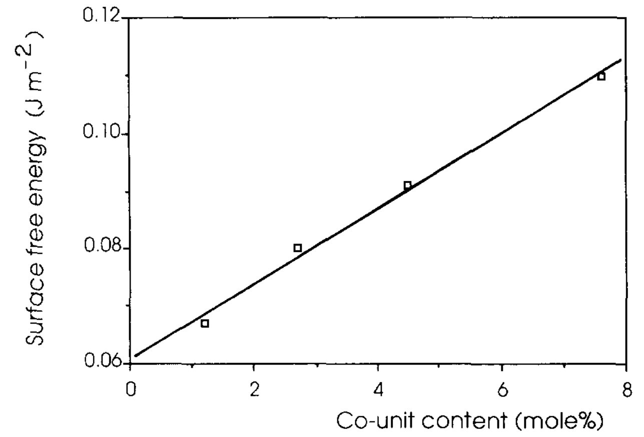

Figure 5 Surface free energy *versus* co-unit concentration for the melt-crystallized copolymers

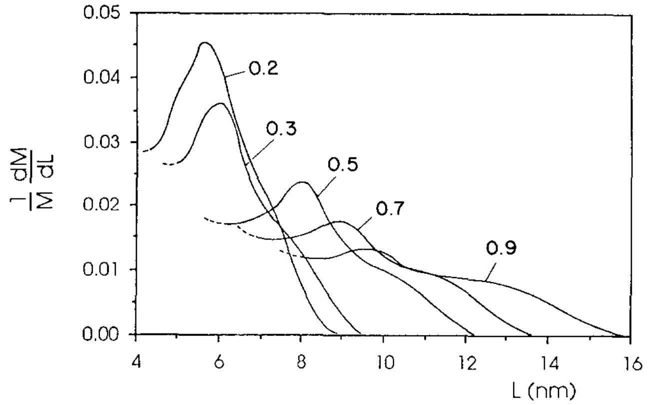

Figure 6 Distribution curves of the crystalline lamellae thickness for the dried gels of copolymer D at various concentrations of the initial solutions (the values indicated are the copolymer weight fractions)

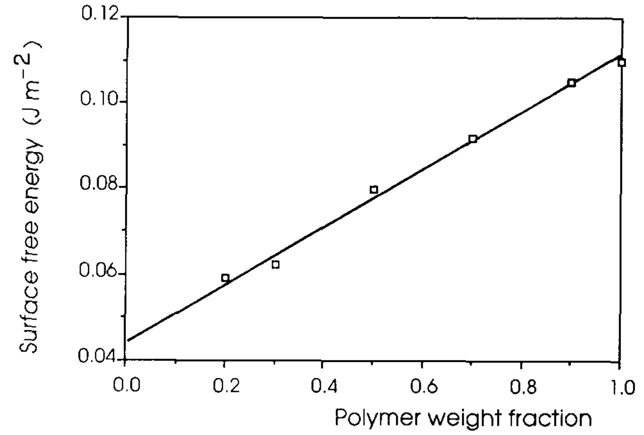

Figure 7 Surface free energy *versus* concentration of the initial solutions for the dried gels of copolymer D

Table 2 Crystal thickness and crystal weight fraction of the dried gels of copolymer D as a function of initial gel concentration C

C (w/w)	L_c (nm)	X_c
0.2	5.8	0.42
0.3	6.2	0.38
0.5	8.1	0.37
0.7	9.2	0.36
0.9	9.7	0.33
1.0	10.0	0.34

experiments that an increase of chain defects is likely to disturb the chain-folding process during crystallization and gradually to turn the natural propensity of linear polyethylene chains for regular folding into random folding[1,2]. Moreover, the extrapolated value of the surface free energy of the copolymers to zero co-unit concentration is fairly close to the value reported for polyethylene single crystals about the melting temperature, $\sigma_e = 0.07 \pm 0.01$ J m^{-2} (refs. 7, 25). This is additional support for our proposal that linear chains are more prone to build up regular chain folding than are branched chains. On the other hand, the higher value of the surface free energy determined in the case of copolymer D, i.e. $\sigma_e = 0.11$ J m^{-2}, is significantly lower than the theoretical value[7] for fringed-micelle crystals, $\sigma_e \approx 0.24$ J m^{-2}. This is a clear indication that copolymers with a high co-unit content still have a good rate of chain-folded macroconformations, but folding is random rather than regular.

Solution-crystallized copolymers

The distribution curves of the crystal thickness of the dried gels of copolymer D are shown in *Figure 6* for various concentrations of the initial solutions. The values of the surface free energy determined from the fitting procedure using the X_c and L_c values of *Table 2* are plotted in *Figure 7* as a function of the polymer weight fraction in the initial solutions. The nearly linear decrease of σ_e with increasing dilution is relevant to a gradual improvement of regular chain folding, as already suggested from mechanical testing[6]. This result gives a much more general meaning to the previous conclusion by Mandelkern and co-workers about the chain topology of copolymer single-crystal mats grown from dilute solutions[12].

CONCLUSION

The determination of the surface free energy of the chain-folding crystal faces of ethylene–butene copolymers having various co-unit concentrations corroborates our previous conclusions from mechanical testing about the chain macroconformation. On the one hand, co-units disturb the melt-crystallization mechanism and turn regular chain-folded macroconformations into fringed-micelle ones; the higher the co-unit content, the higher the disorder in the amorphous overlayer. On the other hand, solution crystallization involves an improvement of regular chain folding; the higher the dilution, the more ordered the amorphous overlayer.

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