Annealing of solution-grown single crystals of ethylene–butadiene copolymers

Ezio Martuscelli, Mariano Pracella and Mario Pirozzi
Laboratorio di Ricerche su Tecnologia dei Polimeri e Reologia del CNR, Via Toiano 2, Arco Felice, Napoli, Italy

(Received 31 January 1977)

The annealing behaviour of solution-grown single crystals of ethylene–butadiene copolymers of differing compositions is examined and compared with that of linear polyethylene. From the plot of melting temperature against the reciprocal of the long spacing features such as the equilibrium melting point T_m^0 and the free energy of folding σ_e have been calculated. Both σ_e and T_m^0 increase with almost a linear trend with the percentage of butadiene along the chain. It is concluded that the surface of single crystals of ethylene–butadiene copolymers is rougher than that of linear polyethylene.

INTRODUCTION

In previous papers[1,2] the morphology, structure, and bromination of solution-grown single crystals of ethylene–butadiene copolymers were investigated together with the effect of intrachain *trans* double bonds on the rate of crystallization from the melt.

Features such as dissolution temperature of the crystals, long spacing, external crystal habit and the free energy of formation of nuclei of critical dimensions were found to be dependent upon the number of *trans* double bonds in the polymer chain[1,2]. The bromination, in suspension, of a sample of single crystals of ethylene–butadiene copolymers, showed that only part of double bonds are accessible to bromine. This result indicated that during crystallization a certain number of double bonds are incorporated as defects in the crystalline lattice of polyethylene[1].

In the present paper the effect of thermal treatment on solution-grown single crystal aggregates of ethylene–butadiene copolymers is investigated. We are mainly interested in studying the influence of a few *trans* double bonds, distributed along the macromolecule, on the values of the surface free energy of folding and of the equilibrium melting point of polyethylene.

Further we are also interested in the distribution of double bonds between crystalline and amorphous regions following the annealing process. Finally we compare the annealing behaviour of single crystals of defect free polyethylene with that of single crystals of polyethylene with $-CH_2-CH=CH-CH_2-$ units acting as chain defects along the macromolecule.

EXPERIMENTAL

Materials

Samples of unfractionated ethylene–butadiene copolymers (1,4-linked) and of linear polyethylene were used in the present work. The methods of synthesis and the characterization of the copolymers are reported elsewhere[1]. The chemical composition of the copolymers, the viscosity-average molecular weight and the conditions of crystallization used to obtain single crystals by precipitation from xylene solutions are reported in *Table 1.*

The details of the morphological characterization of the single crystals were reported in a previous paper[1].

Annealing experiments and measurements

Annealing was carried out by using small pieces of dried single crystal aggregates. These pieces were wrapped in aluminium foil and placed in thin walled test tubes previously filled with nitrogen. The tubes were dipped into the oil bath, at constant temperature, for the annealing. A heat-treatment time of 24 h was used throughout.

A Perkin–Elmer differential scanning calorimater DSC-2 was used to obtain apparent heats of fusion ΔH^*. Except where indicated, all samples were heated at 20°C/min. The area under the melting d.s.c. trace was integrated and expressed in cal/g using a calibration factor determined from melting a known weight of indium for which a value of 6.8 cal/g was taken for the heat of fusion. The melting temperatures of the samples were measured from the maxima of the d.s.c.

Table 1 Composition and crystallization conditions of ethylene–butadiene copolymers. T_{pc}, T_s and T_c are the precrystallization, the seeding and the crystallization temperature respectively. $\bar{M}_\eta$ is the viscosity-average molecular weight and C the concentration

Sample	Composition (mol % butadiene)	$\bar{M}_\eta$	C (% w/w)	T_{pc} (°C)	T_s (°C)	T_c (°C)
Marlex 6009	0.0	128.000	0.08	60	101.5	80
EB1 copolymer	0.7	75.000	0.08	60	97.0	80
EB2 copolymer	1.0	70.000	0.08	60	96.5	80
EB3 copolymer	1.7	75.000	0.08	60	97.5	80
EB4 copolymer	2.85	75.000	0.08	60	97.0	80

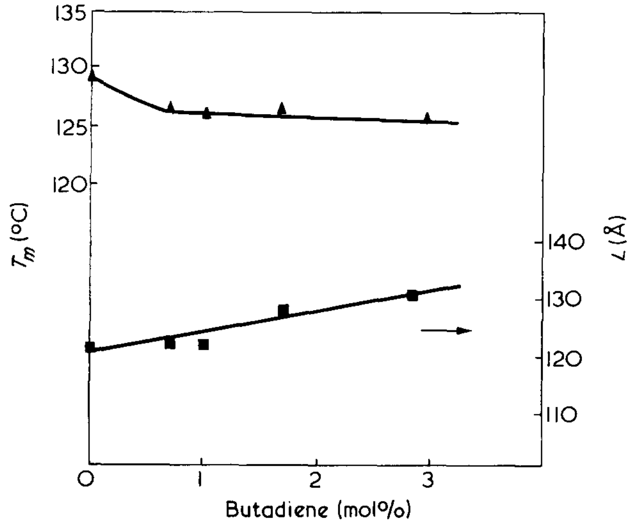

Figure 1 Lamellar thickness L (Å) and melting temperature T_m of unannealed single crystals of ethylene–butadiene copolymers grown at 80°C as a function of the composition

endotherms. The temperature scale was calibrated from the melting points of low molecular weight standard substances.

The thickness of the crystals was determined by means of small-angle X-ray diffraction using a pinhole-collimated Rigaku–Denki apparatus.

RESULTS AND DISCUSSION

The lamellar thickness of single crystals of ethylene–butadiene copolymers grown at 80°C increases with the percentage of butadiene in the macromolecules. The trend is shown in *Figure 1*. In agreement with the kinetic theory of polymer crystallization this behaviour is consistent with a growth mechanism determined mainly by supercooling[3] as the fusion temperatures of unannealed single crystals of ethylene–butadiene copolymers decrease with the butadiene content (see *Figure 1*). According to this theory the most probable fold length is given by the following expression[3,4]:

$$L = \frac{2\sigma_e T_m^0}{\Delta H \Delta T} + \delta L \qquad (1)$$

where ΔT represents the supercooling ($T_m^0 - T_c$), ΔH is the heat of fusion, T_m^0 the melting temperature (or dissolution) of the infinitely extended chain crystal, δL is an additional much smaller term, at least for the usual supercoolings, and σ_e is the end-surface free energy of folding of the crystal.

As shown in *Figure 2* the lamellar thickness of single crystal aggregates of polyethylene and ethylene–butadiene copolymers increases with annealing temperature according to the general behaviour of chain folded lamellar single crystals.

In *Figure 3* the melting temperatures of as-crystallized and annealed single crystal aggregates of polyethylene and ethylene–butadiene copolymers are plotted against the reciprocal of the crystal thickness $1/L$.

A straight line, with negative slope, is obtained for every sample. By using the least square method, equations for the best straight lines which interpolate the experimental points are obtained. These equations are reported for each sample in *Table 2*. The melting temperature T_m of a lamellar crystal with comparatively large lateral dimensions may be related to the lamellar thickness L by the equation[3,4]:

$$T_m = T_m^0 - \frac{2\sigma_e T_m^0}{\Delta H} \cdot \frac{1}{L} \qquad (2)$$

The application of equation (2) to the lines of *Figure 3* provides the values of T_m^0 and σ_e for the samples of single crystals of polyethylene and ethylene–butadiene copolymers

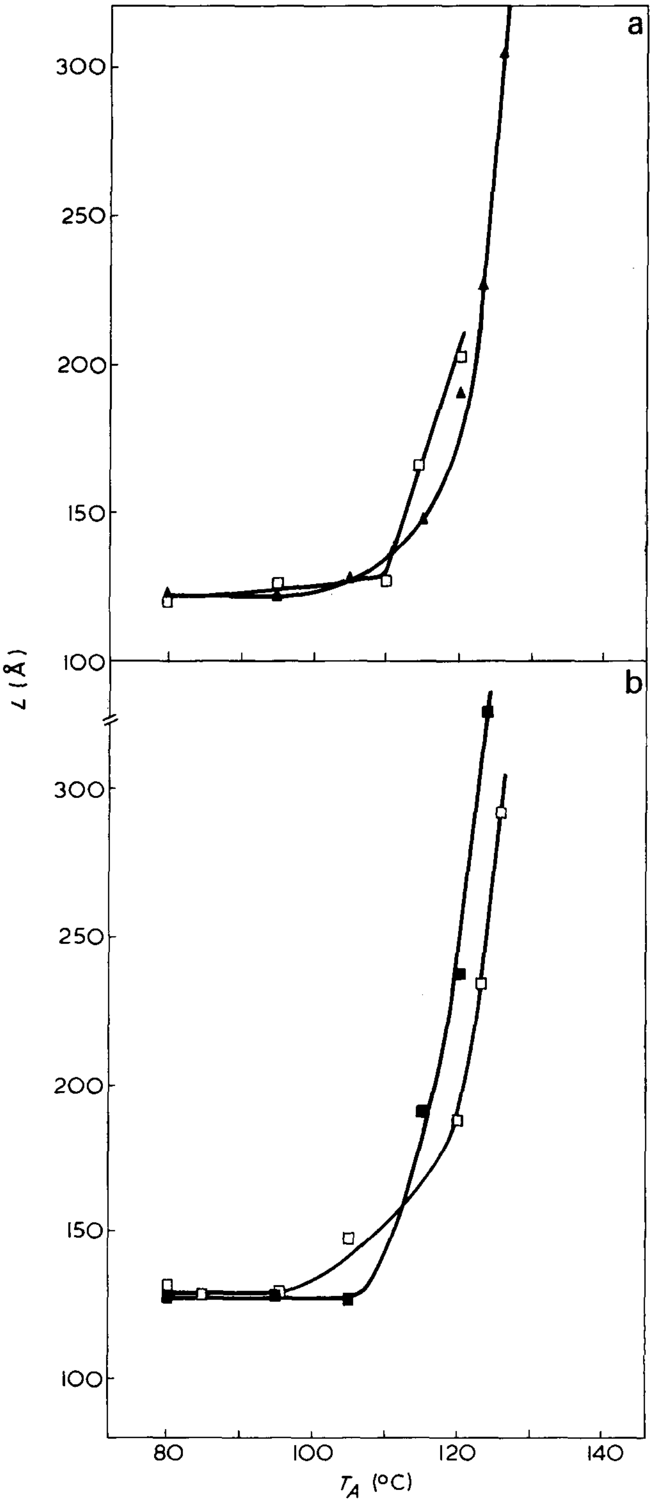

Figure 2 Long spacing of single crystal aggregates of polyethylene and ethylene–butadiene copolymers as function of the annealing temperature (T_A): (a) ▲, Marlex; □, EB1 copolymer; (b) ■, EB3 copolymer; □, EB4 copolymer

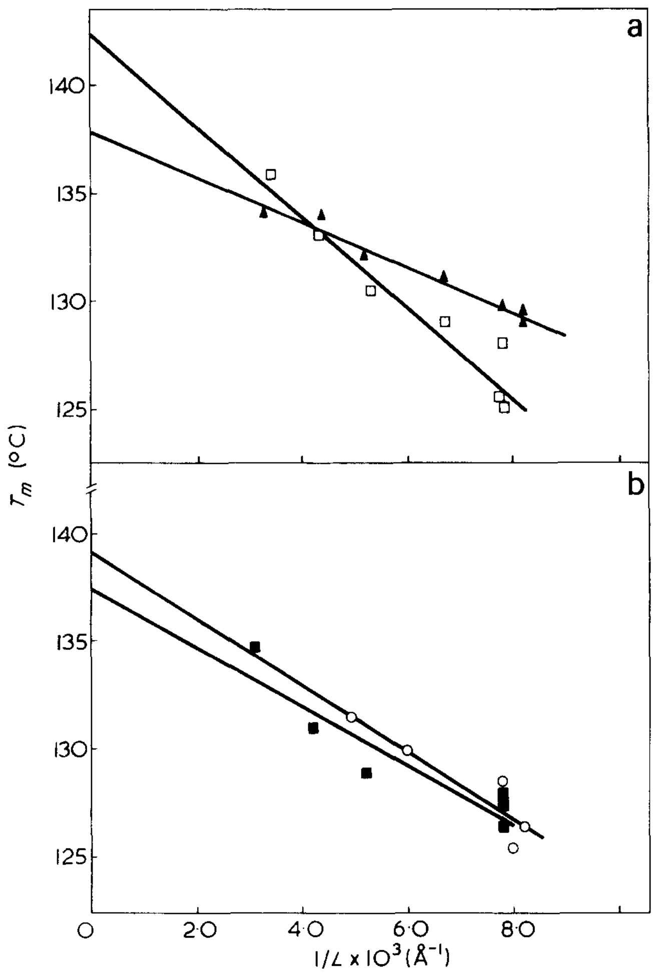

Figure 3 Melting temperature T_m against the reciprocal of the long spacing for single crystal aggregates of polyethylene and ethylene–butadiene copolymers: (a) ▲, Marlex; □, EB4 copolymer; (b) ○, EB1 copolymer; ■, EB3 copolymer

Table 2 Equations of the best straight lines that interpolate the experimental points of *Figure 3*

Sample	
Marlex 6009	$T_m = 137.8 - 1.0417 \times 1/L$
EB1 copolymer	$T_m = 139.2 - 1.5449 \times 1/L$
EB3 copolymer	$T_m = 137.4 - 1.3256 \times 1/L$
EB4 copolymer	$T_m = 142.3 - 2.0854 \times 1/L$

investigated. For the calculation of σ_e we assumed for all the samples the ΔH value of pure polyethylene ($\Delta H = 2.80 \times 10^9$ erg/cm^3)[5]. As shown in *Figure 4* both σ_e and T_m^0 increase with an almost linear trend with the percentage of butadiene along the chain. For linear polyethylene we found values for T_m^0 and σ_e of 138°C and 106 erg/cm^2. In the case of sample EB4 T_m^0 and σ_e are equal to 142.5°C and 205 erg/cm^2, respectively. In a previous paper[2], using a different method based on the correlation of T_m with T_c for bulk material, no significant difference was found in the value of T_m^0 with increasing the amount of double bonds along the macromolecule.

The increasing dependence of σ_e upon the number of constitutional defects, i.e. the number of $-CH_2-CH=CH-CH_2-$ units along the chain, is in agreement with the finding of Martuscelli and Pracella[6] in the case of solution grown crystals of ethylene–propylene copolymers.

On the contrary Martuscelli and Pracella[6] found for ethylene–propylene and ethylene–butene-1 copolymers a decrease in the values of T_m^0 on increasing the number of constitutional chain defects. This different trend may be explained in terms of entropy if it is assumed that in the case of ethylene–butadiene copolymers the entropy of fusion of the crystals is comparatively lower as a consequence of the inclusion of a certain amount of $-CH_2-CH=CH-CH_2-$ units as defects in the crystalline lattice of polyethylene. The number of chain defects incorporated in the lattice should also increase with the percentage of butadiene units along the macromolecules.

As shown in *Figure 5* the apparent enthalpy of fusion ΔH^* of melt recrystallized samples of single crystal aggregates of ethylene–butadiene copolymers decreases with the percentage of butadiene. For linear polyethylene and for sample EB4 we found for ΔH^* values of 44 and 38 cal/g respectively with a percentage reduction of about 14%.

This lowering may be due to a relative larger amount of amorphous material that is not able to crystallize and/or to a larger amount of $-CH_2-CH=CH-CH_2-$ incorporated as defects in the crystalline lattice.

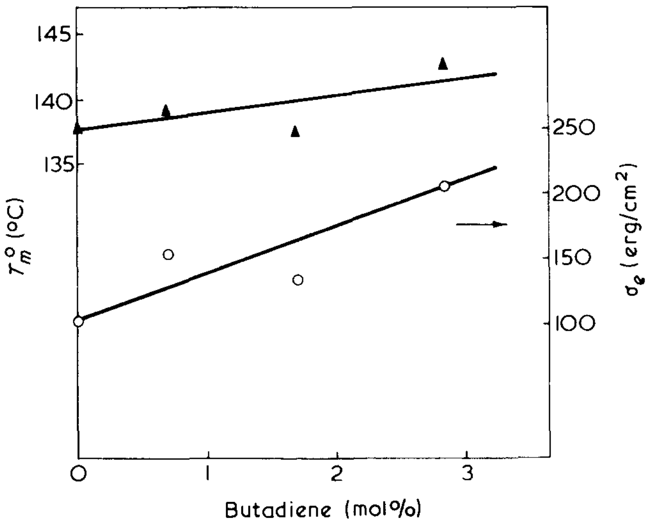

Figure 4 Dependence of σ_e and T_m^0 upon the percentage of butadiene

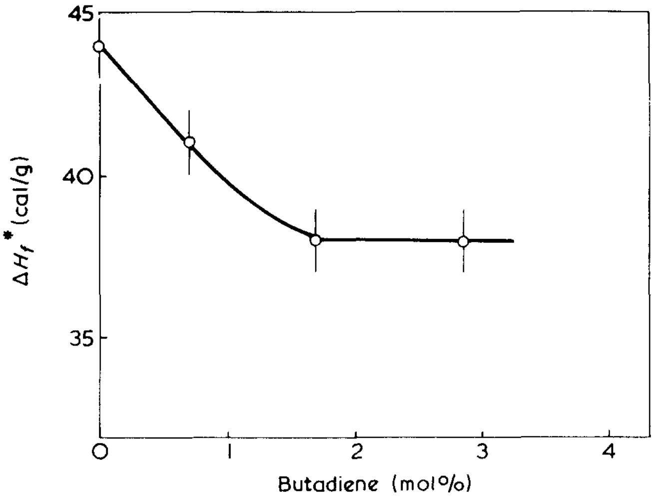

Figure 5 Dependence of ΔH^* of melt recrystallized samples of single crystal aggregates of ethylene–butadiene copolymers upon the percentage of butadiene

Table 3 Comparison between the values of σ_e found by analysis of the dependence of the rate of crystallization from the melt upon the undercooling[2] and that reported in the present paper

Sample	σ_e^a (erg/cm^2)	σ_e^b (erg/cm^2)
Marlex 6009	23	106
EB1 copolymer	30	155
EB3 copolymer	43	135
EB4 copolymer	38	205

[a] From Amelino and Martuscelli data[2]; [b] Present paper

However, the value of the thermodynamic enthalpy of fusion should not be too much affected by unsaturation at least for the range of composition under examination.

The values of the surface free energy of folding σ_e of samples of polyethylene–butadiene copolymers calculated by analysis of the dependence of the rate of the crystallization from the melt upon the undercooling[2] are systematically lower than that reported in the present paper. The values are compared in *Table 3.* The rather large difference in the values of σ_e of *Table 3* may be due to the different method of determination used and/or to a different nature of the surface of folding of the crystals grown from the melt and from dilute solution.

This last aspect of the problem needs to be further investigated. In a recent paper Cernia and others[7] found by means of van der Waals potential energy calculations that the energy values corresponding to the fully extended chain of an ethylene–butadiene copolymer (low butadiene content) and linear polyethylene are nearly equal. Thus in the crystalline lattice of polyethylene $-CH_2-CH_2$ units may be easily replaced with the *trans* –CH=CH– groups. This result based on theoretical calculations is in agreement with our finding that only 44% of double bonds, situated on the surface of solution-grown single crystals, are accessible to bromine in the case of EB4 copolymer[1]. Moreover the same authors[7] reached the conclusion that the three deepest minima of the van der Waals energy of a single chain of ethylene–butadiene copolymers correspond to folded chains with the –CH=CH– group lying on the folded part of the macromolecule.

From this the authors assert that *trans* double bonds, placed along a polyethylene chain, may act as fold supporting. As a consequence the enthalpy of folding q_e corresponding to a crystallographic tight fold of linear polyethylene and ethylene–butadiene copolymer will be of the same magnitude. Then the increasing trend we observed in the value of the free energy of folding σ_e of solution-grown single crystals of ethylene–butadiene copolymers as a function of the butadiene content can only be explained by a relatively increasing tendency of ethylene–butadiene copolymers to form loose loops on the surface of the single crystals with increasing the number of –CH=CH– groups along the macromolecule. This would also account for the large amount of *trans*-double bonds accessible to bromine on the surface of solution grown crystals of EB4 copolymer.

In conclusion there is experimental evidence that the surface of single crystals of ethylene–butadiene copolymers is rougher than that of linear polyethylene.

REFERENCES

1 Cucinella, S. and Mazzei, A. *Chim. Ind. (Milan)* 1971, **53**, 748; Mancarella, C., Martuscelli, E. and Pracella, M. *Polymer* 1976, **17**, 541
2 Amelino, L. and Martuscelli, E. *Polymer* 1975, **16**, 864
3 Keller, A. and Kawai, T. *Phil. Mag.* 1965, **11**, 1165; Lauritzen, J. J. and Hoffman, J. D. *J. Res. Nat. Bur. Stand. (A)* 1960, **64**, 73
4 Hoffman, J. D. *SPE Trans.* 1964, **4**, 315; Hoffman, J. D., and Weeks, J. J. *J. Chem. Phys.* 1962, 37, 1723
5 Hoffman, J. D., Lauritzen Jr., J. J., Passaglia, E., Ross, G. S. Frolen, L. J. and Weeks, J. J. *Kolloid Z. Z. Polym.* 1969, **231**, 564
6 Martuscelli, E. and Pracella, M. *Polymer* 1974, **15**, 306
7 Cernia, E., Conte, G. D'Ilario, L., Pavel, N. V. and Giglio, E. *J. Polym. Sci. (Polym. Chem. Edn)* 1975, **13**, 125