Effect of thermal treatment on solution grown crystals of isotactic propylene/butene-1 copolymers

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The annealing behaviour of solution grown crystals of isotactic propylene butene-1 copolymers is studied in detail. Modifications in both position and number of the d.s.c. peaks in the thermograms of single crystal aggregates as a function of the annealing temperature, are observed and correlated with the presence of different crystalline phases. For all samples a maximum is observed when the overall apparent enthalpy of fusion is reported against the annealing temperature. The annealing temperature corresponding to the maximum is a function of the copolymer composition. The diagram is characterized by a minimum corresponding to a percentage of about 43% by wt in butene-1. The long spacing of crystal aggregates is a function of the annealing temperature. For some samples the long spacing has been correlated with the melting temperature of the crystalline phases and the equilibrium melting point calculated. For copolymer samples at high propylene content the examination of the wide-angle X-ray diffraction patterns leads to the conclusion that a certain number of butene-1 units, incorporated during the crystallization, as defects in the crystalline lattice of polypropylene, following the annealing process, are ejected in the amorphous phase.

INTRODUCTION

The external crystal habit, the morphology and the thermodynamic properties of unannealed solution grown crystals of isotactic propylene butene-1 copolymers, were investigated by the authors as a function of the composition, and the results reported in a previous paper[1]. The dissolution temperature, the density and the apparent enthalpy of fusion of the unannealed crystals of copolymers show a eutectic point corresponding to a composition of about 48% by wt in butene-1[1]. Further, as reported in detail[1], single crystal aggregates of copolymers with butene-1 concentration lower that about 50%, show in the wide-angle X-ray diffraction, only reflections of crystalline polypropylene. On the contrary, the aggregates of copolymers with butene-1 concentration higher than about 50% give only reflections of poly(butene-1) in form I. The copolymer with 53% of butene-1 shows both reflections of polypropylene and poly(butene-1) in form I. In the case of mats of single crystals of pure poly(butene-1), X-ray reflections of the various crystalline forms are co-existent[1].

The dimensions of the unit cell of both polypropylene and poly(butene-1) phase are dependent upon the composition of the copolymers. This result indicated that propylene and butene-1 units may be incorporated as defects in the crystalline lattices of the poly(butene-1) and of polypropylene respectively[1]. In the present paper the annealing and the thermal behaviour of solution grown crystals of isotactic propylene/butene-1 copolymers is investigated.

The research is part of a more general project on the effect of chain defects on the properties of polymeric materials[2].

EXPERIMENTAL

Materials

The unfractionated isotactic random copolymer samples utilized in the present investigation were obtained by means of copolymerization reactions carried out with $TiCl_3-AlEt_2Cl$ catalyst. The composition of the samples, ranges from pure isotactic polypropylene to pure isotactic poly(butene-1). All copolymers, in the range of composition examined, are crystallizable.

The composition of the copolymers was measured by i.r. analysis. Solution grown crystals of isotactic poly(butene-1) and of copolymers were prepared from dilute solutions of isoamyl acetate. Single crystals of isotactic polypropylene were obtained by precipitation from α-chloronaphthalene solution. The details are reported elsewhere[1].

In *Table 1*, the composition of the copolymers, the crystallization conditions and the thickness of the crystals, as measured by small-angle X-ray scattering, are reported.

The suspensions of the crystals were filtered to be laminated and to form mats of thickness 0.5–1 mm. These mats were dried in a vacuum at room temperature for more than ten days and used for heat-treatment experiments.

Table 1 Composition of isotactic random propylene/butene-1 copolymers and crystallization conditions used. T_{PC} is the precrystallization temperature, T_D is the apparent dissolution temperature, T_S is the seeding temperature and T_C the crystallization temperature. The lamellar thickness of the crystals is also reported.

Sample	Butene-1 (% by wt)	Composition (% by mol)	Solvent	Concentration (% w/w)	T_{PC} (°C)	T_D (°C)	T_S (°C)	T_C (°C)	$\Delta T = T_D - T_C$ (°C)	Lamellar thickness (Å)
PP	0.0	0.0	α-Chloronaphthalene	0.039	107	130	136	107	23	130
PP/PB-1	13.5	10.5	Isoamylacetate	0.044	18	115	–	89	26	140
PP/PB-2	26.8	21.5	Isoamylacetate	0.043	25	96	–	60	36	–
PP/PB-3	29.8	24.1	Isoamylacetate	0.039	25	89	–	65	24	–
PP/PB-4	34.5	28.3	Isoamylacetate	0.045	20	90	–	60	30	150
PP/PB-5	45.6	38.6	Isoamylacetate	0.045	21	65	–	44	21	–
PP/PB-6	47.9	40.8	Isoamylacetate	0.045	21	64	–	44	20	–
PP/PB-7	53.3	46.1	Isoamylacetate	0.040	25	70	72	30.5	39.5	138
PP/PB-8	70.0	63.6	Isoamylacetate	0.026	33	66	68	24	42	–
PP/PB-9	97.8	97.1	Isoamylacetate	0.038	30	68.5	75.5	45	23.5	100
PB	100.0	100.0	Isoamylacetate	0.039	25	72.5	–	51.5	21	93.5

Method of heat-treatment

Pieces of dried crystal aggregates were wrapped in aluminium foil and placed in sealed thin-walled test tubes previously filled with nitrogen. These tubes were dipped into the oil bath at a constant temperature for the heat-treatment. An annealing time of 24 h was used throughout.

Measurements

A Perkin–Elmer differential scanning calorimeter DSC-2 was used to obtain apparent heats of fusion $\Delta H_F{}^*$. 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 maximum of the d.s.c. 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 by irradiating X-rays along the surface of the single crystals mat. A Rigaku–Denki apparatus was used.

Wide-angle X-ray spectra were obtained photographically with a flat camera. Nickel-filtered CuKα radiation was used throughout.

RESULTS AND DISCUSSION

Thermograms of unannealed single-crystal aggregates of polypropylene and of PP/PB-9 copolymer show only one endotherm of fusion whilst that of poly(butene-1) and all other copolymers show melting endotherms with multiple peaks and some secondary shoulder.

As reported in detail by us in a previous paper[1], the lower temperature endotherms of fusion of copolymers PP/PB-1, PP/PB-4 and that at intermediate temperature of PP/PB-7 were attributed to the melting of a polypropylene phase with a lower thermodynamic stability due to the inclusion in the lattice of butene-1 units. The higher temperature endotherms of the same samples of copolymers were attributed to a more pure polypropylene phase with higher thermodynamic stability.

The melting endotherms at lower temperature of a sample of PP/PB-7 and those of samples of PP/PB-8 and PP/PB-9 were assigned to a poly(butene-1) form I phase that includes some propylene units as constitutional defects in the crystal lattice.

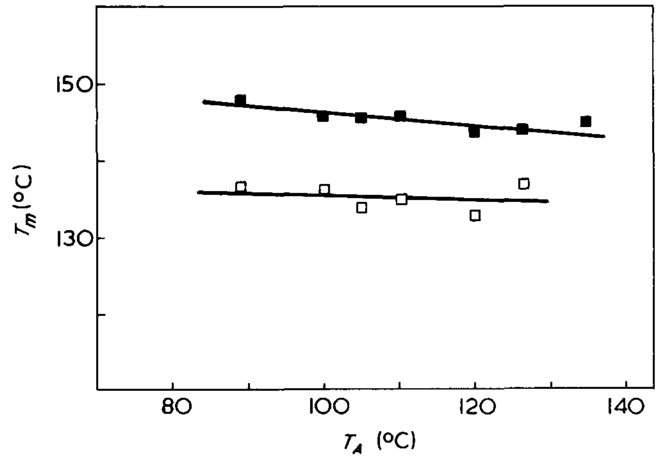

Figure 1 Dependence of melting temperatures upon the annealing temperature for single crystals aggregates of PP/PB-1 copolymer: □, T_m (I); ■, T_m (II)

From X-ray evidence the two peaks in the d.s.c. trace of pure poly(butene-1) are related to the fusion of crystals in form III (lower temperature peak) and in form I (higher temperature peak)[1]. In the case of polypropylene single crystal aggregates the melting temperature is almost independent from the annealing temperature. (T_m = 154° and 152°C for the unannealed sample and for the sample annealed at 145°C respectively.)

The variation in the fusion points of single crystal aggregates of PP/PB-1 sample is reported in *Figure 1*. For annealing temperatures lower than 127°C a slight decrease is observed in both T_m(I) and T_m(II) with increasing T_A.

For higher annealing temperature the d.s.c. peak at lower temperature disappears and only the higher temperature endotherm is observed. This result indicates that the less stable polypropylene phase melts and the material recrystallizes in the more stable phase.

The modificatons in the d.s.c. traces of single crystal aggregates of a sample of PP/PB-1 copolymer as a function of T_A are shown in *Figure 2*. In the d.s.c. thermograms of single crystal aggregates of a sample of PP/PB-4 a sharp third peak appears at lower annealing temperature. The value of the maximum T_m(I) of this peak drastically increases with the annealing temperature whilst the value of T_m (II) and T_m (III) are practically constant. The first peak is observed up to a value of T_A of 89°C.

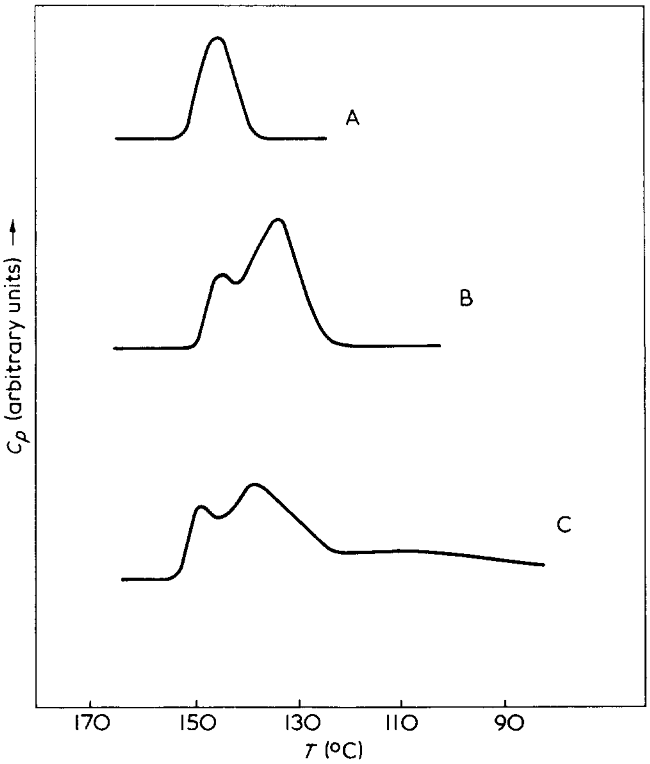

Figure 2 D.s.c. thermograms of single crystals aggregates of PP/PB-1 copolymer as function of the annealing temperature. A, T_A = 135°C; B, T_A = 120°C; C, T_C = 89°C

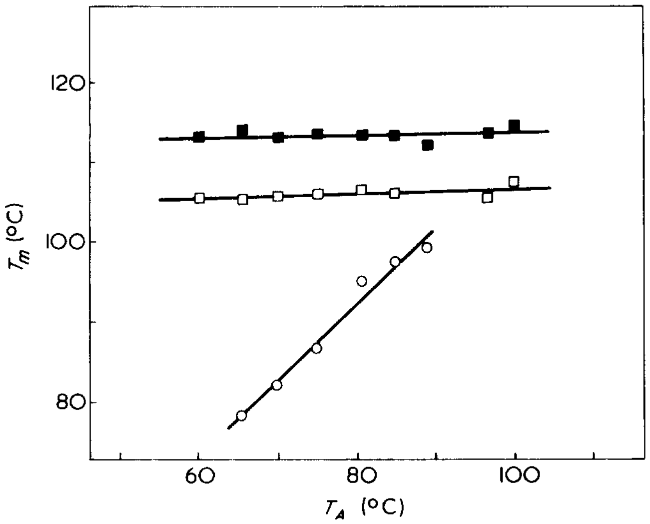

Figure 3 D.s.c. peaks temperatures of crystal aggregates of PP/PB-4 copolymer as function of T_A: ○, T_m(I); □, T_m(II); ■, T_m(III)

The variations of T_m (I), T_m (II), T_m (III) and the modification observed in the d.s.c. traces of single crystal aggregates of a sample of PP/PB-4 are shown in *Figures 3* and *4*, respectively.

The formation of a still less stable polypropylene phase whose stability increases with the annealing temperature should explain the observed variations in the d.s.c. thermograms of this copolymer. The melting temperature T_m(I) of the poly(butene-1) phase in single crystal aggregates of a sample of PP/PB-7 increases with the annealing temperature while the fusion temperature T_m (III) of the polypropylene phase with higher stability is practically constant. Plots of T_m (I) and T_m (III) against T_A are shown in *Figure 5*. The melting temperature T_m (II) of the polypropylene phase with lower stability is detected only on the unannealed sample. As matter of fact the related peak becomes very ill defined following annealing process.

At higher annealing temperature a small peak at a temperature of about 60°C is observed in the d.s.c. traces mats of PP/PB-7 samples. For this copolymer, d.s.c. traces at different annealing temperature are shown in *Figure 6*. The results depicted in *Figures 5* and *6* show that the thermodynamic stability of the poly(butene-1) phase in the PP/PB-7 sample increases with the annealing temperature. The behaviour is likely to be caused by the fact that following the an-

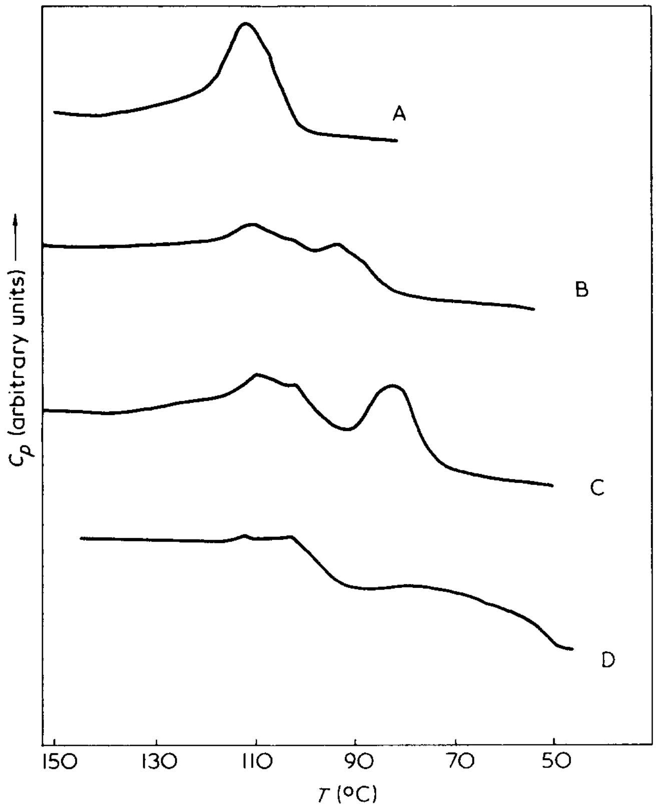

Figure 4 D.s.c. thermograms of crystal aggregates of PP/PB-4 copolymer as function of the annealing temperature. A, T_A = 100°C; B, T_A = 85°C; C, T_A = 75°C; D, T_C = 60°C

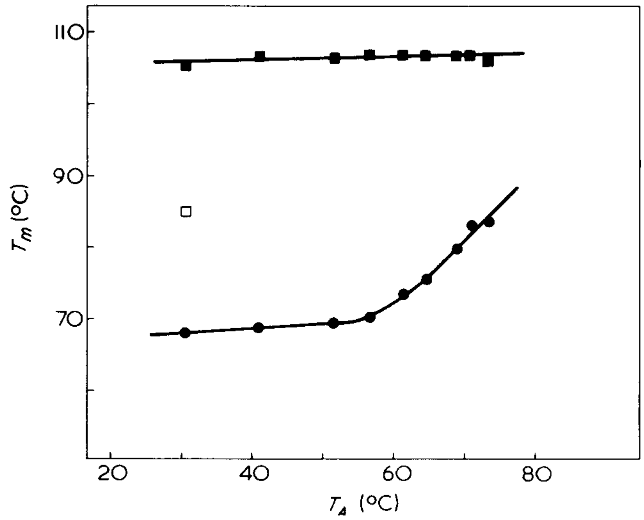

Figure 5 D.s.c. peaks temperatures of crystal aggregates of PP/PB-7 copolymer as function of T_A: ●, T_m(I); □, T_m(II); ■, T_m(III)

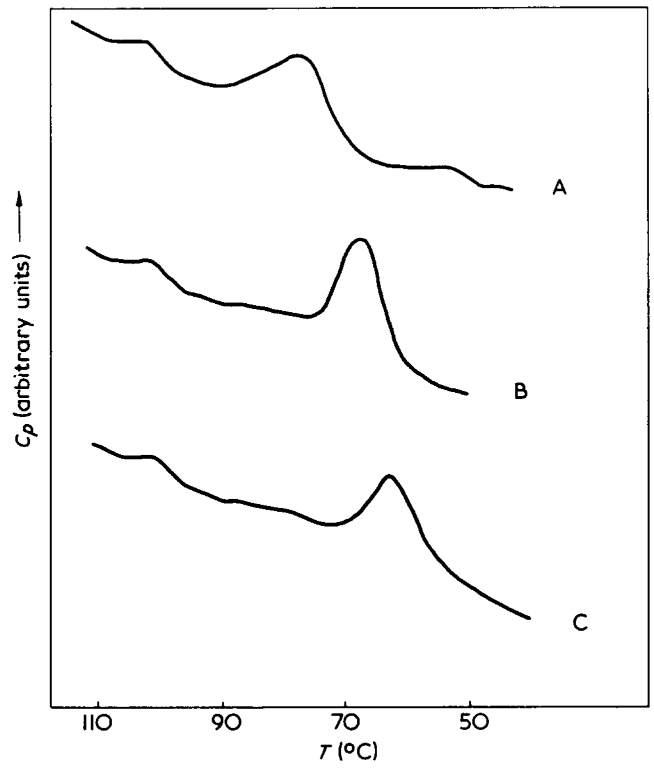

Figure 6 D.s.c. thermograms of crystal aggregates of PP/PB-7 copolymer as function of the annealing temperature. A, T_A = 71°C; B, T_A = 60°C; C, T_A = 41°C

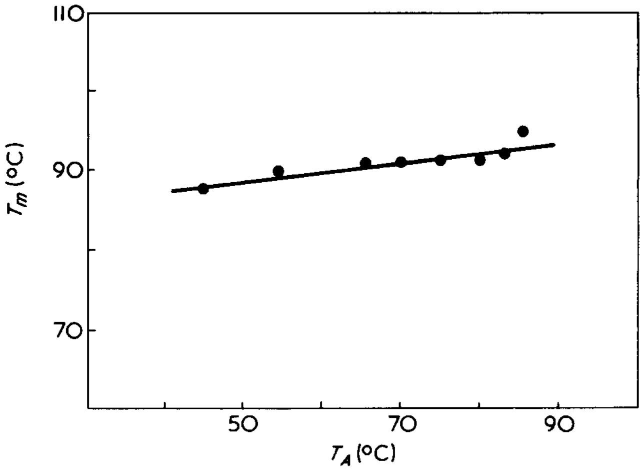

Figure 7 Fusion temperature of PP/PB-9 single crystal mats as function of the annealing temperature

nealing process, propylene units, incorporated in the poly(butene-1) lattice as defects, are ejected in the amorphous phase.

The fusion temperature of PP/PB-9 single crystal mats increases continuously with the annealing temperature. We found for T_m values of 87.5° and 95°C for the unannealed crystals and for mats annealed at 85°C, respectively (see *Figure 7*).

Both the melting temperatures of form III [T_m(I)] and form I [T_m(II)] of crystal aggregates of poly(butene-1) increase with T_A. The trend is shown in *Figure 8*. In *Figure 9* d.s.c. thermograms of mats of single crystals of PB samples corresponding to different values of T_A are shown. A third small peak whose maximum temperature [T_m (III)] is almost independent upon T_A is also observed. For values of T_A higher than 82.5°C the peak related to the fusion of form III of polybutene is not observed any more on the d.s.c. thermograms (see *Figures 8* and *9*). The overall apparent enthalpy of fusion ΔH_F^* of single crystal aggregates of samples of propylene/butene-1 copolymers as a function of the annealing temperature is reported in *Figure 10*.

As shown in this Figure, a maximum is observed in all curves. Single crystal aggregates of polymers with different

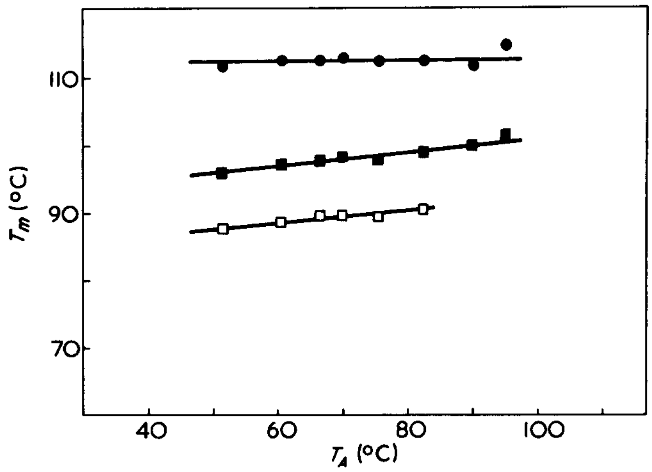

Figure 8 Melting temperatures of form III [□, T_m(I)] and of form I [■, T_m(II)] of single crystal aggregates of poly(butene-1) as function of T_A. ●, refer to T_m(III)

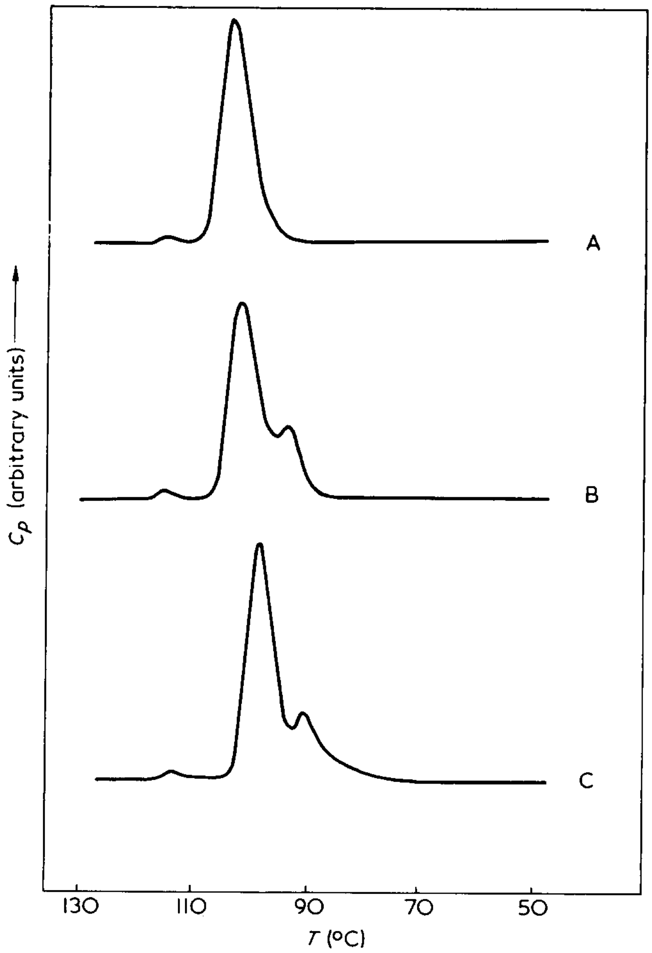

Figure 9 D.s.c. thermograms of single crystal aggregates of poly(butene-1) as function of the annealing temperature. A, T_A = 90°C; B, T_A = 82.5°C; C, T_C = 51.5°C.

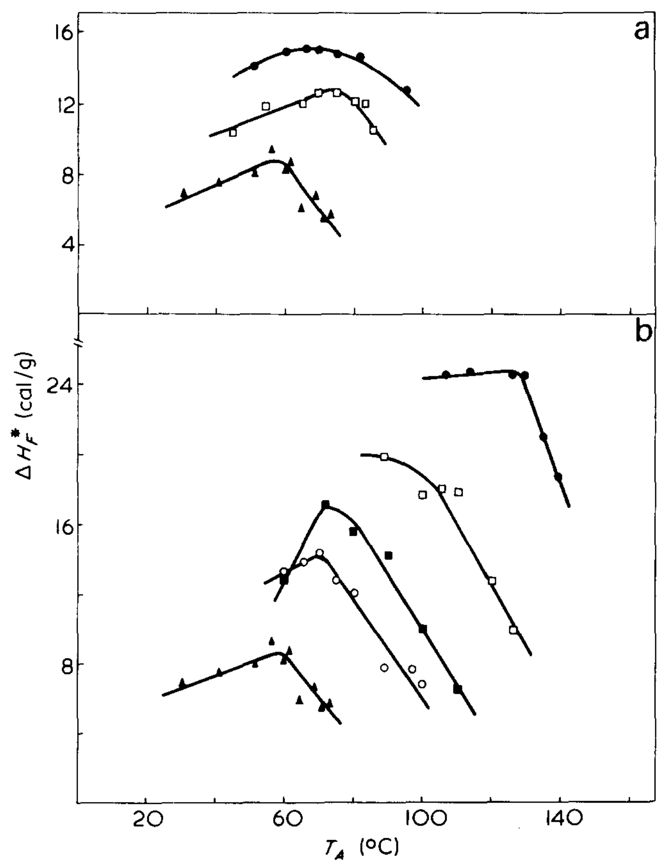

Figure 10 Overall apparent enthalpy of fusion ΔH_F^* of single crystal aggregates of propylene/butene-1 copolymers as function of the annealing temperature: (a) ●, PB; □, PP/PB-9; ▲, PP/PB-7. (b) ●, PP; □, PP/PB-1; ■, PP/PB-2; ○, PP/PB-4; ▲, PP/PB-7

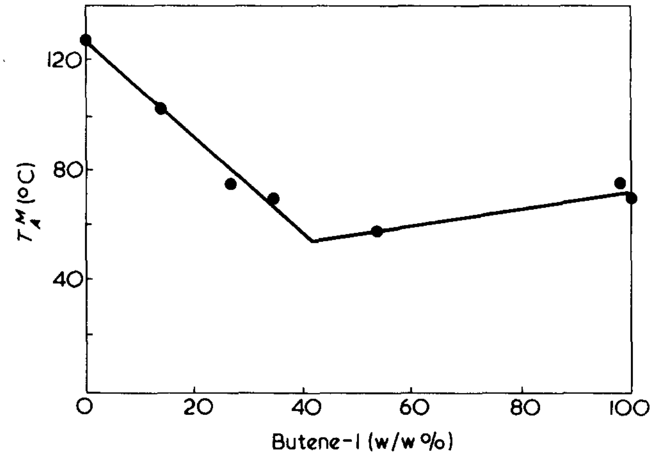

Figure 11 Dependence of the temperature (T_A^M) of the maximum in the $\Delta H_F^* \rightarrow T_A$ curves upon the composition of the copolymers

chemical structure (*trans*-polyalkenamers[4], linear polyethylene and ethylene/α-olefin copolymers[5], polyketones[6] and syndiotactic polypropylene[7]) show the same trend in the $\Delta H_F^* \rightarrow T_A$ curves, observed in the case of propylene/butene-1 copolymers. This behaviour was already interpreted by Martuscelli and Pracella[5] by assuming that for an annealing temperature lower than that of the maxima, the crystals undergo thickening largely by a sliding diffusion mechanism. This process produces a better interlamellar packing together with an increase in the interlamellar order. Above the annealing temperature where a maximum corresponds to the $\Delta H_F^* \rightarrow T_A$ curves the thickening of the crystal is mainly a consequence of a process of partial fusion and recrystallization. This last process causes the lamellae to lose their individuality because of interpenetration effects. At this stage of annealing a new texture is attained, similar to the bulk, characterized by a lower overall degree of crystallinity[5].

In *Figure 11* the values of the temperature T_A^M of the maximum in the $\Delta H_F^* \rightarrow T_A$ curves are reported against the percentage of butene-1 in the copolymers. The diagram is characterized by a minimum corresponding to a percentage of about 43% by weight in butene-1. It is interesting to point out that the same trend was observed by us when the overall apparent enthalpy of fusion of unannealed single crystals and the density were plotted against the composition[1].

All samples of unannealed single crystals mats give rise to a rather sharp X-ray diffraction maximum in the small-angle region. In *Figure 12* for samples PP/PB-7, PP/PB-9 and PB, the long spacing is reported as a function of the annealing temperature. The usual trend observed in the case of polymeric materials is obtained.

In *Figure 13* the melting temperature of the poly(butene-1) phase T_m (I) and that of the polypropylene phase T_m (III) of single crystal aggregates of a PP/PB-7 sample are reported against the reciprocal of the long spacing $1/L$. T_m (I) drastically decreases with $1/L$ though T_m (III) remains almost constant. The extrapolation of the straight lines to $1/L = 0$ gives a value of 116.5° and 107.5°C respectively for T_m (I) and T_m (III).

Under the assumption that the relation[8]:

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

holds for our copolymers and the ratio $\sigma_e/\Delta H_F$[1] is indepen-

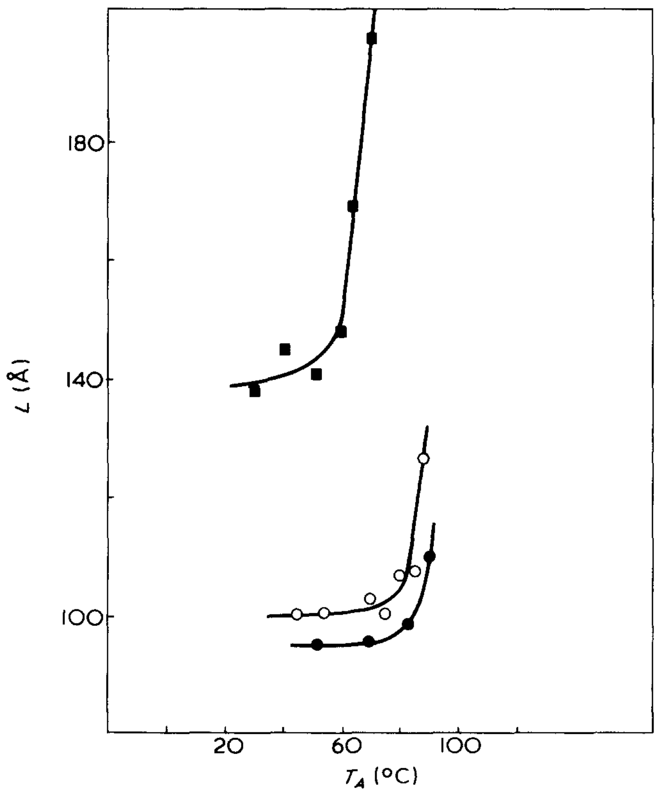

Figure 12 Variation, with the annealing temperature, of the long spacing of single crystal aggregates of samples: ●, PB; ○, PP/PB-9; ■, PP/PB-7

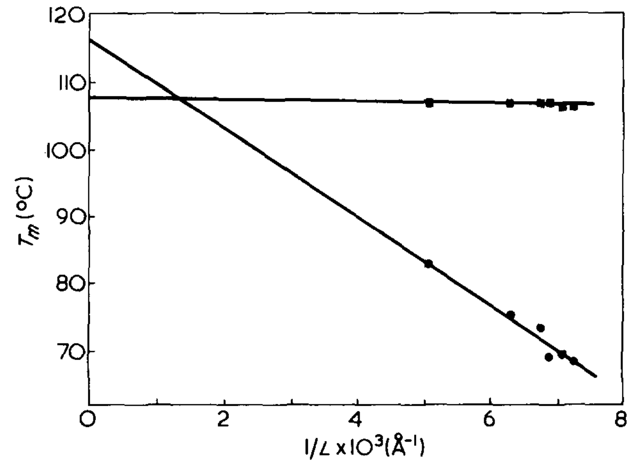

Figure 13 Dependence of the melting temperature of polybutene form I (●) and that of polypropylene phase (■) upon the reciprocal of the long spacing in the case of PP/PB-7 copolymer

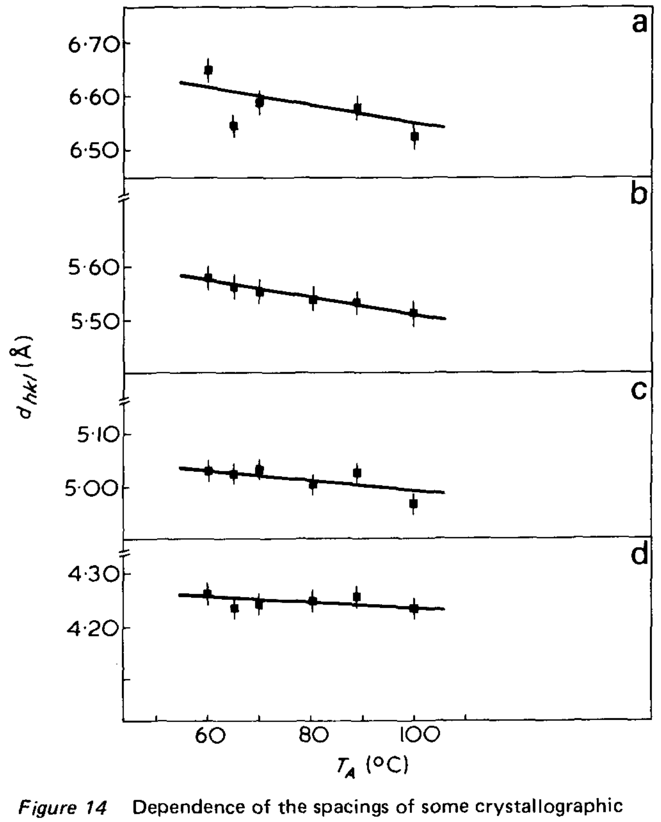

Figure 14 Dependence of the spacings of some crystallographic planes of the polypropylene phase upon the annealing temperature for the PP/PB-4 copolymer. (a) (110); (b) (040); (c) (130); (d) (041)

dent of the annealing temperature, then extrapolated values of T_m(I) and T_m(III) should correspond to the equilibrium melting point T_m° of crystals of poly(butene-1) in form I and of polypropylene. The values we found were noticeably lower than the values reported in the literature (138°C for T_m° of polybutene in form I[9] and 208°C for isotactic polypropylene[10]). This difference must be attributed to the inclusion of propylene and butene-1 units as defects in the crystalline lattice of poly(butene-1) and polypropylene respectively. We do not measure the equilibrium melting temperature of pure polypropylene and poly(butene-1) but the $T_m{}^\circ$ of the defective crystals of the two polymers.

This result is in agreement with the finding the polymers with chain defects along the macromolecules have values of T_m° generally lower than that of the pure material being T_m° also dependent upon the concentration of these defects[4,5].

The d_{hkl} spacings corresponding to the most intense reflections of the polypropylene phase of a PP/PB-4 sample as a function of the annealing temperature are reported in *Figure 14*. As shown in *Figure 14* the values of the spacings continuously decrease with increasing T_A. This result may be only interpreted by assuming that following the annealing process a certain number of butene-1 units, that during the crystallization are incorporated in the polypropylene lattice as defects, are ejected in the amorphous phase with the result of a contraction of the unit cell parameters.

This process of ejection of foreign units from the crystalline lattice of the polymers, following the thermal treatment, should account for the complicated melting behaviour observed in the case of solution grown crystal aggregates of propylene/butene-1 copolymers.

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