# Properties of solution grown crystals of isotactic propylene/butene-1 copolymers

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The external habit of solution grown crystals of isotactic propylene/butene-1 copolymers have been investigated together with some thermodynamic quantities. The dissolution temperature, the density and the apparent enthalpy of fusion of the crystals of copolymers show a eutectic point corresponding to a composition of ~48 % w/w in butene-1. Wide-angle X-ray diffraction analysis of crystal aggregates has been carried out and the results compared with those from the bulk material. An expansion of the unit cell and a contraction is observed for the polypropylene and poly(butene-1) like phases respectively. The values of the $\vec{b}$ axis of the unit cell of polypropylene-like phase and of $\vec{a}\sin\beta$, calculated from the spacing of (110), (040), (130) reflections, as functions of the composition agree with those calculated by Turner-Jones on bulk materials. This result indicates that the process and the mechanism of formation of crystals from dilute solution and from the melt is fundamentally the same. Small-angle X-ray diffraction analysis leads to the conclusion that the ratio $\sigma_e/\Delta H_f$ drastically increases with increase in the concentration of butene-1 units in the case of polypropylene-like phase, and of propylene units for the poly(butene-1)-like phase, along the chain of the copolymers.

## INTRODUCTION

The present paper is part of a more general project leading to the determination of the effect which the insertion of a certain number of chain defects along the macromolecules has on the properties of polymeric materials and further to establish whether during the crystallization from melt and from dilute solution these chain defects are incorporated or ejected from the crystal lattice of the polymer[1].

Certain studies in the literature have concerned themselves with crystallinity and lattice spacing determination of crystallizable bulk copolymers as a function of composition. The importance of these studies relies mainly on the fact that the properties of the material are also functions of the composition and/or of the type of comonomeric units that act as constitutional or configurational defects along the chain of the homopolymer which is able to crystallize.

This paper describes the cocrystallization behaviour from dilute solution of isotactic propylene/butene-1 random copolymers. The composition of copolymers examined ranges from pure isotactic polypropylene to pure isotactic poly(butene-1). All the copolymers, in the range examined, are crystallizable. For low butene-1 concentration we practically have a polypropylene chain with some butene-1 units acting as constitutional chain defects. On the other hand in the region of high butene-1 concentration the copolymers may be considered as defective poly (butene-1) with propylene units as chain defects randomly spaced along the chain.

Density, electron microscopy, differential scanning calorimetry and wide- and small-angle X-ray techniques have been used to study the properties of samples of single crystals isothermally grown from dilute solution.

The main aim of the paper is to investigate the distribution of the comonomer units in the single crystals as a function of the composition and of the crystallization conditions.

The final aim is the construction of the phase diagram representing the melting and dissolution temperature, density, enthalpy of fusion and spacing of the unit cell composition relations for copolymer single crystals.

## EXPERIMENTAL

### *Materials*

The isotactic random copolymer samples used in this investigation were kindly provided by Professor A. Zambelli (ICM, CNR, Milano, Italy). The copolymerization reactions were carried out with a $TiCl_3/AlEt_2Cl$ catalyst. Copolymer compositions were determined by i.r. analysis. In *Table 1* the compositions of the samples of copolymers are reported.

### *Solution grown single crystals preparation*

For isotactic poly(butene-1) and for all copolymers solution grown single crystals were prepared by precipitation from dilute solution in isoamyl acetate. For polypro-

*Table 1* Composition of isotactic random propylene/butene-1 copolymers

| | Butene-1 composition | |
|---|---|---|
| Sample | wt % | mol % |
| PP | 0.0 | 0.00 |
| PP–PB-1 | 13.5 | 10.48 |
| PP–PB-2 | 26.8 | 21.54 |
| PP–PB-3 | 29.8 | 24.15 |
| PP–PB-4 | 34.5 | 28.32 |
| PP–PB-5 | 45.6 | 38.60 |
| PP–PB-6 | 47.9 | 40.81 |
| PP–PB-7 | 53.3 | 46.12 |
| PP–PB-8 | 70.0 | 63.64 |
| PP–PB-9 | 97.8 | 97.09 |
| PB | 100.0 | 100.00 |

*Table 2* Crystallization conditions used in the crystallization of random isotactic propylene/butene-1 copolymers. $T_{pc}$ is the precrystallization temperature, $T_D$ is the apparent dissolution temperature, $T_S$ is the seeding temperature, and $T_c$ is the crystallization temperature

| Sample | Solvent | Concentration (% w/w) | $T_{pc}$ (°C) | $T_D$ (°C) | $T_S$ (°C) | $T_c$ (°C) | $\Delta T = T_D - T_c$ (°C) |
|---|---|---|---|---|---|---|---|
| PP | α-chloronaphthalene | 0.039 | 107 | 130 | 136 | 107 | 23 |
| PP–PB-1 | Isoamylacetate | 0.044 | 18 | 115 | – | 89 | 26 |
| PP–PB-2 | Isoamylacetate | 0.043 | 25 | 96 | – | 60 | 36 |
| PP–PB-3 | Isoamylacetate | 0.039 | 25 | 89 | – | 65 | 24 |
| PP–PB-4 | Isoamylacetate | 0.045 | 20 | 90 | – | 60 | 30 |
| PP–PB-5 | Isoamylacetate | 0.045 | 21 | 65 | – | 44 | 21 |
| PP–PB-6 | Isoamylacetate | 0.045 | 21 | 64 | – | 44 | 20 |
| PP–PB-7 | Isoamylacetate | 0.040 | 25 | 70 | 72 | 30.5 | 39.5 |
| PP–PB-8 | Isoamylacetate | 0.026 | 33 | 66 | 68 | 24 | 42 |
| PP–PB-9 | Isoamylacetate | 0.038 | 30 | 68.5 | 75.5 | 45 | 23.5 |
| PB | Isoamylacetate | 0.039 | 25 | 72.5 | – | 51.5 | 21 |

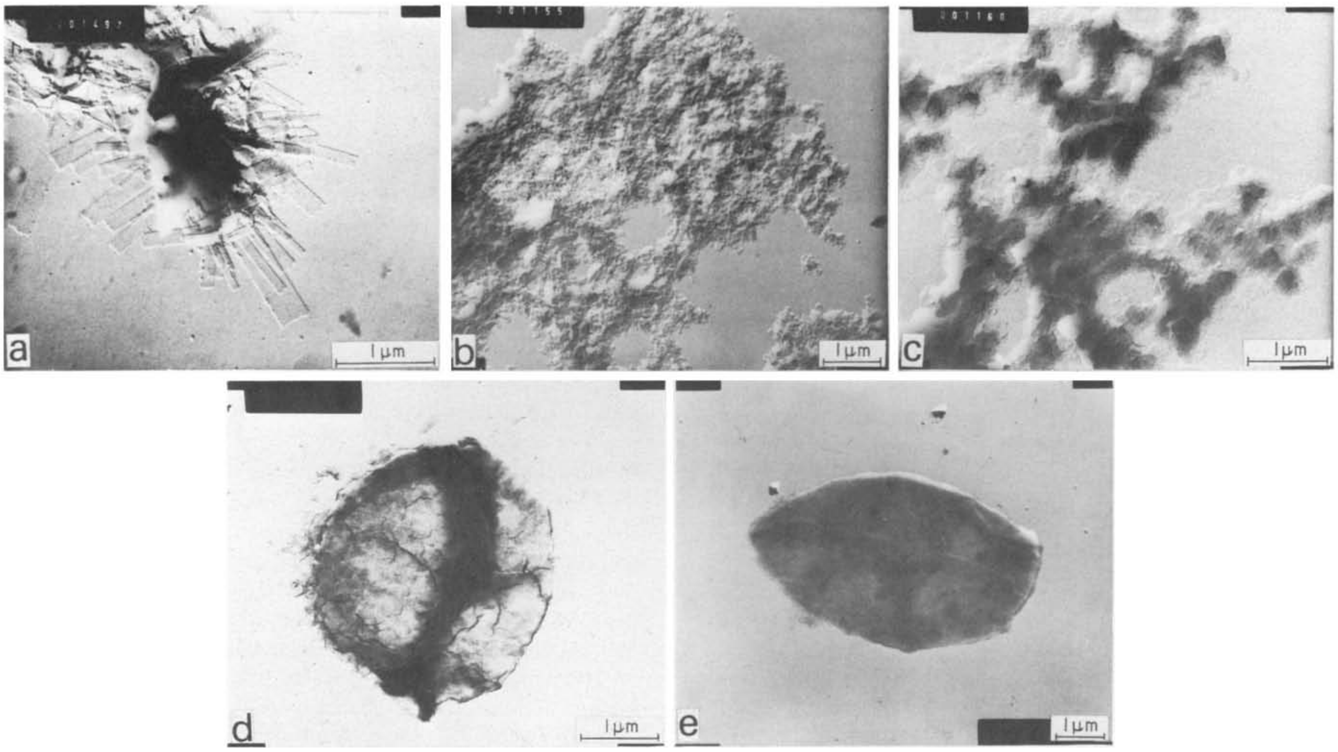

*Figure 1* Electron micrographs of solution grown crystals of: (a) isotactic polypropylene (magnification 22 000 X); (b) sample PP–PB-2 (magnification 14 000 X); (c) sample PP–PB-5 (magnification 18 000 X); (d) sample PP–PB-9 (magnification 17 000 X); (e) isotactic poly (butene-1), (magnification 11 000 X)

pylene, α-chloronaphthalene was used as solvent. The self-seeding[2] technique was used for some of the copolymers. The crystallization conditions are summarized in *Table 2.*

### *Single crystal characterization*

The external crystal habit was examined by means of a Philips E.M. 300 transmission electron microscope.

Wide-angle X-ray diffraction patterns of dried mats of crystals were obtained by using a flat-plate camera with MgO as internal standard in order to enable the sample–film distance to be accurately determined.

Small-angle X-ray diffraction experiments were performed using a pinhole collimated Rigaku–Denki camera. Ni filtered CuKα radiation was used.

Thermal properties of single crystal mats were studied by means of a DSC1-B and DSC2 Perkin–Elmer apparatus. The heating rate used throughout was 20°C/min. The apparent enthalpy of fusion $\Delta H_f^*$ was computed using a calibration factor determined from melting a known weight of indium. A value of 6.8 cal/g was taken for the heat of fusion of the indium.

Density measurements were obtained by flotation using several combinations of liquids and taking as the density of the sample the average value from various experiments. The measurements were performed at 24°C.

## RESULTS AND DISCUSSION

### *Morphology and dissolution behaviour*

Representative electron micrographs of single crystals of isotactic polypropylene, isotactic poly(butene-1) and some copolymers are given in *Figure 1.* The basic morphology of the crystals is lamellar though their external

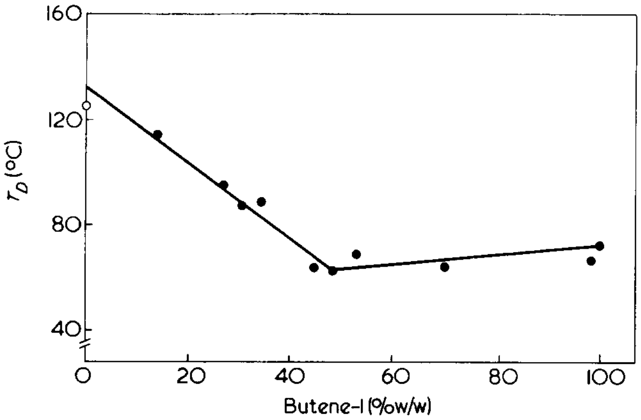

*Figure 2* Dependence of $T_D$ upon the composition

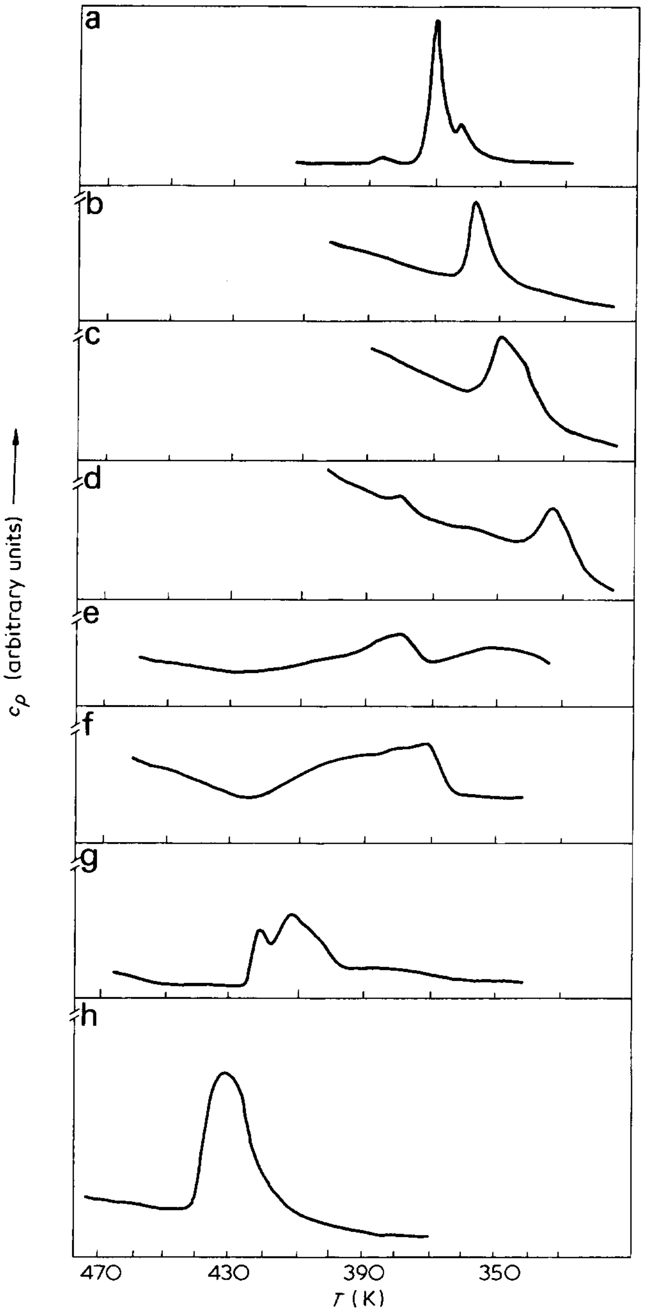

*Figure 3* Examples of d.s.c. thermograms of single crystal aggregates of some random isotactic propylene/butene-1 copolymers and of the homopolymers. (a) PB; (b) PP–PB9; (c) PP–PB8; (d) PP–PB7; (e) PP–PB4; (f) PP–PB2; (g) PP–PB1

appearance is strongly dependent upon the composition.

In the case of polypropylene the crystals are very regular and monolayer with a lath-shaped habit similar to that observed by Kojma[3] (see *Figure 1a*).

In the case of copolymers, on increasing the percentage of butene-1, a deterioration of the external habit is observed. The crystals of samples from PP–PB-1 to PP–PB-7 are as matter of fact very poorly defined and similar in shape to crystals of ethylene/propylene copolymers grown by Martuscelli and Pracella[4] (see *Figures 1b* and *1c*).

Very well defined single crystals of poly(butene-1) and of PP–PB-9 sample have been grown from dilute solution. They have an elongated ovoidal external habit with ridges and cracks indicating that in suspension they are of ovoidal hollow type (see *Figures 1d* and *1e*).

The dissolution temperature $T_D$ defined as the clearing point of suspension of crystals isothermally grown at $T_{pc}$ is dependent upon the composition of the copolymers. The trend shown in *Figure 2*, is of eutectic-type with a minimum in $T_D$ at 64°C corresponding to a composition in butene-1 of ~48 % w/w. For concentrations in butene-1 lower than that of the minimum, $T_D$ decreases linearly with the percentage of butene-1. For concentrations higher than 48%, the slope of the branch of the curve that describes the dependence of $T_D$ upon the percentage of butene-1 is lower.

*Figure 2* indicates that the thermodynamic stability of crystals of copolymers in the concentration range from 13.5 to 48% in butene-1, is lower than that of pure polypropylene. Analogously, single crystals with percentage of butene-1 higher than 48% have a thermodynamic stability lower than that of pure poly(butene-1).

### *Density and melting behaviour*

Typical d.s.c. thermograms of mats of solution grown single crystals of PP–PB copolymers and of polypropylene and poly(butene-1) are given in *Figure 3*. Thermograms of polypropylene and of PP–PB-9 copolymer show only one peak whilst poly(butene-1) and all others copolymers show melting endotherms with multiple peaks.

The melting temperatures, corresponding to the maxima in the d.s.c. endotherms, as a function of composition are given in *Figure 4*. As will be reported in detail later in this

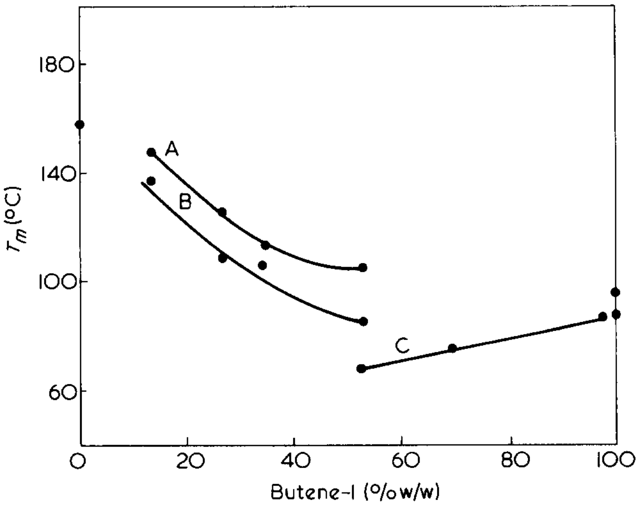

*Figure 4* Melting temperatures from d.s.c. traces as functions of the composition for propylene/butene-1 copolymers. A, Lower temperature peak of the polypropylene phase; B, higher temperature peak of the polypropylene phase; C, melting temperature of the main peak of the poly(butene-1) phase

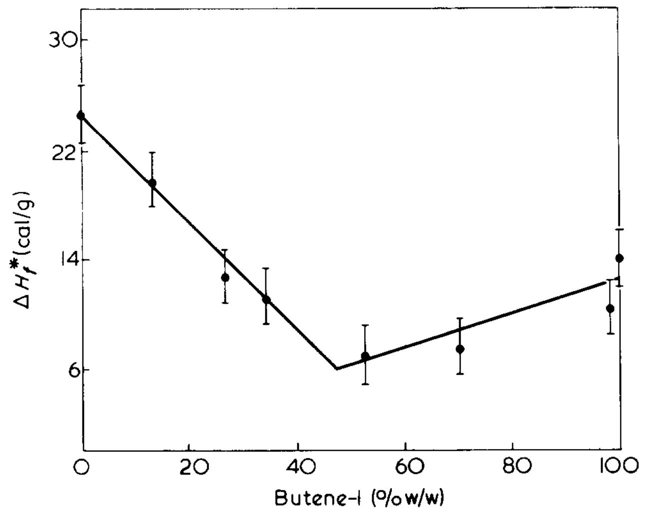

*Figure 5* Overall apparent enthalpy of fusion $\Delta H_f^*$ of single crystals of random isotactic propylene/butene-1 copolymers as a function of composition

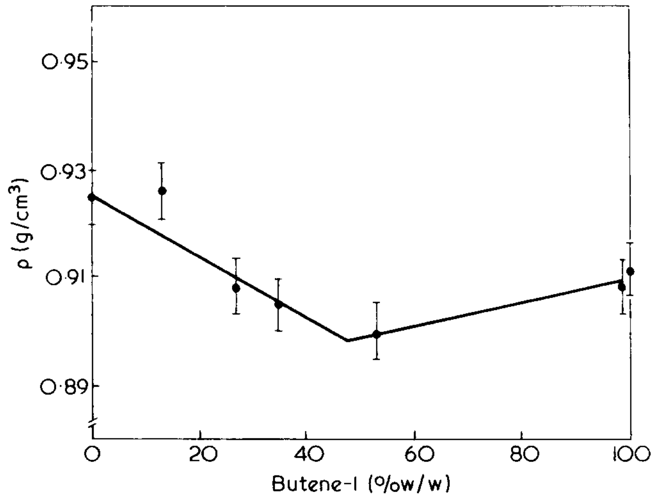

*Figure 6* Overall density (g/cm³) of single crystal aggregates of random isotactic propylene/butene-1 copolymers as a function of composition

paper, single crystal aggregates of copolymer with butene-1 concentration lower that ~50% show, in the wide-angle X-ray diffraction, only reflections of polypropylene. On the other hand the aggregates of copolymers with butene-1 concentration higher than ~50% give only reflections of poly(butene-1) in form 1. The copolymer with 53% butene-1 shows both reflections of polypropylene and poly(butene-1).

In the case of mats of single crystals of pure poly(butene-1), X-ray reflections of the various crystalline forms are coexistent.

On this basis the lower temperature endotherms of fusion of copolymers PP–PB-1, PP–PB-2, PP–PB-4 and that at an intermediate temperature of PP–PB-7 are related to the melting of a polypropylene phase with a lower thermodynamic stability probably due to the inclusion in the lattice of butene-1 units. The higher temperature endotherms of the same samples of copolymers are likely to be attributed to a more pure polypropylene phase with higher thermodynamic stability.

The endotherms at lower temperatures for sample PP–PB-7 and those for samples PP–PB-8 and PP–PB-9 are attributed to a poly(butene-1) phase that will include some propylene units as defects in the crystal lattice. Accordingly the trends of the melting points observed are reported in *Figure 4*.

The overall apparent enthalpy of fusion and the density of single crystal aggregates as functions of the composition are reported in *Figures 5* and *6*, respectively. It is interesting to note that in both curves a eutectic minimum results at a concentration of ~48% in butene-1 at the intersection of the curves that describe the two branches of composition. The second run d.s.c. thermograms of melt recrystallized single crystal aggregates are generally characterized by a main sharp peak with very weak secondary broader peaks. Poly(butene-1) and PP–PB-9 copolymer show on the run II d.s.c. thermograms one fusion endotherm with a well defined maximum.

In *Figure 7* the dependence of the temperatures of fusion of melt recrystallized materials related to the main peaks are reported against the percentage of butene-1. Wide-angle X-ray analysis of the samples of copolymers melt and recrystallized shows that samples from PP–PB-1 to PP–PB-4 crystallize in a polypropylene phase. In sample PP–PB-7 there is a coexistence of polypropylene and poly(butene-1) phases whilst copolymers at higher concentrations crystallize in the poly(butene-1) form 1 phase.

It is interesting to observe that the temperature of fusion of the poly(butene-1) phase in single crystals of PP–PB-7 sample is practically coincident to that of melt recrystallized. The melting temperatures of melt recrystallized samples PP–PB-9 and pure poly(butene-1) are higher than that of the corresponding single crystals. However, the different behaviour in the melting of single crystal aggregates and of melt recrystallized material must be pointed out.

### *Wide- and small-angle X-ray analysis of single crystal aggregates of isotactic propylene/butene-1 random copolymers*

According to the kinetic theory of crystallization of polymer from solution[5] the most probable thickness $L$ of a lamellar crystal is related to the equilibrium melting temperature $T_m^0$, $\Delta H_f$, the surface free energy of folding $\sigma_e$ and the undercooling $\Delta T$ by means of the relation:

$$L\Delta T = (2\sigma_e T_m^0/\Delta H_f) + \delta l \qquad (3)$$

$\delta l$ is an additional term allowing for low values of $\Delta T$ to be neglected.

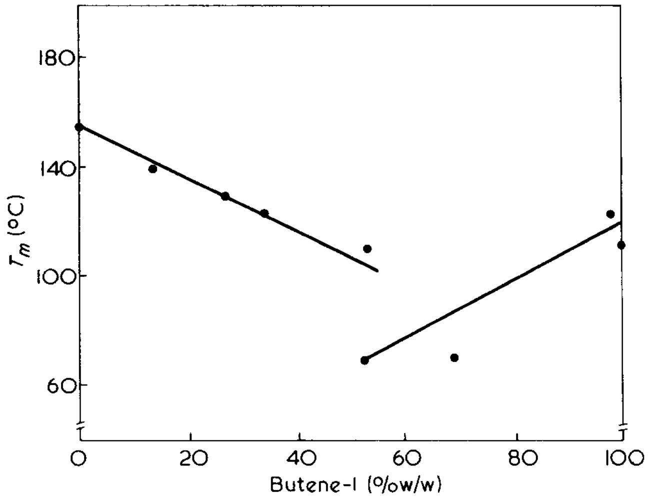

*Figure 7* Dependence of melting temperature of melt recrystallized material (from d.s.c. II run) upon composition (see text)

In *Figure 8* the quantity $L\Delta T$ for single crystal aggregates is given as a function of the percentage of butene-1 in the copolymer samples. $\Delta T$ has been assumed to be $T_D - T_C$. From the examination of the Figure we observe that both in the region of stability of the polypropylene and poly(butene-1) phases the quantity $2\sigma_e T_m^0/\Delta H_f$ increases with increase in number of chain defects along the chain.

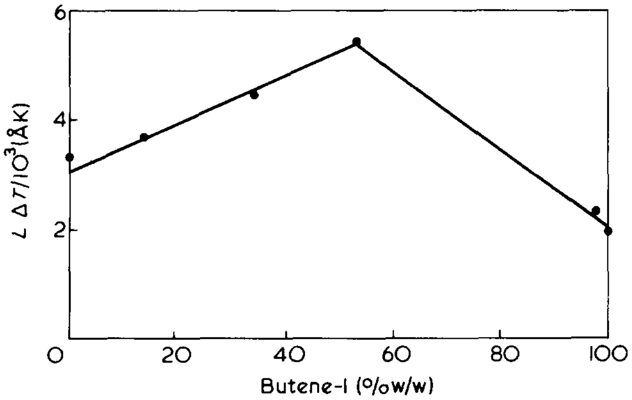

*Figure 8* Variation of the quantity $L\Delta T$ with the percentage of butene-1 in the case of single crystal aggregates of isotactic propylene/butene-1 copolymers

Since it is very unlikely that $T_m^0$ will increase by increasing the number of defects along the chain we have to conclude that the ratio $\sigma_c/\Delta H_f$ drastically increases with increase in the concentration of butene-1 units, in the case of the polypropylene-like phase and propylene units for the poly(butene-1)-like phase, along the chain of the copolymers. In *Figure 9* wide-angle X-ray diffraction spectra, obtained with a flat-plate camera, of a series of samples of solution grown single crystal aggregates of propylene/butene-1 copolymers and of pure homopolymers are shown.

Accurate analysis of the reflections and the determinations of the Bragg spacings leads to the following conclusions.

(a) In the single crystal aggregates of solution grown single crystals of poly(butene-1), reflections of polymorphic phases are coexistent.

(b) Copolymers PP–PB-1, PP–PB-2 and PP–PB-4 show only reflections of the polypropylene phase though an expansion of the unit cell is observed.

(c) In single crystal aggregates of copolymers PP–PB-9

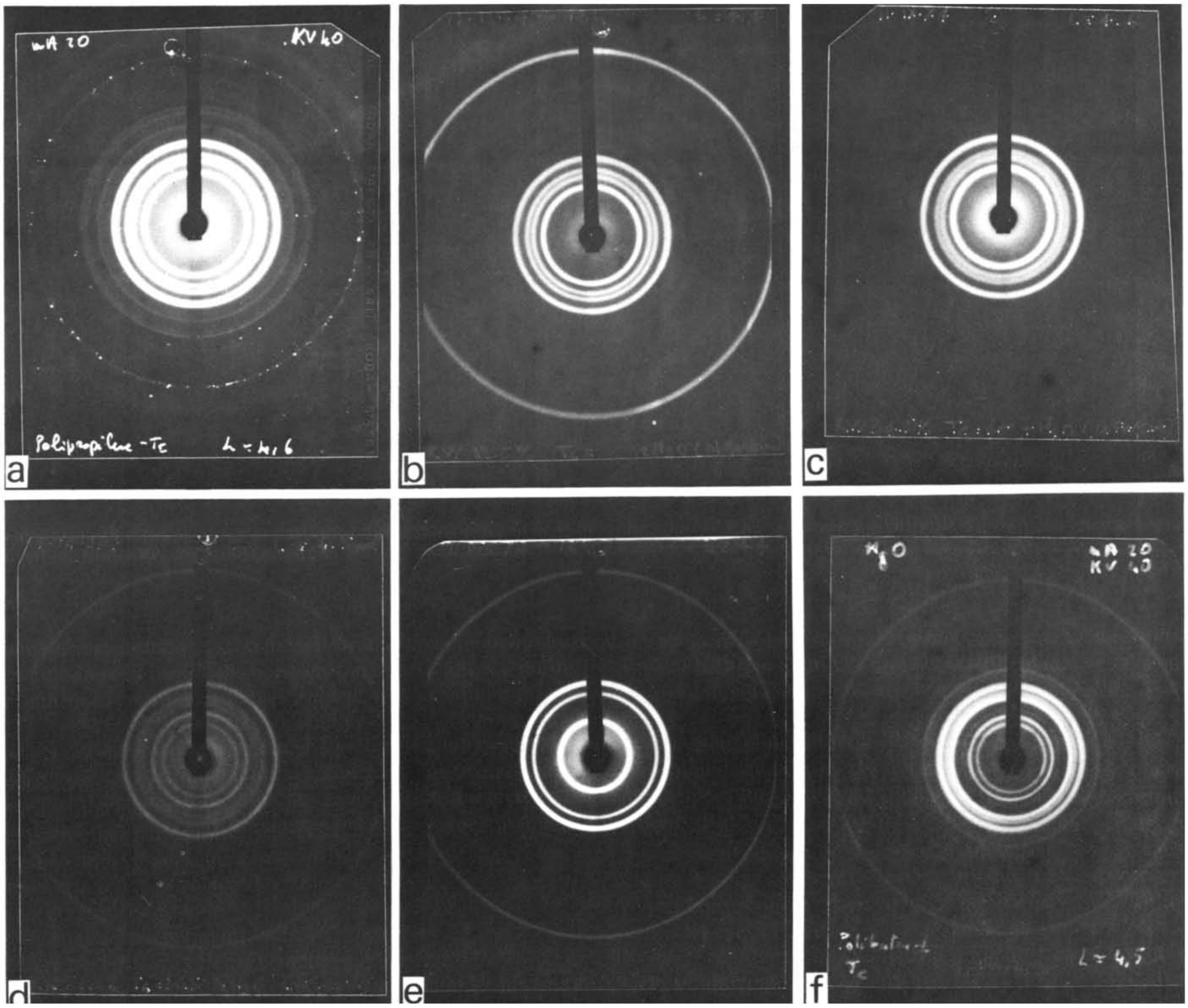

*Figure 9* Wide-angle X-ray diffraction spectra of samples of single crystals aggregates of propylene/butene-1 copolymers: (a) sample PP; (b) sample PP–PB-1; (c) sample PP–PB-4; (d) sample PP–PB-7; (e) sample PP–PB–9; (f) sample PB

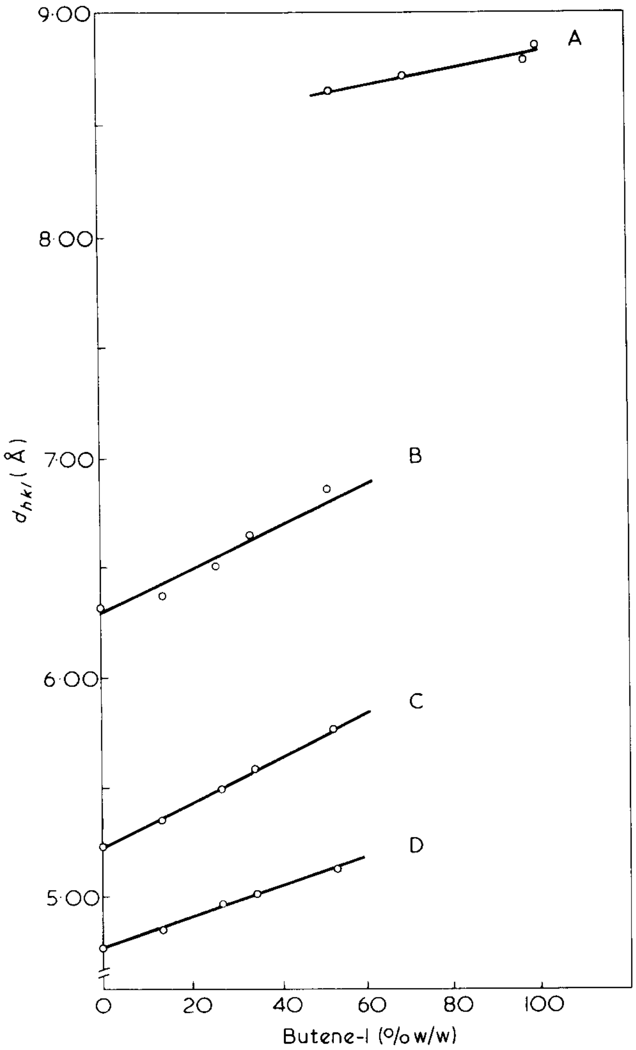

*Figure 10* Bragg spacings of the most intense reflections of polypropylene and poly(butene-1) phases as functions of composition. A, $(110)_{PB}$; B, $(110)_{PP}$; C, $(040)_{PP}$; D, $(130)_{PP}$

and PP–PB-8 only reflections of poly(butene-1) in form 1 are present; a contraction in the unit cell in this case is observed.

(d) in the X-ray diffraction pattern of single crystal aggregates of sample PP–PB-7 reflections of both polypropylene and poly(butene-1) are observed.

These results agree with the findings of Turner-Jones[6] obtained on bulk materials.

The Bragg spacings obtained from the flat-plate camera photographs at room temperature of the most intense reflections of the polypropylene-like phase and of the poly(butene-1) form 1 phase are given in *Figure 10* as functions of the percentage of butene-1. The values of the $\vec{b}$ axis of the unit cell of polypropylene and of $\vec{a}$ sin $\beta$ calculated from the spacing of (110), (040), (130) reflections are shown in *Figure 11* as functions of composition. They agree very well with those calculated by Turner-Jones[6] on bulk materials (see *Figure 11*).

This last result is rather interesting since it is an indication that both on crystallization from dilute solution and from the melt, crystals in polypropylene-like phase with the same amount of butene-1 units incorporated in the crystal lattice are obtained. This should also indicate that the process and the mechanism that lead to the formation of crystals from dilute solution and from the melt is fundamentally the same. It is interesting to note that, just as in the case of bulk propylene/butene-1 copolymers, a small amount of propylene units in the chain stabilizes the form 1 of isotactic poly(butene-1) of sample crystallized from dilute solution. The relative variation $(D-D_0)/D_0$ of the Bragg spacings of the reflections (130), (110), and (040) of polypropylene-like phase as a function of the composition is shown in *Figure 12*. The trend is linear. The slope

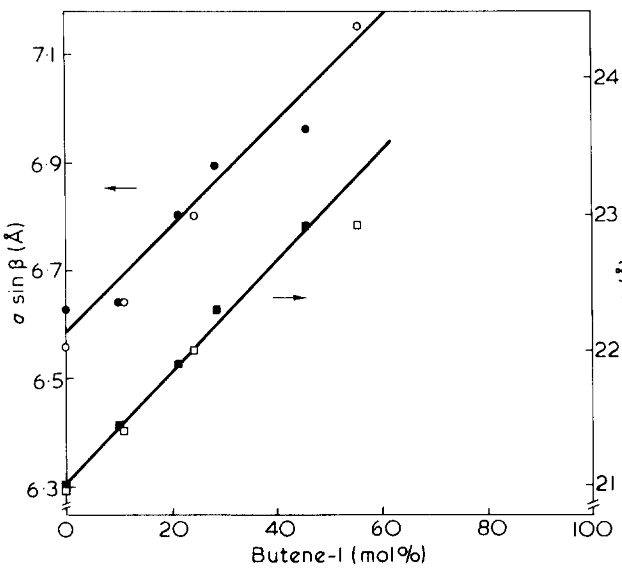

*Figure 11* Values of the $\vec{b}$ axis and of $\vec{a}$ sin $\beta$ of polypropylene phase as functions of composition: ○, □ Turner-Jones data (bulk); ●, ■ present paper (single crystals)

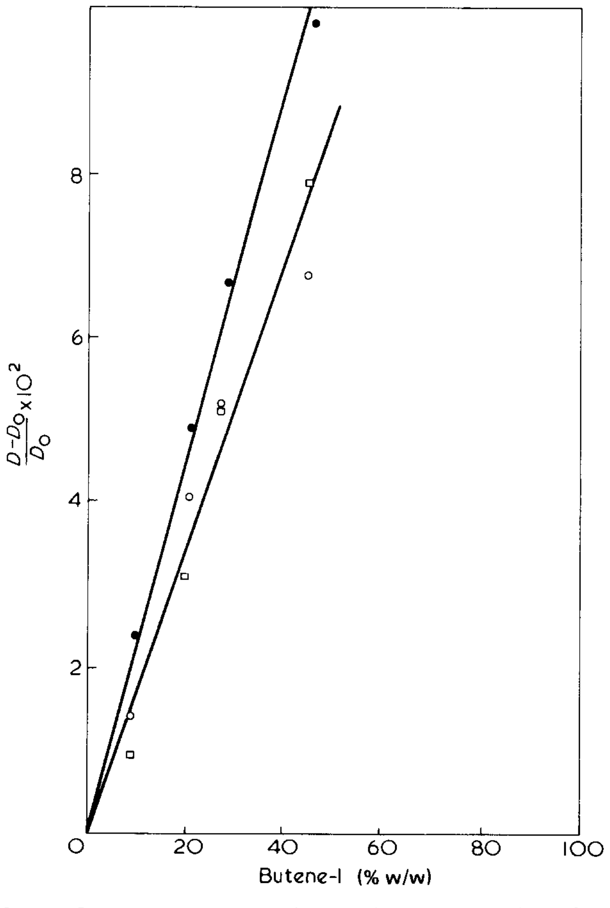

*Figure 12* Relative variation of some of the Bragg spacings of polypropylene phase of single crystal aggregates of propylene/butene-1 copolymers as a function of composition. ● (040); ○ (130); □ (110)

of these lines give a measure of the increase in the distance of the corresponding crystallographic planes. The values of the slopes are $0.23 \times 10^{-2}$, $0.17 \times 10^{-2}$, $0.17 \times 10^{-2}$ for reflections (040), (110) and (130), respectively. The difference found in the values of the slopes shows that the expansion of the unit cell of polypropylene caused by the inclusion of butene-1 units, is probably anisotropic.

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