cal sources in combination with oxidizing cations may be used to promote cationic polymerization of alkyl vinyl ethers and cyclic ethers. Mechanistic details remain to be evaluated but for all systems studied, an important feature is the generation of a chain reaction leading to formation of cationic initiators with obvious implications to quantum amplification in photo-induced phenomena. Detailed studies of individual systems are now in progress and it is clear that other types of cationically susceptible monomers may react similarly given appropriate matching of redox potentials for the promoting free radicals and the oxidizing salts.

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Thermal and mechanical properties of isotactic random propylene–butene-1 copolymers

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INTRODUCTION

The morphology, the crystal structure and the thermal behaviour of solution grown crystals of isotactic propylene–butene-1 copolymers (PP–PB) have been investigated by Martuscelli and coworkers and compared with those of homopolymers[1]. The dissolution temperature, the density and the apparent enthalpy of fusion showed eutectic behaviour with a minimum at a composition of about 48% by wt in butene-1. The crystallinity, present at all compositions, was attributed to the principal homopolymer crystalline phase. In the middle composition range both polybutene-1 (form I) and polypropylene crystalline phase occurred[1]. The experimental results indicated that isotactic PP–PB crystallizable copolymers show a crystal phase inversion for a composition of about 50%. A similar phase inversion has been found by Turner-Jones in the case of melt crystallized materials[2].

The present Note describes investigations on the thermal and tensile behaviour of compression-moulded samples of isotactic PP–PB copolymers.

EXPERIMENTAL

The unfractionated isotactic random copolymer samples used in the present investigation (see *Table 1*) were obtained by copolymerization reactions carried out with a $TiCl_3$–$AlEt_2Cl$ catalyst.

The composition of the samples range from pure isotactic polypropylene to pure isotactic poly(butene-1). All copolymers are crystallizable in the range of compositions examined.

The composition of the copolymers was determined by i.r. analysis.

A Perkin–Elmer differential scanning calorimeter DSC-2 was used to obtain apparent heats of fusion ΔH_f^*. 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 as the heat of fusion.

The melting temperatures of the samples were measured from the maxima in the d.s.c. endotherms. The temperature scale was calibrated from the melting points of low molecular weight standard samples.

The copolymers were tested mechanically using an Instron Universal Testing Equipment Model 1122. Dumbbell shaped specimens were prepared by compression moulding and quickly cooled to room temperature: the specimens of polypropylene were obtained by compression moulding at $P = 300$ kg/cm^2 and $T = 200°C$; the specimens of poly(butene-1) at $P = 300$ kg/cm^2 and $T = 160°C$ and the specimens of copolymers at $P = 300$ kg/cm^2 and $T = 160°C$. The experiments were carried out at a strain rate of $\dot{\epsilon} = 0.9$ min^{-1} at room temperature.

RESULTS AND DISCUSSION

Thermograms of melt-crystallized samples of isotactic PP–PB copolymers and of pure homopolymers show a

Table 1 Composition of isotactic random propylene–butene-1 copolymers

Sample	Butene-1 content	
	wt %	mol %
PP	0	0
PP–PB–5	45.6	38.6
PP–PB–6	47.9	40.8
PP–PB–7	53.3	46.1
PP–PB–8	70.0	63.6
PB	100	100

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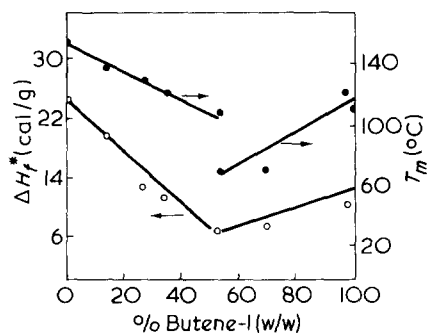
Figure 1 Melting temperature, T_m (●), and overall apparent enthalpy of fusion ΔH_f^* (○) of random isotactic propylene—butene-1 copolymers as a function of composition
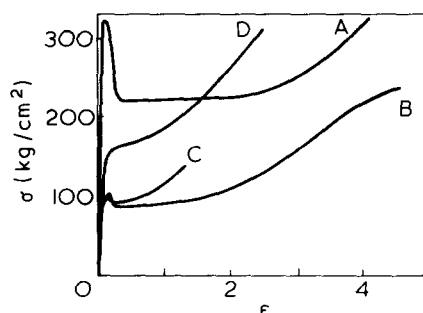

Figure 2 Stress—strain curves of compression moulded samples: A, isotactic polypropylene; B, copolymer with 45.6% by wt of butene-1; C, copolymer with 70.0% by wt of butene-1; D, isotactic poly(butene-1)

single fusion maximum except for sample PP–PB–7, which gives two endothermic peaks, attributed, from X-ray analysis, to the fusion of the polypropylene (higher temperature peak) and poly(butene-1), form I, (lower temperature peak) crystal phases.

As shown in *Figure 1* both the melting temperature of the polypropylene phase (butene-1 content less than 50%) and of poly(butene-1), form I phase decrease linearly with increasing percent of comonomer along the backbone chain. In agreement with the findings of Martuscelli and coworkers on isotactic PP–PB solution grown crystals[1,2] this trend may be accounted for by a co-crystallization process.

As shown in *Figure 1*, the overall apparent enthalpy of fusion of PP–PB isotactic copolymers presents a eutectic minimum at a composition of about 50%. This result, together with the wide-angle X-ray diffraction analysis, indicates that the co-crystallization of butene-1 units in the polypropylene crystal lattice, and *vice versa*, gives rise to the formation of physical defects

which lower the degree of perfection of the solids.

Typical stress—strain curves of poly(butene-1), polypropylene and PP–PB copolymers are shown in *Figure 2*. It can be seen that there is a pronounced difference in the tensile behaviour of these materials. Compression-moulded samples of isotactic poly(butene-1) behave quite differently from polypropylene. Polypropylene has a sharp well-defined reorientation zone or neck. Polybutene stretches throughout the length of the narrow part of the dumbbell shaped sample showing no sharp yield point.

The elastic modulus, E, defined as

$$\lim_{\epsilon \to 0} \frac{d\sigma}{d\epsilon}$$

the yield stress σ_y, (defined as the stress corresponding to the first point with a horizontal tangent) and the ultimate mechanical properties (work to break, W, the stress and elongation to break σ_u and ϵ_u, respectively) are strongly dependent upon the composition of the copolymers. All the tensile data are reported as function of composition in *Figure 3*.

Young's modulus, E, shows a minimum at a composition of about 50%. This result may be accounted for by the corresponding minimum in the value of the crystallinity observed for the same composition. Moreover, the limiting properties show a transition around the same composition (50%). This can be attributed to the crystal phase inversion: polypropylene—poly(butene-1), form I, observed in this material in the middle composition range.

The work to break, W (defined as the area under the stress—strain curve) shows the same trend as all the other mechanical properties discussed above.

From the data reported it can be seen that there is a strong relation between crystal structure, crystallinity, thermal and tensile behaviour of PP–PB copolymers.

CONCLUSIONS

For a butene-1 concentration of less than 50%, isotactic PP–PB copolymers may be considered to be basically a polypropylene chain with butene-1 units acting as constitutional chain defects; for higher butene-1 concentra-
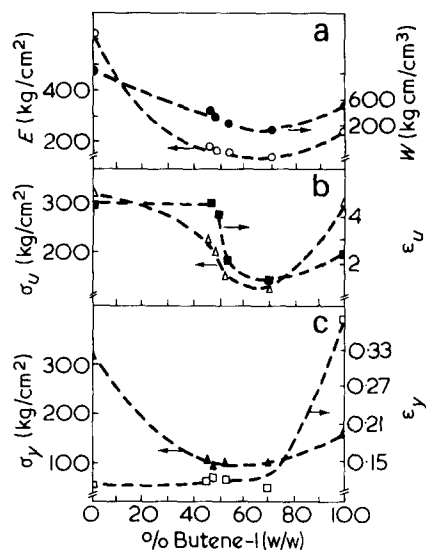

Figure 3 Mechanical properties of random isotactic propylene—butene-1 copolymers as a function of composition: ○, elastic modulus, E; ●, work to break, W; △, stress to break, σ_u; ■, strain to break, ϵ_u; ▲, yield stress, σ_y; □, yield strain, ϵ_y

tions there is defective poly(butene-1) with propylene units as chemical defects[3], in agreement with the general findings of Martuscelli and coworkers on the crystallization behaviour of polymers with chain defects along the chains[3]. When isotactic PP–PB copolymers are allowed to crystallize a certain number of chain defects are incorporated as defects in the crystal lattice of the basic polymers.

This process of partial co-crystallization strongly influences the mechanical properties of PP–PB isotactic copolymers. In fact, all the tensile quantities of polypropylene and poly(butene-1) show a drastic reduction when the amount of comonomer, which acts as a constitutional defect, is increased along the chains. Finally, we wish to point out that the crystal phase inversion observed in the case of PP–PB copolymers for compositions around 50% by wt in butene-1 can also be observed in the mechanical testing of the materials.

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