Effect of converting the crystalline form from α to β on the mechanical properties of ethylene/propylene random and block copolymers

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The crystalline β-form of ethylene/propylene random and block copolymers was obtained by crystallizing in the presence of a two-component β-nucleator. The influence of converting the crystalline copolymers from the α-form to the β-form on the drawing behaviour and impact strength was studied. The results show that the β-phase copolymer has higher impact strength, slightly lower yield strength and a higher degree of stress whitening than the α-phase copolymer. A stretching-induced or impact-induced β–α transformation in parallel with micro-crazing was also noticed.

(Keywords: propylene copolymers; crystalline form; β-nucleator)

INTRODUCTION

In the presence of an effective β-nucleator isotactic polypropylene (PP) crystallizes in the β-form in high purity[1–4]. It was found by us that the β-form of PP has a much higher impact resistance and ductile–brittle transition[5,6] than the α-form. This kind of impact modification of PP has some advantages over the impact modification of PP by blending it with an elastomer[7,8]. Firstly, the stiffness and ultimate strength of PP do not decrease with the α–β transformation, while impact modification traditionally decreases the stiffness of a polymer system, resulting in a lower flexural modulus. Loss in flexural modulus with an increase in elastomer level was observed in all elastomer-modified PP blends. Secondly, the heat distortion temperature of PP is generally enhanced, in spite of the lower melting temperature of the β-form. However, the impact strength of conventional PP at low temperature may not be improved by the α–β transformation because the glass transition temperatures of the α-form and β-form, which determine the low temperature brittleness, are identical.

The mechanical properties of polypropylene are also modified by making random or block copolymers with ethylene[9]. If only a small amount of the ethylene unit is incorporated, the copolymer retains the stiffness and the tensile strength of PP, but has improved mechanical properties at low temperatures. Therefore, it is of interest to examine the mechanical behaviour of β-phase ethylene/propylene copolymers.

The present work deals with the influence of converting the crystalline form from α to β on the drawing and impact behaviour of ethylene/propylene (E/P) random and block copolymers having low ethylene contents and nearly equal molecular weights. In order to convert the crystalline E/P copolymers from the α-form to the β-form, the two-component β-nucleator pimelic acid/calcium stearate was used.

EXPERIMENTAL

Materials and samples

Two ethylene/propylene random and block copolymers[9] having nearly the same melt flow indices and molecular weights, supplied by Tokuyama Soda Co. Ltd, were used in this study. Their characteristics are summarized in *Table 1*. The two-component β-nucleator used in the sample preparation was a mixture of equal weights of pimelic acid and calcium stearate. In order to prepare samples which preferentially crystallize in the β-form, pellets of the copolymer were premixed with 0.1 wt% of the β-nucleator and then extruded at a melt temperature of 200°C. The resulting pelletized extruder blend was denoted as the β-form sample.

Films for property study were prepared by compression moulding. Pellets of the copolymer sample placed between two aluminium foils were premelted at 200°C, then pressed in a laboratory press equipped with heating plates. The films were then quenched by cooling in air.

Instrumentation and experiments

The thermal measurements were carried out on a Perkin–Elmer DSC-2C differential scanning calorimeter equipped with a thermal analysis data station. The instrument was calibrated with high purity metal specimens according to standard procedures.

Wide-angle X-ray diffraction experiments were conducted using a Rigaku Geigerflex model D/max-rB X-ray diffractometer with Ni-filtered CuKα radiation. The

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Table 1 Physical characteristics of the α-form and β-form ethylene/propylene random and block copolymers used in this study

Sample	Polymer type	MFI[a] ($\mathrm{dg\,min^{-1}}$)	Ethylene content (wt%)	$10^{-4}\bar{M}_n$	$10^{-4}\bar{M}_w$	Crystalline form	K	T_c^b (°C)	T_m (°C)	ΔH_f ($\mathrm{J\,g^{-1}}$)	T_g^c (°C)
α-R21	Random	9.6	2.1	4.29	24.3	α	0	103.7	148.7	63.7	7.6
β-R21	Random					β	0.73	108.4	137.6	62.5	8.3
α-B56	Block	9.7	5.6	4.78	25.2	α	0.07	113.0	160.5	73.6	13.0
β-B56	Block					β	0.89	119.6	148.4	73.0	13.7

[a] Melt flow index, measured with a melt indexer according to ASTM D1238

[b] Measured by differential scanning calorimetry at a cooling rate of $20°\mathrm{C\,min^{-1}}$

[c] Measured with a Rheovibron DDV-II EA at 110 Hz

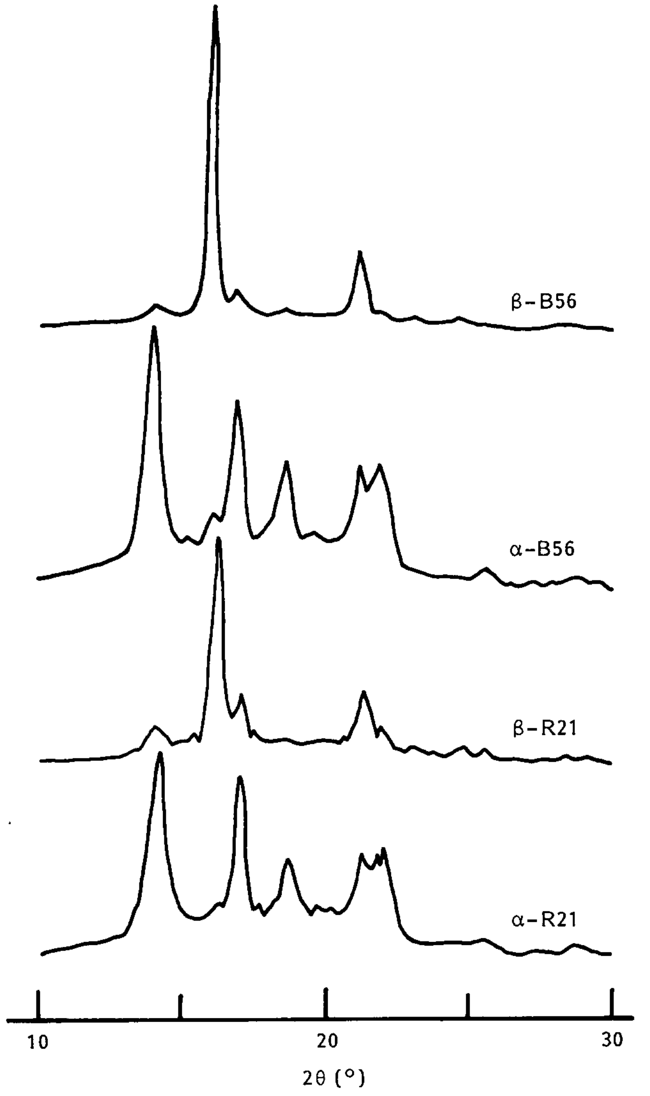

Figure 1 WAXD patterns for the compression-moulded ethylene/propylene copolymers

relative content of the β-form in the specimen was measured in terms of the K value, which is defined as[10]

$$K = \frac{H(300)}{H(300) + H(110) + H(040) + H(130)} \tag{1}$$

where $H(110)$, $H(040)$ and $H(130)$ are the heights of the strong equatorial α-form peaks (110), (040) and (130), and $H(300)$ is the height of the strong β-form peak (300).

The drawing experiments were conducted at a cross-head speed of $50\,\mathrm{mm\,min^{-1}}$ by means of an Instron 1185 tensile testing machine equipped with an environmental chamber. Dumb-bell-shaped samples cut out from the films were used. The notched Izod impact strength of injection-moulded specimens was obtained according to ASTM D256.

The temperature dependence of the storage modulus E', loss modulus E'' and loss tangent $\tan\delta$ was measured at 110 Hz with a Rheovibron DDV-II EA viscoelastometer (Toyo Baldwin Co. Ltd).

RESULTS

The wide-angle X-ray diffraction (WAXD) patterns of the α-form and β-form of E/P random copolymer R21 and block copolymer B56 are shown in *Figure 1*. The formation of the pure β-form in sample β-B56, similar to that in propylene homopolymer, is clearly demonstrated; however, sample R21 contains a substantial amount of the α-form, as shown by the α-form (110), (040) and (130) peaks. The relative amounts of the β-form, as expressed by the K values, in all four samples are given in *Table 1*. It can be seen from *Figure 1* and *Table 1* that the β-nucleator is more effective in inducing the β-form in the E/P block copolymer than in the E/P random copolymer.

The melting curves of the four compression-moulded samples at a heating rate of $20°\mathrm{C\,min^{-1}}$ are given in *Figure 2*. The absence of the melting peak of polyethylene in the vicinity of 130°C and the main peak temperature of 160°C, comparable to that of polypropylene for sample α-B56, reveal that copolymer B56 consists of a propylene block and an E/P elastomer block. For β-B56, the large endothermic peak at 148°C comes from the melting of the β-form of the propylene block, and the endotherms at 162°C and 167°C come from the melting of the original α-form and the recrystallized α-form of the propylene block, respectively. The lower melting temperature and lower T_g, as seen in *Table 1*, signify that α-R21 is a random copolymer. Correspondingly, the melting temperature of β-form R21 is also lower. The evidence from WAXD indicates the existence of more α-form crystals in β-R21. As expected, the ratio of the area under the α-form melting peaks to the area under the melting peaks for β-R21 is also larger compared with that for β-B56.

The tensile drawing behaviour of the four samples is shown in *Figures 3* and *4* through the nominal stress–strain curves recorded at drawing temperatures of 23°C, 70°C and 110°C. At low strains, it can be seen that the yield stress decreases with the conversion of the sample from the α-form to the β-form, demonstrating a lower resistance to the onset of plastic deformation in the

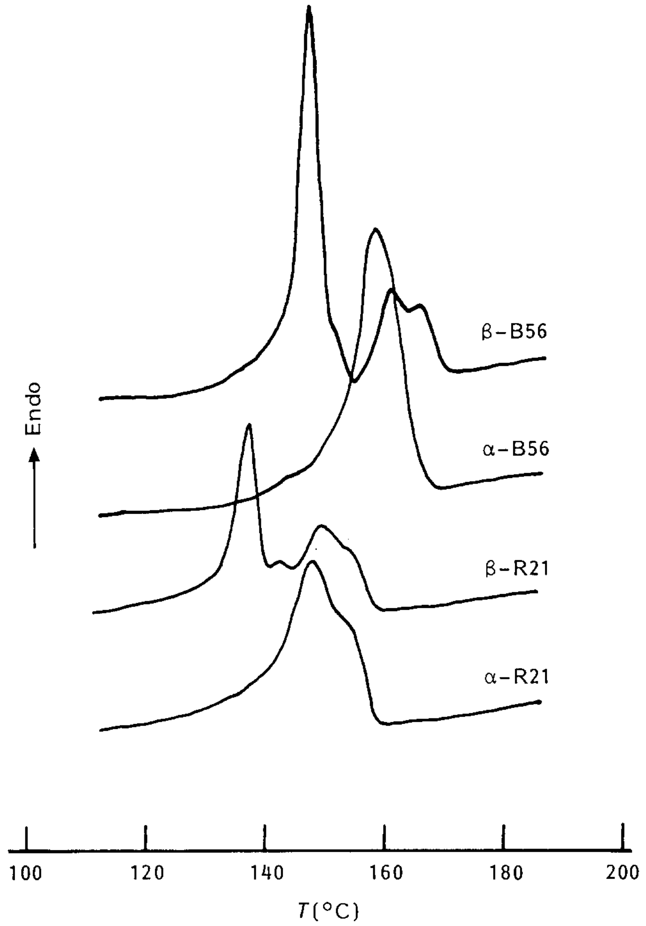

Figure 2 Differential scanning calorimetry melting curves of the compression-moulded ethylene/propylene copolymers (heating rate 20°C min^{-1})

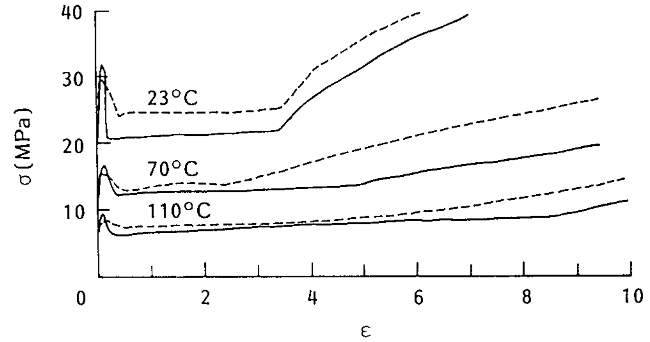

Figure 3 Nominal stress–strain curves of α-phase (——) and β-phase (– – –) random copolymer R21 at 23°C, 70°C and 110°C

β-form sample. Along with this, the drop in the stress from the yield point to the draw plateau is drastically reduced, indicating a broadening of the neck profile, while the draw ratio in the incipient neck decreases from 6.9 to 4.9 for the random copolymer, as indicated in *Figures 5* and *6*. For β-B56 the drawing proceeds uniformly even at a temperature as low as 23°C, and the profile of the drawn β-B56 specimen shows that no neck was formed. Another notable feature is that all β-phase film samples started to whiten beyond yielding, then became completely whitened with further drawing, while the α-phase specimens were partially whitened only at 23°C. Numerous voids created by the tensile drawing scatter light and make the drawn β-phase film whiten. The degree of stress whitening is much higher for β-B56 than for β-R21. This result demonstrates that the tendency to stress whitening increases with increasing β-crystal content in the copolymer, as sample β-R21 has a lower K value than

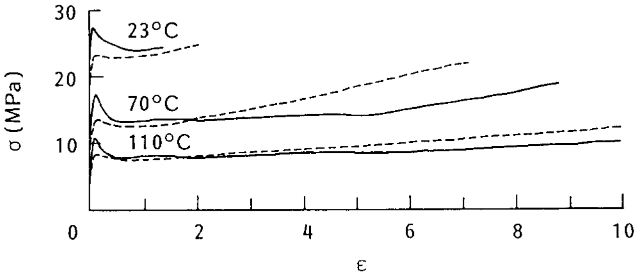

Figure 4 Nominal stress–strain curves of α-phase (——) and β-phase (– – –) block copolymer B56 at 23°C, 70°C and 110°C

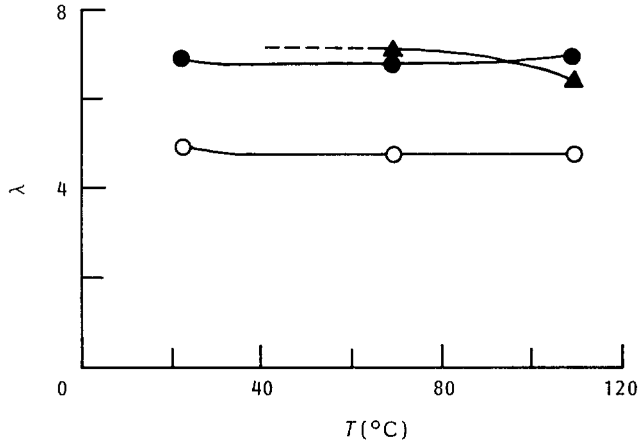

Figure 5 Effect of temperature on the draw ratio λ in the neck for α-phase (●) and β-phase (○) random copolymer R21 and α-phase (▲) block copolymer B56

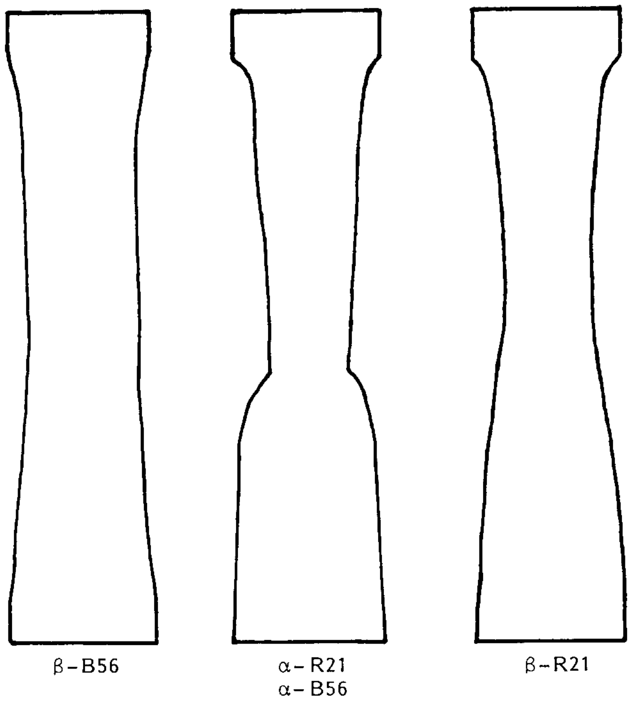

Figure 6 Profiles of drawn samples of ethylene/propylene copolymers. The original test pieces were 60 mm long and 25 mm wide

sample β-B56. It is obvious from *Figure 4* that α-B56 at 23°C broke at an elongation of 10–140%; however, the elongation at break of β-B56 reached 200% or more, indicating the higher toughness of β-B56 at 23°C.

It was observed previously that the β-phase transforms continuously into the α-phase in parallel with the whitening process during the tensile drawing of β-PP homopolymer. In order to follow the β–α transformation of the copolymer, the WAXD technique was used. *Figure 7* shows the variation in the WAXD pattern with the draw ratio for samples β-R21 and β-B56 at 70°C. It is evident from *Figure 7* that the α-form (110), (040) and (130) peaks increase and the β-form (300) and (301) peaks decrease with increasing draw ratio for the two β-phase samples. The draw ratios at which the β-phase disappears completely are different for the two polymers and are approximately equal to 2.5 and 4.0 for β-R21 and β-B56, respectively.

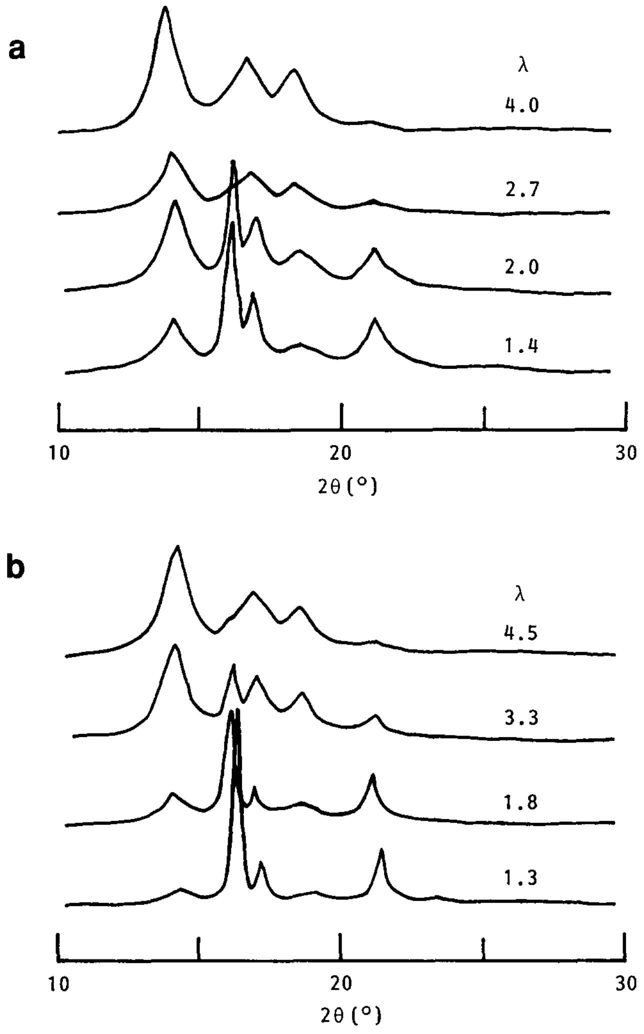

Figure 7 Variation in the WAXD patterns with draw ratio λ for samples β-R21 (a) and β-B56 (b) drawn at 70°C

The results give a clear indication that the stress whitening is caused by a stretching-induced β–α transformation in the copolymer. Sample β-B56 has more β-phase crystals than β-R21, so the stress whitening is much more extensive in β-B56 than in β-R21.

The foregoing results can also be used to explain the quasi-uniform drawing behaviour which appears in β-phase samples. It seems that the stretching produces a local temperature increase that may be compensated by the stretching-induced, endothermic β–α transformation and the extensive stress whitening, which, associated with a volume-increasing process in the β-phase sample, reduces the lateral contraction during neck formation, and so the β-phase sample stretches uniformly without necking.

At large strains, the drawing behaviour differs for α-phase and β-phase samples. The strain hardening of the β-phase film appears earlier than for the α-phase film for both copolymers, which is similar to the results for propylene homopolymer. *Table 2* summarizes the tensile properties of all four copolymer samples. It is rather strange that the formation of micro-crazes in the matrix decreases neither the ultimate strength nor the elongation at break. The notched Izod impact strengths of all four samples at 23°C are also given in *Table 2*. It can be seen from *Table 2* that the β-form samples have higher impact strengths than the α-form samples. Sample β-B56, with an impact strength of 106.8 J m^{-1}, shows the highest degree of stress whitening. This means that the impact modification that occurs upon changing the crystalline form from α to β can be attributed to crazing, and this method of impact modification can greatly enhance the impact strength of E/P block copolymer B56.

Figures 8 and *9* give the dynamic modulus E' and loss tangent $\tan\delta$ as a function of temperature for α-phase and β-phase E/P random copolymer R21 and block copolymer B56, respectively. The peak at about 8°C in

Table 2 Mechanical properties of E/P random copolymers R21 and E/P block copolymers B56

Sample	Temperature (°C)	Yield strength (MPa)		Ultimate strength[a] (MPa)		Elongation at break[a] (%)		Izod impact strength (J m^{-1})		Draw ratio in the neck	
		α	β	α	β	α	β	α	β	α	β
R21	23	31.9	29.6	39.2	39.6	700	610	14.3	20.0	6.9	4.9
	70	16.5	15.1	>23.8	>28.3	>1160	>1100			6.8	4.7
	110	9.3	8.2	>12.3	>14.6	>1200	>1100			6.9	4.7
B56	23	27.2	23.0	24.0	24.6	10–140	200	61.9	106.8	Broken	[b]
	70	17.4	13.3	18.7	22.0	880	700			7.1	[b]
	110	10.7	8.1	>10.7	>12.9	>1350	>1180			6.4	[b]

[a] The > symbol means that the sample was not broken at a gauge length of 15 mm because the sample length at break was beyond the limited height of the environmental chamber

[b] No necking

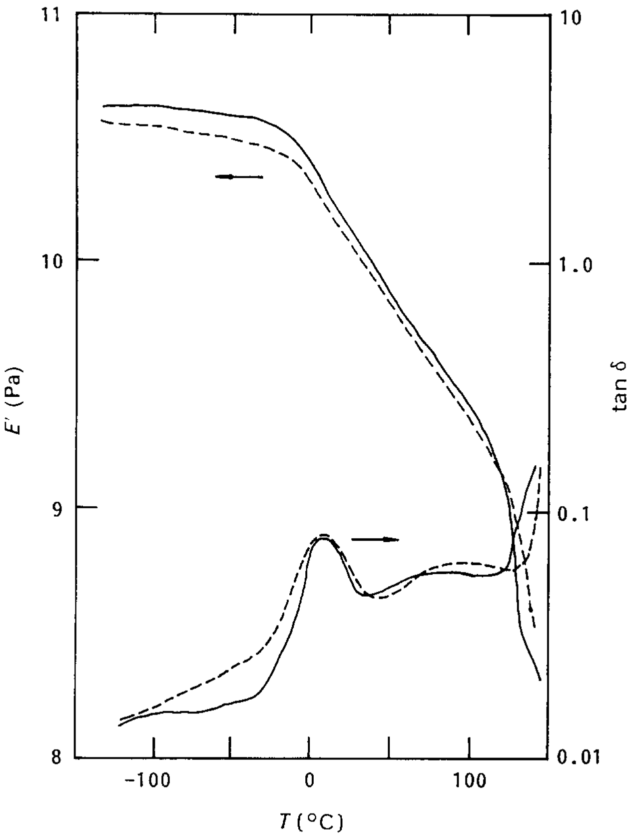

Figure 8 Temperature dependence of E' and $\tan\delta$ for α-phase (– – –) and β-phase (——) random copolymer R21

Figure 8 is the glass transition of the copolymer chains and its intensity increases with conversion from α-R21 to β-R21. Three major transitions are evident from *Figure 9* at approximately −105°C, −35°C and 13°C for α-B56 and β-B56. No shifts in peak position occurred for these three peaks, indicating that these three transitions take place in the amorphous region. The transition at 13°C is the glass transition, the intensity of which also increases with conversion from α-phase to β-phase. An increase in intensity of the glass transition of PP with increasing β-phase content has been observed by Crissman[11] and Jacoby *et al.*[12]. For E/P random and block copolymers we obtained similar results.

DISCUSSION

The Eyring equation

$$\dot{\varepsilon}=\dot{\varepsilon}_0\exp(-\Delta H/RT)\sinh(v\sigma/RT) \qquad (2)$$

was used to interpret the yielding of the E/P copolymer, where ΔH, σ, v, $\dot{\varepsilon}$ and $\dot{\varepsilon}_0$ are the activation energy, applied tensile stress, activation volume, strain rate and a pre-exponential constant, respectively.

For high values of stress, the tensile yield stress σ can be expressed as

$$\sigma=(\Delta H/v)+(RT/v)\ln(2\dot{\varepsilon}/\dot{\varepsilon}_0) \qquad (3)$$

Plots of σ *versus* $\ln\dot{\varepsilon}$ for α-B56 and β-B56 give straight lines, as shown in *Figure 10*. From the intercepts of the lines in *Figure 10* the $\Delta H/v$ values can be estimated.

It can be found from *Figure 10* that the β-phase of B56 has a lower activation energy than the α-phase, assuming that the activation volume is similar for both phases.

In a previous paper, a mechanism for the formation of micro-crazes in β-phase PP was suggested. It seems that these voids originate from a volume contraction during β–α or β–smectic transformation and enlarge with increasing draw ratio, since the crystalline density of the β-form (0.921 g cm^{-3}) is lower than that of the α-form (0.936 g cm^{-3}). This mechanism can also be invoked to explain the higher impact resistance of β-form E/P copolymers, because the β-form shows a higher degree of stress whitening, which is associated with the β–α transformation.

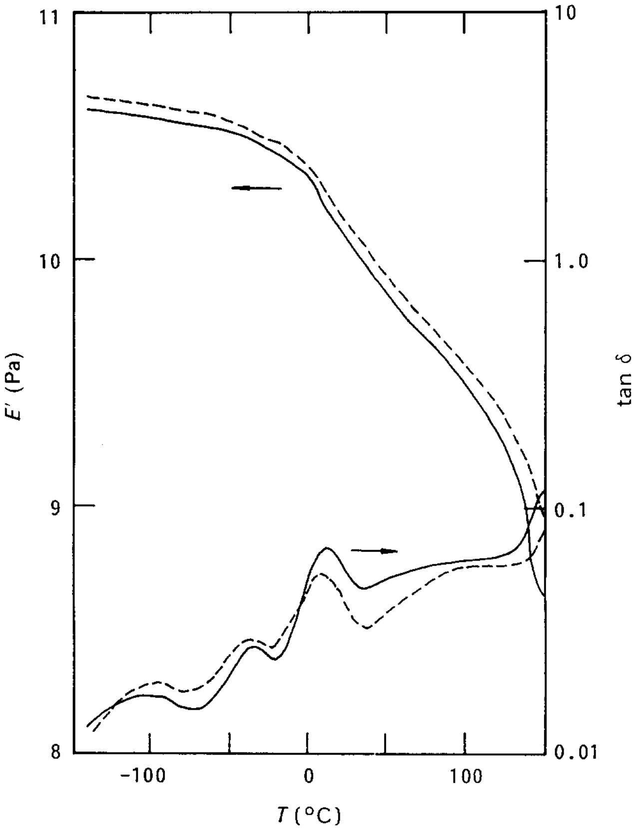

Figure 9 Temperature dependence of E' and $\tan\delta$ for α-phase (– – –) and β-phase (——) block copolymer B56

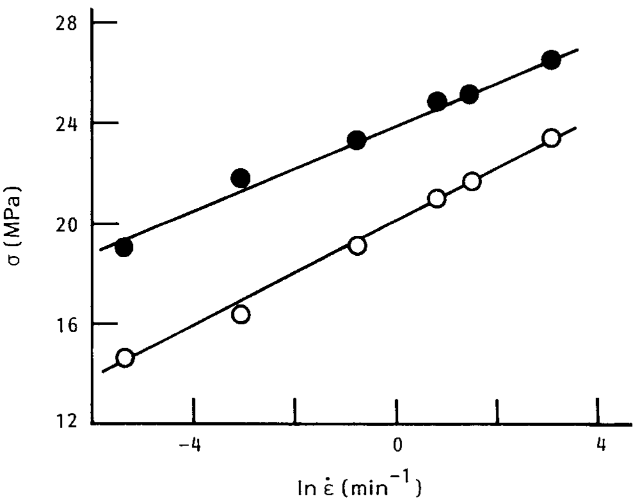

Figure 10 Plots of yield stress *versus* logarithmic strain rate for α-phase (●) and β-phase (○) block copolymer B56 drawn at 23°C

CONCLUSION

This paper has shown that β-form E/P random and block copolymers can be formed by melt crystallization in the presence of a two-component β-nucleator. This β-nucleator is more effective in inducing the β-form in the E/P block copolymer and polypropylene than in the E/P random copolymer.

An evaluation of the mechanical properties of β-form *versus* α-form E/P block copolumer gave the following results.

1. The β-form has a slightly lower yield strength and much higher impact resistance.
2. The β-form draws uniformly without neck formation, and a unique microporous texture having the appearance of white paper is formed beyond yielding.

An evaluation of the mechanical properties of β-form *versus* α-form E/P random copolymer gave the following results.

1. The β-form has a slightly lower yield strength and higher impact resistance.
2. The β-form has a lower draw ratio in the neck and shows stress whitening in tensile drawing, but the degree of stress whitening is lower than that in the E/P block copolymer.

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