PII: S0032-3861(97)00427-8

Presence of low-melting crystallinity in ethylene–propylene elastomers

M. Pizzoli[a,*], M. C. Righetti[a], M. Vitali[a] and P. Ferrari[b]
[a]Dipartimento di Chimica 'G. Ciamician' dell'Università di Bologna and Centro di Studio per la Fisica delle Macromolecole del C.N.R., Via Selmi 2, 40126 Bologna, Italy
[b]Montell Italia, Centro Ricerche 'G. Natta', Piazzale Donegani 12, 44100 Ferrara, Italy
(Received 9 January 1997; revised 3 April 1997)

The thermal behaviour of some ethylene–propylene random copolymers (EPRs) with 55–70 mol% ethylene content was investigated in the temperature range from −100 to +200°C. Irrespective of differences in chemical composition broadness, resulting from different catalytic systems, all samples display a low-melting crystallinity of low degree, developing rapidly when the material is cooled to low temperatures. The poorly crystalline phase, undetectable by X-rays, melts over a broad range of temperature, the lower limit merging with the glass transition and the upper one ending at ~60°C. The crystal size distribution is affected by isothermal treatments performed below room temperature, but the overall degree of crystallinity is not modified. The low-melting crystalline domains are associated with short ethylene segments comprising < 10 CH_2 sequences. Experimental evidence suggests that 55 mol% is the lower limit of ethylene content in EPR copolymers required to achieve a detectable crystallinity which melts below room temperature. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: EPR copolymers; thermal behaviour; low-melting crystallinity)

INTRODUCTION

The physical behaviour of ethylene–propylene random copolymers prepared by Ziegler–Natta polymerization is strictly related to three structural parameters: average chemical composition, compositional heterogeneity and sequence distribution of comonomer units along the chain. Depending on these factors, different kinds of material, either amorphous or partly crystalline, can be obtained. With regard to the composition of the copolymer as a whole, in the range very rich in one of the two components, long crystallizable sequences of ethylene (C_2) or propylene (C_3) units are present in the backbone and the polymers behave as thermoplastic materials. Depending on the predominance of ethylene or propylene units, the physical properties are related to those of high-density polyethylene and isotactic polypropylene respectively, apart from depression of the melting point and crystallinity degree as well as an improvement in transparency and in some mechanical properties such as flexibility and impact strength[1].

In the intermediate range of composition the materials are commonly referred to as ethylene–propylene rubbers (EPR), even though the physical behaviour is affected by the width of compositional distribution among different chains and by the sequence arrangements along the single molecules. The catalytic systems used for the synthesis play a key role in determining whether these elastomers are indeed amorphous at room temperature or retain a certain degree of crystallinity. Catalysts can be divided into two classes, i.e. heterogeneous titanium-based catalysts and homogeneous vanadium-based catalysts. In the former case the product of the reactivity ratios $r_1 r_2$ is greater than unity and the catalyst tends to promote a blocky character in the

copolymer, with relatively long crystallizable ethylene sequences[2]. In addition, the heterogeneity of the catalytic system leads to a multiplicity of active sites and therefore to large compositional fluctuations, which result in a further contribution to crystallinity[2,3]. In the case of vanadium-based catalysts, the $r_1 r_2$ product ranges from 0.1 to 0.5 and a statistical distribution of the monomers along the chain is preferred. As a consequence, more homogeneous copolymers are obtained and no crystallinity at room temperature is displayed by vanadium-based EPR samples covering the mid-concentration range. A third class of catalysts to be mentioned comprises more recently developed systems based on metallocenes which combine the high polymerization activity of $MgCl_2$-supported titanium catalysts with enhanced homogeneity of chemical composition in the copolymer[4,5].

There is not much agreement in the literature[2–8] about the concentration range where ethylene–propylene random copolymers can develop polyethylene-type crystallinity. This is certainly due, in addition to the wide variety of catalytic systems that yield different distributions of composition, to the different techniques used to evaluate the degree of crystallinity. However, it has been suggested that the minimum sequence length of ethylene units is in the region of 10 CH_2 groups for crystallization near room temperature in samples exhibiting a 10% degree of crystallinity[2].

The present paper reports an accurate characterization of the thermal behaviour of two commercial EPR samples in the temperature range from −100 to +200°C. The copolymers have similar average chemical composition, amounting to ~70 mol% of ethylene, but different local sequences and composition distributions resulting from vanadium-based (V-EPR) or titanium-based (Ti-EPR) catalysis. Particular attention has been paid to the

---

* To whom correspondence should be addressed

calorimetric behaviour below room temperature, where the effects of various thermal treatments have been examined. Dynamic mechanical measurements have been performed in the temperature range from -150 to $+150°C$. Some results on EPR samples obtained with the aid of zirconocene catalyst are also reported.

EXPERIMENTAL

Materials

V-EPR was a commercial product (CO054 Enichem Elastomeri) obtained by suspension polymerization with a vanadium-based catalyst. Ti-EPR was synthesized at the 'Giulio Natta' Research Centre of Montell (Italy) by gas-phase polymerization with a titanium-based catalyst supported on $MgCl_2$[9]. The characteristics of the two copolymers are listed in *Table 1*.

Suitable specimens for dynamic mechanical measurements were obtained by using a miniature mixing-injection-moulding machine. Samples (< 1 g) were introduced into the melting cup at 200°C and, after intensive mixing for 2 min, injection-moulded into a small die (30 × 8 × 1.8 mm).

Measurements

Wide angle X-ray scattering measurements were carried out at room temperature using a Philips PW1050/81 powder diffractometer controlled by a PW1710 unit, utilizing a graphite-monochromated Cu Kα radiation (λ = 0.1542 nm, 40 kV, 40 mA). The percentage crystallinity was estimated by integration of the diffracted intensity data in the 5–35° 2θ range and subtraction of the amorphous scattering band intensity.

The calorimetric behaviour was investigated in the temperature range from -100 to $+200°C$, at a heating rate of 20°C min^{-1}, by means of a Perkin-Elmer DSC-7 calorimeter calibrated with high-purity standards. Apart from the d.s.c. results obtained in the first scan on as-supplied samples, excellent reproducibility was found in subsequent thermal scans after rapid cooling (quenching) from $+200$ to $-100°C$. Samples quenched from 200°C to different temperatures were also subjected to isothermal treatments for 3 h in the d.s.c. cell and the next calorimetric curve was recorded after cooling to $-100°C$. The glass transition temperature (T_g) was taken at the midpoint of the specific heat increment associated with the transition and the melting temperature (T_m) at the peak value of the fusion endotherm.

Dynamic storage modulus E' and mechanical loss tangent tan δ were measured with a dynamic mechanical thermal analyser (DMTA, Polymer Laboratories) operated in the dual cantilever bending mode at a frequency of 3 Hz and a heating rate of 3°C min^{-1} over the temperature range from -150 to $+150°C$.

Table 1 Molecular parameters of ethylene–propylene copolymers

		V-EPR	Ti-EPR
C_2 content[a]	(mol%)	66.1	70.6
	(wt%)	56.5	61.5
Intrinsic viscosity[b]	(dL g^{-1})	1.87	2.04
Molecular weight[c]	M_w (10^3)	199	213
	M_n (10^3)	30.8	34.8

[a] from i.r. spectroscopy
[b] in tetrahydronaphthalene at 135°C
[c] From g.p.c. in 1,2-dichlorobenzene at 135°C

RESULTS AND DISCUSSION

X-ray characterization

The X-ray spectrum of V-EPR (see *Figure 1a*) at room temperature is typical of an amorphous material and exhibits only a broad maximum centred at $2\theta = 18°$. On the contrary, Ti-EPR shows two relatively narrow diffraction peaks at $2\theta \approx 21°$ and $23.5°$ superimposed on the amorphous halo (*Figure 1b*). The position of the main crystalline peak corresponds to the (110) strongest reflection typical of polyethylene[10], pointing to the presence of some polyethylene-type crystallinity in Ti-EPR. The degree of crystallinity calculated as described above was found to be in the region of 12%.

The finding that V-EPR and Ti-EPR, though similar in composition, appear respectively amorphous and partly crystalline at room temperature indicates some microstructural differences in the two polymers and confirms the higher probability of longer methylene sequences in titanium-based than in vanadium-based EPR, as mentioned in the Introduction.

Calorimetric behaviour

Figure 2 shows the calorimetric curves of as-received V-EPR and after rapid cooling to $-100°C$. Although the measurements were continued up to 200°C, the curves have been plotted to only 100°C because no thermal event was observed at higher temperature.

An endothermal baseline shift is seen corresponding to the glass-to-rubber transition, starting at about $-60°C$. The specific heat increment at T_g is not followed by a rapid return of the d.s.c. response to a linear baseline and the shape of the calorimetric curve suggests the existence of an endothermic phenomenon of low intensity, covering a wide range of temperature. The small peak located $\sim 20°C$ above room temperature in the first scan is clearly related to room
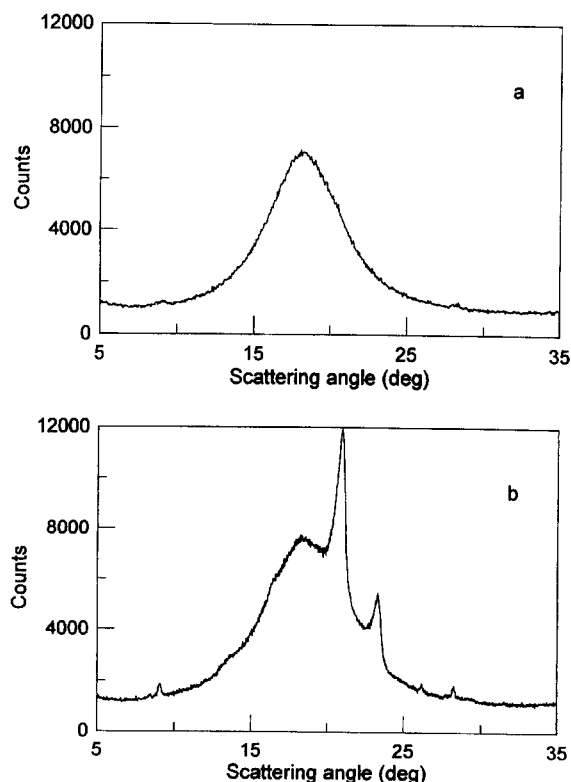

Figure 1 WAXS spectra of V-EPR (a) and Ti-EPR (b)

temperature storage, since heating to 200°C erases the previous thermal history and the subsequent scan (solid line in *Figure 2*) shows only the broad endotherm ranging from about −40°C up to 60°C. Holding the sample for a few hours at room temperature restored a small melting peak very similar to that shown in the first scan of *Figure 2*.

In order to clarify the origin of the endotherm next to the glass transition, the calorimetric behaviour of V-EPR was investigated after annealing at low temperature. For this purpose, samples were heated to 200°C, quenched to a selected temperature (−25, −15 or −5°C) and held isothermally for 3 h. The subsequent heating scans, shown in *Figure 3*, reveal the presence of a small endothermic peak located ∼20°C higher than the temperature of isothermal treatment, in much the same way as previously found for the sample maintained at room temperature. This behaviour is similar to that commonly observed on annealing of partly crystalline polymers[11] and suggests the existence of a low-melting crystal phase in V-EPR. It turns out that even quite short sequences of ethylene units are capable of crystallizing and giving rise to poor and small crystalline entities, most of which develop on cooling whenever the sample is brought below room temperature. The broad endotherm evidenced in the second calorimetric scan of *Figure 2* indicates that
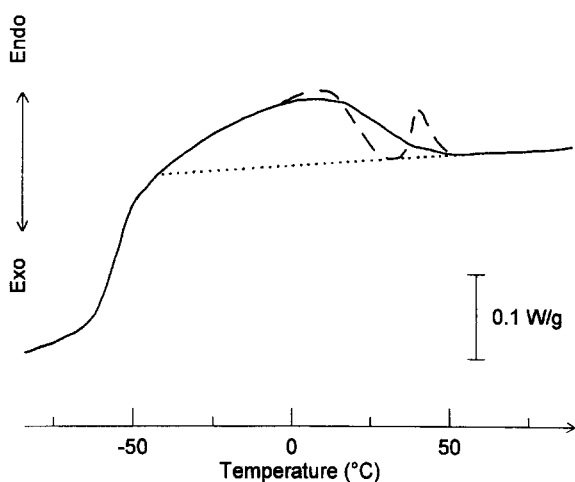

Figure 2 Calorimetric curves of V-EPR: - - -, first scan on as-supplied sample; ————, second scan after rapid cooling to −100°C; · · ·, extrapolated baseline
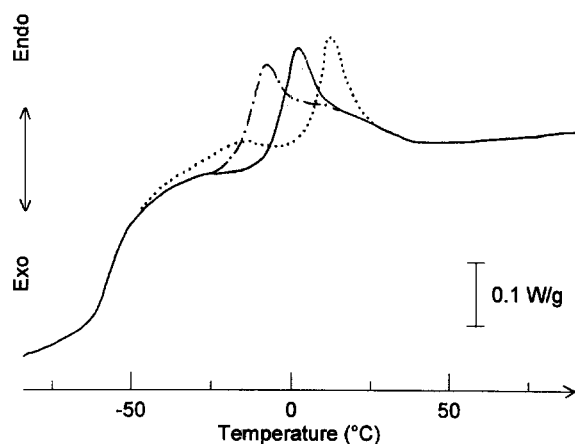

Figure 3 Calorimetric curves of V-EPR after isothermal treatment at −25°C (- • -), −15°C (————) and − 5°C (· · ·)

melting gradually occurs from T_g up to 60°C, in accordance with a wide distribution of crystallite size.

It is apparent from *Figure 3* that thermal treatments at −25 and −15°C are sufficient to allow the formation of relatively less defective crystalline populations, so that all crystallites melt at a temperature higher than the isotherm value and a short linear baseline is observed above T_g. In contrast, only a fraction of ethylene sequences is long enough to crystallize isothermally at −5°C and further crystallization occurs upon cooling to lower temperature. As a matter of fact, besides the sharp peak at 13°C due to annealing, the subsequent heating shows a melting endotherm which merges with the glass transition. If the annealing temperature is further raised, isothermal crystallization involves a decreasing amount of polymer, as evidenced by the small annealing peak of the room-stored sample, and most of the crystallization occurs on cooling to T_g (see broken curve in *Figure 2*).

A rough estimate of the enthalpy associated with the melting region of V-EPR leads to a value of 13 J g^{-1}, which corresponds to a 4.5% degree of crystallinity, assuming 290 J g^{-1} as the heat of fusion of perfectly crystalline polyethylene[12]. No significant effect of thermal history on the experimental melting enthalpy has been observed, which implies that annealing treatments do not increase the degree of crystallinity and affect only the distribution of crystallite size.

The ability of V-EPR to develop a certain degree of crystallinity, revealed by d.s.c. measurements, is not inconsistent with the X-ray results, since most of the crystallites melt at low temperature so that the residual crystal phase at room temperature is below the detection limit of the X-ray technique.

It is clear from *Figure 3* that the thermal treatment at −15°C allows the best resolution between the glass transition and melting phenomena, and the corresponding calorimetric curve can be utilized to evaluate more accurately the glass transition parameters of V-EPR. The values obtained for the glass transition temperature T_g and the specific heat capacity increment ΔC_p are 220 K and 0.60 J g^{-1}K^{-1} respectively. Taking into account that the average value[13] of the product $T_g \Delta C_p$ for most amorphous polymers is equivalent to 115 ± 19 J g^{-1}, the experimental results for V-EPR appear consistent with the published data and suggest that the glass transition parameters are not affected by the low-melting small crystallites present in V-EPR.

One of the equations commonly used to describe the T_g–composition dependence in random copolymers is the Fox relation[14]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

where T_g is the glass transition temperature of the copolymer, T_{g1} and T_{g2} refer to pure homopolymers 1 and 2, and w_1 and w_2 are the comonomer weight fractions. Equation (1) can be used to obtain an estimate of the glass transition temperature of polyethylene, a polymer which cannot easily be vitrified into a wholly amorphous state. By taking 260 K as the T_g of polypropylene[15] and the experimental value for V-EPR, a T_g of 193 K is calculated for polyethylene, in very good agreement with the result obtained by Geil[16] and Boyer[17] for the onset of large-scale motions of unconstrained polymer segments in semi-crystalline polyethylene.

As regards the titanium-based EPR, the calorimetric results confirm the presence of the high-melting crystal phase previously revealed by X-ray measurements. The curves reported in *Figure 4* show a broad melting region above room temperature with a main peak at 123°C, both for the as-received sample and after quenching. The associated enthalpy of fusion corresponds to a crystallinity degree of 14%, in fair agreement with the estimate from X-rays. Apart from the high-temperature melting region, the calorimetric behaviour of Ti-EPR is very similar to that of V-EPR in showing a low-temperature endotherm superimposed on the glass transition. The overall behaviour indicates that the melting region of Ti-EPR covers quite a wide temperature range, extending from T_g up to 130°C, and suggests the presence of low-melting crystallites in addition to the high-melting crystal phase. As already observed in the case of V-EPR, the only difference between the first and second scan lies in the room temperature annealing peak, which disappears after cooling from the melt.

In the attempt to separate the phenomena characteristic of Ti-EPR (glass transition, low-melting and high-melting endotherms), two thermal treatments on the same sample were carried out. The calorimetric curve reported in *Figure 5* refers to the heating of a sample first annealed in an oven at 50°C for 17 h, then quickly transferred to the d.s.c. cell, where it was held isothermally at −15°C for 3 h. As
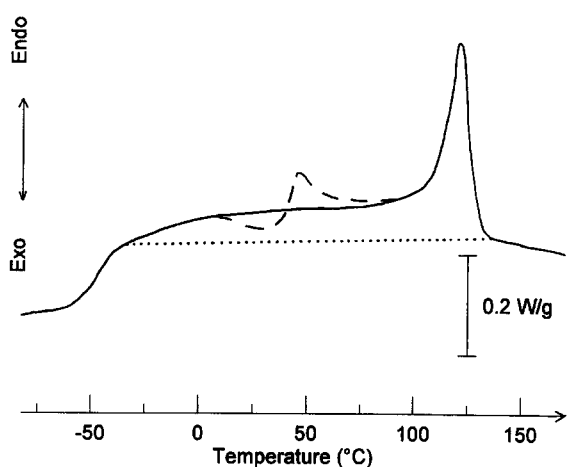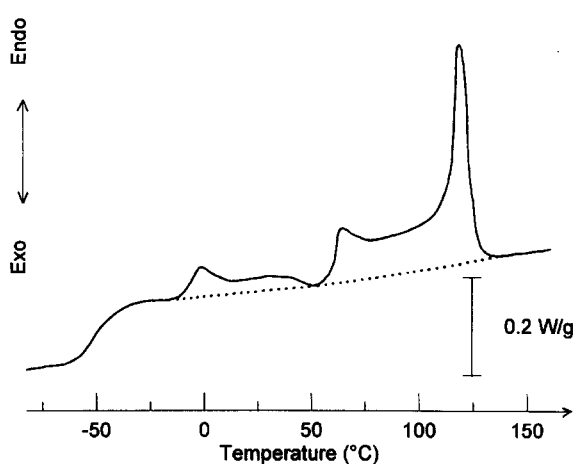
with V-EPR, the treatment at −15°C shifts the onset of the low-melting region to higher temperature and the glass transition appears more defined compared with the unannealed sample of *Figure 4*. Furthermore, annealing at 50°C results in a good separation of the low-melting from the high-melting region and allows values of 6 and 32 J g^{-1} respectively to be calculated for the melting enthalpies relating to the two crystalline populations. The former value corresponds to a lower crystallinity degree than that obtained for V-EPR (13 J g^{-1}) and the difference is easily justified by taking account that, due to the high compositional heterogeneity of Ti-EPR, a significant number of ethylene units are arranged in long high-melting sequences and therefore there are fewer ethylene sequences of suitable length to crystallize below room temperature.

The experimental evidence that both V-EPR and Ti-EPR develop a low-melting crystal phase when cooled below room temperature suggests that the phenomenon is peculiar to the EPR samples investigated, irrespective of the catalytic system used in the synthesis of the copolymer. This hypothesis has been confirmed by examining the calorimetric behaviour of a third rubber (Zr-EPR) obtained through zirconocene-based catalysis, which is known to lead to reduced composition fluctuations[5]. The d.s.c. curves of Zr-EPR shown in *Figure 6* appear quite similar to those previously observed for V-EPR (see *Figure 2*), confirming the existence of a broad melting endotherm next to the glass transition and the occurrence of a small annealing peak in the first scan, due to room temperature storage. The only difference between the two samples concerns the enthalpy associated with the melting region, which is greater for Zr-EPR than for V-EPR (20 *versus* 13 J g^{-1}). The higher crystallinity displayed by the former sample is justified by the slightly higher ethylene content (69.5 mol%) of Zr-EPR compared with V-EPR, which leads to an increased number of ethylene sequences able to crystallize at low temperature.

Calorimetric results for V-EPR fractions

The presence of a certain amount of crystallinity which melts below room temperature has been verified for EPR samples of similar composition (~70 mol% of C_2 units), obtained with different catalytic systems. It turns out that the ability to develop a low-melting crystal phase in these samples is qualitatively—although not quantitatively—independent of the degree of compositional heterogeneity,
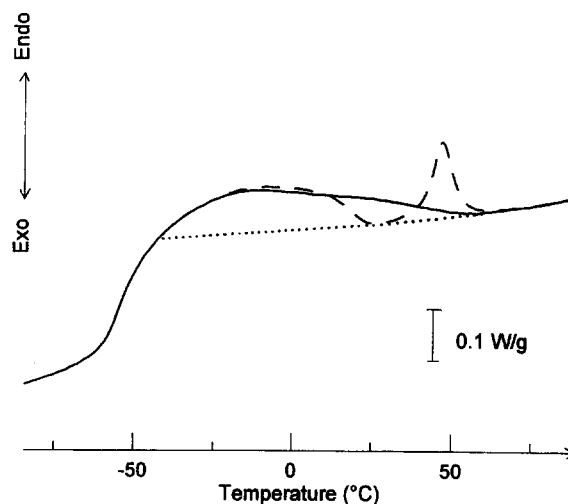

Figure 4 Calorimetric curves of Ti-EPR. Symbols as in *Figure 2*

Figure 5 Calorimetric curve of Ti-EPR after isothermal treatment at 50°C and −15°C (see text for details)

Figure 6 Calorimetric curves of Zr-EPR. Symbols as in *Figure 2*

which is in the order Ti-EPR > V-EPR > Zr-EPR. The broadness of the composition distribution in Ti-EPR is evidenced by its calorimetric behaviour (*Figure 4*), which reveals a melting region extending from T_g up to 130°C in accord with a very wide distribution of ethylene sequence length, including both short and long sequences. The presence of a certain degree of intermolecular heterogeneity in V-EPR was confirmed by its partial dissolution in diethyl ether at room temperature, which yielded two fractions of different composition. The diethyl ether-soluble fraction of V-EPR amounted to 44.8 wt% of the initial sample and was characterized by a C_2 content of 55.4 mol%, whereas the insoluble fraction had a higher C_2 content (73.2 mol%). The calorimetric curves of the two fractions, compared in *Figure 7* with those of unfractionated V-EPR, show that the insoluble fraction develops the largest quantity of low-melting crystal phase whereas the melting region is almost negligible for the soluble fraction. This is evident from examination of both the melting endotherm below room temperature and the characteristic annealing peak located above room temperature in the first d.s.c. scan. The sum of the melting enthalpies characteristic of the two fractions, normalized by taking into account the amount of material recovered for each fraction, gives a value which is consistent with the result obtained for unfractionated V-EPR.

The calorimetric behaviour of V-EPR fractions indicates that chemical composition plays a role in the ability of EPR rubbers to crystallize at low temperature, and the results obtained for the soluble fraction suggest that, below a certain content of C_2 units in the copolymer, the ethylene sequence length becomes too short to allow crystallization. In this connection, a Zr-EPR sample with a C_2 content of 53.1 mol% was examined and was indeed found to remain amorphous down to T_g, its calorimetric curve showing only the endothermic step associated with the glass-to-rubber

transition. Evidently in such a sample the reduction in C_2 content has drastically decreased the probability of occurrence of ethylene sequences of suitable length to crystallize even at very low temperatures.

Dynamic mechanical behaviour

The dynamic mechanical spectra of V-EPR and Ti-EPR are shown in *Figure 8* together with that of a high-density polyethylene (HDPE) sample for comparison. Both EPR samples show two absorption maxima in tan δ between −150 and 0°C and a gradual increase in the mechanical dissipation factor above room temperature.

The low-amplitude tan δ peak located at about − 120°C corresponds to the secondary γ relaxation which is characteristic of all polymers containing sequences of at least three CH_2 units in the backbone[18]. The γ relaxation is usually associated with local motions of methylenic units present in the amorphous regions of the polymer.

In the temperature region of the glass transition, the two copolymers show a much greater β relaxation, whose peak temperature occurs at − 43 and − 41°C for V-EPR and Ti-EPR respectively. The magnitude of the β peak is significantly lower for Ti-EPR than for V-EPR, in accord with the less amorphous character of the former copolymer, as revealed by X-ray and d.s.c. measurements. A slight effect of the low-melting crystal phase on the β relaxation intensity is also observed in the case of V-EPR, whose tan δ maximum (0.8) is lower than usually found for totally amorphous materials, which are characterized by tan δ maxima well above 1[18].

The dynamic modulus E' does not exhibit significant differences between the two copolymers in the glassy state ($T < T_g$). On the other hand, the magnitude of the modulus drop corresponding to the β relaxation is smaller for Ti-EPR than for V-EPR and reflects the physical constraints induced by crystallinity on the cooperative motions of the amorphous polymer segments. By examining the Zr-EPR sample (C_2 content 53.1 mol%), which appeared amorphous down to T_g, it was possible to verify that the modulus decrement of the V-EPR sample over the
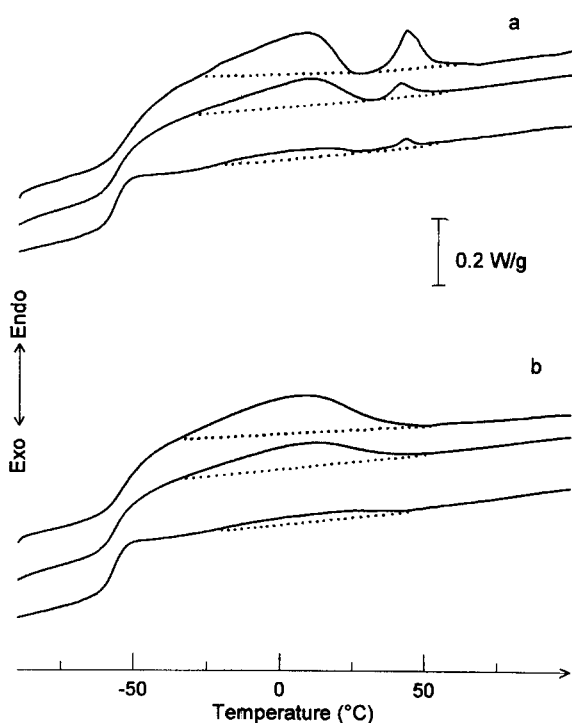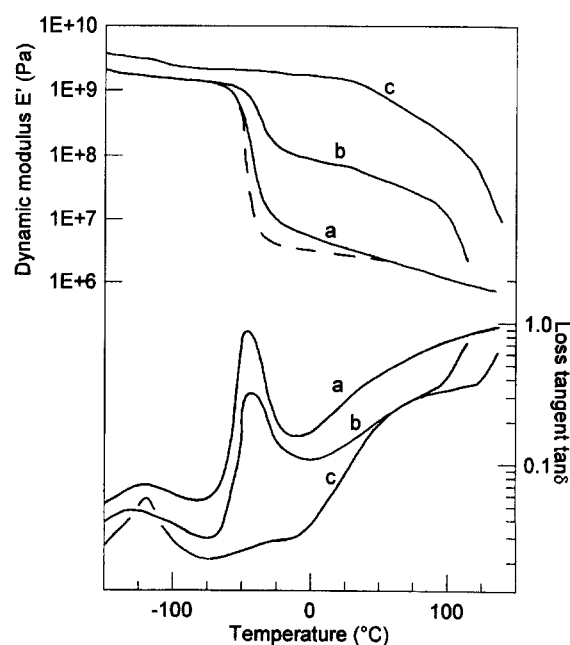

Figure 7 First (a) and second (b) d.s.c. scans on V-EPR: unfractionated sample (middle curve), insoluble fraction (upper curve), soluble fraction (lower curve)

Figure 8 Dynamic mechanical spectra of V-EPR (a), Ti-EPR (b) and HDPE (c). Broken line: see text

temperature range from −50°C to +40°C is not changed by the presence of imperfect small crystallites, which affect only the steepness of the modulus drop. The broken line in *Figure 8* represents the response of the totally amorphous sample and shows a faster and greater modulus decrease than for V-EPR in the β relaxation region. Once the glass transition is exceeded, a further decline in E' with temperature is observed, more marked for V-EPR than for Zr-EPR, the two curves finally merging at ~40°C, i.e. when the poor crystal phase of the former sample is completely molten. At higher temperatures, the regular slight lowering of E' is typical of a rubbery behaviour. Quite differently, the modulus–temperature dependence of Ti-EPR above the glass transition is characterized by two changes in slope (around 30 and 100°C respectively), which are also observed in the dynamic mechanical spectrum of HDPE. The observed reduction in rigidity results from the gradual fusion of the high-melting crystal phase existing in this sample, in line with the calorimetric behaviour of as-supplied Ti-EPR (see *Figure 4*), where progressive melting involved a more significant crystalline fraction above 100°C. The modulus decrease associated with the main melting region of HDPE is shifted to higher temperatures with respect to Ti-EPR, for the reason that the HDPE melting point is ~10°C higher than that of Ti-EPR.

Concluding remarks

The experimental d.s.c. results described in this paper have demonstrated that ethylene–propylene random copolymers with C_2 content in the region of 70 mol% develop a polyethylene-type crystal phase of low degree (2–7%) when cooled below room temperature. Such poor crystallinity melts over a broad range of temperature, extending from the glass transition up to ~50°C, and is not detectable by X-ray measurements performed at room temperature. Only in the presence of a high-melting crystal phase, such as is found in the heterogeneous titanium-based sample, is the WAXS technique helpful in revealing crystalline peaks associated with long ethylene sequences. The highly heterogeneous character of Ti-EPR has been proved by d.s.c., which gave evidence of both a low-melting and a high-melting crystal phase, the latter being characterized by a fusion temperature only 10°C lower than that of HDPE. This means that a significant fraction of the copolymer is very rich in C_2 units and contains long crystallizable sequences responsible for the polyethylene-like crystalline phase, only weakly affected by the presence of the second comonomer.

The EPR samples have also been investigated by DMTA over a wide range of temperature and it was observed that the high-melting crystal phase very similar to polyethylene drastically affects the relaxation spectrum of the heterogeneous Ti-EPR copolymer. On the other hand, samples based on homogeneous catalyst systems show only a slight influence of the poor low-melting crystal phase on the absorption region associated with the glass transition.

The finding that, at an average composition of ~70 mol% C_2, EPR copolymers obtained by catalytic systems which are essentially different (homogeneous vanadium and metallocene-based as well as heterogeneous titanium-based) are similar in crystallization ability below room temperature points to the occurrence of similar ethylene sequences in all samples, despite differences in chemical composition distribution. Taking into account that sequences of 10–12 CH_2 units are known to be responsible for the development of a 10% degree of crystallinity at room

temperature[2], it is clear that crystallization and melting at lower temperatures must be accounted for by shorter sequences. It is remarkable that such sequences are present both in copolymers where all molecules have about the same composition (Zr-EPR) and in molecules with a wide spread of composition (Ti-EPR). From n.m.r. analysis, which allows a detailed study of ethylene diads and triads (I. Camurati, personal communication), the percentage of CH_2 units arranged in sequences of length < 10 has been calculated to be 37% in Ti-EPR, whereas it is $> 50\%$ in V-EPR and Zr-EPR. This difference is itself indicative of a different distribution of comonomers and explains the lower value of low-melting crystallinity (associated with sequences as short as fewer than 10 CH_2 units) in Ti-EPR compared with V-EPR and Zr-EPR. It is likely that much longer CH_2 sequences exist only in Ti-EPR, originating the crystallinity that melts at higher temperature (see d.s.c. peak at 123°C in *Figure 5*).

In the EPR copolymers based on homogeneous catalytic systems, a factor certainly affecting the amount of the low-melting crystal phase is the overall chemical composition, since the magnitude of the broad endotherm that characterizes the fusion of the defective crystal population decreases with decreasing C_2 concentration. A value of ~55 mol% of ethylene units in the copolymer seems to be the lower limit below which the samples remain amorphous, whatever the temperature range investigated.

Taking into account that the melting of short ethylene sequences starts immediately above T_g, a further point to be considered is vitrification. If there were any ethylene sequences left which might crystallize, would this be prevented by vitrification? The results of the present work have shown that, at a given composition, the amount of crystallinity developing at low temperatures is not affected by different thermal histories, which change only the shape of the melting endotherm. In addition, further studies on the crystallization and melting behaviour of V-EPR in the presence of *n*-hexane, which are the subject of a forthcoming paper[19], have shown that the crystallization ability of the polymer is not altered by the enhanced mobility of the system (decrease in T_g) induced by the diluent. The experimental results altogether lead to the conclusion that the crystallization rate of short ethylene sequences is very high and vitrification does not prevent formation of crystallites limited in size and perfection, provided that the sequence length is sufficient for incorporation in a crystallite.

ACKNOWLEDGEMENTS

REFERENCES

1. Cecchin, G., in *Copolimeri, XII Convegno—Scuola AIM*. Pacini, Pisa, 1990, p. 219.
2. Baldwin, F. P. and Ver Strate, G., *Rubber Chem. Technol.*, 1972, **45**, 70.
3. Ver Strate, G., in *Encyclopedia of Polymer Science and Engineering*, Vol. 6. Wiley-Interscience, New York, 1986, p. 522.
4. Koivumäki, J. and Seppälä, J. V., *Eur. Polym. J.*, 1994, **30**, 1111.
5. Galimberti, M., Martini, E., Piemontesi, F., Sartori, F., Camurati, I., Resconi, L. and Albizzati, E., *Macromol. Symp.*, 1995, **89**, 259.

6. Mathot, V. B. F., *Calorimetry and Thermal Analysis of Polymers*. Hanser Verlag, Munich, 1994.
7. Mathot, V. B. F., Scherrenberg, R. L., Pijpers, M. F. J. and Bros, W., *J. Therm. Anal.*, 1996, **46**, 681.
8. Zorina, N. M., Buckina, M. F., Voloshin, V. N., Radenko, G. A. and Kotova, I. P., *J. Polym. Sci. USSR*, 1989, **31**, 1216.
9. Barbè, P. C., Cecchin, G. and Noristi, L., *Adv. Polym. Sci.*, 1986, **81**, 1.
10. Maglio, G., Milani, F., Musto, P. and Riva, F., *Makromol. Chem. Rapid Commun.*, 1987, **8**, 589.
11. Wunderlich, B., *Thermal Analysis*. Academic Press, New York, 1990.
12. Wunderlich, B., *Macromolecular Physics*, Vol. 3. Academic Press, New York, 1980.
13. Boyer, R. F., *J. Macromol. Sci.—Phys. B*, 1973, **7**, 487.
14. Fox, T. G., *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
15. Gaur, U. and Wunderlich, B., *J. Phys. Chem. Ref. Data*, 1981, **10**, 1051.
16. Geil, P. H., in *Order in the Amorphous State of Polymers*, ed. S. E. Keinath, R. L. Miller and J. K. Ricke. Plenum Press, New York, 1987, p.83.
17. Boyer, R. F., *Macromolecules*, 1973, **6**, 288.
18. McCrum, N. G., Read, B. E. and Williams, G., *Anelastic and Dielectric Effects in Polymeric Solids*. Wiley, New York, 1967.
19. Vitali, M. and Pizzoli, M., *Macromol. Chem. Phys.*, in press.