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Maurizio Avella^a; Pietro Greco^a; Mario Malinconico^a

^a Istituto di Ricerche su Tecnologia dei Polimeri e Reologia C.N.R. Via Toiano 6,

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Influence of Microstructure and Sequence Length Distribution on First-Order Thermal Transition in Ethylene-Propylene Rubbers

MAURIZIO AVELLA, PIETRO GRECO
and MARIO MALINCONICO

*Istituto di Ricerche su Tecnologia dei Polimeri e Reologia C.N.R. Via Toiano 6,
80072 Arco Felice (Na)*

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A study on the crystallinity of ethylene-propylene saturated copolymers (EPR) of industrial source is reported. By DSC, with an appropriate choice of annealing experiments, several crystalline areas are found due to polyethylenic-type sequences of different length. The existence of such ordered sequences is confirmed by NMR data and WAXS analysis. The presence of multiple crystalline regions can be interpreted as due to discontinuous sequences distributions, as confirmed by an EPR simplified model made of mixtures of *n*-alkanes in squalane. An attempt is reported to apply classical theories of crystallization in copolymers to our commercial EPR systems.

INTRODUCTION

The physical and mechanical properties of a binary copolymeric system are influenced strongly by the chain microstructure and particularly by the amount of the monomeric units and their distribution along the polymeric chain. This is relevant in ethylene-propylene copolymers, as they can present a plastic or rubber-like behaviour as function of microstructure and composition.¹⁻³

Ethylene-propylene saturated copolymers (EPR) have been widely reviewed by Baldwin and Ver Strate.¹ They consider three structural factors to define a particular copolymer system:

- a) overall composition,
- b) distribution of composition among different chains,
- c) for a given composition and distribution of composition, the ordering of monomeric units along a chain (statistical, alternated or arranged in homogeneous blocks of different lengths).

Crystallinity is a parameter that varies drastically with composition and microstructure of EPR copolymers. It generally decreases as the content of propylene increases, and decreases also when, for a given composition, the structure moves from block to random. Particularly, the fusion of EPRs is generally broad and copolymers which are amorphous at room temperature can develop partial crystallinity upon cooling.^{1,4}

A systematic study on the influence of thermal history on the melting behaviour of EPR was carried out by Ver Strate and Wilchinsky,⁵ which, *inter alia*, show how a fusion of EPR can be induced by annealing a sample at temperatures down the glass transition temperature, T_g . Furthermore, the annealing of a sample at any temperature before the maximum of a melting endotherm, can lead to the formation of crystalline material, part of which melts immediately above the annealing temperature. So, it is possible to produce, by an appropriate choice of experimental condition, multiple regions of enhanced melting by annealing at several different temperatures.

Today, recent development of computerized thermal analyzers allows a deeper understanding of temperature transitions in EPR copolymers. Moreover to determine the distribution of microstructure ¹³C NMR analysis and X-Ray diffraction methods can be used. In the present work we report the results of an investigation on the thermal behaviour of two commercial copolymers obtained with vanadium-based catalysts having different C_2/C_3 ratio. A correlation is drawn between the existence of multiple distinct crystalline regions, as evidenced by a suitable choice of annealing experiments, and microstructure of our EPR copolymers, as obtained by ¹³C NMR and WAXS analyses. Classical Flory's theory

of crystallization in copolymers⁶ is used to demonstrate how such crystalline regions can be related to the presence of discrete multiple blocks of different C₂ lengths.

Moreover an attempt is made to simulate the thermal response of EPR by using mixtures of alkanes and squalane.

MATERIALS

The starting EPRs are two commercial products of Dutral SpA (trade name Dutral Co054 and Co034) and are saturated copolymers, whose characteristics are reported in Table I. They will be coded as EPR054 and EPR034 throughout the paper.

n-decane is Baker reagent grade product, *n*-undecane, *n*-tridecane and *n*-tetradecane are EGA-Chemie pure products, while *n*-pentadecane, *n*-eicosane, *n*-heneicosane, *n*-dodecane, *n*-tricosane and *n*-tetracosane are Aldrich products. The purity of alkanes is not less than 98.5%.

TABLE I
Characteristic of the two commercial copolymers used

Sample	Mw/Mn	C ₂ content (% by moles)	ML (g/min) (1 + 4)(100°C)	Catalytic system
EPR054	3.9	67.2	42	V-based
EPR034	3.6	82.0	42	V-based

TECHNIQUES

¹³C NMR characterization was obtained by random noise, proton decoupled ¹³C NMR spectra on a Bruker WP spectrometer, operating at 50.28 MHz. The spectra were the result of 20 K acquisitions using an acquisition time of 0.52 s, 32 K memories, sweep width of 15,000 pulse width of 12 s (60°C) and a relaxation delay of 3 s. Spectra were obtained at 110°C. Samples were prepared as 3 mg/cm³ solutions of rubber in 1,2,4-trichlorobenzene and sufficient 1,1,2,2-tetrachlorodideuteroethane was added to provide a deuterium lock signal.

Wide angle X-Ray scattering (WAXS) measurements were carried out on a (PW 1050 Model) Philips powder diffractometer (CuK Ni-filtered radiation) to evaluate the crystallinity of EPR samples. The used scanning rate was 0.5 degree/min.

Differential thermal analysis was carried out by using a Mettler TA-3000 differential scanning calorimeter operating under N₂ atmosphere. This apparatus was equipped with a control and programming unit (microprocessor TC-10) and a calorimetric cell (DSC-30), which allowed scans from -170°C to 600°C.

The accuracy of thermal data was assured by conducting repeated scans (not less than 6) on each sample.

RESULTS

¹³C NMR spectral analysis

The spectrum of EPR054 copolymer is shown in Figure 1. A similar spectrum was obtainable for EPR034.

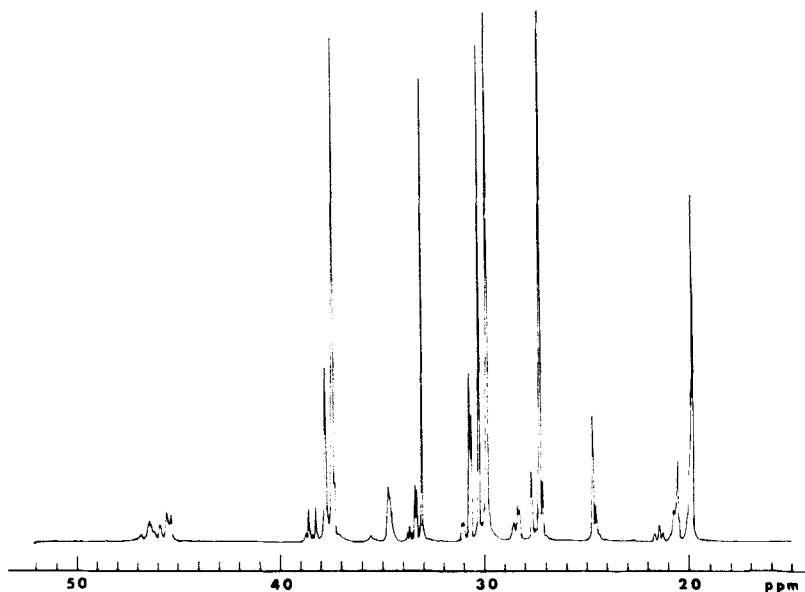


FIGURE 1 50.28 MHz, ¹³C N.M.R. spectrum of EPR054

The assignments of spectral signals to the different structural units are obtained according to Ray *et al.*,⁷ Randall and Hsieh,⁸ Abis *et al.*⁹ On the basis of these spectral assignments, the existence of long isotactic polypropylene sequences can be excluded, as evidenced by the methyl region (19/22 ppm, 0.7% by weight PPP for EPR054 and 0.0% by weight PPP for EPR034).

On the contrary, more pronounced long polyethylenic-type blocks were found (19.8% by weight EEE for EPR054 and 37.9% by weight EEE for EPR034). Also long sequences of the type EPEPE are present as can be seen from the intensity of the signals at 19.8, 30.2 and 33.1 ppm for EPR054 and EPR034, attributable respectively to CH₃ EPE, CH₂ PEP and CH EPE triads. On the basis of such analysis both EPRs should have a substantially random distribution of monomeric units.

WAXS Measurements

The wide-angle diffraction spectra obtained from EPR034 and EPR054 copolymers are shown in Figure 2A and 2B respectively. In

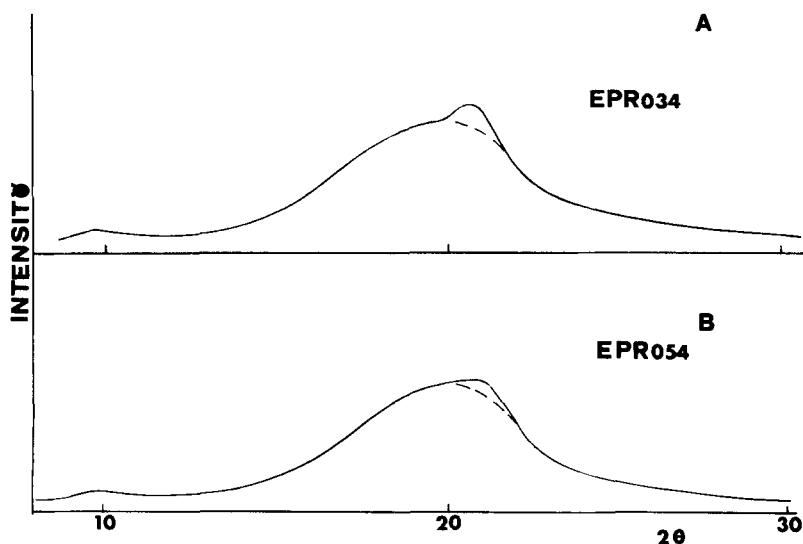


FIGURE 2 X-Ray diffraction curves obtained at room temperatures for: A: EPR034 sample, B: EPR054 sample

TABLE II
Crystallinity by WAXS of the two commercial copolymers used

Sample	Crystallinity X_c (%)
EPR034	4.0 ± 0.3
EPR054	0.9 ± 0.3

both samples the diffraction peak (more marked in EPR034 sample) at $2\theta = 21^\circ$ indicates the presence of a crystalline phase. The degree of crystallinity (X_c) for the samples was obtained utilizing the quantitative analysis of Natta *et al.*¹⁰ and is reported in Table II. The crystalline diffraction peak found at $2\theta = 21^\circ$ is attributable to the intensity of the (1, 1, 0) peak of polyethylenic-type sequences.

The experimental wide-angle diffraction curves of EPRs samples measured after melting (the samples were kept at 100°C for 5 minutes and then cooled at room temperature) present no residue crystallinity. In Figures 3A and 3B respectively are shown the

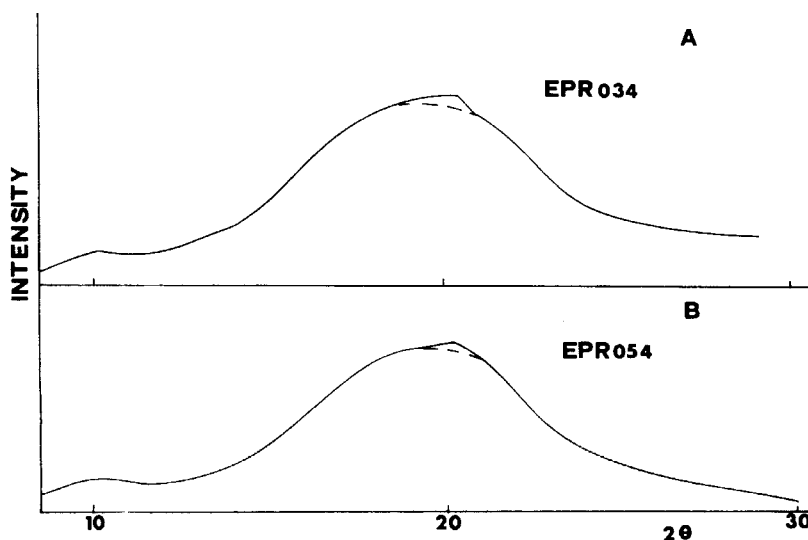


FIGURE 3 X-Ray diffraction curves obtained at $T = 0^\circ\text{C}$ for: A: EPR034 sample, B: EPR054 sample

diffraction spectra, obtained at $T = 0^\circ\text{C}$ after melting, of EPR034 and EPR054 copolymers: also in this case, in both the samples a crystalline diffraction peak at $2\theta = 21^\circ$ is present with a crystallinity degree (X_c) for EPR034 sample equals to $1.0 (\pm 0.3)\%$ and for EPR054 sample equals to $0.6 (\pm 0.3)\%$. Lower temperature crystallinity after melting indicates that only a part of a crystallizable component immediately crystallizes if the temperature is lowered below the room temperature ($T = 0^\circ\text{C}$) according to DSC data.

Furthermore the samples after melting and cooling to or below room temperature, recovered their crystallinity fully after prolonged (1 week) annealing at room temperature.

Thermal analysis of copolymers

By DSC measurements T_g s of EPR054 and EPR034 were measured: thus heating the samples at a scan rate of $10^\circ\text{C}/\text{min}$, values are found respectively of $-48.7 (\pm 0.5)^\circ\text{C}$ and $-42.7 (\pm 0.5)^\circ\text{C}$ according to Baldwin and Ver Strate.¹

Figure 4 shows the DSC thermograms of EPR054 and of EPR034 obtained by heating a sample from 20°C up to 100°C , at a scan rate of $10^\circ\text{C}/\text{min}$.

It must be noted the presence of an endotherm peak at about 45°C for both the copolymers. The temperature at which such peak occurs is not influenced by the composition of EPR copolymer (see Table III). On the contrary, the composition strongly influences the apparent enthalpy of fusion. Particularly, the ΔH_m^* increases,

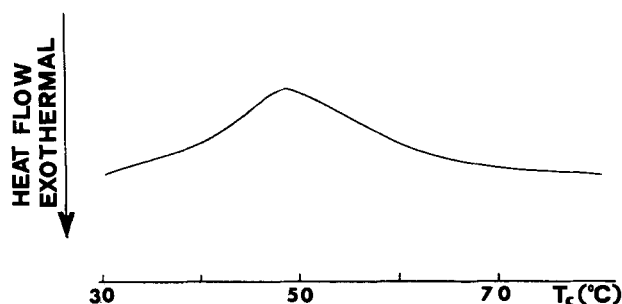


FIGURE 4 DSC melting endotherm for EPR054 sample

TABLE III
Thermal data of the two commercial copolymers used obtained
by heating from 20°C up to 100°C

	EPR054	EPR034
Ethylene content (% by moles)	67.2	82.0
T_m (°C)	45.0 ± 0.5	46.0 ± 0.5
ΔH_m (J/g)	3.2 ± 0.5	18.3 ± 0.5
Crystallinity X_c (%)	1.1 ± 0.5	6.3 ± 0.5

increasing the percent of ethylene, which is the only crystallizable comonomer.^{1,11} At a first sight, this behaviour could indicate that increasing the amount of ethylene, increases quantitatively the amount of crystallizable units, with no modification of the sequences lengths.

The crystallinity X_c is obtained according to the well known equation:

$$X_c = \frac{\Delta H_m^*}{\Delta H_m}$$

where ΔH_m^* is the apparent enthalpy of fusion of the sample. The value of ΔH_m , according to the literature on ethylene copolymers¹² is chosen as the thermodynamic enthalpy of fusion of linear polyethylene, which equals to 288.9 J/g by Wunderlich.¹¹ The crystallinity of EPR054 (1.1 ± 0.5%) is much less than that of EPR034 (6.3 ± 0.5%). If we introduce two parameters, the crystallinity ratio between EPR054 and EPR034, and the ethylene content ratio between EPR054 and EPR034, we can note that while the former is 0.17, the latter is 0.82; it is not possible to attribute the large increase in crystallinity only to the increased amount of ethylene. The crystallizable units in EPR034 are proportionally more than those of EPR054.

To elucidate the existence of lower temperature transition,⁵ a different thermal treatment was effected: a sample was rapidly cooled down to -100°C and then heated up to 100°C at a heating rate of 10°C/min. The thermogram is shown in Figure 5, curve A, for EPR054. Two peaks of fusion are apparent above T_g , the first broad between -35°C and 20°C, and the second sharp at 45°C.

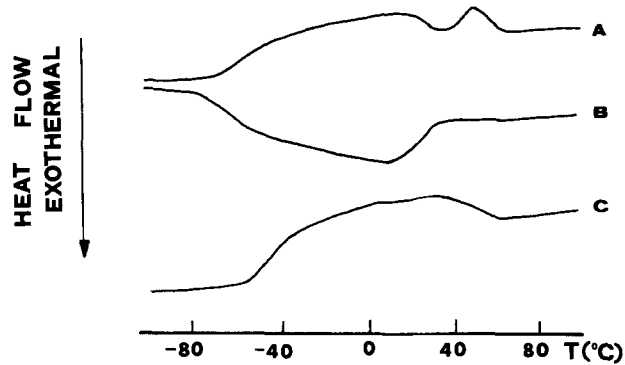


FIGURE 5 DSC thermograms for EPR054: A: 1° run, B: crystallization, C: 2° run

Similar behaviour is observed for EPR034 (see Figure 6 curve A). In Table 4 are compared thermal data on EPR054 and EPR034.

So, we have an overall crystallinity which is higher for EPR034, and an overall crystallinities ratio, 0.64, which is close to the ethylene content ratio, 0.82. On the contrary, the crystallinity at lower temperature is higher for EPR054 than for EPR034, with a ratio of crystallinity of 1.89.

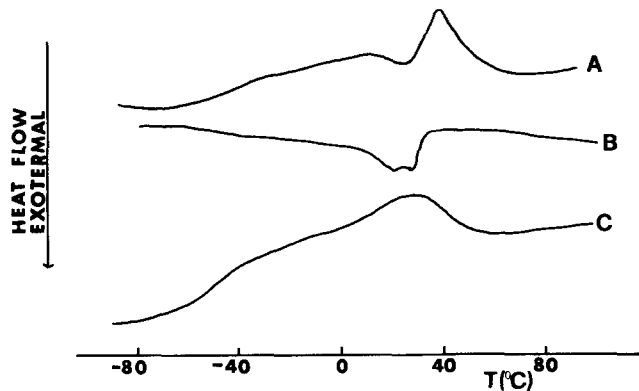


FIGURE 6 DSC thermograms for EPR034 A: 1° run, B: crystallization, C: 2° run

TABLE IV

Thermal data of the two commercial copolymers used obtained heating from -100°C up to 100°C

	EPR054	EPR034
ΔH_m overall (J/g)	18.0 ± 1.0	28.1 ± 1.0
Overall crystallinity X_c (%)	6.2 ± 1.0	9.7 ± 1.0
Crystallinity broad peak* X_c (%)	5 ± 1	3 ± 1

* Calculated by = X_c (overall) - X_c (sharp peak)

Also in this case the results seem to indicate that the different behaviour between the two samples is only due to different distribution of crystallizable units, but not to their different structure. It is quite surprising to found that the intensity of the broad peak, i.e., the amount of sequences responsible of such transition, is higher for EPR054 than for EPR034. In Figure 5, curve B, is reported the cooling behaviour of EPR054 kept at 100°C for 5 minutes and then cooled at a scan rate of $10^{\circ}\text{C}/\text{min}$. Only one broad crystallization peak occurs, whose enthalpic content is 14J/g . EPR034 shows, in the same experiment, (see Figure 6, curve B), two peaks very close together, whose overall enthalpy is 24J/g . (The enthalpies ratio is 0.58). Both samples, heated in a second run at $10^{\circ}\text{C}/\text{min}$ (see Figures 5, 6, curves C) showed only one broad endotherm, while a ΔH_m^* of 15J/g for EPR054 and 26J/g for EPR034. These values indicate that the overall crystallinity is not substantially varied, but the two peaks of first run are overlapped. Several annealing experiments were carried out, cooling rapidly a molten sample from 100°C down to temperature comprised between T_g and R.T., keeping it at that temperature for different time lengths and then cooling rapidly to -100°C .

Figure 7 reports the DSC traces of EPR054 annealed at 0°C for different lengths time. In Figure 8 are reported DSC traces of EPR054 annealed for 120 minutes at different temperatures. It must be noted that at these temperatures there is always some material which can crystallize upon cooling, before it reaches the T_g .

In Table V are reported $T'm$ of samples for different time and temperature of annealing. The experiments show the splitting of the single broad transition in two different peaks. The position and the

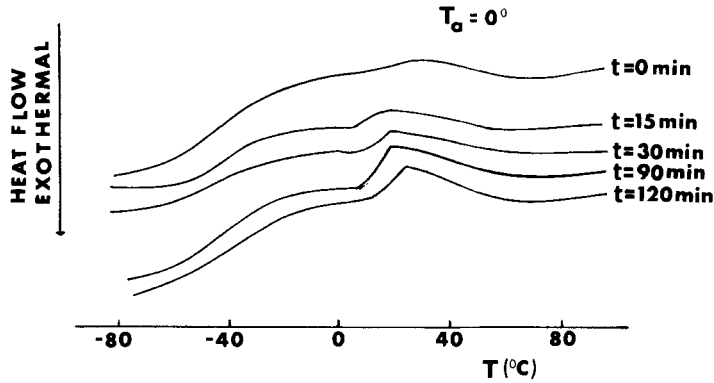


FIGURE 7 DSC traces of EPR054 annealed at $T = 0^\circ\text{C}$ for different time lengths

relative intensities are strongly influenced by the time and temperature of annealing. The ΔH_m^* of overall material is not influenced. Separation is obtained after one week annealing at room temperature.

The $T'm$ increase increasing the time and temperature of annealing. From the above, it is necessary to assume that two distinct crystalline regions are present in EPR copolymers, whose definition is governed by kinetic and thermodynamic factors. These

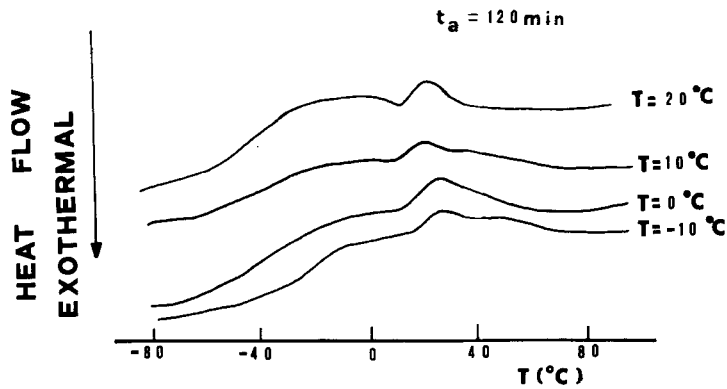


FIGURE 8 DSC traces of EPR054 annealed for $t_a = 120$ minutes at different temperatures

TABLE V

Melting temperatures of EPR054 sample obtained after different temperatures and times of annealing

t_A (min)	$T_A = -10^\circ\text{C}$	EPR054	
	$T'_m(^{\circ}\text{C})(\pm 0.5)$	$T_A = 0^\circ\text{C}$	$T_A = 10^\circ\text{C}$
		$T'_m(^{\circ}\text{C})(\pm 0.5)$	$T'_m(^{\circ}\text{C})(\pm 0.5)$
15	6.0	16.2	26.6
30	5.0	17.2	27.6
45			28.6
60	9.0	15.0	28.5
90	5.9	16.6	29.5
120	8.9	19.8	30.8

results could not be explained if we assume a random distribution of monomeric units along the chains (see the NMR analysis).

Modelling of EPR copolymers

A simplified model of EPR copolymers microstructure can be built up by an appropriate choice of mixtures of long chain alkanes, to simulate the EEEE sequences, and squalane, to simulate non crystallizable EPEP sequences. On the basis of a comparison of melting point of alkanes and melting point of EPR copolymers, we have chosen C_{14} — C_{20} alkanes solution in squalane. All the solutions have a ratio alkanes/squalane 1/1 by moles which falls inside the range of compositions of our EPR copolymers. They are all viscous transparent liquids at room temperature.

In Table VI the variations of melting temperatures of several alkanes in the presence of squalane are shown. The T_m depression of the crystallizable component must be attributed to the diluting effect of the non-crystallizable component (squalane).

In Figures 9A and 9B DSC thermograms of C_{14}/C_{15} and C_{20}/C_{21} mixture are shown respectively. There is only one melting endotherm peak, indicating that mixtures of alkanes having contiguous chain lengths melt (and crystallize) in the same interval of temperatures. On the contrary, it is observed that alkanes with

TABLE VI
Variation of melting temperatures of several alkanes in
presence of squalane

Alkane	T _m (blend)	T _m (pure)
<i>n</i> -Tetradecane	-3.9	5.5
<i>n</i> -Pentadecane	-5.4	9.9
<i>n</i> -Eicosane	30.0	37.0
<i>n</i> -Heneicosane	30.9	41.0

relatively different sequence lengths melt (and crystallize) in the same interval of temperatures (see Figure 10 where the mixture C₁₄/C₂₀ is shown). Similarly, mixtures constituted by two mixtures of alkanes having different contiguous sequences (C₁₄/C₁₅ together with C₂₀/C₂₁) show two endotherms of fusion each attributable to the mixture with contiguous lengths. Zerbi and co-workers¹³ have already shown how, on the basis of spectroscopic and calorimetric evidences, it is possible to follow the formation of thermodynamically stable co-crystals starting from mechanical mixtures of alkanes whose sequence are practically contiguous (C₂₃ and C₂₅).

Such process is very fast at temperatures closer to the T_m of crystals, nevertheless it is already evident at temperatures below the solid-solid transition. These results well agrees with ours, on the evidence of a single T_m in mixtures of contiguous alkanes. The presence, in our case, of squalane as a common matrix, does not modify the experimental evidences. Only the addition of such amorphous liquid causes a shift in the T_m's, so mixtures of contiguous alkanes in squalane co-crystallize, but at lower temperatures than the pure mixture.

DISCUSSION

Thermal transitions of commercial EPR copolymers can be tentatively interpreted on the basis of a comparative analysis of NMR, WAXS, DSC data together with the experiments done on model system.

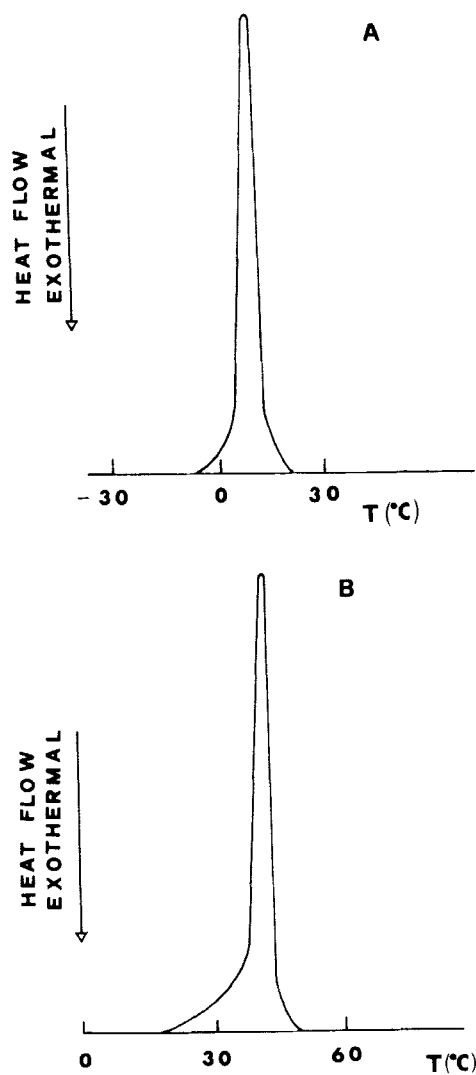


FIGURE 9 Thermograms of alkanes mixtures: A: C_{14}/C_{15} , B: C_{20}/C_{21}

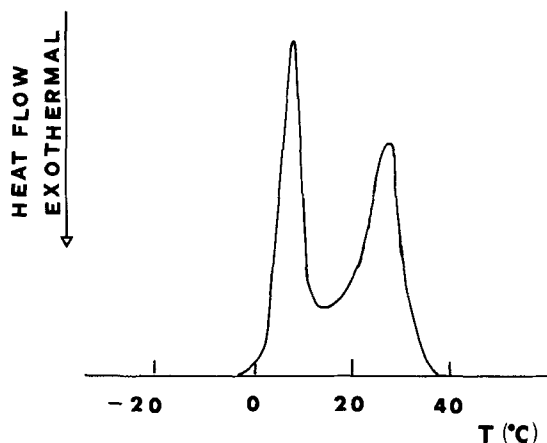


FIGURE 10 Thermograms of $C_{14} - C_{15} - C_{20} - C_{21}$ mixtures

DSC experiments indicate that at least part of the polyethylenic sequences, shown by ^{13}C NMR and WAXS analysis on both copolymers, are blocky. Such sequences can crystallize from the melt, as shown by WAXS spectra obtained at or below R.T. (i.e. 0°C) and DSC analysis. Flory's theory of crystallization⁶ predicts that, gradually cooling a copolymer from its melt, crystallites are formed of any length $Z \geq Z^*$, where Z is the actual length and Z^* is the minimum crystallizable length, which is function of temperature and composition. The theory assumes that in the crystallites are not included sequences of the non-crystallizable component (propylene, in our case, chlorine for Bowmer and Tonelli),¹² even if some authors tried to take into account such influences.^{14,15} At equilibrium there is a discrete distribution of sequences lengths of the crystallizable component $Z \geq Z^*$, but the achievement of equilibrium condition at a given temperature can be obtained only if it is possible the interexchange of sequences among crystallites. As Flory states: "the exchange of sequences between crystallites required to establish this state of equilibrium would be difficult to achieve in an experiment."

The kinetic of crystallization of EPR copolymers and mixtures of normal alkanes in squalane is completely different. But we can make identical thermodynamic considerations: for EPR as for n -alkanes, contiguous sequences co-crystallize, while separated

sequences form, at equilibrium, crystallites with different melting points. Only sequences well separated can form at equilibrium homogeneous and diversified crystalline regions. In the case of our copolymers, the slow kinetic of demixing leads to the co-crystallization from the melt of all the sequences whose length is $Z \geq Z^*$. Nevertheless, with an appropriate choice of annealing temperatures, it is possible to reach, in real time scale, the equilibrium conditions, i.e. the densification of different crystalline areas, each formed by an array of contiguous sequences. This fact implies that our EPR copolymers either present a discontinuous sequences distribution inside each macromolecule, either present macromolecules with different microstructures. Such finding is probably caused by the presence of different catalytic sites, already suggested for the *V*-based catalysts¹⁶ as those used in the preparation of EPR054 and EPR034.

CONCLUSION

The presence of crystalline regions of different T_m in industrial EPR copolymers may be interpreted on the base of Flory's crystallization theory of copolymers together with a careful calorimetric and microstructural analysis. Particularly, a DSC analysis showed that, by a suitable choice of annealing temperatures, an existing broad region of fusion develops well defined peaks, which are related to different average sequences lengths. By a model study on mixtures of crystallizable alkanes in the presence of squalane it is observed that while contiguous sequences tend to co-crystallize at equilibrium, well separated sequences have, as equilibrium condition, the crystallization in homogeneous regions with different melting points. The thermodynamic behaviour of a copolymeric ethylene-propylene system follows similar laws, while the kinetic is different.

More quantitative correlations among enthalpy of fusion, distribution of crystallizable sequences and activity of catalytic sites of polymerization might be tempted in future through the analysis of Taylor-mode samples with well defined microstructure.

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APPENDIX

A further application of Flory's theory can lead to the determination of the parameter, p , i.e. the probability that at an ethylene unit is attached another ethylene unit, for both the crystalline areas. In the equation reported below

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right) = -\left(\frac{R}{\Delta H_m}\right) \ln p$$

T_m are the actual melting temperatures, T_m^0 the thermodynamic melting temperature of polyethylene, R the gas constant and ΔH_m is the enthalpy of fusion per crystallizable unit, which is 980 cal/mol in our case.¹⁶ The values found for p are 0.691 for the higher sharp melting peak, and 0.605 for the lower broad peak. As EPR054 has an ethylene content of 0.672, the theory confirms that the peak at higher T_m is due to long block sequences, while the peak at lower T_m is due to short alternate sequences. The application of the theory to EPR034, which has an ethylene content of 0.820, leads to somewhat surprising results, as the two peak temperatures are still the same of the EPR054, so both groups of sequences in EPR034 must be considered alternated.

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