

Crystalline Characteristics of Ethylene/Propylene/ 1,4-Hexadiene Terpolymers and Related Ethylene Copolymers

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Synopsis

An improved differential thermal analytical technique which permits the rapid, convenient characterization of the thermal behavior of crystalline polymers free of any influence of prior thermal history is presented. Characterization of both crystallization and fusion phenomena is described for ethylene/propylene copolymers subjected to well-controlled thermal scanning techniques. Parameters describing these phenomena are derived. While they are nonequilibrium parameters, they are reproducible and capable of correlation with polymer composition. The crystallization onset temperature determined by this cooling technique was found to relate to the molar ethylene content of the copolymers by an equation similar to the one derived by Flory⁵ based on equilibrium melting point. The relationship was found to hold true for a number of ethylene copolymers, including samples of linear and branched polyethylene, commercial EPDM, and ethylene/vinyl acetate copolymers.

INTRODUCTION

We wish to describe an improved differential thermal analytical technique which permits the rapid, convenient characterization of the thermal behavior of crystalline polymers free of any influence of prior thermal history. The technique was demonstrated in the characterization of various ethylene copolymers, mostly with the class of EPDM's which are constituted mainly of ethylene, propylene, and a small amount of a diene such as ethylidene norbornene, 1,4-hexadiene, or dicyclopentadiene. The crystalline behavior of these materials has been reviewed recently by Baldwin and VerStrate.¹ From density and x-ray measurements at room temperature, the degree of crystallinity was found to depend upon composition, with polymers of higher ethylene content exhibiting higher crystallinity. The degree of crystallinity at a given composition can also vary depending upon the catalyst and synthesis conditions, presumably as a result of changes in the monomer sequence length or compositional distribution. Some heat of fusion data have also been presented² based on samples annealed at room temperature.

Clegg, Gee, and Melia³ presented heating thermograms of a number of ethylene/propylene dipolymers. Unfortunately, the thermal history of the samples was not given.

TABLE I
Thermal Characteristics of E/P/HD, EPDM, and Polyethylene Samples

Sample	Polymer	E, mole-%	M_v^a	T_f , °C	Melting range, °C ^c	$T_m^{c,d}$	ΔH_f^e	Remarks
A1	polyethylene	100		120	75 to 145	135	50	"Marlex" 5003, linear PE, Phillips Petroleum Co.
A2		100		123	75 to 150	140	58	linear PE, experimental sample
A3		100(5)		100	25 to 120	112	36	branched PE, experimental sample
A4		100(5)		100	40 to 120	112	30	DYNH-1, branched PE, Union Carbide Co.
B1	E/P/HD	84.3	87,000	52	-40 to 105	62	24.9	2.0 mole % HD
B2		79.5	190,000	40	-42 to 125	48	20.9	1.3 mole % HD
B3		69.6	150,000	6	-50 to 75	0	11.0	1.3 mole % HD
B4		64.7	110,000	-17	-55 to 15	-25	1.5	1.7 mole % HD
B5		73.2	—	18.5	-50 to 65			1.3 mole % HD
B6		71.8		13	-45 to 75			1.3 mole % HD
B7		63.2		-22	-55 to 15			1.8 mole % HD
B8		61.3	80,000	—	—	—	0	2.0 mole % HD
B21		78.0		32	-45 to 65	43	17.7	1.5 mole-% HD fraction of B2 (55% wt)

B22	80.0	32	-45 to 65	45	19.6	1.1 mole-% HD fraction of B2 (25% wt)
B23	81.7	55, 95	-45 to 120	50	24.4	1.1 mole-% HD fraction of B2 (20% wt)
C1	76.0	200,000	-45 to 125	50	10.1	1.2 mole-% ENB "Vistalon" 3708, Enjay Chemical Co.
C2	77.0	160,000	-35 to 65	45	12.3	1.2 mole-% ENB "EPsyn" 5508, Copolym. Corp.
D1	50.0	123	75 to 175	135, 165		melt blend of polyethylene (sam- ple A-2) and polypropylene (Avison GP)
E1	79	33	-30 to 75	50		experimental samples
E2	84	45	-30 to 80	50		
E3	86.5	60	-20 to 95	70		
E4	88	67	-20 to 95	80		
E5	92	73		87		

a Viscosity-average molecular weight, based on $[\eta] = 1.38 \times 10^{-4} (M_w)^{0.81}$. Intrinsic viscosity $[\eta]$ determined in perchloroethylene at 30°C.

b Onset temperature for crystallization, sample control cooled at 20°C/min.

c From DSC heating curve scanned immediately after the sample has been control cooled (20°C/min) from molten state.

d Minimum peak temperature of the endotherm.

e Not corrected for side-chain content. Assuming there are 2.5 branches/100 C atom, then $E = 95$ mole %.

In the work presented here, rapid reproducible characterization of both crystallization and fusion phenomena free of the influence of prior thermal history is described for ethylene/propylene copolymers subjected to well-controlled thermal scanning techniques. Parameters describing these phenomena are derived. While they are nonequilibrium parameters, they are reproducible and capable of correlation with polymer composition. Deviations from random copolymer structures appear to be detectable.

EXPERIMENTAL

Polymer Samples

The materials studied include both linear and branched polyethylenes (PE, Series A), a series of ethylene/propylene/1,4-hexadiene terpolymers (E/P/HD, Series B), and two samples of commercial ethylene/propylene/ethylidenenorbornene terpolymers (E/P/ENB, Series C). Five experimental samples of ethylene/vinyl acetate copolymers (E/VAc, Series E) have also been included in this study.

The experimental E/P/HD polymers (B1 to B7) were produced by solution polymerization with Ziegler catalysis. Other samples, including series A, C, and D, were commercial polymers, with manufacturers listed in Table I.

The polymer fractions (B21, B22, and B23) were obtained by fractional extraction of sample B2. Samples B21 and B22 are the successive extracts using hexane at 25° and 50°C. The remaining insoluble fraction is designated as B23.

Differential Thermal Analysis

Measurements were carried out with a du Pont 900 DTA instrument equipped with a DSC (differential scanning calorimetric) cell. The cooling scan of the DSC measurement was carried out using either of the two following attachments:

1. The standard cooling can supplied by the du Pont Company: The scan was lifted approximately $\frac{1}{8}$ in. from the platform with a brass ring in order to avoid direct contact between the silver heating block and the cooling surface. Cooling was provided by pumping liquid nitrogen continuously into the screened well of the cooling can.

2. Cooling block: As shown in Figure 1, a double-jacket heat exchanger was tightly mounted on top of the silver heating block of the du Pont DSC cell. Gaseous nitrogen coolant was directed to the cooling assembly during measurements with a controlled rate of cooling.

The stability of the cooling arrangement is extremely important, because any slight thermal or vibrational disturbance in the system may introduce a false output signal. The modifications described above greatly improve the stability over the commercial design in this particular model. The baseline is essentially linear over the broad temperature range examined. The second system is judged even better in this aspect, although the cooling capacity is somewhat reduced due to the use of gaseous coolant. Thus, it was only used for scans above DSC measurements.

In order to eliminate the influence of prior thermal history, the samples were equilibrated for 3 min at 150°C to ensure removal of residual crystallinity; the

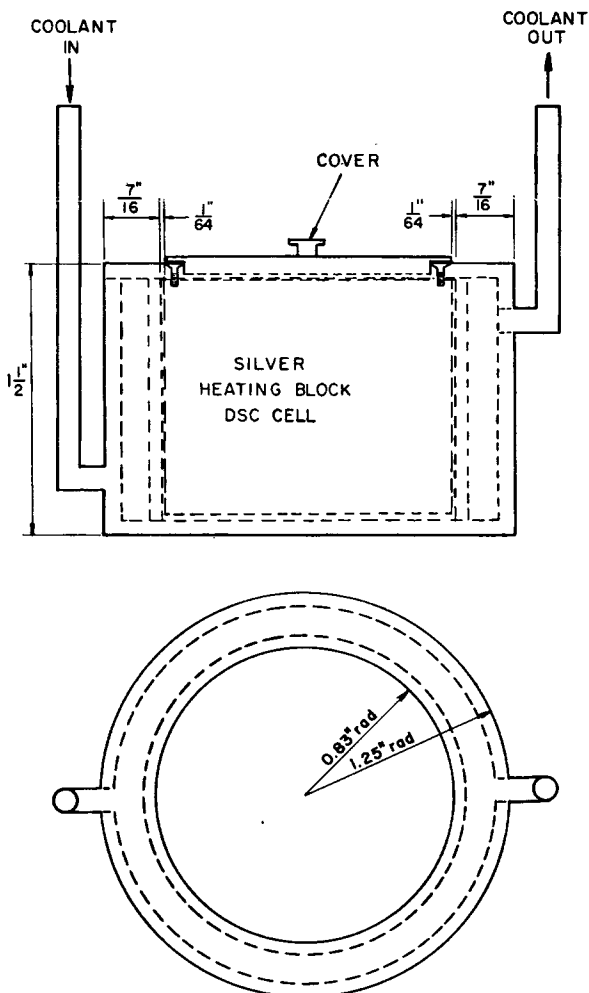


Fig. 1. Cooling block for DSC cell.

cooling scans were then run at $20^{\circ}\text{C}/\text{min}$ immediately after the cooling scans. Without the high-temperature equilibration, nonreproducible crystallization temperatures were observed during the cooling scan; and in the heating thermograms, endotherms with varied peak temperature and peak size depending upon the prior thermal history were observed, to be described in a later section. In the studies on effect of annealing time and temperature, the samples were heated for 3 min at 150°C and placed on a metal surface at the annealing temperature. Following completion of the annealing period, the samples were rapidly quenched in liquid nitrogen, and then the DSC heating scans were taken.

RESULTS

The effects of annealing time and temperature on the DSC thermograms of E/P/HD terpolymers are illustrated in Figures 6 and 7. In view of the strong thermal history effects, thermograms determined with samples equilibrated in

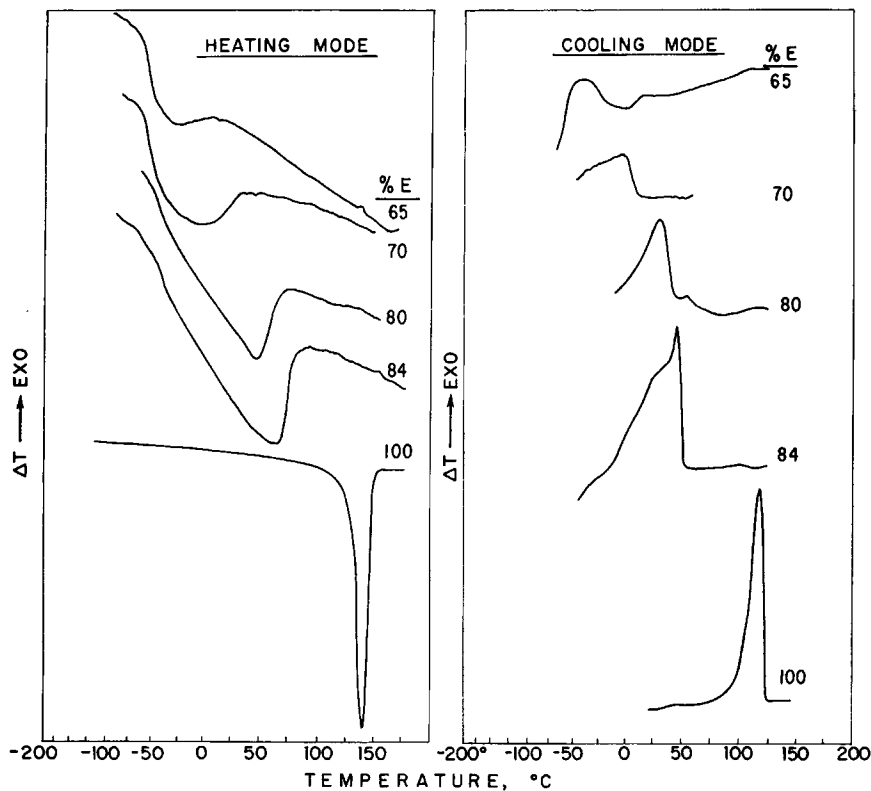


Fig. 2. Heating and cooling thermograms of E/P/HD terpolymers and polyethylene.

the molten state followed by a controlled scanning rate are presented in Figure 2. Various features derived from the heating and the subsequent cooling scans are shown in Table I. In the heating scans, a slope change occurs at -60°C for all the EPDM samples. This corresponds to the glass transition temperature and is followed immediately by a very broad endotherm as the temperature is increased. The size of this endotherm is dependent on polymer composition. The degree of crystallinity, as evidenced by the size of the endotherm, decreases as the ethylene content of the polymer decreases. This is in general agreement with the observations in the literature summarized in reference 1 for other types of EPDM and ethylene/propylene dipolymers. As temperature is further increased, the curve returns to its baseline. Some waviness does occur with some of the polymers (e.g., sample B2, Fig. 6). The thermogram of hexane-soluble fraction B21 (Fig. 2) has an exceptionally linear baseline in the high-temperature region resulting from the removal of the more crystalline and perhaps blockier polymer fractions where two endotherms were observed (Fig. 4). The thermogram of sample B8, a terpolymer containing 61.5 mole% ethylene, the least crystalline polymer of the series, is shown in Figure 5. Essentially no endotherm was observed.

In the cooling thermogram, a sharp exotherm occurs about 10° to 15°C below the peak temperature of the corresponding endotherm in the heating curve. The exotherm can be characterized by the crystallization onset temperature T_f . The latter is defined by the initial departure of the exotherm from the baseline as

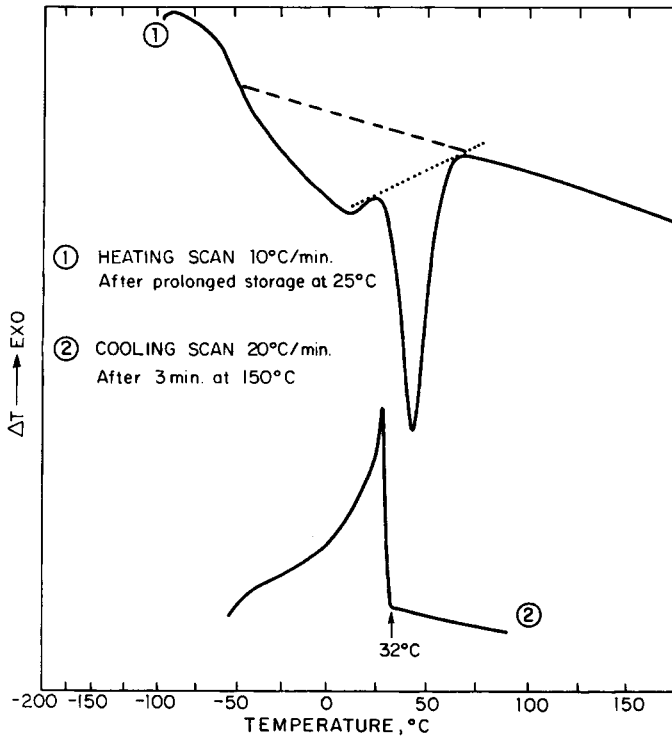


Fig. 3. Thermogram of E/P/HD terpolymer fraction (sample B21).

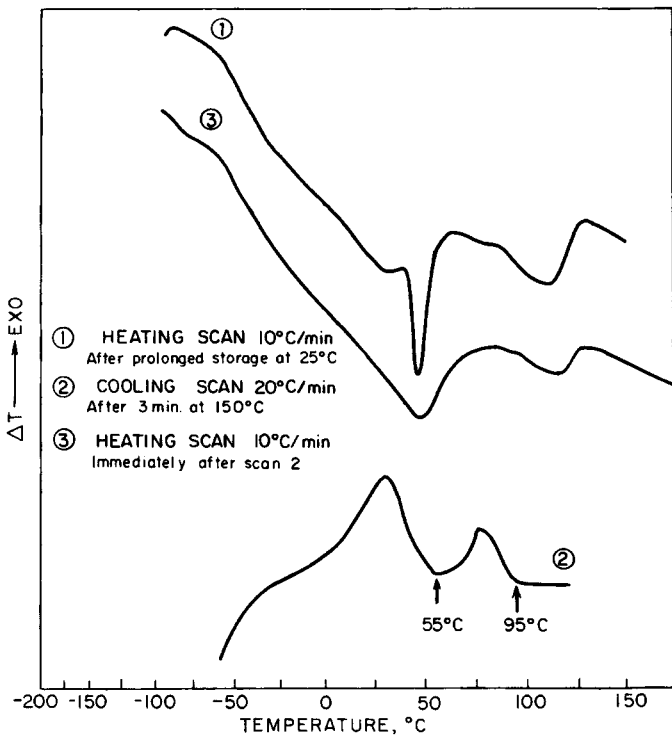


Fig. 4. Thermogram of E/P/HD terpolymer fraction (sample B23).

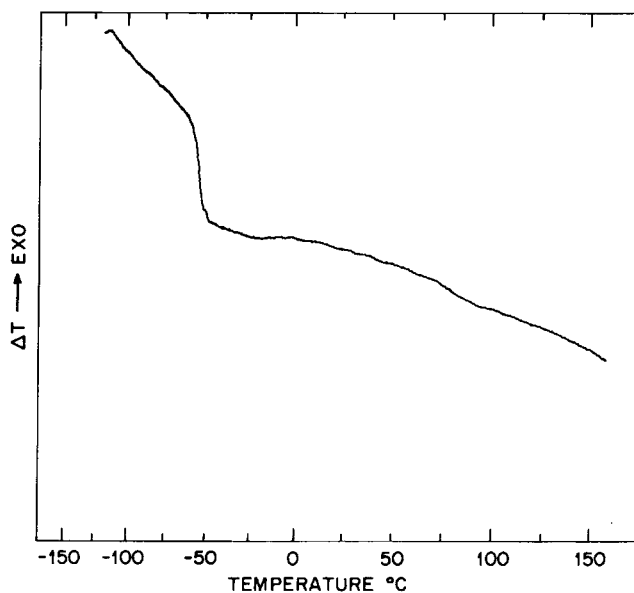


Fig. 5. Thermogram of E/P/HD terpolymer (sample B8).

shown by an arrow in Figure 3. It is reproducible to within 1°C. T_f data for the various samples are also shown in Table I.

DISCUSSION

Heating Thermograms of E/P/HD Terpolymers

As described previously, the thermogram of an E/P/HD terpolymer containing 63 mole % or more ethylene is rather complex. It is linear below its glass transition temperature ($\sim -60^\circ\text{C}$); but as the temperature is raised, it immediately plunges into a broad endotherm before returning to its baseline. The endotherm is interpreted as the melting of crystallites. This is in agreement with the behavior of ethylene/propylene copolymers and other terpolymers reported in the literature.^{3,4} The crystallinity is believed to be associated with ethylene sequences.¹ All samples showed a rather broad endotherm, probably owing to the existence of a broad ethylene sequence length distribution which results in crystals of different sizes with varying degrees of defects and imperfections. The melting range of the polymers is shown in Table I for samples scanned right after being control cooled from the molten state.

Effect of Thermal History

The shape of the endotherm as well as the location of the peak temperature is extremely sensitive to the thermal history of the polymer sample. This is indicated in Figures 6 and 7, which show the important effect of time and temperature of annealing. As shown in Figure 7, the DSC thermograms for samples annealed at room temperature for 10 min at 1 or 20 hr are considerably different from that of the same sample after prolonged room-temperature storage. Both

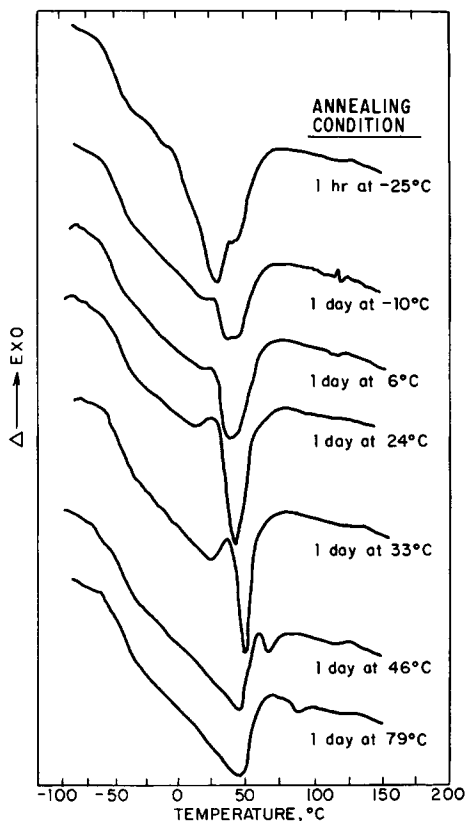


Fig. 6. Thermogram of annealed E/P/HD terpolymer (sample B2). Heating rate, 10°C/min.

the size and the peak temperature of the endotherm increased with the annealing time. The effect of annealing temperature is illustrated with sample B2, as shown in Figure 6. The polymer contains 79.5 mole % ethylene; its thermogram has a broad endotherm covering -42° to 125°C , with a peak temperature of 40°C . The peak temperature can be varied from 30° to 50°C as shown in Table II by varying the annealing temperature. Samples annealed within the 25 – 45°C range result in double endotherms. The peak melting temperature and its intensity increase with the annealing temperature and time, as shown in Table II. An additional endotherm beyond the temperature range of the major melting region was also induced by annealing sample B2 at 79°C (see Fig. 6). This could be due to the presence of a highly crystalline fraction. Examination of the hexane-soluble and hexane-insoluble fractions revealed this could indeed be true, as shown in Figures 3 and 4. The DSC curve is very linear and free of waviness at 55 – 175°C for sample B21, the portion soluble in hexane at 25°C . An additional endotherm centered at 90° to 125°C occurred with sample B23, the portion insoluble in hexane at 50°C . Furthermore, the cooling curve of the latter also showed an additional exotherm corresponding to the higher melting peak.

Cooling Thermograms of E/P/HD Terpolymers

Because of the strong effect of thermal history on the DSC thermograms, crystallinity of the polymer is best analyzed by examining the DSC cooling curve

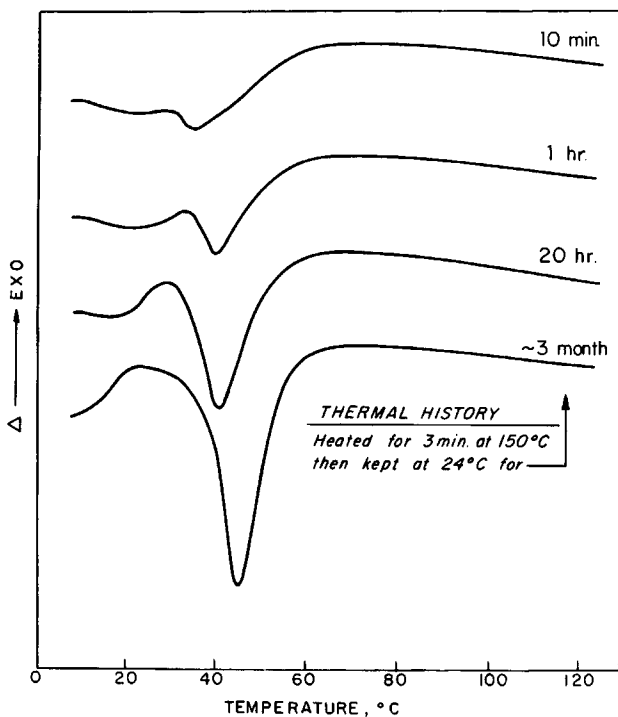


Fig. 7. Thermograms of annealed E/P/ENB terpolymer (sample C2). Heating rate, 10°C/min.

after the sample has been heated above its melting point to eliminate all vestiges of crystallinity. This is not a common technique, because facilities for obtaining a controlled rate of cooling are required. By means of the two attachments described in the experimental section, we were able to examine the crystallization behavior of the polymer samples cooled from the molten state where they were

TABLE II
Effect of Annealing on Melting Temperature of EPDM's^a

Sample	Annealing temperature, °C	Time	Peak temperature, °C ^b	
B2	-25	1 hr	30 (s)	42 (shr)
	-10	24 hr	20-25 (shr)	35-45 (m)
	6	24 hr	25 (shr)	38 (m)
	24	24 hr	15 (m)	43 (s)
	33	24 hr	25 (m)	50 (s)
	46	24 hr	45 (s)	65 (w)
	79	24 hr	45 (s)	86 (w)
C2	25	10 min	36 (w)	
	25	1 hr	40 (m)	
	25	20 hr	41 (s)	
	25	3 months	45 (s)	

^a Sample was heated for 3 min at 150°C, then quenched to the annealing temperature. Relative intensity of the endotherm: s = strong, m = medium, w = weak, shr = shoulder.

^b Minimum point of the endotherm.

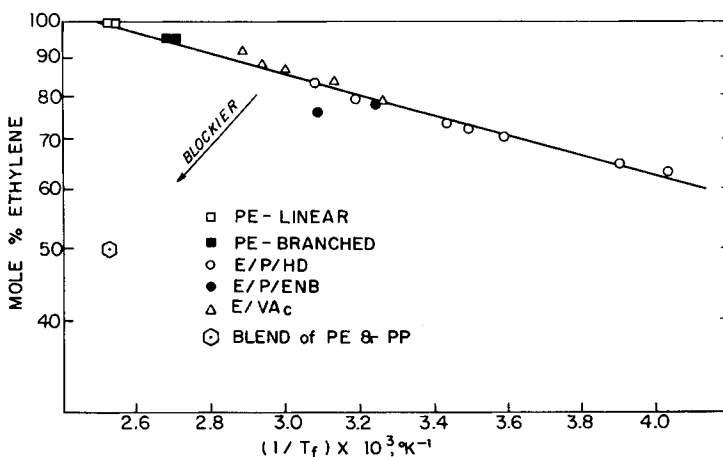


Fig. 8. Compositional dependence of T_f of ethylene copolymers.

free from effects of previous thermal history. Typical cooling curves are shown in Figure 2. The crystallization behavior can be characterized by the temperature (T_f) at which a sharp rise of ΔT occurred.

Effect of Comonomer Composition

The onset of temperature of crystallization (T_f) as defined previously for the various polymers is strongly dependent on composition, as shown in Table I. As a matter of fact, T_f can be correlated with the mole-% of ethylene (E) as shown in Figure 8 and may be represented by

$$1/T_f = k_1 \ln E + k_2 \quad (k_1 \text{ and } k_2 = \text{constants})$$

for all the EPDM's and polyethylene samples examined. The relationship is similar to the one derived by Flory⁵ based on the theory of random copolymers. However, the constants k_1 and k_2 lack theoretical significance because a non-equilibrium freezing temperature instead of the thermodynamic melting point was used. Note that the latter involves difficult and tedious measurements as compared to the simple cooling scan in determining the crystallization onset temperature. The equation relates T_f to polymer composition, and T_f increases as ethylene concentration increases. As shown in Figure 8, the line passes right through the point for linear polyethylene. If we assume that there are 2.5 branches per 100 backbone carbons in branched polyethylene,⁶ the data of the latter fall on the line also. These results conform with the concept that the crystallinity in E/P copolymers with more than 60 mole % ethylene are ethylenic in origin.

We have also examined the crystallization behavior of some ethylene/vinyl acetate copolymers, which are known to have random sequence length distributions.⁷ Their T_f - E relationships are also in line with the correlation. As was discussed previously, the ethylene/propylene copolymers could have different sequence length distributions due to the varied synthesis conditions and catalyst used.^{1,8} This would result in polymers of different crystallinity for a given composition. It is postulated that polymers of a blockier ethylene sequence length distribution will yield a higher freezing point and hence will fall below

the line in Figure 8. For example, sample D1, a physical blend of polyethylene and polypropylene with 50 mole % of the former, has a T_f value of 123°C, and the data point is far below the correlated line. One of the two E/P/ENB samples also falls slightly below the correlated line. The sample is probably somewhat blockier than the rest of the E/P/HD and E/P/ENB terpolymer or E/VAc copolymer samples. The relative chain blockiness defined in such a scheme is, of course, grossly simplified. However, the technique is rather simple and may provide a relative measure of the monomer sequence blockiness in the ethylene copolymers. One is cautioned in the use of the cooling technique in polymer characterization that only pure and uncontaminated samples be used since small amounts of nucleating agent may produce an erroneously high crystallization onset temperature.

The relationship between T_f and composition observed with the copolymer samples suggests that the effect of all the comonomers, including propylene, hexadiene, ethylidenenorbornene, and vinyl acetate, are roughly equivalent, and the variation in T_f can be accounted for solely by the molar ethylene content in the polymer.

The compositional dependence of polymer crystallinity can also be characterized by other thermal parameters, e.g., the heat of fusion (ΔH_f) and the peak temperature of the endotherm (T_m). As discussed previously, these parameters are highly dependent upon the thermal history of the polymer. VerStrate and Wilchinisky² chose to anneal the sample at room temperature for an extended period of time (up to 20 days) before making their measurements. We decided to use heat scanning immediately after a sample is control cooled (20°C/min) from its molten state. The ΔH_f and T_m values of the samples are reported in Table I. ΔH_f was determined from the area of the endotherm below the baseline, and the latter was drawn by extending the baseline of the polymer in the high-temperature region as illustrated by the dashed line in Figure 3. Note that, if the baseline is drawn conventionally as the tangent to the two sides of the endotherm, as illustrated by the dotted line in Figure 3, the value obtained would be considerably lower, even when one is comparing the part of the endotherm above room temperature. This method of drawing baselines is further supported by the heating scan of a noncrystalline sample shown in Figure 5, where the thermogram is essentially linear from -50° to 150°C and the baseline in the lower temperature portion (say, -50° to 100°C) can be represented closely by an extrapolated line from those in the higher temperature range. The results so obtained are shown in Table I. Both T_m and ΔH_f increase as ethylene content is increased.

The parameters T_f , T_m , ΔH_f , and the melting temperature range of the E/P/HD terpolymers appear to change continuously with ethylene concentration right through to 100% ethylene, i.e., polyethylene. The changes in T_f and T_m are rather smooth near polyethylene composition; but rather sharp changes occur with ΔH_f and the melting temperature range when ethylene content is increased from 85% to 100%.

SUMMARY

An improved differential, thermal analytical technique which permits the rapid, convenient characterizations of the thermal behavior of crystalline polymers free of any influence of prior thermal history is presented. By mechanical

modification of a du Pont Model 900 differential thermal analyzer, stable baselines were obtained during the cooling mode. High-temperature equilibration prior to thermal analysis eliminated the influence of prior thermal history on the crystallization and fusion behavior of the polymers.

The technique was demonstrated in the characterization of various ethylene copolymers, mostly with the class of EPDM's which are copolymers of ethylene, propylene, and a small amount of a diene such as 1,4-hexadiene, ethylidene-norbornene, or dicyclopentadiene. Also studied were random ethylene/vinyl acetate copolymers and branched and linear polyethylene. The effect of annealing time and temperature was further demonstrated with this improved technique.

Rapid, reproducible characterizations of both crystallization and fusion phenomena were carried out on these ethylene copolymers subjected to well-controlled thermal scanning techniques. The crystallization onset temperature (T_f) determined by this technique was found to relate to the molar ethylene content of the E/P/HD polymers by an equation similar to the one derived by Flory using equilibrium melting point. The substitution of the latter with the crystallization onset temperature simplifies greatly the experimental measurements. The relationship was found to hold true for samples of linear and branched polyethylene, commercial EPDM, and ethylene/vinyl acetate copolymers. It is suggested that the relative chain blockiness of the ethylene copolymers may be estimated by comparing their crystallization onset temperatures.

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