THERMODYNAMICS OF CRYSTALLINE LINEAR HIGH POLYMERS.
V. EXTENDED-CHAIN COPOLYMERS OF POLYETHYLENE.

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INTRODUCTION

All previous research of this series of papers[1-4] has dealt with the thermodynamics of folded-chain crystals of linear polymers or copolymers. This type of crystal is metastable. However, during the course of the previous research it became clear that in many cases experimentally a heating path approximating zero entropy production could be followed. This mode of heating leads directly from the metastable crystal to the metastable melt. Reorganization, recrystallization and superheating have been avoided by a suitable choice of heating rate. This allowed an "equilibrium" description of the melting process.

Recently extended molecular chain crystals have been prepared in our laboratory.[5-6] These crystals should be close to equilibrium crystals and accordingly of great interest to the understanding of the thermodynamics of linear crystalline high polymers.

In this paper research on the melting behavior of extended-chain copolymer crystals of ethylene with propylene and ethylene with butene-1 will be described. The copolymers are identical to those of the folded-chain copolymer crystals investigated in the previous paper of this series.[4] Significant differences in maximum experimental melting point, melting range, and crystallinity have been found.

EXPERIMENTAL‡

A. Samples

The polymers were identical to those of the last paper.[4] Table 1 gives the characteristics of the reference polyethylene and the copolymers of ethylene and propylene and the copolymers of ethylene and butene-1. The reference polyethylene and butene-1 copolymers were newly characterized by the gel permeation method.

All samples were linear polymers, polymerized at low pressure and temperature.

Table 1.

Sample	Designation	Side Groups/100 Carbons	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
Polyethylene	P_1	0	9,800	130,000	13
Ethylene-propylene	P_2	0.2	-	-	-
Ethylene-propylene	P_3	0.7	-	-	-
Ethylene-butene-1	B_1	0.3	11,000	110,000	10
Ethylene-butene-1	B_2	0.9	9,100	120,000	13
Ethylene-butene-1	B_3	1.0	10,000	88,000	9
Ethylene-butene-1	B_4	1.7	10,000	120,000	12

1

B. Crystallization

Crystallizations were carried o.. [unclear] er elevated hydrostatic pressure. The 5-10 g sample was enclosed in oil-tight brass bellows which in turn were immersed in the hydrostatic oil of the pressure vessel. The pressure was kept constant by automatically pumping oil into or out of the pressure vessel.[7] The accuracy of the pressurestat was ±1.5%. The temperature was regulated by thermostatically controlled heaters from the outside of the pressure vessel. The temperature was controlled to about ±1°C. Reproducible cooling was achieved by means of a linear temperature programmer. All samples were heated to 227°C, then pressurized within four to five minutes to between 4100 and 4900 atm. After remaining at this pressure for 20 hours cooling to room temperature at constant pressure was carried out at a rate of 1.6°C/hour. At room temperature the pressure was released and the sample was removed from the bellows for further analysis.

C. Analysis

The density at 25°C was measured in a toluene-chlorobenzene density gradient column. Commercial glass floats, accurately measured to 10^{-5} g/cm^3, made up the references. By employing small density gradients accuracies of ±0.0002 g/cm^3 could be achieved. About 1-mm^3 pieces were cut from the sample and immersed in toluene under vacuum to avoid adsorbed air bubbles. Density crystallinities were calculated using the expression

$$c_w = \frac{\bar{v}_a - \bar{v}}{\bar{v}_a - \bar{v}_c} \qquad (1)$$

$\bar{v}$ is the sample specific volume, while $\bar{v}_a$ is the amorphous specific volume and $\bar{v}_c$ is the X-ray crystalline specific volume. For $\bar{v}_c$ Swan's value of 1.001 ml/g was used,[8] while $\bar{v}_a$ was assumed to be 1.173 ml/g. The latter is an average value from data by Gubler and Kovacs[9] and Nielsen.[10]

The changes in specific volume with temperature were measured with dilatometers. The procedure employed by Bekkedahl[11] and Aggarwal et al.[12] was closely followed. The bath control over long time intervals was better than ±0.1°C at 140°C. The volume change was followed with a cathetometer. Temperature changes were carried out stepwise. Measurements were only made after no change in height was observed within one hour. When melting was going on generally 12 to 24 hours were needed for each measured point. The specific volume was calculated from the 25°C density, the height of the mercury column and the thermal expansion correction of the reservoir.

The crystallinity calculations were made according to equation (1). The temperature dependence of $\bar{v}_c$ as given by Flory[13] was used.

$$\bar{v}_c = 0.993 + 3.0 \cdot 10^{-4} \, t \qquad (2)$$

Equation (2) is based on X-ray unit cell determinations by Cole and Holmes[14] and by Swan.[8] As a means of avoiding systematic errors such as capillary diameter variation, deviation from the vertical, trapped air etc. a correction was applied to $\bar{v}_a$, such that $\bar{v}_a$ is a linear function of temperature and that the amorphous specific volume is 1.173 ml/g at 25°C.

$$\bar{v}_a = 1.173 + [(v_a(t_0) - 1.173)/(t_0 - 25)](t - 25) \qquad (3)$$

$\bar{v}_a(t_0)$ is a point on the experimental $\bar{v}$ versus t curve at t_0, somewhat above

the melting temperature. This procedure does not introduce a serious error. $\bar{v}_a$ thus calculated for any of the samples does not deviate by more than 0.01 ml/g for the generally accepted values at 140°C.

Differential thermal analysis was performed using the previously described apparatus.[2] A detailed discussion of the apparatus can be found in the thesis of Dr. Bodily.[15] The weight of the sample was controlled to 0.50 ± 0.01 g. The heating rate used was 1.50°C/min in the melting range. The beginning of melting was arbitrarily taken where the temperature difference recording deviated from the base line by 5% of the total melting peak height. The experimental maximum melting point is defined as the temperature where the last detectable amount of heat of fusion is absorbed. The procedure to obtain this point was described previously.[3] The sample iron-constantan thermocouple was calibrated against a certified platinum resistance thermometer. The overall recorded temperature error was about 0.1°C.

For study of the change of the melting range with heating rate the commercial Du Pont 900 Differential Thermal Analyzer[16] was used. With this apparatus controlled heating rates ranging from 0.5°C/min to 80°C/min were available. Small amounts of sample mixed with glass powder were heated in 2-mm diameter glass tubes. The analysis of the data is similar to that mentioned above, although the maximum melting point could not be extrapolated for this equipment.

Calorimetric measurements were carried out with a Perkin-Elmer Differential Scanning Calorimeter.[17] Five to 10-mg samples which were weighed to ±10 micrograms were placed in an aluminum pan and encapsulated by sealing with an aluminum cover. An empty pan was placed in the reference holder. The heating rate was 2.5°C/min. Besides time and temperature, a signal proportional to the differential power input between reference and sample was recorded. The area underneath the melting peak of the differential power recording was measured with a planimeter. This area is proportional to the heat of fusion. Arbitrarily the area of sample P_1 was set equal to 99% crystallinity or 60 cal/g heat of fusion. The disagreement with the density crystallinities can be traced back to difficulties in base line estimation, so that in general only the general trends of ΔH and crystallinity are of interest.

RESULTS

The results of density, DTA, dilatometric, and calorimetric measurements are summarized in Table 2. The crystallization conditions column lists the conditions which were kept for 20 hours before cooling to room temperature at constant pressure with a rate of 1.6°C/hour. The crystallization conditions are such that most of the crystallization took place during the cooling process. Figure 1 shows the DTA-traces of reference polyethylene and ethylene-butene-1 copolymers. Less sample weight (0.43 g) was used for polyethylene in order to avoid scaling out. Figures 2 and 3 give the crystallinity curves for the polymers. The melting points as extrapolated from specific volume plots are indicated by arrows. As can be seen from the figures and Table 2, there is a discrepancy between the melting points found by dilatometry and those by DTA. In order to elucidate this phenomenon, the dependence of DTA peak temperatures on the rate of heating was studied. The results are illustrated in Figure 4. The curves give evidence of superheating.

3

Table 2.

| Sample | Cryst. Conditions | | Density | | Beginning of Melting °C | DTA Main Peak | | Melting Point by Dilatometry (°C) | Calorimetry | |
	Temp. °C	Pressure atm	d^{25} (g/cm³)	Cryst. %		Peak Temp. °C	Extrap. Temp. °C		ΔH (cal/g)	Crystallinity %
P_1	227	4350	0.997	99	124.7	139.8	140.9	138.7	[66.0]	[99]
P_2	227	4350	0.988	93	-	138.7	140.0	137.5	57.3	86
P_3	227	4100	0.968	81	-	-	-	137.5	43.4	65
B_1	227	4350	0.989	94	121.2	139.3	140.3	138.4	56.8	85
B_2	227	4760	0.960	76	98.9	138.7	139.8	138.2	40.6	61
B_3	227	4900	0.949	69	71.7	137.8	139.1	137.2	38.3	57
B_4	227	4300	0.938	62	68.7	140.3	141.1	138.6	32.9	49

On inspection of Table 2 and Figures 1 to 4 the following general trends can be discovered:

(a) The maximum melting point, which corresponds to the last, and perhaps most perfect, crystal in the distribution melting does not change with changing copolymer content. This is in contrast to measurements on the same copolymers crystallized to a folded-chain crystal morphology at atmospheric pressure.[4,13] The dilatometric maximum melting point of all polymers reported on in this paper is $138° \pm 0.8°C$. This temperature is below the maximum melting temperature of polyethylene ($141.4°C$) crystallized in the extended-chain conformation. The small variation in T_m of $\pm0.8°C$ goes largely parallel with the amount of low molecular weight material in the polyethylene and the copolymers, but not parallel with the copolymer content as can be seen from Table 3.

Table 3.

Weight % under 1370 Å Length	Melting Point (°C)	Sample
39	138.7	P_1
41	138.4	B_1
63	138.2	B_2
68	137.2	B_3
44	[138.6]	B_4

The arbitrarily defined beginning of melting on the other hand is within the accuracy of its determination the same for atmospheric-pressure slowly crystallized polymer and high-pressure slowly crystallized polymer. With increasing copolymer content it drops from about 125°C for the homopolymer to 65°C for the B_4-sample.

(b) The crystallinity as calculated by density calculation decreases almost linearly with increasing concentration of foreign groups. As in the atmospheric-pressure folded-chain morphology crystals about 27 CH_2 groups are hindered on crystallization by the introduction of a single copolymer branch. The increase in density achieved in crystallization at elevated pressure decreases from 0.019 g/cm^3 for polyethylene to 0.008 g/cm^3 for sample B_4 indicating that for perhaps three to four copolymer branches per 100 chain atoms the crystallinity for both modes of crystallization is the same. The overall melting curves of Figures 1 to 3 show that there are two different types of crystals melting. One is the fraction which gives rise to the unchanged high maximum melting point. Its melting range is approximately 5°C wide. The other fraction stretches to the temperature at which melting begins. The fraction of the low melting material increases with increasing copolymer content from 27% to 53%, while the fraction of high and sharply melting material decreases quickly from 72% to 8%.

(c) As Table 2 shows, the melting points measured by DTA are somewhat higher than those obtained by dilatometry, indicating that the time allowed for melting was insufficient. Figure 4 gives more detail for samples B_4 and polyethylene. A typical superheating[19] curve is obtained for the high temperature melting crystals. This means that the extended-chain crystals of the polyethylene and copolymer are superheated by as much as 5.5°C when the heating rate is 50°C/min or faster. It can also be seen that the copolymer superheating is somewhat less than that of the polyethylene, indicating either smaller crystals or faster melting rates. The low temperature melting fraction of crystals does not change its melting range in the spread of rates investigated indicating again smaller, less perfect or faster-melting crystals.

From the above it must be concluded that the investigated copolymers form at least partially high-melting extended-chain crystals which can be

5

superheated easily. The unchanged equilibrium melting temperature of these points to the fact that thermodynamically CH_2 and the copolymer units form a solid solution. Although this mode of crystallization is favored at high pressure and temperature, it becomes increasingly more difficult on introduction of more side groups. No high temperature melting peak could be produced on high-pressure crystallization of a branched polyethylene (3.3 side groups/100 chain atoms).

From our previous atmospheric-pressure crystallizations,[4,15] which led to folded-chain crystals and the present results it must be concluded that the copolymers investigated can form either crystals with amorphous defects which act thermodynamically like a rejected species or solid solution crystals. Which alternative is found in the case at hand seems to depend on kinetic considerations. In support of this hypothesis the following additional evidence can be cited: It has been reported[19] that the melt viscosity of polyethylene at high pressure is increased by the introduction of side branches. This could explain why the formation of large extended molecular chain crystals, which requires long-range segmental diffusion, will be more disfavored by the introduction of side branches. Another indication that the inclusion of ethyl and methyl groups in polyethylene crystals in the form of a solid solution or an amorphous defect is a kinetic effect comes from experiments of Flory and coworkers.[12] They found on very carefully (slowly) crystallizing polymethylene copolymers a possible inclusion of less than one side chain per 100 carbons without change in melting point even at atmospheric pressure conditions. Ethyl and propyl or larger amounts of methyl groups could however not be included in the crystalline copolymer without change in maximum melting point.

Acknowledgments

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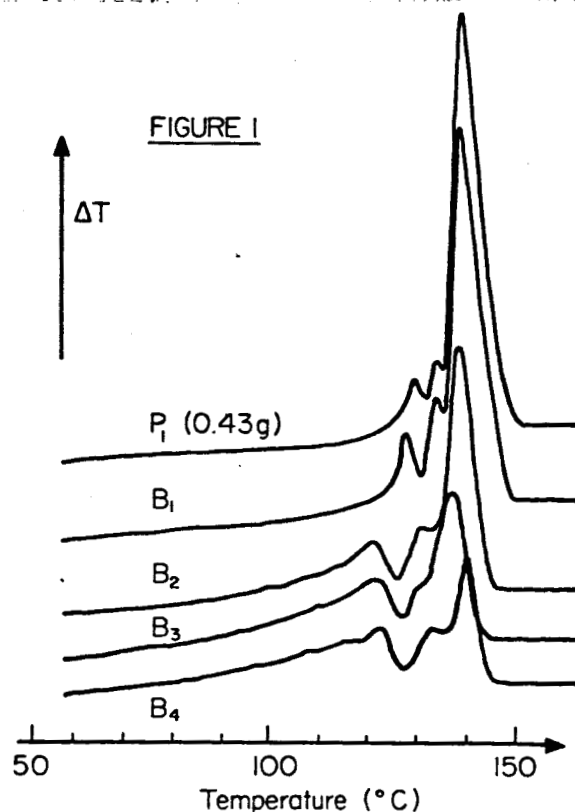19. R. F. Westover, SPE Trans., 1, 14 (1961).

Figure 1: DTA-traces of polyethylene and ethylene-butene-1 copolymers. Successive traces are shifted by varying amounts.
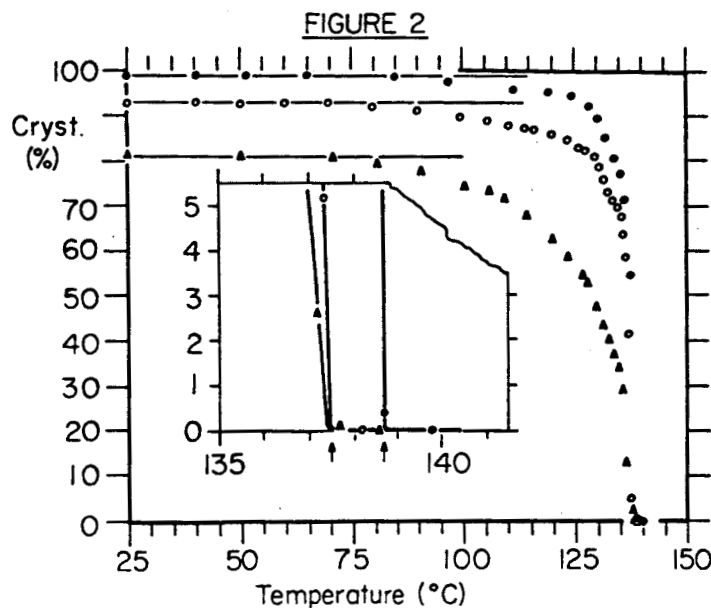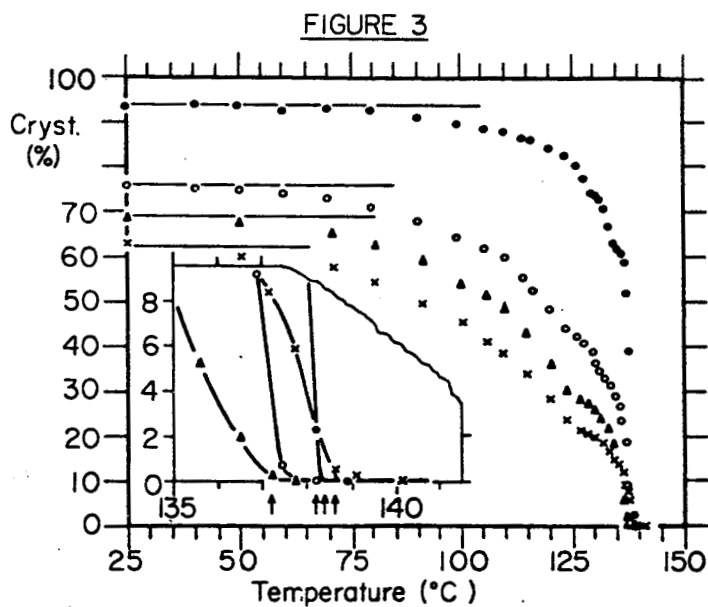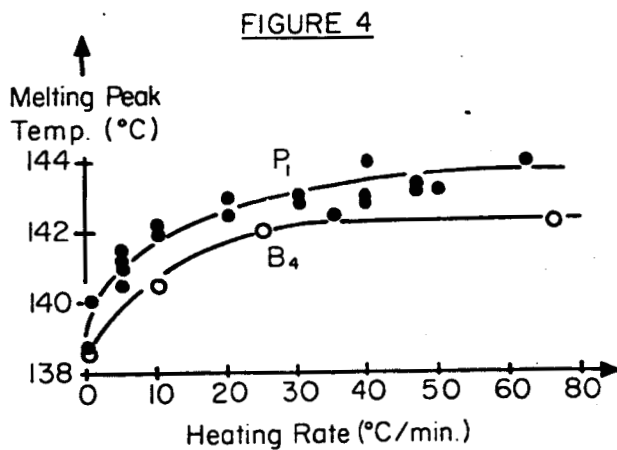

Figure 2: Crystallinity versus temperature of the P-series polymers. Filled circles, P_1; open circles, P_2; triangles, P_3.

7

FIGURE 3

Figure 3: Crystallinity versus temperature of the B-series polymers. Filled circles, B_1; open circles, B_2; triangles, B_3; crosses, B_4.

FIGURE 4

Figure 4: Melting peak temperature measured by DTA as a function of heating rate.