Thermal Analysis of Polyethylene Prepared by γ-Ray-Induced Polymerization in Various Solvents

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Synopsis

Thermal properties of polyethylenes prepared by γ-ray-induced polymerization in various solvents were examined by differential scanning calorimetry. The solvents used were ethyl and n-butyl alcohols, tert-butyl alcohol containing 25 vol% of water, 2,2,4-trimethylpentane, 2,2,5-trimethylhexane, and cyclohexane. The dependence of the profiles of the heating curves for the produced polymers on polymerization temperature varies with the solvent type. This difference was discussed in terms of the degree of undercooling in various solvents during polymerization. In all solvent systems, the melting point and heat of fusion of the polymers decrease continuously with polymerization temperature. This decrease is caused by an increase in branches with reaction temperature. The melting point and heat of fusion are 100–124°C and 30–44 cal/g, respectively, and no superheating is observed. These facts suggest that folded chain crystals are commonly formed in these systems.

INTRODUCTION

In a preceding paper,[1] we showed from electron microscopic observations that polyethylene prepared by γ-ray-induced polymerization in various solvents is commonly composed of lamellar crystals with folded chains and that the polymer morphology is affected by the solvent type as well as polymerization temperature. The solvent effect on the thermal properties of polyethylene produced by crystallization during polymerization has never been studied, though several papers[2-4] on the thermal properties of as-polymerized polyethylene prepared with the Ziegler-Natta catalyst were reported. In these works, however, the physical properties of the polymers may be affected by catalysts, for according to Georgiadis and Manley[4,5] the polymer morphology varies with the catalyst type.

In the present paper, the fine structure of the polyethylene prepared by γ-ray-induced polymerization in various solvents is investigated by differential scanning calorimetry.

EXPERIMENTAL

Polyethylene Preparation

Polyethylenes were prepared by γ-ray-induced polymerization under quiescent conditions in ethyl and n-butyl alcohols, 2,2,4-trimethylpentane (TMP), 2,2,5-trimethylhexane (TMH), and cyclohexane. The polymerization conditions were described before.[1] After polymerization, the product polymer was washed with acetone to fully exchange the reaction medium and subsequently dried under reduced pressure at room temperature for a week. In the case of polymerization above room temperature, the polymer was recovered after the reactor was cooled to room temperature.

Polyethylene produced by polymerization in a 50 l. capacity pilot plant[6] was also used. In this case, ethylene was polymerized in the presence of tert-butyl alcohol containing 25 vol% of water under a pressure of 300 kg/cm^2 and at the dose rate of 2.8×10^5 rad/hr (Co-60 γ rays).

The preparation conditions and number-average molecular weight for the representative polyethylenes are listed in Table I. The number-average molecular weights of the polymers were determined using Tung's equation[7] from the intrinsic viscosities in tetralin solution at 130°C.

DSC Measurements

The thermal behavior of the nascent polymers was examined with a Perkin-Elmer differential scanning calorimeter (DSC), Model DSC 1B. The DSC heating curves of the sample (3 mg) were recorded at heating rate of 8°C/min in a nitrogen stream. Each sample was first melted by heating to about 25°C above the endothermic peak temperature (first run), immediately recrystallized from the melt by cooling in the instrument at the same rate to about 50°C, and remelted under the same experimental conditions (second run). The temperature scale of the calorimeter was calibrated with pure benzoic acid and indium.

TABLE I
Polymerization Conditions and Molecular Weight of the Representative Polyethylenes

Sample No.	Solvent	Polymerization		Molecular weight $\times 10^4$
		Temperature °C	Time min	
1	ethyl alcohol	25	120	0.37
2	n-butyl alcohol	25	120	0.41
3	TMP[a]	25	120	1.8
4	TMH[b]	25	120	0.41
5	cyclohexane	25	120	0.41
6	tert-butyl alcohol[c]	32	60[d]	5.5
7	ethyl alcohol	60	120	0.28
8	n-butyl alcohol	60	120	0.41
9	TMH	60	120	0.92
10	cyclohexane	60	60	0.45
11	tert-butyl alcohol[c]	60	42	2.0
12	ethyl alcohol	80	120	0.26
13	TMH	80	120	0.71
14	n-butyl alcohol	80	120	0.30
15	tert-butyl alcohol	80	42[d]	1.5
16	ethyl alcohol	100	120	0.18
17	TMH	100	120	0.30
18	n-butyl alcohol	90	120	0.18

[a] TMP, 2,2,4-trimethylpentane.
[b] TMH, 2,2,5-trimethylhexane.
[c] Containing 25 vol % of water.
[d] Mean residence time.

RESULTS AND DISCUSSION

Dependence of Profiles of DSC Heating Curves for the Polymers on Polymerization Temperature and Solvent Type

Figures 1–4 show the dependence of the profiles of DSC heating curves (first and second runs) for polyethylenes prepared by γ-ray-induced polymerization in ethyl, n-butyl alcohols, TMH, and cyclohexane, respectively. The polymers formed in tert-butyl alcohol containing 25 vol% of water show heating curves similar to those of samples obtained in ethyl alcohol.

It is clearly seen from the figures that the profiles of DSC heating curves in the first run are strongly dependent on polymerization temperature. The Polymers formed at room temperature show a sharp endothermic peak common to all solvent systems. The tail at the low-temperature side of the main peak becomes broader gradually in any systems as polymerization temperature increases. At higher reaction temperature, discrete double peaks or a broad peak with a shoulder are observable. At still higher reaction temperatures, only a very broad peak is seen.

In addition, it is notable that the polymerization temperature at which the profile of the heating curve for the polymer changes from single to double peak varies with the solvent type. (Hereafter this temperature is referred to as $T_{\text{mult.}}$)
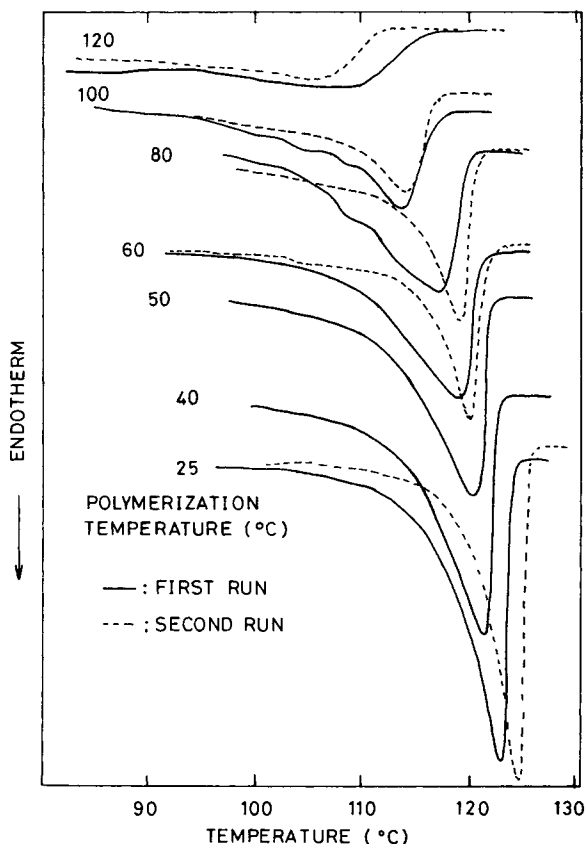

Fig. 1. DSC heating curves for polyethylene prepared by γ-ray-induced polymerization in ethyl alcohol at various polymerization temperatures.
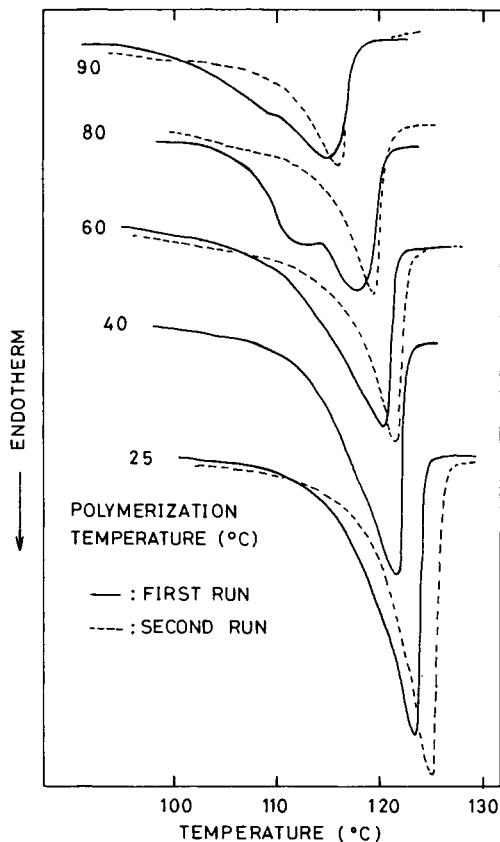
Fig. 2. DSC heating curves for polyethylene prepared by γ-ray-induced polymerization in n-butyl alcohol at various polymerization temperatures.

Since the polymers prepared at higher reaction temperatures show a sharp unimodal molecular weight distribution,[8] these double endothermic peaks do not arise from the fractions of different molecular weights.

Table II summarizes T_{mult} values together with the equilibrium dissolution temperatures[1] of bulk-crystallized linear polyethylene in solvents. It was shown in a preceding paper[1] from the values of the thermodynamic interaction parameter χ_1 (ref. 9) and the molar volume that the affinity of solvent for polyethylene becomes better in the order of ethyl, tert-butyl, n-butyl, TMH, and cyclohexane. Table III lists the degree of undercooling during polymerization in solvents, which is defined as the difference between the equilibrium dissolution temperature of bulk-crystallized polyethylene and polymerization temperature. The underlines in Table III show the polymerization of which DSC double endothermic peaks are explicitly observed in the first run curves.

It is seen from Tables II and III that T_{mult} becomes lower with increasing the affinity of solvent and that the appearance of double endotherms may be correlated with a certain degree of undercooling during polymerization, namely, the double peaks seems to arise to undercooling smaller than 50°–60°C. At small undercooling, the crystallization is slow, i.e., the mobility of polymer chains prior to crystallization is large. This was shown before[1] by the finding that comparatively large lamellar crystals are formed at such small undercooling.

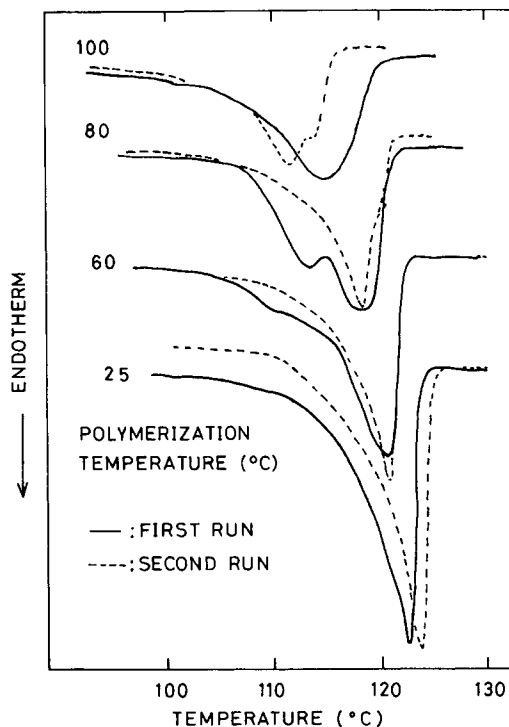The fifth column of Table II shows the temperature at the break point of the

Fig. 3. DSC heating curves for polyethylene prepared by γ-ray-induced polymerization in 2,2,5-trimethylhexane at various polymerization temperature.

TABLE II

Affinity of Solvents for Polyethylene and Polymerization Temperature at which a DSC Double Endothermic Peak Appears

Solvent	Affinity for polyethylene	Equilibrium dissolution temperature °C	DSC double[a] peak temperature °C	Break Point[b] temperature °C
Ethyl alcohol	poor	140	80[c]	80
tert-butyl alcohol[d]	poor	140	80[c]	80
n-butyl alcohol	poor	131.2	80	80
2,2,5-Trimethylhexane	intermediate	121.6	60[c] or 80	60
Cyclohexane	good	107.0	60	(25)

[a] Polymerization temperature at which a DSC double endothermic peak appears.

[b] Temperature at the break point of the curves of the polymer yield against the polymerization temperature (Wada et al.[8]).

[c] Broad single endothermic peak.

[d] Containing 25 vol% of water.

curves of the polymer yield against reaction temperature, which was defined and reported by Wada et al.[8] As seen from Table II, T_{mult} agrees well with the above break point temperature. Wada et al.[8] concluded that heterogeneous and homogeneous polymerizations take place below and above the break point temperature, showing that the mobility of growing polymer chains becomes considerably large above this temperature.

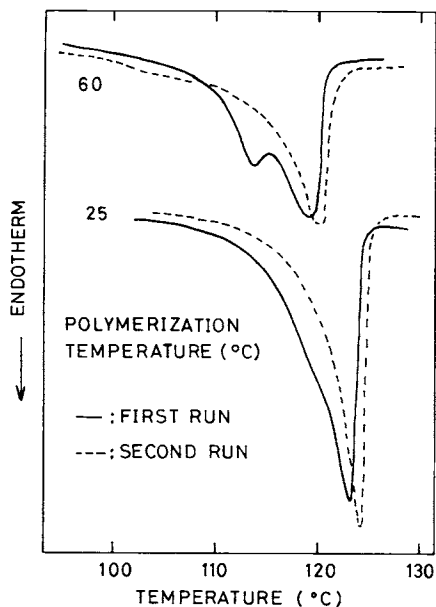During polymerization at small undercooling, the polymers formed at an early

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Fig. 4. DSC heating curves for polyethylene prepared by γ-ray-induced polymerization in cyclohexane at various polymerization temperatures.

TABLE III
Degree of Undercooling during Polymerization in Solvents

| | Degree of Undercooling[a] (°C) | | | |
| Solvent | Polymerization | | Temperature (°C) | |
	25	60	80	100
Ethyl alcohol	115	80	60	40
tert-butyl alcohol	115	80	60	40
n-Butyl alcohol	101.2	71.2	51.2	31.2
2,2,5-trimethylhexane	91.6	61.6	41.6	21.6
Cyclohexane	77.0	47.0	27.0	7.0

[a] Difference between the equilibrium dissolution temperature of bulk-crystallized polyethylene and polymerization temperature.

reaction stage may crystallize gradually, but the polymers formed at the later stage remain in undercooled state when the polymerization is stopped. The latter polymer may crystallize in the cooling process after the polymerization. The crystals shaped rapidly in the cooling process should show less crystal perfection[10] than the crystals grown slowly during polymerization. The former crystals, therefore, may show melting points lower than that formed at the latter condition. Thus, it is inferred that in Figures 1–4, the higher- and lower-temperature peaks in the DSC double endotherms correspond to the melting of crystals formed during polymerization and in the cooling process after the polymerization, respectively.

In polymerization at room temperature, all polymers should crystallize at the same temperature, that is, at room temperature. Under this condition, the polymer crystals may have much the same perfection. Consequently, the polymers formed at room temperature may show a sharp endothermic peak in all solvent systems.

For polymerization above 90°C, the polymers do not show distinct double endothermic peaks. This may be caused by the effects of short chain branches, as discussed below. An increase in branch content with polymerization shifts the main peak to lower temperature.

As for the second run curves, the melting points are slightly higher than those for the first run. This is consistent with the known fact[11] that the bulk-crys-tallized polymer consists of lamellae of large fold length, which melt at temperature higher than the solution-grown crystals. This tendency is different from those of Chanzy et al.[2,3] and Wunderlich et al.[12] The heat of fusion in the second run is generally smaller than that in the first run.

Dependence of Melting Point and Heat of Fusion on Polymerization Temperature for the Polymers

Figures 5 and 6 show the dependence of the melting point (T_m) (expressed by the endothermic peak temperature in the first run) and heat of fusion (ΔH_f) of the polymers prepared in various solvents on polymerization temperature.

Both the melting point and heat of fusion decrease with increasing reaction temperature. Although the data for the tert-butyl alcohol system in a pilot plant are somewhat smaller than for other solvent systems, the data in Figures 5 and 6 may admit us to say that the melting point and heat of fusion are almost independent of solvent type. Lamellar thickness of the polymers increases with polymerization temperature for all solvent systems.[1,13]

The melting point of polyethylene single crystals increases generally with the lamellar thickness.[14] However, the relation between T_m and reaction temperature in Figure 5 is reverse. Such a reverse tendency was also found for the bulk-polymerized polyethylene.[15] This tendency can be explained on the basis of the effect of branches.

Short chain branches are increased at higher polymerization temperature by back-biting mechanism.[16,17] Furukawa et al.[18] confirmed by infrared spec-
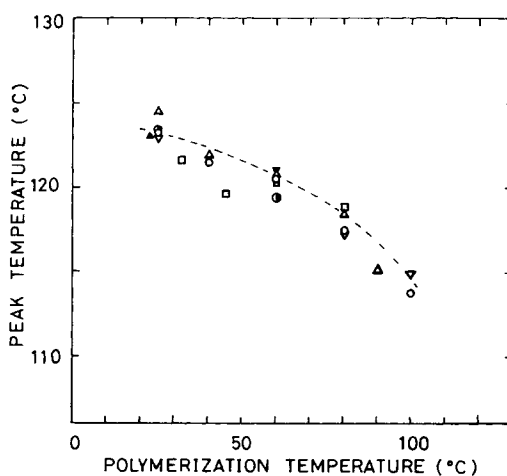

Fig. 5. Dependence of melting point on polymerization temperature for polyethylenes prepared by γ-ray-induced polymerization in various solvents. Polymerization systems: O, ethyl alcohol; □, tert-butyl alcohol containing 25 vol% of water; △, n-butyl alcohol; ▲, 2,2,4-trimethylpentane; ▽, 2,2,5-trimethylhexane; ◑, cyclohexane.
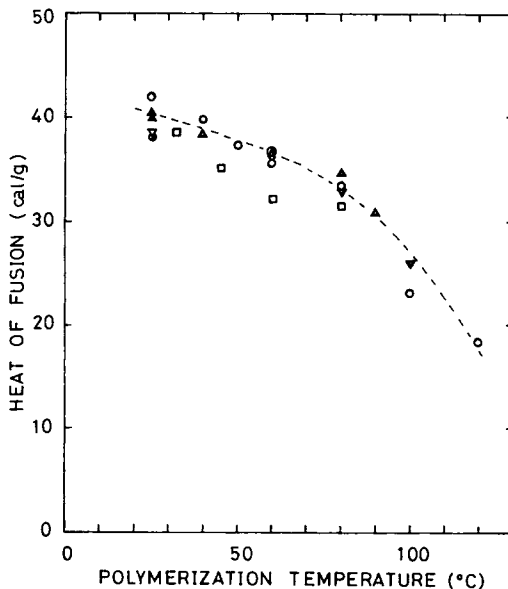
Fig. 6. Dependence of heat of fusion on polymerization temperature for polyethylenes prepared by γ-ray-induced polymerization in various solvents. Symbols are the same as in Figure 5.

troscopy and high resolution NMR that polyethylene prepared in tert-butyl alcohol containing 25 vol% of water contains more short chain branches with an increase in reaction temperature. Yamaguchi et al.[19] reported on long chain branches in the same polymers. These tendencies may be the same in the other solvent systems. Hosoi et al.[20] reported that both an increase in short chain branching with polymerization temperature and an increase of long chain branches in the fractions of high molecular weight polymer bring about a decrease in the melting point of the melt-crystallized polyethylene which was prepared by γ-ray-induced polymerization in bulk. Recently, Martsucelli and Pracella[21] also showed that the melting point and heat of fusion of polyethylene decrease with an increase in branches. Thus, the effect of such short and/or long chain branches must be responsible for the dependence of T_m and ΔH_f on reaction temperature shown in Figures 5 and 6.

Another reason for the small values of ΔH_f of the polymers obtained at room temperature in spite of low branch contents is large undercooling during polymerization. At room temperature, polymer chains grow at large undercooling, which makes polymer chains crystallize so rapidly[10] that there may be no time for the crystals to grow to large size. This postulate is supported by the small sizes of lamellar crystals formed at room temperature.[1]

Thus, the independence of ΔH_f of the polymers on the solvent type despite the large differences in the morphology[1] may be explained in terms of branches on the polymer fine structure.

The endothermic peak temperature of the polymers was almost independent of the heating rate in all solvent systems, suggesting the absence of superheating. This facts is in good agreement with the findings from the electron microscopic observations[1] and selective ozone degradation[13] of the polymers which indicate that the polymers are composed of folded chain crystals.

In addition, the melting point, heat of fusion and the profiles of heating curves

of the polymers scarcely vary with reaction time. These properties are mainly dependent on polymerization temperature. This tendency is similar to that in bulk polymerization.

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