Nonisothermal Melting and Crystallization Studies of Homogeneous Ethylene/α-Olefin Random Copolymers

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ABSTRACT: A study of nonequilibrium melting, nonisothermal, and isothermal crystallization behavior of ethylene/1-octene (EO) random copolymers, produced using metallocene catalysts has carried out. As branch (or defect) content increases, the nonisothermal and isothermal crystallization rates, melting temperatures, and heats of fusion decrease. There is also a branch length effect on melting temperature depression, the melting temperature depression of EO random copolymers with hexyl branches were significantly larger than those of ethylene/1-butene (EB) and ethylene/1-propene (EP) copolymers having ethyl and methyl branches, respectively. The melting temperatures of homogeneous random copolymers have been found to be always lower than those of fractions of heterogeneous copolymers, having approximately the same branch content and molecular weight. Hence, defect distribution in copolymer systems is at least as important a parameter as the defect content. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1893–1905, 1998

Keywords: polyethylene; nonequilibrium melting; copolymers; isothermal crystallization behavior

INTRODUCTION

There has been extensive reporting of melting and structure studies,[1–3] including a review,[4,5] of ethylene/α-olefin random copolymers with a variey of different α-olefins obtained from different sources. The studies used fractions of ethylene copolymers with narrow molecular weight distribution and demonstrated the importance of the comonomer distribution, or sequence length distribution, of the copolymer chains.

Recently available series of homogeneous ethylene/α-olefin random copolymers make it possible to study the melting and the crystallization behavior systematically as a function of branch content by avoiding the heterogeneous molecular weight and sequence length distributions of copolymers produced from Zeigler-Natta catalysts. Heterogeneity in sequence-length distributions of homogeneous ethylene copolymers is less than that of fractions of Zeigler-Natta copolymers. In this article, the effect of heterogeneity of ethylene copolymers on the nonequilibrium melting temperatures will be reported. The crystallization and melting behavior of ethylene/1-octene (EO), ethylene/1-butene (EB), and ethylene/propene (EP) random copolymers produced with metallocene catalysts have been studied as a function of branch content, branch length, and crystallization conditions. In addition, the melting behavior of EO random copolymers from metallocene cata-

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Table I Characteristics of Homogeneous Copolymers

Code[a]	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	$\bar{M}_w/\bar{M}_n$	Density (g/cm^3)	CH$_3$/1000C	T_m (°C)[c]
H7-O	—	43,600	—	0.9180	6.84	113.2
H7′-O	98,400	44,800	2.196	0.9180	7.32	113.3
H10-O	—	48,800	—	0.9126	9.50	107.5
H16-O	—	45,200	—	0.9003	16.34	94.5
H17-O	102,700	48,700	2.108	0.9003	16.92	96.2
L4-O	59,900	27,300	2.194	0.9365	3.98	118.8
L10-O	—	23,700	—	0.9195	9.83	109.2
L13-O	51,800	25,000	2.07	0.9110	12.93[b]	105.0
L18-O	—	24,900	—	0.9027	18.17	94.5
L24-O	46,900	21,800	2.151	0.8975	24.04	90.2
L39-O	48,000	22,800	2.105	0.8700	38.62	48.2
L40-P	58,400	26,800	2.20	0.9046	40.10	92.0
L93-P	59,100	29,100	2.00	0.8849	92.60	49.5
L31-B	55,400	25,400	2.20	0.9048	31.00	94.5

[a] H, M, L; high, medium, and low molecular weight; LPE; Numbers, branch content. O, B, P, octene, butene, and propene comonomer, respectively.
[b] Trans/1000C = 0.298, vinyls/1000C = 0.045.
[c] Measured at DSC heating rate 10°C/min in this work.

lysts is compared to that of ethylene–octene copolymers from heterogeneous catalysts.

EXPERIMENTAL

Materials

The ethylene/1-octene random copolymers were supplied by the Dow Chemical Company, and the ethylene/1-propene and ethylene/1-butene copolymers were from a different source. Branch content, molecular weight, and polydispersity($\bar{M}_w/\bar{M}_n$) were controlled by respective metallocene type catalysts. Chemical characterization data were supplied by the manufacturers. The details of as-received samples are listed in Table I. Here, the code H, L, number, O, B, and P stand for the high molecular weight, low molecular weight, methyl groups per 1000 carbon (i.e., branch content), 1-octene, 1-butene, and 1-propene comonomer, respectively.

Thermal Analysis

Thermal analysis was performed under a nitrogen atmosphere using a Perkin-Elmer Series 7 differential scanning calorimeter (DSC) attached with a cooling accessory. The calibration of the DSC with indium (T_{onset} = 156.60°C, ΔH_f = 28.45 J/g) was carried out several times until deviation from the known onset temperature (T_{onset}) of indium was within ±0.05°C. After completing study, the T_{onset} of indium was remeasured, and the maximum deviation from the known T_{onset} of indium was always within ± 0.15°C. In all melting experiments, the DSC heating rate was 10°C. The peak temperature in the DSC thermogram was chosen as the melting temperature. Samples were prepared in the shape of thin film with the same diameter as the DSC sample pan, to avoid a sample shape effect and provide uniform contact between the sample and the surface of DSC aluminum pan.

Isothermal Crystallization

The isothermal crystallizations were carried out in a silicone oil bath. To avoid contact of the oil and sample, the sample was placed between the two cover glasses, placed in a thin copper jacket, and then sealed in an aluminum bag coated with a thin plastic film, under nitrogen gas. The actual temperature of the sample was precalibrated against the bath temperature reading in a separate experiment. The sealed samples were melted at 150°C for 10 min to remove the thermal history and then transferred to the oil bath, preset at the crystallization temperature. The isothermal crystallization studies were carried out as a function of crystallization temperature and time. After crystallization, the samples were rapidly quenched in liquid nitrogen to room temperature. By this quenching process, it was hoped to separate the isothermally crystallized fraction from the fraction that crystallized on quenching.

RESULTS AND DISCUSSION

Nonisothermal Crystallization

Cooling Rate Effects

Before studying the isothermal crystallization behavior the crystallization temperature range was obtained using nonisothermal crystallization in the DSC. Usually, the isothermal crystallization should be carried out above the nonisothermal crystallization temperature. Figure 1(a) and (b) shows exotherms of H7-O and H16-O, which are of similar molecular weight, but different hexyl branch content, with different cooling rates. As cooling rate increases, the areas of the exotherms increase and the maximum peak temperature shifts to lower temperatures.

There are two different crystallization exotherms. The first is a large exotherm at high temperature (LEHT), and the other a small one at low temperature (SELT). In copolymers produced using Zeigler-Natta catalysts this behavior is well known. LEHT is known to be due to the crystallization of polymer chains with high molecular weight and low branching content, while SELT is caused by polymer chains with low molecular weight and high branching content.[6] In those copolymers segregation of polymer molecules by molecular weight and branch content can occur synergistically. In other words, there is enough time for molecular fractionation, even during nonisothermal crystallization at a cooling rate of 40°C/min.

When we consider that the EO copolymers of Figure 1 were polymerized using metallocene catalysts (uniform site catalyst), the branching distribution should be quite random without localization of branching along the main chain, and there should be no relation between molecular weight and branch content. However, the experimental results show there is still a second lower temperature crystallization process occurring.

Branch Content and Length

Exotherms obtained as a function of branch content at the constant cooling rate of 10°C/min are shown in Figure 2. As branch content increases, the nonisothermal crystallization temperature decreases. Two samples with different molecular weight but the same branch length and content, H10-O (high molecular weight) and L10-O (low molecular weight), show similar crystallization temperatures. The nonisothermal crystallization temperatures are controlled by branch content rather than molecular weight, or by a combination of the two.

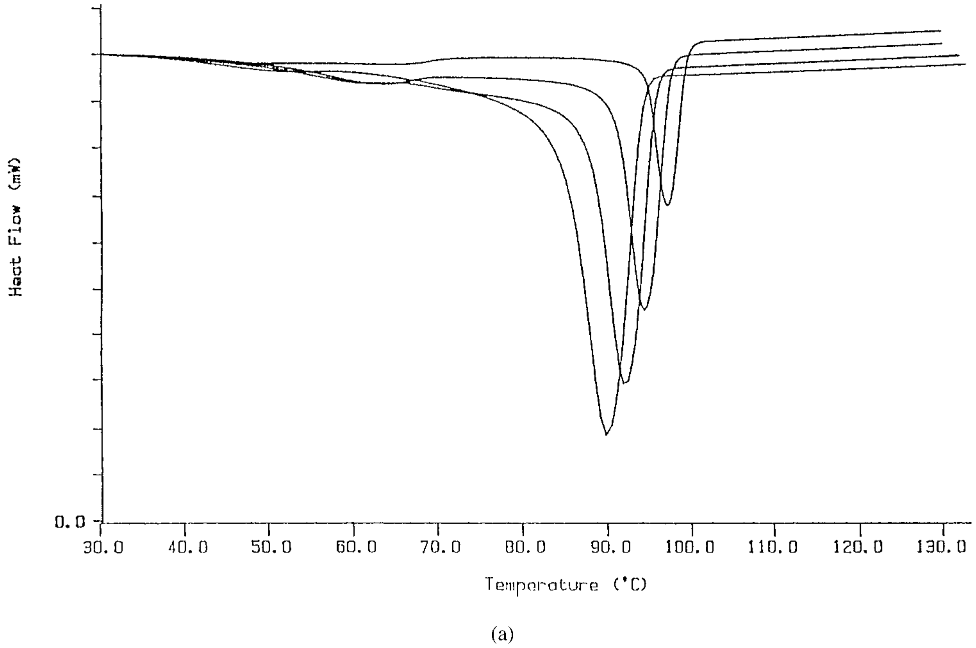
The olefin copolymers with different branch lengths such as hexyl, ethyl, and methyl show quite different nonisothermal crystallization temperatures. For instance, the nonisothermal crystallization temperature of L93-P, having 93 methyl branches per thousand carbon atoms is higher than that of L39-O, having 39 hexyl branches per thousand carbons. Also, the nonisothermal crystallization temperature of L40-P is higher than that of L24-O. In the same manner, the crystallization temperature of L31-B, having 31 ethyl branches, is higher than that of H16-O. In other words, increasing the branch length results in a clear and significant lowering of the nonisothermal crystallization temperature. It appears clear that the longer branches inhibit the crystallization process much more effectively than shorter branches.

Melting Behavior

The melting behavior of semicrystalline material is as important as nonisothermal crystallization behavior for understanding the effect of the polymer structure on the phase transformation process, because it provides information about the character and structure of the crystals formed during nonisothermal crystallization.

Ethylene/1-Octene Random Copolymers

The melting behavior of EO random copolymers quenched to room temperature are shown in Figures 3 and 4 for the high and low molecular weight series, respectively. The peak temperature (at which most probable crystals in the system melt) was chosen as the melting temperature rather than onset temperature at which the melting of crystals starts by definition, or baseline return point, at which the last trace of the crystal melts. The peak melting temperature decreased as branch content increased. Because the melting point is a function of crystal thickness based on the Thompson-Gibbs concept, if surface energy and heat of fusion are constant, melting point



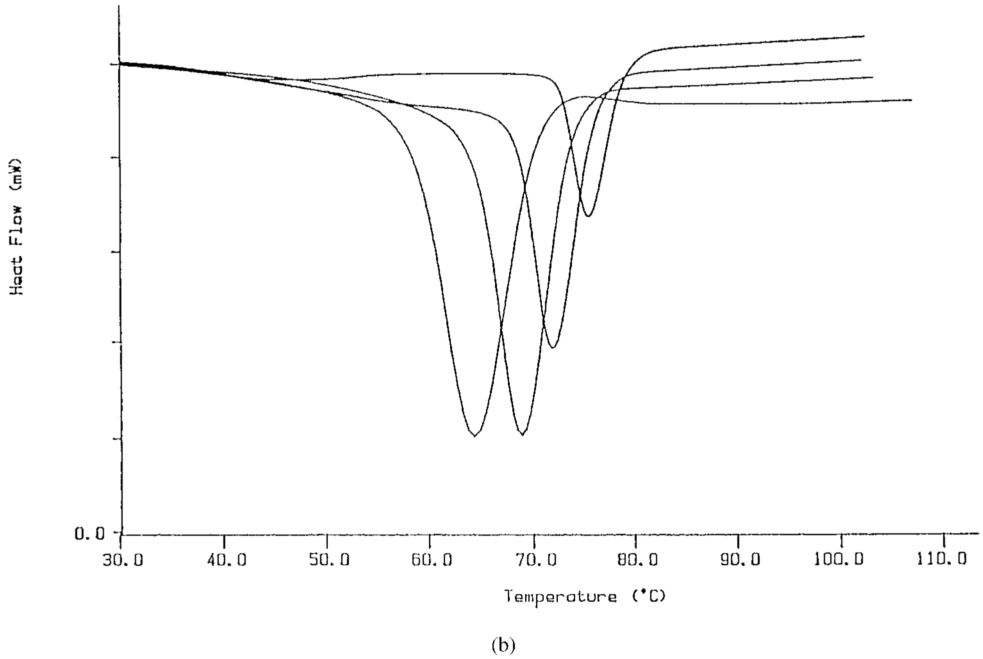


Figure 1 Nonisothermal crystallization thermograms of (a) H7-O and (b) H16-O, at cooling rates, 10, 20, 30, and 40°C/min.

depression with increasing branch content means that the branches restrict the thickness of lamellae. Therefore, lamellar thickness decreases with branch content, and melting point shifts toward a lower temperature.

The shape of the melting thermogram becomes broader with increasing branch content. This means that the distributions of lamellar thickness and/or crystal perfection become broader as branching content increases. In more detail, increasing branch content decreases the sequence length between branch points and results in thinner lamellae if the branches (i.e., defects) are excluded from the crystalline phase. As mentioned earlier, if there is any remaining heterogeneity in the branch distribution, it will cause the

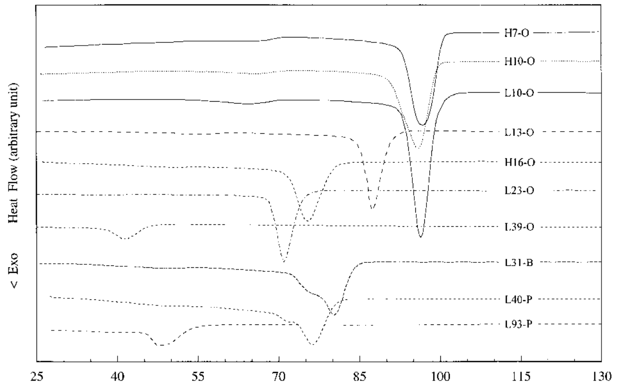


Figure 2 DSC exotherms of EO, EB, and EP copolymers measured at cooling rate of 10°C/min.

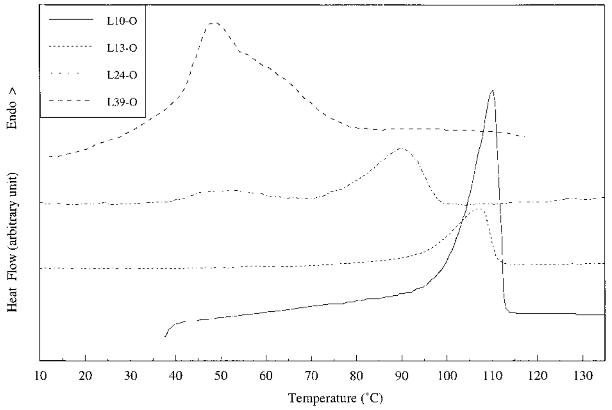


Figure 4 DSC thermograms of as-received EO copolymers (low molecular weight).

crystals to have a broader range of lamellar thickness. Broad melting thermograms could also result from the incorporation of defects in the crystalline phase.

Ethylene/1-Propene (EP) and Ethylene/1-Butene (EB) Random Copolymers

Typical melting curves for L31-B, L40-P, and L93-P crystallized in the same manner as the octene copolymers of Figure 4 are shown in Figure 5. The shape of the melting thermograms is similar to that of the EO random copolymers. As branch content increases, the width of the melting curve broadens, and peak temperatures shift to lower temperatures. The humps around 45°C of L31-B and L40-P are at the same position as the peak temperature of highly branched L93-P. Because their molecular weights are similar to each other and the molecular weight distributions are narrow, the branch distribution is probably the main factor in producing these small humps. On cooling, segregation and crystallization of highly branched molecular sections likely occur. This appears to indicate that there is some heterogeneity in the branch distribution for L31-B and L40-P. In more detail, a localized branch distribution exists for L31-B and L40-P, and the distance between branch points in this localized area must be similar to the distance between two branch points in the randomly distributed area of L93-P. In the same sense, the small humps in the melting endotherms of EO copolymer probably also reflect some heterogeneity in the branch distribution.

Comonomers of propene, 1-butene, and 1-octene produce methyl, ethyl, and hexyl branches, and it is of interest to learn if there is a branch-length effect on the melting behavior. The comparison of melting temperatures in Figure 6

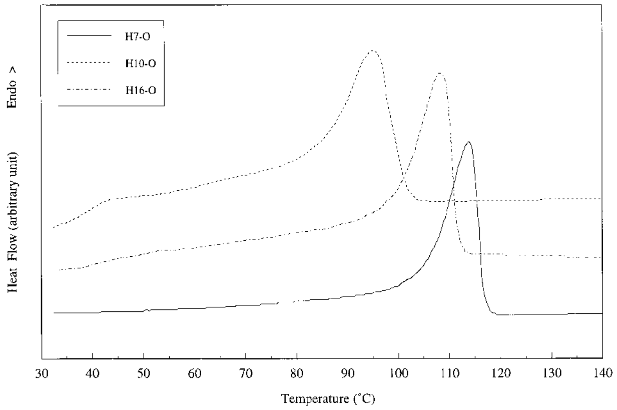


Figure 3 DSC thermograms of as-received EO copolymers (high molecular weight).

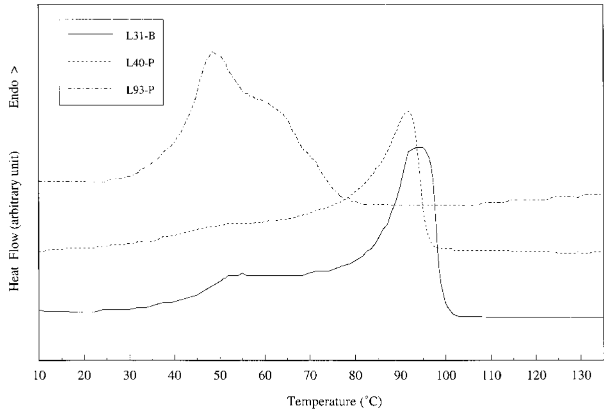


Figure 5 DSC thermograms of as-received EB and EP copolymers.

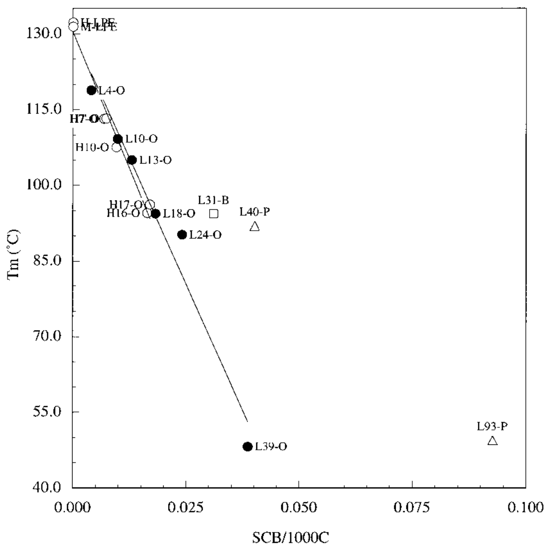


Figure 6 Plot of peak melting temperatures as a function of branch content for EO, EB, and EP copolymers quenched to room temperature.

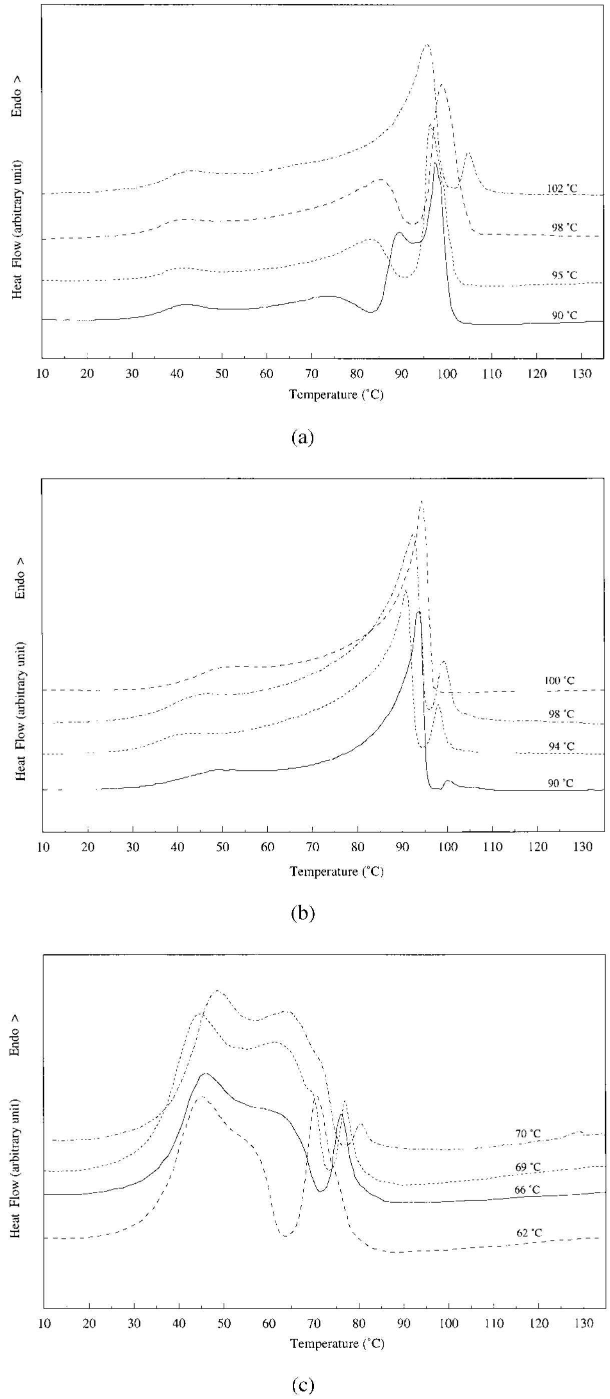
shows L31-B (T_m = 94.5°C) = L18-O (T_m = 94.5°C) = H16-O (T_m = 94.5°C), L40-P (T_m = 92.0°C) > L24-O (T_m = 90.2°C), and L93-P (T_m = 49.5°C) > L39-O (T_m = 48.2°C). These melting temperatures show a similar tendency to that of the effect of the branch length on nonisothermal crystallization temperature.

This result is expected, because the crystals formed at higher crystallization temperatures will have higher melting temperatures than those formed at lower temperatures. It is important to know that branch length affects the melting temperature and the crystallization temperature in a consistent manner. This indicates that there is no abnormal thickening behavior occurring during the heating process in the DSC that might have modfied the trends. The melting temperature of a polymer having a small amount of long side branches corresponds to that of a polymer having a large amount of short branches. In other words, the melting point depression of a copolymer with long side branches is bigger than that of a copolymer with short chain branches. Of course, this does not imply they should have the same thermal, mechanical, and rheological properties. In fact, the isothermal crystallization behavior and the ability to crystallize are quite different.

Isothermally Crystallized LLDPE

Isothermal Crystallization Temperature Effect

The effect of crystallization temperature for a fixed isothermal crystallization time of 24 h followed by cooling to room temperature before scanning is shown in Figure 7(a), (b), and (c) for L31-B, L40-P, and L93-P, respectively. The broad single melting peak typical of a quenched sample is now replaced by three discrete melting peaks,



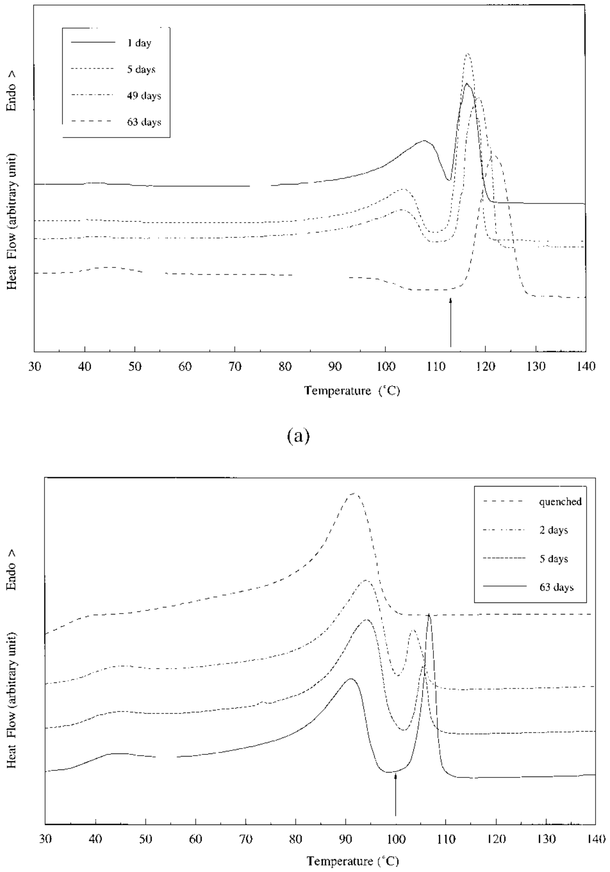
(a)

(b)

(c)

Figure 7 DSC thermograms (a), (b), and (c) of L31-B, L40-P, and L93-P crystallized at the indicated temperatures for 1 day.

except for the L31-B when crystallized at 90°C. The first peak (T1) appears at a higher temperature than the isothermal crystallization temperature (T_c), and results from the isothermal crystallization process. The second peak (T2) found just below T_c and the last peak (T3) around 45°C (far away from T_c) are due to the quenching process. The value of T1 shifts to a higher temperature with increasing crystallization temperature. Evidently, this may be due to the crystallization of molecular sections capable of crystallizing into the thickness of lamellae determined by the crystallization temperature. The area of the first peak T1 of L31-B crystallized at 102°C is much smaller than for samples crystallized below 102°C. This indicates that some molecular sections can be crystallized at this temperature, even though most molecules are in the molten state. Those latter sections will crystallize during cooling, generating the second and third peaks. All molecular sections have a particular crystallization temperature, depending on branch content. Molecules are segregated as a function of branch distribution in the random copolymer even during the fast cooling process below the isothermal crystallization temperature, resulting in the two endotherms, T2 and T3.



(a)

(b)

Figure 8 Melting thermograms (a) of H7-O crystallized at 113°C and (b) of H16-O crystallized at 100°C for indicated times.

Isothermal Crystallization Time Effect

Crystallization is controlled by time as well as temperature. A demonstration of the variation of melting behavior with crystallization time is shown in Figure 8(a) and (b) for H7-O and H16-O, respectively. The quenched sample of H16-O shows a single broad melting peak around 94.0°C in Figure 8(b), with a weak shoulder around 40°C. As isothermal crystallization proceeds, the single broad peak is separated into multiple peaks; however, the 40°C peak remains. The first peak (T1) appears above the isothermal crystallization temperature (T_c), the second peak (T2) below T_c, and the last peak (T3) around 45°C, far away from T_c.

In Figure 8(a) and (b), the T1 just above the crystallization temperature (T_c) grows larger at the expense of the T2 peak, and shifts to higher temperatures with increasing crystallization time. Furthermore, the T2 peak shifts to a lower temperature and the gap between the first and second peaks increases as crystallization time increases. Figures 9 and 10) show that T1 increases rapidly at short crystallization times and then increases slowly as time is increased. Simultaneously, T2 decreases steeply for short crystallization times and then decreases slowly. Long crystallization times are known to result in the crystal becoming more stable by annealing and reorganization. As crystallization time becomes longer, the increase of the T1 temperature levels off. The reason for increasing T1 with crystallization time can be explained. The polymer chain sections that form the most stable crystals at a certain temperature will crystallize first, while other polymer chain sections form unstable crystals or remain in the molten state. The crystallized polymers may thicken by depleting such features as loops, loose chains, cilia, and tie molecules, and may also reorganize internally to lower the free energy, thus becoming more stable. The internal process may be by expulsion of branch points that may have been incorporated into the crystals during the initial crystallization process. Thickening and stabilization of the crystal will cause the increase of melting temperature, be-

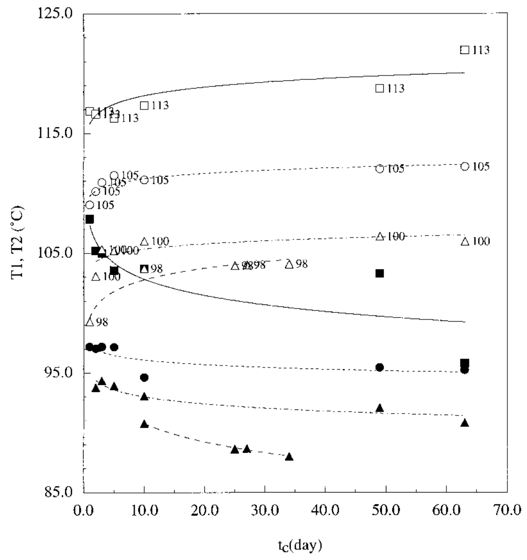


Figure 9 Melting temperature, T1 above T_c and T2 just below T_c, of high molecular weight EO copolymers with crystallization time, at labeled temperatures. Open and closed symbols are T1 and T2, respectively. Square, circle, and triangle are H7-O, H10-O, and H16-O, respectively.

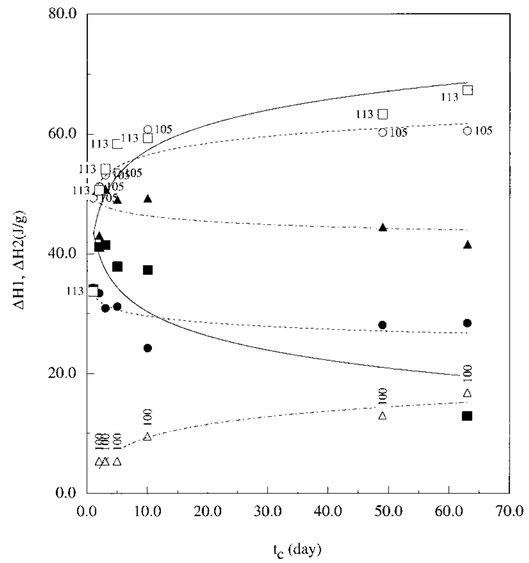


Figure 11 Heat of fusion, $\Delta H1$ above T_c and $\Delta H2$ just below T_c, of high molecular weight EO copolymers with crystallization time at labeled temperatures. Open and closed symbols are $\Delta H1$ and $\Delta H2$, respectively. Square, circle, and triangle mean H7-O, H10-O, and H16-O, respectively.

cause the melting point is a function of lamellar thickness and heat of fusion, based on the Thompson-Gibbs equation.

The reasons for the decrease of the T2 temperature are a little more complex. One way to understand this behavior is to consider the effect of branch distribution on the crystallization process. If the crystallization follows the order of decreasing sequence length, the shorter crystallizable sequences will be incorporated after the longer sequences have been consumed. If this happens, under the assumption that annealing effects are small, the peak melting temperature (T1) should decrease because the average crystal thickness will have decreased statistically, as the sequence lengths crystallizing have also decreased. However, the tendency in Figure 9 and Figure 10 contradicts the above expectation. To explain this, we need to consider the influence of defect incorporation on the behavior. The explanations offered above would be complicated by the incorporation of branch units into the crystal, because the lower heat of fusion of the defective crystal should permit the formation of thicker lamellae, everything else remaining unchanged. This then should result in a negation of the "thinning" prediction above.

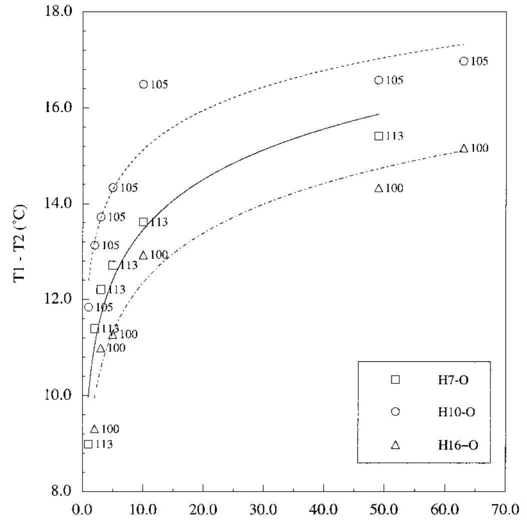


Figure 10 Melting temperature difference (T1–T2) of high molecular weight EO copolymer as a function of crystallization time, t_c(day). Labeled numbers are isothermal crystallization temperatures (°C).

The heats of fusion of the two peaks also vary considerably with crystallization time (Fig. 11). The effects mirror the changes in melting peak location and provide strong confirmation for the segregation with partial incorporation model. As crystallization time increases, the heat of fusion associated with the T1 peak increases, at first rapidy and then more slowly. Concurrently, the heat of fusion of the T2 peak decreases rapidly and then more slowly.

Consider now the relationship between heat of fusion and crystallization time. The heat of fusion (the area under melting curve) is the amount of energy required to break intermolecular forces in transforming the crystalline phase into the amorphous phase. This heat of fusion is directly related to the degree of crystallinity and crystal perfection. Increasing crystallization time has two effects on a semicrystalline system. The preformed crystals will be annealed, the crystals becoming more stable by a molecular reorganization process and annealing, as mentioned before. Annealing behavior was reported even in crosslinked low-density polyethylene[8–10] where molecular mobility was reduced and annealing effects were small. Therefore, the presence of an annealing process in LLDPE is quite reasonable because of more favorable chain mobility. As thickening and reorganization takes place, intermolecular force increases, and the enthalpy of the crystal ($H_{crystal}$) decreases. Thus, the heat of fusion ΔH_f ($= H_{melt} - H_{crystal}$) increases. This means that more energy is needed for the crystals to melt. Simultaneously, new amorphous molecules will be transformed to the crystalline phase. In other words, after a system depletes the polymer chains of the longest A-sequences that can form the largest lamellar thickness, next, the polymer chains with next longest A-sequences will register on the previously formed crystal surface, or on the nucleus, when secondary nucleation is assumed. Both effects will contribute to an increase of the heat of fusion and to the continuous distribution of lamellar thickness above T_c. Thus, the area under the DSC curve above the T_c increases. All the polymer chains, however, cannot participate in crystallization at a particular temperature, because there are highly branched or low molecular weight polymer chains that cannot form stable crystals at high T_c. Those molecules will be crystallized on cooling, generating the second peak, T2. The area of the second peak and the gap between the T1 and T2 peaks depends on whether the fraction of crystallizable sections of polymer molecules are incorporated in the first peak at long crystallization time. More incorporation will cause that second peak to weaken. In the case of narrow molecular weight distribution, the second peak will strongly depend on the branch concentration. Similarly, the polymer chains with high branch contents will primarily have short sequence lengths between branch points. The crystals obtainable from these chains are stable only at low T_c (at high supercooling). Therefore, the area of the second peak of H16-O changes little with the crystallization time, whereas that of H7-O decreases drastically.

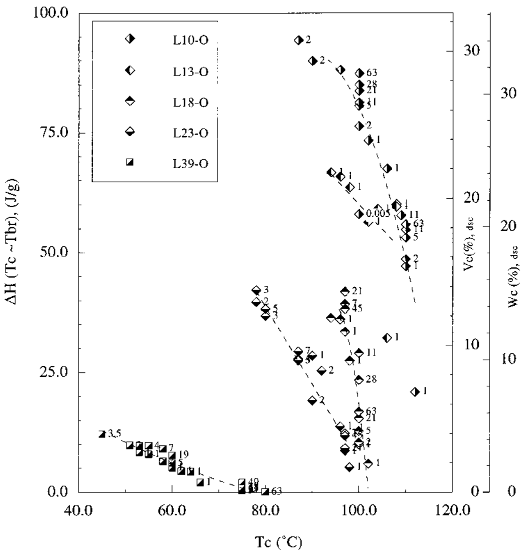


Figure 12 Heat of fusion (ΔH, J/g), degree of weight ($W_c(\%)_{,dsc}$), and volume crystallinity ($V_c(\%)_{,dsc}$) obtained between T_c and baseline return temperatures (T_{br}) as a function of T_c for low molecular weight EO copolymers. Labeled numbers are isothermal crystallization time, t_c(days).

The third peaks (or humps) around 40 and 50°C are not sensitive to crystallization time, except that the peak of quenched H16-O is lower than others crystallized isothermally. It is possible that this peak is a direct result of very slow crystallization at room temperature, as has been seen in many polyolefin systems, such as EPRs, EPDMs and crosslinked polethylenes.[11,12] As expected, because polymer chains crystallizing in this range will be in the molten state at high crystallization temperatures due to their short sequence length, there is no effect of isothermal crystallization time on this peak.

Degree of Crystallinity with Crystallization Temperature, Time, and Branch Content

The relationships between degree of crystallinity, isothermal crystallization time, and temperature are shown in Figure 12 for the low molecular weight series (see ref. 13 for the low molecular weight series of EO copolymers and for the EB and EP copolymers). The indicated numbers are crystallization time (in days) and the degree of volume $V_c(\%)$ and weight crystallinity $W_c(\%)$ obtained from the DSC areas. The heat of fusion decreases as crystallization temperature increases (i.e., supercooling decreases). This is more likely to be due to a reduction of crystallinity rather than a change in crystal perfection. The reduction of crystallinity is due to the much slower rates of crystallization combined the exclusion of more increasingly less imperfect chains as crystallization temperature is increased.

The degree of crystallinity increases with increasing crystallization time due to the primary crystallization process until the spherulites impinge, and then it is due to the secondary crystallization. The crystallinity increase was observed in all samples. Even highly branched LLDPE (L39-O) shows the increase of degree of crystallinity, although the increase is small compared to low branched LLDPE. The degree of crystallinity decreases with branch content because of rejection of branches as defects.

Comparisons of EO, EB, and EP Copolymers

The facts that melting point, crystallization temperature, and heat of fusion (or crystallinity) are all reduced means that the branches function primarily as excludable defects in the crystallizable polymers. In these short chain-branched polymers, the multiple melting behavior is most likely due to the segregation of polymer molecules during crystallization. This segregation is dominated by the branch content for highly branched polymers and by molecular weight for low branched polymers according to this study. The branch as a whole, but also its constituent parts of the branch point and branch end, all play roles as defects in crystallization because their different molecular sizes will not have the same crystallographic features as the polyethylene main chain. If we can assume that the branch defect is rejected from the crystal, then the available fraction of chain lengths capable of crystallization is reduced. This assumption is reasonable because the crystal system has excess free energy when it accommodates defects, causing an unfavorable condition for crystal growth. As long as the system cannot overcome this increased energy barrier or reject the defect to the amorphous phase, the stem growth stops at the defect location. Sections of chain with a long distance between two branch points will crystallize at high crystallization temperatures, and parts consisting of short distances between branch points will crystallize at lower crystallization temperatures. However, in low branch content copolymers, because many stems can deposit before encountering a defect, the defect effect will be less significant. In this case the segregation by molecular weight will continue to be as important as in homopolymers.

It is an important fact that different branch lengths affect melting and crystallization temperature as well as morphology, to different degrees. The melting temperatures of some EO copolymers are significantly lower than EB and EP copolymers that are more highly branched. This means the branch cannot simply be regarded as a point defect but must be considered to be a size defect. On the assumption that predominant exclusion of the branch points occurs, there should be no difference in the behavior of a copolymer containing hexyl branches from one containing methyl or ethyl branches. In terms of the melting points of quench crystallized samples it is clear that a 39 hexyl branch per 1,000 C atom copolymer is equivalent to a 93 methyl branch per 1,000 atom copolymer. The two copolymers also show the same crystallization peak temperature in a rapid cooling experiment. Similar observations can be made for a pair of copolymers containing 19 hexyl branches and 40 methyl branches per 1,000 C atoms. By interpolation it can stated that a 17 hexyl branch per 1,000 C atom copolymer is equivalent to a 31 ethyl branch per 1,000 C atom copolymer. It is very informative to plot the equivalence ratio of small branches to hexyl branches vs. hexyl branch content (Fig. 13), where it can be seen there is an almost linear relationship passing through the expected zero point of 1.0 ratio and zero hexyl content. The depression of melting point is more efficiently achieved than the suppression of crystallization peak temperature. The shape of the curve suggests that as the hexyl group content is increased it takes proportionally more of the smaller branch unit to produce equivalent effects. This cannot simply be due to the exclusion process.

It is well-known that the polyethylene crystal can support the inclusion of methyl branches, and it has been generally assumed that it rejects ethyl and larger branches. Both crystallization kinetics and melting points would be expected to be affected in a copolymer that rejects large branches from its crystals, but a copolymer that accepts branches into its crystals would have its melting point affected more than its crystallization kinet-

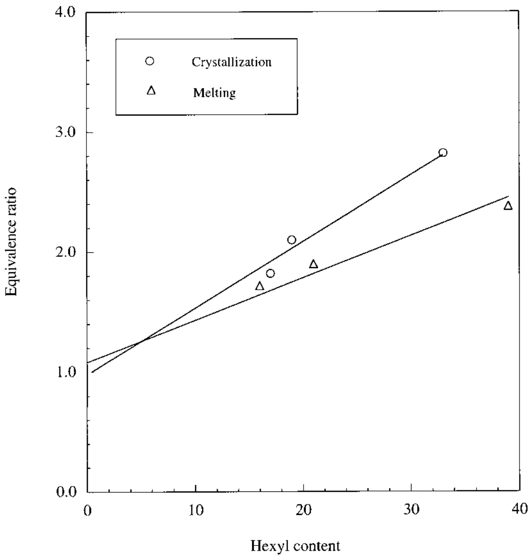


Figure 13 The equivalence ratios [alkyl/hexyl] for crystallization peaks and melting peaks vs. hexyls per 1,000 C atoms.

ics. Indeed, in quenching studies such as many of those conducted here, it would be expected that there would be a significant difference between a EP copolymer and a EB copolymer. Yet, they appear to be very similar in their behavior, and both are very different from the octene copolymers.

There are two ways in which a branch affects the crystallization process. One is based on the mechanism of crystal growth, and the other is based on the location of the branch after crystallization. In crystal growth, the branch will hinder the attachment of the chains to the crystal surface or nucleus, due to the need for it to be rejected from the crystal whenever a molecular section containing the branch attempts to add to the crystal. Long linear branches might be expected to be more effective in this respect, because they could be more efficently attached to the underlying polymer chains. Hence, it is possible that such an effect could contribute to the more effective depression of the crystallization peak. A random copolymer that contains totally excluded comonomer units would be expected to have lost all its crystallinity by about 7% mol content of comonomers, simply on the basis of the minimum lamellar thickness that can be formed. This is known to be the case for isomerized *cis*-polyisoprene.[14] The highest content EP copolymer clearly exceeds this limit, confirming that some proportion of the methyl groups are incorporated into the crystal. Incorporation of the methyl branches is expected to lower the heat of fusion and the melting point; however, it should also increase the lamellar thickness. So, if only exclusion of the hexyl branches occurs, then the lamellar thickness of EO copolymers would be reduced, resulting in larger melting and crystallization temperature depressions compared to those of EB and EP.

The location of the branch after crystallization can affect the T_m and T_c. A branch group can be inside or outside the crystalline phase. As mentioned earlier, in the inclusion case, it is possible for these branches to change the conformation of neighboring chains in order to produce the space for inclusion of the branch defect. The crystallography will be distorted from ideal. As the size of the defect increases, the distortion will be increased. This study did not concentrate on what parts of the branch or what types of the defect are in the crystalline phase and how a long linear branch might be able to enter the crystal. If branches are long enough to crystallize, the defects are the branch end and the branch point, not the entire branch. On the other hand, if the branches are not long enough to crystallize, they can be expelled from the crystalline phase. Although this critical branch length is not known, both the inclusion of the defect and the exclusion of the defect from the crystalline phase cause the depression of T_m, T_c, and ΔH_f. In the case of exclusion to the folds, it is clear that a hexyl branch would cause much more crowding in the surfaces, resulting in highly stressed fold surfaces, unless the interfacial zone increases in thickness, thereby reducing the surface stress. The surface free energy resulting from this stress will also enter into the equations for melting and crystallization, resulting in melting point changes. The inclusion and exclusion possibilities are a complex subject requiring considerably more careful experimentation. Such studies have been conducted,[13] and will be discussed in more detail in later articles.

Comparison of Melting Behavior of Homogeneous and Heterogeneous EO Copolymers

So far, thermal analysis of homogeneous EO copolymers has been discussed based on the analysis of DSC data. The homogeneous EO copolymers showed a linear relationship between melting temperature and branch content (p_B) without a significant molecular weight effect (Fig. 6). In other words, T_m decreases almost linearly with defect content for the homogeneous EO copoly-

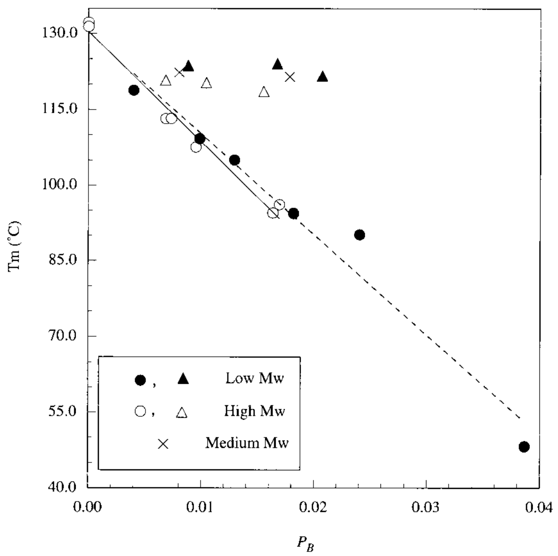


Figure 14 Peak melting temperatures of the homogeneous and heterogeneous EO copolymers cooled fast as a function of branch content.

mers. The values extrapolated to zero defect content coincide with T_ms of the linear polyethylenes.

It is informative to compare the melting points of the heterogeneous EO (HTEO) copolymer with that of the homogeneous EO (HMEO) copolymer to know whether both LLDPEs produced using different catalyst systems have identical thermal properties. For this purpose, the HTEO copolymers with $\bar{M}_r/\bar{M}_w$ 2.0, which had been produced by Dow Chemical using crossfractionation,[15,16] were used. This comparison is represented in Figure 14. The HTEO copolymers do not show the clear linear relationship between T_m vs. P_B found in the case of the HMEO copolymers. Most obvious is the surprise that the melting points of the HTEO copolymer fractions are depressed very little compared to the HMEO copolymers. The difference of T_m between HMEO and HTEO copolymers increases with increasing defect content. For instance, the difference of T_m between both systems is about 25°C at around 2.0% of defect content. Why should this be? The T_m of HTEO copolymer with about 2.0% defect content is even higher than that of H7-O, with defect content of 0.7%.

The HTEO copolymers obtained from the heterogeneous catalyst (i.e., classical Ziegler-Natta catalyst) contain heterogeneous inter- and intramolecular distributions of branches, while the HMEO copolymers from the homogeneous catalyst are believed to have a random distribution of branches along the main chain, and that there is no variation in distribution with molecular weight. The results suggest that there is a nonrandom distribution of branches in individual molecules of the ZN copolymer. It is clear that this nonrandomness results in very long sequences of polymethylenes; so long, in fact, that the depressions of melting point are somewhat less than was observed for the homogeneous copolymer containing only four branches per 1,000 C atoms, even though the average branch content was as high as 22 branches per 1,000 C atoms. Similar major differences have been found in the linear spherulitic growth kinetics and will be reported in a separate publication.[17] The copolymer molecules from ZN catalysts must, therefore, be highly nonrandom. The randomness could take various forms, perhaps related to changes in the character of the catalysts sites with time. Because the copolymer molecules are believed to be polymerized at the surfaces of slurry particles, it seems unlikely that the nonrandomness would be caused by diffusional problems between the monomers. This, in turn, would make it unlikely that the nonrandomness is throughout the molecule. Perhaps the long polymethylene sequences are to be found at one end of the chain due to change of catalyst behavior with time. Regardless of the details of the nonrandomness, which cannot be determined experimentally using spectroscopic methods, it is clear that the differences between the copolymer molecules resulting from metallocene and Zeigler-Natta catalysts go well beyond the simple difference between single-site and multiple-site catalysts. Crystallization and melting behavior are, however, both very sensitive to changes in the spatial distribution of short chain branches and, perhaps, at the present time, constitute the best way of monitoring them.

In conclusion, one of the most important factors governing T_m of olefin-type copolymers is the branch distribution in copolymer systems rather than the branch content. In other words, the crystallization and melting behavior can only be understood in terms of the polymethylene sequence distribution.

CONCLUSIONS

As branch content increases in homogeneous ethylene copolymers, nonisothermal, and isothermal crystallization rates, melting temperatures and heat of fusion (or degree of crystallinity) are decreased. This behavior is explained on the bases of the decrease of lamellar thickness and formation of defective crystal structures, controlled by the role of any particular branch as a defect.

Annealing phenomena were observed in all the LLDPEs including even a highly branched EO copolymer (L39-O) and EP copolymer (L93-P).

There was some evidence for unevenness of branch distribution on the main chain. The endotherm peak around 40–50°C was believed to be due to the molecular segregation by heterogeneity of branch distribution rather than molecular weight.

There is a branch length effect on melting point depression. Long branches cause more melting and crystallization temperature depression than short chain branches. Melting temperature depressions of EO random copolymers with long branches (hexyl) were larger than those of EB and EP random copolymers with ethyl and methyl branches, respectively.

Defect distribution in copolymer systems is the most important factor governing the melting point of olefin type copolymers, and is more important than simply the branch content. The homogeneous random copolymers always exhibit lower melting points than heterogeneous copolymer fractions of equivalent branch content and molecular weight.

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