Phase Structure of Random Ethylene Copolymers: A Study of Counit Content and Molecular Weight as Independent Variables

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ABSTRACT: The phase structure of a series of random ethylene copolymers with 1-butene, 1-hexene, or 1-octene as comonomers, which have narrow molecular weight and composition distributions, has been studied by treating both the counit content and molecular weight as independent variables. Essentially no difference in behavior has been found between the three types of branches in most of the properties analyzed. However, the interfacial content of the ethylene–octene copolymers showed consistently higher values than the others. The interphase is shown to be a relatively important component of the copolymeric lamellae, with thicknesses varying from 10 to ≈45 Å. The melting temperatures and the levels of crystallinity of these copolymers adhere to the reference curves established for the model hydrogenated polybutadienes and random copolymers. It is found to be very important to separate and distinguish the influence of molecular weight and of copolymer composition on the phase structure.

Introduction

In a recent paper the influence of molecular weight on the melting temperature and phase structure was reported for a series of hydrogenated polybutadienes that had about 2.3 mol % branch points.[1] These materials are chemically identical to ethylene–butene copolymers and are characterized by narrow molecular weight and composition distributions, with the ethyl branches being randomly distributed along the main chain.[2,3] They can, therefore, be considered as model random ethylene copolymers. However, one of the limitations associated with these model copolymers is their relatively high concentration of branch units that are available for study. The hydrogenated polybutadienes contain about 2 or more ethyl branches per 100 carbons in the main chain. Thus, the study of properties of lower branch content molecules needs to be relegated to other types of ethylene copolymers. It was found in the previous work that the molecular weight has a drastic effect on many of the phase properties of the polybutadienes, paralleling those of linear polyethylene.[1] For example, the variation of the crystalline and liquidlike content with molecular weight follows an identical trend as the linear polymer. Similarly, the lamellar morphology deteriorates with increasing molecular weight for both the homopolymers and copolymers. On the other hand, other properties, such as the melting temperature of rapidly crystallized samples or the interfacial content, follow a unique pattern with molecular weight for the model copolymers. It was thought that the variation of properties with molecular weight that was observed with the hydrogenated polybutadienes could be a general phenomenon of random ethylene copolymers since three ethylene–hexenes of lower counit content, studied at that time, showed similar trends.[1]

In the present work we examine the importance of the molecular weight as an independent variable when establishing the general properties of ethylene copolymers. We also extend the range of counit contents studied. The influence of molecular weight in copolymer studies of this type has not been universally recognized and has been quite often neglected.[3-6] To pursue our objective, selected thermodynamic and phase structural properties have been studied for different series of random ethylene–1-alkene copolymers. The properties can then be compared to those previously obtained for the model hydrogenated polybutadienes to assess the influence of both copolymer composition and molecular weight. Series of ethylene–1-butene, ethylene–1-hexene, and ethylene–1-octene copolymers having a wide range in counit content and molecular weights were studied. These copolymers have most probably molecular weight and narrow composition distributions. The data obtained significantly augments those previously obtained on similarly constituted copolymers.[1] From the more extensive studies reported here the influence of counit content, molecular weight, and branch type on a given property could be properly assessed.

Experimental Section

Materials. Four different types of random ethylene copolymers have been studied in this work. The ethylene–1-butene, ethylene–1-hexene, and ethylene–1-octene copolymers were synthesized following procedures that are known to produce materials having the most probable molecular weight distribution, with essentially a random distribution of ethyl, butyl, or hexyl branches along the main chain and narrow composition distributions.[8,9] The characterization of the copolymers is given in Table I. Two series of samples are available for each type of copolymer. In one set the molecular weight is fixed at approximately 10^5 and the branching content varies between 0.5 and about 5 branches per 100 carbons in the main chain. In the other set the counit content is kept constant and the molecular weight varied between approximately 2×10^4 and 5×10^5.

The fourth type of copolymer is hydrogenated polybutadiene (HPBD). These samples were kindly supplied to us by Dr. W. W. Graessley[10] and serve as model reference materials. Some of their properties have been previously reported from our laboratory.[1,11-14] Two series of HPBD's are also available. One has a fixed molecular weight of approximately 10^5 and between 2 and 7 ethyl branches per 100 carbons in the main chain. In the other series the molecular weight varies between 5×10^3 and 4.6×10^5 but the branching content is fixed at about 2.3 mol %. The characterization of both series is also included in Table I. With the availability of this variety of samples and molecular constitution, three important variables, the type of branch, the concentration of the branch, and the molecular weight, can be analyzed independently.

Techniques. All the ethylene copolymers were subjected to the same crystallization treatment. Films about 0.5 mm thick were prepared by melting the samples in a Carver press at

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Table I. General Molecular Characteristics of Ethylene Copolymers[a]

copolymer	M_w	M_w/M_n	mol % branch points
ethylene–1-butene	90 000 ± 30 000	2.0 ± 0.2	0.4 < mol % ethyl < 2.8
	108 000 < M_w < 550 000	2.0 ± 0.2	0.4 mol % ethyl br.
	36 000 < M_w < 195 000	2.0 ± 0.2	1.2 mol % ethyl br.
	99 000 < M_w < 200 000	2.0 ± 0.2	2.0 mol % ethyl br.
ethylene–1-hexene	90 000 ± 30 000	2.0 ± 0.2	0.6 < mol % butyl < 4.0
	23 000 < M_w < 307 000	2.0 ± 0.2	1.1 mol % butyl br.
	18 900 < M_w < 240 000	2.0 ± 0.2	1.4 mol % butyl br.
	6 500 < M_w < 121 000	2.0 ± 0.2	1.7 mol % butyl br.
	28 000 < M_w < 280 000	2.0 ± 0.2	2.6 mol % butyl br.
ethylene–1-octene	90 000 ± 30 000	2.0 ± 0.2	0.7 < mol % hexyl < 4.0
	57 000 < M_w 267 000	2.0 ± 0.2	0.8 mol % hexyl br.
	38 300 < M_w < 67 000	2.0 ± 0.2	1.4 mol % hexyl br.
	28 000 < M_w < 99 000	2.0 ± 0.2	2.0 mol % hexyl br.
hydrogenated polybutadiene	100 000 ± 30 000	1.2 ± 0.1	2.2 < mol % ethyl br. < 7.3
	5 000 < M_w < 460 000	1.2 ± 0.1	2.3 mol % ethyl br.

[a] The range of branching content at fixed molecular weight and of molecular weight for a fixed branching content is indicated.

temperatures between 120 and 150 °C and rapidly quenching to −78 °C in a mixture of isopropyl alcohol and dry ice. Different pieces were cut from a given film for the density, calorimetric, and spectroscopic studies.

The branching content was determined using well-developed ^{13}C NMR techniques.[15–19]

Melting temperatures were obtained from the peak melting endotherms using a Perkin-Elmer DSC 2B differential scanning calorimeter at a heating rate of 10 K/min. The degree of crystallinity was determined from the heat of fusion of the endotherms, using the heat of fusion of indium (6.8 cal/g) as standard. The degree of crystallinity was also determined from the analysis of the internal mode region of the Raman spectra. This method was originally developed by Strobl and Hagedorn[20] and further implemented in other works.[21–23] The fractions of the liquidlike and interfacial regions were also determined from the same region of the Raman spectrum in a manner previously described in detail.[21–23] Densities were also measured in most of the copolymers at room temperature in a triethylene glycol/2-propanol density gradient column calibrated with standard glass floats. Degrees of crystallinity $(1 - \lambda)_d$ were calculated from the measured densities using the relation given by Chiang and Flory.[24]

The core crystallite thickness was obtained from the longitudinal acoustic mode (LAM) of the low-frequency region of the Raman spectrum. It was identified with the most probable ordered sequence length in the thickness distribution. The relation between frequency and ordered sequence length proposed by Schaufele and Shimanouchi was applied to all the copolymers analyzed.[25] This relation is given as:

$$\Delta\nu\ (\mathrm{cm}^{-1}) = \frac{m}{2cL}\left(\frac{E}{\rho}\right)^{1/2} \qquad (1)$$

where ν is the observed frequency, m the mode order (1, 3, 5, ...), c the velocity of light, L the ordered sequence length, ρ the density of the crystalline phase (1.00 g/cm^3), and E Young's modulus in the chain direction. The value of E was taken as 2.9×10^{12} dyn/cm^2 for polyethylene.[26,27] The Raman spectra were recorded using an incident radiation of 514.5 nm of a coherent INNOVA argon ion laser Model 90 and a SPEX 1403 double monochromator spectrometer equipped with two 2400 lines/mm planar holographic gratings. The plasma lines were removed from the laser beam using a SPEX 1460 Lasermate premonochromator.

Results and Discussion

The melting temperatures of the ethylene copolymers having a weight-average molecular weight of 90 000 ± 30 000 are plotted against the mole percent of branch points in Figure 1. The copolymers with ethyl, butyl, or hexyl branches follow the same relation as the model hydrogenated polybutadienes. Within the experimental error, they all fall on the reference line (continuous, solid curve) that was previously reported for random copolymers.[9,12] It is noteworthy that the melting temperatures of random ethylene–vinyl acetate copolymers also fall on the same curve.[12]

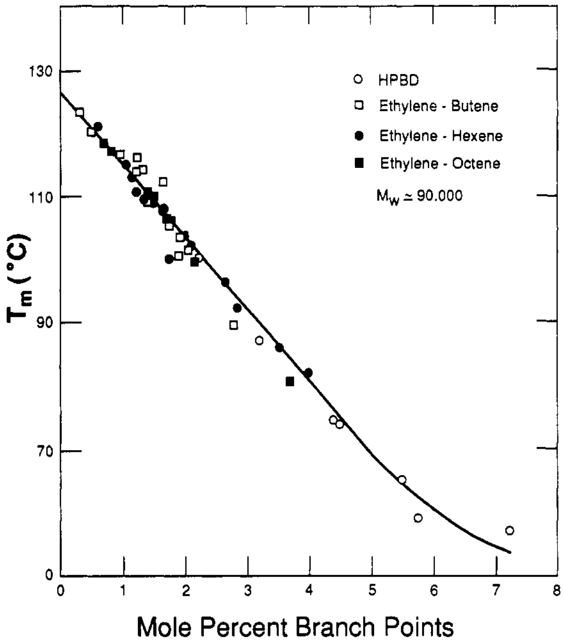

Figure 1. Melting temperatures T_m of rapidly crystallized ethylene copolymers as determined by differential scanning calorimetry. HPBD: hydrogenated polybutadiene. M_w = 90 000 ± 30 000.

It was previously reported that some copolymers obtained with the so-called heterogeneous catalyst gave melting temperatures that were significantly higher than those of the model hydrogenated polybutadienes, even after cross-fractionation.[12] This result was a definite indication of differences in the sequence distribution of these copolymers from the ideal random behavior of the other copolymer fractions that were analyzed at that time.[12] In fact, equilibrium theory predicts that even small differences in the sequence propagation probability, p, of a crystallizing unit will alter the melting temperature in a significant manner.[28] For example, changing p from 0.9800 to 0.9875 alters the melting temperature of the copolymer by 5 °C.[12,28] Melting point differences of this order were also observed by Springer *et al.* for similarly constituted ethylene–butene fractions.[29,30] In their report the compositions of the HPBD's, as well as the other copolymers, were incorrectly extracted from Figures 3 and 4 of ref 12. As a consequence, an anomalous compilation of melting temperatures was given.[29] When this misinterpretation of the data was corrected,[30] it was found that the melting temperatures of the ethylene–butene fractions studied by Springer *et al.* agreed with the nonrandom behavior of the ethylene–butene copolymers that were originally reported.

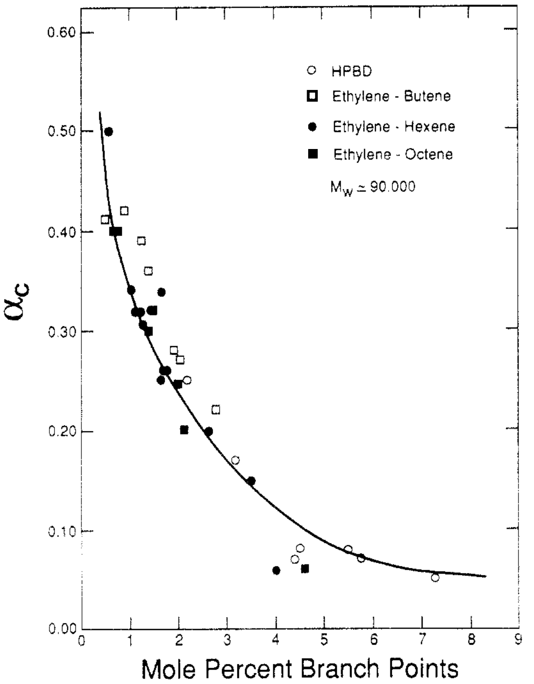

Figure 2. Plot of degree of crystallinity calculated from Raman internal modes, α_c, against mole percent branch points. Solid line from ref 9. HPBD: hydrogenated polybutadiene.

The data in Figure 1 do not show any detectable deviation in melting temperatures between the ethyl side groups and the other branch types. Because of the large size variation in these side groups, the results of Figure 1 indicate that the branches do not enter the lattice to any meaningful extent. A similar conclusion has been reached from other thermodynamic studies,[12,31] selective oxidation studies,[32,33] ^{13}C NMR,[34,35] and WAXS studies.[36-39] Thus, this set of copolymers satisfy the *a priori* requirement of Flory's equilibrium theory that the crystalline phase remains pure.[28,40] In contrast studies have also demonstrated that relatively small side groups, such as methyl, chlorine, and oxygen are included in the crystalline lattice.[31,38,41] Larger size branches are excluded from the lattice. According to equilibrium theory, increasing the counit content in such constituted copolymers will reduce the melting temperature and level of crystallinity. Kinetic restraints will also substantially contribute to this reduction.[13] The number of sequences that crystallize will be reduced along with the crystallite thickness. Consequently we observe that, in this molecular weight range and under the crystallization conditions specified, the melting temperature decreases from 126 °C for linear polyethylenes to approximately 60 °C for polymers having 6 mol % branch points.

Accompanying the reduction of melting temperature with branching content, the level of crystallinity also decreases very rapidly as is illustrated in Figure 2. In this figure, the level of crystallinity, α_c, calculated from the Raman spectra is plotted against the branching content for copolymers of approximately the same molecular weight and containing between about 0.5 and 7 mol % branch points. The solid curve in the figure has been reproduced from previous work.[9] There are no significant differences between the three types of branches or between the copolymers and the hydrogenated polybutadienes. The data fall on the same curve previously given for other random ethylene copolymers.[12] As found in other works,[11,12] the density-determined level of crystallinity depends on the counit content in a manner very similar to that found in Figure 2 for α_c. The density-determined values are, however, between 10 and 15% greater than those obtained from the enthalpy of fusion or α_c. This general observation has been attributed to a contribution from the interphase to the density but not to the enthalpy of fusion or α_c.[12,21]

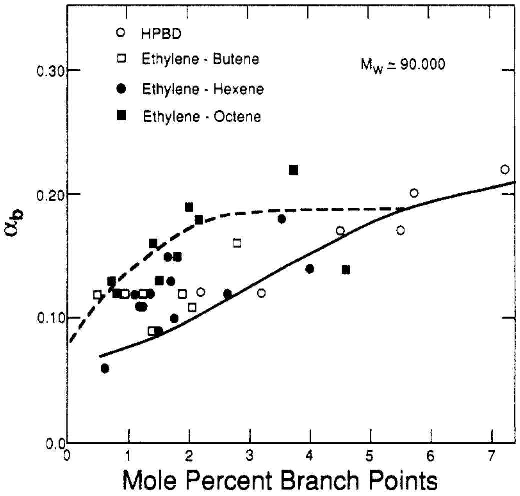

Figure 3. Plot of the interfacial content calculated from Raman internal modes, α_b, against mole percent branch points of the copolymers indicated. HPBD: hydrogenated polybutadiene.

It is also of interest to analyze the variation of the interfacial content with increasing comonomer content, at a fixed molecular weight. The results are given in Figure 3. The method used to determine these interfacial values depends on the accuracy of α_c and α_a (the liquidlike content). Because α_b is calculated from the difference between unity and the sum of α_c and α_a, the errors are additive.[21] This leads to an uncertainty of between 5 and 10% for α_b. Therefore, there is a relatively high dispersion of the data in the figure. Despite this difficulty, two different trends can be distinguished. One is that the interfacial content initially increases with increasing counit content and levels off at a value of about 20% for the higher branching contents. The other is the strong indication that before this leveling off occurs the ethylene–octene copolymers have a higher interfacial content than the other copolymers at comparable compositions. The solid line in Figure 3 has been drawn following the data for the model hydrogenated polybutadienes. The dashed curve represents the data for ethylene–octene copolymers. A great deal of data for the ethylene–butene and ethylene–hexene copolymers lie between the two curves. The increasing interfacial content with the number of branches parallels a preferential accumulation of the branches which are excluded on the crystallite surface. As was pointed out earlier, the branches of interest are excluded from the crystalline phase. The differences observed between the ethylene–octene and the other copolymers studied are probably due to steric differences of the hexyl branches that accumulate at the interphase. When the branching content becomes high, about 3 mol %, the lamellar crystallite habit is lost and very small crystallites are formed under the rapid crystallization conditions employed here.[1,14] In this situation the interfacial content reaches a saturated value.

Computer simulations by Mattice and co-workers[42-44] have indicated that short-chain branches (of unspecified length) are not randomly distributed in the noncrystalline region. Rather they occur preferentially in the anisotropic interfacial region. This segregation caused a growth of the interfacial region at the expense of the isotropic liquidlike region. The extent of the interfacial region is sensitive to the nature of the short-range intramolecular interactions. These theoretical expectations are in qualitative accord with the experimental findings reported here.

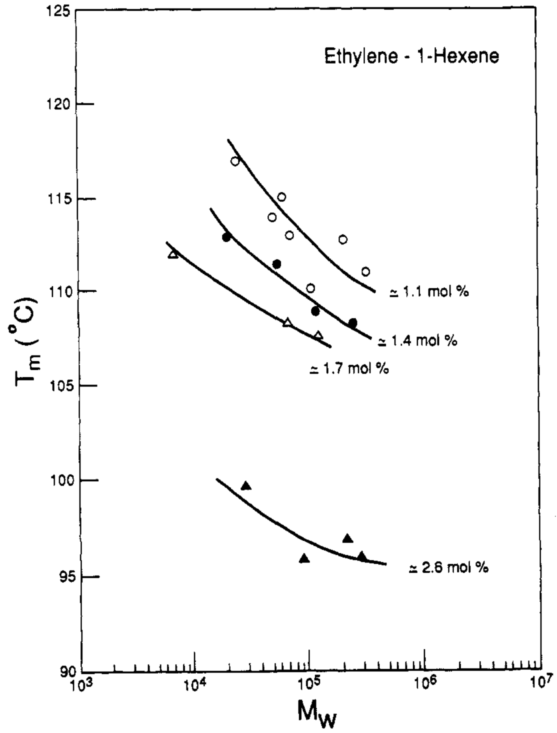

Figure 4. Melting temperatures plotted against molecular weight for different series of ethylene–1-hexene copolymers. Indicated in the figure is the fixed branching content of each series.

More specific identification of the length of the branch is needed for further quantitative comparison. In another type of calculation the number of entangled loops and of tie chains has been reported to increase with the incorporation of a small number of branches in a linear chain.[45–47] The implication of these results to the phase structure is yet to be explored.

Up to now we have considered changes in properties and phase structure as a function of copolymer composition and branch type at essentially a fixed molecular weight. We have previously reported that there is a significant molecular weight dependence of the melting temperature and degree of crystallinity of a series of hydrogenated polybutadienes having approximately 2.3 mol % branches and three ethylene–hexene copolymers with 1.45 mol % branch points.[1] In the present work the study of the influence of molecular weight has been extended to include different types of branches and a wider range of branching content. As an example of the new results, the melting temperatures of different sets of ethylene–1-hexene copolymers, having branch points contents between 1.1 and 2.6 mol % are plotted against molecular weight in Figure 4. For each of these ethylene–hexene series the observed melting temperatures decrease with increasing molecular weight in analogy to the previous result for the hydrogenated polybutadienes.

The influence of molecular weight on the melting temperature is not specific to a given copolymer type. It is a general phenomenon as is illustrated in Figure 5. Here, not only the data for the ethylene–hexenes but the data for the ethylene–butenes and ethylene–octenes are given. Also, the model hydrogenated polybutadienes, previously studied, and linear polyethylene fractions are included for comparison. The data generate a family of curves, each dependent on the counit content but independent of the chemical nature of the counit. The rapidly crystallized linear polyethylene shows a very small variation of the melting temperature with increasing molecular weight. This is a consequence of the fact that the crystallite thickness is independent of molecular weight under these crystallization conditions.[48] The influence of molecular weight on the melting temperature is more accentuated in the copolymers, especially in the series with the lowest branching content (1.1 mol % and lower) and in the range of molecular weight between 20 000 and 300 000. For example, in this molecular weight range, the melting temperatures of the set of copolymers with approximately 1.1 mol % of branch points differ by 7 °C. This difference is almost reduced by half for the series with 2.6 mol % branches. Thus, in a given range of molecular weight, the less branched copolymers form crystallites that are thicker and change over a larger interval than the highly branched copolymers. A similar dependence of the melting temperature with molecular weight was also reported for a series of hydrogenated polybutadienes[49] and for fractions of a high-pressure polymerized polyethylene.[50–53] The melting temperatures level off above a molecular weight of 100 000 for the higher counit copolymer (2.3 and 2.6 mol %). The implication of these results is that if the molecular weight dependence is only studied in this molecular weight range, the general decrease of T_m with M_w would not be observed[29] and incorrect conclusions would be made.

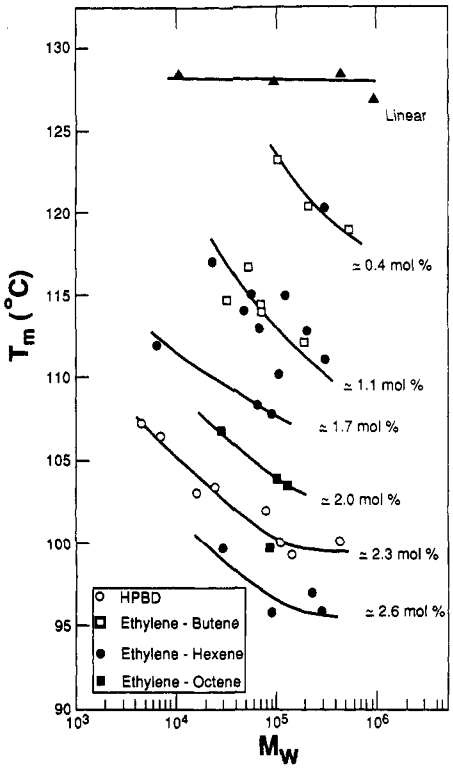

Figure 5. Melting temperatures plotted against molecular weight for series of rapidly crystallized ethylene copolymers having a fixed branching content. The type of copolymer and the branching content, given as the number of branches per 100 carbons, are indicated in the figure. (▲) Rapidly crystallized linear polyethylene fractions.

The possibility that a variation in the sequence distribution with molecular weight explains the melting temperature dependence can be ruled out. ^{13}C NMR analysis has shown that the copolymers possess a random sequence distribution that is independent of molecular weight.[1] In the study of the hydrogenated polybutadienes the reduction of the melting temperature with molecular weight was shown to be a consequence of the formation of smaller crystallite sizes. It was interpreted as a result of an increased entanglement density which is reflected in slower crystallization rates.[13]

The degree of crystallinity, whether determined by either density, heat of fusion, or Raman internal modes, shows a similar dependence with molecular weight. It decreases

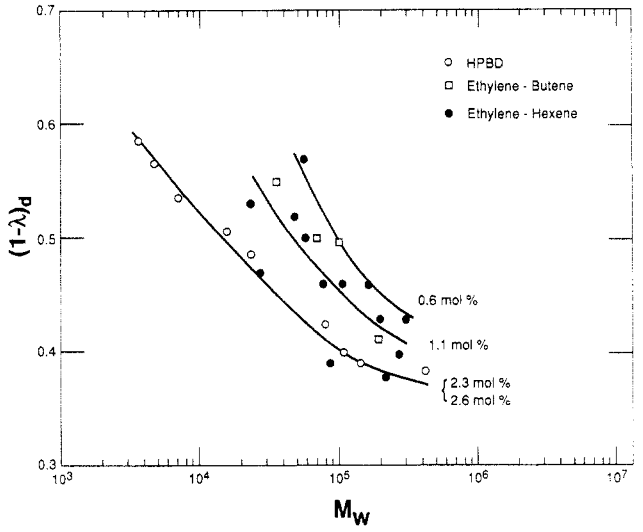

Figure 6. Plot of degree of crystallinity calculated from density measurements $(1 - \lambda)_d$ against molecular weight for different series of ethylene copolymers having a fixed branching content. The copolymers and the branching content are indicated in the figure.

with increasing molecular weight following a trend similar to the variation observed with linear polyethylene fractions. This point is illustrated in Figure 6 for the crystallinity level determined from density measurements for some typical copolymers. A family of curves is generated, depending on counit content. Compared to the crystallinity of linear polyethylene fractions,[1,54] determined by density, a reduction in the level of crystallinity by 20% is observed with the addition of only 0.6 branches per 100 linear carbons. If the number of branches is increased to about 2.5%, the crystallinity level is reduced by close to 40%. No systematic differences in $(1 - \lambda)_d$ are found between the different types of branches.

The change in the interfacial and liquidlike contents with molecular weight, for each type of copolymer, follows the trend previously found in hydrogenated polybutadienes.[1] The liquidlike content increases rapidly with increasing molecular weight at the same time that the core crystalline content decreases.[1] No variation of the interfacial content was observed for the hydrogenated polybutadiene series, with 2.3 mol % of branches, for molecular weights up to ≈500 000. An example of this behavior from the present work is given in Figure 7 for two sets of ethylene–hexenes (1.1 and 2.6 mol % butyl branches) and one ethylene–octene series with 0.8 mol % branches. Up to a molecular weight of about 100 000 all the copolymers follow the behavior found for the hydrogenated polybutadienes, which is indicated by the dashed lines in the figure. However, the highest molecular weight ethylene–hexenes in each series show significantly higher interfacial contents at the expense of a reduction in the amorphous content. The reason for this difference must reside in the character of the lamellae in this molecular weight range coupled with experimental uncertainties intrinsic to the method of measurement. For example, the core level of crystallinity, α_c, of the ethylene–hexene of M_w = 270 000, (2.6 mol % butyl branches) is 14%. Its interfacial content and liquidlike region are 19% and 67%, respectively. In this situation the dissipation of order requires an amount of material that is greater than that of the pure orthorhombic content. The question is raised about the conformation of the chains in this interfacial region. Since in this case we are dealing with small and poorly defined crystallites with large interphases, the experimental methods used to quantify the phase structure, usually based on "ideal lamellae" models, might not apply any longer.

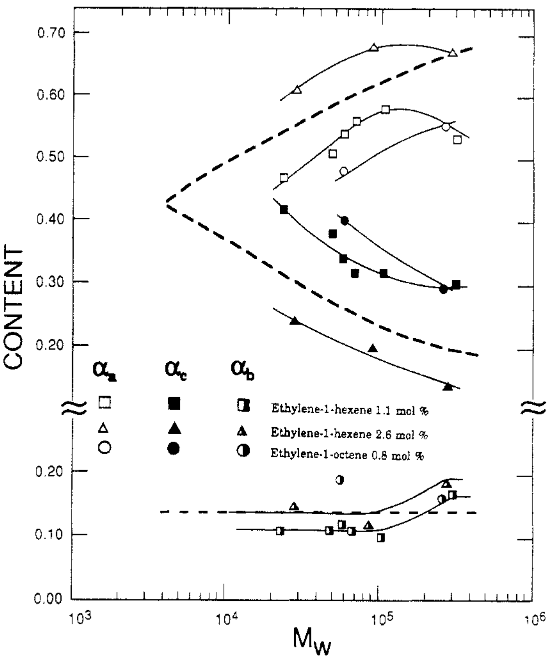

Figure 7. Relative amounts of liquidlike (α_a), crystalline (α_c), and interfacial (α_b) contents as a function of molecular weight for the following series of ethylene copolymers:[1] (- - -) hydrogenated polybutadienes with 2.3 mol % branch units.

When discussing the variation of the interfacial content with increasing counit content of the copolymers with M_w ≈ 90 000 systematic higher values of the ethylene–octene copolymers were observed. This point is again illustrated in Figure 7. The α_b values for the ethylene–octene copolymers are much higher than expected for their counit content. They are comparable to those for the ethylene–hexene copolymers of much higher branch content.

The invariance of the interfacial content with molecular weight (at least up to $M_w = 10^5$) for the copolymers is different from the behavior of linear polyethylenes. For the linear polymer, the interfacial content increases with molecular weight.[55] This change has been attributed to an increased number of entanglements on the crystallite surface.[1] In the copolymers the predominant effect appears to be the accumulation of the branches on the surface that in turn overcomes the entanglement effect. This invariance is consistent with the theoretical simulations of Mattice *et al.* which showed this high percentage of short branches in the layers close to the surface.[43]

The thicknesses of the primary structural regions can be calculated from the Raman spectra. We take as a model a set of lamellar stacks in which the fractions of crystalline, interfacial, and liquidlike regions are given by:

$$\alpha_c = \frac{L_c}{(L_a + 2L_b + L_c)} \frac{\rho_c}{\rho_t} \qquad (2)$$

$$\alpha_b = \frac{L_b}{(L_a + 2L_b + L_c)} \frac{\rho_b}{\rho_t} \qquad (3)$$

$$\alpha_a = \frac{L_a}{(L_a + 2L_b + L_c)} \frac{\rho_a}{\rho_t} \qquad (4)$$

Here L_a, L_b, and L_c are the thicknesses of the liquidlike, interfacial, and crystalline regions, respectively. The experimentally measured density of the specimen is ρ_t, ρ_c = 1.00 g/cm³ is the density of the crystal, and ρ_a = 0.852

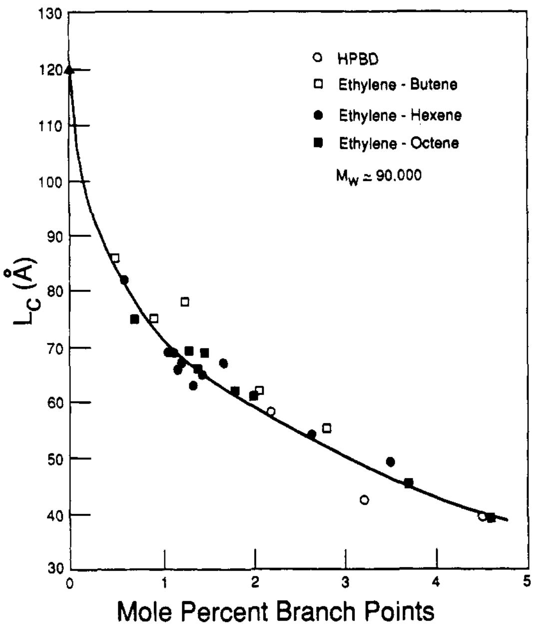

Figure 8. Plot of the core crystallite thickness, L_c, against mole percent branch points of the copolymers indicated. HPBD: hydrogenated polybutadiene.

g/cm^3 is the density of the liquidlike region. L_c can be identified with the most probable ordered sequence length calculated from the low-frequency LAM of the Raman spectrum and corrected for the tilt angle.[56]

The core crystallite thickness, obtained in this manner, is plotted against the branching content in Figure 8 for copolymers having a molecular weight of approximately 100 000. The core crystallite thickness decreases very rapidly from 120 Å for a linear polyethylene of the same molecular weight, crystallized under the same conditions, to 65 Å for the copolymers with about 1.5 mol % branch points. With a further increase of the counit content the core crystallite thickness decreases further. Only very small crystals, calculated to be about 40 Å, are formed with samples having about 4 mol % branch points. All the data in Figure 8 fall on the same curve. No systematic deviations are found for any given type of branch. From the point of view of the core crystallite thickness, the ethylene–butene, ethylene–hexene, and ethylene–octene copolymers represent the same type of crystallite which is also the same as those of the hydrogenated polybutadienes.

It was pointed out previously that in the region of the high counit content, where the true core crystallite thicknesses are lower than about 60 Å, there are problems in interpreting the LAM spectra when using the simplified Shimanouchi relation.[1] For example, in studying the molecular weight series of hydrogenated polybutadienes of 2.3 mol% branches that were rapidly quenched from the melt, the most probable thickness distribution calculated from the LAM did not change with molecular weight.[1] However, the thickness of the core crystallites, calculated from the long spacing, showed a definite decrease with increasing molecular weight. Electron microscopy measurements confirmed the small-angle X-ray scattering results. When the size of the crystals was greater than about 60–65 Å, the three independent experimental methods agreed with one another. At higher counit content the LAM-determined crystallites were greater than those obtained by the other methods. Thus, the true values of the crystallite thicknesses less than about 60 Å in Figure 8 may in fact be smaller. The resolution of this problem requires a more comprehensive theoretical analysis of the LAM for very small crystallite sizes. Irrespective of the reason and the correction that has to be applied to the LAM values, the different type branches will be affected in the same manner, so that the trend with increasing counit content should be the same.

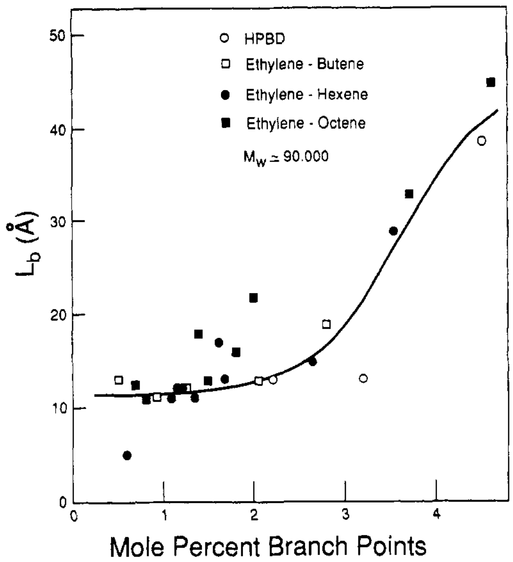

Figure 9. Plot of the interfacial thickness, L_b, against mole percent branch points of the copolymers indicated. HPBD: hydrogenated polybutadiene.

Crystallite thicknesses obtained from stained thin-section electron micrographs have been reported for a series of ethylene–octene fractions.[57] Unfortunately, a distinction could not be made between the molecular weight and composition as indepdnent variables. However, when the low molecular weight fractions (those with the higher counit content) are taken into account, the electron microscopy data follow the patterns of Figure 8 with essentially identical values for the thickness.

The thickness of the interphase, L_b, calculated according to eqs 2–4 is plotted in Figure 9 for the copolymers having a molecular weight of 90 000. The curve drawn in the figure represents an average of the data for the ethylene–butenes, ethylene–hexenes, and hydrogenated polybutadienes. Most of the ethylene–octene data show slightly higher interfacial thicknesses, in agreement with the results described in Figure 3. The calculated interfacial thickness increases very rapidly for branching contents greater than 2 mol %. In this compositional range, L_b increases from 10 Å to about 45 Å. However, this is the concentration range where there is an uncertainty in the L_c values deduced from the LAM spectra. Since this quantity is central to the calculation of L_b, the same uncertainty is introduced. Moreover, in this concentration range the character of the lamellae progressively deteriorates. Eventually lamellae are no longer characteristic of this crystallization mode. Consequently, in this concentration region the model used to calculate L_a or L_b is of limited validity. The interfacial thickness of a linear polyethylene fraction of the same molecular weight, crystallized under the same conditions, was calculated to be about 20 Å.[58] One would expect the copolymers to have larger interfacial thicknesses. However, the interfacial thickness of these copolymers represents a greater percentage relative to the core crystallite thickness. A similar result was obtained with molecular weight fractions of hydrogenated polybutadienes of fixed counit content.[1]

The most probable ordered sequence length of a series of hydrogenated polybutadienes (2.3 mol % branch points) appeared to be constant for molecular weights between 4000 and 500 000. This quantity is directly related to the core crystallite thickness.[1] However, the core crystallite thickness calculated from the small-angle X-ray long period

Table II. Core Crystallite Thickness Obtained from Raman LAM as a Function of Molecular Weight for Different Series of Ethylene Copolymers

M_w	M_w/M_n	mol % branches	L_c (Å)
	Ethylene-1-Butene		
108 000	≈2	0.4	86
211 000	≈2	0.4	82
550 000	≈2	0.4	81
	Ethylene-1-Hexene		
23 000	≈2	1.07	68
48 800	1.9	1.21	67
58 000	2.4	1.08	69
68 000	2.1	1.14	69
104 500	2.4	1.21	67
201 000	≈2	1.10	
307 000	2.15	0.97	64
18 900	2.4	1.43	65
54 000	≈2	1.4	67
112 000	≈2	1.48	≈65
240 000	2.2	1.47	65
6 500	2.9	1.74	
69 400	2.1	1.68	67
121 000	≈2	1.60	67
28 000	≈2	2.60	61
88 000	2.0	2.64	54
223 000	2.2	2.65	50
280 000	≈2	2.7	49
	Ethylene-1-Octene		
57 000	≈2	0.8	69
267 000	≈2	0.8	72
38 300	1.9	1.4	69
67 000	2.3	1.4	66

and corrected by the core crystallinity level decreased rapidly with increasing molecular weight in agreement with the results obtained from electron microscopy.[1] As was pointed out earlier, the theoretical difficulty in interpreting the LAM results for very small crystallite sizes was discussed in this publication.[1] In the present work LAM's have been obtained for the different series of copolymers that have a fixed counit content but varying molecular weight. Table II summarizes these results. With the exception of the set of ethylene-hexenes having 2.6 mol % butyl branches, we find that for each of the series there is essentially no variation in L_c with increasing molecular weight. These results are in accord with the results obtained in hydrogenated polybutadienes.[1] Since it was indicated that the values for L_c obtained from the LAM are not reliable when the true core thickness is less than about 60 Å,[1] we can assume that a similar situation holds for the ethylene copolymers studied here (Table II). Consequently, it is expected that the true crystallite thicknesses of these copolymers, of a given composition, also decrease with molecular weight. The results for the ethylene-hexene series having the highest counit are different in that the L_c values calculated from the LAM's decrease with molecular weight.

Scanning electron micrographs were also obtained for a series of quenched ethylene-octene copolymers having a fixed molecular weight of about 90 000 and a hexyl branching content ranging from 0.7 to 4.6 mol %.[59] The initial lamellar morphology was found to deteriorate with increasing branching content. Lamellae were not observed in the copolymer with 4.6 mol % branches although its crystallinity level was ≃8%. We can conclude that the lamellar structure of quenched random ethylene copolymers with a M_w of approximately 90 000 is lost at a branching content between 3 and 4 mol %. If the branching content is fixed and the molecular weight varied, previous studies showed that lamellar stacks are only observed for relatively low molecular weights in the rapidly crystallized specimens.[1]

Slower crystallization conditions expand the molecular weight range where lamellaelike crystals are still observed. However, the long straight lamellae characteristic of low molecular weight fractions, ≃7000, become short and highly segmented for $M > 100\,000$.[60]

Summary

In summary, the experimental work that has been reported demonstrates that there is no difference between branch types with respect to thermodynamic properties and the phase structure for a series of random ethylene-1-alkene copolymers. The exception to this generalization is in the amount and thickness of the interfacial region. The ethylene-octene copolymers appear to have greater values for these quantities than those containing ethyl or butyl branches at the same composition. This result is in accord with theoretical expectations.[42-44] The experimental results also demonstrate quite clearly that the molecular weight and counit content must be treated as independent variables in assessing these properties.

At a fixed molecular weight there is a significant decrease in melting temperature and crystallinity level with increasing counit content. This type of behavior is expected from equilibrium considerations.[28,40] The rapidly crystallized samples studied here further accentuate this expectation.

At a fixed counit content both melting temperature and crystallization levels decrease with increasing molecular weight, independent of the branch type. This behavior can be attributed to decreasing crystallite thickness with chain length. On the other hand, the interfacial content, which represents a significant portion of the crystallite structure in these type copolymers, is essentially constant with molecular weight. These results are in marked contrast to those found for linear polyethylene. For these polymers a significant increase of the interfacial content was found with increasing molecular weight.

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References and Notes

(1) Alamo, R. G.; Chan, E. K. M.; Mandelkern, L.; Voigt-Martin, I. G. *Macromolecules* **1992**, *25*, 6381.

(2) Rachapudy, H.; Smith, G. G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211.

(3) Krigas, T. M.; Carella, J. M.; Struglinski, M. J.; Crist, B.; Graessley, W. W.; Schilling, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 509.

(4) Heink, M.; Häberle, K. D.; Wilke, W. *Colloid Polym. Sci.* **1991**, *269*, 675.

(5) Bodor, G.; Dalcolmo, H. J.; Schröter, O. *Colloid. Polym. Sci.* **1989**, *267*, 480.

(6) Wilfong, D. L.; Knight, G. W. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 861.

(7) Hosoda, S. *Polym. J.* **1988**, *20*, 383.

(8) Kaminsky, W.; Hähnsen, H.; Kulper, K.; Woldt, R. U.S. Patent 4,542,199, 1985.

(9) Alamo, R. G.; Mandelkern, L. *Macromolecules* **1989**, *22*, 1273.

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(11) Domszy, R. C.; Alamo, R.; Mathieu, P. J. M.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1727.

(12) Alamo, R.; Domszy, R. C.; Mandelkern, L. *J. Phys. Chem.* **1984**, *88*, 6587.

(13) Alamo, R. G.; Mandelkern, L. *Macromolecules* **1991**, *24*, 6480.

(14) Voigt-Martin, I. G.; Alamo, R.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1283.
(15) Randall, J. C. *Rev. Macromol. Chem. Phys.* **1989**, *C29*, 201.
(16) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1975.
(17) Hsieh, E. T.; Randall, J. C. *Macromolecules* **1982**, *15*, 353.
(18) Hsieh, E. T.; Randall, J. C. *Macromolecules* **1982**, *15*, 1402.
(19) Cheng, H. N. *Polym. Commun.* **1984**, *25*, 99.
(20) Strobl, G. R.; Hagedorn, W. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1181.
(21) Glotin, M.; Mandelkern, L. *Colloid Polym. Sci.* **1982**, *260*, 182.
(22) Mandelkern, L.; Peacock, A. *Polym. Bull.* **1986**, *16*, 529.
(23) Failla, M.; Alamo, R. G.; Mandelkern, L. *Polym. Testing* **1992**, *11*, 151.
(24) Chiang, R.; Flory, P. J. *J. Am. Chem. Soc.* **1961**, *83*, 2057.
(25) Schaufele, R. F.; Shimanouchi, T. *J. Chem. Phys.* **1967**, *47*, 3605.
(26) Strobl, R. G.; Eckel, R. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 913.
(27) Synder, R. G.; Alamo, R. G.; Mandelkern, L. *J. Chem. Phys.*, submitted.
(28) Flory, P. J. *Trans. Faraday Soc.* **1955**, *51*, 848.
(29) Springer, H.; Hengse, A.; Hinrichsen, G. *J. Appl. Polym. Sci.* **1990**, *40*, 2173.
(30) Springer, H.; Hengse, A.; Hinrichsen, G. *J. Appl. Polym. Sci.* **1992**, *44*, 189.
(31) Richardson, M. J.; Flory, P. J.; Jackson, J. B. *Polymer* **1963**, *4*, 221.
(32) Shida, M.; Ficker, H. K.; Stone, I. C. *J. Polym. Sci., Polym. Lett.* **1966**, *4*, 347.
(33) Cutler, D. J.; Hendra, P. J.; Cudby, M. A. E.; Willis, H. A. *Polymer* **1977**, *18*, 1005.
(34) Pérez, E.; Vanderhart, D. L.; Crist, B., Jr.; Howard, P. R. *Macromolecules* **1987**, *20*, 78.
(35) Laupetre, F.; Monnerie, L.; Barthelem, L.; Vairon, J. P.; Sauzeau, A.; Roussel, D. *Polym. Bull. (Berlin)* **1986**, *15*, 159.
(36) Bunn, C. W. In *Polyethylene*; Renfew, A., Morgan P., Eds.; Illife: London, Chapter 5.
(37) Vonk, C. G.; Pijpers, A. P. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2517.
(38) Vonk, C. G.; Reynaers, H. *Polym. Commun.* **1990**, *31*, 192.
(39) Howard, P. R.; Crist, B. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2269.
(40) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 223.
(41) Baker, C. H.; Mandelkern, L. *Polymer* **1966**, *7*, 7.
(42) Mathur, S. C.; Mattice, W. L. *Macromolecules* **1988**, *21*, 1354.
(43) Mathur, S. C.; Rodrigues, K.; Mattice, W. L. *Macromolecules* **1989**, *22*, 2781.
(44) Rodrigues, K.; Mathur, S. C.; Mattice, W. L. *Macromolecules* **1990**, *23*, 2484.
(45) Lacher, R. C.; Bryant, J. L.; Howard, L. N.; Sumners, D. W. *Macromolecules* **1986**, *19*, 2639.
(46) Lacher, R. C.; Bryant, J. L.; Howard, L. N. *J. Chem. Phys.* **1986**, *85*, 6147.
(47) Lacher, R. C.; Bryant, J. L. *Macromolecules* **1988**, *21*, 1184.
(48) Mandelkern, L. *Acc. Chem. Res.* **1990**, *23*, 380.
(49) Hser, J. C.; Carr, S. H. *Polym. Eng. Sci.* **1979**, *19*, 436.
(50) Mathot, V. B. F.; Pijpers, M. F. *Polym. Bull.* **1984**, *11*, 297.
(51) Gianotti, G.; Cicuta, A.; Romanini, D. *Polymer* **1980**, *21*, 1087.
(52) Otocka, E. P.; Roe, R. J.; Bair, H. E. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1245.
(53) Hosoi, M.; Naoi, T.; Kawai, T.; Kuriyama, I. *Kobunshi Kagaku* **1972**, *29*, 557.
(54) Mandelkern, L. *J. Phys. Chem.* **1971**, *75*, 3909.
(55) Mandelkern, L. In *Polymer Characterization*; *Advances in Chemistry Series* 227; Craver, C. D., Provder, T., Eds.; American Chemical Society: Washington, DC, 1990.
(56) A tilt angle of 30° has been assumed in all the calculations. If slightly lower or higher values are used, the thicknesses will also change slightly. However, the trend with counit content or molecular weight will be maintained.
(57) Defoor, F.; Groeninckx, G.; Schouterden, P.; Van der Heijden, B. *Polymer* **1992**, *33*, 5186.
(58) Mandelkern, L.; Alamo, R. G.; Kennedy, M. A. *Macromolecules* **1990**, *23*, 4721.
(59) Alamo, R. G.; Mandelkern, L., unpublished results.
(60) Michler, G. H.; Brauer, E. *Acta Polym.* **1983**, *34*, 533.