Crystallization Kinetics of Random Ethylene Copolymers

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ABSTRACT: We report the results of a study of the overall crystallization kinetics of a set of molecular weight and composition fractions of random ethylene copolymers. These copolymers, with ethyl and butyl branches, cover a wide range in molecular weights and co-unit contents. The influence on the crystallization process of molecular weight at a fixed co-unit content, as well as that of co-unit content at a fixed molecular weight, could be assessed by the appropriate choice of fractions. Studying the overall rate of crystallization removes the restriction of having to focus on the growth of well-defined morphological forms, such as spherulites. This latter method severely limits the range of molecular weights and copolymer compositions that can be studied. On the other hand, it has been well-established that the salient features of the crystallization process, such as the temperature coefficient and delineation of regimes, can be obtained with equal reliability by either of the two experimental methods. The most general features of the crystallization process are very similar to those of homopolymers. However, some important exceptions are found. Foremost among these is the fact that the isotherms do not superpose one with the other; deviations from the Avrami relation occur at low levels of crystallinity; and only relatively low levels of crystallinity can be attained after long-time crystallization. These phenomena can be explained by the changing composition of the melt during isothermal crystallization, the restraints that are placed on the concentration of sequences that can participate in steady-state nucleation, and the theoretical limitations on the true equilibrium crystallinity levels. Certain aspects of the crystallization process will be detailed which show that for these purposes a random copolymer behaves as if it were a homopolymer of much higher molecular weight.

Introduction

The properties of crystalline polymers ultimately depend on the structural and morphological features of the system. These characteristics are controlled by the kinetics and mechanisms of crystallization. A variety of studies with different homopolymers have clearly established the important role of molecular weight in controlling the crystallization process and thus the resulting properties.[1-4] Similar factors should also be important in the crystallization of copolymers. In this case, besides molecular weight the influence of co-unit content needs to be assessed. Although there are many reports of the crystallization kinetics of copolymers,[5-8] there is a lack of studies with molecular weight and composition fractions of random copolymers. We report here a detailed study and analysis of the overall crystallization kinetics of molecular weight and composition fractions of random ethylene copolymers. We have chosen for study a set of copolymers where it has been established that the co-units do not enter the crystal lattice.[9-14] With these samples it will be possible to independently assess the influence of molecular weight and copolymer composition on the crystallization kinetics.

There are several distinct advantages in studying the overall rate of crystallization. It has been demonstrated that the temperature coefficient of the crystallization rate and the differentiation of regimes are exactly the same by this method as in the measurement of spherulite growth rates.[2,15,16] However, in studying the crystallization kinetics by calorimetry, or dilatometry, one is not limited in having to observe a specific morphological feature. Stringent restrictions are imposed on the molecular weight range that can be studied with homopolymers[2,16] and copolymers[17] by using microscopic methods. Studies of the overall crystallization kinetics remove these serious limitations.

Experimental Section

Materials. Hydrogenated polybutadienes from two different sources were used in this work. Those labeled HPBD were kindly supplied to us by Dr. William W. Graessley. The details of their synthesis and characterization have already been reported.[18-21] The molecular characteristics of this set of copolymers are given in Table I. Another series, prefixed by the symbol P, were obtained from the Phillips Chemical Co. and have been used in previous reports from this laboratory.[10,17,21,22] Their molecular characteristics are also given in Table I.

An ethylene–hexene copolymer was also studied. This sample, designated, EH-49, was chosen so as to expand the range of co-unit content studied at a fixed molecular weight (≅50 000), as well as to study the effect, if any, of branch length on the crystallization kinetics. This sample was synthesized using $(C_5H_5)_2ZrCl_2$ as catalyst[23] and has a most probable molecular weight distribution. The molecular characteristics of this copolymer are also listed in Table I. It has been established that neither the ethyl nor the butyl branches enter the crystal lattice.[9,10,14]

The copolymer compositions were obtained by conventional high-resolution ^{13}C NMR methods.[10,21,24-26] More detailed analysis of sequence distributions were made for selected fractions that cover the complete molecular weight range. The samples were all found to be random sequence type copolymers irrespective of molecular weight.[27] We thus have available a series of molecular weight fractions, each having ~2.3 mol % branch points, covering the molecular weight range 6.95×10^3–4.6×10^5. At a fixed molecular weight of 5×10^4 there is also available ethyl branched copolymers containing 2.30, 4.14, and 5.68 mol % branch points and a butyl branched copolymer containing 1.21 mol % branch points. Therefore, the influence of molecular weight on the crystallization kinetics, for a fixed copolymer composition, as well as the effect of varying copolymer compositions at a fixed molecular weight can be investigated.

Procedures. The crystallization kinetics were followed using dilatometric techniques that have been previously described in detail.[1,28,29] The amount of sample in the dilatometer varied between 100 and 150 mg. A spacer of ~1 mm less than the diameter of the bulb was used to reduce the amount of mercury necessary to fill the dilatometer. The sample, in the dilatometer, was melted in a silicone oil bath at 150 °C for 15 min and then quickly transferred to another silicone bath set at a predetermined crystallization temperature and controlled at ±0.01 °C. The height of the mercury column at a given time was used to calculate the specific volume v_t of the partially crystalline sample. This quantity was then used to calculate the degree of

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Table I
Molecular Characteristics of Ethylene Copolymers

designation	M_w	mol % ethyl branch points	M_w/M_n
HPBD-6950	6 950	2.36	~1.1
HPBD-24	24 000	2.30	~1.1
HPBD-49	49 000	2.30	~1.1
HPBD-79	79 000	2.44	~1.1
HPBD-460	460 000	2.36	~1.1
HPBD-98	50 000	4.14	~1.1
HPBD-97	50 000	5.68	
P16	16 000	2.10	1.14
P108	108 000	2.20	1.31
P194	194 000	2.00	1.53
EH-49[a]	48 800	1.21[b]	1.87

[a] Ethylene–hexene copolymer. [b] Butyl branches.

crystallinity, $(1 - \lambda)$, assuming the additivity of specific volumes. The relations between the specific volume and temperature for the completely amorphous and crystalline sample are given by[30]

$$v_a = 1.152 + 8.8 \times 10^{-4}T \quad (1)$$

$$v_c = 0.993 + 3.0 \times 10^{-4}T \quad (2)$$

where T is expressed in degrees centigrade.

Accordingly:

$$(1 - \lambda) = (v_a - v_t)/(v_a - v_c) \quad (3)$$

Results and Discussion

Degree of Crystallinity with Time. Representative examples of the time course of the crystallization are given in Figure 1 as plots of $1 - \lambda(t)$ against log t for three fractions, $M = 4.6 \times 10^5$, 4.9×10^4, and 6.95×10^3. Here, $1 - \lambda(t)$ is the fraction of the polymer transformed at time t. Each of these copolymers contains ~2.3 mol % branch points. These isotherms display the general features characteristic of polymer crystallization as well as some that are unique to copolymers. There is a strong negative temperature coefficient, ~4 orders of magnitude over only a 6–7 °C temperature interval, that is typical of nucleation-controlled crystallization. The isotherms have a sigmoidal shape that is typical of a nucleation and growth crystallization process.[1,31] In contrast to homopolymer crystallization, however, the isotherms for a given fraction do not superpose one onto the other. The isotherm shapes are very molecular weight dependent for fractions having the same co-unit content. The level of crystallinity that can be attained isothermally is in the relatively low range of 3–20%, depending on the molecular weight and the crystallization temperature. For a given molecular weight, the isotherms at different crystallization temperatures do not merge with one another at long times as do linear polyethylene fractions.[1] The temperature interval over which isothermal crystallization can take place in an experimentally practical time scale is very dependent on molecular weight. For the highest molecular weight fraction studied, this temperature interval is 94–101 °C; it shifts to 100–108 °C for $M = 4.9 \times 10^4$ and to 104–111 °C for $M = 6.95 \times 10^3$. The overlap of crystallization temperatures for successive fractions only occurs at the extremes in the range. These features will become important as we analyze these data in more detail.

The basic theory of crystallization kinetics as formulated by Avrami,[32] and modified to apply to polymers,[33] allows for the possibility of a variety of different nucleation and growth processes and takes into account the impingement of growing centers. At small extents of the transformation, the Avrami formulation has the same mathematical form

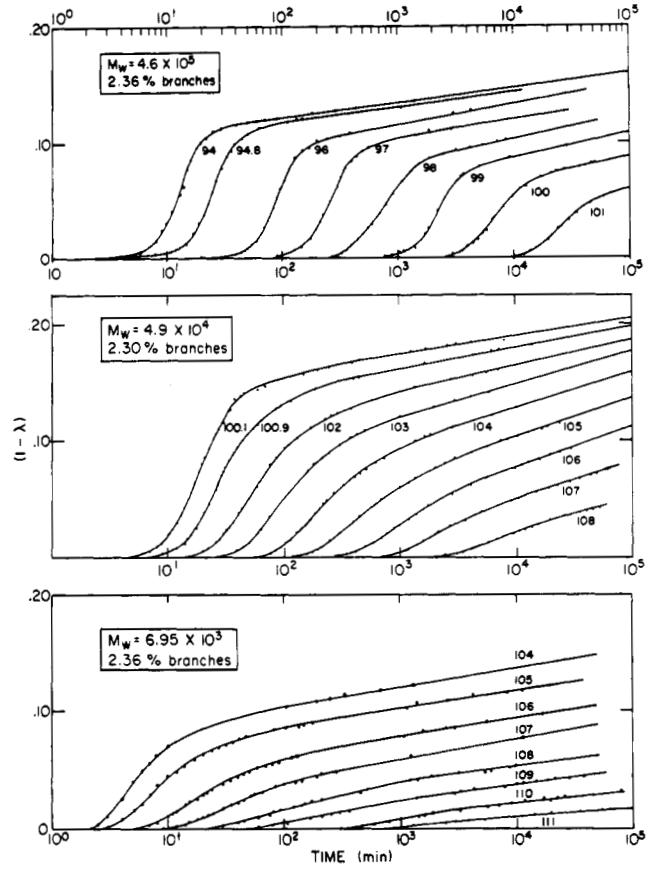

Figure 1. Plot of the extent of transformation, $(1 - \lambda)$, against log time for the crystallization of hydrogenated polybutadienes at the indicated temperatures. The weight-average molecular weights and mole percent branch points of the fractions are also indicated.

as the "free-growth" approximation of Göler et al.[34] and can be written in general form as

$$1 - \lambda(t) = kt^n \quad (4)$$

Here, k is an overall rate constant and n is related to the type and geometry of the nucleation and growth.[31] In Figure 2 the data are analyzed according to eq 1 by a log–log plot of $1 - \lambda(t)$ against t for the same three molecular weight fractions. In this figure, the straight line that is drawn without data points represents eq 4 with $n = 3$. The straight lines that are drawn through the data points, for all the fractions, are parallel to this reference line and hence represent $n = 3$. For the highest molecular weight sample, Figure 2a, straight lines are obtained for almost the entire extent of the transformation. Several different relations between the nucleation and growth rates are consistent with the value of $n = 3$.[31] Upon closer scrutiny we find that small deviations from the simplified theory occur toward the end of the transformation. These deviations become more pronounced with increasing crystallization temperature and decreasing molecular weight. For the lowest molecular weight, Figure 2c, the extent of the transformation that can be represented linearly is progressively reduced with increasing crystallization temperature. It is less than 1% at the highest temperatures. For the intermediate molecular weight (M = 49 000, Figure 2b), adherence to the linear relations lies between the two extremes. There is, therefore, a strong influence of molecular weight and crystallization temperature on the agreement with theory.

The double-log plots of $1 - \lambda(t)$ against t for the P series of hydrogenated polybutadienes follow a somewhat similar

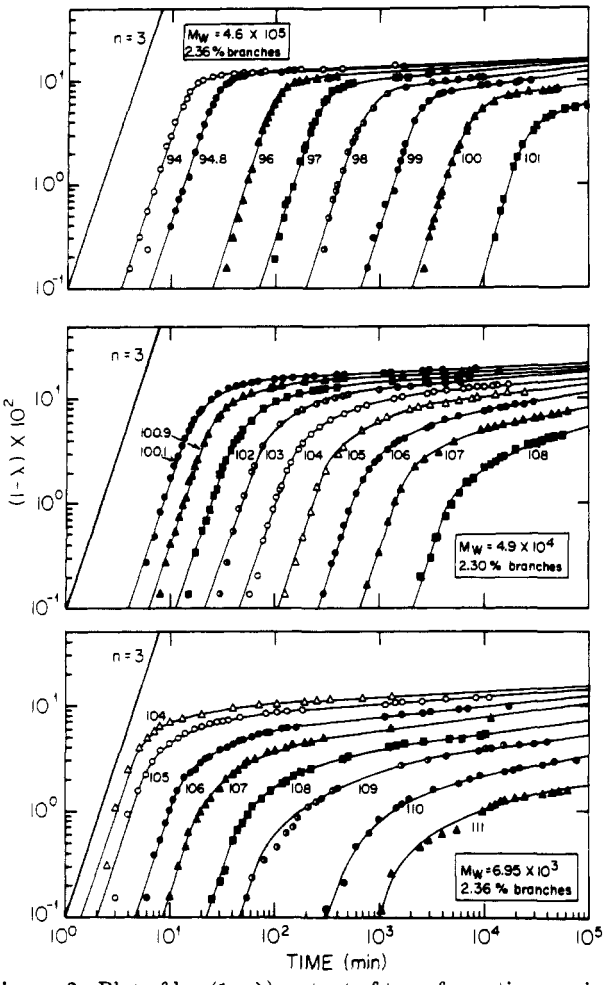

Figure 2. Plot of log $(1 - \lambda)$, extent of transformation, against log time for the crystallization of hydrogenated polybutadienes at the indicated temperatures. The weight-average molecular weights and mole percent branch points of the fractions are also indicated. The solid lines, without any points, are from eq 4 with $n = 3$.

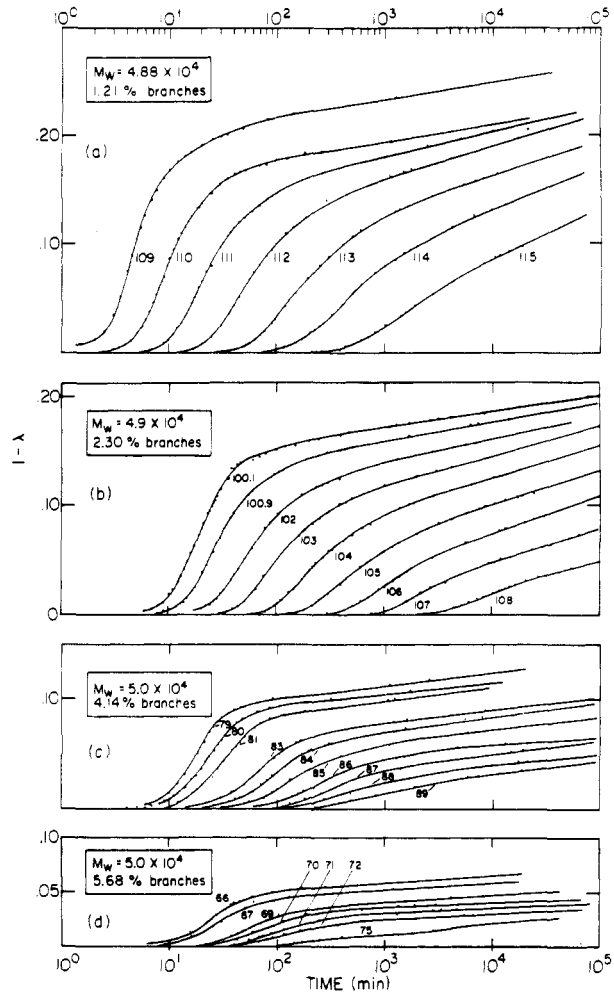

Figure 3. Plot of the extent of transformation, $(1 - \lambda)$, against log time for the crystallization of hydrogenated polybutadienes and one ethylene–hexene copolymer (1.21 mol %) at the indicated temperatures. The weight-average molecular weights and mole percent branch points of the fractions are also indicated.

pattern. The results for the highest molecular weight fraction of this series are similar to that of the previous copolymers. The initial portions of the isotherms can be represented by $n = 3$ and the deviation occurs at progressively lower extends of the transformation with increasing crystallization temperature. However, the situation is quite different for the two lowest molecular weight fractions, P108 and P16, where the initial portions of the transformation are best represented by $n = 2$. The deviations from theory, however, follow the same pattern with molecular weight and crystallization temperature as was previously indicated. These results are consistent with a change in the nucleation process. This could be caused by catalyst residue or the presence of very small quantities of other additives. However, despite these mechanistic differences, it will be found later that the final degree of crystallinity that is attained, and the rate of crystallization, are the same for both sets of polymers.

The influence of co-unit content on the crystallization kinetics is illustrated in Figure 3, where $1 - \lambda(t)$ is plotted against log t for a set of copolymers whose molecular weights are all $\sim 5 \times 10^4$. The branch point concentrations for the hydrogenated polybutadienes Figure 3b–d, are 2.30, 4.14, and 5.68 mol %, respectively. The ethylene–hexene copolymer, Figure 3a, contains 1.21 mol % branch points. The major features previously found for copolymers with a fixed branch content and varying molecular weights, Figure 1, are still observed. However, some features become more accentuated with increasing branching content. For example, although the temperature interval for practical isothermal crystallization is 7–9 °C for all the samples, its absolute location depends on copolymer composition. For the 1.21 mol % ethylene–hexene copolymer the temperature range that can be studied is 109–115 °C and it decreases to 66–75 °C for the hydrogenated polybutadiene with 5.68 mol % branches. A part of this change can be attributed to the decrease in equilibrium melting temperature of ~21 °C at the highest co-unit content[9,35,36] so that the undercoolings at which the crystallizations are conducted would be affected. However, this would only account for a portion of the approximately 40 °C change in the accessible crystallization temperature range for crystallization.

As the co-unit content increases, the isotherm shapes change rather drastically and reflect that the crystallization process is becoming more protracted. For each of the copolymers, the isotherm shape changes with increasing crystallization temperature as was previously noted. The fact that the isotherms do not merge with one another after long-time crystallization becomes quite marked for all the copolymers shown in Figure 3. The level of crystallinity that can be attained isothermally is very dependent on the chain microstructure. It ranges from ~30% for the 1.21 mol % copolymer to ~7% for the 5.68 mol % copolymer and decreases with increasing crystallization temperature. A linear polyethylene fraction of

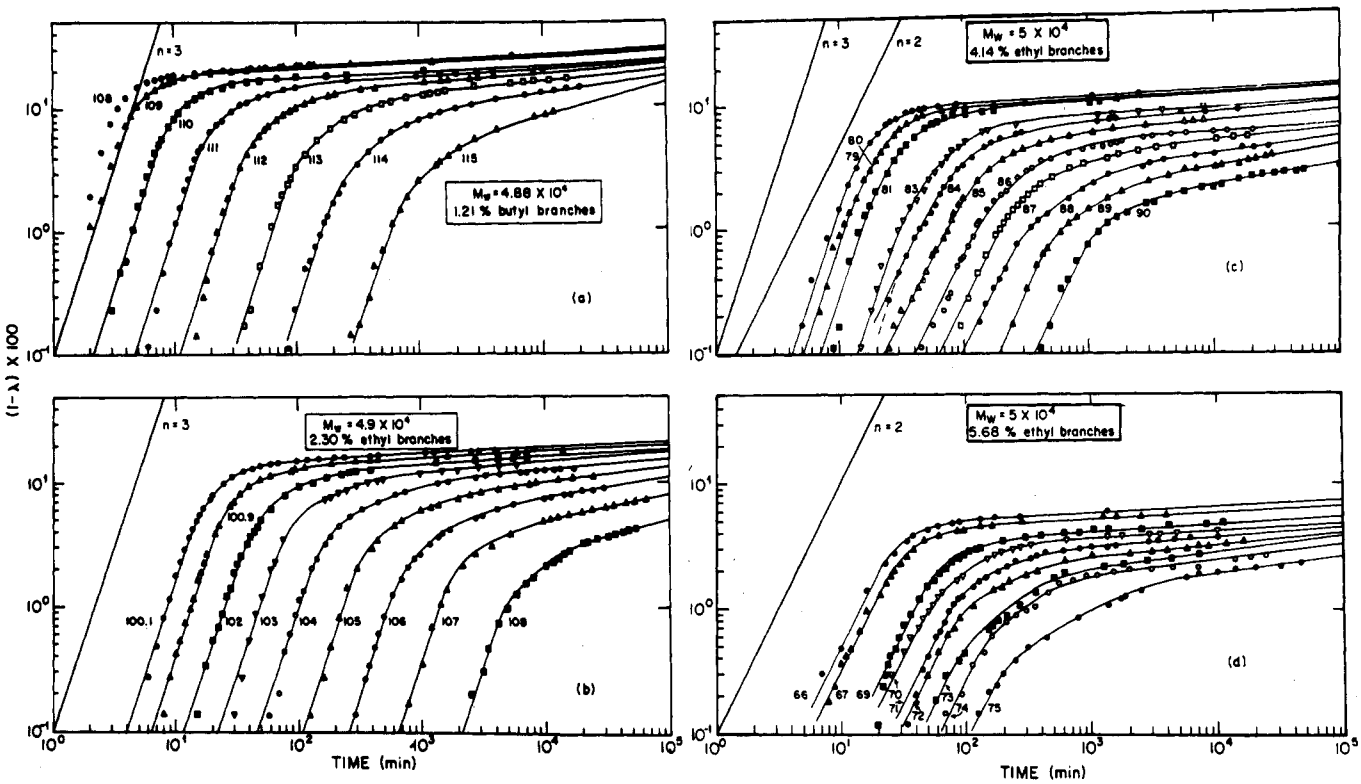

Figure 4. Plot of log (1 − λ), extent of transformation, against log time: (a) ethylene–hexene copolymer; (b–d) hydrogenated polybutadienes. The crystallization temperatures are indicated as are the weight-average molecular weights and mole percent branch points. The solid lines, without any points, are from eq 4 with n = 3 or 2.

the same molecular weight, crystallized under comparable conditions, attains a crystallinity level of ~83%.[1]

The double-log plots of these data are given in Figure 4. The two lowest co-unit content samples follow the pattern previously observed. The isotherms initially follow eq 4 with n = 3 for all crystallization temperatures. However, deviations from theory occur at progressively lower extent of the transformation with increasing crystallization temperature. The data for the copolymer with 4.14 mol % branch points (Figure 4c) are more complex. The isotherms at the lower crystallization temperatures, 79–83 °C, follow the behavior just described. However, the data for 84 °C can be represented either by n = 3, for only a small extent of the transformation (dashed line), or by n = 2 (solid line) for an appreciable portion of the crystallization. The isotherms for 85–90 °C all obey n = 2 with deviations occurring at lower extents of the transformation with increasing temperature. The isotherms for the highest co-unit copolymer (Figure 4d) all adhere to n = 2 initially with the deviations following the established pattern.

The superposition of isotherms, where the $1 - \lambda(t)$ plots are shifted along the horizontal axis to yield a common curve, is important in the analysis of crystallization kinetics.[1,31] A set of superposable isotherms indicates that there is a unique time–temperature variable governing the crystallization process. Superposition is the usual situation for homopolymers in general and linear polyethylene in particular.[1,31] Superposition is observed over the complete extent of the transformation for linear polyethylene fractions covering a very wide molecular weight range, except for the very highest crystallization temperatures.[1] For crystallization temperatures above 129 °C, although the major portions of the isotherms superpose, the final, or tail portion, does not. As is evident from Figures 1 and 3, we would not expect superposition for the copolymers except for the portions of the isotherms that adhere to the simplified theory. For each of the fractions listed in Table I, superposition is only found for that portion of the isotherm that adheres to the theory. Thus, from the point of view of isotherm superposability, the copolymers resemble the high-temperature behavior of the linear polymer. Attempts to obtain superposable isotherms by normalizing the data relative to the crystallinity level extrapolated to some long time, such as t = 10^5, were unsuccessful. The lack of superposability indicates that the deviations from theory are a function of the crystallization temperature.

Deviations from the Avrami theory occur at the ~45% crystallinity level for linear polyethylene. In the molecular weight range 4.70 × 10^4–2.84 × 10^5 the deviations are independent of the crystallization temperature.[1] Panels a and b of Figure 5 indicate that these deviations from the straight lines in Figures 2 and 4 occur at very low levels of crystallinity and are strongly dependent on molecular weight, co-unit content, and the crystallization temperature. In Figure 5a, where the deviation for three fractions each having 2.3 mol % branch points are plotted, we find that at the highest crystallization temperatures deviations occur at crystallinity levels of 1% or less. This value increases slightly with decreasing crystallization temperature. The influence of co-unit content on the deviations from theory is illustrated in Figure 5b. The results here are qualitatively similar to those in Figure 5a. For each copolymer, deviations at the high crystallization temperatures occur at less than 1.5% crystallinity. At the lower crystallization temperatures, there is a marked effect of composition where deviations are observed at the 2–3% crystallinity level for the higher co-unit content copolymer. The highest value that adheres to theory is only 10%. Thus, we find that copolymers deviate from theory at very low levels of crystallinity relative to homopolymers.

Degree of Crystallinity with Molecular Weight. The degree of crystallinity that could be attained iso-

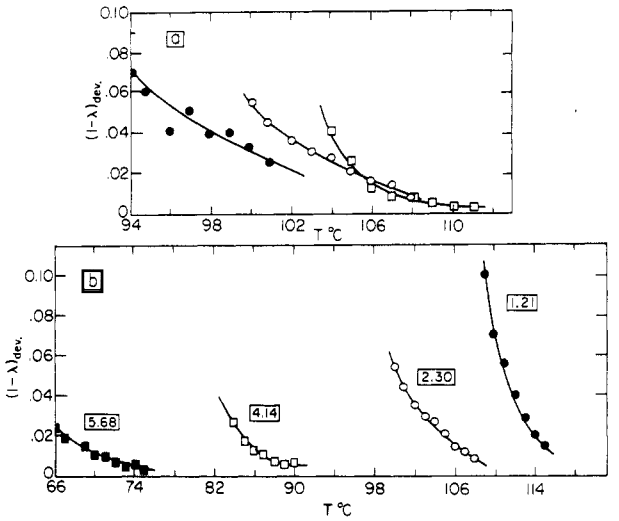

Figure 5. Plot of degree of crystallinity $(1 - \lambda)_{dev}$ at which isotherms deviate from eq 4 (a) Hydrogenated polybutadienes with ~2.3 mol % branch points: □, $M_w = 6.95 \times 10^3$; ○, $M_w = 4.9 \times 10^4$; ●, $M_w = 4.6 \times 10^5$. (b) Copolymers with $M_w \cong 5 \times 10^4$: ●, ethylene–hexene 1.21 mol % branch points; ○, □, ■, hydrogenated polybutadienes. Mole percent branch points indicated.

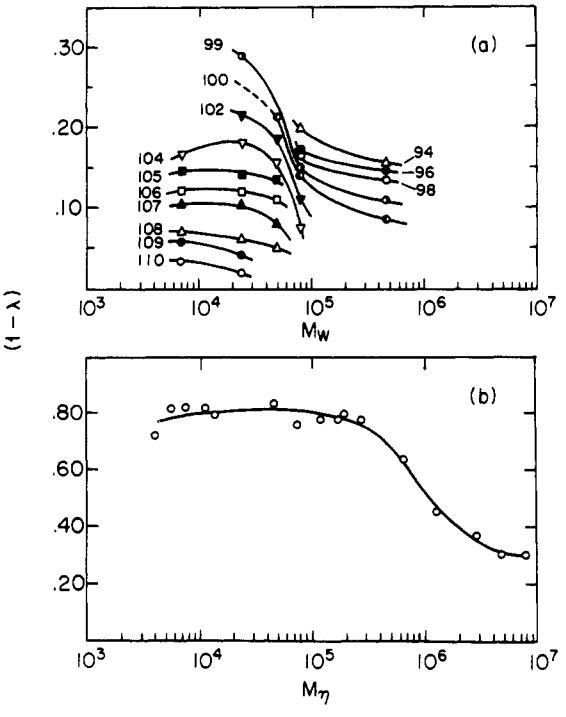

Figure 6. Level of crystallinity attained after isothermal crystallization. (a) Present work for hydrogenated polybutadienes with ~2.3 mol % branch points. (b) Linear polyethylene from ref 1. The crystallization temperatures are indicated in the figure. (The isotherms of linear polyethylene fractions merge in the flat region;[1] therefore, at a given molecular weight, the level of crystallinity at 10^5 min results independent of the crystallization temperature.)

thermally was established by extrapolating the data in Figures 1–4 to five decades of time. This crystallinity level is plotted against the molecular weight in Figure 6a, at the indicated crystallization temperatures, for the hydrogenated polybutadienes having ~2.3 mol % branch points. For comparative purposes, the crystallinity levels for linear polyethylene fractions, isothermally crystallized, are plotted in Figure 6b.[1] Much lower levels of crystallinity are attained by the copolymer relative to the homopolymers. The level of crystallinity is only a few percent at the highest crystallization temperatures but increases to

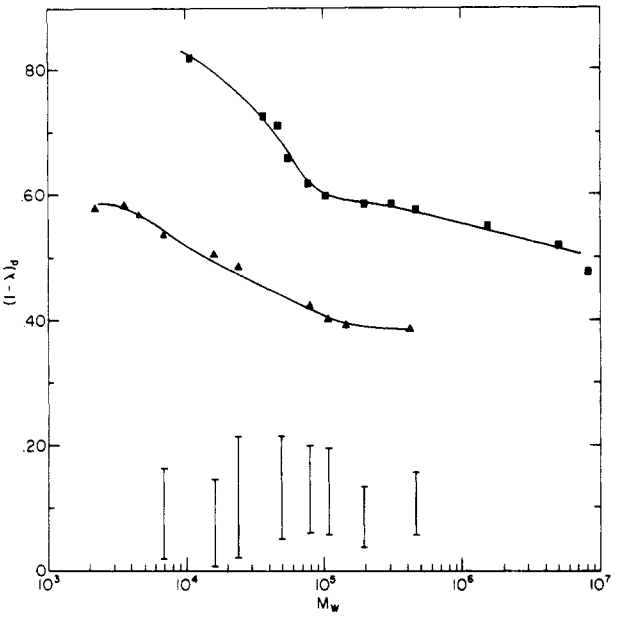

Figure 7. Plot of level of crystallinity, $(1 - \lambda)_d$, attained for hydrogenated polybutadienes with ~2.3 mol % branch points and linear polyethylene for different crystallization conditions. Vertical bars, hydrogenated polybutadienes crystallized isothermally (data from Figure 8); ▲, rapidly crystallized hydrogenated polybutadienes, $1 - \lambda$ from density measurements; ■, rapidly crystallized linear polyethylene from ref 38, $1 - \lambda$ from density measurements.

the 20–30% range as the temperature is lowered. Although there is only a small overlapping range in crystallization temperatures for the copolymer fractions, we can conclude from Figure 6 that, at a given isothermal crystallization temperature, the crystallinity level follows the same trend with molecular weight as seen for homopolymers. For example, for the copolymers the crystallinity level shows only small variations in the molecular weight range between 4000 and 20 000. Above this molecular weight the crystallinity decreases quite steeply with increasing chain length. Linear polyethylene behaves in a qualitatively similar manner. The only difference is that the large decrease in crystallinity begins in the 70–100 000 molecular weight range. An earlier conclusion that the degree of crystallinity is constant with molecular weight for high pressure polymerized branched polyethylenes, as well as hydrogenated polybutadienes, was based on a limited set of data.[37] In view of the more extensive set of data reported here this conclusion was not correct.

Figure 7 is a composite plot of the crystallinity level for isothermal and rapidly crystallized copolymers as well as previous results for rapidly crystallized linear polyethylene.[38] The data for all the copolymers with ~2.3 mol % branch points are plotted in this figure. The crystallinity levels that were attained isothermally are designated by the vertical bars. The molecular weight dependence of the crystallinity level is qualitatively similar for the quenched copolymers and homopolymers. However, for a given molecular weight the crystallinity level is substantially greater for the linear polymer. A comparison of the levels of crystallinity between the quenched and isothermally crystallized copolymers is interesting in that a substantially higher level of crystallinity is attained after rapid crystallization of the copolymers. For example, in the low molecular weight range, the crystallinity level attained isothermally on a density basis range from 2% to 16% for the copolymers, depending on the crystallization temperature. On the other hand, rapidly crystallized samples, in the same molecular weight range, are ~55%

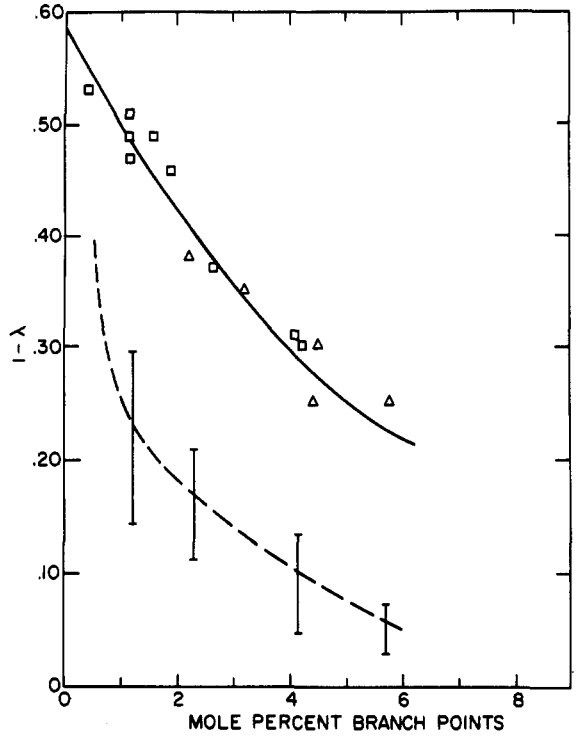

Figure 8. Plot of level of crystallinity, $(1 - \lambda)$, for random ethylene copolymers as a function of mole percent branch points. Molecular weights are all in the range 5×10^4–1×10^5. $(1 - \lambda)$ from density measurements for rapidly crystallized samples: □, ethylene-1-butene; △, hydrogenated polybutadienes,[10,22] vertical bars, isothermally crystallized hydrogenated polybutadienes (present work).

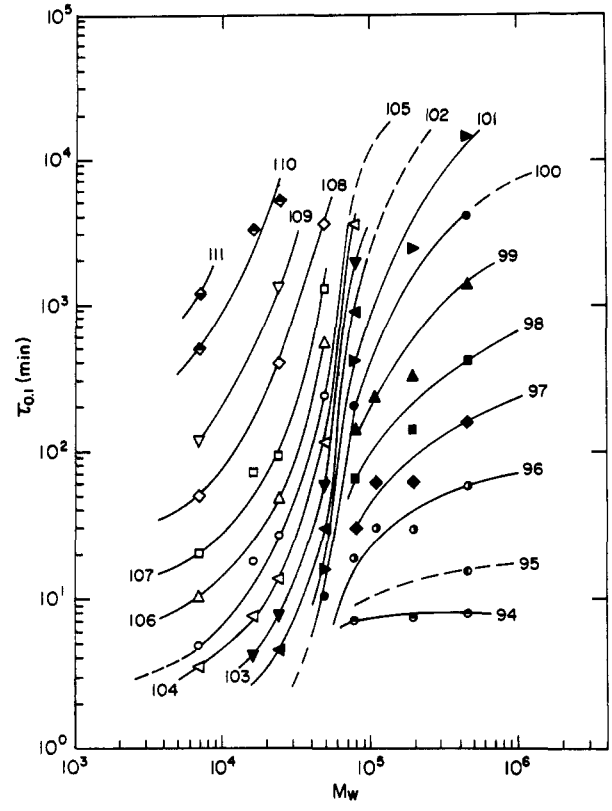

Figure 9. Plot of log crystallization rate ($\tau_{0.1}$) against log M_w for hydrogenated polybutadienes with ~2.3 mol % branch points. Isothermal crystallization temperatures are indicated.

crystalline. Although as the molecular weight increases this difference in crystallinity level decreases, it is still substantial. For $M = 10^5$ the copolymer crystallinity level increases from about 10–15% after isothermal crystallization to 40% after quenching. There is an important implication from these results when copolymer properties are studied at ambient temperature after isothermal crystallization. If a particular measurement is carried out at room temperature, the crystallinity level developed by cooling is so large that it will obscure the isothermal behavior. In general, therefore, properties will depend on the fine details of the cooling process. Linear polyethylene, in contrast, behaves in just the opposite manner. The homopolymer displays a substantial decrease in crystallinity level with decreasing crystallization temperatures.[38] As an example, the homopolymer of $M = 10^5$ has a level of crystallinity of ~80% after isothermal crystallization that is reduced to 60% after quenching. The crystallinity level of homopolymers does of course increase on cooling subsequent to isothermal crystallization.

In Figure 8, the isothermal degrees of crystallinity, obtained by dilatometric measurements, are plotted against the mole percent of branch points for the hydrogenated polybutadienes and the ethylene–hexene copolymer studied here. All of these copolymers have a weight-average molecular weight close to 50 000. The ranges in crystallinity levels that can be attained isothermally are designated by the vertical lines. Also plotted in Figure 8 are previously reported[10,22] crystallinity levels, determined by density for hydrogenated polybutadienes and other ethylene–butene copolymers that were rapidly crystallized at −70 °C. The molecular weight is ~70 000 in this grouping. For both modes of crystallization there is a substantial, and continuous, decrease in the crystallinity level with increasing branching content. For rapidly crystallized samples the crystallinity level is reduced from ~60%, characteristic of the homopolymer of this molecular weight, to ~20% for a copolymer with 6 mol % branch points. The level of crystallinity of the homopolymer of this molecular weight, crystallized isothermally, is ~83%. There is thus a very rapid decrease in crystallinity level with co-unit content for this mode of crystallization. We can also generalize our previous conclusion since for any copolymer composition there is a substantial increase in the crystallinity level with decreasing crystallization temperature.

Crystallization Rates. The influence of molecular weight on the crystallization rate is given in Figure 9 where the log of the time required to develop 10% of the absolute amount of crystallinity, $\tau_{0.10}$, is plotted against the log of the molecular weight. $\tau_{0.10}$ was obtained from plots of the type in Figures 1 and 3, where the actual amount of crystallinity was taken by extrapolating $(1 - \lambda)$ to five decades. Several distinguishing features can be discerned in this plot even though there is not complete overlap of all of the crystallization temperatures. Except for the very lowest temperatures, the crystallization rate decreases ($\tau_{0.10}$ increases) with increasing molecular weight. This dependence is very strong at the highest crystallization temperature while at the lower temperature there is not much change in the rate with molecular weight. These results are qualitatively similar to those reported for linear polyethylene[1] and many other homopolymers.[39-46] Linear polyethylene yields a discrete maximum in the crystallization rate at most crystallization temperatures. The maxima are in the range of $M = 10^4$–10^5 and depend on the crystallization temperature. However, at sufficiently low temperatures, the maximum is no longer observed and the rate does not change very much with chain length. For linear polyethylene, the temperatures at which maxima are observed correspond to undercoolings of ~20 °C or less. The crystallizations of the hydrogenated polybutadienes with ~2.3 mol % branch points are carried out at

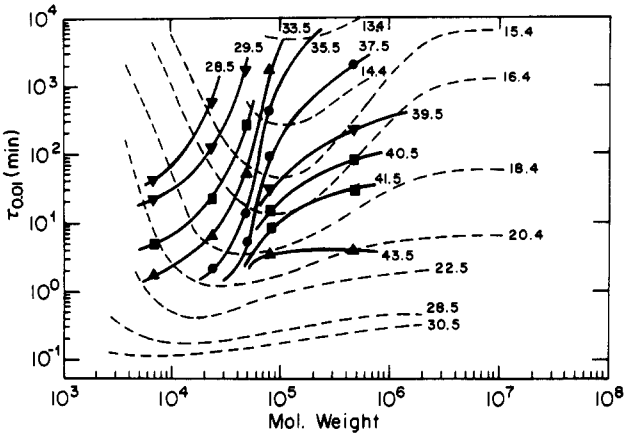

Figure 10. Plot of log crystallization rate ($\tau_{0.01}$) against log M_w for linear polyethylene and hydrogenated polybutadienes with ~2.3 mol % branch points. Linear polyethylene (- - -) from ref 1; hydrogenated polybutadiene (—), present work. Undercoolings at which crystallizations were conducted are indicated.

undercoolings in the range 26–43 °C. At these high undercoolings, maxima would not be observed in linear polyethylene. This factor would appear to be the reason that maxima in the crystallization rates are not directly observed with the copolymers studied here. The plots in Figure 9 indicate the possibility of a minimum in $\tau_{0.10}$ if lower molecular weights were studied.

A comparison between the molecular weight dependence of the crystallization rates of the homopolymers and copolymers, based on undercooling, is given in Figure 10. The equilibrium melting temperatures used to determine the undercoolings were calculated theoretically. (See eq 16 in ref 36.) In order for the copolymer and homopolymer results to coincide, the undercoolings for the copolymer crystallization would have to be reduced by approximately 15 °C and the molecular weight increased by about one decade. With these shifts, the copolymer results would overlap those of the linear polymer and would lie on the right side of the minima. The shapes of the crystallization rate—molecular weight curves for the two polymer types—would then be comparable to one another.[47]

The molecular weight also has an important influence on the crystallization process in the flat regions of the isotherms, i.e., crystallization over very long time periods. This portion of the kinetics has frequently been termed secondary crystallization. However, the crystallization process is continuous over the whole transformation and there is no abrupt change with the major portion of the transformation. Important structural changes take place in the flat portion of the isotherm.[49,50] A convenient way to examine this portion of the isotherm is to analyze the slopes from the Göler et al. type plots in Figures 2 and 4. We have already noted that for linear polyethylene the slopes do not depend on temperature for a given molecular weight. In contrast, for the copolymers there is a definite dependence of the slope on both the molecular weight and the crystallization temperatures, as is illustrated in Figure 11 for the fractions with fixed co-unit content. Although there is an individual curve for each fraction, the slopes are essentially independent of molecular weight at the lowest crystallization temperatures. However, with increasing temperature there is a steady increase in the slope, whose value is greater the higher the molecular weight. Although this slope also increases with molecular weight in linear polyethylene, the effect is much more pronounced with the copolymers.

The influence of co-unit content on the crystallization rate for a fixed molecular weight is illustrated in Figure

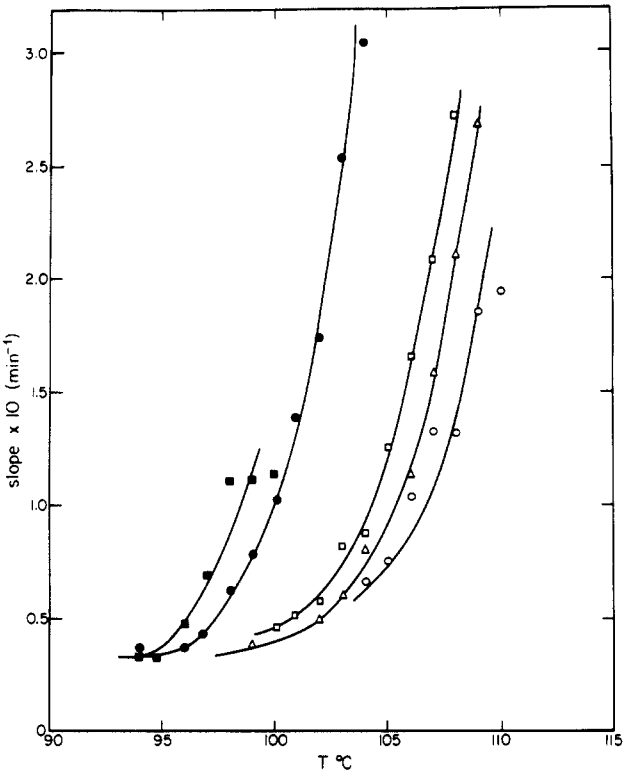

Figure 11. Plot of slope of secondary crystallization as a function of temperature for hydrogenated polybutadienes with ~2.3 mol % branch points and different molecular weights: ○, $M_w = 6.95 \times 10^3$; △, $M_w = 2.4 \times 10^4$; □, $M_w = 4.9 \times 10^4$; ●, $M_w = 7.9 \times 10^4$; ■, $M_w = 4.6 \times 10^5$.

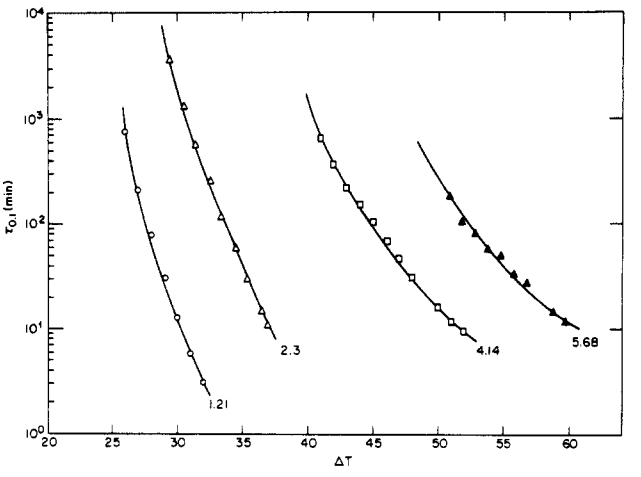

Figure 12. Plot of log crystallization rate, $\tau_{0.1}$, as a function of undercooling, ΔT, for copolymers with $M_w \cong 5 \times 10^4$: ○, ethylene–hexene; △, □, ▲, hydrogenated polybutadienes. Mole percent branch points indicated.

12. The data in this figure show quite vividly the drastic changes in crystallization rate caused by copolymer composition. The shapes of the individual curves in the figure are qualitatively very similar to one another but are displaced along the ΔT axis. In order to maintain a given crystallization rate, a substantial increase in undercooling is required as the co-unit content increases. For example, $\tau_{0.10} = 10^2$ min requires a ΔT of 28 °C for the 1.21 mol % copolymer while a ΔT of 52 °C is necessary for the 5.68 mol % copolymer to maintain the same rate. Conversely, at a given undercooling, the crystallization rate drastically decreases with increasing co-unit content.

A detailed analysis of the slopes in the secondary crystallization region for these copolymers shows that they depend on both the undercooling and the copolymer

composition. At high undercoolings, the slopes are small for each of the copolymers and comparable in magnitude to the molecular weight fractions containing 2.3 mol % branch points. However, the slopes increase rapidly with decreasing undercooling, similar to the changes found with increasing temperature in the molecular weight fractions (Figure 11). The changes in slopes with undercooling parallel one another for each of the copolymers but are much larger for the 1.21 mol % copolymer relative to the 5.68 mol % copolymer.

Temperature Coefficient of the Crystallization Process. The observation of a large negative temperature coefficient in the vicinity of T_m is indicative of a nucleation-controlled crystallization process.[31] Thus, the temperature coefficient of the crystallization rate can be analyzed according to the most general aspects of nucleation theory, without the necessity of invoking any preconceived ideas, or assumptions, as to the specifics of the nucleus structure or the process itself. The steady-state rate for the formation of nuclei of critical size, in condensed systems, $\dot{N}$, can be expressed generally as[51,52]

$$\dot{N} = N_o \exp\{(-E_D/RT) - (\Delta G^*/RT)\} \quad (5)$$

irrespective of the type of nucleation, the shape of the nucleus, or the disposition of the chains within the nucleus. In eq 5, N_o is a constant only slightly temperature dependent for homopolymers but dependent on the concentration of crystallizable units in copolymers.[52,56] E_D represents the energy of activation for transport across the liquid-crystal interface.[57] The free energy change that is required to form a nucleus from a supercooled polymeric liquid possesses a maximum with respect the nucleus size. This maximum is ΔG^*, the height of the free energy barrier that must be surmounted in order for a stable nucleus to be formed. The form of ΔG^* will depend on the specific type of nucleation that is involved. However, for a given type of nucleation, except for numerical factors, the temperature coefficient will be the same for all nucleus shapes and chain dispositions. This important point is often ignored. Therefore, the application of nucleation theory does not allow for the deduction of the chain structure within the nucleus from kinetic studies. The structural factors cannot be deduced solely from studies of the temperature coefficient of crystallization kinetics despite many efforts to invoke this circular argument.[53-55]

We take a cylinder as the model of the nucleus. It comprises ρ polymer chains aligned parallel to the length of the cylinder, each having ξ repeating units along its length. Other nucleus geometries give the same result except for numerical factors. The free energy, ΔG_d, for forming a small crystallite, or nucleus, can be obtained from the equation given by Flory.[35] This general free energy expression has been successfully used to develop nucleation theory pertinent to polymer–diluent mixtures[58,59] and to homopolymers of finite molecular weight.[60-63] For a random copolymer comprising A and B units, with only the A units participating in the crystallization, the free energy, ΔG_d, of forming a three-dimensional homogeneous nucleus can be expressed as[35]

$$\Delta G_d = 2\xi\sigma_u\pi^{1/2}\rho^{1/2} - \xi\rho\Delta G_u + \frac{RT}{x}\frac{z_A}{\bar{z}}\xi\rho + 2\rho\sigma_e - RT\rho\ln\frac{(x-\xi+1)}{x} - RT\rho\xi\ln X_A \quad (6)$$

Here ΔG_u is the free energy of fusion per repeating unit of an infinite molecular weight homopolymer of A units. Over a limited temperature range in the vicinity of T_m it can be approximated by $\Delta H_u(T_m^\circ - T)/T_m^\circ$. In these equations, X_A is the mole fraction of structural units of type A, z_A is the number of segments in an A unit, z_B is the number of segments in a B unit, $\bar{z} = z_A + z_B(1 - X_A)$ is the average number of segments per unit, x is the total number of units of both types (A and B) per polymer molecule, ΔH_u is the heat of fusion per repeating unit, T_m° is the equilibrium melting temperature of the infinite molecular weight homopolymer, σ_u is the interfacial lateral free energy per repeating unit, and σ_e is the interfacial surface free energy per repeating unit.

The dimensions of the critical size nucleus, ξ^* and ρ^*, are given by the saddle point of eq 6. These coordinates are

$$\rho^{*1/2} = \frac{2\sigma_u\pi^{1/2}}{\Delta G_u - RT[(1/x) + 1/(x-\xi^*+1) - \ln X_A]} \quad (7)$$

and

$$\frac{\xi^*}{2}\left[\Delta G_u - \frac{RT}{x} + \frac{RT}{(x-\xi^*+1)} + RT\ln X_A\right] = 2\sigma_e - RT\ln\left(\frac{x-\xi^*+1}{x}\right) \quad (8)$$

The free energy change at the saddle point, obtained by substituting eqs 7 and 8 into eq 6, is

$$\Delta G^* = \pi^{1/2}\xi^*\sigma_u\rho^{*1/2} \quad (9)$$

For the formation, on a surface, of a Gibbs-type two-dimensional coherent nucleus

$$\Delta G_d = 2\xi\sigma_u - \xi\rho\Delta G_u + \frac{RT}{x}\frac{z_A}{\bar{z}}\xi\rho + 2\rho\sigma_e - RT\rho\ln\left(\frac{x-\xi+1}{x}\right) - RT\rho\xi\ln X_A \quad (10)$$

and the dimensions of a critical size nucleus become

$$\rho^* = \frac{2\sigma_u}{\Delta G_u - RT[(1/x) + 1/(x-\xi^*+1) - \ln X_A]} \quad (11)$$

and

$$\xi^* = \frac{2\sigma_e - RT\ln[(x-\xi^*+1)/x]}{\Delta G_u - (RT/x) + RT\ln X_A} \quad (12)$$

with

$$\Delta G^* = 2\xi^*\sigma_u \quad (13)$$

When eqs 6 and 10 are formulated, an additional entropy term is added to the expression for the corresponding homopolymers to allow for the incorporation of sequences of specific length.[35] A recent formulation of nucleation theory applied to random copolymers deals only with an average sequence length and is thus inappropriate.[8]

This nucleation analysis can be considered to be a selection-type process. It represents the initial step in selecting the minimum size and number of sequences that are needed to form a critical size nucleus to allow for crystallization to proceed. If necessary, additional steps can be added to the crystallization process. In the limit of infinite molecular weight $x \to \infty$, eqs 9 and 13 reduce to

$$\Delta G^* = 8\pi\sigma_e\sigma_u^2/(\Delta G_u + RT\ln X_A)^2 \quad (14)$$

$$\Delta G^* = 4\sigma_e\sigma_u/(\Delta G_u + RT\ln X_A) \quad (15)$$

respectively. These equations are those expected from classical nucleation theory appropriate to monomeric

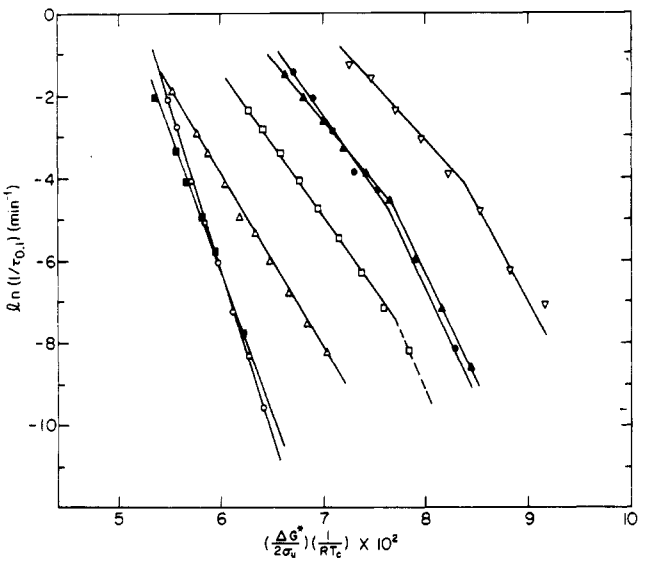

Figure 13. Plot of ln crystallization rate, $1/\tau_{0.1}$, against nucleation temperature function for coherent surface nucleation, from eq 13, for hydrogenated polybutadienes having ~2.3 mol % branch points. Symbols: ▽, $M_w = 6.95 \times 10^3$; ▲, $M_w = 2.4 \times 10^4$; ●, $M_w = 1.6 \times 10^4$; □, $M_w = 4.9 \times 10^4$; △, $M_w = 7.9 \times 10^4$; $M_w = 1.94 \times 10^5$; ○, $M_w = 4.6 \times 10^5$.

systems. They do not, however, take into account the finite length of the chain. If $X_A = 1$, the equations reduce to the previous treatment for homopolymers.[1,31,33]

If for present purposes we assume that the temperature coefficient is a consequence of steady-state nucleation, eqs 9 and 14 or 13 and 15 can be substituted into eq 5 in order to analyze the experimental data. The different choices here involve two- or three-dimensional nucleation, each with either the finite or infinite chain expression. We take as an example finite chain, two-dimensional nucleation theory. In order to follow this procedure, we need to assume values for σ_e since it is not an independently determined quantity. Taking the reasonable value of σ_e = 2000 cal/mol,[62-64] we find that for two-dimensional coherent nucleation the finite chain correction needs only to be made for M = 6950, the lowest molecular weight fraction studied here. Varying σ_e in the range of 1000–4000 cal/mol does not sensibly alter the results. Similar results are obtained for three-dimensional nucleation.

We take $\tau_{0.1}$ as a measure of the crystallization rate and plot this quantity against the appropriate temperature function in Figure 13 in accordance with eq 13 for the copolymers with ~2.3 mol % branch points.[65] We have taken T_m° = 145.5 °C and ΔH_u = 950 cal/mol.[66] We should recognize that using two-dimensional nucleation as an example represents an assumption that needs to be independently justified. A similar assumption is made in the analysis of virtually all crystallization kinetic data.[31] The analysis of the present data according to three-dimensional homogeneous nucleation, eq 14, leads to essentially the same results. As anticipated from our previous discussion, there is not a complete overlap of the kinetic data with respect to the temperature function. However, despite this limitation certain salient features emerge. The data for the three lowest molecular weights can be represented by two intersecting straight lines. The distinct possibility also exists, as is indicated in the figure, that the fraction M = 49 000 can also be represented in a similar manner. On the other hand, the data for the three highest molecular weights define a single straight line. These results are reminiscent of the recent analysis of the crystallization kinetics of linear polyethylene.[2] The

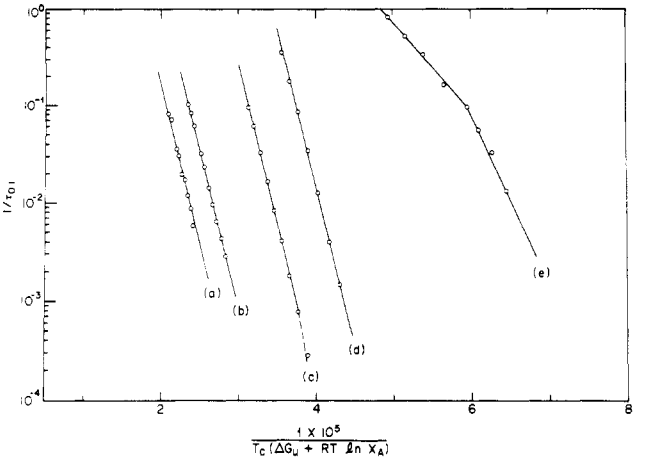

Figure 14. Plot of log crystallization rate, $1/\tau_{0.1}$, against nucleation temperature for coherent surface nucleation, from eq 15 for polymers with $M_w \cong 5 \times 10^4$: (a) hydrogenated polybutadiene, 5.68 mol % branch points; (b) hydrogenated polybutadiene, 4.14 mol % branch points; (c) hydrogenated polybutadiene, 2.30 mol % branch points; (d) ethylene–hexene 1.21 mol % branch points; (e) linear polyethylene from ref 3.

only difference between the results is the molecular weight range where the change in the representation occurs. For linear polyethylenes a single straight line represents the data for fractions $M \geq 8 \times 10^5$. For lower molecular weights the data are represented by two intersecting straight lines. We again find that from the point of view of crystallization kinetics random copolymers behave as much higher molecular weights when compared to the linear polymers.

The change in slope of the two intersecting straight lines can be related to a regime I–II transition, as has been reported in many polymers.[67] For the three lowest molecular weights the ratios of the slopes are ~0.6, being 0.58, 0.67, and 0.58, respectively. These results are consistent with the crystallization process following regime I at the high crystallization temperatures and regime II at the lower ones. The slopes of the straight lines that represent the two highest molecular weights are similar to one another and correspond to that of regime I. For the range in crystallization temperatures studied here the data can be properly assigned to regime Ia as previously defined.[2] The slopes of the straight lines for M = 49 000 and 79 000 correspond to crystallization in regime II. In order to observe regime I for these two fractions, higher crystallization temperatures are needed, which would require an inordinate amount of time.[68] There is a close correlation in the regime behavior between the copolymers and linear polyethylenes. For the homopolymer, the ratio of slopes II/I range from ~1 for very high molecular weights to 0.40 for molecular weights of $\sim 10^4$. The values of II/I slopes observed here would correspond to $M \cong 10^5$ on the linear polyethylene scale. Thus, in the analysis of the slope ratio, copolymers again behave as if they were of higher molecular weights in comparison to the linear polymers. Essentially, the same results are obtained when infinite chain nucleation theory is applied to the data, only a small correction needs to be made for the lowest molecular weight fraction. Regime transitions are observed for the same molecular weights with approximately the same ratio of slopes.

The temperature dependence of the crystallization rate of the copolymers of varying composition, but fixed molecular weight ($M \cong 10^5$), is given in Figure 14. Here the data are plotted according to the dictates of two-dimensional coherent nucleation theory in the infinite molecular weight approximation. For comparative purposes

Table II
Comparison of Slopes from Figure 14

copolymer	mol % branch points	10^{-5}slope, cal/mol	copolymer	mol % branch points	10^{-5}slope, cal/mol
LPE 53000	0	4.2 (I)	HPBD-49	2.30	7.45
		2.1 (II)	HPBD-98	4.14	7.59
EH-49	1.21	7.63	HPBD-97	5.68	8.28

the data for a linear polyethylene fraction of similar molecular weight are also given. The data for all the copolymers, whose compositions range from 1.21 to 5.68 mol % branch points, can be represented by a set of parallel straight lines. The slopes of these lines are listed in Table II. On the basis of our previous discussion, they can be identified as crystallization taking place in regime II. According to theory, the slopes are directly proportional to the product $\sigma_e\sigma_u$. We can conclude from these results that the product $\sigma_e\sigma_u$ is different from the homopolymer but is independent of copolymer composition. This admittedly is a rather surprising result. It is unfortunate that only the product $\sigma_e\sigma_u$ can be obtained from experiment. This limitation is not due to the particular experimental method used here but is imposed on crystallization kinetics, by nucleation theory, irrespective of the particular experimental technique used. If σ_u of the copolymers is independent of composition, then σ_e must also be. Such a conclusion, however, clearly rests on an assumption.

An empirical relation between σ_u and ΔH_u, similar to that used for monomeric systems having spherical nuclei,[69] has often been assumed for polymers.[70-72] However, the validity of a relation of this type has yet to be established for the geometrically asymmetric nuclei characteristic of polymers. Moreover, even if σ_e, the interfacial free energy characteristic of the basal plane, could be extracted from the kinetic data, it cannot be identified with the free energy necessary to make a sharp fold characteristic of the adjacent reentry of ordered sequences.[8,71,72] It is now well-established theoretically[73] and experimentally[4,54,74] that in homopolymers the basal plane of either the mature crystallite or the nucleus from which it is found does not comprise regularly folded chains. For random copolymers, with only one type of unit participating in the crystallite the small incidence of adjacent reentry must be reduced further. Hence, it is quite improper to calculate such a free energy of folding from σ_e.[8]

The interfacial free energies that are deduced here are concerned with nucleation and cannot a priori be identified with those characteristic of the mature crystallites that subsequently develop. If σ_e is indeed independent of copolymer composition, it must only be reflecting the contribution between the junction of the ordered and disordered sequences and perhaps a few units beyond. If these are the only structural contributions to the interfacial region, then σ_e would not be very dependent on the nominal composition. Structural differences in the interfacial region of the mature crystallites would be expected with changing copolymer composition. However, it is not required that the value of σ_e, or the product $\sigma_e\sigma_u$, that is deduced from kinetics be a necessary characteristic of the mature crystallites. The plot in Figure 14 for the linear polyethylene fraction clearly demonstrates crystallization in regimes I and II. The product, $\sigma_e\sigma_u$, in regime II for the homopolymer is a factor of 3.5 times less than that of the copolymers.

Many aspects of the crystallization of random copolymers are similar to that of homopolymers. However, there are also some very important differences. Both the equilibrium and the kinetic aspects of copolymer crystallization are governed to a large extent by the chain microstructure, i.e., the sequence distribution of the crystallizable units. Even on an equilibrium basis, not all the crystallizable sequences can participate in the crystallization process. Equilibrium theory makes clear that only sequences that exceed a certain critical length (not to be confused with the critical sequence length for nucleation) can participate in the crystallization at a given temperature.[36] This requirement explains the broad melting range characteristic of random copolymers and the large decrease in the equilibrium level of crystallinity with counit content.[36,75] For example, from theory the equilibrium level of crystallinity, in the temperature range of current interest, decreases from about 90–95% for the homopolymer to ~20% for the copolymer with 5.68 mol % branch points. Although we are concerned with a kinetic process here, the equilibrium requirements serve as a bound to the problem.

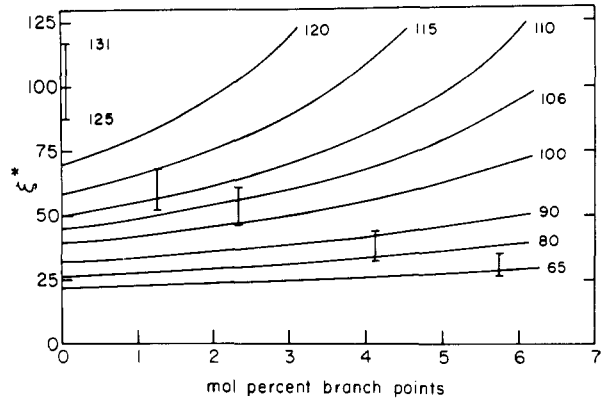

Figure 15. Plot of critical sequence length, ξ^*, for coherent surface nucleation, from eq 12, as a function of mole percent branch points at indicated crystallization temperatures. The value of σ_e was taken to be 2000 cal/mol. Vertical bars represent temperature interval for isothermal crystallization of each copolymer. Values of ξ^* for linear polyethylene were calculated in a temperature interval of 125–131 °C.

The nature of the temperature coefficient that was observed pointed out the importance of nucleation process to copolymer crystallization. We can deduce from eqs 8 and 12 that not all the sequences can participate in nucleation; i.e., not all the crystallizable units are involved. This point is illustrated in Figure 15 for two-dimensional coherent surface nucleation. Here ξ^* calculated from eq 12 is plotted against the mole percent of branch points, for $M \cong 5 \times 10^4$, for different crystallization temperatures. Also indicated in the figure as bars is the experimental temperature range of isothermal crystallization for each of the copolymer fractions and linear polyethylene. For illustrative purposes in this calculation we have used a constant value of σ_e. For a given copolymer composition and crystallization temperature ξ^* is defined. Only sequences containing this or a larger number of units can be involved in forming a critical size nucleus. A significant number of units, therefore, are not allowed to participate in steady-state nucleation. Qualitatively similar results are obtained for other modes of crystallization and values of σ_e. From first principles we know that two-dimensional nuclei do not form stable crystallites unless there is either crystallite thickening or reduction in the interfacial free energy as the mature crystallite develops.[31] A resolution of this dilemma is difficult for homopolymers and is further compounded for random copolymers. The limitation on the sequences, and thus the crystallizable units, that can participate in the steady-state nucleation has important implications to many aspects of the crystallization process.

The isotherms of the copolymers with lower co-unit content, with but minor exceptions, initially follow the Avrami, or Göler et al., formulation with $n = 3$. In this respect they are similar to the homopolymers of modest molecular weight 10^4–10^6.[1] A unique situation is, however, also found with the copolymers having the highest co-unit contents. Here, the value of n changes from 3 to 2. The most general deduction that can be made from this observation is that there is a change in the growth geometry.[31] Electron microscopy studies have shown that in this composition range lamellar-like crystallites are no longer formed.[76] This change in crystallite structure is reflected in the isotherm shape.

The Avrami-type isotherm, and the concomitant deduction of superposition, is based on the implicit assumption that the composition and structure of the melt do not change during the course of the transformation.[31,33] This assumption clearly will not apply to random copolymers where both composition and sequence distribution of the residual melt change continuously during crystallization. The increasing accumulation of the noncrystallizable species and sequences in the residual melt will result in a systematic depression of the melting point and thus the undercooling, even for a process that is actually carried out isothermally. Therefore, a marked alteration in the crystallization rate is to be expected during the course of the isothermal transformation. Calculations have shown that the decrease in nucleation rate becomes more pronounced as the undercooling is lowered and the concentration of the noncrystallizing units increase.[56] The overall rate of crystallization must be consequently affected, resulting in isotherms that do not superpose. The results found here, where the isotherms deviate from theory with the extent of transformation, undercooling, and co-unit content, follow these expectations quite well. Nonsuperposable isotherms have been found in other copolymers such as polybutadiene[5] and long-chain branched polyethylene.[6]

When the crystallization rates are analyzed, consideration must be given to the time restraints that are placed on the process by the nature of the experimental technique. In the dilatometric method used here, the time scale that is covered is approximately 10–10^5 min. The changes in the isothermal crystallization temperature range with molecular constitution must take into account this constraint on the experimental method.

In explaining the right side of the minimum in Figure 10, at least two important structural factors need to be considered. One is the density of entanglements, and other topological restraints to crystallization, that are present in the pure melt. The other is the fraction of sequences of crystallizable units that are allowed to participate in the isothermal crystallization.

For homopolymers, the decrease in crystallization rate (increase in $\tau_{0.1}$) with molecular weight on the right side of the minimum in Figure 10 can be attributed to an increase in the entanglement density. We can initially assume the same dependence for copolymers of a given co-unit content. With simplified rubber elasticity theory, it has been assumed that the plateau modulus, obtained from viscoelastic measurements, is inversely related to M_e, the average molecular weight between coupling junctions, or entanglements.[77] Consequently the number of junction points per molecule is $M/M_e - 1$. It should be noted, however, that the contribution of any interchain entanglements to the equilibrium elastic modulus has been seriously questioned.[78,79] For our present comparative purposes, we shall follow the conventional procedure, recognizing that it rests on a basic assumption. The plateau modulus of a 2.3 mol % hydrogenated polybutadiene is reduced by ~15% relative to the linear polymer.[80] Consequently, following the method outlined, one expects that for a fixed molecular weight there should be a slight increase in the crystallization rate. However, the effect on crystallization rate due to entanglements is compensated by the fact that only 20–40% of the sequences in this copolymer can participate in the crystallization over the experimentally allowed temperature interval. Since there is a molecular weight independent concentration factor in the nucleation rate,[52,56] the crystallization rate will be reduced relative to that of the homopolymer.

The fraction of sequences that can participate in the nucleation, irrespective of how they are distributed among the crystallites, can be estimated in the following manner. The number of sequences, ν, of CH_2 groups, each of which contains a number of units equal to or greater than ξ^* can be expressed as[35]

$$\nu = \nu_a(1 - X_A)X_A^{\xi^*-1} \tag{16}$$

Here ν_a is the number of crystallizable units and X_A is their mole fraction. The fraction of crystallizable sequences, f_c, is then found by dividing the expression in eq 16 by the total number of CH_2 sequences. Thus

$$f_c = \nu/(\text{no. of branches} + 1) \tag{17}$$

By application of eq 17 to the experimental data, it is found that f_c is independent of molecular weight. This fraction is temperature-dependent and for $X_A = 0.977$ varies from ~0.38 at 95 °C to ~0.22 for 110 °C. Therefore, because of the time restraints of the experiment the crystallization temperature must be progressively lowered with increasing molecular weight and consequently, at fixed co-unit content, a larger fraction of sequences is required in order for crystallization to take place within the allowed time frame.

At the same crystallization temperature and value of f_c, as the molecular weight of the copolymer is increased the crystallization rate is reduced because of the increasing entanglement density. However, because of the limited time scale the crystallization must be conducted at progressively lower temperatures as the molecular weight increases.

We can analyze the temperature range of crystallization at a fixed molecular weight in a similar manner. Figure 12 has illustrated that for the same molecular weight, $M = 5 \times 10^4$, crystallization in the allowable time scale is progressively shifted to higher undercoolings with increasing co-unit content. Carella et al.[80] found that the plateau modulus decreases by ~30% when the mole fraction of branch points increases to 5.68%. Consequently, following the conventional argument, we can conclude that the entanglement density increases in the same proportion. In contrast, as is illustrated in Figure 16, the fraction of sequences that can participate in nucleation decreases rapidly with co-unit content at a fixed molecular weight. This factor will significantly retard the crystallization rate and will require a reduction in temperature in order for the transformation to proceed. The experimental temperature range of the crystallization is also indicated in Figure 16. For linear polyethylene the corresponding temperature interval is about 120–130 °C for f_c equal to unity. The value of f_c rapidly drops to the 0.2–0.3 range for copolymers with 2.3 mol % branches and greater. For these copolymer fractions, the crystallization temperature is adjusted accordingly to allow for the fractions of sequences required. The 1.21 mol % copol-

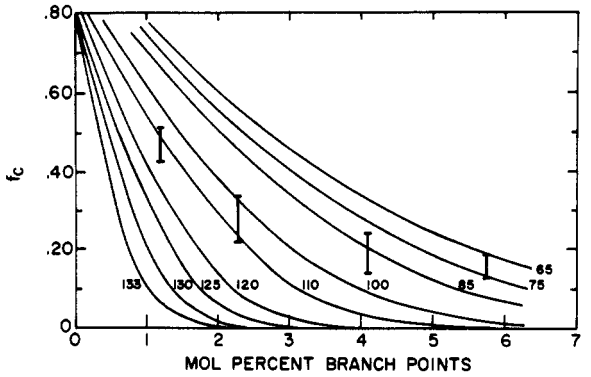

Figure 16. Plot of fraction of sequences, f_c, that can participate in nucleation, calculated from eq 17, against mole percent branch points at indicated crystallization temperatures.

ymer, which is butyl branched, requires a higher value of f_c. This copolymer has a most probable molecular weight distribution. There is, therefore, the distinct possibility that the crystallization rate is influenced by the distribution.

In analyzing the spherulite growth rate of isomerized poly(*cis*-1,4-isoprene), Andrews et al.[7] assumed that it would be attenuated in direct proportion to the probability of finding a sequence of at least ξ^* units long. With this assumption it follows that

$$G = X_A^{\xi^*-1} G_0 \tag{18}$$

or

$$\ln G = (\xi^* - 1) \ln X_A + \ln G_0 \tag{19}$$

Here G is the growth rate of the copolymer and G_0 is the corresponding spherulite growth rate of the homopolymer. For a high value of X_A eq 19 becomes

$$\ln G = (\xi^* - 1)(X_A - 1) + \ln G_0 \tag{20}$$

According to eqs 8 and 12, ξ^* is a function of the undercooling and will vary with copolymer composition at a fixed crystallization temperature. Andrews et al.[7] used eq 20 to analyze their experimental results for the crystallization of random poly(*cis*-1,4-isoprene) copolymers containing up to 9% trans units at a fixed temperature of −26 °C. A plot of ln G against the mole fraction $(1 - X_A)$ was found to be linear.[7] Very large undercoolings are involved at this crystallization temperature. They range from ~65 °C for the homopolymer to ~45 °C for the highest co-unit copolymer. From Figure 15 we find that ξ^* is essentially invariant with copolymer composition at such large undercoolings. Hence, a close to a linear relation would be expected for this special situation. A value of $\xi^* = 75$ was deduced from the slope of this straight line.[7] This value of ξ^* seems unduly high in terms of eq 8 or 12. Figure 14 illustrates that, at best, the crystallization rates of only two copolymer pairs can be compared at the relatively low undercoolings of these experiments. For the two cases that can be compared, (a) with (b) and (c) with (d), the ratio in crystallization rates expected from the theory are 1.5 and 1.9, respectively. Experimentally (Figure 14), we find that the ratios are 17 and 1750, respectively. Thus, there is a larger disagreement between experiment and this theory. A similar result would be expected if the kinetic data for the isoprene copolymer were available at lower undercoolings.

We examine next the crystallization level that can be attained as a function of molecular weight and copolymer composition. The composite plot of Figure 7 indicates that in the isothermal range the level of crystallinity is in the range of 5–20%, depending on the molecular weight and crystallization temperature. Despite the small overlapping region of crystallization temperatures with molecular weight, and the low levels of crystallinity that were reached, a decrease in $(1 - \lambda)$ with molecular weight is discerned at a fixed crystallization temperature. This is qualitatively similar to the behavior of the linear polyethylenes and can be attributed to the dependence of the concentration of entanglements on molecular weight. Unique to copolymers are the relatively low levels of crystallinity that are reached even after long-time crystallization. The underlying basis for this result can be obtained from both the equilibrium restrictions and the kinetic restraints that are imposed on the crystallization process. The equilibrium degree of crystallinity for the 2.3 mol % copolymers is calculated to be in the range of 30–40% in the temperature interval of interest. An estimate of the level of crystallinity that can actually be reached can be obtained from eq 16. Fixing the crystallite thickness as ξ^*, the level of crystallinity, $(1 - \lambda)_{\xi^*}$, can be expressed as[35]

$$(1 - \lambda)_{\xi^*} = \xi^*(1 - X_A) X_A^{\xi^*-1} \tag{21}$$

For two-dimensional coherent nucleation $(1 - \lambda)_{\xi^*}$ is found to be in the range 30–40%. However, mature crystallites with thickness $\xi = \xi^*$ (for two-dimensional nucleation) are thermodynamically unstable.[31] Therefore, for this nucleation mode the crystallites must be thicker. If, for example, the crystallite thickness is taken to be $2\xi^*$, the level of crystallinity that can be reached is reduced to the 15–25% range.

An upper bound to the attainable crystallinity level can also be estimated by allowing crystallite thicknesses of ξ^* and larger to form. The number of such continuous sequences of y crystallizable units can be expressed as[35]

$$\nu_y = \nu_A (1 - X_A)^2 X_A^{y-1} \tag{22}$$

The level of crystallinity, $(1 - \lambda)_u$ for this model is then

$$(1 - \lambda)_u = \sum_{y=\xi^*}^{\infty} y\nu_y / \nu_A \tag{23}$$

With some manipulation eq 23 can be rewritten as

$$(1 - \lambda)_u = 1 - (1 - X_A)^2 \sum_{y=1}^{\xi^*} y X_A^{y-1} \tag{24}$$

from which the crystallinity level, for this model, can be calculated. If ξ^* is taken to be the smallest allowable sequence, the crystallinity level for the upper bound is found to be in the order of 50% or greater, which is much too large a value. Increasing the lower limit in the summation of eq 23 decreases $(1 - \lambda)_u$ accordingly.

From this analysis we can conclude that the $(1 - \lambda)$ values that are actually observed for the isothermally crystallized 2.3 mol % copolymers are determined by the relatively low equilibrium expectations. It is reduced further by the kinetic restraints, particularly by the limitation of allowable sequences and by chain entanglements. A much greater level of crystallinity develops after rapid crystallization from the melt. This increase in $(1 - \lambda)$ results from the allowed participation of the smaller sequence lengths under these crystallization conditions. This enhancement of the crystallization level is a unique property of copolymer crystallization. It is opposite to homopolymer behavior under comparable crystallization conditions.

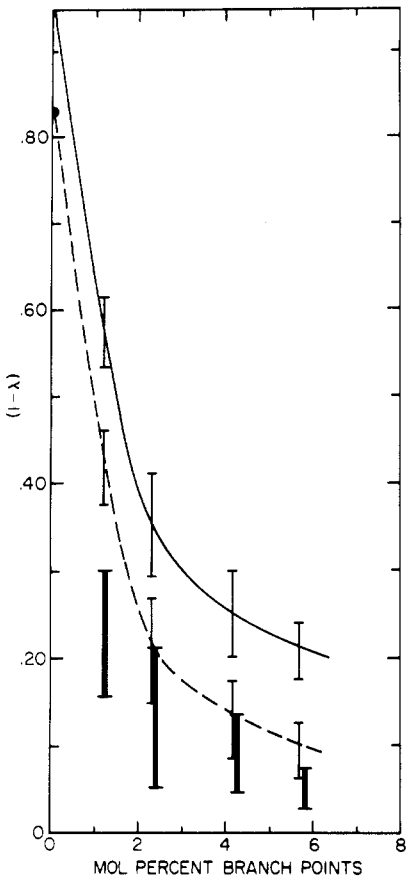

Figure 17. Plot of degree of crystallinity, $(1 - \lambda)$, against mole percent branch points after isothermal crystallization: (—) equilibrium crystallinity calculated from eq 18 of ref 36; (- - -) corrected for entanglement as described in text; heavy vertical bars, experimental results.

The molecular weight dependence of $(1 - \lambda)$, for rapidly crystallized copolymers, parallels that of the linear polyethylenes. It can be explained by invoking the same functional dependence of entanglement density on molecular weight. However, the crystallinity level is ~20% lower for the copolymers. Since the molecular weight between entanglements is greater for the copolymers,[80] the lower level of crystallinity is a reflection of the equilibrium requirements[35,36] and the kinetic restraints.

The level of crystallinity that is attained either isothermally or after rapid crystallization, at a fixed molecular weight, rapidly decreases as the concentration of branch points increases, Figure 8. The observed isothermal crystallinity levels are replotted in Figure 17 along with the value for the homopolymer of the same molecular weight. These crystallinity levels are delineated by the solid, thicker vertical lines. Also plotted are the equilibrium values shown as the solid curve. The vertical lines represent the range in equilibrium values over the temperature interval studied. The two curves follow a very similar pattern. The equilibrium values range from close to 100% for the linear polymer to ~20% for the 5.68 mol % branched copolymer. The observed isothermal values range from 83% for the homopolymers to ~5% of the highest co-unit content copolymer. The rapid decrease in $(1 - \lambda)$ with branching content is thus anticipated on the basis of equilibrium requirements. The precise values reached will depend on the superposition of the kinetic restraints on the equilibrium expectations.

We can estimate the influence of entanglements in the following manner. We assume that the 17% difference in $(1 - \lambda)$ between the expected and observed values for the linear polyethylene fraction, $M = 5 \times 10^4$, is due to the effect of entanglements. In estimating the influence of entanglements on copolymer crystallization we take cognizance of the increase in plateau modulus with branching content.[80] The influence of entanglement is thus proportioned accordingly. For example, for the 5.68 mol % copolymer the concentration of entanglements is reduced 32% relative to the corresponding linear polymer. The percent crystallinity will then be reduced by 11.5 viz. $(17 - 17 \times 0.32)$. The crystallinity levels calculated in this manner are shown in Figure 17 as a dashed line. Relatively good agreement is obtained between the observed and calculated values. The observed crystallinity levels are slightly less than calculated. The discrepancy is somewhat larger with the 1.21 mol % ethylene–hexene copolymer. These small differences can be due to restraints on sequence participation and the molecular weight distribution of the hexene copolymer.

It has been reported and confirmed[48,81] that the melting temperatures of a series of hydrogenated polybutadienes (randomly ethyl branched copolymers), as well as other random ethylene copolymers,[22] decrease with increasing molecular weight at a fixed co-unit content. This behavior is contrary to any equilibrium requirements and to the actual behavior of the homopolymers.[66,82,83] This unusual set of results must be due to the crystallite structures that are actually formed and should depend on the crystallization kinetics. These results give us a guide to establishing equivalent crystallization conditions in order to compare melting temperatures.[81]

From the extensive study of the influence of molecular weight and composition on the crystallization kinetics of random ethylene copolymers certain salient features have emerged. The general aspects of the crystallization process are very similar to those of homopolymers in that the Avrami formulation is followed for the initial portions of the transformation, there is a strong influence of molecular weight, and we are dealing with a nucleation-controlled process. Copolymers on the other hand do not yield superposable isotherms. In many aspects of the crystallization process random copolymers behave as if they were of higher molecular weight. In examining the experimental data several specific examples of this phenomenon can be cited. These include Göler et al. plots, the level of crystallinity that is attained either isothermally or after rapid crystallization, the influence of molecular weight on the crystallization rate, the observation of regime transition, and the ratio of the regime slopes. The restraints on sequence participation, which is unique to copolymers, influence the time scale of the crystallization and the level of crystallinity that can be attained.

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