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The crystallization behavior of random copolymers of ethylene

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Abstract

The crystallization behavior of random ethylene–1-alkene copolymers is reviewed. Major attention is focused on fractions and samples that have well-defined and narrow molecular mass and composition distributions. Emphasis is given to the analysis of thermodynamic properties, the basic elements of phase structure, the purity of the crystalline phase and the supermolecular structure. The molar mass, co-unit content and chemical type are treated as independent variables in the analysis of a large amount of experimental data. As is expected from theoretical considerations, the thermodynamic properties are very sensitive to the sequence distribution of the co-units in the chain. It is found that, except for directly bonded methyl groups, the crystallite structure remains pure, irrespective of the chemical nature of the co-unit. Thermodynamic properties and the major elements of phase structure, with the exception of the interfacial structure, are independent of the nature of the side group for groups larger than methyl. The analyses of a large amount of experimental data makes it clear that the molar mass and co-unit content need to be treated as independent variables.

1. INTRODUCTION

The major focus of this review will be on the thermodynamic properties and phase structure of random copolymers based on polyethylene. Despite this relatively broad subject area that will be covered it needs to be discussed within the general framework of the crystallization behaviour of copolymers. Therefore, a brief summary of the general principles that govern copolymer crystallization is presented before some of the specific thermodynamic and structural properties are discussed. More extensive discussions can be found elsewhere [1,2].

From the point of view of the crystallization behaviour, the definition of

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a copolymer can be subtle. Many different types of structural irregularities can be incorporated into the chain and cause it to behave as a copolymer. In a straightforward way, two (or more) chemically dissimilar monomers or co-units, incorporated into the chain will constitute a copolymer. Depending on the nature of the repeating unit, structural isomers, geometric or stereo can also be present in the chain. Thus, typical examples are the stereoirregular polymers such as poly(styrene) and poly(propylene). The poly(dienes) are examples of chains containing geometric isomers. There can also be head-to-head as opposed to head-to-tail structures in the chain. Long and short chain branches, and also crosslinks, are other sources of structural irregularities. When aromatic rings are in the main chain, different types of isomers (ortho, meta or para) also endow copolymeric character to the chain. Therefore, a careful study must be made of the chain structure of a given polymer before attempting to analyze its crystallization behavior. In addition to identifying the structural irregularities that are present, it is extremely important that their sequence distribution be specified.

For all types of random copolymers the properties of interest deviate in a significant manner from the expected equilibrium behavior [1,3]. Nevertheless, it is important to establish the equilibrium requirement in order to have a base from which to understand the properties that are actually observed. The crystallization of copolymers is but one example of the classical problem of a two-component (or more)-two phase equilibrium. However, the long-chain character of polymers introduces some unique features to the problem, although the principles involved are general. In phenomena of this type, it is necessary to a priori establish, or postulate, the distribution of components between the two phases. Theory, for either monomeric or polymeric systems, does not establish this condition. Rather, theory makes a set of premises with regard to the distribution of components and then proceeds to develop equilibrium conditions based on the assumptions made. For copolymers, where co-units are excluded from the crystal lattice (the crystalline phase is pure) the thermodynamic and structural situation is clear. However, if the co-unit is located within the crystal lattice several different cases need to be clearly distinguished. The distinction has to be made whether the co-unit enters the lattice either as a result of equilibrium requirements or as a non-equilibrium defect. These are obvious distinctly different situations that need to be treated separately. The problem is comparable to that found with monomeric systems. Deciding whether a co-unit does or does not enter the lattice can, admittedly, be difficult.

The equilibrium theory of the fusion of copolymers has been developed by Flory [4,5] for the case where the crystalline phase remains pure. A Bernoullian type chain is considered that is characterized by a parameter p, the sequence propagation probability. This parameter represents the probability that in the copolymer a crystallizable unit is succeeded by another such unit. For this type of chain, under the stipulation that the crystalline phase remains pure, the equilibrium melting temperature T_m can be expressed as

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{-R}{\Delta H_u} \ln p \tag{1}$$

where T_m^0 is the melting temperature of the pure parent homopolymer and ΔH_u is the enthalpy of fusion per repeating unit. This equation gives the very interesting result that the melting temperature of a copolymer does not depend directly on its composition but rather on the nature of the sequence distribution. The reason for this unique result lies in the chain-like character of polymers. The chemical potential of a unit in the chain, in either state, depends on the sequence distribution rather than on the composition [4, 6]. We are not dealing here with the simple monomer that contains isolated impurities.

Three distinct types of sequence distribution can be easily discussed in terms of X_A, the mole fraction of crystallizable units. For an ordered or block copolymer $p \gg X_A$. For such copolymers, there will at most be a slight decrease of the melting temperature from that of the corresponding homopolymer. For an alternating copolymer $p \ll X_A$ and a drastic reduction in the melting temperature occurs. For a truly random copolymer $p = X_A$ so that eqn (1) becomes

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln X_A \tag{2}$$

The prediction that copolymers having the same composition, but constituted in different ways, will have drastically different melting temperatures has been amply demonstrated by experimental observations of a wide variety of copolymer types [1, 3, 7–10]. In general it is expected that the melting temperature, at a given composition, will be very sensitive to the parameter p. (Coleman [165] has analyzed this problem for the case where the addition of a given unit to the chain depends on the preceding unit, i.e. in terms of conditional probabilities and it has recently been reexamined by Allegra et al. [166].)

With our present interest in random copolymers we focus attention on eqn. (2). For a variety of different chemical type copolymers where the crystalline phase is pure, the functional form of eqn (2) is obeyed for copolymers that range from copolyesters and copolyamides to olefin types. The specific chemical nature of the non-crystallizable portion does not affect the results as is predicted by theory. However, in a major shortcoming for real systems, the value of ΔH_u that is obtained is much lower than that obtained by other theoretical methods [1]. This is a reflection of a systematic difference between the observed melting temperature and that expected from equilibrium theory. The reason for this disparity is the inability of real copolymer systems to achieve the structural condition stipulated by the equilibrium requirements. Theory requires that the melting temperature represent the disappearance of very long sequences from the crystallite. Even at equilibrium these sequences only occur in very small concentrations. The crystallization of these sequences will be very difficult because of kinetic restraints, and their detection will require very sensitive experimental techniques. For these reasons the observed melting temperatures of random copolymers will be less than predicted. This difference will become larger as the co-unit content increases and results in an apparent lower enthalpy of fusion. In addition to developing and detecting the necessary long sequences of crystallizable units, the average thickness of the crystallites that develop is less than required by equilibrium requirements and decreases with co-unit content.

The equilibrium theory also gives expectations as to the level of crystallinity for random copolymers. At comparable temperatures the equilibrium degree of crystallinity is severely reduced as the concentration of the non-crystallizing units increases. The fusion of copolymers is expected to occur over a broad temperature range in contrast to the relatively sharp melting of homopolymers [5]. A small, but significant amount of crystallinity will persist for an appreciable temperature interval below the melting temperature. The breadth of this interval increases substantially with the concentration of non-crystallizable units. Thus, equilibrium melting temperatures may be very difficult to detect. The unique features of the fusion of random copolymers (which satisfy all the requirements of a first order phase transition) are a consequence of the broad distribution of sequence lengths that change in the residual melt as fusion progresses. In addition, there is the influence of crystallites of finite thickness. These factors will be severely exacerbated for the real non-equilibrium situations that are usually encountered. The major conclusions of the theoretical development in regard to the crystallinity level and the course of fusion are substantiated by experiment [9, 11–13]. Random copolymers are well known to melt over a broad temperature range irrespective of the specific nature of the structural irregularity or the type of parent homopolymer.

The situation where the co-unit enters the lattice presents an entirely different situation. The presence of a co-unit within the lattice does not necessarily represent a defected structure. It could very well represent the equilibrium condition. As indicated previously, a clear distinction needs to be made between the two cases. When the co-unit acts as a truly defected structure within the crystalline lattice, a variety of formulations can be given to the problem depending on the assumptions made and the details involved. Attempts have been made to calculate the effect of internal defects on the melting temperature [14–16]. If, however, one considers the equilibrium case, then the sequence distribution within the crystallite needs to be known. The reason is that the chemical potential of a unit in both states needs to be equated in order to obtain the melting temperature–composition relation. This is a difficult matter that has not as yet been resolved. There are thus some very major difficulties in analyzing this aspect of the problem.

Many properties of crystalline homopolymers are known to be very dependent on molar mass and crystallization conditions [17–21]. Linear polyethylene has been extensively studied in this connection. Thus, a variety of properties ranging from simple thermodynamic to more complex mechanical ones follow this generalization [18–31]. Random copolymers would be expected to behave in a similar manner. Therefore, in studying the properties of random copolymers, in addition to the sequence distribution and concentration of the units, the molar mass and crystallization conditions need to be specified and independently assessed. In particular the contribution of molar mass and composition need to be treated as independent variables in studying properties. If this precaution is not taken, definitive conclusions can not be made.

Because of the limitations of space we primarily limit our consideration to ethylene-co-1-alkene copolymers. Other random type ethylene copolymers, which have been reviewed elsewhere [2], will only be introduced for very specific purposes. We shall also avoid, in general, discussing samples that are polydisperse in molar mass and composition. They introduce major complications to any serious analyses. Moreover, a sufficient number of studies, involving well-defined and characterized samples, are now available for review.

2. MELTING TEMPERATURE

The analysis of the melting behavior of a polymeric system is usually very informative with respect to molecular structure. In accord with our stated objectives, we shall focus attention here on samples having narrow molar mass and composition distribution as well as those whose distribution is well-defined. In the first category data is available for hydrogenated polybutadienes and cross-fractionated ethylene–1-alkene copolymers. Extensive data is also available for copolymers having narrow composition and most probable molar mass distribution [9, 12, 32–34]. All these copolymers have essentially random sequence distribution. Hydrogenated polybutadiene is a random ethyl branched copolymer of very narrow molar mass and composition distribution [35, 36]. It serves as a very fine model for random ethylene copolymers. Rapidly crystallized samples were analyzed

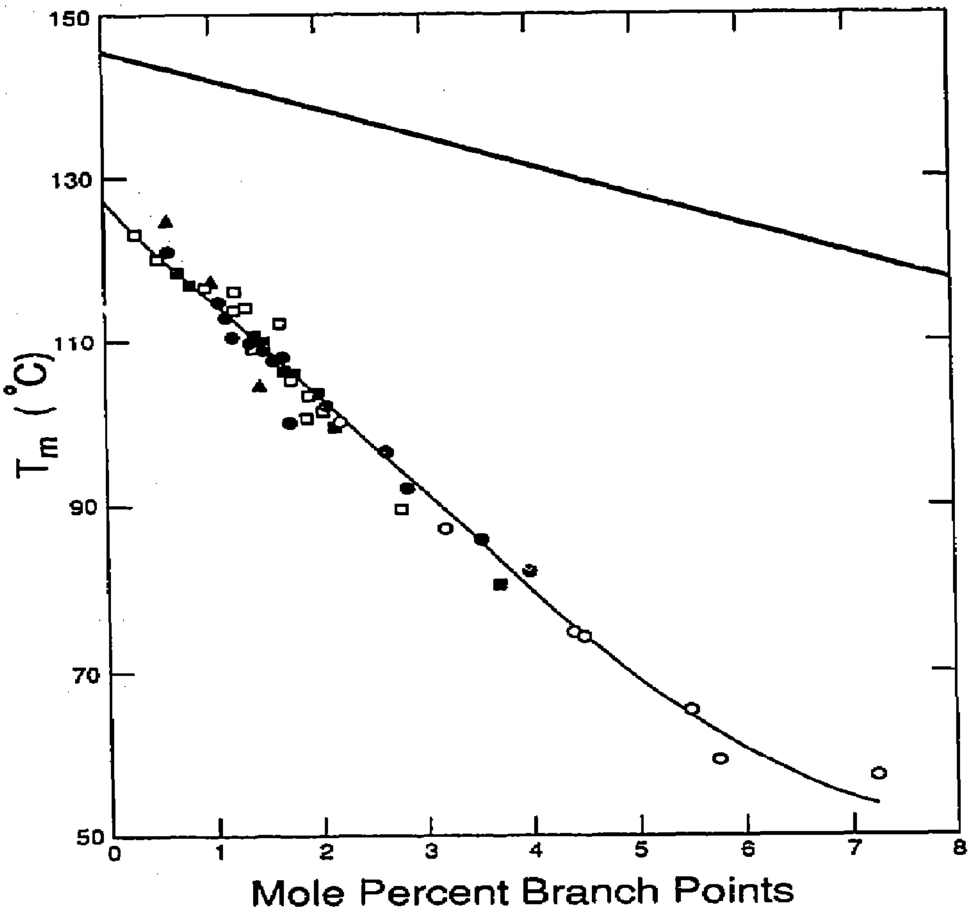

Fig. 1. Melting temperatures of rapidly crystallized ethylene copolymers as a function of branching composition: ○, hydrogenated polybutadienes; □, ethylene–butenes; ●, ethylene–hexenes; ■, ethylene–octenes; ▲, ethylene–octene fractions. Solid thicker line represents equilibrium theory for random copolymers.

to avoid structural and morphological complications present after isothermal or slow crystallization. Although far from equilibrium this crystallization procedure is quite satisfactory for comparative purposes. We shall treat the branch type, co-unit content and molar mass as independent variables in the analysis that ensues.

The melting temperature–composition relation for a variety of copolymers, in the categories described above, is plotted in Fig. 1. (Here, and in all subsequent discussions the co-unit content is expressed as mole percent of branch points.) In this data set, the molar mass is fixed at 90 000 ± 20 000. Also plotted (based on eqn. (2) is the theoretical, equilibrium expectations for a random ethylene copolymer [5]. For this calculation T_m^0 is taken to be 418.5 K and $\Delta H_u = 970\,\mathrm{cal\,mol^{-1}}$ [37, 38]. The most important and significant finding in Fig. 1 is that there is no systematic deviation for the different type copolymers. The same results are obtained at a given co-unit content, irrespective of either the chemical nature of the branch or the polymerization method. Put another way, for this mode of crystallization, at a fixed copolymer composition, there is no effect of the source of the copolymer as long as a narrow composition and constrained molar mass distribution is studied. One can not rule out completely the possibility of small changes in the melting temperature. Exploring this possibility would require even more stringent control of molar mass and a more precise determination of melting temperatures. However, the conclusion can be reached that these copolymers possess essentially the same sequence distribution. The fact that side groups as small as ethyl or as large as hexyl (or even bulkier groups [7]) display identical melting temperature–composition relations is a good indication that they are not incorporated into the crystal lattice; i.e. the crystalline phase remains pure. This point will be discussed in more detail in Section 3.

The expectations from the equilibrium theory that exclude the branches from the crystalline lattice are, therefore, well supported by the experimental results shown in Fig. 1. A decrease in the crystallite size is expected with increasing number of branches in a given chain due to the decreased number of crystallizable units. The melting temperature of the copolymer will accordingly decrease with increasing number of irregularities in the chain. Thus, the melting temperature varies from about 130°C for the linear polyethylene to approximately 70°C for the copolymers with 5 branches per 100 total carbons. The reduction of the melting temperature is very dramatic in the region of low branching, for example, the introduction of only 2 mol% branches in a linear polyethylene chain reduces its melting temperature by as much as 25°C.

The data in Fig. 1 describe a straight line up to 4 mol% branch points. The upward curvature observed in the high co-unit content data for hydrogenated polybutatienes could be related to differences in the sequence distribution. In fact, a comparison of the results from ^{13}C NMR [32, 35] indicates that hydrogenated polybutatienes have essentially a random distribution of ethyl side groups at the low co-unit content, but there is a slight tendency to develop a more ordered sequence distribution at higher co-unit content.

Although the experimental data follow the functional form of the theoretical equation, the melting temperatures are found to be systematically less than theoretical expectations. This result, typical of all types of random copolymers that have been studied, is not surprising since eqn. (1) requires that total equilibrium prevails throughout the system. As indicated in the Introduction, this is a very difficult condition to achieve even under the most stringent crystallization conditions. The results of Fig. 1 are consistent with theory and can be explained by experimental limitations.

Since the copolymers plotted in Fig. 1 were rapidly quenched prior to melting, the depression of their melting temperature with respect to the theoretical expectation will be larger than that obtained after slower crystallization conditions, in this case favoring the formation of thicker crystals. The reported dilatometric determined melting temperatures of some of the hydrogenated polybutadienes and fractions from Fig. 1, slowly crystallized, are a good example of this situation [9]. Increasing the number of randomly distributed branches will cause a decrease in the average crystallite thickness as well as reducing the concentration of the longer sequences required for equilibrium. Both of these factors cause a reduction in the melting temperature relative to the equilibrium expectation.

The equilibrium melting temperature of a copolymer is obviously a quantity of importance. However, except by theory, where certain conditions have to be a priori specified, it is very difficult to attain. The adoption of slow heating rates, subsequent to high temperature crystallization does not alleviate the problem. The conventional extrapolation method of analyzing the dependence of the crystallization temperature on the melting temperature, so successful for homopolymers [39–43], fails in the case of random copolymers, when carried out properly [33]. Extreme caution must be exercised when employing this method with copolymers [33].

The influence of the sequence distribution on the melting temperature is illustrated in Fig. 2. Here an ethylene–butene copolymer, prepared with a heterogeneous type catalyst was fractionated by composition and molar mass. The melting temperatures of the rapidly crystallized fractions are plotted in Fig. 2. In this data set the molar mass is again fixed at 90 000 ± 20 000. The curve from Fig. 1 for the random copolymers is also given as a reference. The melting temperatures of these particular ethylene–butene fractions are significantly higher than the other random copolymers. These differences are about 5°C for 0.5 mol% side groups and increase to 10°C at about 3 mol%.

The differences in melting temperature between these ethylene–butenes and the other copolymers can not be attributed to the chemical nature of the side groups since a direct comparison can be made with the hydrogenated polybutadienes and the other ethylene–butenes. These three type copolymers are chemically identical. On the basis of eqn. (2) we must therefore conclude that the melting point differences are a result of different sequence distributions between the particular ethylene–1-butene copolymers studied and the others. In the composition range of present interest, i.e. the order of a few mole percent co-unit, only very small differences in the parameter p can cause melting point differences of the magnitude observed here. For example, for a random sequence copolymer such as hydrogenated polybutadiene, $p = 0.980$ for 2 mol% side group content. For the melting temperature of the 2 mol% ethylene–1-butene copolymer the calculated value of p would be 0.9875. A similar conclusion is reached in the analysis of the higher co-unit content samples. Therefore,

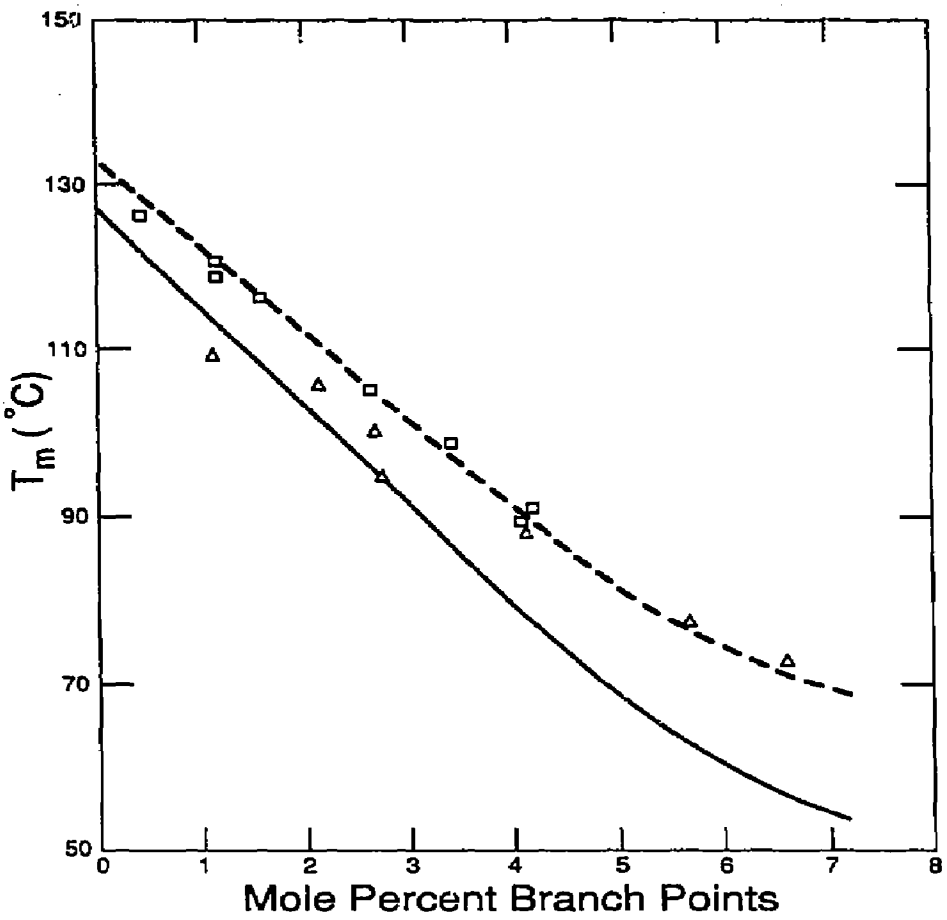

Fig. 2. Melting temperatures of rapidly crystallized ethylene copolymers as a function of branching composition: □, ethylene–butene fractions. △, ethylene–vinyl acetate fractions. Solid line represents random behavior from Fig. 1.

for the type of samples under present discussion the differences in melting temperatures between the ethylene-1-butene and the copolymers represented by the solid line in Fig. 2 are not caused by any inherent difference in the chemical nature of the side group.

Melting point differences of this order were also observed by Springer et al. in similarly constituted ethylene–butene fractions [44, 45]. In their report, the composition of the hydrogenated polybutadienes, as well as the other copolymers, were incorrectly extracted from Figs. 3 and 4 of ref. 9. As a consequence an anomalous compilation of melting temperatures was given [44]. This misinterpretation of the data was corrected subsequently [45]. It was then found that when the correct branching content was used, the melting temperatures of the ethylene–butene fractions studied by Springer et al. agreed with the non-random behavior of the ethylene–butene copolymers that were originally reported. Other examples of differences in sequence distribution caused by different polymerization procedures are the two ethylene–butenes studied by Kimura et al. [46]. In spite of using the same supported catalyst system, the fractions from the slurry polymerization product gave systematically higher melting temperatures than the fractions obtained from the product of a high-pressure tubular reactor. A comparison of these results with those of Fig. 2 points toward differences in the sequence distribution of both copolymers, the product from the tubular reactor having the ethyl branches more randomly distributed. In fact, ^{13}C NMR analyses of both series of fractions indicated a higher tendency for the ethyl branches to group in the slurry polymerized ethylene–butenes [46]. Systematic, although smaller, differences were also found in two series of fractionated ethylene–octene copolymers and interpreted as being a consequence of differences in the sequence distribution [47]. Hosoda [10] studied melting temperature–composition relations of various ethylene–butenes, ethylene–hexenes, ethylene–octenes and ethylene–4-methyl pentenes obtained from different sources. Among the four series of fractions of ethylene–butenes, three of them presented identical melting temperature–composition relations. However, the melting temperatures of the fourth series were between 3 and 10°C higher than the others and are thus characteristic of a more ordered sequence distribution. The ethylene–octenes and ethylene–4-methyl pentenes showed the same behavior between them, but their melting temperatures were lower than those of the ethylene–butenes. The ethylene–hexene copolymers showed melting temperatures intermediate between those of the ethylene–butenes, and the ethylene–octenes (or ethylene–4-methyl pentenes). This decrease of melting temperature with increasing size of the branch, at a fixed branching content, was identified with a different degree of incorporation of branches in the crystal. Although this is an attractive interpretation, there is the distinct possibility that these series of copolymers have different sequence distributions. This possibility was only investigated within ethylene–butenes and not for the copolymers with different types of branches [10]. The conclusion reached by the author of different branching incorporation in the lattice is inconsistent with the data in Fig. 1 and as will be discussed in Section 3; it is untenable in terms of other types of studies. In addition, some of the variation in melting temperatures may be related to the influence of molar mass, which was not treated as an independent variable in this study [10].

A set of ethylene–vinyl acetate copolymer fractions, obtained from free-radical polymerized polymers are also plotted in Fig. 2 [9]. The two lowest acetate content fractions follow the solid line. The others deviate somewhat from the random behavior. In analogy to the situation found in the ethylene–butene fractions, there must also be small differences in sequence distribution between the ethylene–vinyl acetates and the other copolymers. The difference in melting temperatures is more accentuated for concentrations of 4 mol% and higher, indicating a higher tendency of these ethylene–vinyl acetate copolymers to develop a more ordered sequence distribution at high co-unit concentrations. Analysis of these fractions by ^{13}C NMR corroborates that the branches become more ordered with increasing vinyl acetate content [9].

Many properties of crystalline polymers are dependent on chain length [19–31]. The phase structure that defines the crystalline state can be varied over wide limits by changing the molar mass and/or the crystallization conditions [13, 24, 25, 28, 33, 48–51]. Since random copolymers would be expected to behave in a similar manner, the influence of molar mass as an independent variable needs to be investigated in more detail. It has been found for many of the heterogeneous ethylene–1-alkene fractions studied that the less branched fractions have the highest molar mass [10, 44, 52–58]. The melting behavior and other structural properties have usually been studied as a function of branching composition in these series of fractions [10, 44, 57–59] and general conclusions for random copolymers have been drawn. The possible role of molar mass in influencing the results was not recognized.

A definite influence of the molar mass on the melting temperature and degree of crystallinity was observed in low density polyethylene fractions of approximately constant total branching content [60–63]. Similar effects were also observed by Hser and Carr [64] for hydrogenated polybutadienes. These results were confirmed in more detailed studies of hydrogenated polybutadienes having approximately 2.3 ethyl branches per 100 carbons [33]. A decrease in the melting temperature of the order of 7–8°C was observed with increasing chain length in the range between 4500 and 500 000. These results are unexpected since melting temperatures are usually reported to increase with molar mass for both homopolymers and copolymers. The melting temperature–molar mass dependence observed for hydrogenated polybutadienes was confirmed with studies of several series of random ethylene copolymers where the type of branch, the composition and the molar mass were independently varied. Figure 3 shows melting temperature–molar mass relations for compositional series of homogeneous ethylene–1-hexene copolymers [34]. Four different series with branching contents of approximately 1.1, 1.4, 1.7 and 2.6 mol% and molar masses from 10 000 to 500 000 are represented in this plot. For each series illustrated the observed melting temperatures decrease with increasing chain length in analogy to the results for the hydrogenated polybutadienes.

The influence of molar mass on the melting temperature is not specific to a given copolymer type but is a general phenomenon for all types of branches as is illustrated in Fig. 4 [34]. Here data for ethylene–hexenes, ethylene–butenes, ethylene–octenes and the model hydrogenated polybutadienes are presented. Results for linear polyethylene fractions have been included for comparison. The data generate a family of curves each

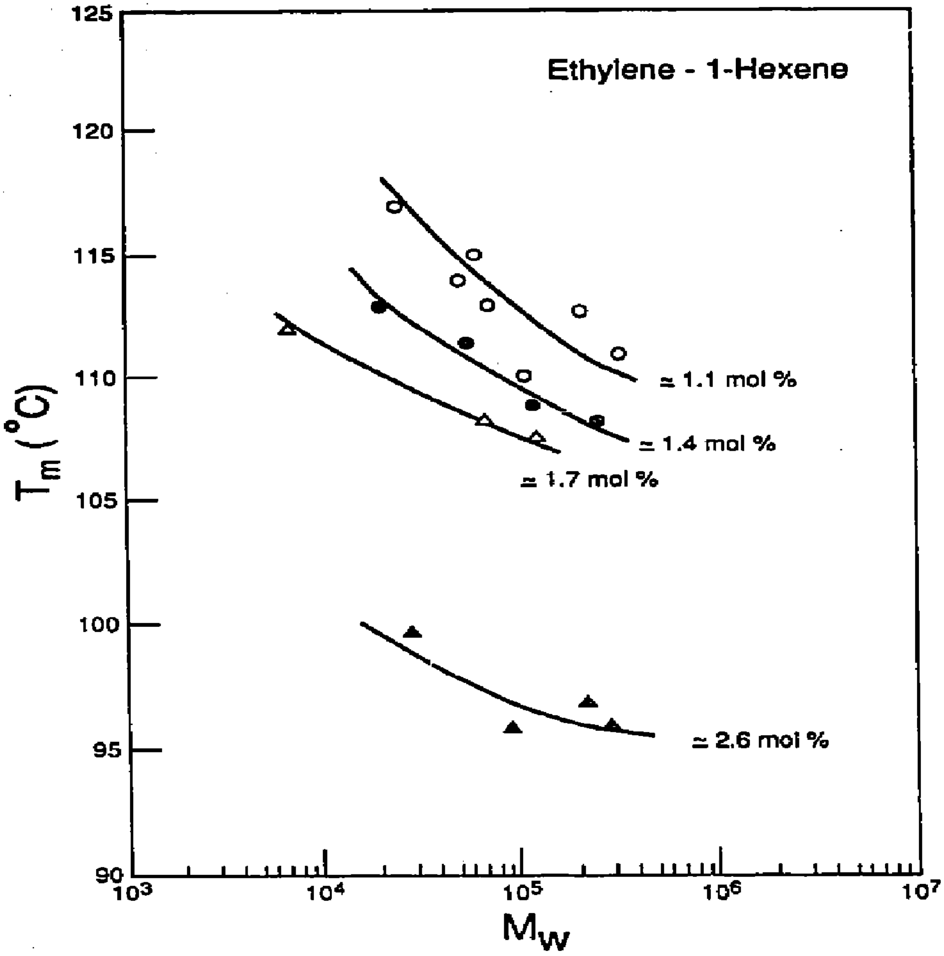

Fig. 3. Melting temperatures plotted against molar mass for different series of rapidly crystallized ethylene–1-hexene copolymers. Each series contains the fixed branching content indicated in the figure.

dependent on the co-unit content, but independent of the chemical nature of the co-unit. The plots indicate that the less branched copolymers display a steeper decrease of the melting temperature with molar mass than those with a higher concentration of branches. For example, in the molar mass range between 2×10^4 and 3×10^5, the melting temperatures of the copolymer series with approximately 1.1 mol% of branch points differ by 7°C. This difference is almost reduced by half for the series that contains 2.6 mol% of branch points. In contrast, the rapidly crystallized linear polyethylene only shows a very small variation of the melting temperature with increasing molar mass. The influence of molar mass is much more marked for the copolymers, especially in the series with the lowest branching content and in the range of molar mass between 5000 and 100 000. The melting temperatures level off above a molar mass of about

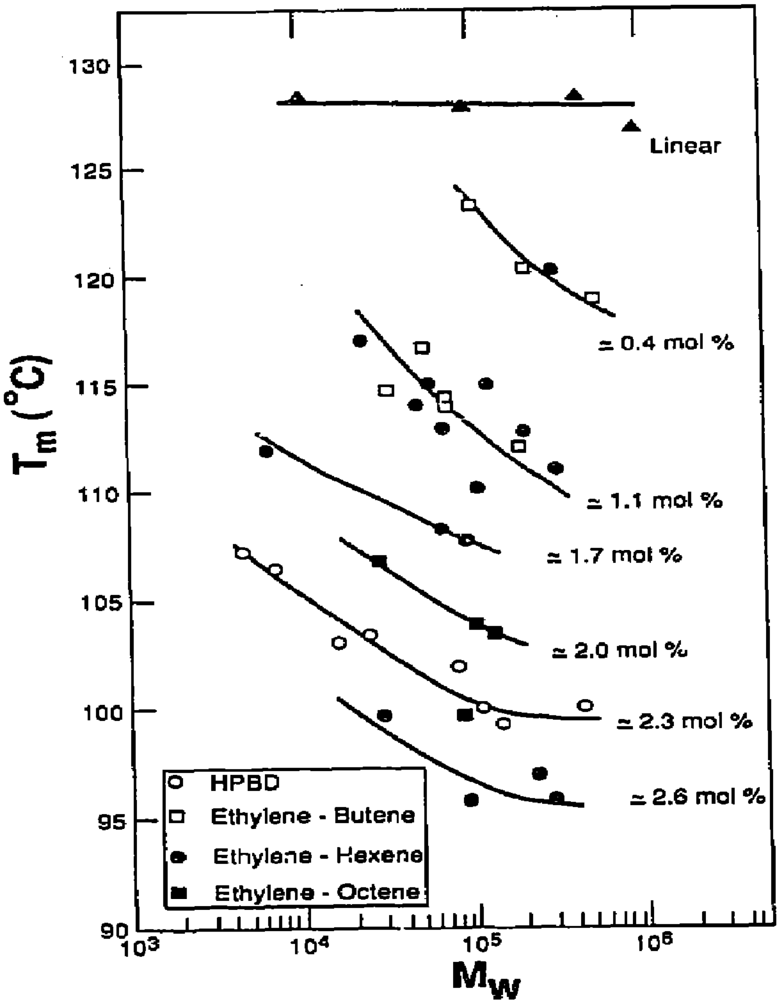

Fig. 4. Melting temperatures plotted against molar mass for series of rapidly crystallized ethylene copolymers having a fixed branching content. The copolymers and number of branches per 100 carbons are indicated in the figure. ▲, rapidly crystallized linear polyethylene fractions.

100 000 for the higher co-unit copolymer (2.3 and 2.6 mol%). The implication of these results is that if the chain length dependence is only studied in this range, the general decrease of T_m with M_w would not be observed [44] and incorrect conclusions would be made.

The reduction of the melting temperature with increasing molar mass in quenched random copolymers is a consequence of the decreased crystallite thickness. An explanation for the formation of smaller crystals with increasing molar mass is related to the slower crystallization kinetics due to the increase in entanglements [13, 33]. These and other aspects of the structure of the copolymer crystals will be analyzed further in Section 5.

The need for considering the influence of the chain length is important not only in studying melting temperatures, as Figs. 3 and 4 demonstrate, but also when studying other aspects of the phase structure. One can not ignore the molar mass effect and consider only the composition relations. For some properties, such as the melting temperature, the effect of increasing co-unit content is opposite to decreasing the molar mass.

3. LATTICE STRUCTURE

A central question that has prevailed in the study of this class of copolymers has been what type of co-unit, if any, enters the lattice. A corollary question is how the branches enter the lattice, i.e. do they do so as a non-equilibrium defect or as an equilibrium requirement. A wide variety of experimental methods have been employed to address this problem. These include analysis of melting temperature–composition relations, lattice expansion, X-ray and neutron scattering, selective oxidation, and NMR, to cite but a few techniques that have been used.

Solid state ^{13}C NMR methods, have the potential to quantitatively describe the distribution of side-groups between the crystalline and liquid-like regions. Thus, this method addresses the problem directly. Several pertinent studies have appeared [65–70] that have greatly aided our understanding. ^{13}C NMR studies of the relaxation behavior of the side-chain carbons of copolymers comprised of $^2H_4$-ethylene copolymerized with protonated 1-alkenes were carried out [67].

The co-units ranged from propene to 1-octadecene. The short T_1 values (the spin–lattice relaxation time) and the single exponential decays of the methyl, α and β carbons supports the concept that the branches are concentrated in a single mobile phase, presumably the liquid-like region. No evidence was found for the incorporation of these side-groups into the crystalline phase. However, some of the directly bonded methyl groups of the 1-propene copolymers may be incorporated within the lattice, according to this NMR study. ^{1}H and ^{13}C spectra and spin–lattice relaxation behavior, in the laboratory frame (T_1) and rotating frame ($T_{1\rho}$), confirm the conclusion with regard to ethyl and butyl branched copolymers [67, 68]. The side chain resonances have short $T_{1\rho}$ times and hence are associated with the mobile disordered region.

Pulsing techniques with ^{13}C NMR have been adopted that allow for a discrimination to be made between resonances assigned to the crystalline or amorphous regions [66]. It was found for an ethylene–propene copolymer that a small quantity of methyl groups are incorporated within the crystal lattice. In contrast, longer branches, ethyl, butyl and hexyl, are located primarily in the liquid-like interfacial regions. The distribution between these two regions depends on the crystallization conditions. Resonances due to the side-groups within the crystalline region, were not detected with the limits of the instrument sensitivity.

Solid state ^{13}C NMR studies have also been reported for a hydrogenated polybutadiene that contained 1.7 mol% ethyl branches [69]. It was concluded, that at the most, about 5% of the total branches were located within the crystalline region. No real, or effective, distinction was made between the crystalline and interfacial region in this particular study. In a study using similar methods, involving a very polydisperse broad composition ethylene–butene copolymer, it was found that about 9% of the total branches were incorporated into the crystal lattice [70].

From these diverse NMR studies that have been directed to this specific problem some general conclusions can be reached. Groups larger than directly bonded methyl are excluded from the lattice. If groups as large as ethyl are accommodated within the lattice, their concentration must be very small.

Chemical methods, usually selective oxidation involving either fuming nitric acid or ozone, have also been used to determine the partitioning of the co-units between the crystalline and non-crystalline region. The method is based on the demonstration with linear polyethylene that the non-crystalline region can be separated from the crystalline core by selective oxidation [71]. The residue, which is presumed to be composed of only the crystalline core is analyzed for branches by conventional IR, ^{13}C NMR or radioactive tagging. A basic problem with this procedure, particularly important for copolymers, is the need to establish the reactivity of the interfacial region and to decide whether it is penetrated by the oxidizing agent. If the interfacial region is not easily removed it has to be considered as being part of the residual crystallite core. It can be expected (see below) that the interfacial region will have a higher content of non-crystallizing co-units. Consequently the experimental results and interpretation will be altered accordingly. With the recognition of this difficulty, it is of interest to examine the results that have been obtained by these chemical methods.

A large number of studies of high pressure, long-chain branched polyethylenes and ethylene copolymers, using these methods have been reported [72–79]. A typical set of results obtained during the selective oxidation by fuming nitric acid of a bulk-crystallized unfractionated (with respect to both molar mass and composition) ethylene–1-butene copolymer is given in Fig. 5. This copolymer contains 3.7 ethyl branches per 100 carbon atoms [72]. The weight loss reaches an apparent plateau after about 6 h of oxidation. About 60% of the sample was removed at this time, corresponding to the initial level of crystallinity of about 40%. Within the same time frame, the ethyl branch content drops to the experimentally negligible value of 0.08%. Within the constraints of the experiment we can conclude rather confidently, that the ethyl branches do not enter the lattice. Put more formally, these groups are easily accessible to the oxidizing agent, while the crystallite core of about 40% of the material remains intact.

Studying similar types of copolymers containing either ethyl, butyl or

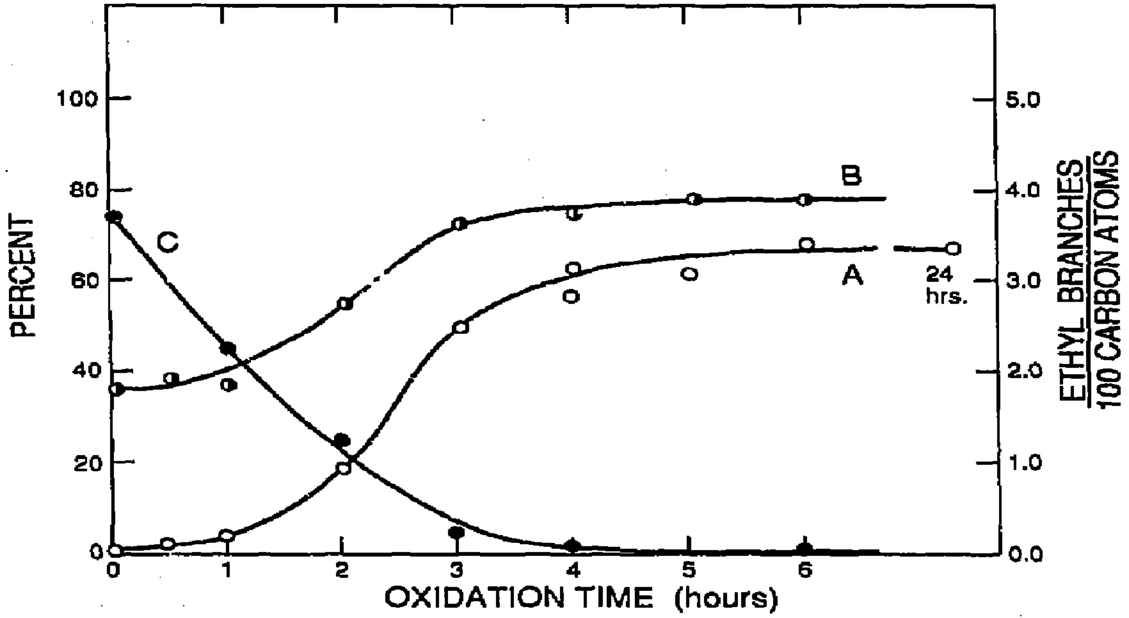

Fig. 5. Percent weight loss (A), percent crystallinity (B) and the number of ethyl branches per 100 carbon atoms (C), of a 0.911-density ethylene–1-butene copolymer versus oxidation time in fuming nitric acid.

hexyl side groups France et al. [79] found that 90%, or more, of the branch groups were removed by this selective oxidation techniques. The results were essentially the same for all three types of branches. In these copolymers the vast majority of the branches are excluded by far from the interior of the crystalline core. Although it is possible that the very small amount of residual branch groups is located within the crystallite interior there is a very strong likelihood that the branches are located in the first few layers of the interface. They would thus be relatively inaccessible to the oxidizing agent.

^{13}C NMR methods, combined with selective oxidation, have been used to determine the location of the side chains in high pressure, free-radical polymerized long chain polyethylene [77–79]. It was found that the ethyl and butyl groups, the most predominant short-chain branch occurring in these polymers, were mainly excluded from the lattice. Not surprisingly, the long chain branches can co-crystallize with the main chain.

Analogous studies with copolymers crystallized from dilute solution have led to very similar conclusions [73, 80]. The directly bound methyl groups were found to be only partially accessible to the oxidizing reagent. In contrast, the ethyl branches were essentially completely removed. For example, for an ethylene–butene copolymer the branch content falls from 1.84 to 0.1 mol%, or a 95% branch loss, over the time it takes for the residual weight to level off. For ethylene–propylene copolymers about 25–33% of the methyl groups are retained within the lattice.

These chemical methods and the NMR results are in essential agreement that the alkyl branches are located outside of the crystalline core. If any side-groups, besides directly bonded methyls, are located within the crystallite their concentration must be very small. If inaccessible they could be located within the first few layers of the interfacial region. In contrast, there is very strong evidence that the directly bonded methyl groups of the ethylene–propylene copolymers are present within the lattice in significant concentrations.

A variety of scattering methods have also been used to address the problem of the distribution of co-units among the phases. Kalepky et al. [81] combined the measurement of the integrated intensities of small-angle neutron and X-ray scattering to determine the extent of partitioning of a randomly chlorinated polyethylene. Based on a two-phase model it was concluded that there was a significant distribution of the Cl groups between the two phases. Roe and Ganiewski [82, 83] studied the same type of copolymer by measuring the absolute intensity of the small-angle X-ray scattering. It was also concluded from these studies that the chlorine atoms enter the lattice. Small-angle X-ray scattering of a series of ethylene–phosphonic acid copolymers has shown that in this case the branch groups are not incorporated into the crystal lattice to any appreciable extent [84]. This is not an unexpected result considering the size of the branch groups.

From a set of wide and small angle X-ray experiments, Vonk and co-workers [85–87] concluded that 20–40% of the side groups of an ethylene–vinyl acetate and ethylene–acrylic acid copolymers and of a high pressure branched polyethylene are included in the lattice. The conclusion is based on the difference between the density obtained from the small-angle invariant and that obtained from the lattice parameters determined by wide angle X-ray diffraction. This difference is attributed to the inclusion of the side groups in the lattice. However, the interpretation of the invariant with the more complex morphology of a copolymer is not straightforward. In addition, as will be discussed below, there are other major reasons, besides branch incorporation, that can cause the lattice to expand. These two factors appear to be the main reason for the conclusion that the bulky side-groups were incorporated to such a large extent [87]. This conclusion is clearly in disagreement with the results just discussed and the melting temperature–composition relations for the ethylene–vinyl acetate copolymer with low co-unit content previously cited.

The analysis of the lattice parameters by means of wide angle X-ray diffraction has been a popular method used to study the internal crystallite structure and presumably its composition. Early in the study of low density polyethylene (the type that contains both short-chain and long-chain branches) it was found that the lattice expands in both the *a* and *b* directions with the *a* spacing being the dimension predominately affected [88]. The cross-sectional area was found to increase with branching. A significant variation of the unit cell density from 1.01 to 0.96 g cm^{-3} resulted. Further, early work with ethylene–propylene as well as with other alkene-1-copolymers also showed a significant increase in the lattice cross-section with branching content [89–91]. These results immediately led to the conclusion that the lattice expansion was caused by the inclusion of the co-units within the crystallite [90, 91]. The influence of the length of the branch on the magnitude of the expansion was also of interest. However, conflicting reports appeared [90–94]. For example, it has been reported that the effect of the butyl group is only imperceptibly different from methyl [94]. In contrast it has been stated rather definitely that methyl and ethyl groups may be accommodated within the lattice but butyl groups are not [94]. It has been clearly shown that the methyl group causes a greater lattice expansion than the *n*-propyl group [93]. In contrast, significant expansion of the *a* and *b* dimensions are claimed for *n*-decane side-groups [92].

The lattice expansion results, and their interpretation, are confusing. The quantitative influence of specific side-groups can be clarified by further experimentation. However, the significance of the lattice expansion itself is in need of further discussion. The initial interpretation that the co-unit must be entering the lattice is in contradiction with the melting temperature data just described and further thermodynamic analysis to be given. Seguela and Rietsch [95] have considered a specific aspect of the problem by analyzing which side groups can be accommodated within the lattice by the introduction along the backbone of the chain of the popularly postulated g^+tg^- defect. Here in place of the usual sequence of three trans C–C bonds, a trans bond is flanked by two gauche bonds of opposite sign. They found that a methyl group could be accommodated at interstitial positions. However, this conformational defect does not provide enough volume to accommodate ethyl and higher alkyl groups. Other types of defects would have to be postulated to allow the larger groups to enter the lattice, if they indeed do so. Granted that lattice expansions are experimentally observed with branches greater than methyl, the question arises whether this requires the co-unit to enter the lattice.

It is well documented that copolymers form very thin crystallites so that the lateral dimension may be altered by the local stress exerted at the basal planes [11]. Bunn [96] suggested that because of the reduced crystallite thickness the *a*-axis expansion could be caused by strain at the interphase due in part to the congregation of co-units in this region. From this point of view the lattice expansion does not necessarily reflect internal defects within the crystallite. In support of this concept has been the observation that the lattice expansion, as described by $ab/2$, is observed in linear polyethylene, both solution and melt crystallized [97] and in the *n*-alkanes [97, 98]. Furthermore, the expansion is inversely proportional to the lamellar thickness. Thus, it is demonstrated that the lattice expansion occurs when the crystallite thickness is decreased. In these cases there are no branches to be included within the lattice. However, similar relations have been found for hydrogenated polybutadienes [99] and a variety of ethylene copolymers [100, 101]. Analysis of the data relating the cross-sectional area of the unit cell to the crystallite thickness has led Vonk [100] to conclude that side-groups such as those occurring in low density polyethylene and ethylene–vinyl acetate copolymers play only a minor role in the expansion of the lattice. The major effect is caused by the reduced crystallite thickness. An exception to this generalization is the behavior of ethyne–propylene copolymers. For this copolymer there is a much greater increase in the cross-sectioned area at a given thickness as compared to the others [100, 101]. Thus, to account for the larger lattice expansion, the smaller CH_3 group can be assumed to be located, in part, within the crystallite lattice. The role played by the interfacial structure in causing the lattice expansion is further illustrated by the changes that occur during selective oxidation. For the copolymer sample described in Fig. 5 the initial *a* dimension is 7.493 Å relative to 7.4175 Å for the corresponding homopolymer [72]. During the course of the oxidation reaction this dimension decreases to 7.433 Å. Although the value of the homopolymer is not quite attained, these results demonstrate that a significant lattice expansion occurs without the co-unit being occluded and that the lattice contracts as the stresses within the interface are being alleviated. Similar results are found for copolymer crystallites formed in dilute solution [102].

The results obtained by a variety of experimental methods, which were described above, have made abundantly clear that side groups greater than methyl are effectively excluded from the crystalline lattice. One would then expect that such copolymers, having the same type of sequence distribution, should have the same thermodynamic properties. This conclusion was substantiated by the melting point relations given in Fig. 1. On this basis one would expect that the melting temperature of ethylene–propylene type copolymers should behave differently. This expectation is indeed fulfilled as shown in Fig. 6. Here the melting temperature of copolymers formed by the decomposition of the diazoalkanes are given [11]. In the synthesis of these copolymers special measures were adopted to assure the random distribution of co-units. Therefore, a valid comparison can be made with these data of the influence of the different type co-units. In Fig. 6, the melting temperature–composition relation falls into two groupings. The methyl branched copolymers are consistently and significantly higher than those with ethyl and *n*-propyl branches. The results for the other copolymers are independent of the nature of the branch as would be expected since the crystalline phase remains pure. These results are for slow heating rates [11]. When extrapolated melting points are used, a maximum in the melting temperature–composition diagram for the methyl branched copolymer is observed [6]. The difference in melting temperatures between copolymers with directly bonded methyl groups and those with longer alkyl branches

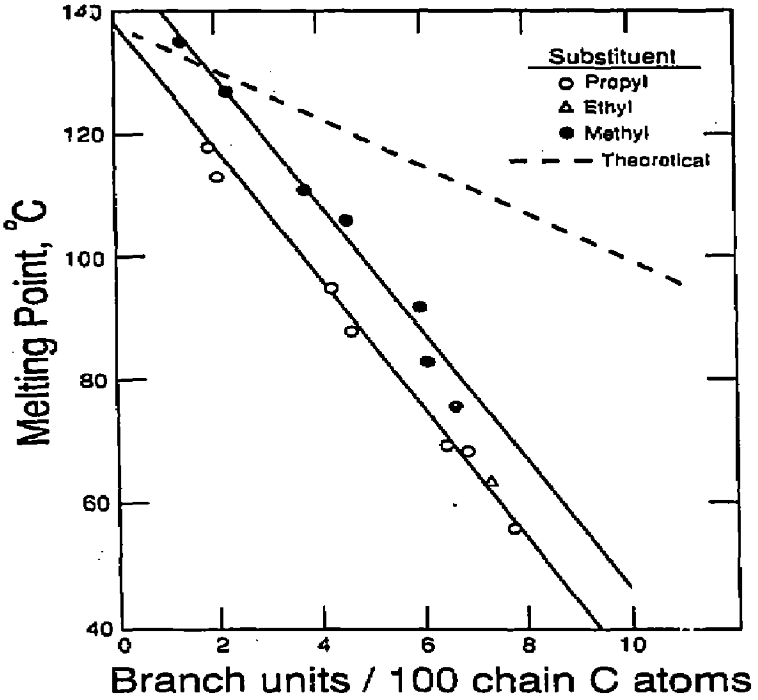

Fig. 6. Melting temperatures as a function of co-unit for a series of random copolymers prepared by the decomposition of diazoalkanes. Dashed line represents equilibrium expectations.

have been observed by others [92]. The initial elevation of the melting temperature with increased concentration of co-unit is strong evidence for solid-solution (or compound formation) of the copolymer with directly bonded methyl groups. The observed melting point relation gives prima facie evidence that the $\mathrm{CH_3}\!>\!\mathrm{CH}-$ group is part of the crystalline phase on an equilibrium basis. This conclusion is in accord with the other evidences reported. The fact that the methyl group is accommodated within the lattice should not only influence the melting temperature but other elements of phase structure as well. As we shall see shortly this expectation is fulfilled.

The melting temperature–composition relation for ethylene–vinyl chloride copolymers [103] is virtually identical to that for ethylene–propylenes [6, 11]. Hence, we can conclude that at least partially the $\mathrm{Cl}\!>\!\mathrm{CH}-$ group is also located within the crystallite on an equilibrium basis. This conclusion is in accord with scattering studies.

From the studies discussed above it can be concluded that a portion of small substituents, such as CH_3, Cl, O, and OH, enter the lattice on an equilibrium basis. Larger side-groups such as ethyl, propyl, butyl, hexyl, methacrylic acid and acetate do not enter the lattice to any appreciable extent. Consequently, the melting temperature and other thermodynamic properties are independent of the chemical nature of the co-unit but depend only on the copolymer composition. In retrospect it should be realized that these definitive conclusions could not be reached by depending on only one experimental method. A variety of techniques need to be utilized so that all aspects of the problem are examined.

4. DEGREE OF CRYSTALLINITY

An important element of phase structure is the degree, or level of crystallinity. It has been shown to be a quantitative concept for both homopolymers and copolymers. The level of crystallinity is plotted in Fig. 7 as a function of co-unit content for copolymers with a molar mass of about 100 000, after rapid crystallization [34]. This plot represents a comprehensive set of data that includes the model hydrogenated polybutadienes,

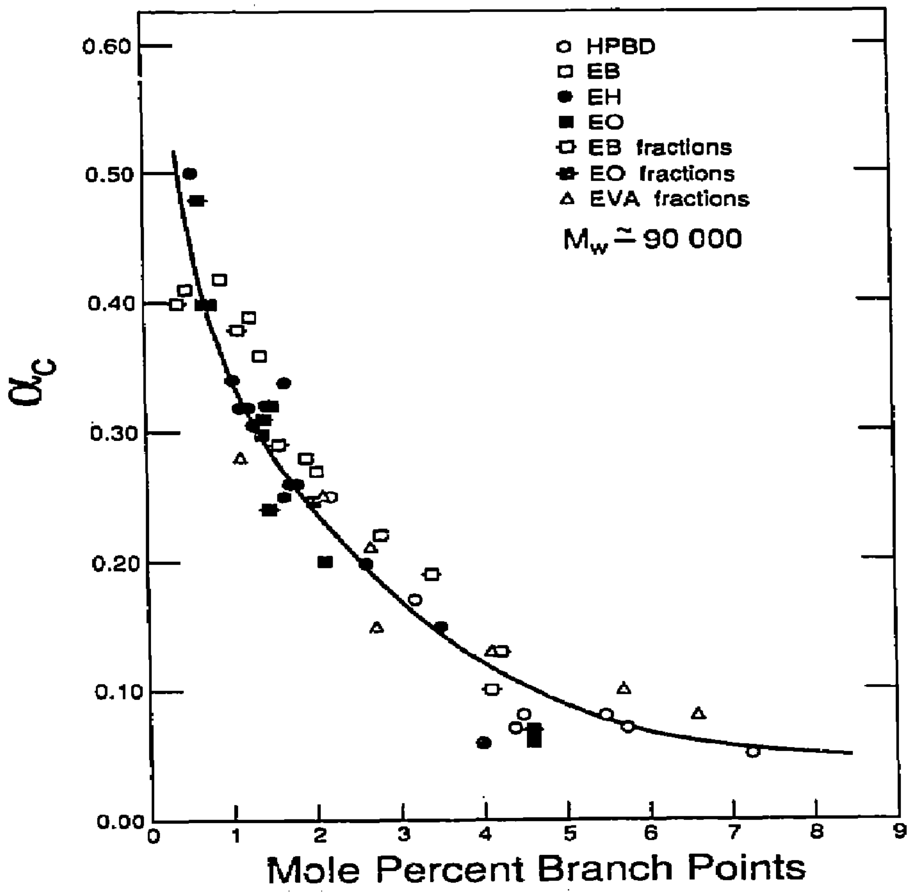

Fig. 7. Plot of degree of crystallinity calculated from Raman internal modes α_c against mole% branch points for the indicated copolymers. Solid line from ref. 12. HPBD, hydrogenated polybutadiene; EB, ethylene–1-butene; EH, ethylene–1-hexene; EO, ethylene–1-octene; EVA, ethylene–vinyl acetate. Samples quenched into a dry ice–isopropanol mixture.

fractions of ethylene–vinyl acetate and ethylene–1-alkenes as well as ethylene–butene, ethylene–hexene and ethylene–octene copolymers with most probable molar mass distributions [12, 34]. The degree of crystallinity α_c was calculated from an analysis of the Raman internal modes [49, 104–106]. It is evident that the introduction of the non-crystallizing co-units into the chain leads to a very rapid and continuing decrease in crystallinity with increasing side group content. Levels of crystallinity vary from about 48% for 0.5 mol% branches to about 7% for 6 mol% branches in the copolymer. The major changes in the crystallinity level occur with the initial introduction of 1–2 mol% of branch groups. An extrapolation of the data indicates that a completely non-crystalline system will be achieved with random type ethylene copolymers at about 10 mol% of branches.

The chemical nature of the branch does not influence the crystallinity values for a given co-unit content. With just minor, non-systematic variations, the data are well represented by the solid curve of Fig. 7. This comprehensive set of data contradicts previous reports [10, 92, 107]. It has also been reported that random sequence copolymers of ethylene–phosphonic acid behave similarly to the ethylene–vinyl acetates [84]. This fact, and the behavior shown in Fig. 7, support the previous conclusion that these units do not enter the crystal lattice.

The differences in melting temperatures observed in Fig. 2 between the ethylene–butenes and some ethylene–vinyl acetate fractions and the random copolymers are not reflected in the crystallinity levels of Fig. 7. The differences in melting temperatures were attributed to small differences in the sequence propagation probability. An explanation for this apparent discrepancy can be found by examining equilibrium theory [5]. Small differences in the parameter p of eqn (1) significantly affect the level of crystallinity at high temperatures (close to melting). At low temperatures, equivalent to the crystallization conditions of these copolymers, and in the range of values for p of interest here, the calculated level of crystallinity is basically unaffected by small changes in p. In the actual non-equilibrium conditions the differences will be even less. It is also expected that slower crystallization conditions would make this difference larger. This is confirmed in a variety of data reported on ethylene–butenes and other ethylene copolymers which were slowly cooled from the melt and had clear differences in the sequence distribution [10, 44, 92].

We should also note that the level of crystallinity that is attained in an actual crystallization process is not a measure of the minimum sequence that participates in the crystallization. Rather it is the sum over all possibilities.

The relation described in Fig. 7 would not be expected to hold for copolymers where the branch is incorporated [illegible] such copolymers as the ethylene–propenes and [illegible] polyethylenes, where it has been established that [illegible]

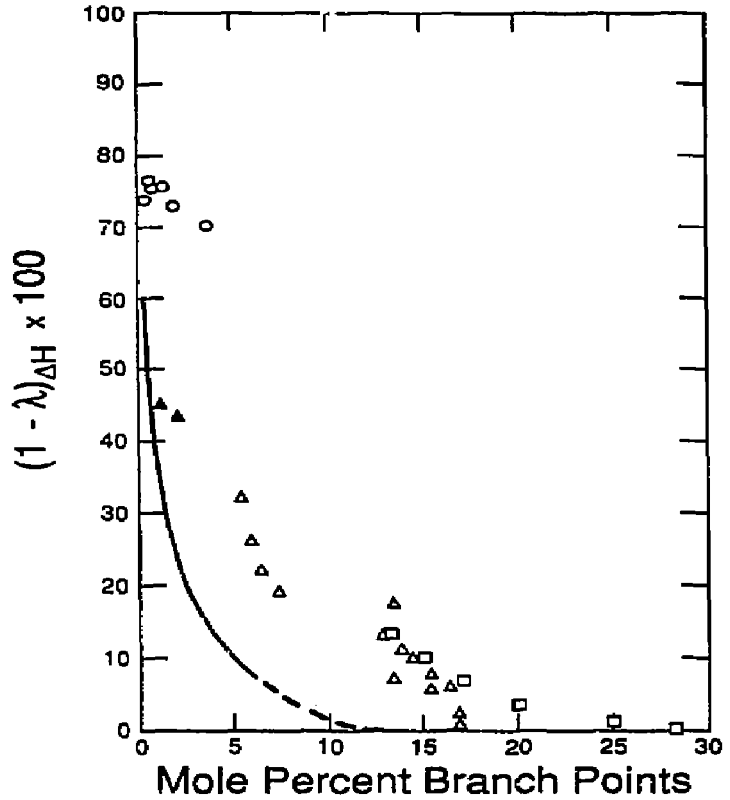

Fig. 8. Plot of degree of crystallinity calculated from heat of fusion versus mol% branch points for ethylene–propylene copolymers: ○, from ref. 92; △, from ref. 108; □, from ref. 109; ▲, from ref. 26. Solid line extracted from Fig. 7.

the co-units between the two phases, higher crystallinity levels should be observed. This expectation is indeed fulfilled as is illustrated in Fig. 8. Here, a compilation of the literature values for the crystallinity level of rapidly crystallized ethylene–propene copolymers is given [26, 92, 108, 109]. The samples reported by Ver Strate et al. [108] and Axelson et al. [26] have molar masses of 200 000 ± 50 000. The molar masses of the rest of the data included in this figure were not reported. For comparative purposes, the solid curve of Fig. 7, for random copolymers where the co-units are excluded, is also given. We note immediately that for this copolymer the crystallinity levels are much higher than those shown in Fig. 7. A considerable amount of crystallinity still remains at about 10 mol% of branch points, a composition at which crystallinity has disappeared for those copolymers where the lattice remains pure.

Since we have found that the molar mass is an independent variable with respect to the melting temperature, we next examine its influence on the crystallinity level. Accordingly, the crystallinity levels calculated from the density, for a set of ethylene–butenes, ethylene–hexenes and hydrogenated polybutadienes are plotted in Fig. 9 as a function of molar mass [34]. The crystallinity levels of linear polyethylene fractions crystallized under the same conditions, are also included for comparison [19]. A family of curves is generated for each co-unit content. Compared to the crystallinity of linear polethylene fractions, 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 approximately 2.5% the crystallinity level is reduced to about 40%. The same type of chain length dependence is observed, irrespective of the branch type. The decrease in the crystallinity level of the copolymers with molar mass is very similar to that for linear polyethylene fractions. This similarity indicates that the mechanism operative in the linear chain is also applicable to the branched ones. Increasing molar mass increases the density of chain entanglements in the melt and thus reduces the ability of a chain to participate in the formation of a crystallite [19, 33, 110]. This phenomenon will be operative in copolymers as well as homopolymers.

In addition to the density, and the analysis of the internal mode region in Raman spectroscopy (examples shown in Figs. 7 and 9), other techniques can be used to determine the level of crystallinity. One of the most popular among investigators is to measure heat of fusion [9, 23, 24, 111–114]. In addition, the deconvolution of the halo obtained by wide angle X-ray scattering and the analyses of relaxation decay curves in ^{13}C NMR have also been used [10, 26, 59, 92, 113, 115]. The crystallinity levels calculated by these techniques do not always coincide for the same specimen crystallized in the same manner. Some of these differences can be attributed to specific aspects of the phase structure [9, 13, 24]. Other possibilities are still under consideration. For example, for a wide variety of bulk and solution crystallized linear polyethylenes and ethylene copolymers, it has been found that the density always yields between 10% and 15% greater values for the degree of crystallinity than does the enthalpy of fusion [9, 18, 24, 113, 116, 117]. Results for a considerable number of ethylene copolymers obtained from different laboratories, are shown in Fig. 10 and support this conclusion [9, 12, 26, 34, 108, 113]. The density determined crystallinity was universally found to be greater than $(1-\lambda)_{\Delta H}$. Data for commercial ethylene–1-propene copolymers have also been included in Fig. 10, [26, 108]. These copolymers also show higher crystallinity levels from density than those from heat of fusion. However, the values are closer to one another than the other copolymers. It has been suggested that the difference between $(1-\lambda)_d$ and $(1-\lambda)_{\Delta H}$ is due to the contribution of the interphase [9, 18, 24, 113, 118]. In fact, values of the interfacial content, calculated by other techniques, agreed quite closely with the difference shown in Fig. 10 [9, 18, 24, 117–119].

This degree of crystallinity calculated from heat of fusion agrees with α_c, the degree of crystallinity calculated from Raman internal modes

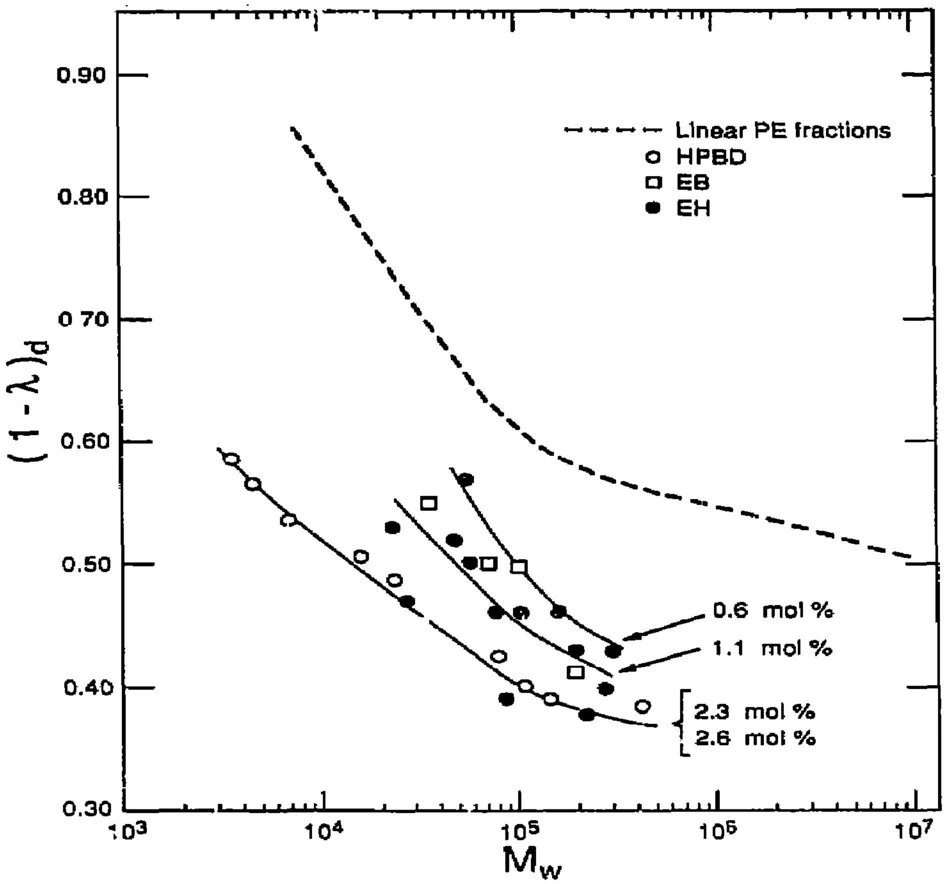

Fig. 9. Plot of degree of crystallinity calculated from density measurements, $(1-\lambda)_d$, against molar mass for different series of ethylene copolymers having a fixed branching content. The copolymers (as in Fig. 7) and the branching content are indicated in the figure. The dashed line represents the behavior of rapidly crystallized linear polyethylene fractions.

[24, 117, 118] and with α_{NMR}, the NMR calculated degree of crystallinity [26] for linear polyethylenes. However, for bulk or solution crystallized ethylene copolymers, $(1-\lambda)_{\Delta H}$ is about 5% higher than α_c or α_{NMR} [9, 24, 113]. The reason is related to the nature of the different measurements. Because the copolymers have a broad melting range, the analysis of fusion needs to be initiated below room temperature. Raman and NMR spectra are measured at room temperature. Hence, $(1-\lambda)_{\Delta H}$ includes the contribution of the small amount of crystallinity that disappears at room temperature.

A comprehensive comparison of $(1-\lambda)_{\Delta H}$ with $(1-\lambda)_X$, the crystallinity from wide angle X-ray scattering (WAXS) has not as yet been reported. The results that are available are not decisive. For example, the $(1-\lambda)_X$ of ethylene–propenes was found to be significantly higher than $(1-\lambda)_{\Delta H}$ [108]. The X-ray determined values were very close to the crystallinity values measured by density. A contribution from the interphase to both

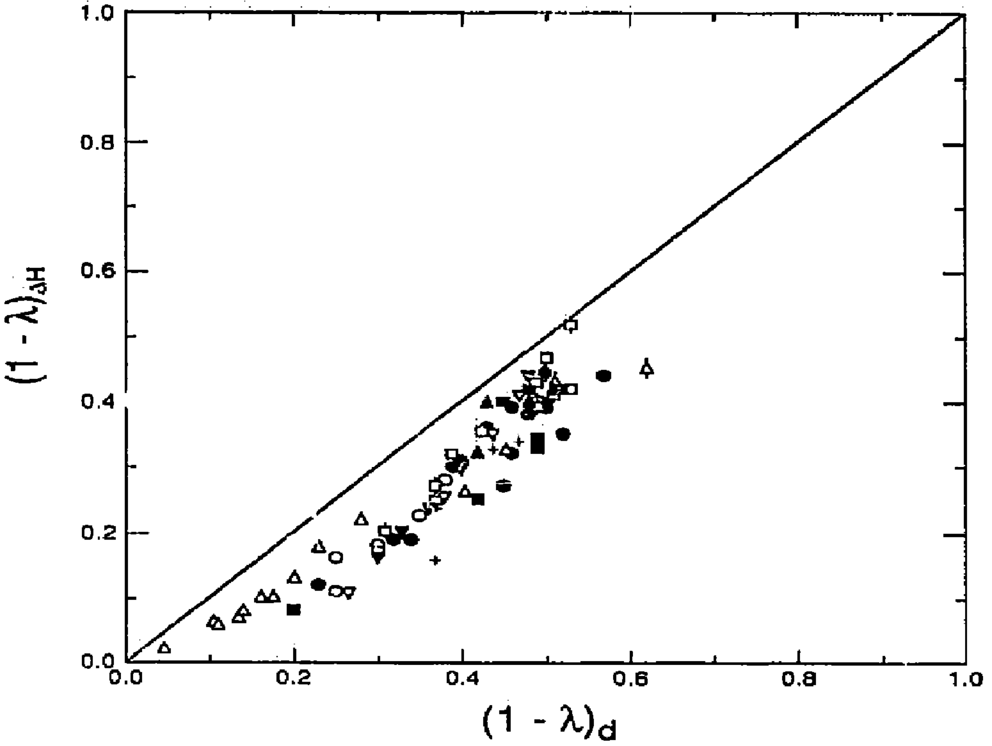

Fig. 10. Plot of degree of crystallinity obtained from heat of fusion, $(1-\lambda)_{\Delta H}$, against the value obtained from density, $(1-\lambda)_d$, for random ethylene copolymers. From ref. 9: ○, hydrogenated polybutadienes; ⎅, ethylene–1-butene fractions; ▲, ethylene–1-octene fractions. From ref. 34: □, ethylene–1-butene; ●, ethylene–1-hexene; ■, ethylene–1-octene. From refs. [26, 108]: △, ⍋, ethylene–propene. From ref. 113: ▽, ethylene–1-butene; ▼, ethylene–1-octene; +, ethylene–1-octadecene.

$(1-\lambda)_d$ and $(1-\lambda)_X$ was given as the reason for this difference. However, similar analyses were carried out with ethylene–butenes, ethylene–octenes and ethylene–octadecenes and led to a different conclusion [113]. In this study $(1-\lambda)_{\Delta H}$ and $(1-\lambda)_X$, were found to be identical and smaller than $(1-\lambda)_d$. A detailed study with linear polyethylenes is needed to serve as a reference to establish the relation between $(1-\lambda)_{\Delta H}$, $(1-\lambda)_X$ and $(1-\lambda)_d$ devoid of the complication of the inclusion of methyl groups within the lattice.

The degree of crystallinity is demonstrated to be a quantitative concept for ethylene copolymers. It can be varied over a wide range of values depending on the composition of the copolymers and/or the molar mass. Each of these quantities is an independent variable. Although different methods of measurement display the same functional behavior, a detailed comparison shows that there are small but significant differences between techniques. As we will discuss later in detail, to acknowledge and define these differences is fundamental to the study of the phase structure of ethylene copolymers.

5. CRYSTALLITE THICKNESS

The crystallite thickness is an important parameter to correlate with properties of random ethylene copolymers. The magnitude as well as the character of the crystallites are directly dependent on the molecular characteristics of the chain and on the crystallization conditions. For fixed crystallization conditions, the branch type, co-unit content and molar mass need to be treated as independent variables. Crystallite thicknesses, obtained from small-angle X-ray scattering [84, 85, 99–101, 120–127], the analysis of the Raman low frequency longitudinal acoustic mode (LAM) [9, 31, 33, 118, 128–130] or from transmission electron microscopy [2, 131–134], are available for a great variety of random ethylene copolymers. The crystallite size distribution is also directly obtained from a proper analysis of any of these methods [118, 124, 127, 134–140]. The LAM yields the distribution of ordered sequence lengths. When corrected for the chain tilt, the "core thickness" is derived.

The variation of the core crystallite thickness with increasing number of branches in the copolymer, as calculated from the Raman LAM, is given in Fig. 11. The results are for rapidly crystallized copolymers with a fixed molar mass of 90 000 ± 20 000. Data for the model hydrogenated polybutadienes, for ethylene–butenes, ethylene–hexenes and ethylene–octene copolymers having the most probable molar mass distribution and fractions from a heterogeneous ethylene–butene copolymer are included in this plot [9, 34]. The introduction of crystallizing structural irregularities into the chain restricts the crystallite thickness due to the depletion of crystallizable sequences with increasing number of branches in the chain. Thus, core crystallite thicknesses decrease very rapidly from the 120 Å for a linear polyethylene of the same molar mass to 65 Å for the copolymers with about 1.5 mol% of branch points. With further increase of the number of structural irregularities in the chain, the crystallite thickness becomes smaller. Copolymers with about 4–5 mol% branches give crystallites that are only about 40 Å thick. A very important conclusion to be drawn from the data is that there is no systematic deviation of the thickness for a given type of branch. Within the margin of the experimental errror in the measurements, the rapidly crystallized ethylene–butene, ethylene–hexene and ethylene-octene copolymers yield identical crystallite thicknesses that are the same as those for the hydrogenated polybutadienes.

In the discussion of the lattice structure it was concluded that branches with two or more carbons did not enter the lattice. On this basis, the results shown in Fig. 11 are to be expected. Following this reasoning, it is also expected that smaller groups that enter the lattice on an equilibrium basis, such as methyl or chlorine, would possess much thicker crystallites. In fact, the LAM measured crystallite thickness of two ethylene–propylene copolymers having 1 and 2 mol% of branch units was close to 130 Å [26].

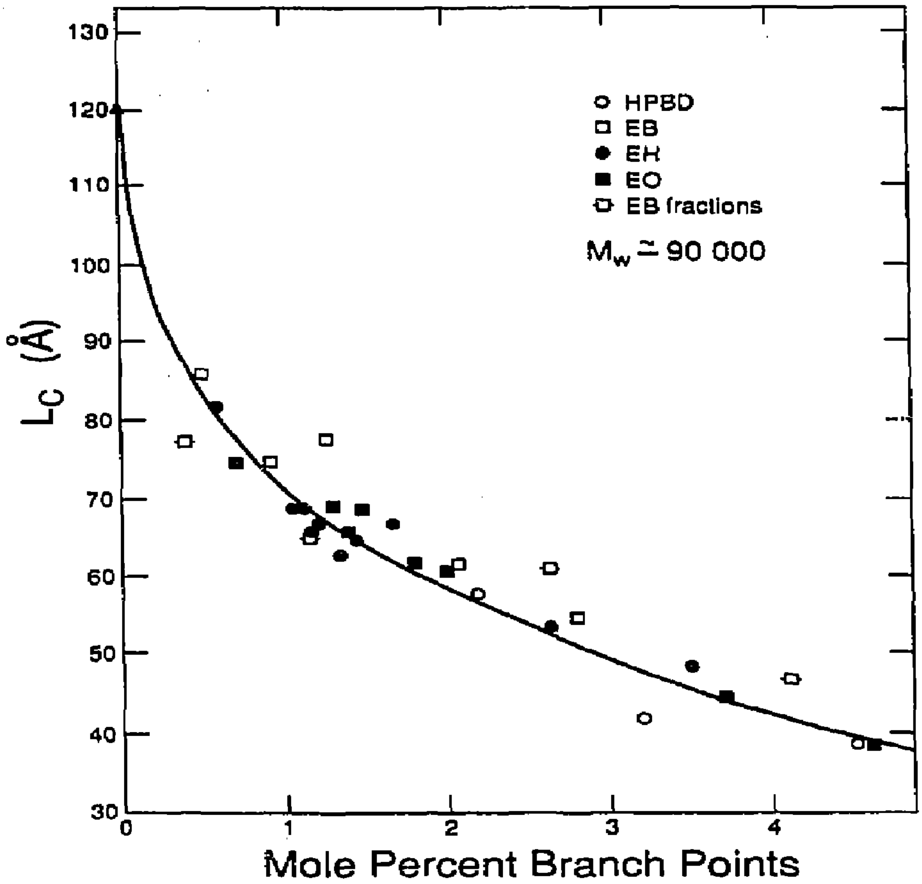

Fig. 11. Plot of the core crystallite thickness L_c against mol% branch points of the copolymers indicated. Designation and crystallization procedures as in Fig. 7.

This thickness is significantly greater than the reference line drawn in Fig. 11 for the random copolymers with branches excluded from the lattice [34]. Similar results were found by Shirayama et al. [92] who compared branch length with size of the crystals formed from a wide variety of ethylene–1-alkene copolymers. The thicknesses from the D_{110} and D_{200} reflections were much higher for the copolymers with directly bonded methyl groups than for the other copolymers.

Some ethylene–butene fractions are included in Fig. 11. The melting temperatures of these fractions are given in Fig. 2 of this review and are consistently higher than the other copolymers. The deviation in melting temperatures was attributed to small differences in the sequence distribution. This difference, however, does not seem to affect the core crystallite thickness of the rapidly crystallized fractions since the data follow the reference line. We can recall that a similar situation was encountered when analyzing the level of crystallinity of these fractions. An explanation of this apparent contradiction is given by equilibrium theory. In agreement with the experimental observations, the minimum sequence length necessary for crystallization, calculated on equilibrium basis, is basically a constant value at low crystallization temperatures and independent of the co-unit content [5,9].

Long spacings from small-angle X-ray diffraction have been obtained from fractions of ethylene–octene and ethylene–butene copolymers [47, 59]. The observed decrease of the long period with increasing branching content in these samples is, at least, partially a consequence of the variation of the molar mass within these series. The molar mass of these fractions decreases with increasing branching content. However, when the molar mass was fixed in a series of hydrogenated polybutadienes, the long period of the rapidly crystallized samples increased slightly with increasing number of ethyl branches [32]. In other series of experiments where the samples were slowly cooled, the long period remain basically constant with branching content [14, 32, 99]. The long spacings calculated from transmission electron micrographs of ethylene–butene copolymers confirmed the basic constancy of the long period [132]. The average values increase with co-unit content while the maximum remained essentially fixed at 200 Å [132]. When the long period is corrected by the degree of crystallinity, the crystallite thickness thus obtained shows a decrease with co-unit content as is illustrated in Fig. 11, in accord with the general observations. Absolute agreement in crystallite thicknesses, as measured by different techniques, is not expected for broad thickness distributions as obtained from isothermally crystallized or slow-cooled samples. For example, the Raman LAM measures the weight average and thus is most sensitive to the thicker crystallites. However the electron microscope method is sensitive to the number average. Since for ethylene copolymers the number of lamellae is small, it is difficult to locate individually placed thick lamellae. However, the Raman LAM technique will easily detect these. In the usual analysis by the X-ray method the lamellae need to be stacked in a reasonably regular array in order to observe a diffraction maximum. As we will discuss shortly, this condition is not always achieved by copolymers. The method used to obtain the degree of crystallinity, in order to correct the long period, will also effect the value of the thickness. When the correlation function is used to obtain morphological information the results will depend on the pre-established model [99, 124, 125].

Thin-section electron microscopy has revealed that lamellae are formed in linear polyethylenes and also in low density branched polyethylenes and ethylene copolymers. The morphological features of the lamellae are very dependent on crystallization conditions, number of branches and molar mass [2, 23, 131, 132, 142]. A study of the influence of the type of branch and composition at a fixed molar mass (about 100 000) was carried out with hydrogenated polybutadienes, ethylene–vinyl acetate, ethylene–butene and ethylene–octene copolymers [132]. Lamellae were found for quenched random copolymers having 1.12 and 2.2 mol% of branches. However, these lamellae were found to be very short, highly curved and segmented. Slower crystallization conditions favor the formation of lamellae. Thus, lamellae were observed up to relatively high branching contents (3.2%) in slowly cooled samples although the level of crystallinity was only about 25%. For low co-unit content copolymers about 1 mol%) long, straight lamellae are obtained. With increasing co-unit content, the lateral extent of the lamellae is reduced, their curvature increases and they become segmented. For branching content of about 4 mol% only very small non-lamellar crystallites are formed in the slowly crystallized specimens. No differences were found in the character of lamellae of copolymers having different chemical type of branches and approximately the same branching content. Thus, in agreement with the pattern established from the melting temperatures and degree of crystallinity, the type of branch does not significantly affect the thickness or character of the lamellae formed in these copolymers. It was also shown that the copolymers that were slightly more ordered gave longer, better formed and better contrasted lamellae than random copolymers [132]. The comparison of these ethylene–butene fractions with the hydrogenated polybutadienes indicated that the co-unit content at which well-defined lamellae are found is higher in the fractions. Thus, a quenched ethylene–butene with 2.64 mol% branches and a greater element of sequential order gave curved and rather segmented, but yet well defined lamellae. In contrast, the lamellae formed in the hydrogenated polybutadiene with 2.2 mol% branches were fewer, smaller and highly segmented [132].

Similar results were obtained with two different series of fractions of ethylene–butenes and ethylene–4-methyl pentenes [133]. The long, straight lamellae formed for low co-unit contents become curved and very segmented for branching contents of about 2.2 mol%. Although the lamellae thickness decreases with increasing degree of branching for both type of branches, the slow crystallization conditions reflected some differences in the crystallite thicknesses between the ethyl-branched and the isobutyl-branched copolymers. The thicknesses of the ethylene–butenes crystals were higher. This effect was attributed to a possible difference in branching inclusion in the crystal, i.e. the larger the branches, the more branches will be excluded. No attempts were made, however, to study possible differences in the sequence probability. Since both ethyl and isobutyl branches are essentially excluded from the lattice, the differences in crystal thickness and melting temperatures observed by Hosoda et al. [133] are most probably related to a slight increase in sequential order in the ethylene–butene copolymers.

Crystallite thicknesses of a series of ethylene–octene fractions have also been obtained from thin section electron micrographs [134]. Unfortunately, for these fractions, a distinction could not be made between the molar mass and composition as independent variables. Thus, thin but long and straight lamellae were observed even at high branching contents due to the low molar mass of these fractions. However, when a comparison is made between samples having similar molar mass and branching content [34, 134], the crystallite thicknesses of these fractions were essentially identical to those obtained from Raman LAM for similarly constituted polymers (Fig. 11).

As mentioned earlier, total agreement between techniques is not always obtained. For example, the most probable ordered sequence length obtained from the LAM needs to be corrected by the tilt angle. This quantity is not usually precisely known so that an uncertainty comes from this correction (between 5 and 20 Å) [32, 131]. It has also been reported that the crystal thicknesses obtained from transmission electron micrographs are 20–30 Å larger than those calculated from the one-dimensional electron density correlation function. To explain these results, it was postulated that the value derived from the SAXS only measures the thickness of the crystalline core, while the crystalline core plus interfacial region is determined by electron microscopy [126, 134, 143]. In other words, it is concluded that the stain does not penetrate the interphase.

So far we have discussed the general patterns of both the crystal thickness and the character of the lamellae focusing on the molar mass of the copolymers and varying the branching content. In what follows, the molar mass will be treated as a variable and the morphological features of the crystals will be analyzed at a fixed co-unit content. Although the data is not as profuse, enough is available in the literature to draw some general conclusions about the molar mass dependence of the structure. A detailed morphological study was carried out by Michler and Brauer on high pressure polymerized polyethylene fractions by transmission electron microscopy [144a]. A series of low molar mass fractions (about 7000) invariably resulted in long straight lamellae which became thinner with increasing co-unit content but maintained high packing regularity and contrast. When the molar mass was increased to about 70 000 long lamellae were still observed but with a tendency for curvature. The lamellae-like crystals of the high molar mass series were, in comparison, short and highly segmented. The lateral dimensions of the lamellae increased from 0.25 μm for molar masses higher than about 100 000 to 1.2 μm for molar masses of about 7000. The crystallite thickness, however, did not appreciably vary with molar mass when the branching content was fixed.

This invariance of the crystal thickness may be a feature characteristic of long chain branched copolymers. Similar studies in a series of hydrogenated polybutadienes showed not only a deterioration of the long straight lamellae structure with increasing chain length, but also a definite reduction of the crystal thickness [33]. In addition to transmission electron microscopy, the crystal thickness of quenched hydrogenated polybutadienes, having about 2.3 mol% ethyl branches and molar masses between 7000 and

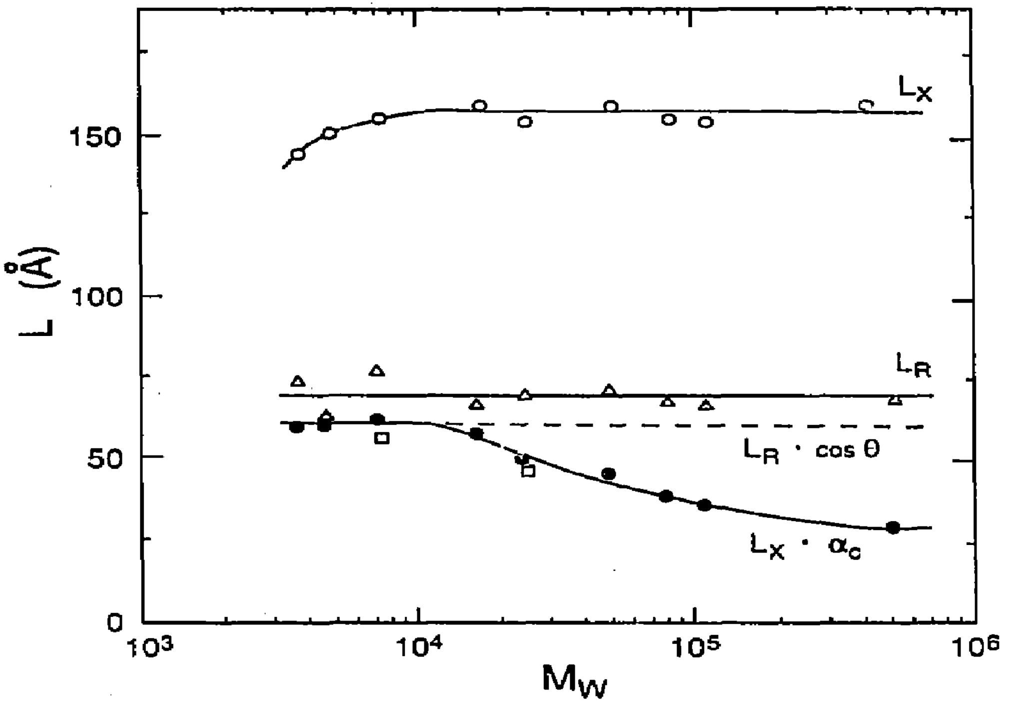

Fig. 12. Plot of sizes against log M_w for hydrogenated polybutadienes: ○, long period from small-angle X-ray scattering; L_X; ●, crystallite thickness from small-angle X-ray scattering, $L_X\alpha_c$; △, most probable value of ordered sequence length from Raman LAM, L_R; – – – – –, crystallite thickness from Raman LAM, $L_R \cos\theta$ with θ taken as 30°.

approximately 500 000, were also measured by SAXS and Raman LAM. A compilation of the results is given in Fig. 12 [33]. The small-angle long period L_X does not vary with chain length, except for the two lowest molar mass samples. To determine the core crystallite thickness, L_X needs to be corrected by the volume crystallinity level. Since crystallinity levels from heat of fusion (or Raman internal modes) differ from those calculated from density, the question arises as to which one is appropriate in the determination of the core. Because the levels of crystallinity decrease with molar mass by either method, both calculations show the same trend; a significant decrease of the core thickness with chain length. However only when the long period is corrected with the Raman determined level of crystallinity (equivalent to the value calculated by heat of fusion), do the values of the core crystallite thickness agree with those obtained from the transmission electron micrographs [33]. As shown in Fig. 12 the crystal thickness from the X-rays decreases from 60 Å to about 30 Å for molar masses ranging from 7000 to 420 000 for the copolymers with 2.3 mol% branches. The thickness derived from the electron micrographs of the copolymer with $M_w = 6950$ (54.5 Å) was very similar to the X-ray value, and so it was the thickness obtained for the copolymer with $M_w = 24\,000$ [33]. Very small and imperfect lamellae-like crystals are found in the quenched sample with $M_w = 108\,000$. Similarly, the electron micrographs of the copolymer with $M_w = 420\,000$ do not show any definitive lamellar organization as expected for such small crystals.

The variation of the crystal thickness with molar mass observed from X-rays or electron micrograph measurements is in good agreement with the decrease of melting temperature with molar mass of the copolymers. The calculated values from the Raman LAM are incompatible with any of the above results. No variation is found in the ordered sequence length, uncorrected or corrected with tilt angle, with molar mass. Only when the thickness of the crystals is about 60 Å or higher, do the numerical values obtained from the three methods agree. However, when the molar mass increases, and the crystallite size decreases, a major difference develops between them. The discrepancy can be attributed to the very small crystallite size and the concomitant large disordered overlayer. The relatively large non-ordered surface layer may have an important influence on the vibration of the ordered sequences in the crystal. For these types of thin copolymer crystallites the simplified Schaufele–Shimanouchi relation [129] may not be applicable to obtain ordered sequence lengths from the observed Raman LAM. An example is already found in the deviations from the ideal non-perturbed rod model observed in short-chain *n*-alkanes. These deviations are associated with intermolecular attraction forces, caused by the ends of the molecule, that influence the vibration associated with the LAM [144b].

6. INTERFACIAL STRUCTURE

Flory [145] pointed out that a demarcation between the ordered crystalline region and the disordered liquid-like region could not be sharply defined in a semicrystalline polymer. The dissipation of order must be gradual. Consequently, an interphase or interfacial region develops that involves a partially ordered set of chain units. The large amount of experimental and theoretical data that support the concept of the interphase in homopolymers has been recently reviewed [119]. For the type of molecules of interest here (random ethylene copolymers in which the branches are excluded from the lattice) the major problem is to assess how the structurally irregular units alter the interfacial and interlamellar region relative to the structure established for homopolymers.

The analysis of the Raman internal modes is a quantitative method for determining the interfacial content of the polyethylenes [18, 24, 104, 105, 146]. The core degree of crystallinity α_c can be defined by this method since the only contribution is from the orthorombic unit cell. The fraction of the liquid-like region α_a can also be quantitatively obtained from the spectrum. From the examination of a large amount of experimental data, it is found that $\alpha_a + \alpha_c \neq 1$ [9, 24, 33, 117, 146, 147]. A partially ordered, primarily trans, anisotropic region must also be included in the proportionated liquid-like and crystalline spectra, to fully represent the observed spectrum. This contribution is defined as the fraction of the interfacial region. Thus

$$\alpha_b = 1 - (\alpha_a + \alpha_c) \qquad (3)$$

The level of crystallinity calculated from different methods was analyzed for linear polyethylenes [24] as well as for copolymers [9, 24, 113, 117]. It was found that the crystallinity content determined from density $(1-\lambda)_d$ is systematically higher than that from heat of fusion measurements $(1-\lambda)_{\Delta H}$. The reason for this discrepancy can be explained by the contribution from the interfacial region. Thus, when the Raman determined interfacial content is added to the crystallinity level obtained from the heat of fusion, or to α_c, the result is very similar to the $(1-\lambda)_d$ values [24, 117–119]. Figure 13 gives an example for rapidly crystallized (quenched) copolymers. The range of crystallinities could be expanded to 80–90% if the linear polyethylenes are included. All the data fall reasonably well on the 45° straight line [9, 12, 33, 34].

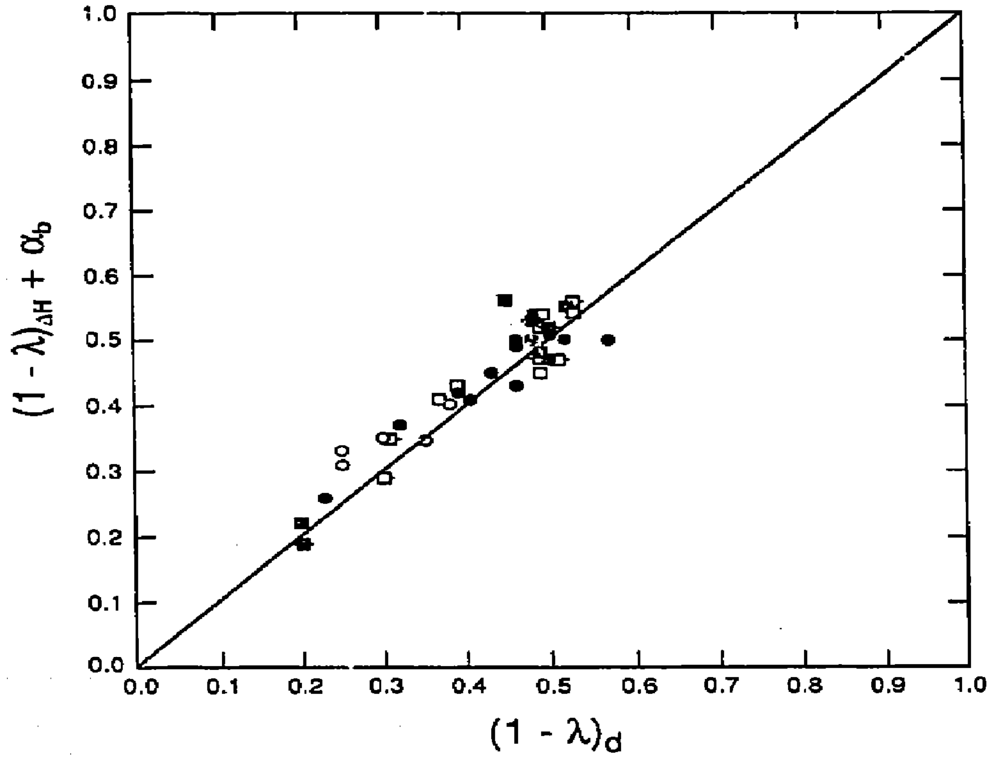

Fig. 13. Plot of the degree of crystallinity calculated from heat of fusion, $(1-\lambda)_{\Delta H}$ plus interfacial content α_b, versus degree of crystallinity from density $(1-\lambda)_d$ for ethylene copolymers. Data from refs. 9 and 34. ○, hydrogenated polybutadienes; -□-, ethylene–1-butene fractions; -■-, ethylene–1-octene fractions; □, ethylene–1-butene; ●, ethylene–1-hexene; ■, ethylene–1-octene.

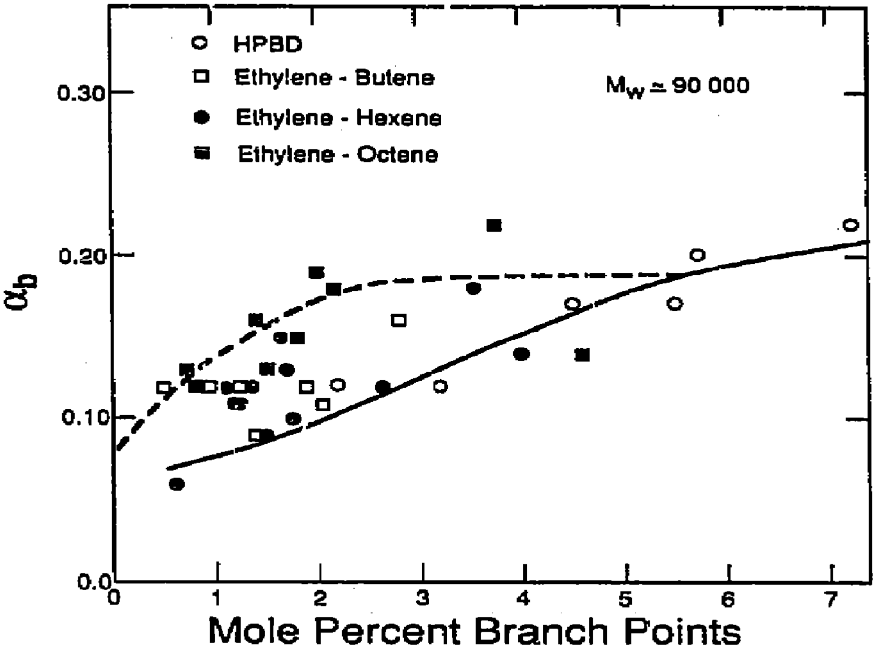

Fig. 14. Plot of the interfacial content calculated from Raman internal modes α_b, against mol% branch points of the copolymers indicated. Crystallization conditions same as in Fig. 7.

The extensive studies carried out with linear polyethylene fractions clearly demonstrated that molar mass and crystallization conditions significantly alter the content of the interphase [24, 148]. It is therefore expected that for random ethylene copolymers besides the effects of increasing co-unit content, the interphase is also affected by changing the molar mass. Thus, the experimental data are analyzed treating both variables independently.

The variation of the interfacial content with increasing branch point units, at a fixed molar mass of 90 000 is given in Fig. 14 for rapidly crystallized samples [34]. The hydrogenated polybutadienes and fractions of ethylene–butene and ethylene–octene copolymers [9] and more recent data for ethylene–butenes, ethylene–hexenes and ethylene–octenes having the most probable molar mass distribution [12, 34] are given in this figure. The solid line is drawn following the data obtained for the model hydrogenated polybutadienes; it shows that the interfacial content increases significantly with increasing co-unit content in the copolymer. Values of 8–10% are found for the copolymers with 1 mol% of branches, but this value almost triples for co-unit contents higher than about 3 mol%.

Several other important trends are seen in the data collected in Fig. 14. For example, the interfacial content increases rapidly in the region between 0 and about 2.5 mol% of branches and levels off at a value of about 20% for the higher branching contents. The increasing interfacial content with the number of branches parallels a preferential accumulation of the branches on the crystallite surface. The region of co-unit where the interfacial content reaches a saturated value coincides with that where the lamellar crystallite habit is essentially lost and only small crystals are formed under rapid crystallization conditions. Before the interfacial content levels off, the ethylene–octene copolymers show higher interfacial contents than the other copolymers at comparable compositions. This is represented by the dashed line in Fig. 14 and has been interpreted as a possible consequence of steric differences of the hexyl branches that accumulate at the interphase [34].

It was pointed out previously that increasing the molar mass in a series of copolymers of fixed composition causes a significant decrease in the level of crystallinity attained. This result is in agreement with expectations from the results with linear polyethylene fractions. The crystallinity content depends on the composition of each set of copolymers, but the functional form with molar mass is practically identical for all of them. A family of curves is, therefore, generated for the level of crystallinity as well as for the liquid-like content. Data for the series of hydrogenated polybutadienes (2.3 mol%), ethylene–hexenes (1.1 mol% and 2.6 mol%) and ethylene–octenes (0.8 mol%) are shown in Fig. 15 [34].

The variation of the interfacial content α_b with molar mass is interesting since it is quite different than that found for linear polyethylene fractions [117]. For a fixed mode of crystallization a continuous increase of α_b with molar mass, consistent with the increased accumulation of units involved in chain entanglements, was observed for linear polyethylene fractions. Rapidly quenched samples showed a variation in α_b from 3 to 16% as the molar mass increases from 7×10^3 to 8×10^6. The interfacial content of copolymers increases with increasing branching composition in the series. However, as seen in Fig. 15, for molar masses lower than about 100 000 it remains basically constant. A slight tendency toward higher α_b values was only found for the highest molar mass studied. The ethylene–octene copolymers show very high α_b in spite of the low co-unit content. The invariance of α_b with molar masses lower than 100 000 indicates that in this range of chain length the interfacial structure is dominated primarily by the need to accommodate the accumulation of branches on the crystallite surface. The effect of the branches dominates the influence of entanglements, which are the major contributors to the molar mass dependence of the interfacial structure of the linear polymer.

The thickness of the interfacial region L_b can also be calculated by different experimental techniques. These involve Raman spectroscopy using the internal and low frequency LAM, small-angle X-ray scattering, and in favorable cases direct observations by electron microscopy. L_b, determined by using a combination of Raman internal modes and the Raman LAM, was found to vary from 14 Å at $M_w = 10^4$ to about 25 Å for linear

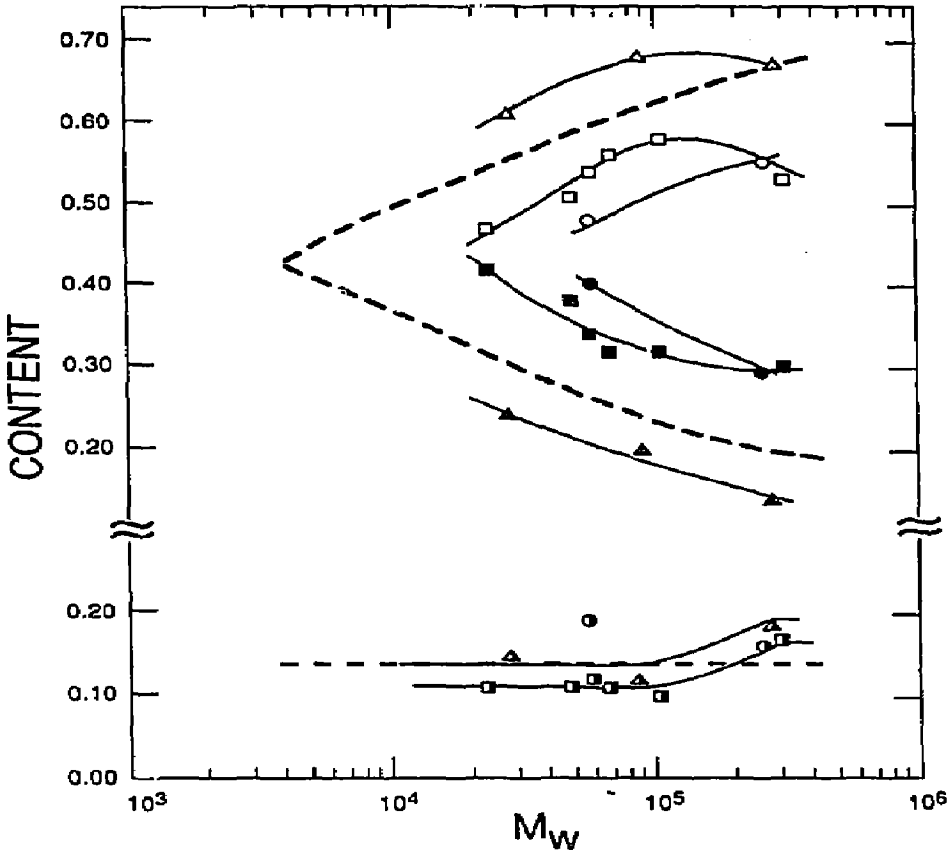

Fig. 15. Relative amount of liquid-like (α_a), crystalline (α_c) and interfacial (α_b) contents as a function of molar mass for the following series of ethylene copolymers. From ref. 33: – – – –, hydrogenated polybutadienes with 2.3 mol% branch units. From ref. 34:

α_a	α_c	α_b	
□	■	◨	Ethylene–1-hexene 1.1 mol%
△	▲	▲	Ethylene–1-hexene 2.6 mol%
○	●	◑	Ethylene–1-octene 0.8 mol%.

polyethylene fractions of $M_w = 10^6$ [28]. Slightly higher values of L_b were found for linear polyethylene fractions having the most probable molar mass distributions [28] and reaches 45 Å in a polydisperse sample ($M_N = 8 \times 10^6$) crystallized under the same experimental conditions [149]. The interfacial thickness of rapidly crystallized copolymers is also known to increase rapidly with increasing branching composition and less with molar mass when the co-unit content is fixed [33, 34]. The variation for different type copolymers having a molar mass of about 90 000 is shown in Fig. 16 [34]. L_b for the model hydrogenated polybutadienes and the most probable ethylene–butenes and ethylene–hexenes is very similar. It only changes from 11 to 14 Å for compositions up to about 2.5 mol% of branches. L_b increases more markedly with co-unit content and reaches a value of about

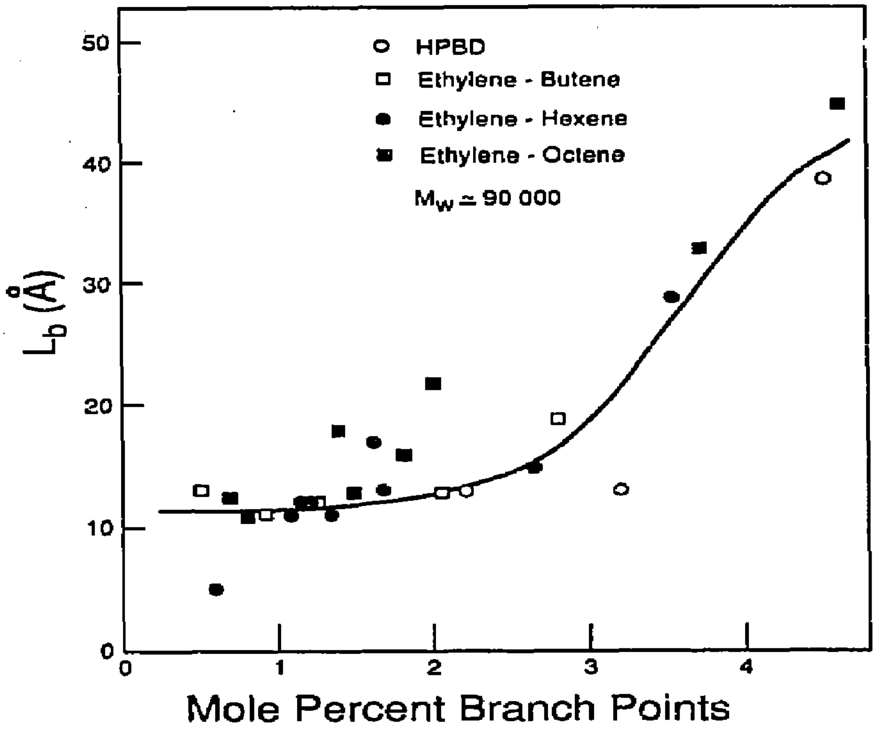

Fig. 16. Plot of the interfacial thickness L_b against mol% branch points of the copolymers indicated: HPBD, hydrogenated polybutadienes.

40 Å at 4.5 mol% branches. The ethylene–octenes show systematically higher values of L_b in agreement with the higher interfacial contents that were obtained for this type of copolymer [34]. Because interphases of about 20 Å were calculated for a linear polyethylene fraction of M_w 90 000 that was crystallized under the same conditions [28], one would expect the copolymers to have higher interfacial thicknesses than those shown in Fig. 16 for low co-unit content. However, because of the small crystallites that are involved, the interfacial thickness actually represents a greater percentage relative to the core crystallite thickness.

Small-angle X-ray scattering studies of a series of ethylene–phosphonic acid copolymers were consistent with the appreciable interfacial content found in random ethylene copolymer crystals by the analysis of the Raman spectra. A two-phase model was inadequate for the interpretation of the invariant in these copolymers [84]. Therefore, scattering from the interfacial region needs to be taken into account when calculating the invariant. The analysis of the angular dependence of the intensity of the small-angle X-ray scattering can also give quantitative information about the interphase [127, 150]. Data based upon the evaluation of the one-dimensional electron-density correlation function was obtained for a long-branched polyethylene having 3.3 branch units per 100 carbons that was isothermally crystallized at 100°C [125, 126]. A transition zone of 16 Å was calculated between the crystalline and liquid-like region. This result is slightly lower than the interfacial values calculated from Raman for copolymers of a similar composition (Fig. 16). However, isothermally crystallized samples are expected to yield smaller interphases [24]. Taking this fact into account, the agreement between these two independent techniques is remarkable. A transmission electron microscopic study was also carried out with long chain branched polyethylene [143]. The lamellae thicknesses were found to be 20–30 Å larger than the value derived from SAXS. Thus, these results, consistent with the above, indicate the presence of a 10–15 Å transition region where the staining medium did not penetrate. As pointed out earlier, a similar conclusion was reached from an electron microscopic study of a series of ethylene–octene copolymer fractions [134].

In summary, several different experimental techniques clearly point out that the interfacial region represents a significant portion of the total crystalline system. This region has been extensively studied with linear polyethylene, as well as ethylene copolymers, and is very dependent on the crystallization conditions, co-unit content and molar mass. Besides these techniques, other theoretical calculations are in qualitative accord with the experimental findings. The computer simulations by Mattice and co-workers [151–153] have indicated that short chain branches (of unspecified length) are not randomly distributed in the non-crystalline region. Rather they occur preferentially in the anisotropic interfacial region causing this region to grow at the expense of the isotropic liquid-like region. In another type of calculations the number of entangled loops and tie chains have been reported to increase with the incorporation of a small number of branches in a linear chain [154–156]. The implication of these results to the phase structure is yet to be explored.

7. SUPERMOLECULAR STRUCTURE

Under certain circumstances the interconnected, basic crystallites can be organized into higher levels of crystalline morphology or supermolecular structures. The commonly observed spherulite represents one structure in this category. The nature of the supermolecular structure can be investigated either by small-angle light scattering, polarized light or electron microscopy. Careful studies of the same specimens have demonstrated that concordant results are obtained with any of these techniques [157]. Detailed studies with homopolymer fractions, such as linear polyethylene [22, 158–160] poly(ethylene oxide) [29] and isotactic poly(propylene) [30, 161] have shown that in fact a variety of morphological forms can be observed. Spherulites are not a unique superstructure. As an example, for linear polyethylene five different light scattering patterns are observed. These correspond to five different superstructures as well as a situation where a superstructure is absent and only randomly arranged lamellae are observed. It is important to recognize that the development of spherulites is not a universal mode of homopolymer crystallization [17, 22]. The superstructures, or lack thereof, develop in a systematic manner, depending on the molar mass and crystallization temperature. Consequently, a morphological map can be constructed representing the superstructure that develops for a given chain length and crystallization temperature [22, 23, 160, 162]. Taking linear polyethylene as a model for homopolymers one finds that, except for the very highest molar masses, where a random type morphology is observed for all crystallization conditions, the cooling rate, or quenching temperature, exerts an important influence on the morphology. The crystalline morphology has also been found to be extremely sensitive to molar mass polydispersity [23, 162, 163].

In studying the supermolecular structure of random copolymers, in addition to the molar mass, polydispersity and crystallization conditions, the co-unit content must also be taken into account as an additional independent variable. In an early study of unfractionated polyethylenes, having both long and short chain branches, and thus properly treated as copolymers, it was found that when first crystallized isothermally at low undercoolings and then cooled to room temperatures spherulitic structures always developed [160]. In contrast, when the same specimens were quenched from the melt, a variety of morphological forms were observed that depended on the branching concentration and proportion of high molar mass species present. The most highly branched samples did not display any well-defined crystalline morphology [160]. The results for the isothermally crystallized samples are somewhat misleading. In contrast to linear polyethylene, only very small amounts of crystallinity develop in the copolymers under these conditions. Most of the crystallinity that is formed is developed on cooling. Therefore, the morphology that is observed is influenced by the small amount of crystallinity formed at the elevated temperature [162].

Detailed studies have been carried out with fractions of the above type of polyethylenes as well as with hydrogenated polybutadienes [23, 162]. The morphological map for the branched polyethylene fractions, when obtained from small-angle light scattering patterns, is given in Fig. 17. The branching concentration of these fractions is in the range 1.5–1.9 mol%. In this figure the molar mass is plotted against the quenching temperature. The solid line delineates the region of spherulite formation. The supermolecular structures, which are identified by letters, are defined as follows. Types a, b and c represent spherulites whose structures deteriorate in the progression a to c. Type d structures are thin rods, or rod-like aggregates. The region labeled h represents randomly oriented lamellae. There is a typical dome shaped region in this plot within which spherulites are observed. Therefore, there is a restricted domain of molar masses and quenching temperatures that yield

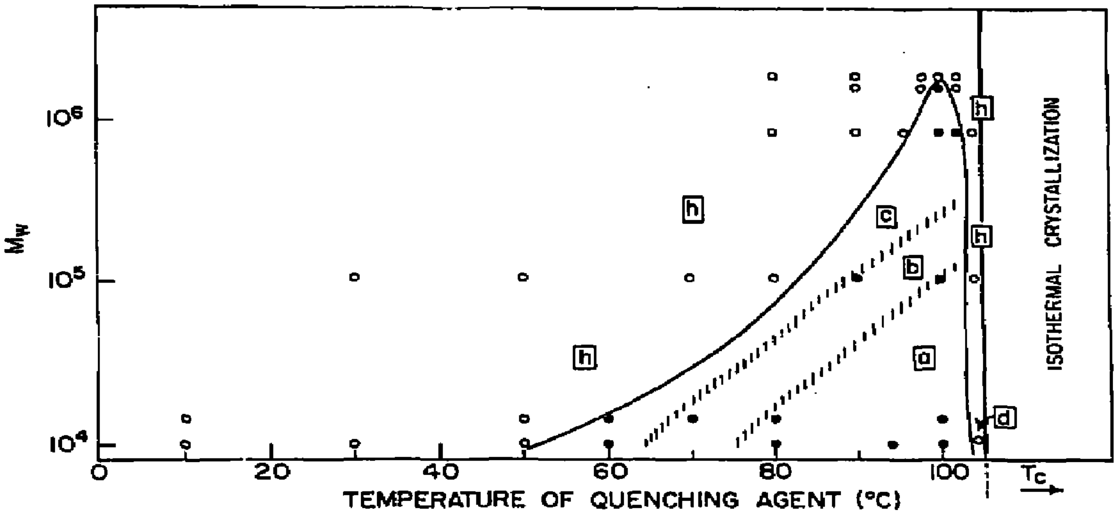

Fig. 17. Morphological map for molar mass fractions of low-density polyethylene (1.5 mol% branched groups) crystallized non-isothermally. Plot of molar mass against quenching temperature. Solid line delineates region of spherulite formation. Morphological forms indicated by letters as defined in text.

spherulitic structures. The lower the molar mass, the larger the temperature range within which spherulites form. This range narrows with molar mass, so that eventually a molar mass is reached above which spherulites do not form. Within the spherulite forming domain better developed structures are formed by lower molar mass and higher quenching temperatures. When crystallized outside the dome, either at high or low temperatures, although lamellar-type crystallites are formed they are randomly arranged relative to one another. Thus, under these circumstances no organized supermolecular structure forms.

Qualitatively similar types of morphological maps have been found for branched polyethylene with about 1 mol% branch points and hydrogenated polybutadienes containing about 2.2 mol% ethyl branches [23]. In the former case the actual top of the dome could not be attained since it is shifted to molar masses greater than 2×10^6. For the hydrogenated polybutadienes the limiting molar mass for spherulite formation is reduced from 2×10^6 found in Fig. 16 to 2×10^5. Thus, small changes in the branching content have a major influence on the supermolecular structure. The morphological studies of Hosoda et al. [133] on slow-cooled fractions of ethylene–butene confirm these results as a general phenomenon. Well developed spherulites were also found for low density polyethylene fractions in the range of molar masses from 10 000 to about 100 000, in agreement with the results of Fig. 17 [144a]. Based on the results available several generalizations can be made. For a given branching concentration, the range of quenching temperatures within which spherulites are formed decreases with molar mass. Most important, as the branching concentration increases the molar mass within which spherulites can be formed decreases markedly. Following this pattern, a branching concentration and/or molar mass will be reached beyond which spherulites will not form at all. The report of Jackson and Flory [164] on spherulite formation in high molar mass diazoalkane copolymers is consistent with this generalization. These authors studied the development of supermolecular structures in random diazoalkane copolymers having either CH_3 or n-C_3H_7 groups attached to the main chain. The structures were studied by polarized light microscopy and the samples were cooled very slowly from the melt. The copolymer with 2 mol% of the n-propyl groups gave very poorly defined spherulitic structures. Copolymers having an n-propyl concentration greater than 2 mol% did not form any ordered superstructures. These results are thus in very good accord with the general conclusions reached above. However, it is very significant to note that for the copolymers with directly bonded methyl group, spherulites do not disappear until the branch concentration was greater than 5.9 mol%. The difference in behavior between the two copolymers obviously reflects the fact that a portion of the directly bonded methyl groups enter the lattice. Thus, the properties of the ethylene–propylene type copolymers are consistently different from the other 1-alkene copolymers because of the difference in internal lattice structure.

8. SUMMARY

In this review we have discussed the crystallization behavior of random ethylene copolymers with major attention being focused on ethylene–1-alkene fractions and copolymers of this type that have well-defined molar mass and composition distributions. Emphasis has been given to the analysis of thermodynamic properties and to the basic elements of phase structure. For a fixed mode of crystallization the molar mass, the copolymer composition and the chemical nature of the co-unit need to be isolated and treated as independent variables. Moreover, analyses are very sensitive to the sequence distribution of the co-units in the chain. It is important, therefore, that this property be established independently. A major conclusion is reached for those copolymers whose internal crystallite structure remains pure: that the thermodynamic properties are independent of the chemical nature of the co-unit. With the exception of the interfacial region, a similar conclusion is reached with regard to the basic elements of phase structure. Copolymers with longer branches, such as the ethylene–octenes, have slightly greater interfacial contents and thicknesses. The major changes in properties occur in the range of 0 to 1–2 mol% of branch points.

The analyses of a large amount of experimental data lead to the conclusion that only small groups, such as CH_3, Cl, O, and OH, enter the crystal lattice and therefore are partitioned between the crystalline and liquid-like regions. If longer branches, such as ethyl groups, enter the lattice they only do so to a very small or negligible extent. The properties of the copolymers containing groups that enter the lattice to an appreciable extent are quite different from those where the crystalline phase remains pure.

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