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DENSITY-BRANCHING RELATIONSHIPS FOR LLDPE

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ABSTRACT

Most commercially available LLDPE's are heterogeneous in the solid state, consisting of separate crystalline and amorphous phases. The crystalline phase may be considered as a solid solution of polyethylene itself and a miscible copolymer. This miscible copolymer can contain as little as 4+ branches/1000 C, depending on the comonomer. At higher comonomer contents, phase separation occurs. A semi-empirical relationship to predict densities of miscible copolymers relates the specific volume (reciprocal density) linearly with the degree of branching and the square root of the side chain molecular weight. It appears valid for comonomers from propylene to octene-1. At higher comonomer incorporations, there is no discernible comonomer effect; specific volume varies linearly with branchiness only. This relationship appears valid for comonomers from propylene to octadecene-1 (and their mixtures). It extrapolates to the EPR region. This model is consistent with previously reported studies of polyethylene crystallinity and copolymer phase separation.

Density of polyethylene has long been used as a convenient parameter to describe polymer crystallinity and the physical properties that are primarily related to it.

For many years, commercial low density (0.910-0.925 g/cm^3) and medium density (0.926-0.940 g/cm^3) polyethylenes were made by high pressure free radical polymerization. These polymers are characterized by a combination of long and short branches off the main polymer chain. High density (0.941-0.965 g/cm^3) polyethylenes were produced by lower pressure, transition metal catalyzed polymerization. Desired densities were obtained by copolymerizing ethylene with alpha-olefins to give only short chain branching. More recently, the full gamut of densities, from below 0.90 to above 0.96, has been produced by lower pressure, transition metal catalyzed copolymerizations. These copolymers are commonly referred to as linear low density polyethylenes (LLDPE). They incorporate a small amount of alpha-olefin comonomer to obtain physical properties associated with lower crystallinity. Typically, butene-1, hexene-1, 4-methylpentene-1, and octene-1 are the comonomers used.

There is a wide variation in properties for these LLDPE's, even at the same level of incorporation of the same comonomer. This scatter in the data can be seen in Fig. 1, which plots polymer density versus comonomer incorporation for a wide variety of commercial and developmental butene-modified polyethylenes. This figure shows that almost a fourfold range of butene incorporation from about 5 to 20 chain branches/1000 C can produce essentially the same 0.92 g/cm^3 density, or conversely, that density can be varied ca. 0.02 g/cm^3 at substantially the same level of comonomer incorporation.

One might have expected that there would be a simple and precise relationship between monomer incorporation and polymer density. Such is obviously not the case. Actually, there appear to be two different types of LLDPE. Some are homogeneous random copolymers that are miscible in the solid state [1, 2] and others are heterogeneous multiphase mixtures [3] that are immiscible in the solid state.

Heterogeneity would not be expected at low levels of comonomer incorporation. If the copolymerization reaction were homogeneous and Bernoullian, just about 0.1% of the butene (for example) would have entered the polymer chain adjacent to another butene molecule. The B-B-B triad would have been almost undetectable. The polymer would have appeared to contain only randomly spaced comonomer units.

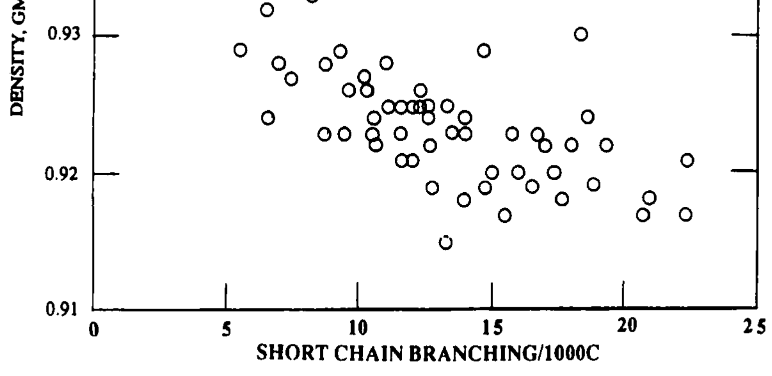

FIG. 1. LLDPE density vs chain branching of butene-1 copolymers.

The situation is analogous to propylene copolymers. Random copolymers with ethylene are homogeneous miscible; impact copolymers are heterogeneous mixtures of homopolypropylene and a broad spectrum of ethylene-propylene copolymers. This distinction has not usually been made for LLDPE.

MISCIBLE RANDOM COPOLYMERS

We assume that this type of copolymer cocrystallizes with homopolyethylene. The comonomer units increase lattice spacing. Each comonomer molecule acts independently of all other comonomer; its effects are strictly local.

This type of copolymer makes the most efficient use of comonomer in decreasing density because of this independence. But there is an upper incorporation limit beyond which the lattice cannot deform sufficiently to accommodate additional comonomer.

The ability of polyethylene crystals to accommodate irregularities in the polymer chain by increasing crystal lattice spacing has been known for many years [4–6]. Martinez de Salazar and Balta Calleja studied the effect of irregularities on crystal dimensions in depth. They concluded that polyethylene crystals readily accommodate irregularities up to a limit beyond which the irregularities are distributed between an amorphous layer at the lateral grain boundaries and within the distorted lamellae of the polyethylene crystal [6].

Correlation between the number of these distortions, as measured by short-chain branching and their effect as measured by density, would be expected to follow the following relationships.

1. Specific volume of copolymer varies linearly with number of side chains, or

$$V_c = V_0 + aB \tag{1}$$

where V_c = specific volume, $(1/\rho)$, cm^3/g
V_0 = specific volume of corresponding unbranched HDPE
B = short chain branching/1000 C

2. Relationships for different comonomers should converge to the same value of V_0. This assumption should hold within each type of catalyst but not necessarily across all catalyst systems. V_c and V_0 can also be affected by postreaction processing conditions, but this complication was ignored. The consistency of data presented later indicates that for the systems considered, this was a relatively minor effect.
3. Rate of volume increase per branch for different comonomers should vary with the effective volume of the side chain introduced, but it is independent of catalyst or synthesis conditions.
4. The effective volume of linear aliphatic side chains is approximately proportional to $M_c^{0.5}$, where M_c is the molecular weight of the side chain (not comonomer). The square root is appropriate because the side chains, being sandwiched between polyethylene lamellae, are essentially immobilized. For a constrained random walk, the effective length of the side chain would be almost exactly proportional to the square root of its

length. This relationship for much, much longer chains was assumed to be valid even down to ethyl side chains as a first approximation.

5. Only a small, limited number of branches can be incorporated homogeneously before they begin to interfere with each other. Interferences will behave as localized regions of heterogeneity. It necessarily follows that any nonrandom incorporation will cause the onset of heterogeneity at lower comonomer incorporation levels.
6. In any given population of copolymers, homogeneous copolymers will fall on an envelope line that represents the maximum specific volume at a given branchiness. Heterogeneous copolymers will be found at lower specific volumes and higher branchiness.

According to this model, homogeneous copolymers can be characterized by the relationship

$$V_c = V_0 + k_c BM_c^{0.5} \tag{2}$$

where k_c is an empirically determined proportionality constant—the same over a wide range of comonomers. As mentioned above, V_0 need not necessarily be the same for all systems.

The literature provides several populations of data to test this model: (A) propylene, butene-1, pentene-1, and octene-1 modified LLDPE's made with unspecified but presumably chromium catalyst [7]: hexene-1 and 4-methylpentene-1 copolymers prepared with titanium-chromium tergel catalyst [8]. Because the methyl side chain of propylene-modified LLDPE would presumably be too short for the square-root function to apply, these data were ignored in calculating V_c and k_c. Envelope lines tangent to low branchiness data were drawn, and their slopes and intercepts were correlated by least squares to yield

$$V = 1.0485 + 0.000540BM_c^{0.5} \tag{3}$$

with a correlation coefficient of 0.96. As shown in Figs. 2 and 3, agreement is satisfactory. Equation (3) provides a reasonable envelope and appears to have the appropriate slope for each of the comonomers from butene to octene. As shown in Fig. 3, the correlating lines for propylene copolymers have the expected slope but are displaced slightly from the data. This shift in V_0 could reflect either a different thermal history for these polymers or that propylene dispersion is not completely random so that a small amount of phase separation has taken place. Considering the assumption made in deriving Eq. (3), agreement is better than expected.

Figure 3 also shows that there is no discernible difference between hexene-1 and isomeric 4-methylpentene-1 as far as their effect on density is concerned. This does not suggest that both comonomers have identical effects on other physical properties such as strength or clarity.

In short, some LLDPE's seem to consist largely of crystal-miscible random copolymers. These polymers achieve densities of 0.92–0.93 with very low comonomer incorporation and, in general, have excellent film properties.

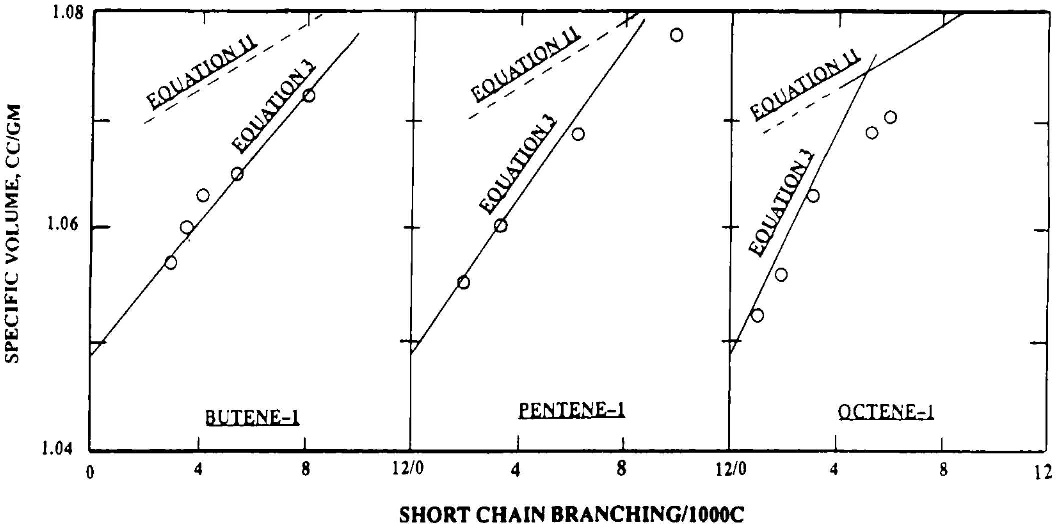

FIG. 2. LLDPE specific volume vs chain branching of miscible copolymers.

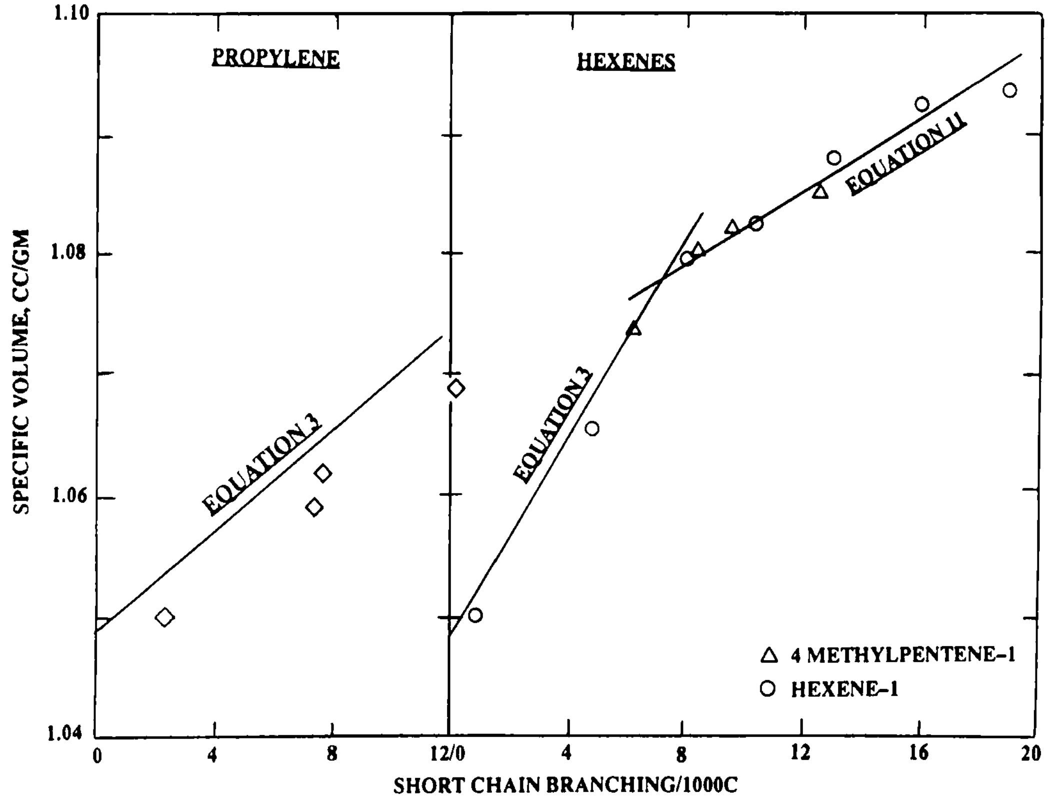

FIG. 3. LLDPE specific volume vs chain branching of propylene and of hexene copolymers.

AMORPHOUS COPOLYMERS

When comonomer incorporation levels are sufficiently high, a separate amorphous phase forms. Such polymers are considered as simple mixtures whose volumes are additive.

These copolymers are assumed to consist of W_c parts by weight crystalline copolymer and $(1 - W_c)$ parts amorphous. The crystalline component contains W_1 parts comonomer and has specific volume V_1 $(= V_0 + k_c B M_c^{0.5})$. Amorphous fraction contains W_2 parts comonomer and has specific volume V_2.

$$V = W_c V_1 + (1 - W_c) V_2 \tag{4}$$

and

$$W = W_c W_1 + (1 - W_c) W_2 \tag{5}$$

Eliminating W_c and rearranging:

$$\frac{V_2 - V}{V_2 - V_1} = \frac{W_2 - W}{W_2 - W_1} \tag{6}$$

Equation (6) can be transformed into a form with the same variables as Eq. (2) by using the relationship

$$W = 0.001(nB) \tag{7}$$

where n is the number of carbon atoms in the comonomer molecule. Equation (7) is readily derived from stoichiometry.

Equation (6) then becomes simply

$$V_a = V_1 + k_a B \tag{8}$$

subject to the limitations relative to Eq. (2):

$$V_1 > V_0 \tag{9}$$

$$k_a < k_c M_c^{0.5} \tag{10}$$

Here, k_a can depend on the volume and branchiness of the amorphous phase material. Data for a wide range of ethylene copolymers are plotted in Fig. 4. These data are correlated by the relationship

$$V_a = 1.0670 + 0.001521B \tag{11}$$

with a correlation coefficient above 0.98.

Equation (11) seems to apply regardless of comonomer, catalyst, or synthesis conditions. At any given level of comonomer incorporation, Eq. (11) represents the minimum density envelope for LLDPE.

Data for butene-1, octene-1, and octadecene-1 [1] fall on the same line as well as do limited data for the three-component systems ethylene–propylene–octene

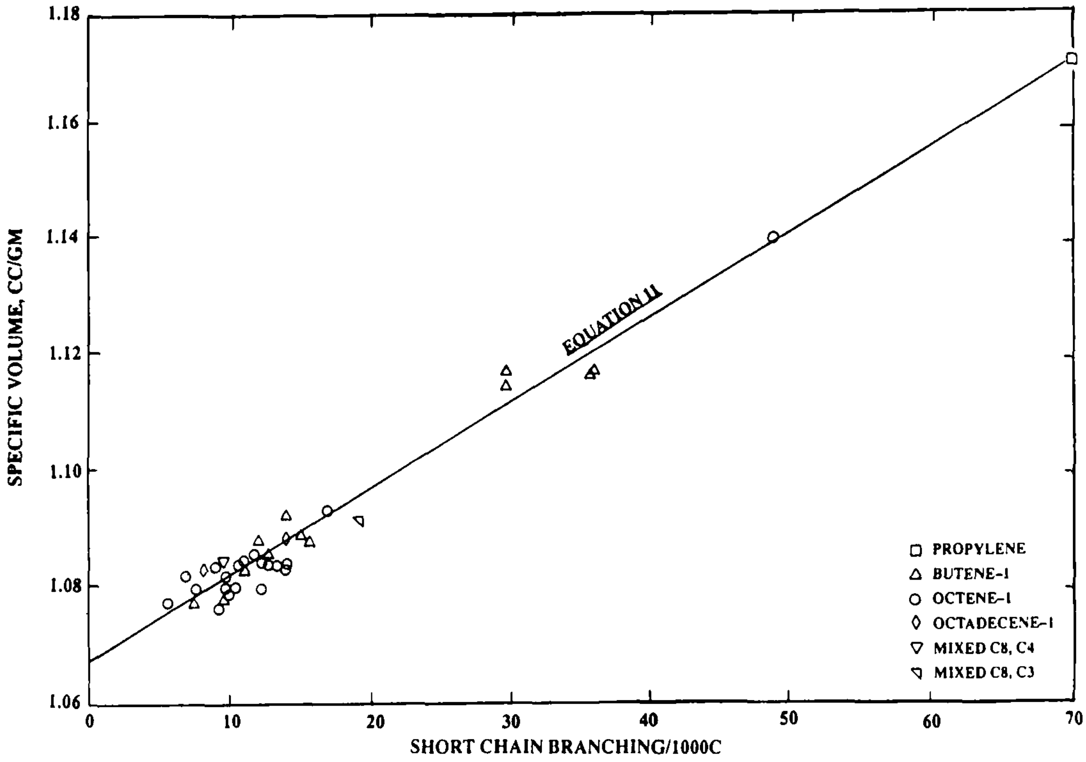

FIG. 4. LLDPE specific volume vs chain branching of random-amorphous polymers.

and ethylene-butene-octene [1]. And as shown in Fig. 3, hexene-1 and 4-methylpentene-1 copolymers also follow Eq. (11).

This relationship also extrapolates to the amorphous EPR region, being consistent with the data of Baldwin and VerStrate—a density of 0.854 and a linear extrapolation of high ethylene crystallinity to zero at 15 mol% propylene (V = 1.1710, B = 70.0) [9]. It was completely unexpected that a single straight line would include such a wide variety of comonomers. Looked at another way, it indicates that amorphous polyolefins are much the same in density and branchiness.

Equations (3) and (11) can be tested by Mirabella and Ford's LLDPE data [3]. As shown in Table 1, the sum of individual volumes yields a close approximation to measured density. Even better agreement (1.0889 vs 1.0893) is obtained when the sum of fraction weights is normalized to 100%. It is interesting that the same density could have been reached with 20% less butene if the catalyst had given a fully random miscible copolymer.

HOMOPOLYETHYLENE

Data for many commercial LLDPE's indicate a higher comonomer incorporation to achieve a given density than would be predicted by Eqs. (3) and (11). These copolymers are mixtures of crystal-miscible random copolymers of unspecified (but

TABLE 1. Fractionation of LLDPE [3]

Fraction	Weight of fraction, %	Butene in fraction, wt%	Branching B	Predicted V_i	$W_i\ V_i$
A	27.5	13.4	33.5	1.1180	0.3075
B	36.5	7.8	19.5	1.0967	0.4003
C	20.2	2.4	6.0	1.0660	0.2153
D	15.7	0	0	1.0485	0.1646
Calculated sum	99.9	7.02	17.56	–	1.0877
Measured	–	7.0	17.5	–	1.0893

less than maximum) composition and amorphous material. Mathematically, this is equivalent to regarding the system as a ternary mixture of

A. Miscible copolymer of composition and density determined by the intersection of Eqs. (3) and (11)
B. Amorphous copolymer
C. Homopolyethylene

The envelope that completely encloses most of the data would linearly connect these three components. Points outside the envelopes would be there because of experimental errors.

The third relationship is a linear connection between amorphous copolymer (1.1710, 70) and homopolymer (1.0485, 0) i.e.,

$$V_e = 1.0485 + 0.001750B \qquad (12)$$

This line appears to be a reasonable lower envelope for commercial butene copolymers, as shown in Fig. 5. The intersections of Eqs. (3), (11), and (12) for butene copolymer form a triangle with vertices at (1.0485, 0), (1.0873, 13.32), and (1.1710, 70.0).

Measured density and branchiness yield three equations in three unknowns that can be solved for the relative amounts of the three hypothesized components.

For butene-1 copolymers:

$$W_c + W_a + W_e = 1 \qquad (13.1)$$

$$1.0485W_c + 1.0873W_a + 1.1710W_e = V \qquad (13.2)$$

$$13.32W_c + 70.0W_a = V \qquad (13.3)$$

For example, the copolymer designated "LLDPE-A" by Mirabella and Ford, shown in Fig. 5, has measured parameters $V = 1.0893$ and $B = 17.5$. From these

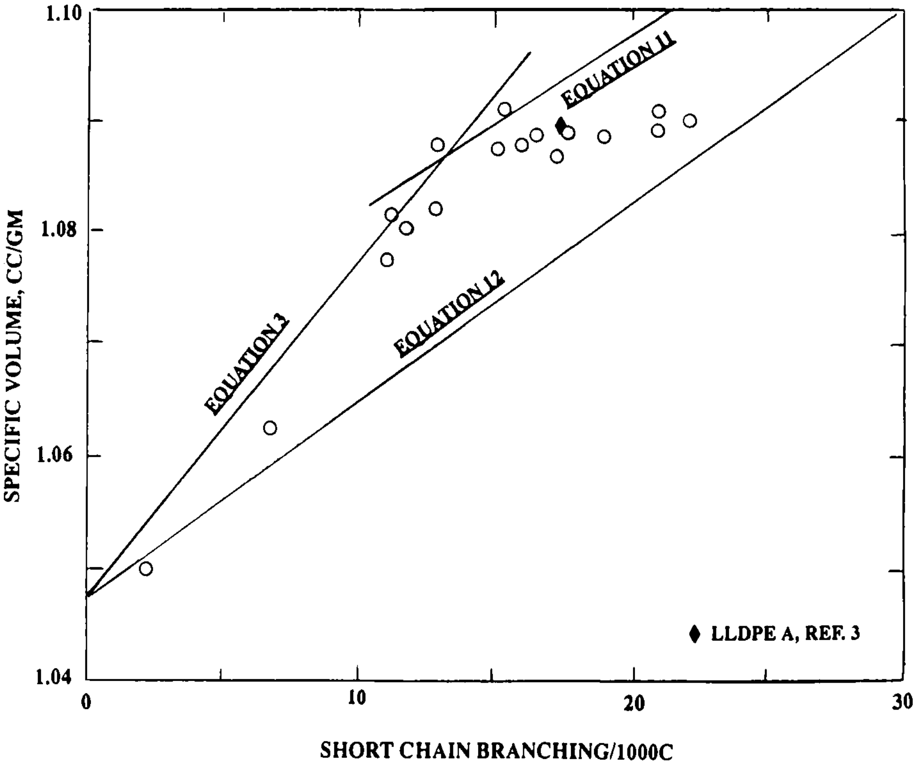

FIG. 5. LLDPE specific volume vs chain branching of commercial butene copolymers.

data Eqs. (13) calculate 22% random, 66% amorphous, and 12% homopolymer. Ratios of these values can be used to correlate and predict physical properties that are related to homogeneity and crystallinity.

PHASE SEPARATION

The intersection of Eqs. (3) and (11) defines the maximum comonomer level without phase separation. But if comonomer units are not inserted randomly along the polymer backbone, or the system is nonhomogeneous, as defined previously by Ross [10]; there can be local areas with greater-than-average comonomer concentrations. These will form local amorphous regions. Under these circumstances, specific volumes will be less than predicted by Eq. (3).

Actually, there should be a somewhat gradual transition from miscible to nonmiscible copolymers as branching is increase, rather than an abrupt change from one regime to the other. Conceptually, however, it is useful to idealize the model to a system of straight lines.

Martinez de Salazar and Balta Calleja [6] have shown that as the number of crystal defects (principally branching) increases, polyethylene crystal volume rises smoothly over the range of ~2–70 branches/1000 C. The rate of volume increase was high at low levels of branching (<10) and almost constant at higher levels. Alternatively, their polymers may be separated into two groups, $B < 10$ and $B > 10$. Each group can be correlated by a straight line. These lines intersect at $B \approx 12$, as would be expected for a butene-modified polyethylene. See their Fig. 3. (Their measured densities are higher than predicted by Eqs. (3) and (11). This most probably is the result of their sample preparation techniques, which were designed to enhance the formation of large crystals for their crystallographic studies.)

Phase segregation has been proposed to explain the extraordinary fracture toughness of LLDPE compared to LDPE and HDPE. Mirabella et al. found phase segregation in commercial LLDPE containing 15–20 branches/1000 C [11]. The present model predicts that phase separation can occur at this level of branching.

The present model is also consistent with phase compositions calculated from the thermodynamics of mixing. This agreement suggests that spinodal decomposition may explain the crystallization behavior of LLDPE [12]. Rough calculations for the system ethylene–butene suggest that typical LLDPE might separate into two phases containing ~15 and ~50–100 branches/1000 C, respectively. This model predicts 13 and 70.

CONCLUSIONS

1. At low comonomer incorporation levels, specific volume of LLDPE varies linearly with degree of branching and the square root of side-chain molecular weight.
2. These copolymers are largely crystal miscible with ethylene homopolymer.
3. At higher comonomer incorporation levels, maximum increase in specific volume depends on degree of branching and is independent of comonomer molecular weight.
4. A single correlation line appears to be valid up to the EPR region.
5. The present correlations are consistent with prior crystal deformation measurements as well as previously demonstrated phase separation studies.

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