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independent of N as a function of scaled time s. Then the linear combination

$$\hat{C}(s,\alpha) = \sum_N w(t,N)C(sN^\alpha;H_N) / \sum_N w(t,N) \qquad (A.2)$$

will equal the scaled correlation function. To minimize the variance of the estimate of $\hat{C}(s,\alpha)$, the weights $w(t,N)$ must be chosen so that each term in the linear combination contributes an equal variance. This implies

$$w(t,N) = 1/V(t,N) \qquad (A.3)$$

The success of the scaling hypothesis can then be judged by the squared difference between the scaled averaged function and the original data:

$$\chi^2(\alpha) = s^{-1}\int_0^{s_0} \mathrm{d}s \sum_N [C(sN^\alpha;H_N) - \hat{C}(s,\alpha)]^2 / V(sN^\alpha,N) \qquad (A.4)$$

The best scaling exponent is that which minimizes $\chi^2(\alpha)$. In the integral in eq A.4 we have chosen s_0 to be such that for at least two values of N, $C(sN^\alpha;H_N)^2 > V(sN^\alpha,N)$; i.e., the signal is greater than the noise.

The advantages of the above procedure are that it makes no assumptions about the form of $\hat{C}(s)$, that all of the available data are used with the proper statistical weight, and that the procedure is stable (i.e., a minimum in $\chi^2(\alpha)$ is ensured).

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Branch Formation in Low-Density Polyethylene

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ABSTRACT: Formation of short branches in low-density polyethylene (LDPE) has been investigated by using a rotational isomeric state model for the chain statistics. It is assumed that the probability of an intramolecular rearrangement of the Roedel type is proportional to the probability that reacting groups are separated by a distance $r^* \pm \Delta r$ and adhere sufficiently closely to "three in a line" geometry. Excluded-volume effects are ignored. The calculations rationalize many of the structural features observed in LDPE. They support previous proposals that ethyl groups are formed mainly by two successive Roedel-type rearrangements. The greater rate postulated by others for the second rearrangement and the measured 1:1 ratio of the two structures resulting from the second rearrangement (2-ethylhexyl and 1,3-paired ethyl branches) are predicted by the calculations. Butyl branches are calculated to be more prevalent than amyl branches. The calculations indicate that previous studies utilizing ^{13}C NMR may have overestimated the contribution of long-chain branches to the resonances associated with branches six and longer. Our model predicts that the concentration of hexyl, heptyl, and other intermediate-length branches is unlikely to be negligibly small. Therefore, previously reported estimates for the number of long branches in LDPE based on NMR measurements are probably too high.

Low-density polyethylene (LDPE), prepared by the free radical initiated polymerization of ethylene at high ethylene pressure, is a versatile material because different physical properties can be obtained, depending on the reaction conditions used for its preparation. The number and type of short branches, which exert a strong influence on morphology and solid-state properties, are observed to vary from one sample of LDPE to the next.[1] An attractive mechanism for formation of short branches is intramolecular hydrogen atom abstraction in a cyclic intermediate.[2] In contrast, long branches can be defined as those which arise via an intermolecular hydrogen transfer.[3,4] The long branches may have a range of lengths, with an upper limit approaching the length of the main chain.

Among experimental techniques employed to characterize short-chain branching in various samples of low-density polyethylene are infrared spectroscopy,[5-9] radiol-

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ysis,[10-12] and ^{13}C nuclear magnetic resonance (NMR) spectroscopy.[1,9,13-16] Application of these techniques has led to the general conclusion that all low-density polyethylenes contain butyl groups. The nature and relative amounts of other small branches vary considerably from study to study and from sample to sample.

The preferred technique for quantitative characterization of short branches is ^{13}C NMR because the specific identity and concentration of short branches can be extracted from the spectra. This method can distinguish between *n*-alkyl branches containing up to five C atoms.[14,17] *n*-Alkyl branches with six or more C atoms cannot presently be distinguished from each other although their total concentration can be determined from the intensity of a characteristic band given by all *n*-alkyl branches of length six or greater.[14,17] A careful and comprehensive investigation of 15 LDPE samples has shown that methyl branches are formed only when the copolymerizable monomer propylene is present during polymerization.[1] Ethyl branches are usually present, and their concentration can vary over wide limits, depending on polymerization conditions. Propyl branches are usually not present in detectable concentrations although their presence in one sample made using propylene comonomer has been firmly established.[1] Butyl branches are usually found in substantially higher concentrations than other branches.[1,9,12,14,15] Amyl branches, as well as *n*-alkyl branches longer than C_5, have been found in relatively low concentrations.[1,12,14,17]

^{13}C NMR has also provided limited information concerning the distribution of branches along the chain. When butene comonomer is present in small concentrations during polymerization, "isolated" ethyl groups, i.e., ethyl groups that are at least four carbon atoms removed from other branch points, are formed by random copolymerization.[1] However, in the absence of butene comonomer, ethyl groups occur mainly as 1,3-paired ethyls and as constituents of 2-ethylhexyl branches.[1,12]

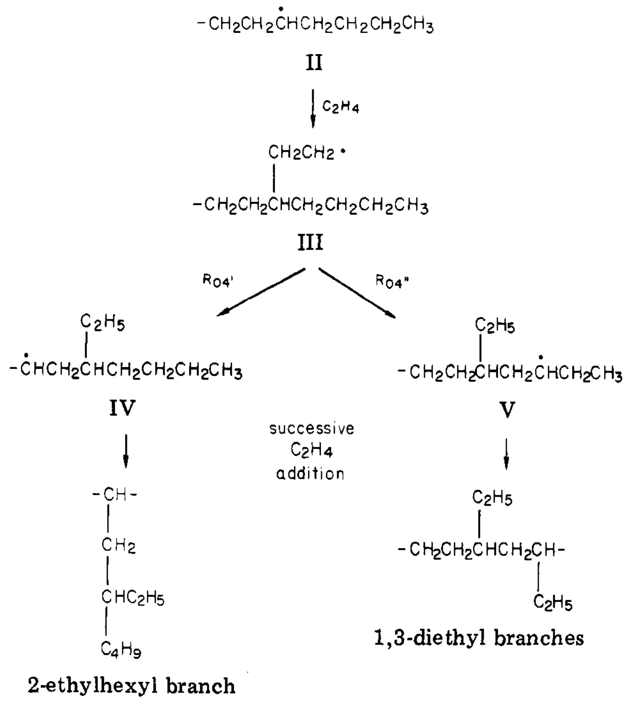
Formation of butyl branches can be explained by an intramolecular radical rearrangement (R_{04}) proposed by Roedel:[2]

$$\underset{\mathrm{I}}{-(\mathrm{CH_2})_x\underset{4}{\mathrm{CH_2}}\underset{3}{\mathrm{CH_2}}\underset{2}{\mathrm{CH_2}}\underset{1}{\mathrm{CH_2}}\underset{0}{\mathrm{CH_2}}\cdot} \xrightarrow{\mathrm{R_{04}}} \underset{\mathrm{II}}{-(\mathrm{CH_2})_x\dot{\mathrm{C}}\mathrm{HC_4H_9}}$$

Subscripts $0j$ in R_{0j} are based on sequential numbering of the carbon atoms, starting at zero at the radical site. Successive addition of ethylene to the rearranged free radical II yields a pendant butyl branch on the polymer chain. C_5, C_6, etc. branches might arise similarly via R_{05}, R_{06}, etc. rearrangements.

The presence of 2-ethylhexyl branches and of 1,3-paired ethyls on the polymer chain could be accounted for by an extension of the Roedel mechanism.[8] Such structures would be formed as depicted in Scheme I. Thus the addition of one molecule of ethylene to II would yield III. This radical could undergo a rearrangement, designated R_{04}', to yield the rearranged radical IV. Successive addition of ethylene to IV would give a 2-ethylhexyl branch on the polymer backbone. An alternate rearrangement of III, designated R_{04}'', would yield the rearranged radical V. Successive addition of ethylene to V would give 1,3-diethyl substituents on the polymer backbone. To account for the relative amounts of ethyl and butyl groups in LDPE, Willbourn postulated that the R_{04}' and R_{04}'' rearrangements were much more probable than the R_{04} rearrangement.[8] One objective of this work was to compare the calculated relative rates for R_{04}, R_{04}', and R_{04}'' rearrangements, using a rotational isomeric state model for unperturbed polyethylene.[18-20]

Scheme I



Another objective of this work pertains to the use of ^{13}C NMR for estimating the concentration of long-chain branches (LCB) in polyethylene. Let P_{0m} be the probability of an R_{0m} rearrangement. If the probability for formation of C_6, C_7, etc. branches by the Roedel mechanism were negligibly small, i.e., if $\sum_{m=6}^{\infty} P_{0m} \ll P_{04}$, then the sum of the concentration of branches longer than C_5 determined by NMR would equal the number of branches formed by intermolecular H transfer, i.e., equal to the number of long branches. The small amyl/butyl ratio in LDPE shows that P_{05} is much smaller than P_{04}. However, this observation does not by itself justify the assumption $\sum_{m=6}^{\infty} P_{0m} \ll P_{04}$. Whereas P_{0m} must undergo a monotonic decrease at sufficiently large m,[21] it may experience maxima and minima at small m.[22-30] Bovey et al. reported good agreement between the concentration of branches longer than C_5 measured by NMR and the concentration of long branches estimated by solution viscosity measurements.[14] These results, as well as those obtained in some,[31,32] but not all,[1] subsequent investigations, have provided some support for the critical assumption that $\sum_{m=6}^{\infty} P_{0m} \ll P_{04}$ and for the use of ^{13}C NMR as a direct measure of long-branch concentration in LDPE. An objective of this work was to calculate P_{0m} for m up to 13, using a rotational isomeric state model to determine whether there is a theoretical basis for equating the content of branches longer than C_5 with the long chain branch content of LDPE.

Calculations

Evaluation of P_{0m}. The probability P_{0m} of an R_{0m} rearrangement at a particular temperature is assumed to be proportional to the probability p_{0m} that carbon atom 0 will find itself at a distance $r^* \pm \Delta r$ from a hydrogen bonded to carbon atom m, the C_m–H···C_0 angle, α, simultaneously being between $\pi - \Delta\alpha$ and π. The latter requirement arises because the preferred geometry for hydrogen atom abstraction is "three in a line".[33] The value of $\Delta\alpha$ is the maximum departure from linearity for C_m–

$H\cdots C_0$ which will permit hydrogen atom abstraction. If our interest is in p_{0m} of sufficiently small m, evaluation can proceed through discrete enumeration of all configurations of the short end of the chain between C_0 and C_m. Weighting, however, must take account of the configurational properties of the long tail as well.

The desired weighting scheme is obtained by using a rotational isomeric state model which successfully accounts for configuration-dependent properties of unperturbed polymethylene.[18-20] The configuration partition function, Z, is formulated as

$$Z = \mathbf{J}^*\mathbf{U}^{(n-2)}\mathbf{J} \qquad (1)$$

where $\mathbf{J}^*$ = row (1,0,0), $\mathbf{J}$ = col (1,1,1), and the statistical weight matrix is

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix}_i \qquad (2)$$

Here columns index the state of bond i, rows index the state of bond $i - 1$, and the order of indexing is t, g$^+$, g$^-$ (trans, gauche$^+$, gauche$^-$). Statistical weights for first- and second-order interactions are denoted by σ and ω, respectively. Specification of dihedral angles, φ, for bonds 2 through $m - 1$ fixes the distance between C_0 and C_m. If φ_m is also specified, the $C_0\cdots H-C_m$ angles, as well as the $C_0\cdots H$ distances, are also fixed. The probability that bonds 2 through m have dihedral angles φ_2, φ_3, ..., φ_m is

$$p_{\varphi_2,\varphi_3,\ldots,\varphi_m} = Z^{-1}\mathbf{J}^*(\mathbf{U}'_{\varphi_2}\mathbf{U}'_{\varphi_3}\ldots\mathbf{U}'_{\varphi_m})\mathbf{U}^{(n-m-1)}\mathbf{J} \qquad (3)$$

where $\mathbf{U}'_{\varphi_i}$ is obtained from $\mathbf{U}_i$ by zeroing all columns except that used when bond i has the desired dihedral angle. The estimate for p_{0m} is the sum of all $p_{\varphi_2,\varphi_3,\ldots,\varphi_m}$ which yield at least one $C_0\cdots H$ distance within $r^* \pm \Delta r$ and a value between $\pi - \Delta\alpha$ and π for that $C_0\cdots H-C_m$ angle. It proves convenient to rewrite eq 1 and 3 as

$$Z = \mathbf{J}^*\mathbf{U}^{(m-1)}\,\text{col}\,(1,y,y) \qquad (4)$$

$$p_{\varphi_2,\varphi_3,\ldots,\varphi_m} = Z^{-1}\mathbf{J}^*\mathbf{U}'_{\varphi_2}\mathbf{U}'_{\varphi_3}\ldots\mathbf{U}'_{\varphi_m}\,\text{col}\,(1,y,y) \qquad (5)$$

where y is the limiting ratio of the second and first elements in $\mathbf{U}^n\mathbf{J}$ as n approaches infinity. The column $(1,y,y)$ is easily evaluated because y converges rapidly as n increases.[19]

Evaluation of p_{04}' and p_{04}''. The hydrogen atom abstractions in the R_{04}' and R_{04}'' rearrangements differ from that in the R_{04} rearrangement in that a branch is already present near the end of the chain. Weighting of the configurations required for the R_{04}' and R_{04}'' rearrangements will therefore be different from that for those producing the R_{04} rearrangement. Probabilities must now be evaluated by using branched-molecule rotational isomeric state theory.[34] In the spirit of eq 4, it is convenient to write the configuration partition function for III as

$$Z = \mathbf{J}^*\mathbf{U}^2\mathbf{U}_4(\mathbf{U} \ominus \mathbf{U})\{[\mathbf{U}_6\,\text{col}\,(1,y,y)] \otimes \mathbf{J}\} \qquad (6)$$

where

$$\mathbf{U}_4 = \begin{bmatrix} 1 & 1 & \tau \\ \omega & 1 & \tau\omega \\ 1 & \omega & \tau\omega \end{bmatrix} \qquad (7)$$

$$\mathbf{U}_6 = \begin{bmatrix} 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \qquad (8)$$

$$\mathbf{U} \ominus \mathbf{U} = \begin{bmatrix} \omega & \omega & \tau & \tau & \tau\omega & \tau^2\omega & 1 & \omega & \tau \\ \omega & 1 & \tau & \tau & \tau & \tau^2\omega & \omega & \omega & \tau\omega \\ \omega & 1 & \tau\omega & \tau\omega & \tau\omega & \tau^2\omega^3 & 1 & 1 & \tau\omega \end{bmatrix} \qquad (9)$$

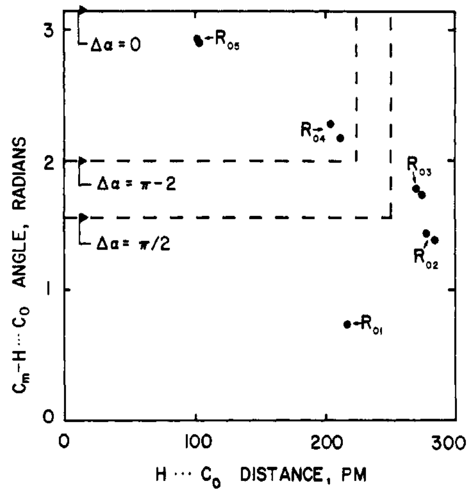


Figure 1. $C_m-H\cdots C_0$ angle, α, and $H\cdots C_0$ distance for m less than 6 and distances smaller than 300 pm. Dashed lines are described in the text.

and the remaining $\mathbf{U}$ are given by eq 2.[34,35] Here $\otimes$ denotes the direct product, and two simultaneous first-order interactions merit a statistical weight of $\sigma\tau$. Indexing for the columns of $\mathbf{U} \ominus \mathbf{U}$ is tt, tg$^+$, tg$^-$, g$^+$t, g$^+$g$^+$, g$^+$g$^-$, g$^-$t, g$^-$g$^+$, g$^-$g$^-$, where the second index denotes the state of the first bond in $CH-CH_2CH_2\cdot$, and the first index denotes the state of the first bond in $CH-(CH_2)_x-$.

Expressions analogous to eq 5 are

$$p_{\varphi_b,\varphi_5,\varphi_6} = Z^{-1}\mathbf{J}^*\mathbf{U}^2\mathbf{U}_4(\mathbf{U}'_{\varphi_5} \ominus \mathbf{U}'_{\varphi_b})\{[\mathbf{U}'_{\varphi_6}\,\text{col}\,(1,y,y)] \otimes \mathbf{J}\} \qquad (10)$$

pertinent for formation of a 2-ethylhexyl branch, and

$$p_{\varphi_3,\varphi_5,\varphi_b} = Z^{-1}\mathbf{J}^*\mathbf{U}\mathbf{U}'_{\varphi_3}\mathbf{U}'_{\varphi_4}(\mathbf{U} \ominus \mathbf{U}'_{\varphi_b})\{[\mathbf{U}_6\,\text{col}\,(1,y,y)] \otimes \mathbf{J}\} \qquad (11)$$

pertinent for formation of 1,3-paired ethyl branches.

Parameters. Structural parameters and interaction energies are those used successfully to rationalize configuration-dependent properties of polymethylene.[19,20] The length of the C–C bond is 153 pm, the supplement of the C–C–C angle is 68°, $\varphi_t = 0°$, and $\varphi_{g\pm} = \pm 112.5°$. The C–H bond length is 110 pm, and hydrogen atoms are positioned so that they equally subtend the available space. Energies are $E_\sigma = 500$ cal mol^{-1}, $E_\tau \geq E_\sigma$, and $E_\omega = 2000$ cal mol^{-1}. Statistical weight w is exp $(-E_w/RT)$.

Results and Discussion

Assignment of $r^* \pm \Delta r$ and $\Delta\alpha$. We assume r^* is approximately the same as the length of a C–H bond. Reasonable assignments for $r^* \pm \Delta r$ and $\Delta\alpha$ can then be obtained by demanding that they produce agreement with the known occurrence of very short branches in low-density polyethylene. Specifically, the assignment must permit formation of butyl and amyl branches but forbid formation of methyl and propyl branches.[1]

Figure 1 depicts the $C_0\cdots H-C_m$ angle, α, and $C_0\cdots H$ distances for configurations in which that distance is less than 300 pm. If the calculation is to rationalize the known formation of butyl side chains, $r^* \pm \Delta r$ must be somewhat greater than 200 pm. A value of at least 1 rad is also required for $\Delta\alpha$ if formation of butyl side chains is to be permitted. However, any combination with $r^* \pm \Delta r > 270$ pm and $\Delta\alpha > 1.4$ rad must be rejected, for the calculation would then predict formation of propyl side chains.

Computations were carried out using $\Delta r = 112$ pm and $\Delta\alpha = \pi - 2$ and also $\Delta r = 125$ pm and $\Delta\alpha = \pi/2$. In each case r^* was $^1/_2\Delta r$. These two sets of assignments are de-

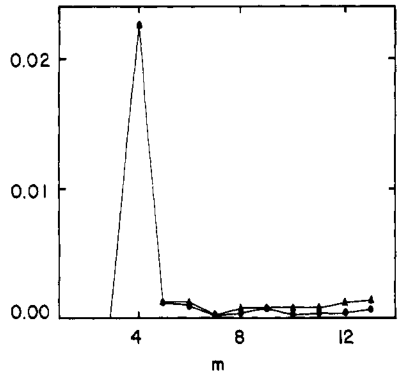


Figure 2. p_{0m} for a temperature of 300 °C. Assignments for filled circles are Δr = 112 pm and $\Delta\alpha = \pi - 2$ and for triangles they are Δr = 125 pm and $\Delta\alpha = \pi/2$.

noted by dashed lines in Figure 1. As will be seen below, similar qualitative conclusions are drawn with both sets of assignments.

p_{0m} for *m* Less Than 14. Figure 2 depicts p_{0m} computed for a temperature of 300 °C. By far the largest p_{0m} is p_{04}, as expected. The calculation therefore rationalizes the observation that butyl side chains are common in low-density polyethylene.[1,13] This figure also shows p_{05} is much smaller than p_{04}. Hence the calculation rationalizes the observation that amyl side chains are much less prevalent than butyl side chains in low-density polyethylene.[1,13] Both sets of assignments for r^*, Δr, and $\Delta\alpha$ yield the same p_{04} and p_{05} because no new configurations contribute to these p_{0m} when the assignments change (Figure 1). Zero is obtained for p_{0m}, $m < 4$, because r^*, Δr, and $\Delta\alpha$ were selected in a manner which forces this result.

The choice of assignments for r^*, Δr, and $\Delta\alpha$ has a small effect on p_{0m} for *m* between 6 and 9, and a larger effect for *m* greater than 9. Several conclusions, however, can be drawn from either set of assignments. In both cases p_{06} is only slightly smaller than p_{05}. Therefore hexyl branches should be nearly as common as amyl branches in low-density polyethylene. A much smaller p_{0m} is obtained when *m* is 7, leading to the expectation that heptyl branches will be virtually absent.

If p_{0m} were to continue to decrease as *m* rose above 7, it would indeed be true that $\sum_{m=6}^{\infty} p_{0m} \ll p_{04}$. The results depicted in Figure 2, however, show that p_{0m} goes through a minimum at $m = 7$. Nonyl branches might be expected to be nearly as prevalent as hexyl. Detailed behavior of p_{0m} at still higher *m* becomes more sensitive to the assignment of r^*, Δr, and $\Delta\alpha$. Neither sets of assignments employed, however, show a rapid decline in p_{0m} when *m* is in the range 8–13. On the contrary, these p_{0m} suggest nonnegligible p_{0m} might be obtained over an appreciable range of *m*. Either set of assignments used yields $p_{05} < \sum_{m=6}^{\infty} p_{0m}$. While p_{04} may well be larger than $\sum_{m=6}^{\infty} p_{0m}$, this sum may not be negligible compared to p_{04}.

Most of the above conclusions can also be drawn from results of calculations in which $\varphi_{g\pm}$ is ±120° rather than ±112.5°. When $\varphi_{g\pm}$ is ±120°, the p_{0m} show a much more pronounced alternating character. If *m* is even and larger than 5, the p_{0m} computed with $\varphi_{g\pm} = \pm 120°$ are roughly 3 times as large as those depicted in Figure 2. This result arises because the chain conforms more closely to a diamond lattice when $\varphi_{g\pm}$ is ±120°.

Temperature dependence of the p_{0m} is depicted in Figure 3. An increase in temperature produces an increase in p_{0m}, with the effect becoming less dramatic as *m* rises above 9. Configurations conducive to an R_{0m} rearrangement must contain gauche placements, and they frequently contain neighboring bonds which occupy gauche placements of opposite sign. This situation is particularly so when *m* is small. Configurations required for an R_{0m} rearrangement can compete more effectively with lower energy, predominantly trans, configurations if *RT* increases relative to E_σ and E_ω.

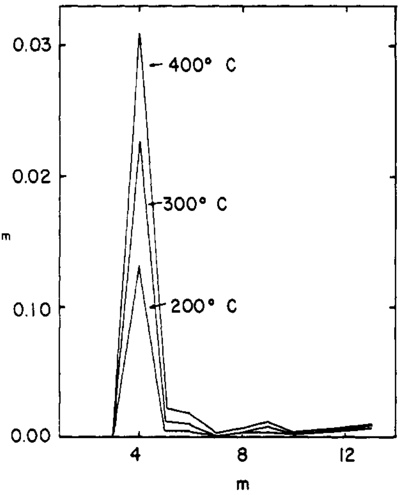


Figure 3. p_{0m} for temperatures of 200, 300, and 400 °C, using Δr = 112 pm, $\Delta\alpha = \pi/2$.

The conclusion that $\sum_{m=6}^{\infty} p_{0m}$ is not negligibly small compared to p_{04} implies that reported LCB values for LDPE by ^{13}C NMR are likely to be too high. Contrary to the basic hypothesis of the NMR method for long-chain branching, the concentration of branches having intermediate length (C_6, C_7, C_8, etc.) in LDPE is unlikely to be negligibly small. Therefore it is not surprising that LCB values obtained by NMR and hydrodynamic measurements are not always in agreement.[1] Nevertheless, good agreement has been reported between LCB concentrations determined by NMR and by solution viscosity methods in some cases.[14,31] In these latter investigations, solution viscosity was related to molecular structure by the equation

$$g^\epsilon = [\eta]_B/[\eta]_L \tag{12}$$

Here $[\eta]_B$ and $[\eta]_L$ are the limiting viscosity numbers for branched and linear molecules having the same molecular weight, *g* is the ratio of the mean-square radius of gyration of branched molecules to that of linear molecules, and ϵ is a parameter variously estimated to range from 0.5 to 1.5. Calculations show that the number of LCB estimated by solution viscosity methods is very sensitive to the structural model assumed for the branched molecules and to the value chosen for ϵ.[36] In one experimental investigation good agreement with NMR LCB values was obtained for $\epsilon = 0.75$,[31] whereas in another investigation agreement was obtained for a different value of ϵ, 0.50.[14] Thus, there is considerable uncertainty in the accuracy of LCB estimates obtained by solution viscosity methods. The reported agreement with NMR estimates therefore does not provide strong support for the accuracy of NMR values nor for the assumption that the concentration of intermediate length branches is negligibly small.

While results of the calculations reported here give reason to question the absolute accuracy of LCB concentrations concentrations by NMR, relative values obtained by NMR and solution viscosity methods appear to be more reliable. This is indicated by Foster's results, which show an excellent correlation between LCB concentrations obtained by the two methods.[31] A correlation coefficient equal to 0.98 was obtained for seven samples. Whether

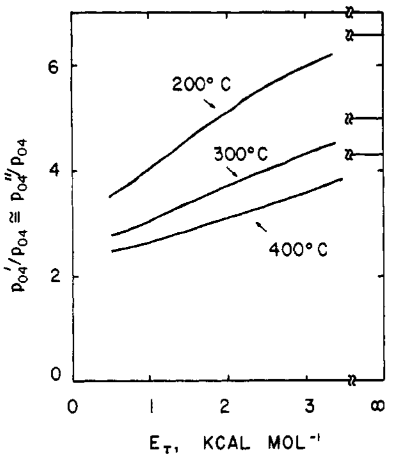


Figure 4. Dependence of p_{04}'/p_{04} and p_{04}''/p_{04} on E_τ.

such a good correlation holds for LDPE polymers prepared over a broad range of experimental conditions is presently undemonstrated.

Relative Probabilities for R_{04}, R_{04}', and R_{04}'' Rearrangements. Identical values are obtained for p_{04}' and p_{04}'' if $\tau = 0$ ($E_\tau = \infty$). If $\infty > E_\tau \geq 500$ cal mol^{-1} and T is in the range 200–400 °C, p_{04}' is less than p_{04}'', but the difference is less than 0.1%. Therefore the content of 2-ethylhexyl branches in low-density polyethylene must equal the content of 1,3-paired ethyl branches if these branches arise solely via R_{04}' and R_{04}'' rearrangements and the probability of the necessary rearrangements is governed by the configurational statistics of the unperturbed polymethylene chain. The calculated 1:1 ratio for these two structures is indeed in agreement with the 1:1 ratio determined by ^{13}C NMR.[12]

Figure 4 depicts the ratio of p_{04}' (or p_{04}'') to p_{04} as a function of E_τ in the temperature range 200–400 °C. This ratio exceeds unity for all conditions of interest, and it has a large value (3–6) at typical ethylene polymerization temperatures of 200–300 °C. The results are consistent with $p_{04}p_{04}'$ (or $p_{04}p_{04}''$) $> p_{04}^2$, where p_{04}^2 denotes the anticipated probability of having the two successive rearrangements required to produce 2-ethylhexyl or 1,3-paired ethyl branches if both rearrangements were of the *same* probability. These calculations therefore support Willbourn's ad hoc assumption that the R_{04}' and R_{04}'' rearrangements are much more probable than the R_{04} rearrangement.[8] Chain configurations giving rise to an R_{04} rearrangement have two successive bonds occupying gauche states of opposite sign. This pair of bonds contributes a factor of $\sigma^2\omega$ to the statistical weight of the chain. Competing configurations have a substantially larger statistical weight. The competing configurations are subject to additional repulsive first- and second-order interactions if a trifunctional branch point occurs in the fragment undergoing cyclization, as is the case in the R_{04}' and R_{04}'' rearrangements. For this reason p_{04}' and p_{04}'' are larger than p_{04}. It is questionable whether 2-ethylhexyl or 1,3-paired ethyl branches could be detected in low-density polyethylene if the probability for their formation were no larger than p_{04}^2.

The above rationalization of the calculated result, showing p_{04}' and p_{04}'' being larger than p_{04}, should apply in other cases as well. In general, then, we anticipate p_{0m}' and p_{0m}'' will be larger than p_{0m}. These calculations indicate an initial rearrangement will tend to be followed by a second rearrangement. Extension of this argument suggests the second rearrangement increases the probability of a third rearrangement, etc. There will consequently be a tendency for clustering of short branches, especially, as discussed below, in polymers made at low ethylene concentrations.

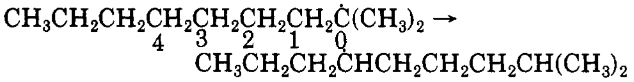
Table I
Relative Rates of Radical Rearrangements by Various Methods

	generated	relative rate of R_{0m}		relative
m	branch by R_{0m}	by NMR	calcd	rate of $R_{0'm}$
1	CH_3	0	0 (forced)	0
2	C_2H_5		0	0
3	C_3H_7	0	0 (forced)	1
4	C_4H_9	100	100	100
5	C_5H_{11}	19	4–6	5

The predicted tendency for clustering of branches in some low-density polyethylenes is consistent with LDPE melting point measurements. Clustering of branches would be expected to increase the melting point above that of a polymer having an equal number of short branches distributed randomly along the chain.[37] Hydrogenated polybutadiene is taken as a model for an ethyl-branched polyethylene with a random distribution of short branches. The 110–116 °C melting point of isothermally crystallized LDPE's containing 8–16 short branches/1000 C atoms[38] is indeed significantly greater than the 99 °C melting point of an isothermally crystallized hydrogenated butadiene containing a slightly greater number of branches, 19 branches/1000 C atoms.[39]

The extended Roedel mechanism for branch formation in LDPE, which is strongly supported by our calculations, accounts for the wide ethyl:butyl ratio range found for this polymer.[1] At very high ethylene concentrations the rate of ethylene addition to III will be greater than the rate of the unimolecular R_{04}' and R_{04}'' rearrangements. Consequently, mainly butyl branches will be formed and these will tend to be randomly distributed along the polymer chain. However, at low ethylene pressures the rate of ethylene addition to III will be smaller than the rate of R_{04}' and R_{04}'' rearrangements. Under these conditions the number of ethyl branches will be greater than the number of butyl branches and the branches will tend to occur in clusters, with the clusters distributed almost randomly along the polymer chain.

Comparison of Relative Rates of Radical Rearrangements by Various Methods. The relative rates of free radical rearrangements estimated by three different methods are summarized in Table I. Numers in the NMR R_{0m} column are average intensities of various alkyl groups, relative to butyl, for seven LDPE's made without propylene or butene comonomer.[1] As discussed above, ethyl branches in LDPE homopolymer are believed to form mainly by two successive rearrangements so their concentration does not give a valid measure of R_{02}. Consequently, no value is given for R_{02} in the NMR column. The fourth column shows R_{0m} for m = 1–5 calculated for 200–300 °C, using Δr = 112 pm and $\Delta\alpha = \pi - 2$. The $R_{0'm}$ column lists relative rates of rearrangements for vibrationally excited 2-nonyl free radicals in the gas phase that were determined from analyses of reaction products.[40] The $R_{0'm}$ rearrangements are illustrated below for m = 4:



$$CH_3CH_2CH_2\underset{4}{CH_2}\underset{3}{C}H_2\underset{2}{C}H_2\underset{1}{C}H_2\underset{0}{\dot{C}}(CH_3)_2 \rightarrow CH_3CH_2CH_2\dot{C}HCH_2CH_2CH_2CH(CH_3)_2$$

Analogous to the previous R_{0j} nomenclature, subscripts $0'j$ in $R_{0'j}$ are based on sequential numbering of carbon atoms starting at the free radical site. Table I shows qualitative agreement between the three methods for estimating the relative rates of the radical rearrangements. Quantitative agreement would not be expected between $R_{0'm}$ and NMR R_{0m} values, considering the different, albeit analogous, processes involved. The zero calculated value for R_{02} and the zero measured value for $R_{0'2}$ support the view that ethyl branches in LDPE are not formed by an R_{02} rearrangement. It has been suggested that the steric probability for cyclic transition states leading to propyl and butyl branches should be similar and that the absence of propyl branches in LDPE therefore argues against the Roedel R_{04} mechanism for butyl formation.[41] Our calculations show, however, that the high concentration of butyl branches and the absence of propyl branches can be readily reconciled by conformation considerations.

Comparison of calculated and NMR estimates for R_{05} in Table I shows that the calculated C_5H_9 concentration is considerably lower than that measured by NMR. The discrepancy is due in part to the method used to calculate p_{0m}. A configuration satisfies the tolerances if its $C_0 \cdots H$ distance and $C_0 \cdots H–C_m$ angle place it within the pertinent rectangle denoted by dashed lines in Figure 1. No distinction is drawn between configurations which fall at the top of this rectangle, and therefore conform very closely to "three in a line" geometry, and configurations which barely lie above the bottom border of the rectangle. However, the former configurations should actually have a higher propensity for rearrangement than the latter. If the upper part of the rectangle were to be more heavily weighted than the lower part, it is clear from Figure 1 that p_{05} would increase relative to p_{04}, thereby bringing the calculation into better agreement with the NMR result.

Conclusions

The preceding results and discussion lead to the following conclusions:

(1) Calculations using a rotational isomeric state model for the chain statistics can account for many structural features encountered in LDPE.

(2) Butyl, amyl, and intermediate-length branches are formed by Roedel-type free radical rearrangements. The calculation readily rationalizes the preponderance of butyl groups in the polymer.

(3) Contrary to the basic assumption of the ^{13}C NMR method for long chain branching estimates in LDPE, the calculations indicate that the concentration of intermediate-length branches (C_6, C_7, C_8, etc.) is not negligibly small. Consequently, NMR estimates for long-branch concentrations in this polymer are likely to be somewhat too high.

(4) The calculations support the conclusion that ethyl groups in LDPE homopolymers are formed mainly by the extended Roedel mechanism involving two successive free radical rearrangements. The greater rate postulated by others for the second rearrangement and the measured 1:1 ratio of the two structures resulting from the second rearrangement (2-ethylhexyl and 1,3-paired ethyl branches) are predicted by the calculations. The identity of branches and the extent of clustering of branches should be strong functions of polymerization conditions.

(5) The calculations rationalize the absence of methyl and propyl branches in LDPE homopolymers.

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