gests that considerable frequency dispersion may be present in the PC film above T_g.

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Registry No. Bisphenol A polycarbonate, 24936-68-3; bisphenol A–carbonic acid copolymer, 25037-45-0.

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Complex Branch Formation in Low-Density Polyethylene

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ABSTRACT: Formation of complex branches, which might arise from two intramolecular rearrangements of the Roedel type, has been investigated in polyethylene. A rotational isomeric state model is used for the polyethylene chain statistics, with inclusion of the effect of a trifunctional branch point on weighting of all configurations. It is assumed that reactive configurations are those in which pertinent carbon atoms are separated by a distance $r^* \pm \Delta r$, there simultaneously being approximate adherence to "three-in-a-line" geometry. This approach has recently been shown to rationalize several characteristics of branching in low-density polyethylene, including the common occurrence of butyl, less frequent presence of amyl, and occassional detection of 1,3-paired diethyl and 2-ethylhexyl branches (Mattice, W. L.; Stehling, F. C. *Macromolecules* **1981**, *14*, 1479). Present calculations successfully rationalize the observation of 1,3-paired ethyl butyl and tetrafunctional butyl branches, but they provide no explanation for the formation of tetrafunctional ethyl branches. They also suggest that 2-butylhexyl is an attractive candidate for unassigned resonances in the ^{13}C NMR spectra of low-density polyethylene.

Free radical initiated polymerization of ethylene at high pressure gives rise to low-density polyethylene. In addition to long branches,[1,2] this material contains short branches which influence morphology and solid-state properties. The number and type of short branches vary from one sample to the next.[3-13] Quantitative characterization of short branches is most easily achieved with ^{13}C NMR.[3-8,10-13] Short branches reported in low-density polyethylene include butyl,[3-8,11-13] ethyl,[3-8,11,13] amyl,[5,6,10-13] 1,3-paired diethyl,[11,13] 2-ethylhexyl,[11,13] 1,3-paired ethyl butyl,[13] tetrafunctional ethyl,[13] tetrafunctional ethyl butyl,[13] and tetrafunctional butyl.[13] Additional resonances, arising from short branches of unknown composition, are also found.

Intramolecular hydrogen atom abstraction via a cyclic intermediate is an attractive mechanism for formation of short branches.[14] Analysis of probabilities for observation of configurations conducive to this abstraction, using a rotational isomeric state model for the chain statistics,[15,16] can successfully rationalize occurrence of several known types of short branches.[17] The rotational isomeric state model can be reasonably parameterized so that a single Roedel-type rearrangement would be most likely to yield a butyl branch, could also give rise to longer branches, but would not produce branches shorter than butyl. Simple extensions of this mechanism have been proposed as a source of 2-ethylhexyl,[18] 1,3-paired diethyl,[18] and tetrafunctional butyl[14] branches. The rotational isomeric state

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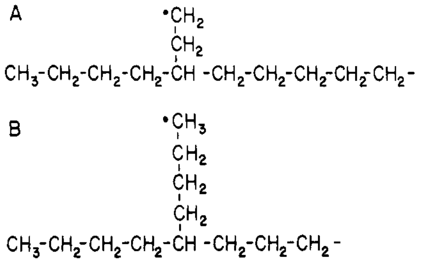

A: $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH(CH_2{-}{\cdot}CH_2){-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}$

B: $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH(CH_2{-}CH_2{-}CH_2{-}{\cdot}CH_3){-}CH_2{-}CH_2{-}CH_2{-}$

Figure 1. Fragments whose intramolecular rearrangements are considered in Figures 2 and 3.

model[17] provides support for the possibility that the necessary consecutive Roedel-type rearrangements would be of sufficiently high probability so that 2-ethylhexyl and 1,3-paired diethyl branches could be observed in low-density polyethylene.

Recently[13] evidence for the existence of additional types of complex and paired branches has been obtained from ^{13}C NMR spectra. The double back-biting mechanism[10,18] has been proposed as the origin for several of these branches.[13] The major objective here is evaluation of probabilities, using the rotational isomeric state approach, for the second of the two necessary rearrangements. Calculations identify a complex short branch which is an attractive candidate for unassigned resonances in ^{13}C NMR spectra of low-density polyethylene.

Calculations

Calculations were performed in the same manner as that employed in our earlier investigation of the formation of 2-ethylhexyl and 1,3-paired diethyl branches.[17] Using branched molecule rotational isomeric state formalism,[19] we can write the configuration partition function, Z, as

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

for the molecule depicted in Figure 1A and as

$$Z = \mathbf{J}^*\mathbf{U}^2\mathbf{U}_4(\mathbf{U} \ominus \mathbf{U})\{[\mathbf{U}_6 \text{ col } (1,y,y)] \otimes [\mathbf{U}_7\mathbf{U}\mathbf{J}]\} \tag{2}$$

for the molecule depicted in Figure 1B. Statistical weight matrices appearing in these expressions are[15,19,20]

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{3}$$

$$\mathbf{U}_4 = \begin{bmatrix} 1 & 1 & \tau \\ \omega & 1 & \tau\omega \\ 1 & \omega & \tau\omega \end{bmatrix} \tag{4}$$

$$\mathbf{U}_6 = \begin{bmatrix} 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{5}$$

$$\mathbf{U}_7 = \begin{bmatrix} 1 & \sigma\omega & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma\omega \end{bmatrix} \tag{6}$$

$$\mathbf{U} \ominus \mathbf{U} = \begin{bmatrix} \omega & \omega & \tau & \tau & \tau\omega & \tau^2\omega & 1 & \omega & \tau \\ \omega & 1 & \tau & \tau & \tau & \tau^2\omega & \omega & \omega & \tau\omega \\ \omega & 1 & \tau\omega & \tau\omega & \tau\omega & \tau^2\omega^3 & 1 & 1 & \tau\omega \end{bmatrix} \tag{7}$$

and $\mathbf{J}^*$ = row (1, 0, 0) and $\mathbf{J}$ = col (1, 1, 1). The limiting ratio, as n approaches infinity, of the second and first elements in $\mathbf{U}^n\mathbf{J}$ defines y. Thus y takes account of the remainder of the polyethylene chain, in the approximation that additional branch points are at least eight carbon atoms removed from the branch point depicted in Figure 1A,B.

Following the procedure employed previously,[17] we desire the a priori probability for chain configurations with the proper separation and angular correlation for three atoms. Let C· denote the carbon atom that is to abstract a hydrogen atom from carbon atom C_i. Separation of atoms C· and C_i is denoted by r, and the C_i–H···C· angle is denoted by α. We desire probabilities for configurations in which r is within a tolerance Δr of a critical distance r^*, the angle α simultaneously deviating from π by no more than $\Delta\alpha$. The latter requirement arises from the preferred angular geometry for hydrogen atom abstraction being "three in a line".[21] The maximum allowed departure from linearity is thus $\Delta\alpha$. Our previous work used $\Delta r = r^*/2$ and either $r^* = 112$ pm, $\Delta\alpha = \pi - 2$ or $r^* = 125$ pm, $\Delta\alpha = \pi/2$. These assignments prohibit formation of methyl, ethyl, or propyl branches via a single rearrangement, cause butyl to be the most prevalent branch, and predict formation of amyl and longer branches in smaller amounts. Both sets of assignments yield identical results for the rearrangements studied here.

The a priori probability, p_i, for observation of the ith configuration is calculated[16,19] as

$$p_i = Z_i'/Z \tag{8}$$

where Z_i' differs from Z only in modification of statistical weight matrices for those bonds whose configuration is specified. Two columns (six or eight columns in $\mathbf{U} \ominus \mathbf{U}$) are rendered null in modified statistical weight matrices. The only column(s) retaining nonzero elements is that indexed by the state required for the specified configuration. The probability, p, for a specified rearrangement is the sum of all p_i for configurations that simultaneously satisfy the tolerances for r and α.

Structural parameters and two interaction energies are those used to rationalize configuration-dependent properties of linear polyethylene.[15,22] Bond lengths are 153 and 110 pm for C–C and C–H, respectively, the supplement of the C–C–C angle is 68°, and dihedral angles for trans and gauche states are 0° and ±112.5°. C–C–H angles are assigned so that hydrogen atoms equally subtend the available space. First- and second-order interaction energies, E_σ and E_ω, are 500 and 2000 cal/mol, respectively. An additional first-order interaction energy, E_τ, is required for bonds to a trifunctional carbon atom. While an exact value for this energy is not available, it must be no smaller than E_σ. Calculations were performed using various E_τ ranging upward from E_σ. Excluded volume effects are ignored.

Results and Discussion

Table I summarizes types of branches that result from intramolecular hydrogen atom abstraction in structures depicted in Figure 1A,B. The branch listed is the one that would arise if hydrogen atom abstraction were to be followed by continual addition of ethylene without further rearrangement.

Figures 2 and 3 depict calculated probabilities for configurations conducive to hydrogen atom abstraction from the indicated carbon atoms. Two curves are shown in each figure. These curves depict results obtained using $\tau = \sigma$ and $\tau = 0$. They therefore bracket the anticipated value for τ. Additional calculations (results not shown) were performed with temperatures of 200 and 400 °C. Probabilities for observation of reactive configurations increase with an increase in temperature. As noted earlier,[17] the probability increases with temperature because the lowest energy configurations do not have a geometry favorable for intramolecular hydrogen atom abstraction. Higher energy configurations with the desired geometry can com-

Table I
Types of Branches Formed

precursor	reactive carbon	resulting branch
Figures 1A and 2	C_1	1,4-paired methyl ethyl
	C_2	1,3-paired diethyl[a]
	C_3	1,2-paired ethyl propyl
	C_4	tetrafunctional ethyl butyl[a]
	C_5	1-ethylpentyl
	C_6	2-ethylhexyl[a]
	C_7	3-ethylheptyl
	C_8	4-ethyloctyl
	C_9	5-ethylnonyl
Figures 1B and 3	C_1	1,4-paired methyl butyl
	C_2	1,3-paired ethyl butyl[a]
	C_3	1,2-paired propyl butyl
	C_4	tetrafunctional butyl[a]
	C_5	1-butylpentyl
	C_6	2-butylhexyl
	C_7	3-butylheptyl

[a] Branch reported in low-density polyethylene. See text for citations.

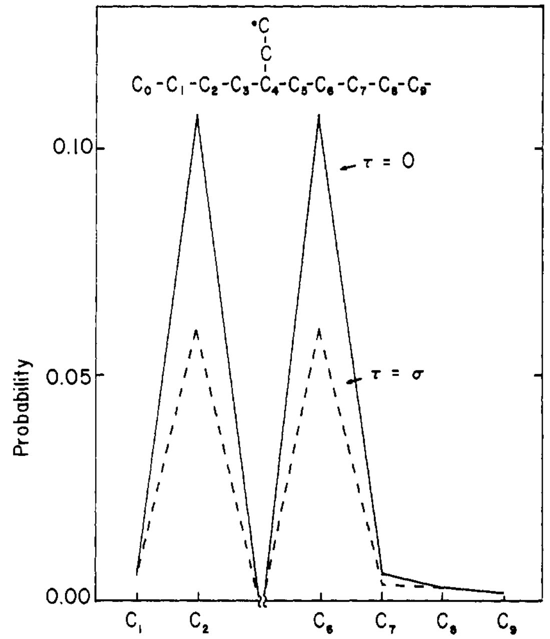

Figure 2. Probabilities at 300 °C for configurations conducive to intramolecular abstraction of a hydrogen atom bonded to the indicated carbon atoms.

pete more effectively with unreactive, low-energy conformations at higher temperatures. While changes in temperature alter computed probabilities, the manner in which these probabilities vary with C_i is qualitatively the same at all temperature examined.

Figure 2 shows that nearly identical probabilities are obtained for rearrangements giving rise to 2-ethylhexyl and 1,3-paired diethyl branches, as reported previously.[17] Probabilities for these rearrangements exceed, by at least an order of magnitude, those for any of the other rearrangements dealt with in Figure 2. Abstraction of hydrogen atoms bonded to C_3, C_4, or C_5 is forbidden because the tolerances for r^*, Δr, and $\Delta\alpha$ were assigned so that they exclude configurations required for production of methyl, ethyl, or propyl side chains via a single rearrangement.[17] Figure 2 shows that the calculation can rationalize the observation of 2-ethylhexyl and 1,3-paired diethyl branches.[17] However, it provides no explanation for the reported observation[13] of tetrafunctional ethyl butyl or tetrafunctional ethyl branches. Formation of those branches might arise by abstraction of a hydrogen atom from C_4. The necessary rearrangement requires configurations that, in a linear chain, would produce hydrogen atom abstractions giving rise to isolated ethyl branches. Our calculation is parameterized so that it forbids formation of isolated ethyl branches, and it therefore assigns a probability of zero to intramolecular hydrogen atom abstraction from C_4 in the fragment dealt with in Figure 2.

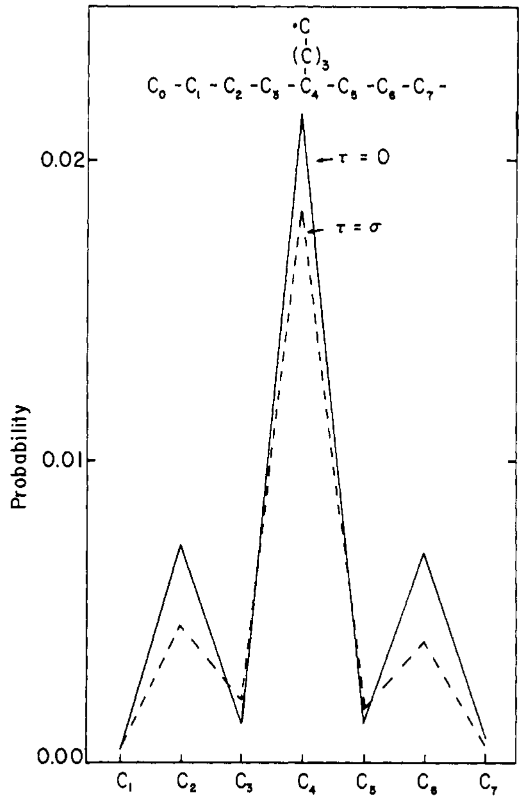

Figure 3. Probabilities at 300 °C for configurations conducive to intramolecular abstraction of a hydrogen atom bonded to the indicated carbon atoms.

Figure 3 depicts probabilities for configurations conducive to intramolecular hydrogen atom abstraction starting from the fragment depicted in Figure 1B. C_4 is now the atom from which hydrogen atom abstraction is most likely. The resulting branch would be tetrafunctional butyl, which has been reported in low-density polyethylene.[13] The number of carbon atoms in the cyclic intermediate is five, which was also the case in rearrangements having the highest probabilities in Figure 2. This cyclic intermediate is found to be more probable in Figure 2, by a factor of 3–5, than is the case in Figure 3. A difference of a factor of 2 would be expected as a simple consequence of the difference in number of potentially abstracted hydrogen atoms bonded to C_4 in Figure 3 and to C_2 or C_6 in Figure 2. The additional factor of approximately 2 arises from the effect of the trifunctional branch point on weighting of the configurations. It must be recalled that Figures 2 and 3 evaluate only configurational effects. They do not take into account different intrinsic reactivities of secondary and tertiary hydrogen atoms.

Subsidiary maxima occur in Figure 3 for abstraction of hydrogen atoms from C_2 and C_6. Probabilities are nearly identical for configurations conducive to these two rearrangements. Intramolecular hydrogen atom abstraction from C_2 could give rise to 1,3-paired ethyl butyl, which has been reported in low-density polyethylene.[13] If abstraction were from C_6, the resulting branch would be 2-butylhexyl. We are not aware of any experimental identification of 2-butylhexyl branches in low-density polyethylene. The calculation depicted in Figure 3, along with the reported observation of 1,3-paired ethyl butyl, makes 4-butylhexyl an attractive candidate for a contributor to unidentified resonances observed in ^{13}C NMR spectra of low-density polyethylene samples.

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Registry No. Polyethylene, 9002-88-4.

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