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Ties, Loops, and Tight Folds in Ethylene–1-Alkene Copolymers with Different 1-Alkene Components

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ABSTRACT: The characteristic ratio, C, has been evaluated by rotational isomeric state theory for polyethylene chains that contain randomly placed short branches. The size of the short branches ranges from methyl to octyl. Calculations were restricted to chains with few branches, where C is nearly a linear function of branch content. The calculations provide numerical values for $(\partial \ln C/\partial P_b)_0$, where P_b is the probability that a repeat unit has a short branch and zero as a subscript denotes the initial slope. Within the context of the Gambler's Ruin model, these $(\partial \ln C/\partial P_b)_0$ are used for evaluation of $(\partial \ln P_T/\partial P_b)_0$, $(\partial \ln \langle B\rangle/\partial P_b)_0$, $(\partial \ln \langle L\rangle/\partial P_b)_0$, and $(\partial \ln P_{tf}/\partial P_b)_0$, where P_T denotes the probability of a tie, $\langle B\rangle$ and $\langle L\rangle$ denote the average number of bonds in a tie and loop, and P_{tf} denotes the probability of a tight fold. The values of $(\partial \ln C/\partial P_b)_0$ and $(\partial \ln P_T/\partial P_b)_0$ are identical, and they decrease with branch size up to ethyl and then approach a plateau. In contrast, $(\partial \ln P_{tf}/\partial P_b)_0$ increases with branch size and does not reach a plateau for the branches studied. The value of $\langle L\rangle$ is independent of P_b, and $(\partial \ln \langle B\rangle/\partial P_b)_0$ shows an initial increase with branch size and then reaches a plateau. Implications of these results for the tensile and tear strengths of the bulk polymer are discussed.

Introduction

The properties of copolymers of ethylene with a small amount of a 1-alkene, which bear the popular name linear low-density polyethylene, depend on the nature of the minor component. The presence of short branches and absence of long branches leads to unique properties for these copolymers. The short branches are of uniform type because they arise from the 1-alkene comonomer. In contrast, the material obtained from the free-radical-initiated polymerization of ethylene at high pressure contains both short and long branches, and the short branches are not of uniform type.[1,2] The ethylene–1-alkene copolymers generally have better tensile and tear strengths. Ethylene–1-alkene copolymers with a range of properties can be obtained by appropriate selection of the type and amount of 1-alkene used in the copolymerization. The molecular basis for this dependence of properties is not known.

The molecular morphology in these copolymers must be considered in the development of a rational explanation of the dependence of physical properties on the type of short branches introduced. Flory's theory of the equilibrium melting points of copolymers pictures the comonomer units as being confined to the amorphous phase.[3] An exception is provided by methyl branches, which can be incorporated in the crystalline regions of polyethylene.[4-9] Theoretical studies[8] of ethylene–1-butene copolymers show that few ethyl branches lie in the crystal. Electron micrograph studies[9] indicate the presence of fairly long lamellae with reduced crystalline perfection for slow-cooled hydrogenated polybutadiene samples containing 2.2 and 3.2 mol % ethyl branches that are randomly distributed. At a lower counit content (less than 1.5 mol % branch groups present in slightly ordered sequence distributions), the electron micrographs did not reveal any significant differences in the lamellar structure between ethylene–butene and ethylene–octene copolymers, and in both cases well-developed crystals with good internal perfection were formed. It can be assumed that close packing of the chain segments in the crystallites requires exclusion of short branches larger than ethyl from the crystalline regions.

Yoon and Flory have described a model for the amorphous regions in semicrystalline polyethylene.[10] On the basis of their model, DiMarzio et al.[11] and Guttman et al.[12,13] developed analytical models for several properties of a homopolymer in the amorphous phase of a lamellar semicrystalline polymer. When the interlamellae spacing is sufficiently large and the interfacial region is small, the statistics of loops and bridges are described by the classic Gambler's Ruin problem. Among the properties that are accurately described are the probability of a tie or bridge, the average number of bonds in a bridge, and the average number of bonds in a loop that returns to the original crystalline lamella. These properties are denoted by P_T, $\langle B\rangle$, and $\langle L\rangle$, respectively. Unusual conformational effects arising from any intermolecular interactions near the amorphous–crystal interface are not included in the development of the relationships that define these properties in the Gambler's Ruin approach. The relative interfacial content[14] increases very rapidly with increasing counit content and is independent of the chemical nature of the counit or branch group.

The characteristic ratio, C, is the crucial quantity required for characterization of chain segments in the amorphous region via the Gambler's Ruin approach. Small numbers of randomly placed methyl and ethyl branches will modify the configurational properties of chain segments in the amorphous phase because these branches produce a decrease in C.[15,16] Trends expected upon a systematic change in the size of the short branches are described here. Characteristic ratios are evaluated by using rotational isomeric state theory[17] with inclusion of the interactions between articulated side chains and atoms in the main chain.[18,19] These C are then combined with the Gambler's Ruin to obtain configurational statistics for chains in the amorphous regions. Intermolecular interactions that may occur near the amorphous–crystal interface are ignored.

Computational Methods

A random number generator was used to construct 1000 different chains, each with 500 ethylene or 1-alkene units and the desired probability that a monomer is the 1-alkene. Attachments of branches to the backbone with *d* or *l* stereochemistry were equally probable, and there was no correlation in the stereochemistry at successive branch points. For purposes of computational convenience, the first and last units were ethylene, and there was at least one ethylene unit between successive 1-alkene units, thereby suppressing short-range interactions between neighboring short branches. These assumptions are admissible because our interest is in the influence of the short branches on C when the branch content is extremely small. The characteristic ratio was calculated for each chain, and the average overall chains generated are taken to be C for a polymer of that composition.

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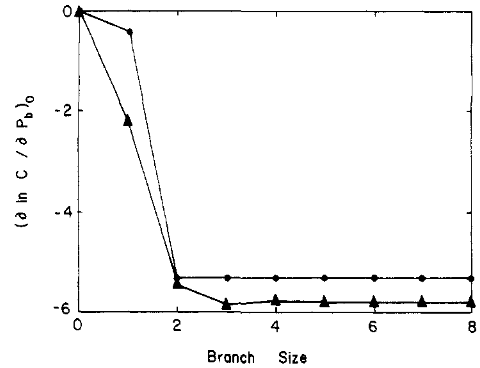

Figure 1. Variation in $(\partial \ln C/\partial P_b)_0$ and $(\partial \ln P_T/\partial P_b)_0$ with the number of carbon atoms in the short branch when $\tau = \sigma$ (triangles) and $\tau = 0$ (circles).

The parameters in the rotational isomeric state treatment are those commonly used for unperturbed linear polyethylene. The bond length is 154 pm, the bond angle is 112°, gauche states are located at 120° from the trans state, and first- and second-order interactions are weighted with $\sigma = 0.43$ and $\omega = 0.034$. Two values, 0 and σ, were used for the additional statistical weight, τ, required at a trifunctional branch point.[20]

The conformational properties of the chains in the amorphous regions were calculated from eq 1–7. The pertinent equations from Guttman and DiMarzio[13] are

$$<L> = 2w/l \qquad (1)$$

$$<B> = (w/l)^2/C \qquad (2)$$

$$P_T = Cl/w \qquad (3)$$

where w denotes the width of the amorphous region between the crystalline lamellae and l denotes the bond length. When a numerical value for w is required, it was taken to be 10 nm. After incorporation of a minor modification that takes into account the mass of the atoms in the branches, the probability for a tight fold is

$$P_{tf} = 1 - (d_a/d_c)(w/1.28r) \qquad (4)$$

where d_a and d_c are the densities of the amorphous and crystalline regions, respectively, and r is given by

$$r = [(N_b + N_{mc})/N_{mc}][P_T<B> + (1 - P_T)<L>] \qquad (5)$$

The computation of P_{tf} from eq 4 was made with a value of 0.85 for the ratio of the densities. The numbers of carbon atoms in branches and in the main chain, respectively, are N_b and N_{mc}. The effect of short branches on $<B>$ and P_T can be separated from the influence of w by focusing attention on suitably defined initial slopes obtained from $(\partial \ln C/\partial P_b)_0$, where P_b is the probability that a monomer unit is the 1-alkene:

$$(\partial \ln <B>/\partial P_b)_0 = -(\partial \ln C/\partial P_b)_0 \qquad (6)$$

$$(\partial \ln P_T/\partial P_b)_0 = (\partial \ln C/\partial P_b)_0 \qquad (7)$$

At small P_b, ln C is sufficiently close to a linear function of P_b so that $(\partial \ln C/\partial P_b)_0$ is easily evaluated from ln C at finite P_b. Similarly, $(\partial \ln P_{tf}/\partial P_b)_0$ is easily calculated from ln P_{tf} at small P_b. However, the latter parameter is dependent on the value of w as far as numerical values are concerned.

Results and Discussion

The variation in the initial slope, $(\partial \ln C/\partial P_b)_0$, with the size of the short branch is depicted in Figure 1. Initial slopes are negative because C decreases upon the initial incorporation of branches. A similar decrease has been reported previously for the incorporation of methyl[15] and ethyl[16] branches in polyethylene. The values of C from Mark's work are slightly smaller than those reported here because they were obtained with chains of 200 bonds. The initial slope in not sensitive to plausible variation in τ for branches larger than methyl. As the branches increase in size, one quickly reaches a point where $(\partial \ln C/\partial P_b)_0$ becomes independent of the number of bonds in the branch.

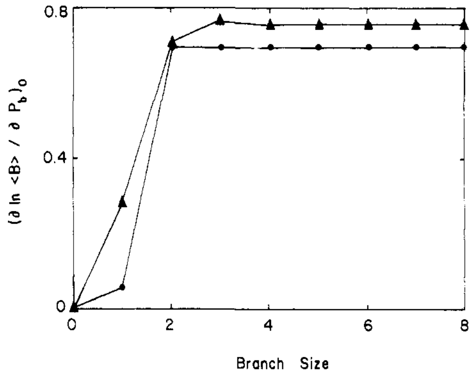

Figure 2. Variation in $(\partial \ln <B>/\partial P_b)_0$ with the number of carbon atoms in the short branch when $\tau = \sigma$ (triangles) and $\tau = 0$ (circles).

The changes seen in C upon changing the substituent from hydrogen to methyl to ethyl are subject to qualitative rationalization by consideration of pentane, 3-methylpentane, and 3-ethylpentane. The probability that the two internal bonds in pentane will adopt trans states is

$$1/(1 + 4\sigma + 2\sigma^2 + 2\sigma^2\omega)$$

For the 3-methylpentane and 3-ethylpentane, this probability becomes

$$1/(3 + 4\tau + \omega + \tau^2\omega)$$

and

$$(2\omega + \tau)/(2 + 6\omega + 9\tau + 3\tau\omega + 6\tau^2\omega + \tau^3\omega^3)$$

At 300 K, the numerical values are 0.32, 0.21, and 0.08, respectively, for pentane, 3-methylpentane, and 3-ethylpentane when $\tau = \sigma$. They become 0.32, 0.33, and 0.03, respectively, for $\tau = 0$. The foregoing analysis shows that there is a decrease in the probability for trans states at the two main chain bonds connected to the carbon atom at the trifunctional branch point as one goes from the unbranched molecule to cases where methyl or ethyl branches are present for $\tau = \sigma$, and when ethyl branches are present for $\tau = 0$. A decrease in C is therefore expected.

The average number of bonds in a loop, $<L>$, depends only on the thickness of the amorphous region and bond length, as is shown by eq 1. It is unaffected by the incorporation of branches because $<L>$ does not depend on C.

Figure 2 depicts the variation of $(\partial \ln <B>/\partial P_b)_0$ with branch size. This parameter, in contrast to $(\partial <B>/\partial P_b)_0$, is independent of the thickness of the amorphous region. The results depicted in Figure 2 are a direct consequence of the fact that $<B>$ is inversely proportional to C, as shown in eq 2. They are, of course, independent of the nature of the proportionality constant. The average number of bonds in a tie becomes larger as the branch size increases from methyl to ethyl, but there is little change upon a further increase in the number of bonds in the branch. Equation 7 shows thet $(\partial \ln P_T/\partial P_b)_0$ is identical with $(\partial \ln C/\partial P_b)_0$, which follows immediately from the fact that P_T is directly proportional to C in eq 3. For this reason, $(\partial \ln P_T/\partial P_b)_0$ is depicted in Figure 1. Both $(\partial \ln P_T/\partial P_b)_0$ and $(\partial \ln <B>/\partial P_b)_0$ become essentially independent of the size of the short branch if that branch is at least as large as propyl.

Qualitatively different behavior is seen for $(\partial \ln P_{tf}/\partial P_b)_0$, as is shown in Figure 3. The degree of tight folding

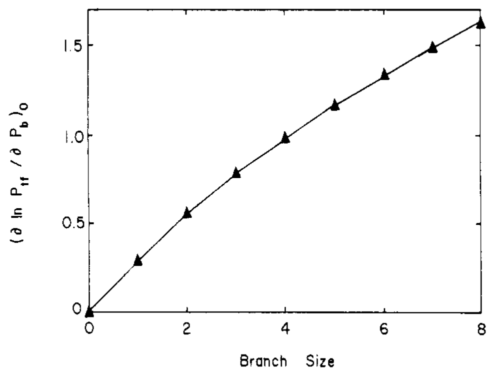

Figure 3. Variation in $(\partial \ln P_{tf}/\partial P_b)_0$ with the number of carbon atoms in the short branch when w = 10 nm.

obtained from the Gambler's Ruin remains sensitive to the nature of the short branch for branches as large as octyl, and the trend suggests that a plateau would not be reached until the branch was substantially larger. The positive values for $(\partial \ln P_{tf}/\partial P_b)_0$ mean that short branches increase the probability for a tight fold. The effect becomes larger as the number of bonds in the short branch increases. Placement of short branches in the amorphous region, without any change in chain conformation, would lead to an increase in density. The original density of the amorphous region can be preserved if introduction of short branches is accompanied by an increase in the number of tight folds.

The results depicted in Figures 1–3 have several implications for the molecular origin of the variation in physical properties with the nature of the 1-alkene in ethylene–1-alkene copolymers. Figure 1 shows that the presence of a few short branches produces a decrease in the probability of a tie. Therefore, the improved tensile and tear strength of the ethylene–1-alkene copolymers cannot be attributed to an increase in the number of ties. The effects of short branches on the probability of a tie and the number of bonds in a loop reach a plateau when the branch becomes as large as propyl. If the change in tensile and tear strengths at constant w and P_b were caused by changes in the number of ties or the average number of bonds in a loop, these strengths should become independent of the size of the short branch when the branches are at least as large as propyl.

Lacher et al.[21] recently reported the existence of entangled loops in the amorphous regions in a semicrystalline polymer. Entangled loops that originate from opposite crystal faces provide a means of tying the two crystals together, even though they are not a tie of the type that is considered in the evaluation of P_T. A qualitative description of the influence of entangled loops is accessible if one admits the plausible hypothesis that the probability for entangled loops is a function of the probability for any type of loop. This latter probability is $1 - P_T$. The information in Figure 1 then leads to the prediction that, at constant w and number of branches, the number of entangled loops increases as the branch size increases from methyl to ethyl, but it becomes independent of branch size when the branches are at least as large as propyl. If entangled loops are responsible for the effect of the 1-alkene on tensile and tear strengths, the tensile and tear strengths at constant w and P_b should become independent of branch size when the branches reach the size of propyl.

The probability of a tight fold continues to increase with the size of the short branch for branches as large as octyl. The results depicted in Figure 3 predict a continual improvement in tensile and tear strengths, at constant w and P_b, as the short branch changes from propyl to octyl if its origin lies in an increase in the probability of tight folds. More laborious computations will be necessary for an assessment of any modifications in these trends due to the intermolecular interactions in the interfacial region.

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Registry No. (Ethylene)(propylene) (copolymer), 9010-79-1; (ethylene)(1-butene) (copolymer), 25087-34-7; (ethylene)(1-pentene) (copolymer), 26221-69-2; (ethylene)(1-hexene) (copolymer), 25213-02-9; (ethylene)(1-heptene) (copolymer), 26221-72-7; (ethylene)(1-octene) (copolymer), 26221-73-8; (ethylene)(1-nonene) (copolymer), 57816-71-4; (ethylene)(1-decene) (copolymer), 26221-74-9.

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