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On the Amorphous Structure of Ethylene-1-Alkene Copolymers

Among the largest volume products of the chemical industry today are the so-called low-density polyethylenes, with US production of about 4.5 million tons in 1986 and it is expected to increase.[1] A significant fraction of this production consists of linear low-density polyethylenes, typically ethylene–X copolymers containing 0.5–4.5 mol % of the X counit and delivered in the (semi-)crystalline state. The X counits form side chains on the otherwise linear polyethylene backbone. These side groups play an essentially geometric role in the crystallization process: though relatively small, they are large enough to have a strong preference not to enter the ethylene crystal structure and thus seem to contribute indirectly to the amorphous structures in the uncrystallized region in which the crystal lamellae are embedded. We introduce an opposing planes model that accounts for side chain effects by modifying crystal entry probabilities as a function of branch percent. For a given crystal size, crystallinity, and branching, estimates of amorphous structures (tie and link probabilities) can be computed from the model. Results from a series of calculations using crystal thickness of 90 Å and amorphous thickness of 150 Å yield a sharp maximum in probability of intercrystalline connections at around 4% branches.

Background. For the purpose of this paper, X is restricted to the class of 1-alkenes, although the remarks apply qualitatively in any similar setting of a copolymer with a small percentage of short branches on an otherwise linear backbone in which the branches are excluded from the backbone crystal structure. Let n_b denote the number of carbon atoms in the 1-alkene X. There is significant change in properties between the $n_b = 3$ and $n_b > 3$ cases. In all cases, an ethyl group in X enters the backbone, thus forming a side chain with $n_b - 2$ carbons. In the case of $n_b = 3$, the methyl side group enters the crystal structure at equilibrium, while for $n_b > 3$ the side chain strongly prefers not to defect the crystal.[2] Thus in the following we assume $n_b > 3$. Many properties of these short-branched copolymers seem to depend more on the number of branches than on the specific chemistry or size of the branch, as long as the branch is excluded from crystallization.[3-5]

Recent theoretical studies of Mathur and Mattice have begun to consider effects specifically attributable to side chains. A lattice-based simulation[6] has provided numerical evidence that side chains large enough to be excluded from crystallization tend to collect preferentially in the interphase regions near crystal faces, a conclusion in qualitative agreement with the experimentally observed thickening of the interphase with branch probability.[7] Another study used Monte Carlo methods to calculate the effect of branching on the characteristic ratio in the amorphous region.[8] Again for a branch size larger than one unit, an estimate of −0.7 for $(\partial \ln C/\partial p)_{p=0}$ is obtained, where p = branch probability. (Figure 1 of the reference has an incorrect vertical scale. The correct scale should read from 0 at the top to −0.8 at the bottom, scaled linearly.[9]) Thus the characteristic ratio decreases with increasing branch probability p for small p. This estimate for the initial slope of $\partial \ln C/\partial p$ can be used to approximate characteristic ratios. Let p denote branch probability and C^p_∞ the characteristic ratio of the copolymer with branch probability p. Then $C^p_\infty \approx \tilde{C}^p_\infty$ where

$$\tilde{C}^p_\infty = C^0_\infty(1 - 0.7p) \qquad (1)$$

(An alternative approximation would be $C^p_\infty \approx C^0_\infty e^{-0.7p}$. For $p \leq 0.1$, these two approximations result in the same values of n^p_a using eq 2 and thus produce exactly the same computational results.)

The effect of side groups on amorphous structure has also been considered. For example, the simulation in ref 6 indicates an increased tie probability along with the thickened interphase. Increases in tie[10] and link[11] probability were also found to be a consequence of thickening interphase in models of linear polymers. And a calculation similar to the one described below has already been seen to predict increased tie and link probabilities for branched copolymers based on crystal exclusion of the branches.[12] (A consequence of decreasing characteristic ratio is decreasing tie probability in the gambler's ruin model, as pointed out in ref 8, but this is probably not a realistic conclusion for branched copolymers, as the gambler's ruin model takes into account neither interphase phenomena nor branching effects.)

The Model. *The noncrystallizing counits, as well as the small sequences of regular units, will be rejected from the crystallite.* This statement, quoted from page 1296 of ref 2, can be used as the basis of an opposing planes model yielding estimates of tie probability P_{tie} and link probability P_{link} as functions of branch probability p. (A *tie* is a subchain bridging the amorphous region between two crystals. A *link* consists of two subchain loops, based on distinct crystallites, having nonzero gauss linking number. See ref 11 for background.) Chains in the model reside on the unit cubical lattice between two parallel planes representing crystal faces. At the faces, the crystal entry probabilities are modified by a factor representing the probability of a pure (unbranched) sequence sufficiently long to enter the crystal.

Input parameters for the calculation are *amorphous thickness* W_a, *crystal thickness* W_c, and *branch probability* p. W_a and W_c are converted to lattice units n^p_a and n_c, respectively, by using the equations

$$n^p_a = \frac{W_a}{\tilde{C}^p_\infty l}$$

$$n_c = \frac{W_c}{l \cos \alpha} \qquad (3)$$

where $\tilde{C}^p_\infty$ is the Mathur–Mattice approximation of characteristic ratio given by eq 1, $l = d \sin(\theta/2)$ is segment length (d = bond length, θ = bond angle), and α = orientation angle of extended chains across the crystal structure. (n^p_a and n_c are rounded to the nearest integer.) For the ethylene–1-alkene copolymers, we take $C^0_\infty = 6.8$, $l = 1.27$ Å ($d = 1.53$ Å, $\theta = 112°$), and $\alpha = 30°$. At the layer representing the crystal–amorphous interface, crystal entry probability is set to $(1-p)^{n_c}/6$ with the other five directions having equal probability. At layers deeper than one unit into the amorphous region, probabilities are set for pure isotropy. The resulting opposing planes model can be solved to produce calculated values for P_{tie} and P_{link}. (Equation 5 of ref 11 is used to estimate P_{link}. The distribution $\{d_k\}$ is calculated numerically and adjusted for density effects as described in ref 12.)

Results. Results from one series of calculations, using $W_a = 150$ Å and $W_c = 90$ Å, are depicted in Figure 1, where amorphous structure estimates are plotted against p. A sharp maximum in P_{link} occurs at $p = 3.75\%$. The sum $P_{\text{tie}} + P_{\text{link}}$ is the probability that an amorphous subchain is a bridge (physical connection) or one loop of a link (topological connection) holding two crystallites together. This sum, also shown in Figure 1, attains a maximum at 4.1%. These pronounced peaks in P_{link} and $P_{\text{tie}} + P_{\text{link}}$ at around 4% counit are typical of several such calculations

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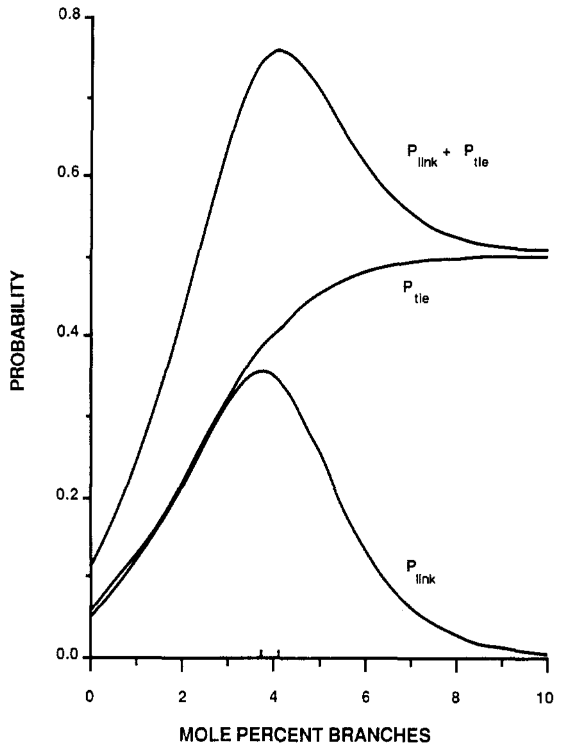

Figure 1. Probabilities of physical and topological intercrystalline connections calculated from the model with input parameters $W_a = 150$ Å and $W_c = 90$ Å. P_{link} attains a maximum at $p = 3.75\%$. $P_{tie} + P_{link}$ attains a maximum at $p = 4.1\%$.

made recently. The maxima are caused by two conflicting effects of reluctance of the side chains to enter the crystal structure. On one hand, longer amorphous loops are produced, thus tending to increase the liklihood of linking for a given pair of opposing loops. On the other hand, heavier amorphous loops are produced, so at constant density there are fewer opposing pairs.

Discussion. The maximum values at around 4% branching illustrated in Figure 1 occur where substantial morphological change has been observed in the laboratory[7] and may have a role in explaining this as well as changes in certain mechanical properties as functions of branch content.[4,5] Two ameliorating points must be kept in mind, however. First, the fixed input parameters W_a and W_c represent only a hypothetical copolymer series as p varies. In practice, W_c varies from around 150 Å to a floor of 50 Å (for ethylene–1-alkenes) as p increases from 0 to around 4%, while W_a varies in the opposite direction.[7] For p exceeding 5%, the crystalline state becomes increasingly difficult to observe. Second, there is evidence that the increases in tie and link probability for small p are accompanied by increases in the number of interphase loops and decreases in the number of completely amorphous subchains. Any quantitative study of tight or small-reach loops must take into account variation in interphase content, a phenomenon not considered in the present computations. A thorough study, taking into account experimentally determined variation in amorphous, interphase, and crystal dimensions as functions of p, may produce substantial indirect evidence as to the extent to which topological linking occurs between amorphous loops and what influence these links have on morphological and mechanical properties.

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R. C. Lacher*
Department of Computer Science
Florida State University
Tallahassee, Florida 32306

J. L. Bryant
Department of Mathematics, Florida State University
Tallahassee, Florida 32306

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Vitrification of Water in a Hydrogel

Polymers prepared from 2-hydroxyethyl methacrylate (PHEMA) imbibe about 43 wt % water at equilibrium and, in this respect, are rather insensitive to inclusion of cross-linking comonomers, such as dimethacrylates.[1] A number of techniques have been used to investigate these PHEMA hydrogels[2-7] and distinctions made about the environment of water molecules, using such adjectives as "bulk", "bound", and "interfacial".[6] Dynamic mechanical analysis (DMA), using torsion pendulums,[8-12] revealed a γ-transition in dry PHEMA, near −131 °C (1 Hz),[12] which was attributed to side-chain motion.[8] As water content was increased, the γ-transition was gradually replaced by a β-transition, which varied from −77 to −109 °C (1 Hz).[12] As is customary in DMA work,[13] the value of a transition was taken as the maximum of the mechanical loss (tan δ). In the present work an alternative approach is pursued[14,15] according to which a transition temperature is assigned by reference to changes in the modulus of elasticity (E'). In a preliminary report, this approach resulted in discernment of a vitrification process with a glass transition temperature, T_g, similar to values reported for water.[16]

Homogeneous solutions of HEMA (3.0 mL), triethylene glycol dimethacrylate (0.6 mL), both from Aldrich, and distilled water (2.2 mL) were exposed in glass molds to γ-rays from a ^{137}Cs source: dose rate = 0.8 Mrad/h; dose = 4.8 Mrad; ambient temperature = 40 °C. The highly cross-linked hydrogel products were soft and transparent; they contained little residual monomer. After prolonged equilibration in distilled water, the water content of the hydrogels was 40–43 wt %. For comparison, similar specimens were made with glycerol in place of water. This was done at the maximal solubility of glycerol in the mo-