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TOPOLOGICAL STRUCTURE OF SEMICRYSTALLINE POLYMERS*

J. L. Bryant and R. C. Lacher

Introduction

Semicrystalline polymers are among the largest volume products of the chemical industry today. Long-chained polymers ($\sim 10^4 - 10^6$ monomers), such as polyethylene or polystyrene, are cooled from a melt, forming lamellar crystals that are separated by a non-crystalline or amorphous region. The crystals are usually in the range of 50-500 Å thick and the region between two lamellae ranges from 50 to 200 Å [14]. The size of the chains is such that a single chain may enter many of the crystals as well as reenter the same crystal many times. In addition there is a small interphase at the faces of the crystals in the amorphous region, about 10-12 Å thick for polyethylene, in which the chains proceed from the totally ordered state of the crystal to apparent random disorder [5]. Again for polyethylene it has been estimated that about 70% of the chain segments that emerge from a crystal face reenter the crystal without ever leaving the interphase [5].

A significant fraction of the semicrystalline polymers produced consists of linear low-density polyethylenes. A typical chain has a polyethylene backbone with a small

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percentage of branches (0.5 - 4.5 mol %) of a 1-alkene copolymer X that has n_b carbon atoms. An ethyl group of X enters the backbone of the chain forming a side chain of n_b-2 carbons. An important consequence of the presence of the side chains is that when they are long enough they have a strong preference not to enter a crystal [1]. 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][15][19].

In this paper we discuss models with which we may investigate the topological connections between the crystal lamellae in a semicrystalline polymer and the extent to which they contribute to physical properties of the polymer.

The Model

Under the broad context of *opposing planes models* the region between two crystals is represented as the region in $\mathbb{R}^3$ between the planes (crystal faces) $y = 0$ and $y = n$ (See, e.g., [5], [6], [7], [8], [9], [10], [11], [12], [13], [16], and [17]). A chain, which is confined to lie within the slab defined by the planes, is classified as a *loop* or a *tie* according to whether it has its endpoints on the same plane or opposite planes. Free chains, although important in other contexts, will not be considered here. In one form of this model a chain emerging from a crystal face is modeled as a random walk

on the integer cubic lattice between the two planes starting at y = 1 or y = n - 1. (See Figure 1.) (Here we assume that n is an integer. Random walks that we shall consider have probability 1 of being absorbed at y = 0 or y = n [4].) The unit for the lattice corresponds to the statistical unit for the polymer [5][8]; e.g., for polyethylene this is about 3.5 monomers [5]. The statistical unit is the minimal length of a polymer chain that exhibits near total flexibility. Typically, amorphous thickness is found in ranges corresponding to values of n between 15 and 40, although it may range anywhere from 10 to 80.

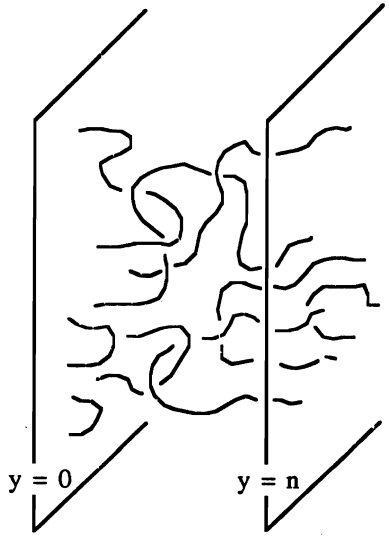

Figure 1.

The purely isotropic version of this model, wherein each of the transitional probabilities is set equal to 1/6, was introduced by Guttman, DiMarzio, and Hoffman in [7]. Other versions of the latticebound walk model include the environment for Mansfield's Monte Carlo simulations [16], and the interphase-sensitive models of Flory, Yoon, and Dill [5], and Marqusee and Dill [17].

Applying so-called "gambler's ruin" statistics, Guttman, *et al.*, [7] compute the distribution of loops and ties for the pure isotropic model; namely,

$$P_L = (n - 1)/n \text{ and } P_T = 1/n,$$

where P_L and P_T denote the probability that an individual walk will become a loop or tie, respectively. (If a gambler starts with \$k, bets \$1 on each bet that has a probability 1/6 of winning, 1/6 of losing, and 2/3 of a standoff, and sets a goal of winning \$n, then the probabilities of success and failure are k/n and (n - k)/n, respectively.)

These parameters are derived from recurrence relations obtained from the principle: "Take a step and see what happened." That is, if α_k is a parameter associated with a walk that starts with $y = k$, $0 < k < n$, and if p_k, q_k, and r_k are the probabilities of taking a step +1, -1, and 0, respectively, in the y-direction, then, in general, α_k will satisfy a (possibly) nonhomogeneous recurrence relation of the form

$$(*) \qquad \alpha_k = p_k\alpha_{k+1} + q_k\alpha_{k-1} + r_k\alpha_k + f_k$$

with specified boundary values for α_0 and α_M and nonhomogeneous term f_k. For pure isotropy, $p_k = q_k = 1/6$ and $r_k = 2/3$. Other parameters of interest, such as the expected value of the length of a chain, of a loop, or of a tie, are easily computed from these equations. In the isotropic case they are, respectively,

$$\langle C \rangle = 3n - 2,$$

$$\langle L \rangle = 2n,$$

$$\langle T \rangle = n^2$$

(See [7].) For example, the value $\langle C \rangle = 3n - 2$ indicates that, of the chain segments emanting from a crystal, only about one-sixth are expected to pass through the interphase into the isotropic region because of density considerations. This is consistent with the results of Flory, *et al.* [5].

The question now arises as to what extent loops based on opposite planes are linked (homologically). Unfortunately, recurrence schemes that apply so well to single-chain statistics do not seem to be directly applicable to computing homological linking between opposing loops. The first attempts at computing the incidence of homological linking between unbranched polymers were reported in [9] and [10], and we shall review briefly some of the results of those papers.

Homological Linking of Unbranched Polymers

We shall call a walk based on the plane $y = 0$ (respectively $y = n$) an L(left)-walk (respectively, an R-walk). Similarly, we may speak of an L-loop or an

R-loop. Given an L-walk L and an R-walk R, define the *offset linking number* olk(L,R) as follows: If each of L and R is a loop, complete it to a closed curve by joining its endpoints with an arbitrary path in its base plane, offset the lattice for R by the vector $(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$, and define olk($L$,$R$) to be the homological linking number of the resulting (disjoint) closed curves. (Use the natural orientation determined by the direction of the walk.) Otherwise, set olk(L,R) = 0. We say that L and R *link* if olk(L,R) $\neq$ 0.

In [9], [10], and [11] results of the following computer simulations were described. For each n - 2 $\leq$ n $\leq$ 24, using a random exit pattern, or n = 6, 12, $\cdots$ 54, using a uniform exit pattern--perform a number of trials, each of which consists of generating one L-walk from (0,1,0) and a family of R-walks from a square of side 2n in the plane y = n - 1, symmetric about (0, n-1,0), with starting density d. The value of d is usually set at 1/6 for reasons discussed above. From these trials estimate the parameters:

P_{link} = Link Probability = the probability that an L-walk has nonzero offset linking number with some R-loop;

D_{link} = Link Density = the expected number of R-walks an L-walk links;

W_1 = Total Winding = the expected sum of the absolute values of the offset linking

numbers of an L-walk with all R-walks.

W_2 = Square Link Density = the expected sum of squares of the offset linking numbers of an L-walk with all R-walks.

In [10] a simple geometric model is proposed to estimate link density. In this model a loop is represented as an isosceles triangle parallel to the y axis that has its base on a boundary plane and a fixed breadth to reach ratio b. (See Figure 2.) Computer simulations yield an estimate of 1.19 for b for the planar separations observed (but there is some evidence that b behaves as a concave function of reach). One obtains a fairly nice expression for the link density in the simplified model:

$$D(n) = 2b^2 d \sum_{i=1}^{n-1} d_i \sum_{j=n-1}^{n-1} (i+j+1/2-n)^2 d_j,$$

where $d_k = \frac{1}{k(k+1)}$ is the probability that a loop will have reach k, $0 < k < n$. The double sum in this expression has the limit $(\pi^2/3) - 3$ as $n \to \infty$ [10]. Substituting the values b = 1.19 and d = 1/6 yields

$$\lim_{n\to\infty} D(n) \doteq .1368.$$

Estimates of the link density from the random walk trials indicate that it is approaching 90% of D(n) for n = 54 [11]. (See Figure 3.) Some of this loss can be accounted for from the truncation of the plane of starts for R-walks in the simulation. Thus, the simulation statistics and D(n) seem to be in rather close agreement.

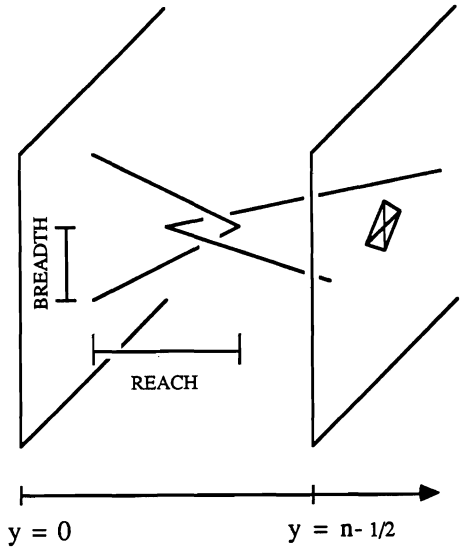

Figure 2. Simplified model of linking.

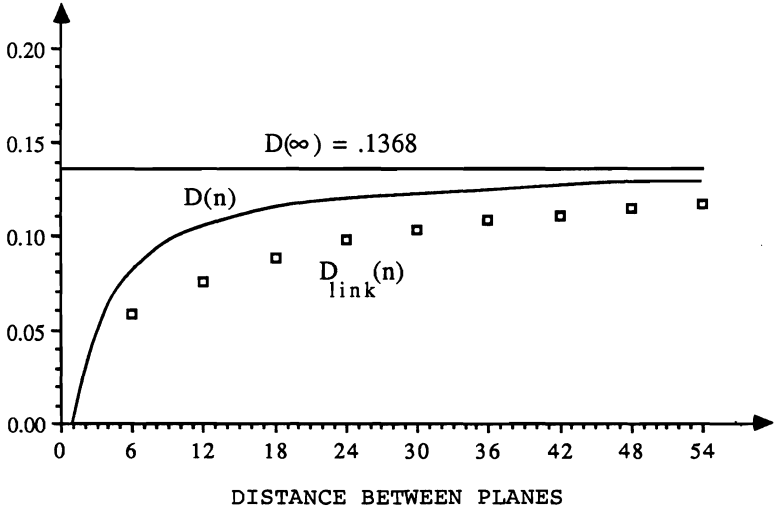

Figure 3. Comparison of computations of link density from the simplified model (D(n)) with computer simulations ($D_{link}(n)$).

A formula for the link probability may also be obtained from the simplified model. The derivation from [11] yields:

$$P(n) = 1 - 1/n - \Sigma_{i=1}^{n-1} d_i \prod_{j=n-i}^{n-1} [1-2b^2 d(i+j+1/2-n)^2 d_j].$$

As indicated in Figure 4, agreement with simulation statistics is quite good.

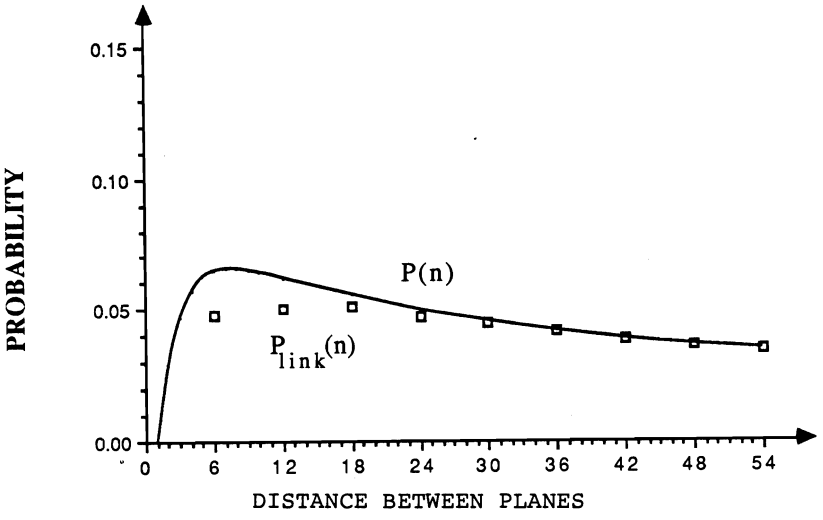

Figure 4. Comparison of link probability from the simplified model (P(n)) with computer simulations ($P_{link}(n)$).

The results of these simulations seem to indicate that each of the linking parameters is most certainly non-negligible in the physically significant ranges of n. For example, D_{link} overtakes the density of ties (=1/n) around n = 13 and $P_{link} \geq .04$ for $n \leq 36$. Thus, the evidence indicates that homological linking is quite

prevalent, at least in the models, and that for larger values of n it may contribute significantly more to the strength of a polymer than the ties between crystals. The next problem then is to try to discover experimental evidence that such linking occurs. Recent results with branched copolymers may provide some answers.

Topological Connections in Branched Copolymers

The difference equations (see page 4(*)) together with computations from the simplified linking model, similar to those above, can be used to estimate the probabilities P_{tie} and P_{link} of a tie and link, respectively, for the ethylene-1-alkene copolymers. (See [11].) These quantities vary as functions of amorphous thickness, W_a, crystal thickness, W_c, and branching density p. The values of W_a and W_c in turn depend on p [20]: measured in angstroms, they satisfy, approximately, the equations (**)

$$W_a = 100 + 5000p$$
$$W_c = 150 - 2500p,$$

$0 \leq p \leq 0.06$. Crystal width W_c appears to have a minimum, however, at around 50Å [1]; the crystals begin to break down as p varies from 0.04 to 0.05. The associated lattice units n_a^p and n_c are obtained from the equations

$$n_a^p = \frac{W_a}{C_\infty^p \ell}$$

$$n_c = \frac{W_c}{\ell \cos\alpha}.$$

The quantity ℓ ($\doteq$ 1.27Å) is the effective bond length of an extended polyethylene chain, $\alpha(\doteq 30°)$ is its orientation angle in a crystal, $C_\infty^p \doteq C_\infty^0 \times (1-0.7p)$ is an approximation of the characteristic ratio of amorphous ethylene-1-alkene based on calculated estimates of Mathur-Mattice [18], and $C_\infty^0(\doteq 6.8)$ is the typical value of the characteristic ratio of amorphous linear polyethylene at room temperature. The characteristic ratio of a polymer is defined to be the ratio

{expected end-to-end length of a chain of length n}/$\ell\sqrt{n}$.

For a tightly packed polymer this ratio is (essentially) constant.

Initial calculations reported in [12] determined P_{tie} and P_{link} as functions of branch density p for an idealized polymer whose amorphous and crystal thickness are held constant at 150 Å and 90 Å, respectively. An "isotropic" setting is assumed: transitional probabilities are set at 1/6 when $1 < y < n-1$; the probability of taking a step into the plane $y = 0$ or $y = n$, respectively, is defined to be $\frac{1}{6}(1-p)^n c$ and the remaining five probabilities are set equal to each other. In this model P_{tie} approaches 1/2 asymptotically and P_{link} has a sharp maximum at $p \doteq .0375$. Figure 5 shows the graph of P_{tie}, P_{link}, and $P_{tie} + P_{link}$. The sharp maximum at $p \doteq .04$ occurs where changes in mechanical properties [19], [15] and substantial morphological changes have been observed

experimentally [20]. Thus, we may have the first substantial evidence of linking of amorphous chains.

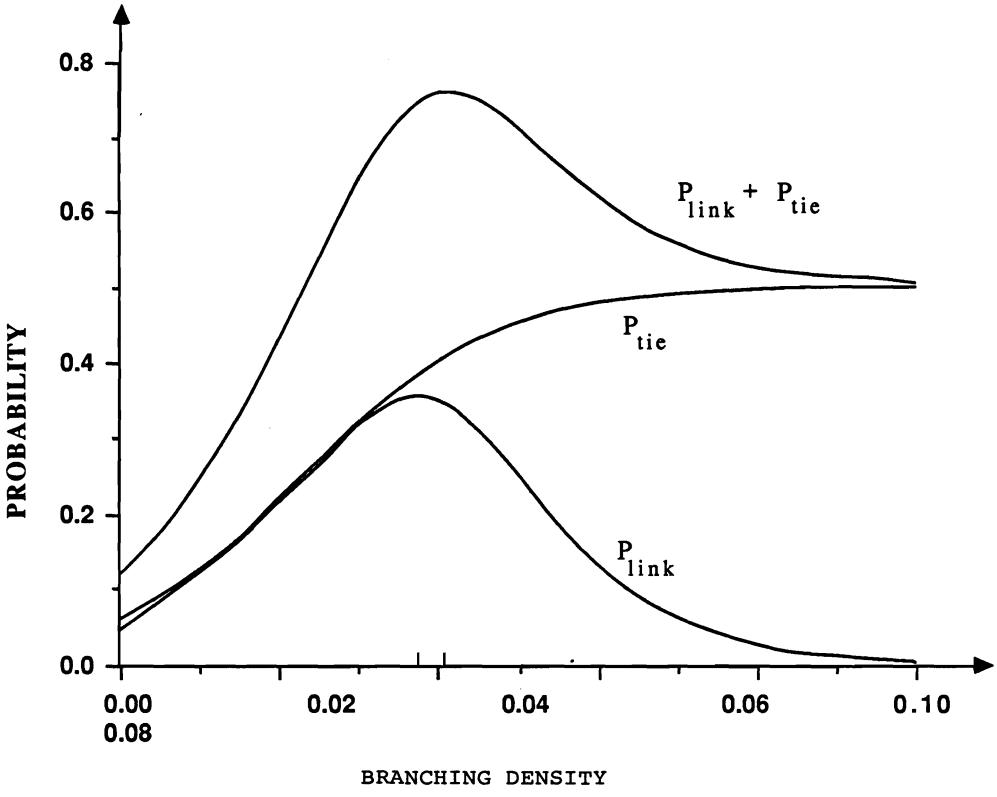

Figure 5. Probabilities for an idealized copolymer, having varying branching density, but amorphous and crystal thickness held constant at 150 Å and 90 Å, respectively.

Somewhat more chemically realistic calculations are reported in [13] in which P_{tie} and P_{link} are computed allowing crystal and amorphous thickness to vary with p as in (**). In this case both P_{tie} and P_{link} exhibit

maxima in the p-range of .025 to .030, and P_{link} exceeds P_{tie} for p > .012. The graphs are found in Figure 6.

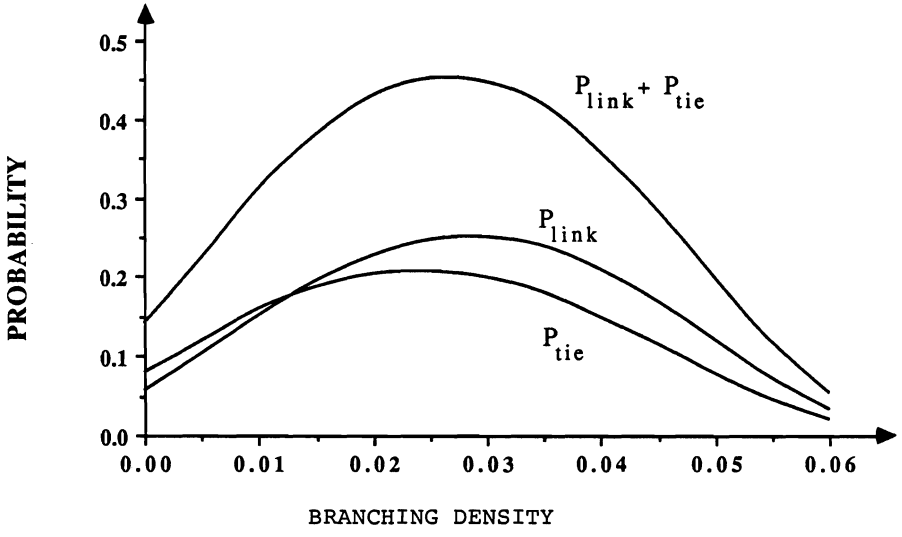

Figure 6. Probabilities for copolymers having amorphous and crystal thickness varying with branching density as in (**).

Questions and Conjectures

Although the asymptotics for link density as computed in the simplified model were worked out in [10], the asymptotics for link probability have not been determined. That is, one would like to know $\lim_{n\to\infty} P(n)$, given

$$P(n) = 1 - 1/n - \Sigma_{i=1}^{n-1} d_i \, \Pi_{j+n-i}^{n-1} [1-2b^2 d(i+j+1/2-n)^2 d_j].$$

Conjecture: $\lim_{n\to\infty} P(n) = 0$. Specifically, $n \cdot P(n) \sim 0(\log(n))$.

What are the asymptotics for the random walk models? Evidence presented above would indicate that link density and link probability exhibit the same asymptotic behavior as their analogs, D(n) and P(n), in the simplified model, and one is led to conjecture that they are the same. The asymptotics for total winding W_1 and square link density W_2 are unknown. Of these two parameters, W_2 is perhaps the easier to pursue. In [2], for example, a heuristic argument is given that W_2 approaches a nonzero constant as $n \to \infty$. Because of the inequalities $D_{link} \leq W_1 \leq W_2$, we would conjecture that each of these linking densities approaches a nonzero constant as $n \to \infty$.

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