Statistics of Branched, Random-Flight Chains

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ABSTRACT: Distributions of the radii of gyration for some typical branched, long, random-flight chains were computed using our previously published formulation of random-flight statistics. The observations were much the same as those previously reported for short, branched chains, *viz.*, that the probability of observing the dimensionless polar radius of gyration, ξ_3, between values of 1.0 andsl.5 increases with branching at the expense of the distribution at higher values of ξ_3, while the probability of ξ_3, below about 0.8, goes very rapidly to zero with decreasing ξ in all cases. The results also show a significant difference between the distributions for a three-branch regular star molecule of lengths $n = 30$ and 100, and only above about $n = 100$ can we consider the distributions of such chains to have attained their asymptotic value.

Distributions of the one-, two- and three-dimensional radii of gyration of random-flight chains are of importance in many areas of polymer science and have thus received considerable attention in the literature. Until recently, treatments were restricted to linear chains. There is now available, however, a generalized formulation of the statistics of random-flight chains that is applicable to any type of chain branching.[1-3] In this formulation, dimensionless radii of gyration are defined[4] as follows

$$\begin{aligned} \xi_1^2 &= \pi^2\beta^2 S_x^2 \\ \xi_2^2 &= \pi^2\beta^2(S_x^2 + S_y^2) \qquad (1) \\ \xi_3^2 &= \pi^2\beta^2 S^2 = \pi^2\beta^2(S_x^2 + S_y^2 + S_z^2) \end{aligned}$$

where S_x, $(S_x^2 + S_y^2)^{1/2}$, and S represent the one-, two- and three-dimensional cases. The term β^2 $(= \frac{3}{2}nl^2)$ is the Gaussian parameter commonly used to characterize the distribution of end-to-end distances of assemblies of linear chains, n is the number of statistical segments per chain, and l^2 is the mean square length of each segment. The results of the analysis give the distribution functions in terms of an inverse Fourier transform integral,[1,2,3] where ϕ is the transform variable.

$$W^0(\xi_j) = \frac{n(n+1)}{\pi^3}\,\xi_j\,|\mathbf{D}(\phi)|^{j/2} \times \int_{-\infty}^{\infty} \frac{\exp[-in(n+1)\xi_j^2\phi/\pi^2]\,d\phi}{|\mathbf{D}(\phi)|^{j/2}} \qquad (2)$$

$$j = 1,\ 2,\ \text{or } 3$$

In eq 2, $i = (-1)^{1/2}$ and $\mathbf{D}(\phi)$ is a complex matrix given as a sum of two real matrices **P** and **M**.

$$\mathbf{D}(\phi) = \mathbf{P}^T\mathbf{P} - i\phi\mathbf{M} \qquad (3)$$

The development shows that **M** is independent of branching and is a simple $n \times n$ matrix with diagonal elements equal to 2 and all the off-diagonal elements equal to 1. Matrix **P**, however, depends on the nature of branching but is easily written for any chain. The masses are first numbered consecutively 0 to n starting in any branch. In the first row, $P_{11} = 2$ and the remaining elements equal 1. The rest of **P** is then the transpose of the $n \times (n-1)$ associated matrix of the directed graph[5] of the masses 1 through n.

Earlier, Forsman and Hughes[4] presented a matrix method for treating the statistics of linear chains, which was then modified[6] to account for any type of branching. The method considered in this paper is, however, more powerful, in that it yields distributions and not just mean-square radii. We should also like to add that the same matrices used in this treatment of chain statistics can be used to predict the linear viscoelastic behavior of assemblies of branched, unentangled, free-draining, random-flight chains.[7]

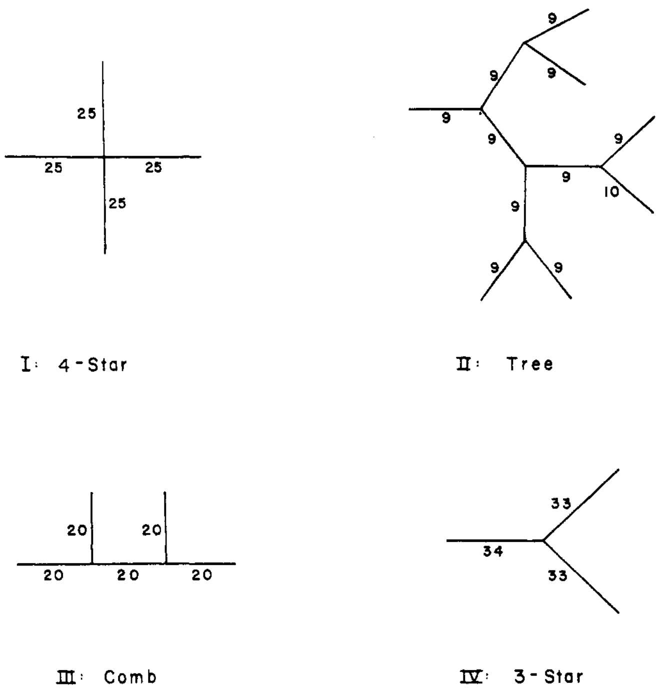
We recently[8] used eq 2 to solve for the probability functions of some typical branched, short chains. As expected, molecules with branches attached nearer to the central segments were predicted to be more compact than molecules in which the branches were located near the end segments. Of somewhat more interest was the observation that W^0 (ξ_3) for values of ξ_3 between 1.0 and 1.5 increased with branching at the expense of the distribution for values of ξ_3 greater than about 1.5, while the probability for observing ξ_3 below about 0.8 went *very* rapidly to zero with decreasing ξ_3 in all cases.

Results and Discussion

Computations of the distribution of ξ_1, ξ_2, and ξ_3 for several types of branched chains of 100 statistical segments have now been completed. Only the results for W^0 (ξ_3) are given here, however, since these are of greatest interest. For the three commonly considered forms of branching shown in Figure 1, Figure 2 shows these distributions. They are a four-branched regular star (or cruciform) molecule, a comb molecule, and a tree molecule suggested by Dobson and Gordon.[9] The plot for a linear chain of $n = 100$ is also included for comparison. The computed distributions for the linear chain and those for the star and comb molecules give second moments that are in excellent agreement with values obtained analytically.[6,10] It should be noted, however, that it is inappropriate to compare the results reported here on the tree molecules with those of Kajiwara[11] since he gives results averaged over isomers of monodisperse chains.

Figure 2 shows that our previous observations on short chains hold for long chains as well. The effect of n on the distribution function of three-branch regular star chains is shown in Figure 3. In contrast to the behavior of the linear chain,[12] the probability density for a chain of 30 segments differs considerably from that for chains of 100 segments. Furthermore, the maximum of the distribution moves to lower values of ξ_3 with increasing n, as in the case of linear chains.[13]

As described earlier,[1,3] perturbation methods can be applied to this treatment of random-flight statistics to give the limiting form of the expansion factor α_S as a function of the segment–solvent interaction for assemblies of branched chains. In addition, distribution functions such as those presented in this paper can also be used, along with a suit-



I: 4-Star II: Tree

III: Comb IV: 3-Star

Figure 1. Branched chains with $n = 100$. The number of statistical segments in each branch is indicated.

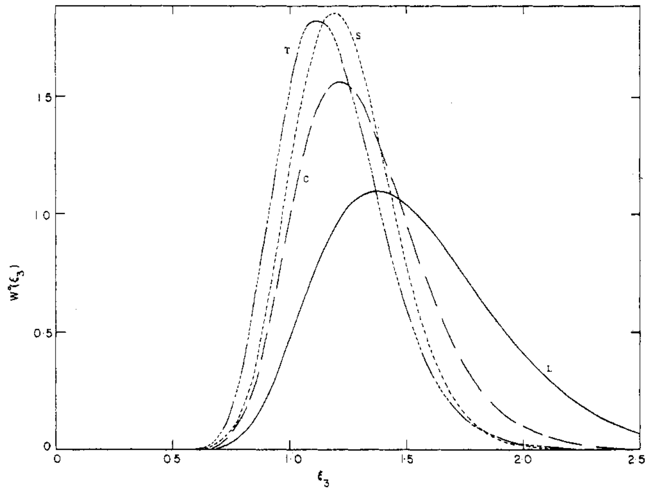


Figure 2. Distribution of ξ_3 of branched molecules shown in Figure 1: L, linear; S, star; T, tree; and C, comb.

able Boltzmann factor, to give the distribution in the perturbed state as

$$W(S) = W^0(S) \exp\left(\frac{-\Delta F_m}{kT}\right) \tag{4}$$

where ΔF_m is the free energy of interaction between the solvent and the polymer molecule as a function of radius of gyration.[14-16] An expression for ΔF_m suggested by Flory[15,16] is

$$\Delta F_m = Az\langle S^2\rangle_0^{3/2}/2S^3 \tag{5}$$

In eq 5, z is the polymer–solvent interaction parameter given by

$$z = n^{1/2}b(n/4\pi\langle S^2\rangle_0)^{3/2}$$

where b is the binary cluster integral.[17] The constant A was determined to be $3^{3/2}$ for spherically symmetric chains. Casassa and Orofino[18] used the correct distribution of segments about the center of mass and found that the value of A used in eq 5 for linear chains should be $1.213 \times 3^{3/2}$ instead of $3^{3/2}$ as predicted by Flory.[15,16] The formulation of chain statistics upon which the work presented in this paper is based[3] also yields segment densities, and they are now being computed for the branched chains considered here. Equation 4 and 5, along with these segment densities, can be used to obtain numerical solutions for the excluded volume effect as a function of n. These have already been evaluated for linear chains and will be published in a future paper.[19,20]

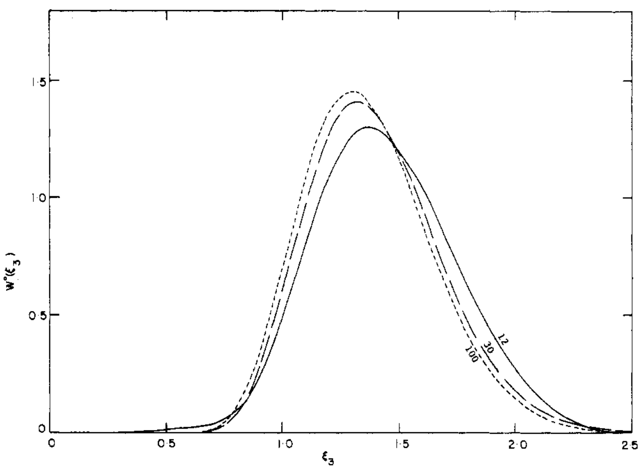


Figure 3. Distribution of ξ_3 for a three-branch regular star molecule as a function of n.

Additional Comments

This material was presented in part at the 103rd meeting of the American Chemical Society, Polymer Chemistry Division, held at Detroit, May 1–4, 1973. The Fortran IV program used for computing the distribution as well as the one- and two-dimensional distributions for various cases considered in this paper can be supplied on request by one of us (W. C. F.). Computation of each distribution for $n = 100$ took about 1 min of computer time on an IBM 370-165.

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The Conformational Analysis of Crankshaft Motions in Polyethylene[1]

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ABSTRACT: Conformational changes involving sequences of only a few bonds (crankshaft motions) in chain segments residing in amorphous domains have for some time been proposed as the basis for the γ relaxation in polyethylene. The energetics of the Schatzki (five bonds between stem bonds) and Boyer (three bonds between stem bonds) crankshaft motions have been investigated here by means of conformational energy calculations. In the isolated chain the five-bond motion is found to be as Schatzki proposed, a single barrier determined by the sum of the barriers in the rotating colinear stem bonds. The Boyer crankshaft motion in the isolated chain is found to involve two barriers separating a strained stable intermediate state from the initial and final states. One of the barriers can be described as semirigid motion about the stem bonds much in the manner of the Schatzki motion. The other barrier, passage over which is required to complete the motion, can be described as a "flip–flop" of two gauche bonds of opposite sense separated by a trans bond $\cdots$ G′(TGT)– → $\cdots$ G(TG′T)– where the first gauche bond is one of the stem bonds and the other is the center bond in the three-bond sequence interior to the stem bonds. Calculations of the effect of a surrounding matrix indicate that motion over the flip–flop barrier to the stable strained intermediate requires very little swept out volume and is not significantly influenced by the matrix. The motion over the other barrier involves considerable swept out volume and is significantly inhibited by the matrix. From these results, it is also concluded that the Schatzki motion cannot take place in a glassy matrix. A model for the amorphous component of the γ relaxation in polyethylene is proposed in terms of the motion between $\cdots$ G′TGT sequences (frozen in at the glass temperature, or β transition) and the strained intermediate state over the flip–flop barrier (and perhaps also influenced by the complete motion over both barriers). The breadth of the transition is ascribed to several relaxation times associated with differing barrier systems resulting from several possible conformations adjacent to the $\cdots$ G′TGT sequences and perhaps also to the double barrier nature of each system. The height of the calculated barriers is consistent with the location of the γ process in the T, ν domain. The increase in intensity of the transition with temperature is ascribed to the energy differences between the initial and intermediate states. The energy of the strained intermediate state should be sensitive to mechanical deformation and thus the flip–flop barrier motions should be mechanically active.

The identification of molecular mechanisms associated with the relaxation behavior of polymers has suffered from a lack of tractable models for which comparisons of predicted and measured properties can be made. In particular a useful quantitative description of the highly cooperative long-range segmental motions associated with the glass–rubber transition seems to be highly elusive. A number of suggestions of varying degrees of completeness have been made concerning the nature of other transitions. The α transition in polyethylene is thought to be a process taking place within the chain-folded crystalline lamellae.[2] Hoffman, Williams, and Passaglia[3] have proposed a site model involving a rotation of the chain as a nearly rigid unit. McCullough[4] has presented a more detailed and sophisticated treatment of this motion. Other proposed motions associated with the crystalline phase have involved defect structures such as chain-end induced row vacancies,[3,5] motion of a defect chain twist[3] (Reneker defect[6]), and fold reorientations.[7] Another mechanistic suggestion involves the amorphous phase contribution to the γ transition in polyethylene (and other linear polymers). The low temperature (−120°, 1 Hz) at which this transition occurs and its modest activation energy (~11–15 kcal/mol[2]) suggests that it must involve a molecular motion of a particularly simple type[8–11] (crankshaft motions) uncoupled from the longer range highly cooperative segmental motion usually associated with glass–rubber transitions (and considered by many to be responsible for the β transition on polyethylene[2,3]).

Recently, computational methods have been developed that permit the calculation of the minimum energy path for conformational changes involving the cooperative motion of a number of bonds.[12–14] In addition, advances in conformational computational methods[15] have resulted in much improvement in the energy functions and parameters for hydrocarbons to be used in quantitative conformational calculations.[16] Thus, it now seems opportune to undertake the calculation of the energetics of the conformational changes associated with mechanisms proposed as underlying relaxations in polymers. In the present work we have undertaken the investigation of crankshaft motions in polyethylene in an attempt to answer some of the questions outlined below concerning them.

Inquiring into what might be the shortest range motion energetically feasible in polyethylene, Schatzki[8] presented a very specific model for the γ mechanism. He proposed that the conformational transition that could take place with the least energy barrier between stable strain-free conformations in the amorphous phase is of the type depicted in Figure 1. Since the initial and final states together represent a ring structure, it is helpful to visualize the conformational situation as a substituted *cis*-decalin. The substituent bonds 1 and 7 are colinear and Schatzki pointed out that the transition from the initial to the final state can be accomplished by simultaneous rotation about bonds 1 and 7 with the rest of the bonds held rigid. Further, the overall barrier to the motion should be well approximated by the sum of the two individual barriers to rotation of