Reduction in the Unperturbed Dimensions of Poly(vinyl chloride) upon the Random Incorporation of Chloromethyl Branches

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ABSTRACT: Rotational isomeric-state calculations of the mean-square unperturbed dimensions have been performed for poly(vinyl chloride) chains that contain isolated chloromethyl branches. The influence of the branches is reported as $\partial \ln \langle s^2\rangle_0/\partial p_{\mathrm{branch}}$, and compared with the values of $\partial \ln \langle s^2\rangle_0/\partial p_{\mathrm{m}}$. Here $\langle s^2\rangle_0$ is the mean-square unperturbed radius of gyration, p_{branch} is the probability that a monomer unit will contribute a chloromethyl branch, and p_{m} is the probability for a meso diad. Both partial derivatives are evaluated in the limit where $p_{\mathrm{branch}} \rightarrow 0$. $\partial \ln \langle s^2\rangle_0/\partial p_{\mathrm{branch}}$ is negative throughout the entire range of p_{m}, and it is always more negative than $\partial \ln \langle s^2\rangle_0/\partial p_{\mathrm{m}}$. This result shows that the introduction of a chloromethyl branch produces a contraction of the chain, and the contraction is more severe than that produced by a small change in the ratio of meso to racemic diads. An analysis of the origin of the negative values for $\partial \ln \langle s^2\rangle_0/\partial p_{\mathrm{branch}}$ shows that the results should apply also to the influence of an isolated 2,4-dichlorobutyl branch on the unperturbed dimensions of the chain.

Introduction

The incorporation of a few short branches into an otherwise linear polymer can have important consequences for its properties. An excellent example is provided by the prototype of a semicrystalline polymer, polyethylene. The ethylene–1-alkene copolymers are the version of this polymer that contain short branches of a specific size. When the short branches are larger than methyl, the chains organize themselves so that the short branches do not occur in the crystalline regions. Simulations show that the short branches are not uniformly distributed in the amorphous regions, but instead occur preferentially in the anisotropic interfacial region, accompanied by an increase in the interfacial content.[1,2] The increase in the interfacial content is observed experimentally,[3,4] as is the nonuniform distribution of short branches in the amorphous region.[5]

Short branches also occur as minor constituents in other types of polymers, either as a natural consequence of the mechanism of the polymerization, or via the intentional introduction of a small amount of a comonomer that will contribute the branch. The focus here will be on a common glassy polymer, poly(vinyl chloride). The presence of different types of short branches has been documented in this material, with the most abundant short branch being the chloromethyl group.[6]

An important difference in these two systems lies in the fact that one is semicrystalline, but the other is amorphous. In the case of the ethylene–1-alkene copolymers, accurate rotational isomeric-state calculations that reveal the influence of the short branch on the mean-square unperturbed dimensions[7] provide little insight into the effect of the branch on the bulk material. The reason for this failure is that the dominant influences of the short branch arise from its strong exclusion from the crystal, and its moderate preference for the anisotropic interfacial region over the isotropic amorphous region, both of which can be attributed to intermolecular interactions. In contrast, it is intramolecular interactions of short range that are considered in the computation of the unperturbed dimensions.

The same phenomenon cannot be active in the influence of the chloromethyl branches on poly(vinyl chloride) because there is no crystalline region from which the branches might be excluded, the entire system being amorphous. Such being the case, it is of interest to assess the influence of the chloromethyl branch on the unperturbed dimensions of the poly(vinyl chloride) chain. That assessment is reported here, based on rotational isomeric-state calculations that treat the chloromethyl group as an articulated side chain.[8,9] The rationalization of the results permits a reasonable prediction for the influence of the 2,4-dichlorobutyl branch on the unperturbed dimensions of poly(vinyl chloride). This branch is also found in poly(vinyl chloride), although usually at lower content than the chloromethyl branch.[6]

Computational Procedure

An isolated chloromethyl branch on a portion of a poly(vinyl chloride) chain is depicted in Figure 1. The covalent structure of the polymer is defined by four parameters, denoted by x, p_{m}, p_{branch}, and p_{mb}. The number of monomer units is denoted by x, the probability for a meso diad is denoted by p_{m}, the probability that a monomer unit will contribute a chloromethyl branch is denoted by p_{branch}, and p_{mb} is the probability for a meso placement at $CH_2CHClCH(CH_2Cl)CH_2$. The value of p_{mb} is relevant only when $p_{\mathrm{branch}} > 0$. The interest here is confined to very small values of p_{branch}, in recognition of the small content of chloromethyl branches in typical samples of poly(vinyl chloride).[6] Since p_{branch} is small, the formation of chloromethyl branches by two consecutive monomer units is of such rare occurrence that it will be ignored.

For convenience, it is assumed that neither end of the chain contributes a chloromethyl branch, and that monomer units i and $i-1$ cannot both contribute chloromethyl branches. These assumptions simplify the formulation of the conformation partition function, and they have no influence on the results when p_{branch} is very small, as is the case in all of the calculations of interest here. If monomer unit $i-1$ did not contribute a chloromethyl branch, as will usually be the case, the structure of monomer unit i is determined by the procedure diagrammed in Figure 2. Pseudorandom numbers in the range 0–1 are denoted by r_1 and r_2. Monomer unit i will contribute a chloromethyl branch if $r_1 < p_{\mathrm{branch}}$. Otherwise it will contribute an unbranched monomer unit. If this monomer unit contributes a branch, the configuration of the asymmetric carbon atoms in monomer units i and $i-1$ will be meso if $r_2 < p_{\mathrm{mb}}$, and racemic otherwise. If monomer unit i does not contribute a branch, the diad formed by monomer units i and $i-1$ will be meso if $r_2 < p_{\mathrm{m}}$, and racemic otherwise.

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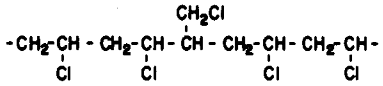

$-CH_2-CH(Cl)-CH_2-CH(Cl)-CH(CH_2Cl)-CH_2-CH(Cl)-CH_2-CH(Cl)-$

Figure 1. A small portion of a poly(vinyl chloride) chain in the vicinity of a chloromethyl branch.

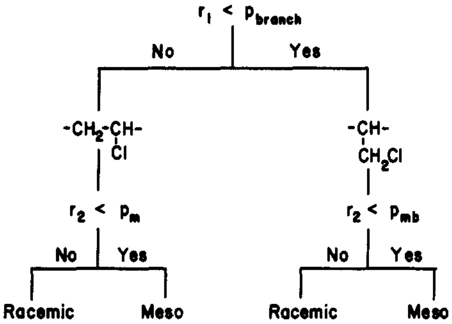

Figure 2. Scheme for generation of the structure of monomer unit i when monomer unit $i-1$ does not contribute a chloromethyl branch.

The chain will contain $2x - 1 - n_b$ C–C bonds in the backbone, where n_b is the number of chloromethyl branches. The symbol n will be used for $2x - 1 - n_b$, in conformity with the usual definition of n in rotational isomeric-state calculations for unbranched chains. The conformation partition function, Z, is written as a serial product of n statistical weight matrices, $\mathbf{U}_i$.

$$Z = \mathbf{U}_1\mathbf{U}_2 \dots \mathbf{U}_n \tag{1}$$

When $p_{\mathrm{branch}} = 0$, the expression for Z and the $\mathbf{U}_i$ is identical with that used by Mark in his treatment of unbranched poly(vinyl chloride).[10] The five statistical weights occurring in his $\mathbf{U}_i$ are denoted by η, τ, ω, ω', and ω''. In the present application, additional statistical weight matrices are required for three bonds near each chloromethyl branch, and two additional statistical weights are to be found in the statistical weight matrices for one of these bonds.

The first new statistical weight matrix is for the bond indicated by the dash in $CH_2CHCl–CH(CH_2Cl)CH_2$. The composition of this matrix depends on the stereochemistry of the carbon atoms at each end of that bond. By use of the dl notation to denote the stereochemistry, the matrices are

$$\mathbf{U}_{dd} = \begin{bmatrix} \eta & \tau & \eta\tau \\ \eta & \tau\omega & \eta\tau\omega \\ \eta\omega & \tau\omega & \eta\tau \end{bmatrix} \tag{2}$$

$$\mathbf{U}_{dl} = \begin{bmatrix} \eta\tau & \eta & \tau \\ \eta\tau\omega & \eta & \tau\omega \\ \eta\tau & \eta\omega & \tau\omega \end{bmatrix} \tag{3}$$

The statistical weights appearing in these matrices arise from interactions that are similar to the ones represented by the same symbols in Mark's treatment of unbranched poly(vinyl chloride).[10] Matrix $\mathbf{U}_{ll}$ is obtained from $\mathbf{U}_{dd}$, and $\mathbf{U}_{ld}$ is obtained from $\mathbf{U}_{dl}$, by transposition of elements according to the scheme

$$\begin{gathered} u_{1,2} \leftrightarrow u_{1,3} \\ u_{2,1} \leftrightarrow u_{3,1} \\ u_{2,2} \leftrightarrow u_{3,3} \\ u_{2,3} \leftrightarrow u_{3,2} \end{gathered} \tag{4}$$

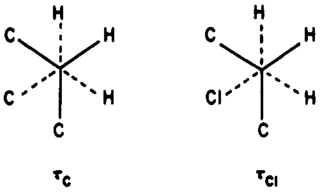

Figure 3. Conformations that contribute the first-order statistical weights τ_C (left) and τ_{Cl} (right). In the structure $CHClC^1H(C^3H_2Cl)C^2H_2$, the view is along the bond between atoms with superscripts 1 and 2 for τ_C, and along the bond between atoms with superscripts 1 and 3 for τ_{Cl}.

The statistical weight matrix for the next bond in the main chain must incorporate the interactions that arise from the chlorine atom in the three conformations of the articulated chloromethyl side chain. For this reason, the dimensions of the matrix expand to 3 × 9. In the formulation that is adopted below, the atom denoted by superscript i in $C^1HClCH^2(CH_2Cl)C^3H_2$ is trans to the chlorine atom in the chloromethyl branch in the ith 3 × 3 block. The forms are[8]

$$\mathbf{U}_{dd} = \begin{bmatrix} \omega' & \omega' & \tau_C & \tau_{Cl} & \tau_{Cl}\omega' & \tau_C\tau_{Cl}\omega' & \omega' & \omega'^2 & \tau_C\omega' \\ \omega' & 1 & \tau_C\omega & \tau_{Cl}\omega' & \tau_{Cl}\omega' & \tau_C\tau_{Cl}\omega\omega'^2 & \omega'' & \omega'' & \tau_C\omega\omega'' \\ \omega' & \omega & \tau_C\omega' & \tau_{Cl}\omega'' & \tau_{Cl}\omega\omega'' & \tau_C\tau_{Cl}\omega'^2\omega'' & 1 & \omega & \tau_C\omega' \end{bmatrix} \tag{5}$$

$$\mathbf{U}_{dl} = \begin{bmatrix} \omega' & \tau_C\omega' & 1 & \tau_{Cl}\omega'' & \tau_C\tau_{Cl}\omega'^2\omega'' & \tau_{Cl}\omega'' & \omega' & \tau_C\omega'^2 & \omega' \\ \omega' & \tau_C & \omega & \tau_{Cl} & \tau_C\tau_{Cl}\omega' & \tau_{Cl}\omega & \omega'' & \tau_C\omega'' & \omega\omega'' \\ \omega' & \tau_C\omega & \omega' & \tau_{Cl}\omega' & \tau_C\tau_{Cl}\omega\omega'^2 & \tau_{Cl}\omega'^2 & 1 & \tau_C\omega & \omega' \end{bmatrix} \tag{6}$$

Each of the three 3 × 3 blocks in $\mathbf{U}_{ll}$ and $\mathbf{U}_{ld}$ can be generated from the corresponding block in $\mathbf{U}_{dd}$ and $\mathbf{U}_{dl}$ by the transposition of elements depicted in eq 4. Figure 3 depicts the conformations that contribute the new first-order interactions denoted by τ_C and τ_{Cl}. The exact values of τ_C and τ_{Cl} are of little consequence because, as will be brought out below, the conclusions that flow from these calculations are remarkably insensitive to these assignments.

The statistical weight matrices for the bond denoted by the dash in $CH(CH_2Cl)CH_2–CHCl$ are of dimensions 9 × 3, with all three 3 × 3 blocks in a given matrix being identical. The form depends on the stereochemistry of the carbon atoms at the two ends of this fragment. The expressions are

$$\mathbf{U}_{dd} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} \eta\omega' & \tau\omega & 1 \\ \eta & \tau\omega' & \omega \\ \eta\omega' & \tau\omega\omega' & \omega \end{bmatrix} \tag{7}$$

$$\mathbf{U}_{dl} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} \eta & \omega & \tau\omega' \\ \eta\omega' & 1 & \tau\omega \\ \eta\omega' & \omega & \tau\omega\omega' \end{bmatrix} \tag{8}$$

where ⊗ denotes the direct matrix product. As before, $\mathbf{U}_{ll}$ is obtained from $\mathbf{U}_{dd}$, and $\mathbf{U}_{ld}$ is obtained from $\mathbf{U}_{dl}$, by the transformation in (4).

The dihedral angles for the three rotational isomers were separated by angular displacements of 120°. Two-hundred independent chains were generated for each combination of x, p_m, p_{branch}, p_{mb}, τ_C, and τ_{Cl} investigated. For each chain, the mean-square unperturbed end-to-end distance, $\langle r^2\rangle_0$, and mean-square radius of gyration, $\langle s^2\rangle_0$, were evaluated by the usual combination of the 5 × 5 and 7 ×

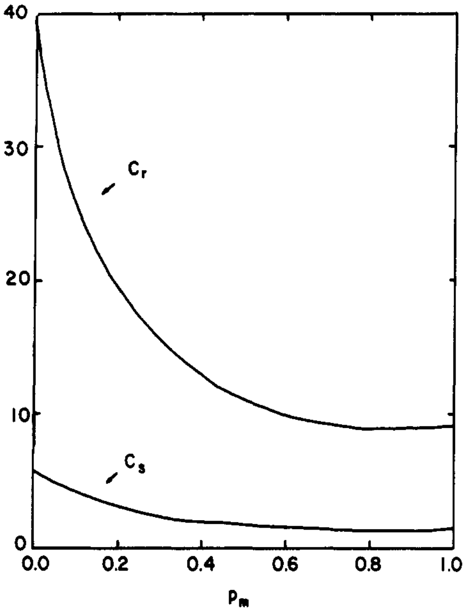

Figure 4. Characteristic ratios C_r and C_s, as functions of p_m, for $x = 250$ ($n = 499$). No chloromethyl branches are present.

7 generator matrices, respectively, with the expression for Z in eq 1.[11]

Results and Discussion

The sign and magnitude of the effect of an isolated chloromethyl branch on the unperturbed dimensions of poly(vinyl chloride) is most conveniently presented as the dimensionless partial derivative $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$, evaluated in the limit where $p_{\text{branch}} \rightarrow 0$. (For chains with degrees of polymerization that are of interest here, the numerical values of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ are nearly identical with the numerical values of $\partial \ln \langle r^2\rangle_0/\partial p_{\text{branch}}$.) In order to provide an intuitive appreciation for the size of this partial derivative, we will also present values of $\partial \ln \langle s^2\rangle_0/\partial p_m$, likewise evaluated in the limit where $p_{\text{branch}} \rightarrow 0$. The latter derivative describes the influence on $\langle s^2\rangle_0$ of changing the stereochemical configuration so that the chain contains an additional meso placement; the former derivative describes the influence when the structure of a monomer is changed so that it forms a chloromethyl branch. Are these changes in the same direction, and are they of comparable magnitude?

For assistance in understanding the results, Figure 4 depicts the dimensionless characteristic ratios, as a function of p_m, for chains with $p_{\text{branch}} = 0$. The characteristic ratios are defined as $C_r = \langle r^2\rangle_0/nl^2$ and $C_s = \langle s^2\rangle_0/nl^2$. Results depicted in Figure 1 were evaluated at $x = 250$. For this reason, they are slightly larger, particularly at small p_m, than the results reported for shorter chains by Mark.[10] The racemic chain is highly extended; the dimensions fall sharply as p_m rises above zero, then pass through a minimum in the vicinity of $p_m = 0.9$, and finally rise weakly as p_m approaches 1. The large extension of the racemic chain produces $C_r > 6C_s$; i.e., the distribution for its end-to-end vector is non-Gaussian, even at $x = 250$.

The slope of the line labeled C_s in Figure 4 is $\partial(\langle s^2\rangle_0/nl^2)/\partial p_m$. Division by C_s produces $\partial \ln \langle s^2\rangle_0/\partial p_m$, which is depicted in Figure 5. This partial derivative is strongly negative when $p_m = 0$, because the introduction of a meso diad into a racemic chain produces a break in the extended structure, leading to a large reduction in $\langle s^2\rangle_0$. The derivative becomes less negative as p_m increases, and it turns weakly positive as p_m rises above 0.9. For a very highly isotactic chain, conversion of one of the few racemic diads into a meso diad produces a small increase in the unperturbed dimensions.

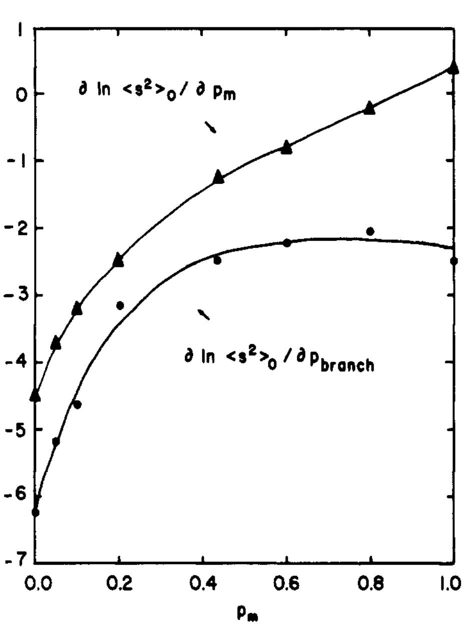

Figure 5. Partial derivatives $\partial \ln \langle s^2\rangle_0/\partial p_m$ and $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$, both evaluated in the limit where $p_{\text{branch}} \rightarrow 0$, for chains with $x = 250$. The values of the statistical weights peculiar to the vicinity of the branch point are $\tau_C = \tau_{Cl} = 4$ and $p_{mb} = 0.5$.

Figure 5 also depicts the behavior of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ for the same chains. This partial derivative was evaluated in the limit where $p_{\text{branch}} \rightarrow 0$, using $\tau_C = \tau_{Cl} = 4$ and $p_{mb} = 0.5$ for the parameters that are unique to the vicinity of a chloromethyl branch. This partial derivative also is strongly negative at $p_m = 0$ and is in fact slightly more negative than $\partial \ln \langle s^2\rangle_0/\partial p_m$. The mean-square unperturbed dimensions of an exclusively racemic chain will be reduced by the random introduction of either a single meso diad or a single chloromethyl branch, but the reduction will be somewhat more severe with the introduction of the chloromethyl branch. The value of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ remains negative throughout the entire range of stereochemical composition, in contrast to the behavior of $\partial \ln \langle s^2\rangle_0/\partial p_m$. Introduction of a chloromethyl group will always bring about a reduction in the unperturbed dimensions, no matter what the stereochemical composition of the chain may be. For chains in which p_m is in the vicinity of 0.43, $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ is about twice as negative as $\partial \ln \langle s^2\rangle_0/\partial p_m$.

Other calculations were carried out to determine the sensitivity of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ to variation in the values assigned to τ_C, τ_{Cl}, and p_{mb}. Of course, the values of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ change somewhat, but the changes are small. The qualitative conclusions drawn in the preceding paragraph remain valid for changes of 1 order of magnitude in τ_C and/or τ_{Cl}, and upon variation of p_{mb} over the range 0–1. The directions of the relatively small changes are such that $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ becomes more negative upon an increase in τ_C, a decrease in τ_{Cl}, or a decrease in p_{mb}.

The rationalization for the fact that $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ is negative at all values of p_m is as follows. Figure 4 shows that C_r is much larger than 2 at all values of p_m. Therefore the chains are much more extended than one would expect if the bonds were subject to free rotation, for which case C_r would have a value only slightly greater than 2. The larger values of C_r, at all p_m, imply that there is a tendency for the propagation of specific local conformations of the chain. This tendency is greatest for the racemic chain,

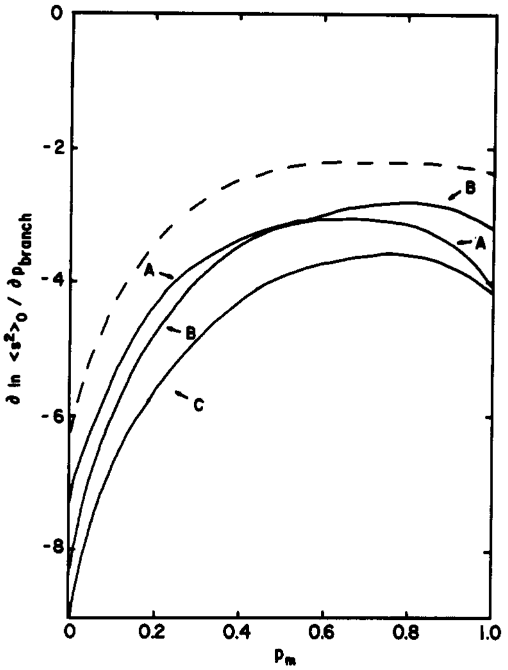

Figure 6. Lack of sensitivity of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ to variations in τ_C, τ_{Cl}, and p_{mb}. The solid lines depict values of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$, in the limit where $p_{\text{branch}} \to 0$, calculated when all elements in the following statistical weight matrices are assigned the same value: Curve A, the 3 × 3 matrices in eqs 2 and 3; curve B, the 3 × 9 matrices in eqs 5 and 6; curve C, the matrices in eqs 2, 3, 5, and 6. The dashed line is the result for $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ from Figure 5.

but it is present at all values of p_m. The introduction of a chloromethyl branch produces a local disruption in the tendency for propagation of specific local conformations found in those portions of the chain that do not contain a branch. That disruption produces a concentration in the dimensions, because it causes the local trajectory of the chain to change from the one that would propagate the preferred conformation. If one were to think about a localized portion of the chain, rather than the overall dimensions, the results presented in Figure 5 show that this localized portion will, on average, be contracted if it contains a chloromethyl branch.

The physical origin of the result that $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ is not sensitive to large variations in the values of τ_C, τ_{Cl}, and p_{mb} is presented with the aid of Figure 6. The curve depicted as the dashed line is the result presented for $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ in Figure 5. In curve A of Figure 6, the statistical weights are adjusted so that all three conformations at the CHCl–CH(CH$_2$Cl) bond are equally probable and independent of the conformations at neighboring bonds. In curve B, the adjustment causes all three conformations at the CH(CH$_2$Cl)–CH$_2$ bond to be equally probable and independent, and it also assigns equal probability and independence to the three conformations of the chloromethyl branch. Curve C combines the effects of curves A and B. There is little difference between curves A and B. An arbitrary assignment of equal probability to the three conformations for the bond immediately preceding the chloromethyl branch has nearly the same effect as the assignment of equal probability to the three conformations for the bond following this branch.

Throughout the entire range of p_m, the values of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ obtained with either of these arbitrary assignments are slightly more negative (but by an amount that lies between 1 and 2) than the values computed with a more realistic model, depicted by the dashed line in Figure 6. The realistic model does not assign equal probabilities to the three conformations of the bonds on either side of the chloromethyl branch, and the conformations at these bonds are dependent upon the conformations adopted at their neighbors. The reason that the results from the realistic model are so similar to the results from the artificial models is that all of the models have in common the introduction of a disruption in the preferred conformation for an unbranched poly(vinyl chloride) chain. It is the disruption itself, rather than the details of the disruption, that are of the greater importance for the determination of the behavior of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$. For this reason, large variations in the assignments of the values of τ_C, τ_{Cl}, and p_{mb} in the realistic model produce relatively small changes in the values of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$.

The observation that the calculated values of $\partial \ln \langle s^2\rangle_0/\partial p_{\text{branch}}$ are not sensitive to the details of the statistical weights unique to the chloromethyl branch implies that the results presented here are of broader application. In particular, they should provide an excellent approximation to the influence of an isolated 2,4-dichlorobutyl branch, which has also been documented in poly(vinyl chloride),[5] on the unperturbed dimensions of this polymer.

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