Statistical Chain Dimensions of Poly (vinyl acetal)-Type Molecules

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Summary

Acetalization of poly(vinyl alcohol) molecules results in acetal ring formation between two successive hydroxyl groups. This will dominate the chain stiffness of poly(vinyl acetal) in different ways, depending on the stereospecificity of poly(vinyl alcohol) used as the starting material. The present paper first deals with calculations of statistical dimensions of hypothetical poly(vinyl acetal) chains with a 100% degree of substitution and different stereospecificities (isotacticity and syndiotacticity). The calculations are essentially identical with those made by Wall and Markovitz, but recent stereochemical knowledges of the acetal ring and poly(vinyl alcohol) are taken into account. The results show that the chain dimension of poly-(vinyl acetal) chain derived from isotactic poly(vinyl alcohol) is much larger than that of poly(vinyl acetal) derived from the syndiotactic one. The treatment used above is extended to more realistic chains that have any degree of stereoregularity and of substitution. As has been anticipated intuitively, it is ascertained that the chain dimensions increase with increase in the degree of substitution for each stereospecificity.

Each pair of two neighboring hydroxyl groups in a poly(vinyl alcohol) (PVA) molecule can be acetalized with aldehydes to form a m-dioxane ring of cyclic acetal, which is supposed to have the chair conformation. The acetal ring formation will dominate the chain flexibility in several ways, depending on the relative stereochemical position of the two successive hydoxyl groups.

As has been pointed out by Matsumoto and Ohyanagi [1, 2], the m-dioxane ring has two steric isomers, corresponding to the stereo-specificity of starting PVA molecule; the isotactic portion of PVA affords cis-4, 6 derivatives of m-dioxane, whereas the syndiotactic portion affords trans-4, 6 derivatives, as schematically illustrated in Fig. 1. In the figure, bonds designated (a) and (e) indicate the C—C bonds radiating axially and equatorially in the plane of the dioxane ring [3], respectively.
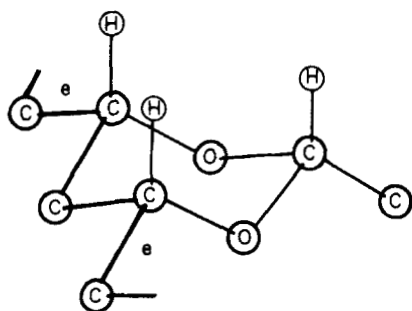
(a)
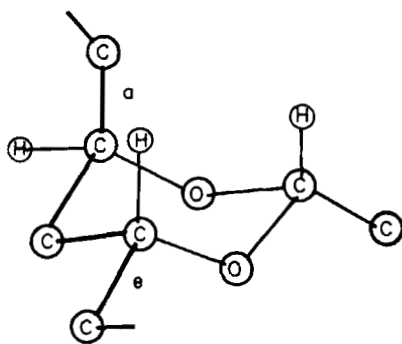
(b)

FIG. 1.   Schematic representation of the cis-4, 6 derivative (a) and the trans-4, 6 derivative (b) of a m-dioxane ring which appear followed by acetalization of PVA. In the figure, C—C bonds, designated by "e" and "a," show bonds radiating equatorially and axially in the plane of the dioxane ring, respectively.

Now we represent a pair of C—C bonds extending axially in the plane of dioxane ring with (a, a) and that extending equatorially with (e, e). Then it seems reasonable to presume that in the case of iso-tactic PVA, the population of the (e, e) form would be much higher than that of the (a, a) form. This may be attributed to a steric hin-drance that will be given rise when the (a, a) form is realized. Such an expectation has been proved experimentally by means of NMR with acetoacetal of pentane-2, 4-diol [4], and formal of heptane-2, 4, 6-triol [5] as model substances. It follows, therefore, that poly(vinyl acetal) chains derived from PVA rich in the isotactic sequence will assume a rather extended configuration, while those derived from PVA rich in the syndiotactic sequence will assume a somewhat con-tracted one. An intermediate configuration between these will appear in poly(vinyl acetals) from atactic PVA.

The purpose of the present paper is to calculate statistical chain dimensions of poly(vinyl acetal)-type molecules exhibiting free in-ternal rotations as functions of the degree of acetalization and of the tacticity of PVA with each stereospecificity. This result makes it possible to estimate the chain stiffness when the unperturbed chain dimension is obtained experimentally.

FUNDAMENTAL ASSUMPTIONS

The following assumptions are made for the PVA chain; the PVA chain is constituted by a head to tail connection with respect to the repeating unit, the number of atoms in the chain is large enough for statistical treatments, and the chain is linear with no branches. Fur-ther, the excluded volume effect is neglected and the internal rota-tions around all the C—C bonds, except those which constitute the dioxane (acetal) ring, are assumed to be free of any restriction.

In general, poly(vinyl acetals) may be regarded as copolymers composed of vinyl alcohol and acetal. For the sake of simplicity, however, the calculation will be made first for a hypothetical poly (vinyl acetal)-type chain, whose degree of acetalization is 100%,* and this result will be extended to poly(vinyl acetal)-type chains having more real structures.

CHAIN DIMENSIONS OF 100% ACETALIZED ISOTACTIC PVA MOLECULES

For convenience in explaning the present calculation, a schematic

*According to the statistical treatment of Flory [6], poly(vinyl acetal) molecules having a higher degree of acetalization than 86. 5% will not be possibly to obtain with the usual acetalization techniques. However, an attempt has been made recently to obtain poly(vinyl acetal) with 100% acetalization using a special procedure [7].
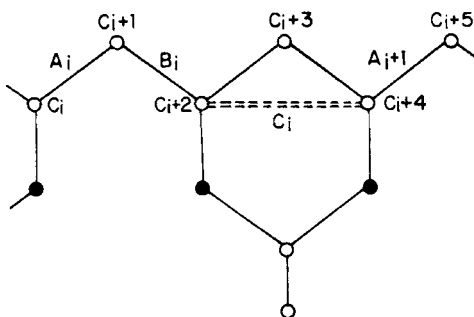
FIG. 2. Molecular model for acetalized PVA molecule. For details, see the text.

chain model for isotactic PVA–100% acetal is given in Fig. 2. A bond vector that joins the carbon atoms C_i and C_{i+1} is designated $\mathbf{A}_i$, and that joining C_{i+1} with C_{i+2} is designated $\mathbf{B}_i$. For the reason given above, two bonds $\mathbf{A}_{i+1}$ and $\mathbf{B}_i$ are assumed to extend equatorially in the plane of acetal ring. Rotation of bonds between C_{i+2} and C_{i+3} as well as between C_{i+3} and C_{i+4} will be frozen completely as a result of the acetal ring formation. This permits us to replace the bond joining C_{i+2}, C_{i+3}, and C_{i+4} by one hypothetical rigid bond designated by $\mathbf{C}_i$. On the other hand, the bonds $\mathbf{A}_i$ and $\mathbf{B}_i$ can be rotated independently with each other but keeping a fixed bond angle between $\mathbf{A}_i$ and $\mathbf{B}_i$, and this freedom of internal rotation alone will afford flexibilities to the polymer chain.

Now consider three successive bonds $\mathbf{B}_i, \mathbf{C}_i$, and $\mathbf{A}_{i+1}$. The situation of these bonds is similar to that of a double bond interposed by two single bonds, as seen in 1, 4-polybutadiene. Thus we may expect that the treatments employed by Wall [8] or Markovitz [9] for calculating mean-square end to end distances is applicable to the present problem.

As is illustrated in Fig. 3, each of the bond vectors, $\mathbf{A}_i, \mathbf{B}_i$, and $\mathbf{C}_i$, is numbered successively from the one to the other end of chain. Let α be angle between vectors $\mathbf{A}_i$ and $\mathbf{B}_i$ [hereafter α will be denoted alternatively by $(\mathbf{A}_i, \mathbf{B}_i)$]. By a simple geometric consideration, angle β, i.e., $(\mathbf{B}_i, \mathbf{C}_i)$ is equal to $(\mathbf{C}_i, \mathbf{A}_{i+1})$, thus being $\beta = (1/2)\alpha$, and $(\mathbf{B}_i, \mathbf{A}_{i+1})$ is equal to α. A strain effect which will be induced in the bonds by formation of the acetal ring is not taken into account. Now we write absolute values of $\mathbf{A}_i$ and $\mathbf{B}_i$ by a, and those of $\mathbf{C}_i$ and of the end to end distance vector, $\mathbf{L}$, which contains p units of (A,B,C) by b and L, respectively. Then we get

$$\mathbf{L} = \mathbf{A}_1 + \mathbf{B}_1 + \mathbf{C}_1 + \mathbf{A}_2 + \mathbf{B}_2 + \mathbf{C}_2 + \cdots + \mathbf{A}_p + \mathbf{B}_p + \mathbf{C}_p \qquad (1)$$

A scalar product of $\mathbf{L} \cdot \mathbf{L}$ is expressed by
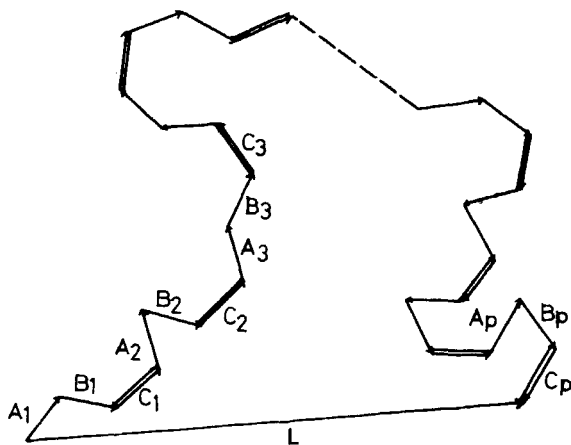
FIG. 3. Possible chain configuration for 100% acetalized isotactic PVA.

$$\mathbf{L} \cdot \mathbf{L} = \mathbf{A}_1 \cdot \mathbf{A}_1 + \mathbf{B}_1 \cdot \mathbf{B}_1 + \mathbf{C}_1 \cdot \mathbf{C}_1$$

$$+ \mathbf{A}_2 \cdot \mathbf{A}_2 + \mathbf{B}_2 \cdot \mathbf{B}_2 + \mathbf{C}_2 \cdot \mathbf{C}_2 + \cdots + \mathbf{C}_p \cdot \mathbf{C}_p$$

$$+ 2(\mathbf{A}_1 \cdot \mathbf{B}_1 + \mathbf{B}_1 \cdot \mathbf{C}_1 + \mathbf{C}_1 \cdot \mathbf{A}_2 + \mathbf{A}_2 \cdot \mathbf{B}_2 + \cdots + \mathbf{B}_p \cdot \mathbf{C}_p)$$

$$+ 2(\mathbf{A}_1 \cdot \mathbf{C}_1 + \mathbf{B}_1 \cdot \mathbf{A}_2 + \mathbf{C}_1 \cdot \mathbf{B}_2 + \mathbf{A}_2 \cdot \mathbf{C}_2 + \cdots + \mathbf{A}_p \cdot \mathbf{C}_p)$$

$$+ \cdots$$

$$+ 2(\mathbf{A}_1 \cdot \mathbf{B}_p + \mathbf{B}_1 \cdot \mathbf{C}_p) + 2\mathbf{A}_1 \cdot \mathbf{C}_p \qquad (2)$$

where clearly

$$\mathbf{A}_1 \cdot \mathbf{A}_1 = \mathbf{B}_1 \cdot \mathbf{B}_1 = \mathbf{A}_2 \cdot \mathbf{A}_2 = \mathbf{B}_2 \cdot \mathbf{B}_2 = \cdots = \mathbf{B}_p \cdot \mathbf{B}_p = a^2$$

$$\mathbf{C}_1 \cdot \mathbf{C}_1 = \mathbf{C}_2 \cdot \mathbf{C}_2 = \mathbf{C}_3 \cdot \mathbf{C}_3 = \cdots = \mathbf{C}_p \cdot \mathbf{C}_p = b^2$$

As has been pointed out by Wall [8] in the calculation for saturated hydrocarbon and polybutadiene chains, the following relations should be applicable to the present case, for every internal rotation around $\mathbf{A}_i$ and $\mathbf{B}_i$ is completely free:

$$\mathbf{A}_1 \cdot \mathbf{B}_1 \quad = \mathbf{A}_2 \cdot \mathbf{B}_2 \approx \mathbf{A}_3 \cdot \mathbf{B}_3 = \cdots = \mathbf{A}_p \cdot \mathbf{B}_p = a^2\lambda$$

$$\mathbf{B}_1 \cdot \mathbf{C}_1 \quad = \mathbf{C}_1 \cdot \mathbf{A}_2 \approx \mathbf{B}_2 \cdot \mathbf{C}_2 = \mathbf{C}_2 \cdot \mathbf{A}_2 = \cdots = ab\mu$$

$$\langle \mathbf{A}_1 \cdot \mathbf{C}_1 \rangle = \langle \mathbf{C}_1 \cdot \mathbf{B}_2 \rangle = \langle \mathbf{A}_2 \cdot \mathbf{C}_2 \rangle = \cdots = ab\lambda\mu$$

where $\lambda = \cos \alpha$ and $\mu = \cos \beta$. Since angle $(\mathbf{B}_i, \mathbf{A}_{i+1})$ is equal to 2β, hence to α, we obtain

$$\mathbf{B}_1 \cdot \mathbf{A}_2 \quad = \mathbf{B}_2 \cdot \mathbf{A}_3 = \mathbf{B}_3 \cdot \mathbf{A}_4 = \cdots = a^2\lambda$$

and

$$\langle \mathbf{A}_1 \cdot \mathbf{A}_2 \rangle = \langle \mathbf{B}_1 \cdot \mathbf{B}_2 \rangle = \langle \mathbf{A}_2 \cdot \mathbf{A}_3 \rangle = \langle \mathbf{B}_2 \cdot \mathbf{B}_3 \rangle$$

$$= \cdots = a^2\lambda^2 = \langle \mathbf{A}_j \cdot \mathbf{A}_j \rangle \lambda^2 = \langle \mathbf{B}_j \cdot \mathbf{B}_j \rangle \lambda^2$$

$$\langle \mathbf{C}_1 \cdot \mathbf{C}_2 \rangle = \langle \mathbf{C}_2 \cdot \mathbf{C}_3 \rangle = \cdots = b^2\lambda\mu^2$$

$$\langle \mathbf{C}_1 \cdot \mathbf{C}_3 \rangle = \langle \mathbf{C}_2 \cdot \mathbf{C}_4 \rangle = \cdots = b^2\lambda^3\mu^2$$

$$= \langle \mathbf{C}_j \cdot \mathbf{C}_{j+1} \rangle \lambda^2$$

$$\langle \mathbf{B}_1 \cdot \mathbf{C}_2 \rangle = \langle \mathbf{B}_2 \cdot \mathbf{C}_3 \rangle = \cdots = ab\lambda^2\mu$$

$$= \langle \mathbf{B}_j \cdot \mathbf{C}_j \rangle \lambda^2 \tag{5}$$

Equation (5) may be generalized in the form

$$\langle \mathbf{X}_j \cdot \mathbf{Y}_m \rangle = \langle \mathbf{X}_j \cdot \mathbf{Y}_{m-1} \rangle \cdot \lambda^2 \qquad \text{for } j < m \tag{6}$$

where $\mathbf{X}$ and $\mathbf{Y}$ represent any vector of $\mathbf{A}, \mathbf{B},$ and $\mathbf{C}$. However, Eq.(6) is valid only when $j + 2 \leqslant m$, if $\mathbf{X} = \mathbf{Y} = \mathbf{C}$. Taking the average of each term appearing on both sides of Eq. (2) over all possible conformations and substituting Eqs.(3), (4), (5), and (6), we obtain

$$\langle \mathbf{L} \cdot \mathbf{L} \rangle = \langle \mathbf{L}^2 \rangle_{\text{of}} = 2pa^2 + pb^2$$

$$+ 2[p\mathbf{A}_j \cdot \mathbf{B}_j + p\mathbf{B}_j \cdot \mathbf{C}_j$$

$$+ (p-1)\mathbf{C}_j \cdot \mathbf{A}_{j+1} + p\langle \mathbf{A}_j \cdot \mathbf{C}_j \rangle$$

$$+ (p-1)\mathbf{B}_j \cdot \mathbf{A}_{j+1}$$

$$+ (p-1)\langle \mathbf{C}_j \cdot \mathbf{B}_{j+1} \rangle$$

$$+ (p-1)\langle \mathbf{A}_j \cdot \mathbf{A}_{j+1} \rangle$$

$$+ (p-1)\langle \mathbf{B}_j \cdot \mathbf{B}_{j+1} \rangle$$

$$+ (p-1)\langle \mathbf{C}_j \cdot \mathbf{C}_{j+1} \rangle$$

$$+ (p - 1)\langle \mathbf{A_j} \cdot \mathbf{B_{j+1}} \rangle$$

$$+ (p - 1)\langle \mathbf{B_j} \cdot \mathbf{C_{j+1}} \rangle$$

$$+ (p - 2)\langle \mathbf{C_j} \cdot \mathbf{A_{j+2}} \rangle$$

$$+ \cdots \tag{7}$$

or

$$\langle L^2 \rangle_{of} = p(2a^2 + b^2)$$

$$+ 2p(a^2\lambda + 2ab\mu) - 2ab\mu$$

$$+ 2(p - 1)(a^2\lambda + 2ab\lambda\mu) + 2ab\lambda\mu$$

$$+ 2(p - 1)(2a^2\lambda^2 + b^2\lambda\mu^2)$$

$$+ 2(p - 1)(a^2\lambda^3 + 2ab\lambda^2\mu) - 2ab\lambda^2\mu$$

$$+ 2(p - 2)(a^2\lambda^3 + 2ab\lambda^3\mu) + 2ab\lambda^3\mu$$

$$+ \cdots \tag{8}$$

When $p \gg 1$, Eq. (8) may be reduced, by rearranging the terms, to

$$\frac{1}{p}\langle L^2 \rangle_{of} = \frac{2(1 + \lambda)}{1 - \lambda} a^2 + \frac{4\mu}{1 - \lambda} ab + \frac{1 - \lambda^2 + 2\lambda\mu^2}{1 - \lambda^2} b^2 \tag{9}$$

The suffix "of" means that the chain is subjected to no excluded volume effect, and to free internal rotation, as usual. Assuming 70°32′ for α and 1.54 and 2.51Å for a and b, respectively, as in normal hydocarbon molecules, and putting these values into Eq. (9), we can evaluate the mean-square effective chain length per unit segment composed of $(\mathbf{A_i}, \mathbf{B_i}, \mathbf{C_i})$, that is, $\langle L^2 \rangle_{of}/p = 37.87Å^2$.

CHAIN DIMENSIONS OF 100% ACETALIZED SYNDIO-TACTIC PVA MOLECULE AND 100% ACETALIZED ATACTIC PVA MOLECULE

As will be understood easily by studying any molecular model of syndiotactic PVA–100% acetal, it is clear that if either one of bonds $\mathbf{B_i}$ and $\mathbf{A_{i+1}}$ radiates equatorially in the plane of acetal ring, the other bond is obliged to radiate axially. This situation differs from that for isotactic PVA–100% acetal; both of $\mathbf{B_i}$ and $\mathbf{A_{i+1}}$ are either equatorial or axial with respect to the plane of acetal ring, the latter conformation being forbidden, however, owing to its strong steric hindrance. It may be supposed for an acetal of syndiotactic PVA molecule that a set of ways of connections (a, e) and (e, a) would be
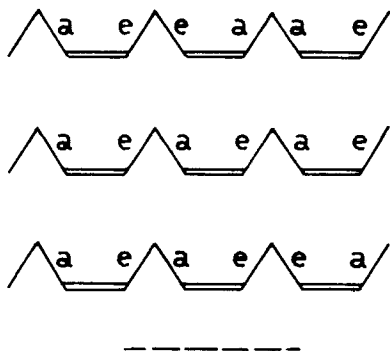
FIG. 4. Schematic representation of some possible types of connections (a, e) and (e, a). For details, see the text.

distributed statistically along the main chain* [for the symbols (a, e) etc., see above]. Figure 4 illustrates some possible types of these connections which will appear in the main chain.

Referring to the aforementioned description, we easily find that angle (B_i, C_i) can be put equal to β and γ (= 90°), corresponding to the equatorial and axial connection of **B** onto **C**, respectively. By a geometric consideration, angle (B_i, A_{i+1}) is equal to 2β, hence to α. This situation is the same as for acetals of isotactic PVA.

On the other hand, atactic PVA subjected to 100% acetalization may be represented by a model chain along which the connection forms (a, e), (e, a), and (e, e) are distributed randomly. Thus acetals of atactic PVA have more complicated structures than acetals of syndiotactic and isotactic PVA. On the basis of this preliminary knowledge, calculations of $\langle L^2 \rangle_{of}$ will be made along the same lines as described in the last section.

The values of $\langle L^2 \rangle_{of}$ for acetals of syndiotactic and atactic PVA chains may be represented by Eq. (7). Averages of scalar products, $\langle A_i \cdot B_j \rangle$, $\langle B_i \cdot A_j \rangle$, $\langle A_i \cdot A_j \rangle$, and $\langle B_i \cdot B_j \rangle$ are the same as appear in acetals of isotactic PVA, whereas $\langle B_i \cdot C_j \rangle$, $\langle C_i \cdot A_j \rangle$, and $\langle A_i \cdot C_j \rangle$, containing vector **C**, are different from those in acetals of isotactic PVA; averages of the latter products are taken over all possible conformations and configurations, differing from the case of averaging the former products.

Now we represent the configuration for hydroxyl groups in PVA

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*It has been found recently that for formal of syndiotactic heptane-2, 4, 6-triol, the (e, a) form was easily transformed to the (a, e) and vice versa [5], while for acetoacetal of d, 1-pentane-2, 4-diol, such an equilibrium was not observed [4].

chain in terms of the "diad" expression and denote the fraction of isotactic part in PVA chain by t. Then the fraction of syndiotactic part is given by $(1-t)$, and the fraction of (e, e) form associated with the three types of acetal forms in acetals of PVA thus becomes equal to t. The assumption made above seems to be plausible if one keeps in mind the observation that the rate of reaction of acetalizing PVA in homogeneous systems is almost independent of the stereospecific structure of PVA [4]. Another support of this assumption may be found in an experimental result obtained by NMR [5]; the intensity ratio of two signals assigned to the (e, e) and (e, a) form in formalized PVA is consistent with the content ratio of the isotactic and syndiotactic portions of PVA sample used as the starting material.*
It follows then that the fraction of $\{(a, e) + e, a)\}$ is equal to $1 - t$. The probabilities that $\mathbf{B_i}$ is connected with $\mathbf{C_i}$ equatorially and axially are $(1 + t)/2$ and $(1 - t)/2$, respectively. Thus $\langle \mathbf{B_i} \cdot \mathbf{C_i} \rangle$ can be expressed by

$$\langle \mathbf{B_i} \cdot \mathbf{C_i} \rangle = ab\kappa \tag{10}$$

with

$$\kappa = \frac{1 + t}{2} \mu + \frac{1 - t}{2} \nu$$

where $\cos \gamma$ is written ν. In the same way as above we get

$$\langle \mathbf{C_i} \cdot \mathbf{A_{i+1}} \rangle = ab\kappa \tag{11}$$

$$\langle \mathbf{A_i} \cdot \mathbf{C_i} \rangle = \langle \mathbf{C_i} \cdot \mathbf{B_{i+1}} \rangle = ab\lambda\kappa$$

$$\langle \mathbf{C_i} \cdot \mathbf{C_{i+1}} \rangle = b^2\lambda\kappa^2$$

$$\langle \mathbf{B_i} \cdot \mathbf{C_{i+1}} \rangle = \langle \mathbf{C_i} \cdot \mathbf{A_{i+2}} \rangle = ab\lambda^2\kappa \tag{12}$$

The equations can be expressed generally by

$$\langle \mathbf{X_j} \cdot \mathbf{Y_m} \rangle = \langle \mathbf{X_j} \cdot \mathbf{Y_{m-1}} \rangle \lambda^2 \tag{13}$$

which is valid only for $j + 2 \leqslant m$ if $\mathbf{X} = \mathbf{Y} = \mathbf{C}$, however. As was done previously, each term in Eq. (7) is substituted by Eq. (13). For a large enough value of p, we then arrive at

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*When the formalizing reaction is made under some equilibrium conditions, the resultant product tends to show a higher content of the (e, e) form than that expected from the tacticity of original PVA [10]. For this reason, the present assumption is not necessarily acceptable in a rigorous sense.

$$\frac{1}{p}\langle L^2 \rangle_{of} = \frac{2(1 + \lambda)}{1 - \lambda} a^2 + \frac{4\kappa}{1 - \lambda} ab + \frac{1 - \lambda^2 + 2\lambda\kappa^2}{1 - \lambda^2} b^2 \qquad (14)$$

It is found easily that Eq. (14) can be reduced to Eq. (9) derived for isotactic PVA–100% acetal if κ is put to μ corresponding to t = 1. The chain dimensions $(1/p)\langle L^2 \rangle_{of}$ for the syndiotactic PVA–100% acetal (t = 0) and atactic PVA–100% acetal (t = 0.5) calculated by using Eq. (14) are 26.06 and 31.76Å^2, respectively.

CHAIN DIMENSIONS OF PARTIALLY ACETALIZED PVA MOLECULES

In this case it is necessary to add bonds of vinyl alcohol unit into our hypothetical chain; two types of vectors D and E are introduced as chain members in addition to **A**, **B**, and **C**. A possible configuration of such a chain is schematically shown in Fig. 5. The partially
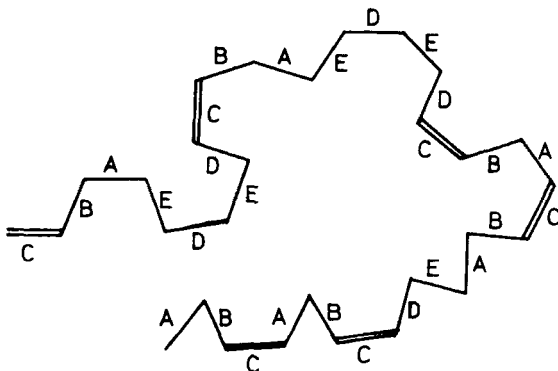

FIG. 5. Possible chain configuration for partially acetalized atactic PVA.

acetalized PVA chain will, therefore, be similar to the polybutadiene-type chains obtainable with both 1, 4- and 1, 2-type polymerizations, and the calculation of the end to end distance made by Markovitz [9] for polybutadiene may also be applicable to the present case. Suppose that PVA used as the starting material is atactic and has an isotactic fraction denoted by t and that the acetalization proceeds randomly irrespective of the local stereoregularity of PVA chain. Then the probability that an acetalized monomeric unit is found in the chain is equal to the degree of acetalization; in other words, the unit sequence of (**A**, **B**, **C**) is located randomly among the unit sequen·

ces of (D, E). It is further provided that the partially acetalized PVA has n acetal connections and m vinyl alcohol units, and the chain consists of p units as a whole, i.e., $n + m = p$. Thus the fractions of acetal and vinyl alcohol units are given by $g = n/p$ and $h = m/p$, respectively. The degree of polymerization, P, counted on the basis of vinyl unit, is written

$$P = (1 + g)p \tag{15}$$

and the degree of acetalization is given by

$$\frac{2g}{1 + g} \tag{16}$$

Making use of a procedure similar to that employed in the previous section, the scalar product $\mathbf{L} \cdot \mathbf{L}$ is formed and then averaged. This leads to

$$\langle L^2 \rangle_{of} = \langle \mathbf{L} \cdot \mathbf{L} \rangle = 2a^2n + b^2n + 2a^2m + 2 \text{ average of}$$

[Σ(products of neighboring bonds)

$+ \Sigma$(products of bonds twice removed)

$+ \Sigma$(products of bonds three times removed)

$+ \cdots$] $\tag{17}$

Each product appearing in Eq. (17) is listed below in the same way as adopted by Markovitz [9], but we write the averaged products, e.g., $\langle A_i \quad B_i \rangle$, for brevity, as $\mathbf{A} \cdot \mathbf{B}$. The number of such products that will appear in a chain on the average is given in parentheses beside each product. Terms of order unity are neglected in comparison with terms of order m or n in this number.

Products of neighboring bonds:

$\mathbf{A} \cdot \mathbf{B}(n) = \mathbf{D} \cdot \mathbf{E}(m) = \mathbf{E} \cdot \mathbf{D}(mh) = \mathbf{E} \cdot \mathbf{A}(mg) = a^2\lambda$

$\mathbf{B} \cdot \mathbf{C}(n) = \mathbf{C} \cdot \mathbf{A}(ng) = \mathbf{C} \cdot \mathbf{D}(nh) = ab\lambda$

Products of bonds twice removed:

$\mathbf{A} \cdot \mathbf{C}(n) \quad = \mathbf{C} \cdot \mathbf{B}(ng) = \mathbf{C} \cdot \mathbf{E}(nh) = ab\lambda\kappa$

$\mathbf{B} \cdot \mathbf{A}(ng) \ = \mathbf{B} \cdot \mathbf{D}(nh) = a^2\lambda$

$\mathbf{D} \cdot \mathbf{A}(mg) = \mathbf{E} \cdot \mathbf{B}(mg) = \mathbf{D} \cdot \mathbf{D}(mh) = \mathbf{E} \cdot \mathbf{E}(mh) = a^2\lambda^2$

Products of bonds three times removed:

$$\mathbf{A} \cdot \mathbf{A}(ng) = \mathbf{B} \cdot \mathbf{B}(ng) = \mathbf{A} \cdot \mathbf{D}(nh) = \mathbf{B} \cdot \mathbf{E}(nh) = a^2\lambda^2$$

$$\mathbf{E} \cdot \mathbf{C}(mg) = \mathbf{C} \cdot \mathbf{D}(nh^2) = \mathbf{C} \cdot \mathbf{A}(ngh) = ab\lambda^2\kappa$$

$$\mathbf{C} \cdot \mathbf{C}(ng) = b^2\lambda\kappa^2$$

$$\mathbf{D} \cdot \mathbf{B}(mg) = \mathbf{D} \cdot \mathbf{E}(mh) = \mathbf{E} \cdot \mathbf{A}(mgh) = a^2\lambda^3$$

Products of bonds four times removed:

$$\mathbf{A} \cdot \mathbf{B}(ng) = \mathbf{A} \cdot \mathbf{E}(nh) = \mathbf{B} \cdot \mathbf{D}(nh^2)$$
$$= \mathbf{B} \cdot \mathbf{A}(ngh) = \mathbf{E} \cdot \mathbf{A}(mg^2) = \mathbf{E} \cdot \mathbf{D}(mgh) = a^2\lambda^3$$

$$\mathbf{C} \cdot \mathbf{B}(ngh) = \mathbf{C} \cdot \mathbf{E}(nh^2) = \mathbf{D} \cdot \mathbf{C}(mg) = ab\lambda^3\kappa$$

$$\mathbf{C} \cdot \mathbf{A}(ng^2) = \mathbf{C} \cdot \mathbf{D}(ngh) = \mathbf{B} \cdot \mathbf{C}(ng) = ab\lambda^2\kappa$$

Products of bonds further removed involve terms of order λ^5 and smaller. For the present purpose, contributions of these terms can be neglected, and they will be excluded below.

Products of bons five times removed:

$$\mathbf{C} \cdot \mathbf{A}(ngh^2) = \mathbf{C} \cdot \mathbf{D}(nh^3) = \mathbf{E} \cdot \mathbf{C}(ngh) = ab\lambda^4\kappa$$

$$\mathbf{B} \cdot \mathbf{B}(ngh) = \mathbf{B} \cdot \mathbf{E}(nh^2) = \mathbf{A} \cdot \mathbf{D}(nh^2) = \mathbf{A} \cdot \mathbf{A}(ngh)$$
$$= \mathbf{E} \cdot \mathbf{B}(mg^2) = \mathbf{E} \cdot \mathbf{E}(mgh) = \mathbf{D} \cdot \mathbf{A}(mg^2)$$
$$= \mathbf{D} \cdot \mathbf{D}(mgh) = a^2\lambda^4$$

$$\mathbf{C} \cdot \mathbf{B}(ng^2) = \mathbf{C} \cdot \mathbf{E}(ngh) = \mathbf{A} \cdot \mathbf{C}(ng) = ab\lambda^3\kappa$$

$$\mathbf{C} \cdot \mathbf{C}(ngh) = b^2\lambda^3\kappa^2$$

$$\mathbf{B} \cdot \mathbf{A}(ng^2) = \mathbf{B} \cdot \mathbf{D}(ngh) = a^2\lambda^3$$

Products of bonds six times removed:

$$\mathbf{C} \cdot \mathbf{A}(ng^2h) = \mathbf{C} \cdot \mathbf{D}(ngh^2) = \mathbf{B} \cdot \mathbf{C}(ngh) = \mathbf{E} \cdot \mathbf{C}(mg^2) = ab\lambda^4\kappa$$

$$\mathbf{B} \cdot \mathbf{B}(ng^2) = \mathbf{B} \cdot \mathbf{E}(ngh) = \mathbf{A} \cdot \mathbf{A}(ng^2) = \mathbf{A} \cdot \mathbf{D}(ngh) = a^2\lambda^4$$

$$\mathbf{C} \cdot \mathbf{C}(ng^2) = b^2\lambda^3\kappa^2$$

Products of bonds seven times removed:

$$\mathbf{C} \cdot \mathbf{A}(ng^3) = \mathbf{C} \cdot \mathbf{D}(ng^2h) = \mathbf{B} \cdot \mathbf{C}(ng^2) = ab\lambda^4\kappa$$

If the values tabulated above are put into Eq. (17) and the same

numerical values for a, b, and λ are used as in the previous section, the result is expressed by

$$(1/p)\langle L^2 \rangle_{of} = 9.193 + 6.944g + 23.10g\kappa - 0.5855g^2$$

$$- 0.0954g^2\kappa + 4.666g^2\kappa^2 + 0.1756g^3$$

$$+ 0.0954g^3\kappa \qquad (18)$$

The values $\langle L^2 \rangle_{of}/p$ obtained by use of this approximate expression for 100% acetals are in agreement with those obtained by Eq. (14), as seen from Table 1. The ratio of the mean-square end to end distance to the degree of polymerization, $\langle L^2 \rangle_{of}/P$, is related to $\langle L^2 \rangle_{of}/p$ with the aid of Eq. (15):

TABLE 1. Values of $(\langle L^2 \rangle_{of}/P)^{1/2}$(Å) as Functions of Degree Poly(vinyl acetal)-Type Chains with 100% Acetalization Using Eqs. (14) and (18)

			$(\langle L^2 \rangle_{of}/p)^{1/2}$, Å	
Type of PVA chain	g	t	Eq. (14)	Eq. (18)
Syndiotactic	1	0	26.04	25.94
Isotactic	1	1	37.87	37.70
Atactic	1	0.5	31.76	31.62

TABLE 2. Values of $(\langle L^2 \rangle_{of}/P)^{1/2}$(Å) as Functions of Degree of Acetalization (A in mole %) and Fraction of Isotactic Portion (t)

	A(g)				
t	100(1)	80(0.666)	70(0.537)	60(0.429)	0(0)[a]
0	3.60	3.48	3.43	3.37	3.03
0.3	3.83	3.66	3.58	3.51	3.03
0.5	3.98	3.78	3.69	3.60	3.03
0.8	4.20	3.96	3.84	3.72	3.03
1.0	4.34	4.07	3.94	3.81	3.03

[a]The values evaluated using Eq. (18) differ from 3.08Å by ca. 2%.

$$\frac{\langle L^2 \rangle_{of}}{P} = \frac{1}{1+g} \frac{\langle L^2 \rangle_{of}}{p} \qquad (19)$$

Table 2 gives values of $\langle L^2 \rangle_{of}/P$ evaluated using Eqs. (18) and (19) for various values of t and g, and these results are represented graphically in Fig. 6.
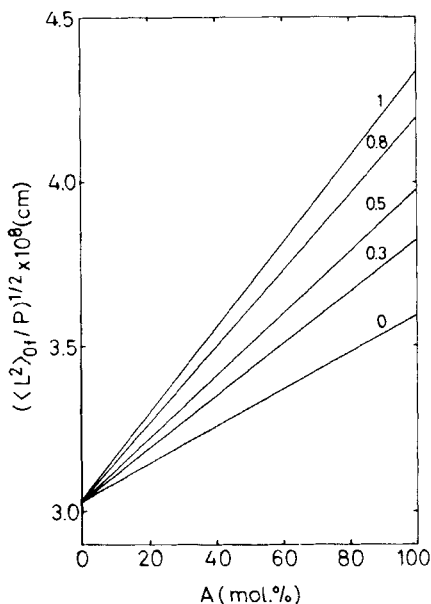
FIG. 6.   Values of $(\langle L^2 \rangle_{of}/P)^{1/2}$ as a function of the degree of acetalization. The number attached to the right end of each curve indicates the fraction, t, of isotactic portion in PVA.

DISCUSSION

The values of $(\langle L^2 \rangle_{of}/P)^{1/2}$ calculated above allow us to expect that the statistical dimensions of poly(vinyl acetal)-type chains are distinctly larger than those of other vinyl-type polymer chains (3.08 Å), and acetals derived from isotactic PVA assume more extended configurations than those derived from the syndiotactic one. This agrees with our intuitive anticipation. Referring to the numerical result given in Table 2, we can calculate values of $\langle L^2 \rangle_{of}^{1/2}$ for poly(vinyl acetals) with 80 mole% acetalization and the degree of polymerization of 5000 as a function of the fraction of isotactic por-

tion in PVA, t. These values are 220, 239, and 257 Å for t values 0, 0.5, and 1.0, respectively. It turns out that the unperturbed dimensions, $\langle L^2 \rangle_0^{1/2}$, should come to 440, 478, and 514 Å, corresponding to each t value, if one tentatively assumes that the steric factors, σ, i.e., the ratio of $\langle L^2 \rangle_0^{1/2}$ to $\langle L^2 \rangle_{of}^{1/2}$, be 2.0 for all of poly(vinyl acetal)-type chains. The difference expected among these three values will be large enough for experimental detection by light scattering as well as by intrinsic viscosity determination. Thus we believe that the effect of stereoregularity on the unperturbed dimension of PVA may be amplified by acetalizing PVA as highly as possible.

The acetal ring formation in PVA chain restricts the internal rotation around the skeletal C—C bonds, and this effect will surely, be reflected in such physical properties as rheological properties, glass transition, solubility, etc. In fact, it has been reported that the glass transition temperature, T_g, of poly(vinyl formal) [11] is obviously higher than that of PVA [12, 13] and becomes higher with increase in the degree of formalization [11]. This fact may be attributed to the increase of the mean segmental length caused by the acetal ring formation, as pointed out above. Acetalization with higher aldehydes than formaldehyde tends, however, to lower the glass transition temperature when the carbon number of the alkyl group increases [11]. This trend is interpreted in terms of the effect of the bulkiness of side groups on the free volume [14, 15].

As stated in the previous sections, the difference in the stereochemical structures of isotactic and syndiotactic PVA—acetals is associated with which one of the (e, e) and the (e, a) or (a, e) forms is preferred at the 4, 6 position of the dioxane ring. Taking into consideration that the (e, e) and (e, a) forms correspond to cis and trans configuration, respectively, the stereochemical situation for these two acetals is comparable to that for amylose (cis) and cellulose (trans) in polysaccharides as well as for natural rubber (cis) and gutta percha (trans) in 1, 4-polyisoprenes, whose physical properties are strongly dependent on their absolute configurations [16, 17]. Thus such a comparison may permit us to predict some possible differences in the physical properties which might appear for isotactic and syndiotactic PVA—acetals. However, any difference expected for these PVA—acetals might not be as prominent as the aforementioned substances exhibit, since a greater difference in the distortion of molecular shape that could occur for a combination of the (a, a) and (e, a) forms is quite unrealistic; the distortions of molecular shape associated with the (e, e) and (e, a) forms are not greatly different. Such a consideration may be justified if one notes the fact that the differences in $(\langle L^2 \rangle_{of}/P)^{1/2}$ calculated for cis and trans forms of polysaccharides of 1, 4-polyisoprenes are larger than those for isotactic and syndiotactic PVA—acetals (see Table 3) [18].

TABLE 3.   Collected Values of $(\langle L^2 \rangle_{0f}/P)^{1/2}$ for Various Polymers with Steric Isomers

Polymer	Characteristic repeat unit	$(\langle L^2 \rangle_{0f}/P)^{1/2}$, Å
PVA	Common for all vinyl polymers	3.08
Isotectic PVA–100% acetal	Acetal ring with (e, e)	4.34
Syndiotache PVA–100% acetal	Acetal ring with (e, a)	3.60
Atactic PVA–100% acetal[a]		3.98
Amylose	α-Glucoside	4.26
Cellulose	β-Glucoside	7.90
Gutta percha	C = C (trans)	5.80
Natural rubber	C = C (cis)	4.02

[a]This corresponds to t = 0.5.

Acknowledgment

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Zusammenfassung

Die Acetalisierung von Polyvinylalkohol ergibt ein Acetalringbildung zwischen zwei in der Kette benachbarten Hydroxylgruppen. Dadurch wird die Kettensteifheit von Polyvinylalkohol in verschiedener Weise beeinflusst, je nach der Stereospezifität des als Ausgangsmaterial benutzten Polyvinylalkohols. Die vorliegende Arbeit beschreibt Berechnungen der statistischen Dimensionen von hypothetischen Polyvinylacetalketten mit 100%igem Substitutionsgrad und verschiedenen Stereospezifizitäten (isotaktisch und syndiotaktisch). Die Berechnungen sind im wesentlichen identisch mit den von Wall und Markovitz gemachten, jedoch wurden neuere stereochemische Befunde des Acetalringes und von Polyvinylalkohol berücksichtigt. Die Ergebnisse zeigen, dass die Kettendimension von aus isotaktischem Polyvinylalkohol abgeleiteten Poly(vinylacetal)-ketten grösser ist als die von aus syndiotaktischem Polyvinylalkohol abgeleitetem Poly-(vinylacetal). Die angeführte Behandlung wird auf realistischere Kettenmodelle ausgedehnt, die alle Arten von Stereoregularität und Substitution aufweisen. Wie intuitiv angenommen wurde, wird nun bestätigt, dasse die Kettendimensionen mit dem Substitutionsgrad jeder Stereospezifizität zunehmen.

Résumé

L'acétalisation de molécules de l'alcool polyvinylique resulte dans la formation d'un cycle acétal entre deux groupes hydroxylés successifs. Ce fait dominera la rigidité de la chaîne du poly(vinyl acétal) dúne maniére différente selon la stéréospécificité de l'alcool

polyvinylique, utilisé comme matiére de départ. Le présent mémoire est consacré aux calcules de dimensions statistiques des chaines hypothétiques de poly(vinyl acetal), substitues 100% et avec des stéréospécificités différentes (isotacticité et syndiotacticité). Les calculs sont essentiéllement identiques à ceux faits par Wall et Markovitz, mais les connaissances récentes sur le cycle acetal et l'alcool polyvinylique sont prises en considération. Les résultats montrent que les dimensions de chaînes de poly(vinyl acétal), derivées de l'alcool polyvinylique isotactique sont beaucoup plus grandes que du poly(vinyl acétal) obtenu d'un alcool syndiotactique. Ce traitement est étendu à des chaines plus réalistes possédant un degré de stéréorégularité et de substitution. Comme s'était anticipé par intuition, on S. est assuré que les tailles de chaines augmentent avec l'accroissement du degré de substitution pour chaque stéréospecifité.