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# Unperturbed Dimensions and Local Stiffness of Poly(vinyl chloride) with Stereochemical Sequences Composed of Repeating Units

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ABSTRACT: The unperturbed dimensions, preferred local conformations, and conformational entropies have been examined in rotational isomeric state models of poly(vinyl chloride) with stereochemical sequences defined by 46 repeating patterns. All possible repeats of 1−7 diads were considered, as well as selected repeats of 8−11 diads. Most of these chains have unperturbed dimensions close to the averages in a typical atactic poly(vinyl chloride). One exception is the chain with the repeating stereochemical sequence *mmr*, where *m* and *r* denote *meso* and *racemo* diads, respectively. This repeating stereochemical sequence yields the smallest unperturbed dimensions obtainable with poly(vinyl chloride), due to three competing preferred conformations within the *mm* unit and the inability of this short unit to complete a single turn of the $3_1$ helix typical of an isotactic vinyl polymer. The series $mr_x$, $x = 1, 2, ...$, exhibits unperturbed dimensions with a strong odd−even effect superimposed on a general tendency for an increase toward the asymptotic limit defined by the syndiotactic chain. The larger unperturbed dimensions are obtained when $x$ is odd. Given the strong preference for the *tt* conformation in an *r* diad, the preferred conformations of $mr_xm$ have the appearance of a bend when $x$ is even, with both *m* diads tending to depart from the same side of the $r_x$ rod. When $x$ is odd, these *m* diads have a greater probability of departing the $r_x$ rod in opposite directions, producing a greater extension of the chain. In contrast with the odd−even effect observed in the unperturbed dimensions, the average conformational entropy per bond exhibits a monotonic decrease as $x$ increases through the series $mr_x$. Similar behavior is seen in the $mr_x$ series in a rotational isomeric state model for polystyrene. The screening of the 46 repeating stereochemical sequences of poly(vinyl chloride) identifies *mmr* and $mr_x$ as being worthy of further study with multichain simulations at bulk density.

## Introduction

The mean-square unperturbed dimensions of vinyl polymers often depend strongly on stereochemical composition, as documented in numerous examples cited in books on the rotational isomeric state model.[1−3] The unperturbed dimensions have usually been computed as a function of $p_m$, the probability for a *meso* ($m$) diad, invoking the assumption of Bernoullian statistics. This approach entailed averaging of the mean-square unperturbed dimensions over several different chains at each $p_m$, $0 < p_m < 1$, to adequately account for the randomness of the stereochemical sequence.

The advent of metallocene catalysts[4] provides the potential opportunity for greater control of the stereochemical sequence of vinyl polymers. This control might include preparation of stereochemically pure isotactic and syndiotactic polymers, in which the only diads are *m* or *racemo* (*r*), respectively. It might also include controlled synthesis of chains in which the fundamental repeat for the stereochemical sequence extends over a range longer than a single diad, e.g., *mr*, *mmr*, etc. This potential capability in synthesis creates an interest in the anticipated behavior of chains in which the stereochemical sequences consist of repetitions of a short string of diads. This interest will assist in the identification of sequences that are most likely to yield novel properties and in the development of an understanding of the origin of trends in the properties of a family of chains with systematically related repeat units.

Poly(vinyl chloride) is a well-known atactic polymer. For decades its stereochemical composition has been manipulated over a narrow range by performing the polymerization at different temperatures. Bovey reports that $p_m$ can vary from 0.37 (for polymerization at −78 °C) to 0.46 (for polymerization at 100 °C).[5] Most of the commercial material falls within this range.

Given an interest in using vinyl chloride to prepare polymers with properties different from those of the usual atactic material, it becomes worthwhile to inquire which repeating stereochemical sequences, besides those of the pure isotactic and pure syndiotactic polymer, might behave differently from the conventional atactic material. A simple screen for such sequences is the computation of the mean-square dimensions, with the search for stereochemical sequences that produce dimensions different from those of the average for conventional atactic chains. That excerise, as employed here, identifies *mmr* and $mr_x$ ($x = 1, 2, ...$) as being the repeating stereochemical seqeuences that are of greatest potential interest.

## Method

The stereochemical sequence of the chain is described using *m* and *r* diads.[6] The notation of *d*, *l* pseudoasymmetric centers, as defined on p 174 of Mattice and Suter,[2] will be used in the discussion of a few specific conformations. Descriptions of stereochemical sequences using *m* and *r* diads, or *d* and *l* pseudoasymmetric centers, are equivalent, the one description being converted into the other by simple transformations using a matrix **Q**.[6]

$$\mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \tag{1}$$

Figure 1 depicts short segments of an extended isotactic

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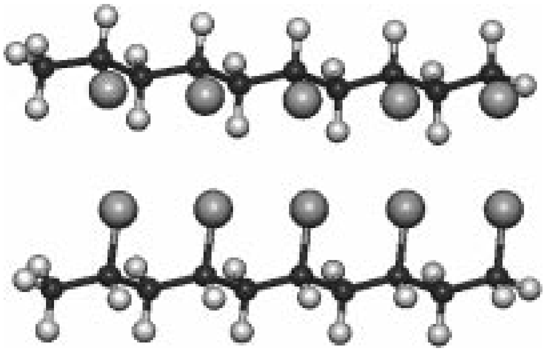

**Figure 1.** Segments of extended isotactic chains composed of repeating *d* (top) or *l* (bottom) pseudoasymmetric centers.

chain composed entirely of *m* diads and *d* (top) or *l* (bottom) pseudoasymmetric centers.

Calculations of the mean-square unperturbed end-to-end distance, $\langle r^2 \rangle_0$, employ the classic rotational isomeric state model for the distribution of conformations in chains unperturbed by long-range interactions.[1] The values of $\langle r^2 \rangle_0$ are converted to the characteristic ratio, $C_n$,

$$C_n = \frac{\langle r^2 \rangle_0}{nl^2} \tag{2}$$

where $n$ denotes the number of C−C bonds of length $l$. The asymptotic limit, $C_\infty$, is obtained by linear extrapolation of $C_n$ vs $1/n$ to $1/n = 0$.

$$C_\infty = \lim_{1/n \to 0} C_n \tag{3}$$

Three rotational isomeric states are used for each internal bond. First- and second-order interactions are employed in the 3 × 3 statistical weight matrices, $\mathbf{U}$. In the description of the chain with $m$ and $r$ diads,[6] the statistical weight matrix for the $C^\alpha$−C bond is

$$\mathbf{U}_p = \begin{bmatrix} \eta & 1 & \tau \\ \eta & \omega & \tau \\ \eta & 1 & \tau\omega \end{bmatrix} \tag{4}$$

where $C^\alpha$ denotes the carbon atom bearing a chlorine atom. The matrix for the next bond, which completes the diad, is either $\mathbf{U}_m$ or $\mathbf{U}_r$,

$$\mathbf{U}_m = \begin{bmatrix} \eta\omega_{XX} & 1 & \tau\omega_X \\ \eta & \omega & \tau\omega_X \\ \eta\omega_X & \omega_X & \tau\omega\omega_{XX} \end{bmatrix} \tag{5}$$

$$\mathbf{U}_r = \begin{bmatrix} \eta & \omega_X & \tau\omega_{XX} \\ \eta\omega_X & 1 & \tau\omega \\ \eta\omega_{XX} & \omega & \tau{\omega_X}^2 \end{bmatrix} \tag{6}$$

depending on whether the diad is $m$ or $r$. Rows and columns are indexed in the order $t$, $g$, $\bar{g}$ (defined by Flory et al.[6]), with columns indexing the states of the present bond and rows indexing the states of its predecessor.

Equivalently, the chain can be described using the better known $t$, $g^+$, and $g^-$ rotational isomeric states (for *trans*, *gauche*$^+$, and *gauche*$^-$),[7] along with $d$, $l$ pseudoasymmetric centers and statistical weight matrices defined by

$$\mathbf{U}_p = \mathbf{Q}\mathbf{U}_d = \mathbf{U}_l\mathbf{Q} \tag{7}$$

$$\mathbf{U}_m = \mathbf{U}_{dd}\mathbf{Q} = \mathbf{Q}\mathbf{U}_{ll} \tag{8}$$

$$\mathbf{U}_r = \mathbf{U}_{dl} = \mathbf{Q}\mathbf{U}_{ld}\mathbf{Q} \tag{9}$$

Descriptions based on $m$ and $r$ diads, and on $d$ and $l$ pseudoasymmetric centers, are equivalent, as is apparent from the relationships in eqs 7−9 and the fact that $\mathbf{Q}^2$ yields the identity matrix.

As described on p 175 of Mattice and Suter,[2] our definitions of the torsion angles and pseudoasymmetric centers differ from those employed by Flory et al.,[6,7] but the differences do not affect the form of the statistical weight matrices. In conformity with current usage, we place the zero of the torsion angle, $\phi$, at the *cis* arrangement, whereas Flory et al. placed their zero at the *trans* arrangement. Our $g^+$ state is obtained by a clockwise (positive) rotation of ~60° from *cis*, which means that our $g^+$ state is the $g^-$ state of Flory et al. (obtained by a counterclockwise rotation of ~120° from *trans*), and vice versa. We also invert the definition of the pseudoasymmetric centers, so that our $d$ is the $l$ of Flory et al., and vice versa. The combined changes in the location of the zero for $\phi$ and the definitions of the pseudoasymmetric centers cancel one another, insofar as the form of the statistical weight matrices is concerned. Therefore, our $\mathbf{U}$'s have exactly the same form as those described initially by Flory et al.

The statistical weights appearing in the matrices are for first-order interactions in the $t$ and $\bar{g}$ states ($\eta$ and $\tau$, respectively) and second-order interactions between two carbon atoms in the backbone, between a carbon atom and a chlorine atom, and between two chlorine atoms ($\omega$, $\omega_X$, and $\omega_{XX}$, respectively).

Calculations of the probabilities of various conformations were performed using a priori and conditional probabilities deduced from the usual manipulation of the conformation partition function that is specified by the serial product of the statistical weight matrices, as described in pages 93−101 of Mattice and Suter.[2] The conformational entropy per bond was calculated from the probabilities as[8]

$$S = -R(p_t \ln p_t + p_g \ln p_g + p_{\bar{g}} \ln p_{\bar{g}}) \tag{10}$$

where $p_t$, $p_g$, and $p_{\bar{g}}$ denote the probabilities for the $t$, $g$, and $\bar{g}$ states, respectively, and $R$ is the gas constant.

The geometry and statistical weights are closely related to those described recently by Smith et al.[9] The bond angles are 112° and 116° for $\angle$C−$C^\alpha$−C and $\angle C^\alpha$−C−$C^\alpha$, respectively. Within a *dd* (*ll*) diad, the torsion angles are −178° (178°), 61° (60°), −60° (−61°) at the $C^\alpha$−C bond and 178° (−178°), 60° (61°), −61° (−60°) at the C−$C^\alpha$ bond, both given in the sequence $t$, $g^+$, $g^-$. Within a *dl* (*ld*) diad, these torsion angles are 175° (−175°), 66° (62°), −62° (−66°) at the $C^\alpha$−C bond and at the C−$C^\alpha$ bond. The statistical weights were calculated as Boltzmann factors, using the energies $E_\eta = -0.9$, $E_\tau = -0.5$, $E_\omega = 3.0$, $E_{\omega X} = 2.3$, and $E_{\omega XX} = 4.0$, all expressed in kcal mol$^{-1}$. The temperature was 373 K. Calculations of $C_\infty$ were performed using the program V2.RIS, for which the FORTRAN source code is listed in Appendix C of Mattice and Suter.[2]

A few values of $C_\infty$ for polystyrene are reported near the end of the paper. The geometry and statistical weights employed for polystyrene are closely related to

**Table 1. $C_\infty$ at 373 K for Poly(vinyl chloride) Chains with Repeating Stereochemical Sequences of 1−7 Diads**

| min no. of diads in repeat | repeating sequence | $C_\infty$ | min no. of diads in repeat | repeating sequence | $C_\infty$ |
|---|---|---|---|---|---|
| 1 | *m* | 9.7 | 7 | *mmmmmmr* | 9.5 |
|  | *r* | 29.9 |  | *mmmmmrr* | 9.8 |
| 2 | *mr* | 20.9 |  | *mmmmrmr* | 11.0 |
| 3 | *mmr* | 6.8 |  | *mmmrmmr* | 7.9 |
|  | *mrr* | 10.7 |  | *mmmmrrr* | 11.9 |
| 4 | *mmmr* | 9.6 |  | *mmmrmrr* | 9.6 |
|  | *mmrr* | 8.4 |  | *mmrmmrr* | 8.0 |
|  | *mrrr* | 22.6 |  | *mmrmrmr* | 10.1 |
| 5 | *mmmmr* | 9.2 |  | *mmmrrrr* | 14.4 |
|  | *mmmrr* | 11.3 |  | *mmrmrrr* | 10.6 |
|  | *mmrmr* | 8.5 |  | *mmrrmrr* | 10.8 |
|  | *mmrrr* | 9.9 |  | *mrmrmrr* | 11.8 |
|  | *mrmrr* | 11.1 |  | *mmrrrrr* | 12.4 |
|  | *mrrrr* | 15.1 |  | *mrmrrrr* | 14.6 |
| 6 | *mmmmmr* | 8.7 |  | *mrrmrrr* | 12.9 |
|  | *mmmmrr* | 9.9 |  | *mrrrrrr* | 18.2 |
|  | *mmmrmr* | 10.3 |  |  |  |
|  | *mmmrrr* | 13.3 |  |  |  |
|  | *mmrmrr* | 9.4 |  |  |  |
|  | *mmrrrr* | 11.2 |  |  |  |
|  | *mrmrrr* | 22.0 |  |  |  |
|  | *mrrrrr* | 23.0 |  |  |  |

those in the rotational isomeric state model constructed by Rapold and Suter.[10] The bond angles are 112° and 114° for $\angle$C−C$^\alpha$−C and $\angle$C$^\alpha$−C−C$^\alpha$, respectively. The statistical weights are $\eta = 2.2$, $\tau = 0$, $\omega = 0.078$, and $\omega_X = 0.008$. The assignment $\tau = 0$ makes $\omega_{XX}$ irrelevant. Torsion angles for $g^\pm$ are ±70°. For *t* the torsion angles are 175° at the C$^\alpha$−C bond in an *ll* or *dl* diad and at the C−C$^\alpha$ bond in a *dd* or *dl* diad. They are −175° otherwise.

## Unperturbed Dimensions

Table 1 presents values of $C_\infty$ for poly(vinyl chloride), using all repeating stereochemical sequences comprised of 1−7 diads. The completely syndiotactic chain has a very high $C_\infty$, as was shown previously,[11] due to its propensity for propagation of long sequences of *t* states. In contrast, the $C_\infty$ for the isotactic chain is not much different from the results for typical atactic polymers, reported to be in the range 9.6−10.9[12] and found to be about 11−12 in previous descriptions of rotational isomeric state models of poly(vinyl chloride).[11,13]

The results in Table 1 can be used to estimate $C_\infty$ for an atactic chain. Consider the atactic chain with $p_m$ of $^1/_2$ and Bernoullian statistics. The crudest estimate (very crude indeed!) is based on repeating sequences of a single diad. It is the first point in Figure 2, $^1/_2(9.7 + 29.9)$, which is calculated as the average of the first two entries in Table 1. The next crudest estimate incorporates repeating stereochemical sequences of two diads in the estimate. It is the second point in Figure 2, calculated as $^1/_4[9.7 + 2(20.9) + 29.9]$, which is the estimate for the atactic poly(vinyl chloride) based on the first three entries in Table 1 (for *mm*, *mr* ≡ *rm* and *rr*). The remaining entries in Figure 2 were calculated in a similar manner. Each entry uses all relevant data from Table 1, up to repeats of the range indicated. The $C_\infty$ in Figure 2 exhibit an odd−even effect. (The origin of the odd−even effect will receive more attention below.) The entries for odd *x* appear to converge to a limit near 11 as *x* increases. This value is a plausible limit for the values with even *x* also. The limiting value is in reasonable agreement with the estimates cited at the end of the preceding paragraph.

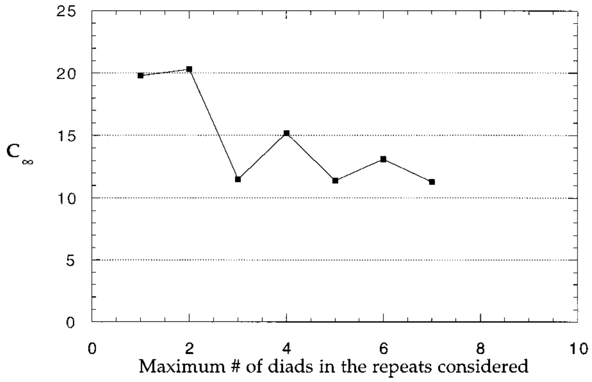

**Figure 2.** $C_\infty$ for a chain with $p_m = {}^1/_2$ and Bernoullian statistics, as estimated from the chains in Table 1. The maximum number of diads in the repeats considered is plotted on the horizontal axis.

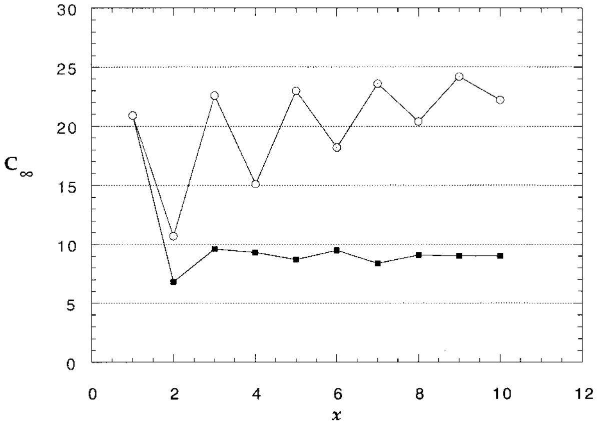

**Figure 3.** $C_\infty$ for poly(vinyl chloride) chains with repeating stereochemical sequences $m_xr$ (bottom, filled squares) and $mr_x$ (top, open circles).

Figure 3 presents $C_\infty$ for chains with repetitions of the stereochemical sequences $m_xr$ and $mr_x$, i.e., sequences of *x* occurrences of one type of diad that are interrupted, at specified intervals, by a single occurrence of the other type of diad. The range of *x* employed in this figure extends beyond the upper limit for the lengths of the repeating stereochemical sequences of the chains considered in Table 1. The chain with the repeating stereochemical sequence *mr*, which is the member with $x = 1$ in both series, has a $C_\infty$ that is roughly midway between the results calculated for the isotactic and syndiotactic chains. Some of the higher members of these series display more interesting behavior than does *mr*.

The most interesting member of the $m_xr$ series is the one with $x = 2$, i.e., a repeating stereochemical sequence given by *mmr*. It has the lowest $C_\infty$ of all of the 46 chains considered in the figures or in Table 1. Its value of $C_\infty$ is roughly 60% as large as the result for conventional atactic poly(vinyl chloride). In view of the number of chains addressed in Table 1, it is safe to conclude that no other unperturbed poly(vinyl chloride) chain has mean-square dimensions smaller than those found in the chain with repeating stereochemical sequence *mmr*.

The higher members of the $m_xr$ series, with $x > 2$, exhibit $C_\infty$ that are close to those observed with atactic poly(vinyl chloride) and predicted for isotactic poly(vinyl chloride). For this reason the chains with repeating stereochemical sequences $m_xr$, $x > 2$, are not as interesting as the chain with repeating stereochemical sequence *mmr*.

Not surprisingly, the $mr_x$ series tends to show an increase in $C_\infty$ as $x$ increases. The limit as $x \to \infty$ must be 29.9, which is the value of $C_\infty$ for the syndiotactic chain. The expected increase in $C_\infty$ with increasing $x$ is observed in Figure 3, but it is not monotonic. Superimposed on the general increase is a strong odd−even effect at small $x$, $C_\infty$ being larger when $x$ is odd than when $x$ is even.

The interesting $C_\infty$ calculated for the repeating stereochemical sequences *mmr* and $mr_x$ survive reasonable variation in the parametrization of the rotational isomeric state model for poly(vinyl chloride). The model described by Mark[11] assigns all bond angles as 112°, uses 180° and ±60° for $\phi$, and uses slightly different values of the energies for the short-range interactions. With these minor changes, it still yields a low value of $C_\infty$ (6.8) for the chain with repeating stereochemical sequence *mmr* and finds an odd−even effect with the series $mr_x$.

## Rationalization of the Values of $C_\infty$ for Several Interesting Sterochemical Sequences

The preferred conformations of the chains can be deduced from the probabilities of the three rotational isomeric states at an internal bond and from the joint probabilities for rotational isomeric states at two consecutive bonds. As expected from prior work,[11] a C−C bond in the syndiotactic chain has a high probability (0.92) for the *t* state, which rationalizes the large value of $C_\infty$ for a very long string of *r* diads. The isotactic chain has a preference for *tg* helices,[11] but this preference is not as strong as the preference for *tt* in the syndiotactic chain. For example, if we consider four consecutive bonds beginning at $C^\alpha$−C in a long syndiotactic chain, the preferred conformation is *tttt*, with probability 0.81. The remaining 80 conformations of that fragment contribute a combined probability of 0.19. For an isotactic chain (taken in this example to be composed of *d* pseudoasymmetric centers), the preferred conformations for four consecutive bonds (also beginning at $C^\alpha$−C) are $tg^-tg^-$ or $g^+tg^+t$, each with a probability of about 0.25. The remaining 79 conformations account for the other half of the population. The syndiotactic chain has a greater local stiffness than does the isotactic chain.

An alternative comparison of the local stiffness in unperturbed isotactic and syndiotactic poly(vinyl chloride) is via the conformational entropy per bond specified by eq 10. This entropy is 1.88 cal mol$^{-1}$ deg$^{-1}$ for unperturbed isotactic poly(vinyl chloride). It has the much smaller value of 0.60 cal mol$^{-1}$ deg$^{-1}$ for unperturbed syndiotactic poly(vinyl chloride), revealing the greater stiffness of the latter chain.

The chain with repeating sequence *mr* prefers the *tt* sequence at the two bonds in the *r* diad, with different permutations of *tg* being preferred at the two bonds in the *m* diad. These permutations are $tg^-$ and $g^+t$ if the meso dyad is *dd* in the notation of pseudoasymmetric centers, and the permutations are $tg^+$ and $g^-t$ if it is *ll*. Within a four-bond sequence there are two favored conformations with a combined probability of about 0.85, which suggests more local rigidity than seen in the isotactic chain but less rigidity than seen in the syndiotactic chain, consistent with the relationship between the $C_\infty$ of these three chains. The conformational entropy per bond, 1.02 cal mol$^{-1}$ deg$^{-1}$, lies between the results obtained for the isotactic and syndiotactic chains.

The repeating stereochemical sequence *mmr* yields the smallest $C_\infty$ for any poly(vinyl chloride) chain. However, this result does not arise because it is the chain with the greatest local flexibility. Its average conformational entropy per bond, 1.20 cal mol$^{-1}$ deg$^{-1}$, is well below the result (1.88 cal mol$^{-1}$ deg$^{-1}$) obtained with the unperturbed isotactic chain. The small $C_\infty$ for the chain with repeating stereochemical sequence *mmr* does not imply exceptional local flexibility; instead, it arises because the preferred, locally stiff conformations happen to join one another in a manner that produces compact chains. The chain has three preferred conformations of the *mmr* unit. The *tt* sequence is preferred within the *r* diad, as is usual for an *r* diad in poly(vinyl chloride). The *mm* sequence prefers the two *tg* helices (*tgtg* and *gtgt*), and *gttg* has a probability comparable with one of the helices. If the *m* diads are constructed from *d* pseudoasymmetric centers, the three sequences are $tg^-tg^-$, $g^+tg^+t$, and $g^+ttg^-$. The combined probability of these three conformations of the *mmr* sequence is 0.73. The two short *tg* helices, *tgtg* and *gtgt*, have nearly the same probability in *mmr* as the combined probabilities of *tgtg* and *gtgt* in the isotactic chain. However, the *tg* helices of four bonds can propagate further through the neighboring *m* diads in the isotactic chain, but in the chain with repeating stereochemical sequence given by *mmr* these short helices are terminated by the *tt* conformations in the *r* diads on either side. Since the two consecutive *m* diads cannot complete a single turn of the $3_1$ *tg* helix, the *tt* placements in the *r* diads at either end must be oriented in different directions, as illustrated in Figure 4. Therefore, the chain with the repeating stereochemical sequence *mmr* has a smaller $C_\infty$ than the isotactic chain. Higher members ($x > 2$) of the $m_xr$ series can propagate longer *tg* helices through the $m_x$ sequence, including helices that complete a single turn.

The series with repeating stereochemical sequences $mr_x$ prefers *tt* conformations in the *r* diads, with *tg* or *gt* at the *m* diad. The odd−even effect in $C_\infty$ does not arise from an odd−even effect in the average conformational entropy per bond in this series. These entropies, which are 1.02, 0.87, and 0.80 cal mol$^{-1}$ deg$^{-1}$ for $x = 1$, 2, and 3, respectively, exhibit a monotonic decrease as $x$ increases. The average conformational entropies (in cal mol$^{-1}$ deg$^{-1}$) per bond for the members of this series with $x \geq 2$ are approximated as

$$S = \frac{0.6x + 1.4}{x + 1} \tag{11}$$

The pronounced odd−even effect seen in $C_\infty$ must arise from an odd−even effect in the ability of the locally stiff conformations to support high extension of a long chain. The origin of the odd−even effect becomes apparent in Figure 5. The pseudoasymmetric centers at either end of $r_x$ are both of the same pseudochirality if $x$ is even (*dld*, *dldld*, etc.), but they are of opposite pseudochirality if $x$ is odd (*dldl*, *dldldl*, etc.). This difference affects the relationship between the preferred trajectories of the two *m* diads at the ends of the $r_x$ segment. This fragment has a shape that is reminiscent of a bend when $x$ is even, but it is more extended when $x$ is odd.

## Polystyrene vs Poly(vinyl chloride)

Some of the effects reported here for poly(vinyl chloride) are likely to appear in a few other vinyl

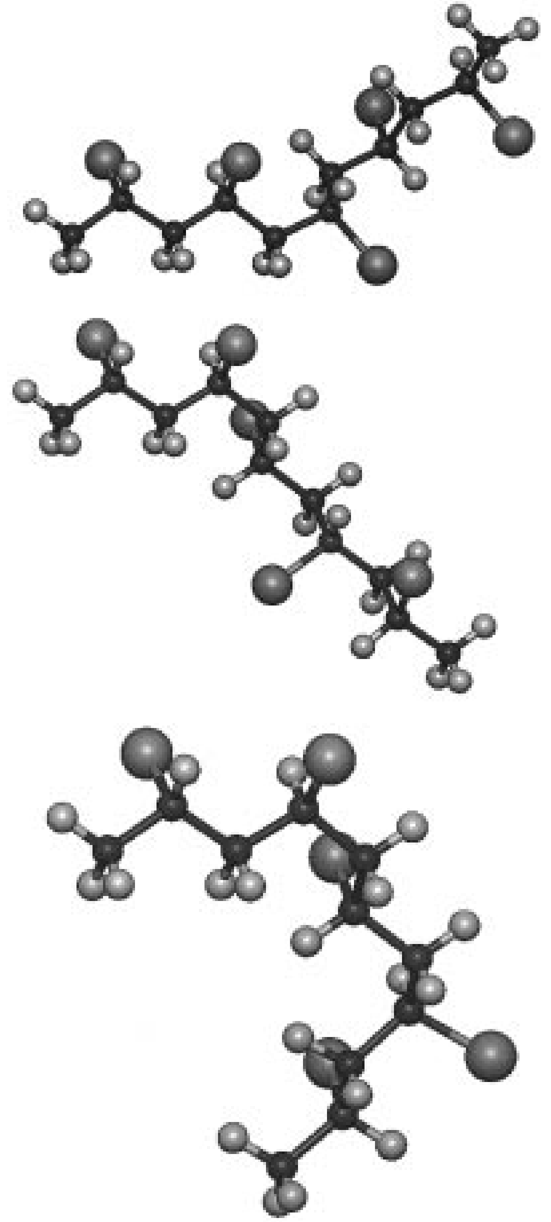

**Figure 4.** A methyl-terminated *rmmr* fragment with the three preferred conformations. The *m* diads are represented by *d* pseudoasymmetric centers. The conformation of the *mm* fragment is $tg^-tg^-$ (top), $g^+tg^+t$ (middle), and $g^+ttg^-$ (bottom). The conformation is *tt* in the *r* diads, and the *r* diad at the left has the same orientation in all three parts of the figure.

polymers. Consider polystyrene as an example. The rotational isomeric state model constructed by Rapold and Suter predicts $C_\infty$ for syndiotactic and atactic ($p_m = {}^1/_2$, Bernoullian statistics) polystyrene that are not much different from those in Table 1 and Figure 2 for poly(vinyl chloride). The smallest $C_\infty$ (6.6) for polystyrene is found when the repeating stereochemical sequence is *mmr*, as is the case also with poly(vinyl chloride), and $C_\infty$ for the series $mr_x$ exhibits an odd−even effect, as shown in Figure 6. The odd−even effect in $C_\infty$ in the series with repeating stereochemical sequence $mr_x$ can be anticipated in any vinyl polymer in which *tt* placements are strongly preferred in an *r* diad. Therefore, it might appear also in polymers such as poly(α-methylstyrene),[14] poly(*N*-vinylcarbazole),[15] and poly(methyl vinyl ketone).[16]

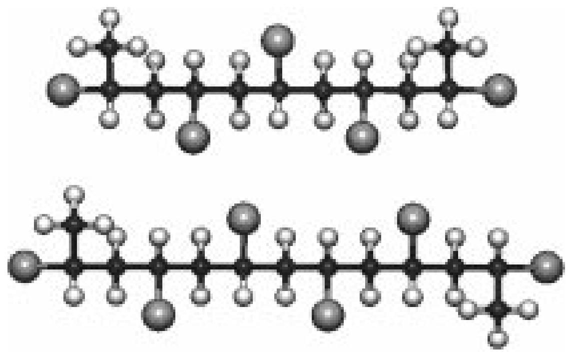

**Figure 5.** Methyl-terminated *mrrm* (top) and *mrrrm* (bottom) fragments, each with *tt* placements in the *r* diads, and a permutation of the preferred *tg* conformation in the *m* diads. The sequences of pseudoasymmetric centers are *ddldd* and *ddldll*, respectively. The conformations are $g^+t(tttt)tg^-$ and $g^+t(tttttt)tg^+$, respectively, where parentheses enclose the bonds in the $r_x$ portion. Point groups are $C_{1h}$ (top) and $C_2$ (bottom). Both fragments are oriented so that the plane of the backbone in the $r_x$ fragment is perpendicular to the paper.

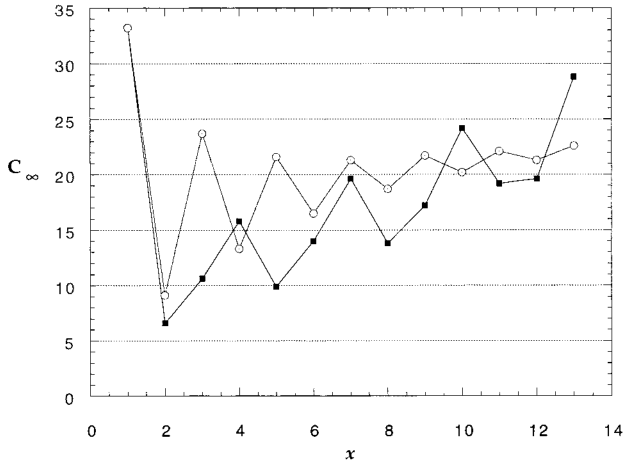

**Figure 6.** $C_\infty$ for polystyrene chains with repeating stereochemical sequences $m_xr$ (filled squares) and $mr_x$ (open circles).

The rotational isomeric state models for polystyrene and poly(vinyl chloride) differ strongly in their predictions for the isotactic chain. Isotactic poly(vinyl chloride) has a $C_\infty$ that is not much different from the result for the atactic chain, as is seen in comparison of Table 1 and Figure 2. In contrast, the rotational isomeric state model of Rapold and Suter finds an enormous $C_\infty$ for isotactic polystyrene. For this reason, $C_\infty$ exhibits qualitatively different behavior in the $m_xr$ series in the two polymers. This series is uninteresting for poly(vinyl chloride) when $x \geq 2$, as described above. For polystyrene, however, the $m_xr$ series exhibits an oscillation, with a period of three, superimposed on a general increase, as shown in Figure 6. The rotational isomeric state model for polystyrene propagates very long *tg* helices. The high extension of these helices accounts for the general trend, and the presence of three units per turn accounts for the oscillation with a period of three. Such behavior is a generalization of the oscillation in the $mr_x$ series. If the sequence of *x* units of a single type of diad, either $m_x$ or $r_x$, strongly propagates a single conformation, $C_\infty$ as a function of *x* will show a general increase. Superimposed on this increase is an oscillation with a period specified by the repeat in the manner in which the conformational defects depart from the preferred conformation. This repeat is two diads for the *tt* sequences in $r_x$ of both polymers and three diads for the *tg* helices in $m_x$ of polystyrene. The 3-fold oscillation is not seen in $m_x$ for poly(vinyl chloride) because the tendency for propagation of a *tg* helix is smaller in this polymer than in polystyrene.

## Summary and Implications

Table 1 and Figure 3 present results for poly(vinyl chloride) chains with 46 different repeating stereochemical sequences. Most of these repeating stereochemical sequences have uninteresting $C_\infty$. Their unperturbed dimensions are not significantly different from those observed with conventional atactic poly(vinyl chloride). Apart from the two pure stereochemical forms (completely isotactic and completely syndiotactic), the only remarkable chains are those with repeating sequences *mmr* and $mr_x$. The former is remarkable for its unusually low mean-square unperturbed dimensions, which are atypical of poly(vinyl chloride). Properties controlled by, or related to, $C_\infty$ are likely to be novel, making it an interesting chain for further study in simulations of multichain systems at bulk density.

The $mr_x$ series is interesting for the pronounced odd−even effect in $C_\infty$ that is superimposed on the trend of increasing unperturbed dimensions as *x* increases. Highly syndiotactic poly(vinyl chloride) has limited solubility, due to its high crystallinity.[17] A balance between solubility and crystallinity might be achieved by judicious selection of *x* in $mr_x$. Such a selection might be attempted by the design of a catalyst that has a strong preference for replication of a sequence of *r* diads, interrupted systematically by a defect (*m*), with the defect being followed immediately by a return to the preferred *r* diad. If catalysts were available that would prepare the first few members of this series, such as $mr_x$, $x = 1, 2, 3$, the properties of these three polymers might appear chaotic, because their $C_\infty$ do not appear to show a trend. The $C_\infty$ are 20.9, 10.7, and 22.6, respectively. The rotational isomeric state analysis provides an explanation for what might otherwise appear to be chaotic behavior. The lower members of this series merit further study in simulations of multichain systems at bulk density. In particular, it will be interesting to learn whether properties of the multichain systems should also exhibit an odd−even effect.

Some of the effects reported here for poly(vinyl chloride) are likely to appear in a few other vinyl polymers. The odd−even effect in $C_\infty$ in the series with repeating stereochemical sequence $mr_x$ can be anticipated in any vinyl polymer in which *tt* placements are strongly preferred in an *r* diad.

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## References and Notes

(1) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.
(2) Mattice, W. L.; Suter, U. W. *Conformational Theory of Large Molecules. The Rotational Isomeric State Model in Macromolecular Systems*; Wiley: New York, 1994.
(3) Rehahn, M.; Mattice, W. L.; Suter, U. W. *Adv. Polym. Sci.* **1997**, *131/132*.
(4) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 133.
(5) Bovey, F. A.; Hood, F. P.; Anderson, E. W.; Kornegay, R. L. *J. Phys. Chem.* **1967**, *71*, 312.
(6) Flory, P. J.; Sundararajan, P. R.; DeBolt, L. C. *J. Am. Chem. Soc.* **1974**, *96*, 5015.
(7) Flory, P. J.; Mark, J. E.; Abe, A. *J. Am. Chem. Soc.* **1966**, *88*, 639.
(8) McQuarrie, D. M. *Statistical Mechanics*; Harper & Row: New York, 1976; p 48.
(9) Smith, G. D.; Ludovice, P. J.; Jaffe, R. L.; Yoon, D. Y. *J. Phys. Chem.* **1995**, *99*, 164.
(10) Rapold, R. F.; Suter, U. W. *Macromol. Theory Simul.* **1995**, *3*, 1.
(11) Mark, J. E. *J. Chem. Phys.* **1972**, *56*, 451.
(12) Sato, M.; Koshiishi, Y.; Asahine, M. *J. Polym. Sci., Part B* **1963**, *1*, 223.
(13) Boyd, R. H.; Kesner, L. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 375.
(14) Sundararajan, P. R. *Macromolecules* **1977**, *10*, 623.
(15) Sundararajan, P. R. *Macromolecules* **1980**, *13*, 512.
(16) Suter, U. W. *J. Am. Chem. Soc.* **1979**, *101*, 6481.
(17) Wilkes, C. E. *Macromolecules* **1971**, *4*, 443.

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