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Conformational end effects in unperturbed chains and star-branched polymers

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Abstract

End effects in unperturbed chains with a specified number of bonds, n, have previously been characterized using the conformations at individual bonds and the mean square unperturbed dimensions of subchains situated at various positions along the chain. Both criteria have found that the end effects are extremely weak in typical flexible chains, such as unperturbed polyethylene. Of course, these criteria detect no end effect at all in a freely jointed chain. This conclusion requires modification if the end effects are defined differently, using the mean square radius of gyration of the $n+1$ chain atoms about chain atom i, denoted $\langle s_i^2\rangle_0$. The values of $\langle s_i^2\rangle_0$ depend on i in all chains, including the freely jointed chain. The range for the volume specified by $\langle s_i^2\rangle_0^{3/2}$ suggests that the average density of chain segments about a terminal atom is roughly 1/3 of the average density of chain segments about the atom midway along the contour of any long unperturbed chain. The severity of these end effects in finite chains depends on the detailed local structure, becoming more severe for more extended chains. The end effect detected by $\langle s_i^2\rangle_0$ in regular freely jointed star-branched polymers becomes more severe as the number of branches increases.

Keywords: End effects; Conformation; Star-branched polymers

1. Introduction

End effects on the conformations of typical flexible unperturbed chains can be characterized in two distinctly different ways. The characterization can either use a large set of chains with different numbers of bonds, n, or instead it can use a single chain with a large value of n. Previous investigations of the end effects in simple unperturbed chains, as characterized with the rotational isomeric state (RIS) model [1], can arrive at different conclusions about the severity of the end effects, depending on which one of these two methods is used for the investigation.

The first type of investigation typically examines the average value of a conformation-dependent physical property, such as the mean square unperturbed end-to-end distance, $\langle r^2\rangle_0$, or its characteristic ratio,

$$C_n \equiv \frac{\langle r^2\rangle_0}{nl^2} \tag{1}$$

as a function of n. The end effect is revealed by the manner in which C_n approaches its asymptotic limit, C_∞. The approaches of C_n and the analogous characteristic ratio defined using the mean square unperturbed radius of gyration, $\langle s^2\rangle_0$,

$$C_{s,n} \equiv \frac{\langle s^2\rangle_0}{nl^2} \tag{2}$$

to their asymptotic limits depend on a k-weighted sum over k of the average of the dot product of unit vectors oriented along bonds i and $i+k$, where i indexes a bond remote from the nearest chain end [2].

$$\left[\frac{\mathrm{d}C_n}{\mathrm{d}(1/n)}\right]_{1/n=0} = -2\sum_{k=1}^{\infty} k\langle \mathbf{u}\cdot\mathbf{u}_{i+k}\rangle_0 \tag{3}$$

$$\left[\frac{\mathrm{d}C_{s,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} = C_{s,\infty} - \sum_{k=1}^{\infty} k\langle \mathbf{u}_i\cdot\mathbf{u}_{i+k}\rangle_0 \tag{4}$$

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The sum over $k\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$ is susceptible to numerical evaluation using RIS models [2] such as the ones described by Abe et al. for polyethylene (PE) [3] or Flory et al. for polydimethylsiloxane (PDMS) [4]. Several hundred bonds are required for C_n to approach within 1% of C_∞ for these two polymers. The end effects are more severe in PE than in PDMS, with the values of the sums over $k\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$, being 17 and 9, respectively [2]. Of course, $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$ is equal to zero at all $k \neq i$ if the chain is freely jointed (FJ). Then Eq. (3) detects no end effects whatsoever, i.e., the FJ chain has $C_n = 1$ at all n. Weak end effects in the FJ chain are still apparent with Eq. (4), however, with $C_{s,n}$ depending slightly on n.

$$C_{s,n} = \frac{1}{6}\left(\frac{n+2}{n+1}\right) \tag{5}$$

Alternatively, the end effects can be studied by selection of a chain with a specified (and large) value of n, and then examining the behavior of a conformation-dependent property of its subchains, each with a number of bonds smaller than n, as one proceeds along the chain from one end to the other. When the subchain contains only three bonds, the relevant property is the probability that bond i is in state η, denoted $p_{\eta;i}$. In his second book [5], Flory described illustrative results obtained by Jernigan [6] using the RIS model for PE, calculated using values of the statistical weights for the first- and second-order interactions of $\sigma = 0.54$ and $\omega = 0.088$. These calculations yield a probability for a gauche$^+$ (g^+) state of 0.202 at the internal C–C bonds when n is large. The first four rotatable bonds at a chain end have $p_{g^+;i}$ of 0.231, 0.198, 0.202, and 0.202 for $i = 2$–5, respectively. When defined using $p_{\eta;i}$, the small end effect is confined to the bonds very near a chain end. The slight enrichment in the gauche state at bond 2 is due to the second-order interaction that strongly penalizes successive gauche states of opposite sign. This penalty, which is incorporated in the RIS model using $\omega < 1$, has less effect on bond 2 than on bonds $2 < i < n-1$ because only one of the neighbors of bond 2 or bond $n-1$ might be in a state that would induce the penalty. Therefore, the population of the g^+ state is higher at bond 2 and bond $n-1$ than at bonds with $2 < i < n-1$, which have rotatable nearest neighbors on both sides. If the calculation is performed with $\omega = 1$, this end effect disappears completely, with $p_{g^+;i} = 0.2596$ at all i, $1 < i < n$. The simple unperturbed chain with independent bonds has no conformational end effect whatsoever, when the end effect is evaluated using $p_{\eta;i}$.

A similar conclusion about the lack of importance of end effects on the conformation of a long unperturbed chain is reached when the chain of specified n is examined using the mean square end-to-end distance of the subchain between chain atoms i and j, denoted $\langle r_{ij}^2\rangle_0$. Subchains with $|j-i|$ bonds can appear at $n+1$–$|j-i|$ different positions in the main chain. Once again using the RIS model for PE for purpose of illustration, the characteristic ratios, $C_{ij} = \langle r_{ij}^2\rangle_0/(j-i)l^2$, have been calculated for subchains of 100 bonds in a chain with $n = 300$ [7]. The results are 6.534 and 6.538 for the subchains located at the chain end and in the middle of the chain, respectively. The slightly enhanced preference for a gauche state at bond 2, discussed in the previous paragraph, is responsible for the slightly smaller unperturbed dimensions for the subchain located at the chain end. However, the effect is so small that it would defy detection in an experiment. Even this small end effect would disappear completely if the bonds were allowed to be independent, i.e., if the RIS calculation had used $\omega = 1$ instead of $\omega = 0.088$.

The perceived severity of end effects in unperturbed chains can depend on the manner in which they are defined, as illustrated above by definitions that employ $[\mathrm{d}C_n/\mathrm{d}(1/n)]_{1/n=0}$ or $[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0}$, evaluated using a set of chains with different values of n, or using instead $p_{\eta;i}$ and $\langle r_{ij}^2\rangle_0$ for a single chain of large n. The first set of criteria found significant end effects in unperturbed PE, but the end effects identified for PE by the second set of criteria are trivial. Both sets of criteria find virtually no end effects in the FJ chain.

Here we demonstrate that the latter strategy, based on a single chain of large n, can detect strong end effects that are present in all unperturbed chains, including the FJ chain, if the appropriate parameter is used for the analysis. The chain of n bonds is examined using a set of $n+1$ mean square unperturbed radii of gyration, denoted $\langle s_i^2\rangle_0$. Each $\langle s_i^2\rangle_0$ is the mean square distance of all chain atoms from chain atom i. It is, therefore, related to the average density of $n+1$ chain atoms in a volume element of size $\langle s_i^2\rangle_0^{3/2}$, with larger values of $\langle s_i^2\rangle_0$ implying smaller average densities. The dependence of $\langle s_i^2\rangle_0$ on i finds nontrivial end effects in FJ chains. More detailed models have end effects that approach those of the FJ chain as $n \to \infty$. The manner in which the asymptotic limit is reached depends on the local chain structure. The end effects detected in this manner become more severe if the linear chain is transformed into a star-branched polymer with f branches and n/f bonds in each branch.

2. The limiting form for an unperturbed chain

In a specified conformation, the squared radius of gyration of the $n+1$ chain atoms of identical mass about their center of mass is obtained from the sum of all of the r_{ij}^2, using a double sum over i and j.

$$s^2 = \frac{1}{(n+1)^2}\sum_{i=0}^{n-1}\sum_{j=i+1}^{n} r_{ij}^2 \tag{6}$$

If instead we seek the squared radius of gyration of the same atoms about chain atom i, the sum over i is no longer required, and the desired result is the average value of the r_{ij}^2 obtained using a single sum over j.

$$s_i^2 = \frac{1}{n+1}\sum_{j=0}^{n} r_{ij}^2 \tag{7}$$

Averaging over all of the conformations of the FJ chain, using $\langle r_{ij}^2\rangle_0 = |j-i|l^2$, leads to a simple expression for the dimensionless characteristic ratio, $c_{s,n,i} \equiv \langle s_i^2\rangle_0/nl^2$.

$$c_{s,n,i} = \frac{1}{2} - \frac{i}{n}\left(\frac{n-i}{n+1}\right) \tag{8}$$

Expressing the position of the reference atom as its fractional distance along the contour of the chain, $x = i/n$,

$$c_{s,n,i} = \frac{1}{2} - x(1-x)\left(\frac{n}{n+1}\right) \tag{9}$$

The $c_{s,n,i}$ achieve their maximum values when $x = 0$ or 1, i.e., when the reference atom is located at an end of the chain.

$$c_{s,n,0} = c_{s,n,n} = \frac{1}{2} \tag{10}$$

This maximum value is independent of n. The minimum value of $c_{s,n,i}$ is achieved when the reference atom is located half way along the contour of the chain.

$$c_{s,n,n/2} = \frac{1}{4}\left(\frac{n+2}{n+1}\right) \tag{11}$$

When $n = 2$, $c_{s,n,n/2} = 1/3$. The value of $c_{s,n,n/2}$ approaches 1/4 as $n \to \infty$. For very long FJ chains, $c_{s,n,i}$ decreases by a factor of two as i increases from 0 to $n/2$. This result is intuitively obvious from the ratio of the maximum numbers of bonds in the subchains that emanate from chain atom 0 (or n) and from chain atom $n/2$.

All of the $c_{s,n,i}$ are larger than $C_{s,n}$, because only for $C_{s,n}$ are the squared distances measured from the center of mass. Since atoms at the end of the chain tend to be further from the center of mass than the atom located midway along the contour of the chain, the chain has $c_{s,n,0} > c_{s,n,n/2} > C_{s,n}$. The relationship between the sizes of $\langle s^2\rangle_0^{1/2}$, $\langle s_{n/2}^2\rangle_0^{1/2}$, $\langle s_n^2\rangle_0^{1/2}$, and $\langle r^2\rangle_0^{1/2}$ in a long FJ chain is sketched in Fig. 1, where the values are in the ratio $\langle s^2\rangle_0^{1/2}:\langle s_{n/2}^2\rangle_0^{1/2}:\langle s_n^2\rangle_0^{1/2}:\langle r^2\rangle_0^{1/2} = 1:(3/2)^{1/2}:3^{1/2}:6^{1/2}$.

The importance of conformational end effects in the FJ chain cannot be unequivocally evaluated until the operational definition of these end effects is elaborated, as summarized in Table 1. The FJ chain has no end effects at all if they are defined in terms of the dependence of C_n on n, because $C_n = 1$ at all n. Also the values of $\langle r_{ij}^2\rangle_0$ and $\langle s_{ij}^2\rangle_0$ are completely independent of the subchain's position, which is specified by $(i+j)/2$. In contrast, end effects for exactly the same FJ chain are always present if they are defined using either $\langle s_i^2\rangle_0$ or the average density of chain atoms about atom i, i.e., $(n+1)/\langle s_i^2\rangle_0^{3/2}$. The end effects pervade the entire FJ chain, even in the limit as $n \to \infty$. The range for the volume obtained as $\langle s_i^2\rangle_0^{3/2}$ implies that the average density of chain segments about an end bead is $(1/2)^{3/2}$, or approximately 1/3, of the average density of chain segments about the bead midway along the chain.

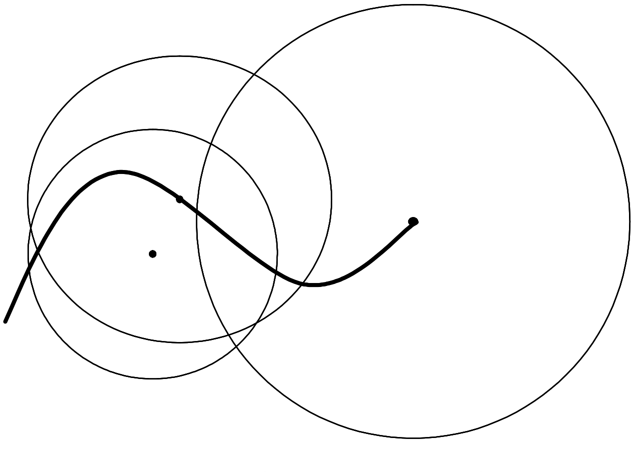

Fig. 1. Schematic depiction of the dimensions that define the end effect in a long FJ chain. The smallest circle, which represents $\langle s^2\rangle_0^{1/2}$, is located at the center of mass of the chain. The single conformation depicted has an end-to-end distance that is larger than the radius of the smallest circle by a factor of $6^{1/2}$, which represents the relationship between $\langle r^2\rangle_0^{1/2}$ and $\langle s^2\rangle_0^{1/2}$. The other circles are located at the midpoint along the chain and at a chain end. The radii of the three circles are in the ratio $\langle s^2\rangle_0^{1/2}:\langle s_{n/2}^2\rangle_0^{1/2}:\langle s_n^2\rangle_0^{1/2} = 1:(3/2)^{1/2}:3^{1/2}$.

3. Numerical results for freely rotating chains

For comparison with the expectation for models of unperturbed chains that incorporate a more detailed description of the short-range interactions, and hence have different values of $C_{s,\infty}$, it is useful to normalize the result for the FJ chain in Eq. (9) through division by the characteristic ratio for its mean square radius of gyration, Eq. (5).

$$\frac{c_{s,n,i}}{C_{s,n}} = 6\left(\frac{n+2}{n+1}\right)\left[\frac{1}{2} - x(1-x)\left(\frac{n}{n+1}\right)\right] \tag{12}$$

Table 1
Detection of end effects in FJ chains

Property	Result	End effect?
$\langle r^2\rangle_0$	$C_n = 1$ at all n	No
$\langle r_{ij}^2\rangle_0$	$\langle r_{ij}^2\rangle_0 = \lvert j-i\rvert l^2$ for all subchain positions, $(i+j)/2$	No
$\langle s_{ij}^2\rangle_0$	$\langle s_{ij}^2\rangle_0 = \lvert j-i\rvert(\lvert j-i\rvert+2)(\lvert j-i\rvert+1)^{-1}l^2/6$ for all subchain positions, $(i+j)/2$	No
$\langle s_i^2\rangle_0$	$\langle s_0^2\rangle_0 = \langle s_n^2\rangle_0 > \langle s_{n/2}^2\rangle_0$	Yes

Since any unperturbed chain has $\langle r_{ij}^2 \rangle_0 \to C|j-i|l^2$ in the limit as $|j-i| \to \infty$, the form for $c_{s,n,i}$ vs. x in this limit must approach the behavior described in Eq. (12) and depicted in Fig. 2. The extreme values are identical maxima at the ends, which approach a value of 3 as n increases,

$$\frac{c_{s,n,0}}{C_{s,n}} = \frac{c_{s,n,n}}{C_{s,n}} = 3\left(\frac{n+1}{n+2}\right) \tag{13}$$

and a minimum of 3/2, as $n \to \infty$, when the reference atom is located midway along the contour of the chain.

$$\frac{c_{s,n,n/2}}{C_{s,n}} = \frac{3}{2} \tag{14}$$

A convenient measure of the severity of the end effect is provided by the differences in the mean square radii of gyration of all chain atoms about an end atom and about a penultimate atom.

$$\frac{c_{s,n,1} - c_{s,n,0}}{C_{s,n}} = \frac{-6}{n}\left(\frac{n-1}{n+2}\right) \tag{15}$$

This difference is the initial slope of the simple modification of Fig. 2 in which the abscissa is i instead of i/n. Eq. (11) states that the initial slope depends on n, but this equation cannot capture any influence of detailed short-range interactions because it is based on the FJ chain.

Fig. 3 depicts $(c_{s,n,1} - c_{s,n,0})/C_{s,n}$ vs. $1/n$ for several simple freely rotating (FR) chains with different fixed bond angles, θ. The results for the FR chains with $\theta = 90°$ are identical with the results for the FJ chain. A line with a slope of -6, as required by Eq. (14), is an accurate description of the data for the FR chains at large n. Deviations appear at smaller n, as expected from Eq. (15). These deviations depend on the nature of the detailed structure, as represented by θ for the FR chains. They imply that the end effect becomes more severe, with $(c_{s,n,1} - c_{s,n,0})/C_{s,n}$ further from zero, as θ (and hence $C_{s,\infty}$) becomes larger.

Fig. 4 depicts $c_{s,n,n/2}/C_{s,n}$ vs. $1/n$ for the same set of FR chains. The results for the FR chain with $\theta = 90°$ are equal to 3/2 at all n, as required by Eq. (14) for the FJ chain. For FR chains with other values for θ, $c_{s,n,n/2}/C_{s,n}$ has a nonzero dependence on $1/n$. If $\theta > 90°$, so that $C_{s,\infty} > 1/6$, the values of $c_{s,n,n/2}/C_{s,n}$ are less than 3/2.

The end effects in finite FR chains, as measured by the difference between $c_{s,n,0}/C_{s,n}$ and $c_{s,n,n/2}/C_{s,n}$, become more severe as the FR chain becomes more extended, as shown in Fig. 5.

4. Freely jointed regular star-branched polymers

The end effects detected with $\langle s_i^2 \rangle_0$ become more severe when the FJ chain is transformed into a FJ regular star-branched polymer with the same n. The regular star-branched polymer has f branches, each with n/f bonds. Indexing of the atoms starts at zero at the atom at the free end of the branch that contains atom i. The atom at the branch point bears index n/f, and the atoms in the remaining branches are indexed $n/f+1$ through $2n/f$. Starting from

$$s_i^2 = \frac{1}{n+1}\left[\sum_{j=0}^{n/f} r_{ij}^2 + (f-1)\sum_{j=n/f+1}^{2n/f} r_{ij}^2\right] \tag{16}$$

and using $\langle r_{ij}^2 \rangle_0 = |j-i|l^2$, one obtains

$$c_{s,n,i} = \frac{(f^2 + 3nf - 2n)}{2f^2(n+1)} - x(1-x)\frac{n}{n+1} \tag{17}$$

Taking the $n \to \infty$ limit for the first term on the right-hand side of Eq. (17) yields a simple expression in terms of the

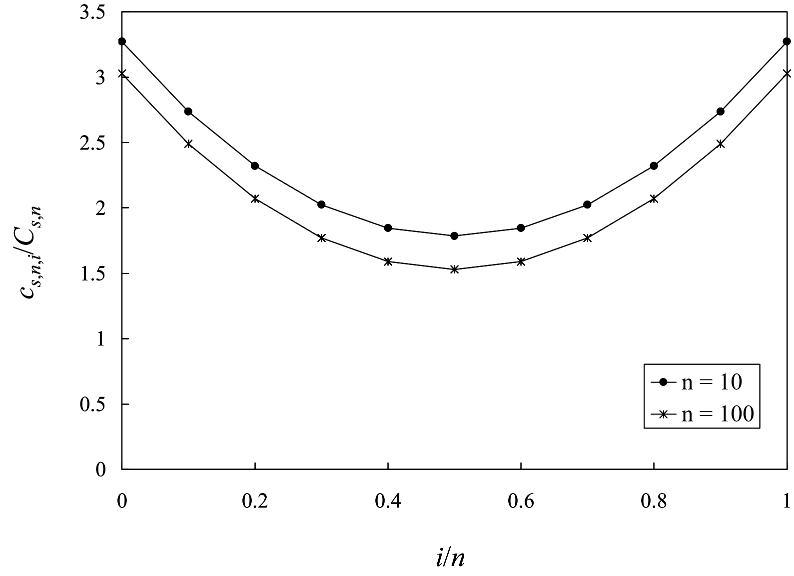

Fig. 2. Values of $c_{s,n,i}/C_{s,n}$ vs. $i/n = x$ for FJ chains of 10 and 100 bonds.

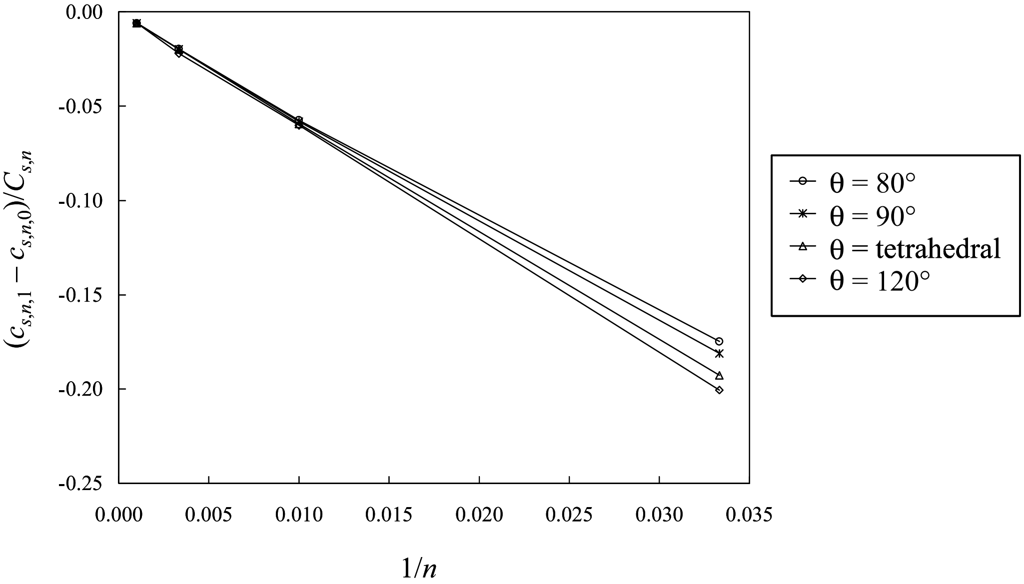

Fig. 3. Behavior of $(c_{s,n,1} - c_{s,n,0})/C_{s,n}$ vs. $1/n$ for FR chains with θ that are (a) 120°, (b) tetrahedral, (c) 90°, and (d) 80°.

Zimm–Stockmayer g factor, which for regular FJ star-branched polymers is $g = (3f-2)/f^2$ [8].

$$\lim_{n\to\infty} c_{s,n,i} = \frac{g}{2} - x(1-x) \tag{18}$$

In the same limit, the result reduces to Eq. (9) for the linear chain with $g = 1$. The physically sensible range for x in Eq. (18) is from 0 to $1/f$. Table 2 shows that the end effect, as measured by the ratio of the $c_{s,n,i}$ for the atom at the branch point and an atom at a free end, moves further from 1 as the f increases. The end effect becomes more severe as the number of branches increases.

5. Conclusion

When measured using the mean square distance of the $n+1$ chain atoms from chain atom i, conformational end effects pervade the entire unperturbed chain. In the limit as $n \to \infty$, this conclusion is equally valid for FJ chains and other unperturbed chains with more detailed short-range interactions. The results imply that the average density of chain atoms about a terminal atom is roughly 1/3 of the average density of the chain atoms about an atom midway along the contour of a long unperturbed chain, independent of the nature of the detailed local structure. At small n, this end effect can be enhanced beyond that expected for the FJ

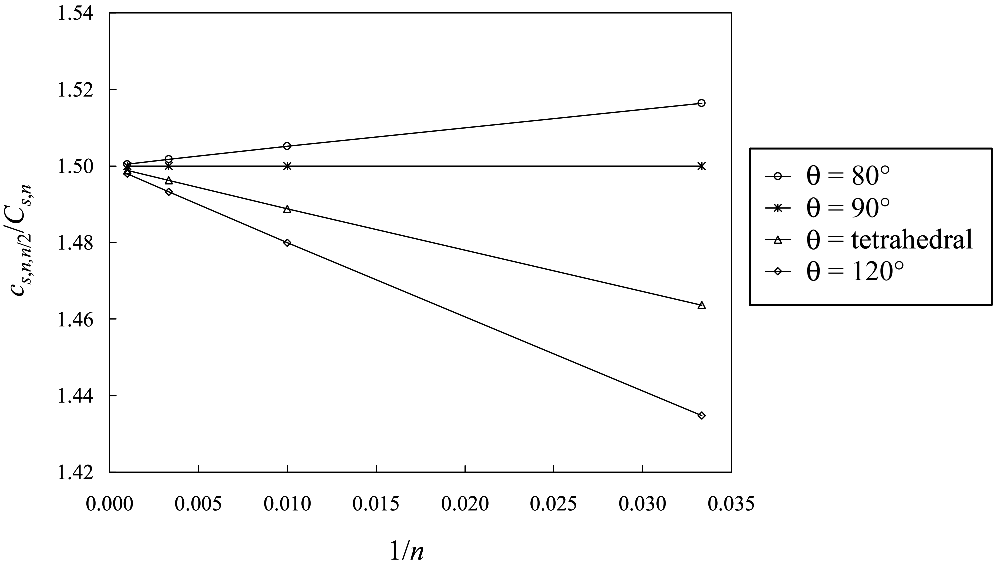

Fig. 4. Behavior of $c_{s,n,n/2}/C_{s,n}$ vs. $1/n$ for FR chains with θ that are (a) 120°, (b) tetrahedral, (c) 90°, and (d) 80°.

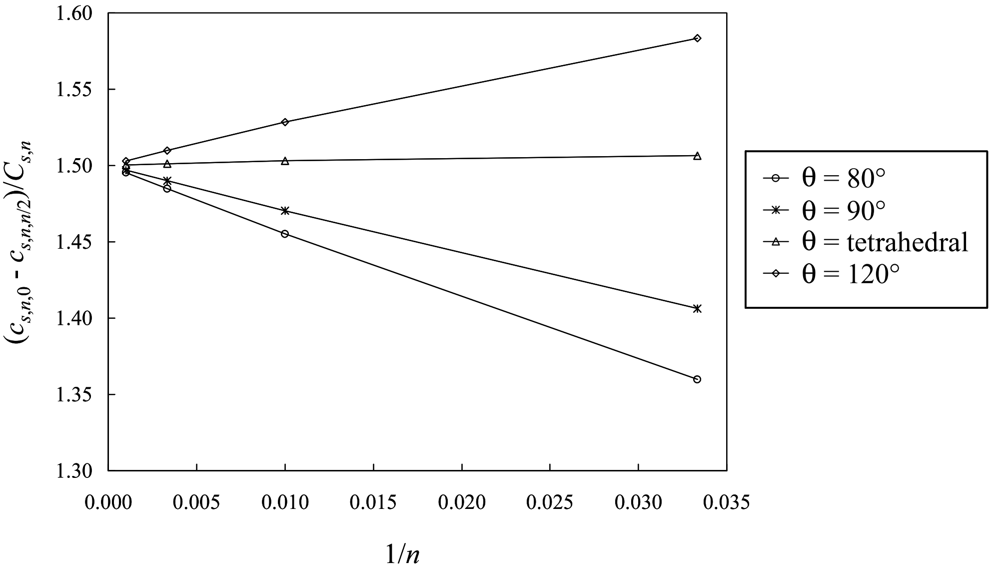

Fig. 5. $(c_{s,n,0} - c_{s,n,n/2})/C_{s,n}$ vs. $1/n$ for FR chains with θ that are (a) 120°, (b) tetrahedral, (c) 90°, and (d) 80°.

Table 2
Severity of the end effects in FJ regular star-branched polymers with a large number of bonds

f	$c_{s,n,0}$	$c_{s,n,n/f}$	$c_{s,n,n/f}/c_{s,n,0}$
2	1/2	1/4	1/2
3	7/18	1/6	3/7
4	5/16	1/8	2/5
5	13/50	1/10	5/13
6	2/9	1/12	3/8
7	19/98	1/14	7/19
8	11/64	1/16	4/11
9	25/162	1/18	9/25
10	7/50	1/20	5/14

chain if the detailed local structure produces an expansion of the chain. In FJ regular star-branched polymers, the end effect measured in this manner becomes more severe as the number of branches increases.

This end effect may play a role in the initial cross linking event when the reaction is performed on a long chain at infinite dilute in a Θ solvent. If the probability of this cross linking reaction is proportional to the local density of chain segments, it is more likely (by a factor of $2^{1/2}$) to involve the atom midway along the contour of the chain as the atom at a specific chain end. On the other hand, if the cross linking reaction is performed in the dense melt, the probability of an intramolecular cross link is more likely (also by a factor of $2^{1/2}$) for the atom midway along the chain as for the atom at a specified chain end.

Acknowledgements

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References

[1] Flory PJ. Foundations of rotational isomeric state theory and general methods for generating configurational averages. Macromolecules 1974;7:381.

[2] Mattice WL, Helfer CA, Sokolov AP. The persistence length and the finite chain length effect on characteristic ratios. Macromolecules 2004; 37:4711.

[3] Abe A, Jernigan RL, Flory PJ. Conformational energies of n-alkanes and the random configuration of higher homologs including polymethylene. J Am Chem Soc 1966;88:631.

[4] Flory PJ, Crescenzi V, Mark JE. Configuration of the poly(dimethylsiloxane) chain. III. Correlation of theory and experiment. J Am Chem Soc 1964;64:146.

[5] Flory PJ. Statistical mechanics of chain molecules. New York: Wiley; 1969. p. 82.

[6] Jernigan RL, Flory PJ. Configurational correlations in chain molecules. J Chem Phys 1969;50:4165.

[7] Mattice WL, Suter UW. Conformational theory of large molecules. The rotational isomeric state model in macromolecular systems. New York: Wiley; 1994. pp. 141, 418.

[8] Zimm BH, Stockmayer WH. The dimensions of chain molecules containing branches and rings. J Chem Phys 1949;17:1301.