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On the Size and *g*-factor of Uniform Star Polymers in a Dilute Solution: A Monte Carlo Simulation

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ABSTRACT

The size of uniform star polymers in a dilute solution was investigated using Monte Carlo simulation and a self-avoiding walk (SAW) model with the pivot algorithm. Chain conformations were simulated in a 3D cubic lattice. The size of these polymer chains, reflected through the mean square radius of gyration ($<R_g^2>$), was examined and compared with that of linear analog chains.

The results showed that star polymers have a smaller size compared to linear chains with the same total number of segments. The radius of gyration increased with the total number of segments, but it decreased with an increase in the number of arms. This indicated that the segment-repelling effect due to the "excluded volume" had a smaller influence when compared to the effect of the molecular structure restriction. Simulated *g*-factor values were compared with various theoretical predictions and agreed well, even with a Zimm-Stockmayer prediction for ideal chains with no excluded volume effect. This indicated that the solvent practically had no effect on the relative size compared to the linear analog and that the *g*-factor of ideal chains could be used as a good estimator for the *g*-factor of real chains in a dilute solution.

Key words: Monte Carlo simulation, pivot algorithm, radius of gyration, self-avoiding walk, uniform star polymers

INTRODUCTION

A star polymer is one of a group of polymers with a complex molecular topology, which is of interest because it increasingly finds its way into practical applications. Moreover, it can also serve as a model topology that can be used to test molecular theories. A uniform star polymer is a specific star molecule that has the same number of segments in each of its arms. The chain characteristics of such polymers in terms of size and relative size compared to that of a linear analog have been investigated theoretically using various approaches (Zimm and Stockmayer, 1949; Daoud and Cotton, 1982; Miyake and Freed, 1983).

Some numerical investigations of uniform star polymers using a self-avoiding walk (SAW) model and Monte Carlo simulation have also been reported (Muzur and McCrackin, 1977; Kajiwara and Burchard, 1982; Whittington *et al*., 1986; Barrett and Tremain, 1987; Wilkinson *et al*., 1988; Zifferer, 1997) and reviewed (Douglas *et al*., 1990; Zifferer, 1999). However, these results are typically simplified or limited to relatively short chain molecules and a small number of samples, due to the time-consuming simulation usually required. The typical algorithms used to

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simulate chain conformations are inappropriate because they generate a large rejection rate. The acceptance fraction for this molecular topology is much less than that of a simple linear analog because molecular restrictions at the center significantly promote high intramolecular interactions. Recently, a new algorithm based on the bond fluctuation model (Di Cecca and Freire, 2002) was developed and applied to address this issue. This model is still quite complicated to implement, however.

A pivot algorithm is a dynamic Monte Carlo algorithm reported to be quite efficient for simulating linear SAW chains in a canonical ensemble with free endpoints (Madras and Sokal, 1988). This algorithm, with its reasonable acceptance fraction of sampling, has allowed the exploration of large polymers within a reasonable amount of time. This algorithm was applied in the present work to investigate the conformation and size of uniform star polymers with a relatively large chain length.

In this work, chain conformations were simulated and the molecular size of uniform star polymers with various numbers of segments and arms investigated in a dilute solution using the pivot algorithm. The relative size of these polymers compared to those of linear analogs was also examined. The simulated results were compared with the results from several theoretical predictions reported earlier to determine an appropriate theoretical approach for estimating the size and relative size of uniform star polymers.

MATERIALS AND METHODS

Related theories for predictions of molecular size

The self-avoiding walk (SAW) model has been widely used to describe chain conformations of polymer molecules in a dilute solution (Sokal, 1995). The chain conformations obtained from this model can be used to calculate molecular size and shape, which are key molecular characteristics. One of the parameters typically used to represent molecular size is the mean square radius of gyration ($<R_g^2>$), which is defined as the mean square distance between the structural units and the center of gravity of the polymer chain.

For polymers with a complex topology, the molecular size typically decreases when compared to its linear analog. To determine their relative size, the *g*-factor (Equation 1), defined as the ratio of the mean square radius of gyration of a branched polymer ($<R_g^2>_{br}$) to that of a linear analog with the same total number of segments ($<R_g^2>_{lin}$), is typically used.

$$g = \frac{< R_g^2 >_{br}}{< R_g^2 >_{lin}} \qquad \text{(Equation 1)}$$

For uniform star molecules having *f*-arms with no long range intramolecular interaction (*i.e.*, ideal chains with no excluded volume effect), an analytical solution for describing relative size has been reported by Zimm and Stockmayer (1949).

$$g(f) = \frac{3f - 2}{f^2} \qquad \text{(Equation 2)}$$

For uniform star polymers in a dilute solution with excluded volume, Miyake and Freed (1983) predicted the *g*-factor in a three dimensional lattice using renormalization group treatments as follows:

$$g(f) = \frac{3f-2}{f^2}\left\{1 - \frac{\varepsilon}{8}\left[\frac{13(f-1)(f-2)}{2(3f-2)} - \frac{4(f-1)(3f-5)\ln 2}{3f-2} + \ln f\right] + O(\varepsilon^2)\right\} \qquad \text{(Equation 3)}$$

where $\varepsilon = 4\text{-}d$ and d is the spatial dimension.

For chains in a dilute solution, $d = 3$. Note that the prediction from the renormalization group will be reduced to the results of Zimm and Stockmayer when $d = 4$.

For a similar system, Daoud and Cotton (1982) developed the scaling theory for estimating the *g*-factor of uniform star polymers. Their results

indicated that the mean square radius of gyration of *f*-arm star polymers should decrease with $f^{4/5}$ as shown in Equation 4:

$$g(f) = 1.83 f^{-4/5} \qquad \text{(Equation 4)}$$

The relationship between the mean square radius of gyration and the total number of segments (*N*) for uniform star polymers can be expected to be represented by Equation 5:

$$< R_g^2 >= A(f) N^{2\nu(f)} \qquad \text{(Equation 5)}$$

The theoretical results from the renormalization group and scaling theory suggested that the critical exponent ($\nu(f)$) of such a relationship is independent of the number of arms, and should be equal to that of linear polymers, while the pre-factor ($A(f)$) has a high dependence on the number of arms (Whittington *et al.*, 1986).

Simulation method

Chain conformations of uniform star polymers with a total number of segments (*N*) between 60 and 300 and a number of arms (*f*) between 2 and 6 were created using Monte Carlo simulation. For each case, the first conformation was simulated using a dimerization and non-reversal random walk (NRRW) algorithm (Sokal, 1995) to initialize the equilibrium start for the pivot algorithm (Madras and Sokal, 1988), avoiding an unnecessary thermalization period.

In the pivot algorithm, a site on the conformation was chosen randomly and used as a pivot point. A random symmetry operation (*i.e.*, all possible rotations and reflections) was then applied to the part of the segments subsequent to the selected pivot point. The resulting conformation was accepted if it was self-avoiding, otherwise it was rejected. To test for the self-avoidance condition, a data structure called a "hash table" was implemented. For each case, 100,000 pivot moves after the initialization were considered. The square radii of gyration of all conformations in each case were analyzed and averaged for comparison with theoretical predictions.

RESULTS AND DISCUSSION

Radii of gyration of uniform star molecules

Figure 1 shows the relationship between the mean square radius of gyration and the total number of segments. The results indicated that the

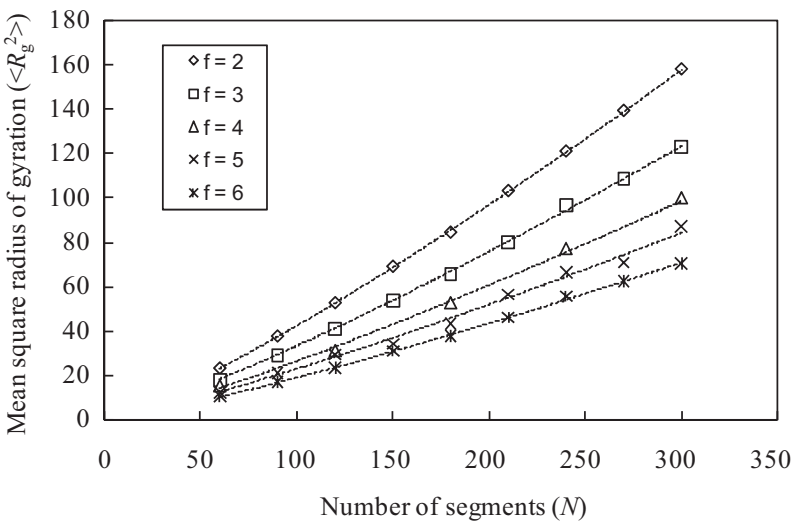

Figure 1 Relationship between mean square radius of gyration and number of segments. Lines are power law trend lines.

molecular size increased exponentially with the total number of segments, but it decreased with an increase in the number of arms. For a polymer molecule with complex topology, there are typically two competing factors influencing its molecular size. The first is the molecular restriction due to chemical bonding that reduces the overall molecular size; the other is the repelling effect due to excluded volume that increases and expands the overall molecular size. The fact that the molecular size decreased with an increase in the number of arms simply indicated that for a star molecule the molecular restriction due to chain topology had a stronger influence on its molecular size.

To determine the critical exponent of uniform star polymers with various numbers of arms, the linear relationship between $\ln(\langle R_g^2 \rangle)$ and $\ln(N)$ was plotted (Figure 2). The parallel linear relationship confirmed the theoretical prediction that the critical exponent was independent of the number of arms. In the present work, the critical exponent was estimated to be 0.6019±0.0025, which was close to the critical exponent of 0.588-0.6 reported earlier for linear chains (Sokal, 1995).

***g*-factor of Uniform Star Molecules**

The *g*-factor of uniform star polymers with various numbers of segments is shown in Figure 3. The results indicated that the *g*-factor was practically independent of the total number of segments, but it significantly decreased with an increase in the number of arms.

Figure 4 compares the simulated *g*-factor with the results from several theoretical predictions. All theoretical predictions described the tendency of *g*-factor dependency on the number of arms well; however, the predictions based on the renormalization group treatment slightly overestimated the *g*-factor and gave the largest discrepancy ($r^2 = 0.9970$). This discrepancy might be reduced if the renormalization group treatment were extended to include the terms of order ε^2. These results agree with previous works (Lue and Kiselev, 2001; Lue and Kiselev, 2002), which indicated that the results from the renormalization group had difficulty in describing the relative size of star molecules with a large number of arms.

The predictions of scaling theory ($r^2 = 0.9976$) and Zimm and Stockmayer ($r^2 = 0.9977$) could describe the magnitude of the *g*-factor well. This was surprising because Zimm and

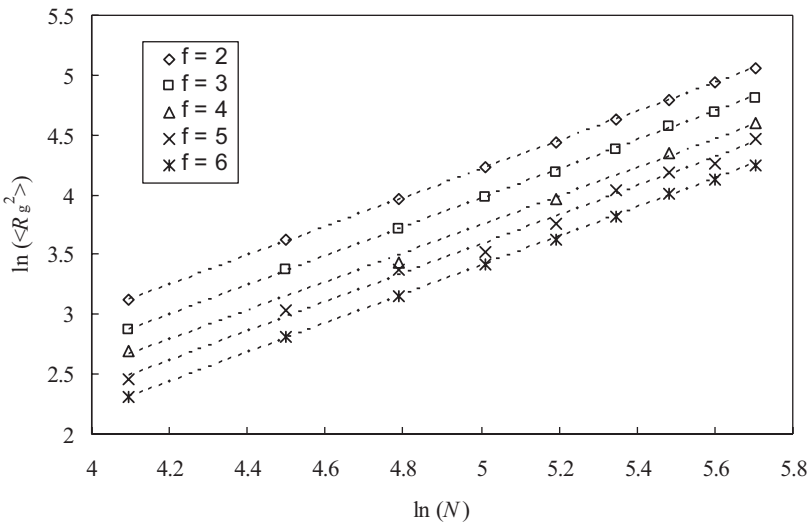

Figure 2 Relationship between $\ln(\langle R_g^2 \rangle)$ and $\ln(N)$. Lines are linear best fit ($r^2 = 0.9943$-0.9999).

Stockmayer's theoretical treatment did not consider the excluded volume effect. This implied that although a solvent could significantly influence the actual size of molecules, it did not affect the *g*-factor of branched molecules; these results support the opinion that the *g*-factor is insensitive to the solvent quality (Douglas *et al.*, 1990). Thus, the investigation on the size of branched molecules could be greatly simplified by estimating molecular size from the size of a SAW linear analog and the *g*-factor of the ideal chains having the same topology, which would require much less computational effort. In fact, this hypothesis has been applied in several works on the simulation of gel permeation chromatography of polymers with complex topologies (Tobita and Saito, 1999; Tobita and Saito, 2000).

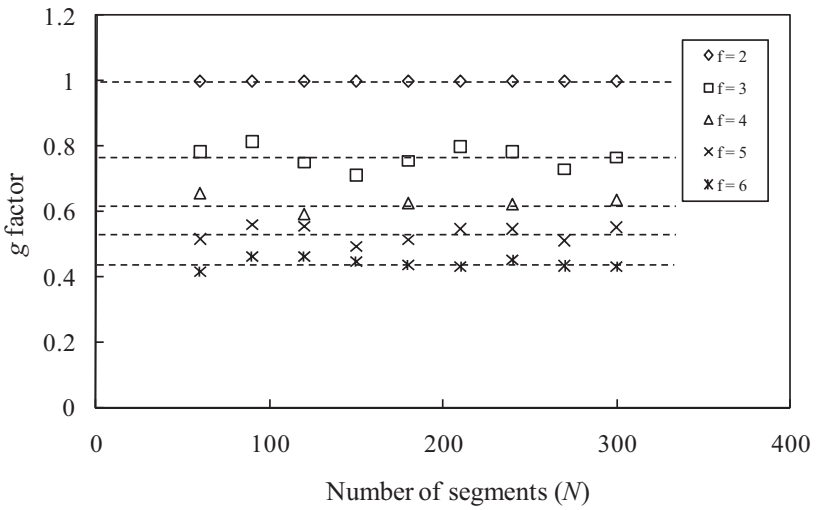

Figure 3 *g*-factor for uniform star polymers with various numbers of segments. Lines are average *g*-factor values.

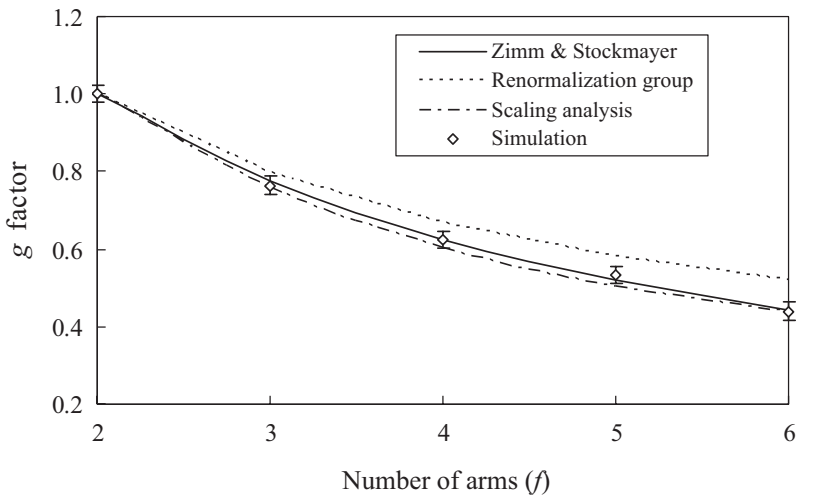

Figure 4 Comparison between simulated *g*-factor values (symbols with error bars) and theoretically predicted *g*-factor values (lines).

CONCLUSION

In this work, the size of uniform star polymers in a diluted solution and their relative size compared to that of linear analog were investigated using Monte Carlo simulation and a self-avoiding walk model with the pivot algorithm. The results were compared with various theoretical predictions. The *g*-factor predicted by ideal chains with no excluded volume best described the simulated results, supporting the hypothesis that the relative size of the branched molecule compared to the linear analog was insensitive to the presence of solvent.

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