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Radius of Gyration and Viscosity of Linear and Star Polymers in Different Regimes

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ABSTRACT: The mean-square radii of gyration and intrinsic viscosities of isolated three-dimensional linear and star polymers in excluded volume, Θ, and collapsed conditions have been determined by Monte Carlo simulations. The theoretical scaling laws in the different solvent conditions have been confirmed. The collapse of the star polymers is more gradual than that of the linear chains. The scaled transition curves for the intrinsic viscosity results are less sharp than those obtained with the radius of gyration of both types of chains. Many-armed stars and linear chains in the collapsed regime are well represented by the rigid sphere model.

Introduction

The investigation of the properties of linear and star molecules is an active area of research; several aspects of molecular topology as probed with a variety of experimental and theoretical methods have recently been reviewed.[1] In this paper off-lattice Monte Carlo simulation techniques are used to compute the radii of gyration and intrinsic viscosities of isolated star and linear polymers in different regimes: excluded volume, Θ, and collapsed.

The overall shape of a polymer can be characterized by its mean-square radius of gyration, $\langle S^2 \rangle$. It is well-known[2] that $\langle S^2 \rangle \sim N^{2\nu}$ where $N + 1$ is the number of units on the chain and ν is a universal exponent for self-avoiding (excluded-volume or EV) chains. In three dimensions this exponent is given by renormalization group theory as[3] 0.59. For random walks (non-excluded volume or NEV chains) simple statistical arguments lead to $\nu = 1/2$ in all dimensions. If attractive forces are present, it is possible for the chain to collapse.[4] In this regime the density of a three-dimensional chain is $\sim N/\langle S^2 \rangle^{3/2}$, but since the density must be independent of N in the collapsed state, the exponent becomes $\nu_c = 1/3$.

As the temperature is lowered for a system with both attractive and repulsive interactions, there will be a critical temperature T_Θ (the Θ temperature) where the two interactions effectively balance. Above this temperature the repulsions dominate and the chain has EV behavior; below T_Θ the attractions dominate and the chain is collapsed into a dense globule. In three dimensions the chain displays Gaussian-type (non-excluded volume) behavior at the Θ temperature. The values of the exponent ν in the three different regimes in three dimensions are thus $\nu_{EV} = 0.59$, $\nu_\Theta = 0.50$, and $\nu_c = 1/3$, and these values are expected to apply to both linear and star polymers.

An important hydrodynamic property of polymer solutions is the intrinsic viscosity, $[\eta]$. As a polymer collapses from an open coil to a dense globule, $[\eta]$ will decrease because fewer chain units will be exposed to the solvent. The intrinsic viscosity has been related to the mean-square radius of gyration by the Flory relationship[5]

$$[\eta] = 6^{3/2}\phi\langle S^2 \rangle^{3/2}/M \qquad (1)$$

where ϕ should be a constant for long chains dependent only on the solvent quality and M is the molecular weight (proportional to $N + 1$). The value of ϕ is dependent on the solvent regime. Theoretical estimates of ϕ have been made for the EV and Gaussian models.[1,5] Only numerical simulations, however, can currently provide an adequate description of the fluctuating hydrodynamic interactions required for precise calculations of $[\eta]$ in different regimes.

Method

The chain systems studied herein consist of $N + 1$ beads placed so that the distance between neighboring beads is not constant but follows a Gaussian distribution with root-mean-square value b. The beads also represent[6] hydrodynamic frictional units. For the star polymers the number of beads per arm is N/f where f is the number of arms. Linear chains were modeled as star polymers with two equal arms joined to a central vertex. Systems with f = 2 and 12 (linear and 12-arm star polymers) and $N + 1$ = 25, 49, 85, and 109 have been studied.

Nonneighboring beads interact through a Lennard-Jones potential:

$$U(R_{ij}) = 4\epsilon[(\sigma/R_{ij})^{12} - (\sigma/R_{ij})^6] \qquad (2)$$

Here R_{ij} is the separation distance between beads, ϵ is the well depth, and σ is the value of R_{ij} for which $U(R_{ij})$ changes sign. Reduced temperatures, T^*, are measured in units of k_BT/ϵ where k_B is Boltzmann's constant and T is the temperature. R_{ij} and σ are measured in units of b. We have set $\sigma/b = 0.8$ because that value was adequate to reproduce a realistic expansion of the chains in three dimensions employing the number of beads which can be reasonably handled in numerical computations.[7] Previous investigations[7] have shown that for a value of $1/T^* = 0.10$ the polymers is in the good solvent regime (EV), that high values of $1/T^*$ correspond to the collapsed state, and that at least for short chains $1/T^* = 0.30$ was in the transition region for our model. A more recent study[8] with longer chains has shown that, at the Θ point, $1/T^*$ is closer to 0.275.

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The properties of interest in this study are the mean-square radius of gyration and the intrinsic viscosity. The mean-square radius of gyration, $\langle S^2 \rangle$, is defined by

$$\langle S^2 \rangle = [1/(N+1)^2] \sum_{m=1}^{N+1} \sum_{n \geq m}^{N+1} \langle (\mathbf{R}_m - \mathbf{R}_n)^2 \rangle \quad (3)$$

(where $\mathbf{R}_m$ and $\mathbf{R}_n$ are the positions of the mth and nth units and $\langle\ \rangle$ denotes an average over polymer configurations). While Brownian dynamics is probably the most accurate method with which to determine $[\eta]$ values, it is prohibitively expensive for long chains. Alternative approaches have been proposed which make use of equilibrium averages from Monte Carlo simulations.[9,10] It has been shown that the "lower bound" method[10] is computationally very efficient and gives results which are more consistent with experimental data than methods based on the commonly used preaveraged approximations.[5] We have used lower bound calculations to determine the viscosity; details of the implementation are contained in a previous paper.[11] This method derives the lower bounds from perturbation theory and makes use of a configuration independent diffusion matrix (describing the hydrodynamic interactions between units) which contains optimized variational parameters in terms of the friction constants for the units. Monte Carlo calculations over a sample of rigid equilibrium conformations are performed in order to obtain averages required in the final formulas given by the variational procedure. Although the method is in this respect similar to the usual calculation of equilibrium averages (which provides upper bounds), it has the great computational advantage of not requiring the inversion of the diffusion matrix at every simulation step. The lower bound for viscosity is calculated in reduced units such that $[\eta]^* = [\eta]M/Lb^3$ where L is Avogadro's constant.

Different Monte Carlo sampling methods have been employed for the three regimes. In the EV regime ($1/T^*$ = 0.07, 0.10, and 0.20) the pivot algorithm was used. A very extensive analysis of the pivot algorithm by Madras and Sokal[12] has demonstrated the efficiency of this method for generating polymer configurations of isolated chains. Effectively independent configurations are generated in CPU time $O(N)$. The form of the pivot algorithm employed in this work starts with a moderate-energy random-chain configuration. A bead is then selected at random, and its coordinates with respect to the preceding bead (i.e., the neighbor closest to the chain center) are resampled from the Gaussian distribution. After moving the selected bead to its new location, the rest of the beads on the chosen arm are shifted by the same amount and then rotated with respect to the moved bead (the "pivot"), according to three randomly chosen Euler angles. These beads therefore change their coordinates, but the distances between them remain exactly the same.

In the Θ regime ($1/T^*$ = 0.275) we modified the pivot algorithm described above so that the final rotation about the moved bead was not performed; the beads on the chosen part of an arm are therefore translated but not rotated. In some cases we also used an alternative method based on single moves.[7] These two modifications result in considerable increased correlation times. In the collapsed regime ($1/T^*$ = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0) only single bead moves were allowed. Different methods are needed in the three regimes in order to optimize the statistical efficiency of the sampling (as the attractions increase the chain becomes more compact and the probability of moving a portion of an arm decreases dramatically).

In all cases a Metropolis energy criterion is used to test for acceptance or rejection of the new trial configuration. Typically in the EV regime the first 10 000 configurations of each sequence are discarded for equilibration and the system properties are obtained by averaging over the subsequent 50 000 configurations; in the Θ and collapsed regimes the first 800 000 configurations are discarded and the averaging is performed over the subsequent 2 400 000 configurations.

For the radius of gyration calculations all the equilibrium configurations are used, but for the intrinsic viscosity in the EV regime only a representative 500 configurations are employed and in the Θ and collapsed regimes only 600 configurations are used since these calculations are quite computationally demanding. The errors entailed by using fewer samples are not expected to be significant since the underlying distribution of the intrinsic viscosity is much narrower[13] than that of the radius of gyration. Eight dependent sequences of configurations are generated by using different random number seeds to initialize the procedure. In all cases batch means and standard deviations are determined from these eight independent sequences.

Results

The simulation results are listed in Table I. The errors reported are 1 standard deviation of the mean. In a previous study[8] with a variety of models we have reported results for $1/T^*$ = 0.1 and 0.275 for some of the chain lengths. Although the present values have been obtained in independent runs they agree closely with the previous calculations. From Table I, it is clear that the chains become more contracted as $1/T^*$ increases since both $\langle S^2 \rangle$ and $[\eta]$ decrease and the collapse is sharper for larger N (for infinite chains one would expect a discontinuity). This is illustrated in Figure 1 where we have plotted the square of the expansion factor for the radius of gyration against $1/T^*$ for the linear chain; the expansion factor is defined by the ratio of the mean-square radius of gyration at a given temperature to that at the Θ temperature, $\alpha^2 = \langle S^2 \rangle / \langle S^2 \rangle_\Theta$. Experimental data for the radius of gyration at different temperatures have provided coil–globule transition curves similar to those reported here.[4,14] In Figure 2 we have similarly plotted the square of the expansion factor for the intrinsic viscosity, $\alpha_\eta^2 = ([\eta]/[\eta]_\Theta)^{2/3}$. The viscosity ratio is raised to the 2/3 power so that it would be equivalent to α^2 if the proportionality $[\eta] \sim \langle S^2 \rangle^{3/2}$, established[5] for long Gaussian chains, could be maintained in the whole temperature range. In these calculations we have assumed that $1/T^*_\Theta = 0.275$ characterizes the Θ point.

Similar plots are obtained for the star polymers, but the transition is more gradual. The same trends have been observed in previous simulations of star polymers.[15,16] All of these results are summarized in Figure 3 for the 109 bead chains. In this figure the results are plotted as a function of T^* so that the variation of the dimensions with changing temperature for a given solvent can be directly appreciated. It should be noted that the values of $\langle S^2 \rangle$ and $[\eta]$ for both linear and star chains become the same in the collapsed state for all the chains studied (see Table I).

In previous work[15] we have obtained results for dimensions and hydrodynamic properties for shorter chains ($18 \leq N \leq 54$). However, those chain lengths were not long enough to show the sharpening of the collapse transition for increasing values of N, except in the case of linear chain dimensions.

The results for the Flory parameter, ϕ, also included in Table I deserve some comment. A detailed analysis of the change of ϕ with varying chain lengths, types of chain,

Table I
Simulation Results[a]

$N+1$	ϵ/k_BT	$\langle S^2\rangle/b^2$	$[\eta]M/Lb^3$	ϕ, 10^{-23} mol^{-1}
		Linear		
25	0.07	6.99 ± 0.02	79.96 ± 0.98	1.77 ± 0.03
	0.10	6.89 ± 0.02	74.42 ± 2.51	1.69 ± 0.06
	0.20	6.33 ± 0.02	69.37 ± 0.77	1.79 ± 0.03
	0.275	5.78 ± 0.01	65.90 ± 1.17	1.94 ± 0.04
	0.40	4.72 ± 0.03	55.48 ± 0.88	2.22 ± 0.05
	0,50	3.52 ± 0.03	40.98 ± 0.37	2.54 ± 0.05
	0.60	2.57 ± 0.02	32.12 ± 0.45	3.20 ± 0.08
	0.70	1.92 ± 0.01	24.66 ± 0.39	3.79 ± 0.08
	0.80	1.55 ± 0.01	20.58 ± 0.16	4.37 ± 0.05
	0.90	1.33 ± 0.01	17.41 ± 0.13	4.64 ± 0.05
	1.00	1.19 ± 0.01	15.51 ± 0.14	4.91 ± 0.06
49	0.07	15.85 ± 0.05	273.05 ± 5.72	1.77 ± 0.05
	0.10	15.35 ± 0.09	264.53 ± 8.87	1.80 ± 0.08
	0.20	13.50 ± 0.08	225.07 ± 4.45	1.86 ± 0.05
	0.275	11.68 ± 0.01	200.78 ± 2.28	2.06 ± 0.03
	0.40	7.16 ± 0.17	123.12 ± 5.55	2.63 ± 0.21
	0.50	4.10 ± 0.07	78.65 ± 1.92	3.89 ± 0.19
	0.60	2.71 ± 0.01	53.77 ± 0.48	4.93 ± 0.08
	0.70	2.17 ± 0.01	40.44 ± 0.75	5.20 ± 0.13
	0.80	1.86 ± 0.01	33.54 ± 0.64	5.42 ± 0.12
85	0.07	30.44 ± 0.18	697.38 ± 8.45	1.70 ± 0.04
	0.10	29.53 ± 0.09	690.38 ± 3.79	1.76 ± 0.02
	0.20	24.92 ± 0.11	565.05 ± 10.44	1.86 ± 0.05
	0.275	20.28 ± 0.04	477.92 ± 12.46	2.15 ± 0.06
	0.40	8.31 ± 0.35	212.51 ± 13.22	3.64 ± 0.45
	0.50	4.29 ± 0.04	109.61 ± 2.06	5.06 ± 0.16
	0.60	3.18 ± 0.02	76.97 ± 1.71	5.56 ± 0.16
	0.70	2.69 ± 0.02	59.89 ± 1.76	5.57 ± 0.24
109	0.07	40.45 ± 0.16	1100.3 ± 19.79	1.75 ± 0.04
	0.10	39.48 ± 0.20	1053.7 ± 16.65	1.74 ± 0.04
	0.20	32.89 ± 0.24	869.0 ± 34.24	1.89 ± 0.09
	0.275	25.82 ± 0.11	691.79 ± 10.65	2.16 ± 0.04
	0.40	8.52 ± 0.37	283.74 ± 20.14	4.67 ± 0.64
	0.50	4.61 ± 0.06	123.42 ± 4.16	5.11 ± 0.27
	0.60	3.57 ± 0.04	84.45 ± 3.90	5.13 ± 0.32
		Star		
25	0.07	2.26 ± 0.01	34.48 ± 0.58	4.17 ± 0.09
	0.10	2.25 ± 0.01	33.90 ± 1.11	4.12 ± 0.14
	0.20	2.18 ± 0.01	32.06 ± 1.07	4.08 ± 0.15
	0.275	2.11 ± 0.01	30.46 ± 0.54	4.07 ± 0.08
	0.40	1.98 ± 0.01	29.70 ± 0.38	4.38 ± 0.06
	0.50	1.84 ± 0.01	26.37 ± 0.52	4.33 ± 0.09
	0.60	1.70 ± 0.01	24.75 ± 0.31	4.56 ± 0.06
	0.70	1.56 ± 0.01	23.11 ± 0.31	4.87 ± 0.07
	0.80	1.42 ± 0.01	19.98 ± 0.26	4.85 ± 0.07
	0.90	1.28 ± 0.01	17.92 ± 0.27	5.05 ± 0.09
	1.00	1.17 ± 0.01	15.60 ± 0.36	5.05 ± 0.12
49	0.07	4.40 ± 0.02	101.54 ± 2.80	4.51 ± 0.16
	0.10	4.37 ± 0.01	99.45 ± 1.66	4.45 ± 0.09
	0.20	4.14 ± 0.02	90.14 ± 2.67	4.39 ± 0.16
	0.275	3.88 ± 0.01	85.93 ± 1.38	4.60 ± 0.08
	0.40	3.41 ± 0.01	74.80 ± 1.29	4.88 ± 0.09
	0.50	2.98 ± 0.01	66.49 ± 1.68	5.29 ± 0.14
	0.60	2.55 ± 0.01	53.34 ± 0.68	5.36 ± 0.08
	0.70	2.18 ± 0.01	43.07 ± 0.42	5.49 ± 0.07
	0.80	1.90 ± 0.01	37.32 ± 0.52	5.85 ± 0.11
	0.90	1.69 ± 0.01	31.23 ± 0.66	5.84 ± 0.15
85	0.07	7.91 ± 0.02	250.38 ± 4.36	4.61 ± 0.10
	0.10	7.77 ± 0.04	244.75 ± 4.11	4.63 ± 0.11
	0.20	7.16 ± 0.04	227.01 ± 5.21	4.85 ± 0.16
	0.275	6.51 ± 0.01	199.49 ± 4.04	4.92 ± 0.11
	0.40	5.23 ± 0.01	156.83 ± 1.88	5.37 ± 0.08
	0.50	4.71 ± 0.01	120.33 ± 1.46	5.80 ± 0.09
	0.60	3.28 ± 0.01	89.07 ± 1.32	6.14 ± 0.12
	0.70	2.73 ± 0.01	70.47 ± 0.61	6.39 ± 0.08
109	0.07	10.40 ± 0.04	387.38 ± 4.95	4.73 ± 0.09
	0.10	10.17 ± 0.04	379.00 ± 12.52	4.79 ± 0.18
	0.20	9.23 ± 0.03	344.45 ± 10.79	5.04 ± 0.19
	0.275	8.22 ± 0.01	293.67 ± 5.56	5.11 ± 0.11
	0.40	6.22 ± 0.02	210.94 ± 3.55	5.57 ± 0.12
	0.50	4.71 ± 0.01	151.57 ± 3.20	6.08 ± 0.15
	0.60	3.60 ± 0.01	112.22 ± 2.73	6.72 ± 0.19

[a] Here $N+1$ is the number of beads, ϵ/k_BT the inverse reduced temperature, $\langle S^2\rangle$ the mean-square radius of gyration, $[\eta]$ the intrinsic viscosity, and ϕ the Flory parameter.

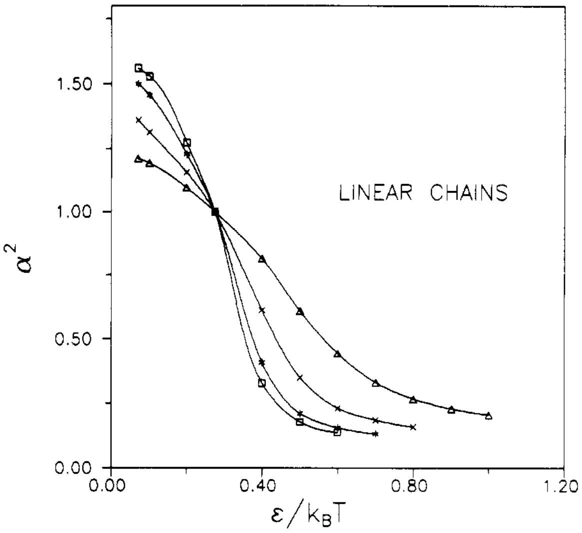

Figure 1. Radius of gyration expansion factor, α^2, as a function of $1/T^*$, where T^* is the reduced temperature, for chains of different lengths: $N+1 = 25$ (△); $N+1 = 49$ (×); $N+1 = 85$ (*); $N+1 = 109$ (□).

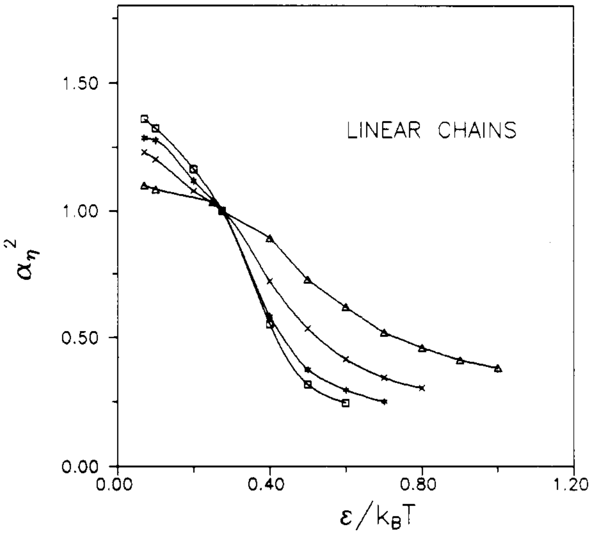

Figure 2. Intrinsic viscosity expansion factor, α_η^2, as a function of $1/T^*$, where T^* is the reduced temperature, for chains of different lengths: $N+1 = 25$ (△); $N+1 = 49$ (×); $N+1 = 85$ (*); $N+1 = 109$ (□).

and different models has been carried out previously[8] for the excluded volume and Θ regimes. The conclusions are reinforced by the present calculations; the ratios of values of ϕ for excluded volume chains to those of equivalent chains at the Θ point are generally smaller than unity since the chain expansion allows for increased partial draining of the solvent through the polymer coil. This effect was already found in previous simulations in which the intrinsic viscosity was calculated by means of the less efficient upper bound method[6] and is also predicted from renormalized group theory and approximate hydrodynamic treatments.[1] Only the results for small star chains do not show statistically significant variation with temperature in the excluded volume regime. Previous studies[6,8] and the present results agree in displaying values of ϕ which are considerably higher for stars than for linear chains in all solvent regimes. This is also consistent with the experimental behavior derived from intrinsic viscosity and radius of gyration data on different linear and star chains.[17]

The new results obtained now for the collapse state also suggest an approach toward a rigid sphere model. From the values in Table I, it can be observed that for both linear and star chains ϕ increases as temperature decreases. Of course, the longest star chains obey more closely this globular behavior. Therefore, ϕ has only a weak dependence on the solvent conditions for star chains, in sharp

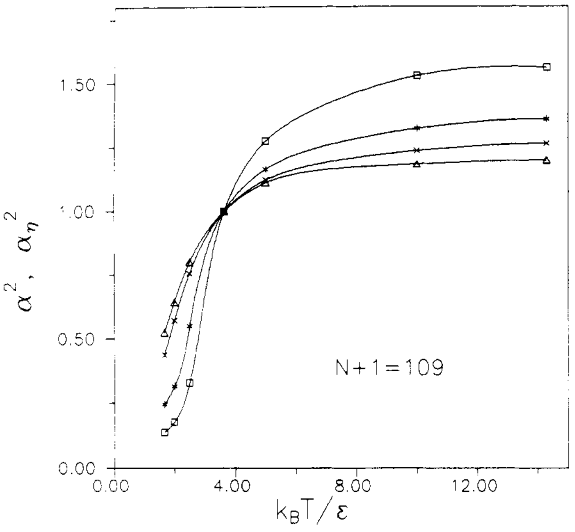

Figure 3. Expansion factors for 109 unit chains: α_η^2 star (△); α^2 star (×); α_η^2 linear (*) α^2 linear (□).

contrast to the behavior shown by equivalent linear chains.

The equation for the radius of gyration of a rigid sphere of uniform density combined with the Einstein formula for its viscosity provides the limiting value, $\phi = 9.23 \times 10^{23}$ mol^{-1}. According to eq 1, for a given viscosity and molecular weight, the highest value of ϕ obtained from our simulations (for the star chain with $N + 1 = 109$ and $1/T^* = 0.6$) will give a polymer effective radius exceeding by 10% that predicted by the rigid sphere limiting value. Moreover, it should be noted that our calculations yield a lower bound for ϕ and also that the hydrodynamic treatments based on modified versions of the Oseen tensor are less efficient as the density of interaction centers increases. In any case, the values of ϕ obtained in the present work for the collapse state are considerably closer to the rigid sphere limit than those obtained from the previous upper bound calculations.[15] Although in that study the results for ϕ in the excluded volume and Θ regimes were fairly well reproduced with the upper bound method,[6] higher uncertainties lead to results in the collapse state[15] which overestimated the rigid sphere limit by more than 100%.

The coil–globule transition can be described by modified versions of the Flory mean-field theory[2,4] and perturbation theory.[5] These approaches when applied to sufficiently long chains lead to equations for the expansion factor with the scaling form

$$\alpha^2 \sim F(Z) \qquad (4)$$

where $F(Z)$ is a scaling function. In eq 4 the scaling variable Z accounts for both the number of bonds on the chain and the temperature; it is given by

$$Z \sim N^{1/2}(1 - T^*_\Theta/T^*) \qquad (5)$$

The ν exponents describing the EV, Θ, and collapsed regimes can be used to predict the scaling behavior of α in our definition of the expansion factor. Then at large values of Z the scaling function should behave as $Z^{0.36}$ in the EV regime and as $Z^{-2/3}$ in the collapsed regime.

Figures 4 and 5 contain log–log plots of the square of the expansion factor against the absolute value of the scaling variable for linear and star chains, respectively. The straight lines in these figures have been drawn with slopes 0.36 and $-2/3$ for the EV and collapsed regimes, respectively. Data for the larger linear and star chains agree reasonably well with the scaling prediction in the collapsed regime. It has been difficult to observe this scaling behavior in previous simulations. The star chains are just beginning to reach their asymptotic limit in the EV regime although the linear chains display asymptotic behavior already at these values of Z.

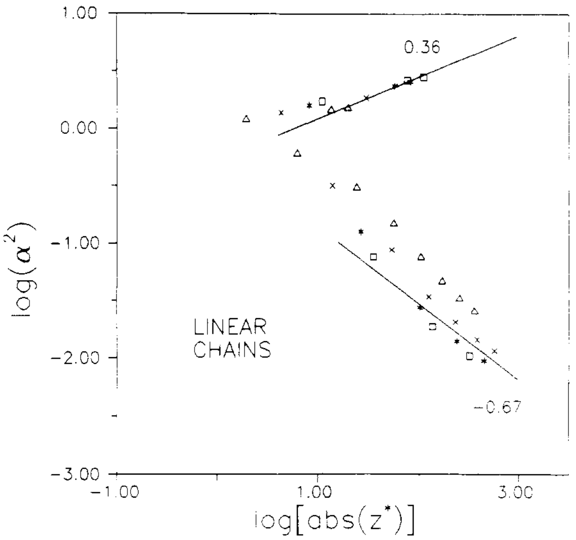

Figure 4. Scaled plots of log (α^2) vs log [abs(Z^*)] for linear chains (symbols as in Figure 1); $Z^* = N^{1/2}(1 - T^*_\Theta/T^*)$. The straight lines have been drawn with the limiting theoretical slopes.

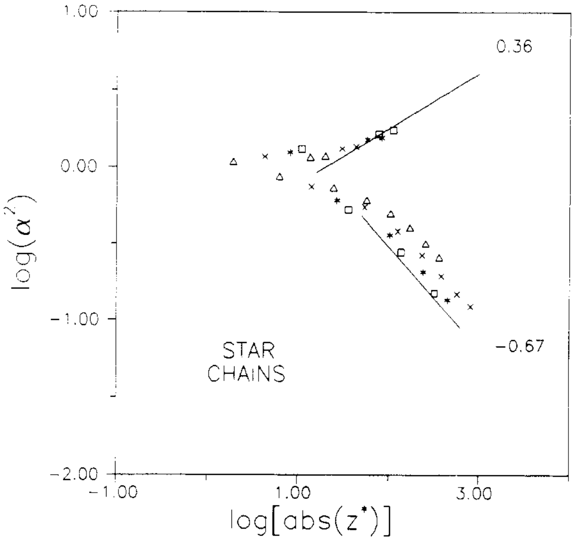

Figure 5. Scaled plots of log (α^2) vs log [abs(Z^*)] for star chains (symbols as in Figure 1); $Z^* = N^{1/2}(1 - T^*_\Theta/T^*)$. The straight lines have been drawn with the limiting theoretical slopes.

The behavior of the intrinsic viscosity parallels that of the radius of gyration. From eq 1

$$[\eta]/[\eta]_\Theta = (\langle S^2\rangle/\langle S^2\rangle_\Theta)^{3/2} \qquad (6)$$

Hence, α_η^2 is expected to have the same scaling behavior as α^2. This is demonstrated in Figures 6 and 7 for linear and star chains, respectively. The data again agree very well with the scaling predictions in the collapsed state but have not yet reached the limiting behavior in the EV regime because of the increased draining effects in expanded chains as previously discussed.

Conclusions

The off-lattice simulations employed in this study have enabled us to obtain accurate data on the mean-square radius of gyration and the intrinsic viscosity for linear and 12-arm star polymers. Our results for the power law behavior of the radius of gyration confirm those results of other workers[18–30] for the EV and Θ regimes obtained using a variety of different simulation approaches. Our results for the collapsed state show clearly the expected behavior.

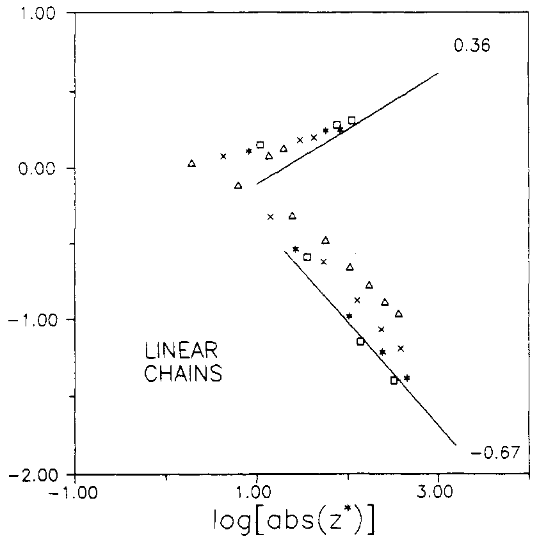

Figure 6. Scaled plots of log (α_η^2) vs log [abs(Z^*)] for linear chains of different lengths; notation as in Figure 4.

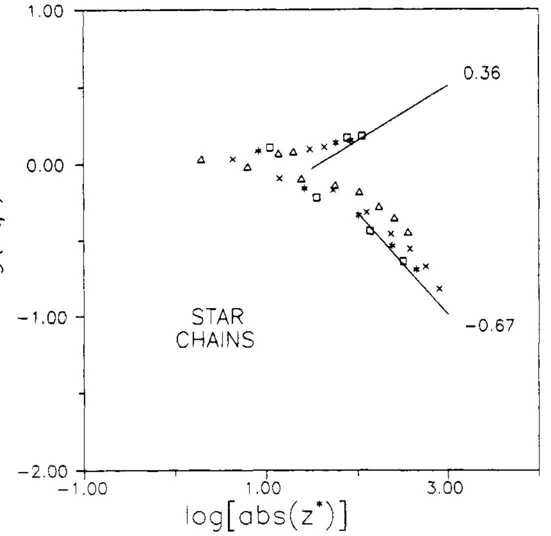

Figure 7. Scaled plots of log (α_η^2) vs log [abs(Z^*)] for star chains of different lengths; notation as in Figure 4.

It should be mentioned that previous simulations could not clearly reproduce the correct collapse state temperature or chain length dependences of dimensions consistent with this scaling behavior.[15,20,21,27]

We have also investigated the behavior of the intrinsic viscosity in all the regimes. The high efficiency of the lower bound method has allowed us to extend previous upper bound studies of Rey et al.[15] to chains long enough to observe a clear transition, sharpening as the chain length increases. As far as we are aware, this is the first study of the scaling behavior of the intrinsic viscosity in the collapsed regime. The Flory parameter ϕ is shown to approach fairly closely to the rigid sphere limit in this regime.

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