Monte Carlo simulations of randomly branched polymers with annealed and quenched branching structures

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We present three-dimensional off-lattice Monte Carlo simulations on randomly branched polymers with annealed and quenched branching structures when monomers interact with each other through excluded volume interactions. The values of the critical exponent for the mean-square radius of gyration are estimated on the basis of scaling analysis as $\nu_a = 0.49 \pm 0.01$ (annealed) and $\nu_q = 0.45 \pm 0.01$ (quenched), which suggest that annealed and quenched randomly branched polymers belong to different universality classes. We further confirm the existence of a scaling parameter that was deduced earlier by the perturbation theory and the Flory-type argument. [S1063-651X(96)09005-X]

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I. INTRODUCTION

The study of models of branched polymer chains has attracted considerable interests due to its fundamental importance to biological molecules and to technical applications in synthetic physical chemistry [1–4]. Branched polymers may have regularly branched structures as in the case of star-shaped and comb-shaped polymers [5] or they may have randomly branched structures. In the latter systems, there exist two possible types of solutions of randomly branched polymers (RBPs): those with annealed branching structures and those with quenched. The majority of previous analytical works [6–8] and numerical simulations [9–16] in this field have been devoted to systems of annealed RBPs, in which the rearrangement of branching points may take place and the branching structure is controlled by maintaining a constant branching activity; the repulsive interactions between polymer segments not only swell the polymer, but also affect the average number of branching points. Much less attention has been given so far to quenched branched polymers [17]. Unlike annealed branched polymers, quenched branched polymers have more stable structures; the statistics of the branching points is unaffected by the introduction of the interaction potential for two polymer segments. An important example is the transfer RNA molecules [18,19]. Quenched RBPs are expected to exhibit different static and dynamic behaviors from annealed ones. They are more compact and the quenched polymeric branching structures prevent any structural changes. Very recently, it has been suggested [20,21] that the static properties of these two types of polymers belong to different universality classes.

In the present work, we shall verify some of the recent theoretical results by studying dilute solutions of RBPs with annealed and quenched branching structures using the nonlocal Monte Carlo (MC) pivot algorithms. Our main interest is to obtain simulation data on the structure of a model of annealed and quenched RBPs, especially in the scaling region of the mean-square radius of gyration. We shall also present a discussion on the choice of an appropriate scaling variable that one should use to extract the characteristic critical exponent in the asymptotic limit of a large molecule weight. The resulting scaling behavior of the simulation data for the radius of gyration indicates that quenched RBPs belong to a universality class different from that of annealed RBPs. The critical gyration exponents are estimated as $\nu_a = 0.49 \pm 0.01$ (annealed) and $\nu_q = 0.45 \pm 0.01$ (quenched). The former is consistent with the values reported earlier [16,22].

II. RBP MODEL AND SIMULATION METHOD

The RBP model being numerically studied here is a tree-like molecule of links of N identical rigid bonds of length l, freely jointed together in D ($=3$) dimensional space; a hard spherical bead is attached to every end of the bonds. The bonds are connected through junctions that may grow two or three branches. It is assumed that the beads (monomers) interact with each other through a hard-sphere-type excluded volume potential, the hard-sphere diameter being denoted as d in the following. The quantities of interest here are the mean-square radius of gyration $\overline{S^2}$ and the average number of branching units n_3. These quantities were obtained for several values of N (typically $10 \leq N \leq 2000$) as well as for several values of the interaction parameter d. Although our model may differ from the actual structures of real systems, the scaling behavior and the critical exponent should be system independent, according to the universality hypothesis.

For quenched RBPs, the topology of the branching structure is fixed while other degrees of freedom are accessible to the polymers. We assumed that, during the initial preparation, no monomer-monomer interactions are present and different structures occur with the same probability. The introduction of the monomer-monomer interaction leads to stretching of the polymer, but does not affect the branching structures. On the other hand, for annealed RBPs interacting through the excluded volume interaction, the configurational

phase space of rotating the bonds is sampled simultaneously with the degree of freedom of rearranging branching structures. Due to this difference, different computer algorithms are proposed below.

The nonlocal MC pivot algorithm to simulate annealed RBPs used in this study is similar to that proposed by Madras and Sokal [23], while the MC algorithm to simulate quenched RBPs is an altered version of the same. The basic steps to simulate annealed RBPs are as follows. An initial self-avoiding branched molecule is produced and equilibrated over certain runs. To obtain a new configuration, a branching position is chosen at random and one of the neighboring bonds is cut to produce two pieces of the polymer. The smaller portion of the polymer is identified and rotated as a rigid body to a new position by specifying randomly chosen values for the three Euler angles (α, β, γ). Note that the Euler angle β between the new and old z axes is actually chosen so that $\cos \beta$ is evenly distributed in the interval $-1 \leqslant \cos \beta \leqslant 1$. Subsequently, an arbitrary point on the larger portion of the polymer is located for reconnecting the two pieces. The new configuration is accepted only when the new branching point contains less than three branches originally and only when the hard-sphere monomers of the rotated portion do not overlap with those of the unrotated portion. Otherwise, the new configuration is rejected, the old configuration is recovered, and the cutting-reconnecting procedure starts over again. Such a nonlocal algorithm efficiently produces radically different configurations after a relatively small number of successful moves. Madras and Sokal showed that this algorithm satisfies the condition of detailed balance [23].

The key requirement to simulate quenched RBPs is to maintain the statistics of the branching positions unaffected by the excluded volume interaction, while the hard-sphere monomers are allowed to interact. We adopted the algorithm that otherwise is the same as that for the annealed case except for the last step; whether or not overlapping takes place between the monomers of the rotated and the unrotated portions after the reconnection, the configuration is always accepted as an intermediate one. Such a configuration is then regarded as a nonequilibrium state and is allowed to relax to the equilibrium state. Any possible overlapping is gradually eliminated by randomly rotating an arbitrarily chosen part of the polymer, until a configuration with no overlapping monomers is achieved. This nonoverlapping configuration is subsequently equilibrated over a number of runs (typically $N-2N$) before a measurement is taken.

To simulate annealed RBPs, the measurement of the physical properties was taken every five MC steps in order to avoid temporal correlation of the configurations. For a given set of N and d, a typical run that was performed contains $2 \times (10^5 - 10^6)$ MC steps. To simulate quenched RBPs, measurements were taken only after five new structures were made and equilibrated to avoid temporal correlation of the *branching structures*. For a given set of N and d, a typical run that was performed contains $5 \times (10^4 - 10^6)$ new branching structures. Table I shows the original data that we obtained from the simulation. In Fig. 1, the mean-square radius of gyration $\overline{S^2}$ and the mean number of tribranches n_3 are plotted as functions of N for several values of d. The open symbols represent data for annealed RBPs and the solid symbols for quenched RBPs. Regardless of the differences in d, n_3 of the quenched case always remains the same as that for $d=0$, as expected.

III. SCALING ANALYSES

In order to analyze the simulation data, it is essential to have a firm theoretical understanding of the interacting RBPs with annealed and quenched branching structures. In contrast to the case of linear polymers, where there exists a consistent description for the mean-square radius of gyration $\overline{S^2}$ of self-avoiding chains [1–3], the behavior of interacting RBPs is not completely understood. We recall that linear polymers obey the so-called two parameter model, in which a scaling parameter z relating the excluded volume with the total number of monomers is clearly defined [2]. At large z, the ratio between $\overline{S^2}$ of self-avoiding chains and that of random walks is expected to have a power-law dependence in z [3]. The question is whether we can understand the data in Fig. 1 by using a similar description. Both perturbation theory [8,21] and Flory-type theory [24–26] show that

$$\overline{S^2}/(\overline{S^2})_0 \sim z^{2(4\nu-1)/\epsilon} \tag{1}$$

and

$$z = \frac{u\Lambda^2}{(4\pi)^4} \left(\frac{16\pi^2 N}{\Lambda} \right)^{\epsilon/4}, \tag{2}$$

where $(\overline{S^2})_0 = l^2 (\pi N/\Lambda)^{1/2}/4$ is the mean-square radius of gyration of ideal chains when no interactions are present [27,28], ν is the gyration exponent, $\epsilon = D_c - D$ with $D_c = 8$ being the upper critical dimensionality [29,8], u is the excluded volume, and Λ^2 is the activity of the trifunctional units.

The validity of Eqs. (1) and (2) can be demonstrated by using a perturbation theory that treats u as the perturbation parameter [2]. We have recently shown through a first-order perturbation that the z parameter in Eq. (2) indeed exists for both annealed and quenched cases [8,21], similar to the z parameter in the two-parameter theory for linear polymers. Based on the perturbation expansions for the mean-square radius of gyration $\overline{S^2}$, the second virial coefficient A_2, and the partition function Q, we have further applied the renormalization group technique, which allows us to determine the critical exponent ν for for small ϵ:

$$\nu_a = \tfrac{1}{4}[1 + \tfrac{1}{9}\epsilon + O(\epsilon^2)] \tag{3a}$$

for annealed RBPs and

$$\nu_q = \tfrac{1}{4}[1 + \tfrac{1}{10}\epsilon + O(\epsilon^2)], \tag{3b}$$

for quenched RBPs. At $D=3$, however, we cannot determine rigorously the values of ν_a and ν_q based on a series containing only one correctional term. We are fortunate to have an exact solution for ν_a: Parisi and Sourlas [22] have demonstrated that ν_a has an exact value of $\tfrac{1}{2}$ for $D=3$. This value can be used as a benchmark for the determinations of ν_a and ν_q by using other methods.

The Flory-type argument is an effective procedure for estimating the critical exponent ν approximately. In the case of

TABLE I. Numerical results for the conformation properties.

d	N	Annealed		Quenched	
		$\overline{S^2}$	n_3	$\overline{S^2}$	n_3
0.25	10	1.564	2.066	1.570	2.073
	20	2.614	4.979	2.600	4.971
	50	5.065	13.671	5.064	13.762
	100	8.597	28.135	8.416	28.394
	200	15.078	57.080	14.374	57.694
	300	21.168	86.048	19.952	86.714
	400	27.068	114.879	25.371	116.497
	600	39.140	172.720	35.458	174.899
	800	51.191	230.537	45.051	233.524
	1000	63.622	288.284	55.303	291.456
	1500	92.859	432.381		
	2000	123.199	577.502		
0.50	10	1.842	2.018	1.821	2.069
	20	3.413	4.802	3.322	4.995
	50	7.769	13.211	7.383	13.735
	100	14.766	27.145	13.619	28.286
	200	28.328	55.083	24.832	57.644
	300	42.224	83.405	35.727	87.260
	400	55.517	111.021	45.874	116.442
	600	82.313	166.988	65.926	174.726
	800	108.427	222.786	84.792	232.389
	1000	135.955	278.843	102.729	293.394
	1500	195.202	416.826		
	2000	268.453	560.201		
0.75	10	2.234	1.919	2.167	2.082
	20	4.338	4.569	4.164	4.980
	50	10.607	12.599	9.660	13.772
	100	20.711	25.801	18.142	28.450
	200	40.912	52.322	33.760	57.674
	300	61.320	78.469	48.654	86.549
	400	80.514	105.292	62.966	116.346
	600	121.836	157.843	89.717	174.446
	800	160.942	211.967	117.749	233.768
	1000	202.318	264.940	142.138	292.983
	1500	297.598	399.276		
	2000	411.121	533.141		
0.99	10	2.587	1.770	2.484	2.079
	20	5.203	4.265	4.861	4.993
	50	12.956	11.734	11.436	13.735
	100	25.941	24.208	21.754	28.497
	200	51.270	49.097	40.772	57.830
	300	76.772	74.385	58.030	87.381
	400	101.948	98.876	74.832	115.239
	600	151.627	148.433	108.714	175.094
	800	204.690	199.773	141.093	234.419
	1000	254.156	249.741	171.797	293.302
	1500	377.612	372.312		
	2000	531.196	498.249		

linear polymers, the seemingly crude Flory argument produces the appropriate form for the scaling parameter z, which can be identified by, for example, the perturbation expansion. In the case of RBPs, the Flory-type argument also produces the correct form for z given in Eq. (2) and a good approximation for the critical exponents ν_a and ν_q. Follow-
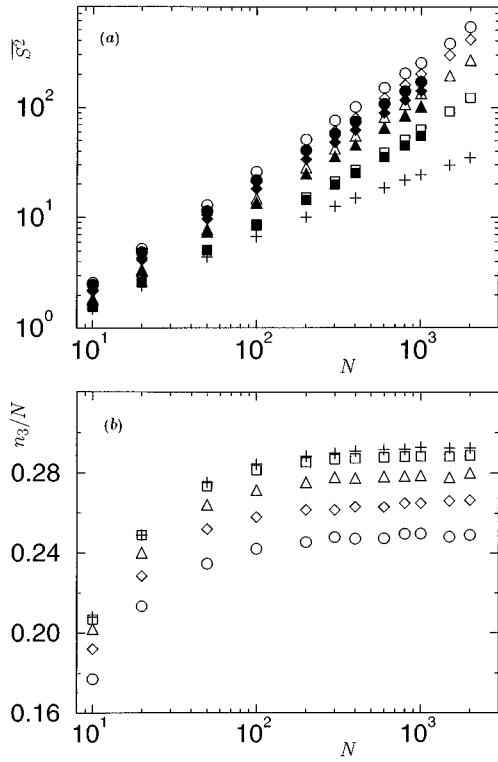
FIG. 1. (a) Mean-square radius of gyration $\overline{S^2}$ and (b) mean number of tribranching points n_3 vs the monomer number N for different values of hard-sphere diameter d. Here the open symbols represent data for the annealed cases and solid symbols for the quenched cases. The circles correspond to $d=0.99$, diamonds to $d=0.75$, triangles to $d=0.50$, squares to $d=0.25$, and crosses to $d=0.0$. For quenched branch polymers, n_3 is the same as that of the $d=0$ case (cross symbols).

ing the discussion presented by Daoud and Joanny [24], here we briefly review the Flory-type argument by explicitly maintaining Λ^2 in the formula.

For quenched RBPs, within Flory's approximation, the free energy F_q is the sum of the elastic energy $F_e = \beta^{-1}\overline{S^2}/(\overline{S^2})_0$ and a term contributed from the repulsive interaction [3] $F_i = \beta^{-1} u N^2/(\overline{S^2})^{D/2}$. Minimizing $F_q = F_e + F_i$ with respect to $\overline{S^2}$ yields $\nu_q(\text{Flory}) = 5/(2D+4)$ [24–26] and $\overline{S^2}/(\overline{S^2})_0$ obeying Eqs. (1) and (2). It is worth mentioning that at $D=3$, $\nu_q(\text{Flory}) = \frac{1}{2}$ was previously thought to be in agreement with the annealed exponent $\nu_a = \frac{1}{2}$ determined by Parisi and Sourlas [22].

As regards the annealed branched polymers, there is an additional entropy term F_s contributing to the free energy, which corresponds to the rearrangement of the branching units. Gutin, Grosberg, and Shakhnovich [20] have considered a simple model, in which only ends and branched points are allowed to exist (no linear parts), in order to estimate F_s by using de Gennes's diagrammatic method [28]. For an N monomer molecule in which the average number of bonds connecting two arbitrary external ends is L, they found $F_s = \beta^{-1}L^2/N$. To generalize to the case where the branching units are connected by linear parts, each containing several monomers, we may group the monomers between the branching units in imaginary blobs [24]; the branched molecule can then be represented as a molecule made exclu-

sively of branching units and blobs. The physical behavior of the blob model should be qualitatively similar to that of Gutin, Grosberg, and Shakhnovich's model [20] consisting of the same number of trifunctional units. In such a blob model, the average number of monomers in one blob is roughly Λ^{-1}. Accordingly, F_s of a branched polymer of N monomers with L bonds between two arbitrary ends is the same as the system consisting of $N/(\Lambda^{-1})$ blobs with $L/(\Lambda^{-1})$ blobs between those two ends: $F_s = \beta^{-1}[L/(\Lambda^{-1})]^2/[N/(\Lambda^{-1})]$ $= \beta^{-1}L^2/(N/\Lambda)$. Furthermore, noting that the mean-square radius of gyration for one blob is $\Lambda^{-1}l^2$ and there are in total $L/(\Lambda^{-1})$ blobs between these points, we can estimated the elastic energy as $F_e = \beta^{-1}\overline{S^2}/\{[L/(\Lambda^{-1})](\Lambda^{-1}l^2)\}$ $= \beta^{-1}\overline{S^2}/(Ll^2)$, which is independent of Λ. Minimizing $F_a = F_e + F_i + F_s$ with respect to L and $\overline{S^2}$ yields the same form of $\overline{S^2}$ as in Eqs. (1) and (2) and a gyration exponent $\nu_a = 7/(3D+4)$ [20]. Equation (1) now contains the branching activity Λ in comparison with equations in Ref. [20]. At $D=3$, $\nu_a = 0.54$, which shows $\nu_a > \nu_q$.

The physical meaning of Λ^2 is somewhat different in the two cases considered here. In the annealed case, Λ^2 is the fugacity of the branching structures, which is affected by the presence of the excluded volume interactions, and thus Λ is a function of u. In the quenched case, Λ^2 is the fugacity of the branching structures when the polymers were initially made without the presence of the excluded volume interaction and is independent of u. It is difficult, however, to analytically evaluate the parameter Λ that must enter Eq. (2) for numerical analysis when the excluded volume interactions exist. An alternative method will be to "measure" Λ through measuring n_3, which is simultaneously determined in the simulation, since the two quantities are related by [28]

$$n_3 = \Lambda N, \qquad (4)$$

where the large-N limit is considered. de Gennes showed Eq. (4) in Ref. [28] for the case of branched polymers without interaction of the monomers, which is the same case as our quenched polymers. We showed earlier [8] that the same relation is followed even in the case of annealed RBPs although Λ depends on the interactions. Using the n_3/N data as demonstrated in Fig. 1(b), we can estimate Λ by examining the large-N asymptotic behavior and substitute that value into Eq. (2). Since we are only interested in the large-N behavior in order to determine the critical exponent ν, we may also replace Λ in Eq. (2) by n_3/N directly during the actual data analysis. We may show that the two procedures produce the same value for the exponent ν within the given error quoted below. The analysis described below follows the second procedure.

As for the estimation of the average excluded volume per bond u, it is a subtle problem even for linear polymers [30]. We shall follow the treatment suggested in Ref. [30]. Consider a single bond that is associated with two beads at the ends. If $d < l/2$, the region excluded per bond, when a third bead is introduced, is simply the volume of two half spheres of radius d. If $d \geq l/2$, however, these two half spheres overlap and the actual excluded region is the volume of two half spheres of radius d minus the volume of the overlapping region. The excluded volume averaged over one bond is then given by
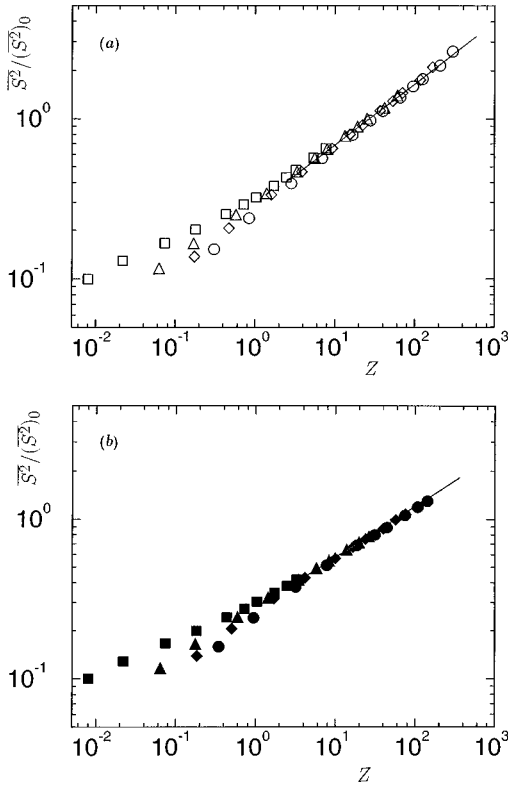
FIG. 2. Scaled mean-square radius of gyration $\overline{S^2}/(\overline{S^2})_0$ for (a) the annealed case and (b) the quenched case, plotted as a function of the scaled excluded volume z defined in Eq. (2) on a log-log scale for various monomer numbers N and hard-sphere diameters d. $(\overline{S^2})_0$ is the mean-square radius of gyration of ideal chains when no interactions are present. The meaning of the symbols are the same as in Fig. 1. The two straight lines indicate asymptotic behavior with slopes $2(4\nu-1)/5$, where $\nu_a=0.49$ and $\nu_q=0.45$, respectively.

$$u = \begin{cases} \dfrac{4}{3}\,\pi\left(\dfrac{d}{l}\right)^3, & d < \dfrac{l}{2} \\[2ex] \pi\left[\left(\dfrac{d}{l}\right)^2 - \dfrac{1}{12}\right], & d \geq \dfrac{l}{2}, \end{cases} \tag{5}$$

which is used to compute the value of z, Eq. (2).

Using Eqs. (1), (2), (4), and (5), we present in Fig. 2 a log-log plot of the function $\overline{S^2}/(\overline{S^2})_0$ against z. It can be observed from Fig. 2 that the data points for large z lie closely along a straight line for both annealed and quenched RBPs and that the slope of the straight line for annealed RBPs is higher than that for the quenched ones. This implies that the scaling behavior in Eq. (1) is indeed valid for large z and that the critical exponent of annealed RBPs for $\overline{S^2}$ is greater than that of quenched ones. These observations agree with the theoretical results discussed above. Using data points with $z \geq 3$, we have estimated the gyration exponents

$$\nu_a = 0.49 \pm 0.01 \tag{6a}$$

for the annealed case and

$$\nu_q = 0.45 \pm 0.01 \tag{6b}$$

for the quenched case.

The earliest numerical estimates of ν, based on MC scaling of (annealed) lattice trees suggested that $\nu_a=0.45$ for three-dimensional trees [9]. The most recent calculation is by van Rensburg and Madras [16] for lattice trees, which yields $\nu_a=0.4960$. Our value ν_a is in satisfying agreement with that obtained by van Rensburg and Madras for lattice animals [16], and that from the exact field-theory calculation ($\nu_a=0.5$) [22]. For comparison, the Flory-type argument yields $\nu_q=0.5$ and $\nu_a=0.54$, which show a similar relative difference between the values of the two exponents.

In determining the critical exponents, we did not take into account possible correction terms to the scaling behavior in Eq. (1). The simulation data in Fig. 2 show interesting deviation from the scaling behavior represented by the straight lines in the log-log plots. It is well known that the coefficient of the correction-to-scaling term is proportional to u^*-u, where u^* is a characteristic excluded volume corresponding to the fixed point in the field theory analysis of critical systems [31]. As displayed in Fig. 2, different values of u show different behavior. Those curves with small excluded volume (small d) satisfying $u<u^*$ exhibit positive curvature, while those curves with large excluded volume satisfying $u>u^*$ exhibit negative curvature. The effective exponents determined by the small-u curves are always smaller than the actual value, while the effective exponents are larger otherwise. A similar qualitative behavior for linear polymers [32] was discussed and analyzed by Nickel [33] and a crossover model that takes the correction-to-scaling terms into account in a closed form was put forth by Chen and Noolandi [34,35]. Without a better knowledge of the behavior of the correction-to-scaling terms for RBPs, it is difficult to give a meaningful analysis of the simulation data at small z in Fig. 2.

IV. CONCLUSION

In conclusion, the present MC simulations show that randomly branched polymers with annealed and quenched branching structures have different gyration exponents and thus belong to different universality classes. This verifies the previous conformational space renormalization analysis and Flory-type arguments which yield different gyration exponents for the two cases. It would be interesting to verify these results experimentally.

ACKNOWLEDGMENT

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