What Is the Size of a Ring Polymer in a Ring−Linear Blend?

Balaji V. S. Iyer,[†] Ashish K. Lele,[†] and Sachin Shanbhag*[,‡,§]

Complex Fluids and Polymer Engineering Group, Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411008, India; Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida 32310-6046; and School of Computational Science, Florida State University, Tallahassee, Florida 32306-4120

Received April 20, 2007; Revised Manuscript Received June 4, 2007

ABSTRACT: In melts, ring polymers assume more compact conformations compared to linear chains with the same degree of polymerization N_r, i.e. $R_r \sim N_r^{\nu}$ with $\nu \approx 0.4$, where R_r is the radius of gyration. Upon gradually substituting some of the ring polymers with linear chains, the ring molecules swell. In the limit of infinite dilution, their size scales as $R_r \sim N_r^{0.5}$. We present a scaling argument based on the blob model to capture this transition. Ring−linear blends are modeled as a semidilute solution of ring polymers in a Θ-solvent consisting of linear chains. The model predicts that the size of the ring polymer remains unchanged up to the overlap concentration c_r^*. Beyond c_r^* the size of the ring shrinks according to $R_r \sim c_r^{\beta}$, where $\beta = 2\nu - 1 = -1/5$ for $\nu = 0.4$. The overlap concentration depends on the degree of polymerization of the ring according to $c_r^* \sim 1/\sqrt{N_r}$. These predictions were tested by performing Monte Carlo simulations of ring−linear blends using the bond-fluctuation model. The results of the simulation for $N_r = 150$ and 300 blended at different concentrations with linear chains of the same degree of polymerization validate the scaling model.

1. Introduction

Although the statistical properties of flexible and semiflexible linear polymers are well understood theoretically,[1] the same cannot be claimed for ring or cyclic polymers. The properties of the simplest class of such molecules, namely nonconcatenated rings which are topologically equivalent to a "trivial knot", are difficult to determine since the corresponding partition function must somehow exclude (potentially using an infinite number of invariants) the fraction of closed loops that are not in the same topological class.

Starting from the mid-1980s a substantial body of experimental work has been developed on viscoelastic and tracer diffusion studies of polystyrene and polybutadiene rings[2−5] comparing the properties of linear and cyclic polymers. In general, they indicate that, compared to their linear counterparts, rings assume more compact conformations, are less viscous, and possess lower plateau moduli.[6,7] Experimental limitations have not stalled the theoretical[8−11] and computational investigation of ring polymers.[12−20] Theoretical efforts have largely focused on the statics and dynamics of rings in a fixed array of obstacles, while computational studies have addressed rings in isolation and in melts. A significant fraction of computational studies utilize the lattice-based bond-fluctuation model (BFM), in part because most of the established simulation strategies that aid the equilibration of linear chains[21] in off-lattice Monte Carlo (MC) and molecular dynamics models, such as end-bridging[22] and configurational bias MC,[23] cannot be trivially extended to prevent the formation of concatenated rings by accident. The popular "slow push off" method of Auhl et al.,[24] which involves dialing up excluded-volume interactions of chains, prepacks phantom random walks into a simulation box so as to start from a configuration that is similar to the equilibrium distribution. However, this method cannot be easily generalized to melts of rings since it is probable that concatenated rings will be formed during the prepacking process. The MD simulation of a polyethylene ring melt by Hur et al.[20] using a united-atom description is the only study we are aware of that uses an off-lattice description to study a dense system of rings. However, from the standpoint of rheology the systems simulated are relatively small (70 chains of 300 united atoms, corresponding to about 3 entanglements using the entanglement molecular weight of linear polyethylene). The BFM predicts that the equilibrium size of rings $R_r \sim N_r^{0.4}$, where R_r is the radius of gyration and N_r is the number of monomers in the ring. It may be noted that estimates using some MC methods report a $R_r \sim N_r^{0.45}$ dependence,[25,26] which has been attributed to finite size effects.[12]

While the conformational and diffusion properties of pure ring and linear melts have been investigated quite extensively, blends of rings and linear chains have not been studied adequately (apart from Geyler and Pakula,[26] who studied such systems using a cooperative relaxation model). These blend systems are important because most experimental data on "pure rings'' are in fact data on ring−linear blends due to contamination or limitations of purification methods. As a first step toward understanding the behavior of ring−linear systems, we examine the statics, in particular, the average size of the rings as a function of the relative composition of the ring and linear species. These results may be viewed in light of recent dynamic experimental data on systematic ring−linear blends.[27]

Rings are expected to enlarge when they are blended with linears. The sensitivity of the extent of swelling to the concentration of the linears is an unaddressed question. In this paper we present a scaling model for the size of a ring polymer based on the blob model for semidilute solutions.[28] Ring−linear blends are modeled as a "semidilute solution" of ring polymers in a Θ-solvent comprising linear chains. The scaling model and its predictions are explained in section 2.1. The BFM simulation method for ring−linear blends is presented in section 2.2. The

* Corresponding author: phone (850) 644-6548; e-mail sachins@scs.fsu.edu.
† National Chemical Laboratory.
‡ FAMU-FSU College of Engineering.
§ Florida State University.

10.1021/ma0709295 CCC: $37.00
Published on Web 07/07/2007

predictions of the model are tested using the BFM simulations in section 3.

2. Model and Methods

2.1. Scaling Model. It has been conjectured (and observed) that a flexible ring polymer takes a collapsed conformation in a melt of pure ring polymer chains due to the topological constraint of nonconcatentation.[8,17,29] A scaling argument for the size of noncatenated ring polymers involves writing the free energy as[8]

$$F(R_r) = \frac{R_r^3}{N_r} + \frac{N_r}{R_r^2} \tag{1}$$

where the first term is proportional to the number of neighbors and denotes the increase in free energy due to the nonconcatenation constraint, and the second term denotes the Gaussian free energy increase that favors the expansion of the coil. Minimizing the free energy $dF/dR_r = 0$ leads to $R_r \sim N_r^{2/5}$.

Further, a ring molecule is expected to swell with addition of linear chains due to the relaxation of the nonconcatenation constraint[8] (see Appendix). In this section we present a scaling argument to capture the size dependence of a ring molecule on its concentration in a ring−linear blend. A small fraction of rings in a melt of linear chains constitutes the starting point for the scaling model.

A ring−linear blend at low concentration of rings in a linear melt can be thought of as a dilute solution of rings. Since a ring polymer does not experience excluded volume interactions in a melt, its conformation is identical to that in a Θ-solvent. At the overlap or threshold concentration c_r^*, the concentration in the solution is the same as the concentration of monomers (Kuhn segments) within an individual ring. This concentration is given by the ratio of number of monomers in a single ring chain, N_r, to the pervaded volume of the ring chain in dilute solution, $(R_r^{dil})^3 \sim N_r^{3/2}$:

$$c_r^* = \frac{N_r}{(R_r^{dil})^3} \sim \frac{N_r}{N_r^{3/2}} \sim N_r^{-1/2} \tag{2}$$

At the threshold concentration, c_r^*, the correlation length, ξ, i.e., the mean distance between Kuhn segments on neighboring ring chains, is of the order of the radius of gyration of the ring chain, R_r^{dil}. Beyond the threshold concentration c_r^* the ring−linear blend enters the semidilute regime, and the correlation length ξ decreases from R_r^{dil} with increasing c_r. Further, we expect the correlation length to be independent of N_r, beyond the overlap concentration. Thus, the concentration dependence of the correlation length is given by

$$\xi = R_r^{dil}\left(\frac{c_r^*}{c_r}\right)^m \sim N_r^0 \tag{3}$$

Since c_r is independent of N_r, we obtain $m = 1$ using $R_r^{dil} \sim N_r^{1/2}$ and the scaling relationship for c_r^* given by eq 2. Thus, the correlation length scales inversely as the concentration in the semidilute regime

$$\xi(c_r) \sim \left(\frac{c_r}{c_r^*}\right)^{-1} \tag{4}$$

Considering the ring chain to be composed of blobs of size ξ consisting of, say, N_b Kuhn segments, the ring chain can be examined at length scales less than ξ and of the order of ξ. Below the correlation length scale, ξ, we argue that the ring encounters on average only linear neighbors, and a chain section in a blob of size ξ behaves as if it was under Θ-conditions. Thus,

$$\xi \sim N_b^{1/2}$$
$$N_b \sim \left(\frac{c_r}{c_r^*}\right)^{-2} \tag{5}$$

from eq 4. For a coarse-grained picture on length scales of the order of ξ we argue that ring on an average only sees ring chain neighbors. The nonconcatenation constraint becomes operational at this length scale, and hence the ring bears a lattice-tree structure.[8,10]

At the length scale ξ we consider the ring to be composed of N/N_b segments of length ξ with only ring neighbors. Based on conjecture proposed by Cates and Deutsch,[8] the radius of gyration of such a structure would scale as

$$\begin{aligned} R_r &\sim (N_r/N_b)^{2/5}\xi \\ &\sim \left(\frac{c_r^0}{(c_r/c_r^*)^{-2}}\right)^{2/5} (c_r/c_r^*)^{-1} \\ &\sim (c_r/c_r^*)^{-1/5} \end{aligned} \tag{6}$$

from eqs 3 and 4. Note that $N_r \sim c_r^0$ since it is independent of concentration. The above scaling argument indicates that in the semidilute regime the radius of gyration of a ring scales with concentration of ring as $(c_r/c_r^*)^{-1/5}$.

We can follow a similar line of reasoning for the case of linear chains in a melt of rings starting from a small fraction of linear chains up to the semidilute regime. In the semidilute regime the linear chains can also be considered to be composed of blobs of size ξ. Because of the absence of nonconcatenation constraint in the linear chain, the scaling at length scales less than ξ persists up to and beyond length scales of the order of ξ. This yields a radius of gyration of the linear in the semidilute regime as

$$\begin{aligned} R_l &\sim (N_l/N_b)^{1/2}\xi \\ &\sim \left(\frac{c_l^0}{c_l^{-2}}\right)^{1/2} c_l^{-1} \\ &\sim c_l^0 \end{aligned} \tag{7}$$

since $N_b \sim c_l^{-2}$, $\xi \sim c_l^{-1}$, and the number of monomers (Kuhn steps) in a linear chain N_l is independent of concentration.

It is observed from eq 7 that in the case of linear chains the radius of gyration is independent of concentration c_l. This is expected for a linear chain as the constraints imposed on it do not change, when a linear neighbor is replaced with a cyclic molecule.

Finally, we estimate the concentration $c_r^\dagger$ at which the ring polymer shrinks to unperturbed dimensions. Using eq 6, we can write

$$R_r(c_r) = R_r(c_r^*)\left(\frac{c_r^*}{c_r}\right)^{1/5}$$

$$R_r(\text{melt}) = R_r(c_r^*)\left(\frac{c_r^*}{c_r^\dagger}\right)^{1/5} \quad (8)$$

which implies

$$c_r^\dagger = \left(\frac{R_r(c_r^*)}{R_r(\text{melt})}\right)^5 c_r^*$$

$$\sim \left(\frac{N_r^{1/2}}{N_r^{2/5}}\right)^5 N_r^{-1/2}$$

$$\sim N_r^0 \quad (9)$$

This implies that the concentration at which a ring molecule attains unperturbed dimensions in a ring−linear blend is independent of molecular weight, which suggests that the number fraction of ring neighbors is unity at concentration $c_r^\dagger$, i.e., in a melt of pure rings.

2.2. Bond-Fluctuation Model. Like Szamel and co-workers,[13,14,18] we employ Shaffer's version of the BFM (referred to as S-BFM henceforth).[30] S-BFM shrinks the number of allowed bond vectors from 108 in the original BFM proposed by Carmesin and Kremer[31] to 26, leading to polymer chains that are comparatively less flexible.

To generate an equilibrated blend of ring and linear molecules, we modified the initialization method described in our earlier publications.[32,33] We systematically placed N_{pr} nonconcatenated rings, each consisting of N_r monomers or beads, on a 3D cubic lattice in a simulation box of size $L_{box} \times L_{box} \times L_{box}$ with periodic boundaries. Throughout this report, length is expressed in units of lattice spacing. In S-BFM, excluded volume and chain connectivity are imposed by ensuring that two beads do not occupy the same lattice site and that the length of the bond connecting consecutive beads belongs to the set $\{1, \sqrt{2}, \sqrt{3}\}$. S-BFM enforces chain uncrossability by prohibiting moves that lead to configurations in which the midpoints of bonds intersect. In a trial move, a randomly chosen bead is displaced by one lattice unit in any one of the six possible directions. It is accepted if it does not violate the excluded volume, chain connectivity, and chain uncrossability constraints. After shuffling the rings for approximately $t = 25000N_rN_{pr}$ trial moves to distribute them evenly in space, we randomly inserted N_{pl} linear chains, each with N_l monomers, in the simulation box. Configurations that led to multiple occupancy of lattice sites were discarded, and the process was continued until all the N_{pl} chains were successfully embedded. In all the cases simulated, this process took no longer than 5 min of CPU time on a modern workstation, although we expect that a more sophisticated insertion method may be required for longer chains. To simulate meltlike behavior, the total fractional occupancy of the lattice was maintained at $\phi = \phi_r + \phi_l = 0.5$, where ϕ_r and ϕ_l represent the fractional occupancy of ring and linear molecules, respectively (see Appendix). Keeping the rings frozen in place, we allowed the linear chains to move for approximately $t = 25000N_lN_{pl}$ trial moves, subject to the same constraints, to randomize the initial configuration.

In the past, the equilibration of linear chains[32,33] was accelerated by allowing chains to pass through each other initially. Such moves were forbidden in the subsequent phase of initialization. Unfortunately, the same technique cannot be utilized for rings, since it can alter the topology and potentially transform a system of nonconcatenated rings to one with a sizable fraction of concatenated rings. During equilibration, a trial move was attempted for a randomly selected bead, belonging to either a ring or linear chain. One Monte Carlo step (MCS) corresponds to $N_{pl}N_l + N_{pr}N_r$ trial moves. For linear chains, we monitored the autocorrelation function of the end-to-end vector $p_l(t) = \langle \mathbf{R}(t)\cdot\mathbf{R}(0)\rangle/\langle R^2(0)\rangle$, where $\mathbf{R}(t) = \mathbf{r}_{N_l}(t) - \mathbf{r}_1(t)$ is the vector connecting the positions of beads 1 and N_l at time t, and $\langle\cdot\rangle$ is an average over all the chains in the system. Similarly, for rings we monitored the decay of the autocorrelation $p_r(t)$ of the "diametrical'' vector connecting beads 1 and $N_r/2$, $\mathbf{r}_{N_r/2}(t) - \mathbf{r}_1(t)$. The system was assumed to be equilibrated after both p_l and p_r dropped below 0.1. This took on the order of 5×10^7 MCS or ~15 CPU days on a modern processor for the system sizes studied.

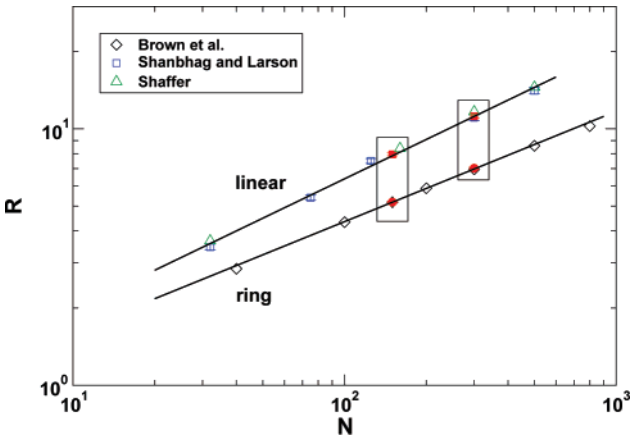

Figure 1. Combined linear regression on pure linear and ring data simulated using Shaffer's version of the bond-fluctuation model indicates that the radius of gyration of linears scales as $R_l \sim N_l^{0.51\pm0.01}$ while that of rings scales as $R_r \sim N_r^{0.43\pm0.01}$.[18,32,34] Open symbols indicate results from earlier publications. Filled symbols are results on pure rings and linears from this work corresponding to $N = 150$ and $N = 300$. The range of simulations of mixtures carried out in this paper is highlighted for perspective.

3. Discussion

Previous S-BFM studies explored the chain length dependence of static and dynamic properties of pure linears and pure rings.[18,32,34] The data from these references for $N \geq 30$[32,33,35] have been collated in Figure 1, along with data on pure rings and linears simulated in this paper. The radius of gyration of linear chains scales as $R_l \sim N_l^{0.51\pm0.01}$, and that of rings scales as $R_r \sim N_r^{0.43\pm0.01}$. This is consistent with the idea that configurations of linear chains obey Gaussian statistics in the melt, while ring molecules are more compressed due to the nonconcatenation constraint with neighboring molecules.

In this study, we considered two series of ring−linear blends. In each series, identical numbers of beads were used to represent the two species, i.e., $N_r = N_l = N$. As indicated in Figure 1, we examined $N = 150$ and $N = 300$, at a total fractional occupancy $\phi = \phi_r + \phi_l = 0.5$. The lengths of the linear and ring polymers were held constant, and we varied the composition of the ring−linear blend from $\phi_r = 0.5$ to $\phi_r = 0.0$, corresponding to the range between pure rings to pure linear chains, respectively. Table 1 summarizes the details of the systems studied.

Table 1. Description of the Systems Simulated[a]

ϕ_l	ϕ_r	N_{pl}	N_{pr}
	$N = 150$		
0.500	0.000	720	0
0.479	0.021	690	30
0.458	0.042	660	60
0.438	0.063	630	90
0.375	0.125	540	180
0.313	0.188	450	270
0.250	0.250	360	360
0.188	0.313	270	450
0.125	0.375	180	540
0.063	0.438	90	630
0.042	0.458	60	660
0.021	0.479	30	690
0.000	0.500	0	720
	$N = 300$		
0.500	0.000	360	0
0.450	0.050	324	36
0.375	0.125	270	90
0.250	0.250	180	180
0.167	0.333	120	240
0.100	0.400	72	288
0.050	0.450	36	324
0.025	0.475	18	342
0.000	0.500	0	360

[a] The size of the simulation box $L_{box} = 60$, and the total density $\phi_r + \phi_l = 0.5$.

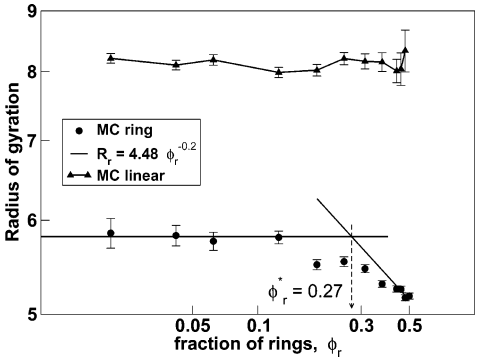

Figure 2. A log−log plot of the mean-squared radii of gyration of rings (circles) and linear chains (triangles) for a blend of ring and linear molecules with $N_r = N_l = 150$ at different compositions. As the fraction of the rings ϕ_r decreases, the cyclic molecules swell as linear chains pervade the volume occupied by them. The simultaneous effect on the size of the linear chains is negligible. We used the last four data points in the semidilute region to fit the straight line to R_r.

To measure the size of the rings and linear chains, we calculated the average radius of gyration

$$\langle R_g^2 \rangle = \frac{1}{N}\sum_{i=1}^{N}\langle(\mathbf{r}_i - \mathbf{r}_{cm})^2\rangle \tag{10}$$

where the summation index i runs over all the $N = N_r$ or N_l beads of a molecule located at $\mathbf{r}_i$, and the center of mass $\mathbf{r}_{cm}$ is defined by

$$\mathbf{r}_{cm} = \frac{1}{N}\sum_{i=1}^{N}\mathbf{r}_i \tag{11}$$

As mentioned earlier, angular brackets $\langle\cdot\rangle$ represent an average over all the molecules in the system. Figures 2 and 3 depict the radius of gyration of the rings and linear species for $N = 150$ and 300, respectively. As predicted by the scaling model (see eq 7), the size of the linears R_l appears to be

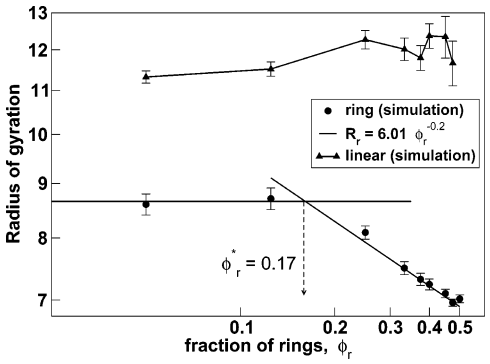

Figure 3. A log−log plot of the mean-squared radii of gyration of rings (circles) and linear chains (triangles) for a blend of ring and linear molecules with $N_r = N_l = 300$ at different compositions. We used the last six data points in the semidilute region to fit the straight line to R_r.

independent of the concentration of the rings ϕ_r and is approximately equal to the size of coil in the pure linear melt ($R_l(\phi_r = 0) = 7.95 \pm 0.10$ and 11.20 ± 0.17 for $N = 150$ and 300, respectively). The size of the error bars increases as $\phi_r \rightarrow 0.5$ because N_{pl} decreases (see Table 1).

The size of the ring polymers is not sensitive to ϕ_r at small concentration of rings. This is expected for a "dilute solution" of rings in an environment of linear chains, as a ring molecule cannot perceive the presence of other rings. In both Figures 2 and 3, the size of the ring polymer remains roughly constant, so long as $\phi_r < \phi_r^*$. Beyond the overlap concentration, $\phi_r > \phi_r^*$, the dispersion of rings enters the semidilute regime, and the size decreases in accordance with $R_r \sim \phi_r^{-1/5}$ as predicted by the scaling model (eq 6).

This well-defined, albeit weak, dependence on the concentration is in sharp contrast with *dynamical* properties of ring polymers, which are extremely sensitive to linear contaminants.[7] More recently, it has been reported that the terminal relaxation time of a polystyrene ring−linear blend (both components of molecular weight 200 kDa) with 5 vol % of the linear component is greater than the relaxation time of the linear chain itself.[27]

The intersection of dilute and semidilute regimes defines the overlap threshold concentration, ϕ_r^* which is equal to 0.27 and 0.17 for $N = 150$ and 300, respectively (see Figures 2 and 3). On the basis of the results for $N = 300$ and eq 2, we expect $\phi_r^*(N = 150) \approx 0.24$, which is in fair agreement with the observed value. It is interesting to note that in the pure ring melt, $R_r(N = 300, \phi_r = 0.5)/R_r(N = 150, \phi_r = 0.5) = 1.35 \pm 0.01 = (300/150)^{0.43}$. However, dilute rings are more expanded, and $R_r^{dil}(N = 300)/R_r^{dil}(N = 150) = 1.48 \pm 0.05 = (300/150)^{0.56\pm0.05}$ and suggests a larger slope. Although it is inappropriate to infer power laws from merely two data points, the reported trend is expected. The pressure imposed by the nonconcatenation constraint in a ring melt, which causes compression, is relaxed in a dilute dispersion of rings. Indeed, in a clever calculation, Brown et al.[18] capitalized on a unique geometrical feature of S-BFM which allows the chain uncrossability constraint to be easily switched on or off. When ring contours were allowed to cross each other, they found that the rings were swollen and obeyed a power law $R_r \sim N_r^{0.5}$.

In Figure 4, the two series are collapsed onto a master curve by normalizing the absicca with ϕ_r^*, and the ordinate with the size of the dilute rings R_r^{dil}. The universality observed essentially validates the scaling model proposed. The suggestion

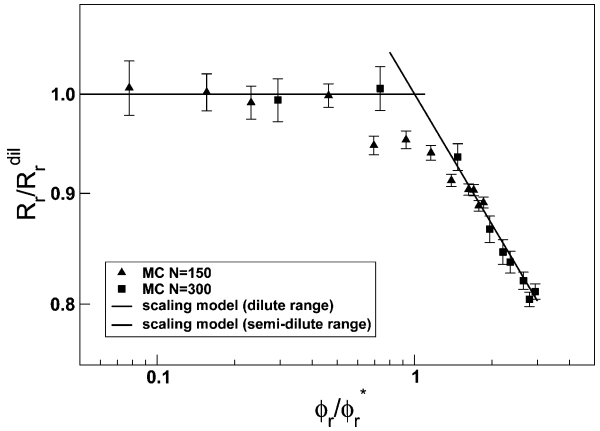

Figure 4. Master curve in which Figures 2 and 3 are superimposed by normalizing the axes.

that a ring polymer attains unperturbed dimensions only in the pure ring melt (eq 9) is also borne out in the master curve.

Although the agreement between the scaling model and S-BFM appears to be excellent, it is important to point out remaining ambiguities. The scaling model, in general, predicts that if $R_r \sim N_r^{\nu}$ for a pure ring melt, the concentration dependence of the size of a ring in a ring−linear blend in the semidilute regime is given by $R_r \sim \phi_r^{2\nu-1}$. As mentioned earlier, for $\nu = 0.4$, it implies $R_r \sim \phi_r^{-0.2}$. However, the S−BFM model yields $\nu = 0.43$. Thus, from the scaling argument, we would expect a weaker concentration dependence $R_r \sim \phi_r^{2\nu-1} \sim \phi_r^{-0.14}$. However, it may be pointed out that ν appears to approach 0.4, when only $N_r > 100$ are considered or when finite size effects are corrected for as suggested by Müller et al.[12] Finite size effects are also evident in Figure 2. As N_r increases from 150 to 300, the quality of agreement with the scaling model improves (see Figure 3). The scaling model assumes that the rings obey Gaussian statistics, an assumption that becomes increasingly more suitable as N_r increases.

Finally, in the ring−linear blends studied by Geyler and Pakula,[26] using a quasi-cubic lattice and a simple cooperative relaxation scheme, there is no evidence for a ϕ_r^* (see Figure 3 in their paper[26]) that characterizes a transition from the dilute to the semidilute regime. They observe a linear correlation $R_r^2 \sim \phi_l$ throughout the concentration window explored. However, in the absence of associated error bars, it is unclear how much confidence ought to be placed in the most dilute solutions of rings (which correspond to averages over only 4 rings for $N_r = 128$). Since $\phi_r^* \sim 1/\sqrt{N_r}$, we conjecture that the transition was pushed toward $\phi_l \rightarrow 1$ and went unobserved due to the large noise-to-signal ratio. Further, the BFM is a well-established model in which issues such as ergodicity and weighting of configuration states are better understood.[34]

4. Conclusions

We proposed a scaling model to predict the size of a ring polymer in a ring−linear blend. We found that in the dilute region the sizes of the components are independent of the concentration, and in the semidilute region while $R_l \sim c_r^0$ continues to be independent of concentration, $R_r \sim c_r^{-1/5}$. In addition, for ring polymers, we also found that the overlap concentration $c_r^* \sim N_r^{-1/2}$, and the concentration at which the ring attains unperturbed dimensions $c_r^{\dagger} \sim N_r^0$.

Acknowledgment. S.S. acknowleges Dimitris Vlassopoulous for sharing his viscoelastic data on ring−linear blends and CRC-PG 020837 at Florida State University for financial support.

Appendix

The number fraction of ring segments ϕ_r/ϕ is given by

$$\frac{\phi_r}{\phi} = \frac{N_{pr}N_r}{N_{pr}N_r + N_{pl}N_l} \tag{12}$$

where N_{pr} and N_{pl} are the number of ring and linear chains in the system, respectively. In this study, ring and linear polymers are consist of identical number of monomers ($N_r = N_l$). If the total density, $\phi = \phi_r + \phi_l$, of the system remains constant, then $N_{pr} + N_{pl}$ is also a constant for a given volume of the blend. Therefore, we have from eq 12 $(\phi_r/\phi_r^*) \sim (N_{pr}/N_{pr}^*) \sim (c_r/c_r^*)$, where ϕ_r^* is the number fraction at threshold concentration. Using this in eq 6, we have

$$R_r \sim \left(\frac{\phi_r}{\phi_r^*}\right)^{-1/5} \tag{13}$$

In the spirit of eq 1, the free energy of a ring−linear blend can be written as

$$F(R_r) = \frac{\phi_r}{\phi}\frac{R_r^3}{N_r} + \frac{N_r}{R_r^2} \tag{14}$$

where the free energy increase due to the nonconcatenation constraint is assumed to be proportional to the fraction of ring neighbors of any given ring. Minimizing this free energy, one obtains

$$R_r \sim (\phi_r/\phi)^{-1/5} N_r^{2/5} \tag{15}$$

Comparing the scaling results in eq 13 with the free energy based scaling results in eq 15, we see that the results of free energy minimization corroborate with the concentration scaling arguments.

References and Notes

(1) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(2) Roovers, J. *Macromolecules* **1985**, *18*, 1359−1361.
(3) Mckenna, G.; Hadziioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. *Macromolecules* **1987**, *20*, 498−512.
(4) Roovers, J.; Toporowski, P. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 1251−1259.
(5) Mckenna, G.; Hostetter, B.; Hadjichristidis, N.; Fetters, L.; Plazek, D. *Macromolecules* **1989**, *22*, 1834−1852.
(6) The latter observation is controversial, since the presence of a small fraction of knotted or "Olympic" rings and linear contaminants in these samples cannot be ruled out, which could explain the presence of a plateau modulus.
(7) McKenna, G. B.; Plazek, D. J. *Polym. Commun.* **1986**, *27*, 304−306.
(8) Cates, M.; Deutsch, J. *J. Phys. (Paris)* **1986**, *47*, 2121−2128.
(9) Rubinstein, M. *Phys. Rev. Lett.* **1986**, *57*, 3023−3026.
(10) Obukhov, S.; Rubinstein, M.; Duke, T. *Phys. Rev. Lett.* **1994**, *73*, 1263−1266.
(11) Iyer, B. V. S.; Lele, A. K.; Juvekar, V. A. *Phys. Rev. E* **2006**, *74*, 021805.
(12) Müller, M.; Wittmer, J.; Cates, M. *Phys. Rev. E* **1996**, *53*, 5063−5074.
(13) Brown, S.; Szamel, G. *J. Chem. Phys.* **1998**, *108*, 4705−4708.
(14) Brown, S.; Szamel, G. *J. Chem. Phys.* **1998**, *109*, 6184−6192.
(15) Deutsch, J. M. *Phys. Rev. E* **1999**, *59*, R2539−R2541.
(16) Müller, M.; Wittmer, J.; Barrat, J. *Europhys. Lett.* **2000**, *52*, 406−412.

(17) Müller, M.; Wittmer, J.; Cates, M. *Phys. Rev. E* **2000**, *61*, 4078−4089.
(18) Brown, S.; Lenczycki, T.; Szamel, G. *Phys. Rev. E* **2001**, 6305.
(19) Ozisik, R.; von Meerwall, E.; Mattice, W. *Polymer* **2002**, *43*, 629−635.
(20) Hur, K.; Winkler, R.; Yoon, D. *Macromolecules* **2006**, *39*, 3975−3977.
(21) In a brute-force simulation, the equilibration time would be on the order of the reptation time which scales roughly as the third power of the length of the chains. These equilibration strategies aim to reduce the equilibration time below the reptation time.
(22) Mavrantzas, V.; Boone, T.; Zervopoulou, E.; Theodorou, D. *Macromolecules* **1999**, *32*, 5072−5096.
(23) Siepmann, J.; Frenkel, D. *Macromolecules* **1992**, *75*, 59−70.
(24) Auhl, R.; Everaers, R.; Grest, G. S.; Kremer, K.; Plimpton, S. J. *J. Chem. Phys.* **2003**, *119*, 12718−12728.
(25) Weyersberg, A.; Vilgis, T. A. *Phys. Rev. E* **1994**, *49*, 3097−3101.
(26) Geyler, S.; Pakula, T. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 617−623.
(27) Kapnistos, M.; Lang, M.; Rubinstein, M.; Roovers, J.; Chang, T.; Vlassopoulos, D. Presented at the Society of Rheology Annual Meeting, 2006.
(28) de Gennes, P. *Scaling Concepts in Polymer Physics*, 1st ed.; Cornell University Press: Ithaca, NY, 1979.
(29) Arrighi, V.; Gagliardi, S.; Dagger, A.; Semlyen, J.; Higgins, J.; Shenton, M. *Macromolecules* **2004**, *37*, 8057−8065.
(30) Shaffer, J. S. *J. Chem. Phys.* **1994**, *101*, 4205−4213.
(31) Carmesin, I.; Kremer, K. *Macromolecules* **1988**, *21*, 2819−2823.
(32) Shanbhag, S.; Larson, R. G. *Phys. Rev. Lett.* **2005**, *94*, 076001.
(33) Shanbhag, S.; Larson, R. G. *Macromolecules* **2006**, *39*, 2413−2417.
(34) Shaffer, J. S. *J. Chem. Phys.* **1995**, *103*, 761−772.
(35) The average number of monomers per entanglement (for linear chains) has been reported to be around $N_e \approx 30$.

MA0709295