a higher molecular weight of PAA.

Acknowledgment. This work was supported by the Polymers Program of the National Science Foundation through Grant DMR 84-07847 and in part by the Army Research Office through Contract DAAG 29-82-K-0019.

Registry No. PEG*–PAA complex, 106250-10-6.

References and Notes

(1) Bekturov, E. A.; Bimendina, L. A. *Adv. Polym. Sci.* **1981**, *41*, 99.
(2) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*.
(3) Anufrieva, E. V.; Pautov, V. D.; Geller, N. M.; Krakoviak, M. G.; Papisov, I. M. *Dokl. Akad. Nauk SSSR* **1975**, *220*, 353.
(4) Bednář, B.; Li, Z.; Huang, Y.; Chang, L.-C. P.; Morawetz, H. *Macromolecules* **1985**, *18*, 1829.
(5) Chen, H. L.; Morawetz, H. *Eur. Polym. J.* **1983**, *19*, 923.
(6) Chen, H. L.; Morawetz, H. *Macromolecules* **1982**, *15*, 1445.
(7) Bednář, B.; Morawetz, H.; Shafer, J. A. *Macromolecules* **1984**, *17*, 1634.
(8) Anufrieva, E. V.; Pautov, V. D.; Papisov, I. M.; Kabanov, V. A. *Dokl. Akad. Nauk SSSR* **1977**, *232*, 1096.
(9) Oyama, H. T.; Nakajima, T. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2987.
(10) Takahashi, A.; Hayashi, N. ; Kagawa, I. *Koka* **1957**, *60*, 1059.
(11) Cuniberti, C.; Perico, A. *Eur. Polym. J.* **1977**, *13*, 369.
(12) Oyama, H. T.; Frank, C. W. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1813.
(13) Cheung, S.; Winnik, M. A.; Redpath, A. E. C. *Makromol. Chem.* **1982**, *183*, 1815.
(14) Tanford, C. *Physical Chemistry of Macromolecules*; Wiley: New York, 1961; p 178.
(15) Char, K.; Frank, C. W.; Gast, A. P.; Tang, W. T. *Macromolecules*, submitted.
(16) Antipina, A. D.; Baranovskii, V. Yu.; Papisov, I. M.; Kabanov, V. A. *Vysokomol. Soedin., Ser. A* **1972**, *14*, 941 (translated in *Polym. Sci. USSR (Engl. Transl.)* **1972**, *14*, 1047).
(17) Ikawa, T.; Abe, K.; Honda, K.; Tsuchia, E. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1505.
(18) Papisov, I. Mm.; Baranovskii, V. Yu.; Kabanov, V. A. *Vysokomol. Soedin., Ser. A* **1975**, *17*, 2104 (translated in *Polym. Sci. USSR (Engl. Transl.)* **1975**, 17, 2428.

Topological Constraints and Their Influence on the Properties of Synthetic Macromolecular Systems. 1. Cyclic Macromolecules

G. ten Brinke[†] and G. Hadziioannou*

IBM Almaden Research Center, San Jose, California 95120-6099. *Received May 31, 1986*

ABSTRACT: Monte Carlo simulations of closed random walks on a body-centered cubic lattice are used to investigate the influence of the average knot structure on the root mean square radius of gyration R_g and scattering function $P(q)$ of flexible ring polymers obtained by cyclization under Θ-conditions. Calculations are carried out for walks of 10 to 160 steps. Considered as an equivalent chain model for ring polystyrene, this corresponds to molecular weights $M_n \leq 120000$. Up to 37% of the ring molecules are shown to be knotted. The influence of the number and kind of knots on R_g is presented in some detail. Removing part or all of the unknotted rings produces a more pronounced maximum in the Kratky plot of the scattering function. Comparisons are made with experimental small-angle neutron scattering data for cyclic polystyrene in deuteriated cyclohexane.

1. Introduction

The recent synthesis of ring-shaped polystyrenes via anionic polymerization has led to a number of interesting experimental studies involving these polymers.[1-6] It is believed that a detailed investigation of the properties of ring polymers, in dilute solution and in the melt, may ultimately result in a better understanding of the first principles governing the behavior of macromolecules.

Experiments carried out in dilute solution at the Θ-temperature for linear polystyrene (cyclohexane, 35 °C) show a positive second virial coefficient A_2 for ring polystyrene.[1] Theoretically, this was already predicted by Vologodskii et al.,[7,8] who showed that the condition of conservation of the topological state of the system (absence of linkage, or linkage of a definite type such as catenates) leads to entropy-type interactions between the chains. These interactions were shown to be quite appreciable and effectively forbid any mutual penetration of unlinked polymer rings. Hence, intermolecular excluded volume effects will be present in dilute solutions of ring polymers in Θ-solvents of the corresponding linear polymers. For linear polymers, the Θ-temperature (normal Θ-temperature) is generally considered to be the temperature of unperturbed dimensions, vanishing second virial coefficient, and onset of phase separation.[9] Candau et al.[10] showed that for star polymers, these three properties do not necessarily occur at the same temperature. Combining the strongly increased density inside the coil of a highly branched polymer with a segment density dependent χ-parameter, they were able to show that the temperature of unperturbed dimensions, Θ_α, is in general lower than the temperature, Θ_{A_2}, of vanishing second virial coefficient. Both are below the Θ-temperature of the corresponding linear polymer. The density inside the coil of a ring polymer is also higher than for a linear polymer, but the difference is too small[11] to give rise to similar effects.

The topological interaction between two unlinked ring polymers is always present and gives rise to a positive second virial coefficient at the normal Θ-temperature. However, if rings of all types of knot structures are present in proportions dictated by ring closure under Θ-conditions, the Θ-temperature of linear polymers should be the temperature of unperturbed dimensions of ring polymers, too. If, on the other hand, ring closure takes place under conditions giving rise to a nearly complete absence of knots, as is the case for cyclization in good solvents, the situation is somewhat different. It is generally believed that knot-free rings (trivial rings) should also show intramolecular excluded volume behavior due to the topological constraints, even at the normal Θ-temperature. So far, numerical simulations have not been able to confirm this. des Cloizeaux et al.[12] went as far as investigating unknotted

---

[†] Permanent address: Department of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.

0024-9297/87/2220-0480$01.50/0

rings of 280 steps, and still did not observe a large difference in the molecular weight dependence of R_g from the random walk predictions. The asymptotic regime is apparently far away.

Experimentally, slightly different values are found for the Mark–Houwink exponent, a, of the intrinsic viscosity of ring polystyrenes in cyclohexane at 35 °C.[2,13] This should come as no surprise, since the above discussion shows that the situation for ring polymers is very much like that of gels and glasses. In all cases, a correct description involves two ensembles, the "preparative ensemble" and the "final ensemble".[14]

It is the purpose of this paper to investigate the influence of the knot structure on the root mean square radius of gyration and scattering function of ring polymers in the molecular weight range of interest. This is accomplished by using Monte Carlo calculation of a random walk lattice model and using the equivalent chain concept[15] to establish the connection with real polymer systems. Semlyen and co-workers[16] combined Monte Carlo calculations with the rotational isomeric state model to calculate the scattering function for short cyclic poly(dimethylsiloxanes). However, no effort was made to distinguish between knotted and unknotted rings.

2. Theoretical Model

To study the influence of knots on various properties of ring polymers, the Monte Carlo method is used to create closed walks on a lattice. Only random walks will be considered since it is well-known[17,31] that the probability of knot formation for self-avoiding walks is very small. To investigate the knot structure, it is obviously necessary to avoid true intersections. This is realized by a procedure introduced by Vologodskii et al.[17] Every time the end point of a step coincides with the end point of a previous step, it is shifted by a very small distance in a randomly chosen direction. For a long random walk, the probability of returning to the origin after a given number of steps becomes vanishingly small. To avoid unnecessary calculations, it is therefore desirable to introduce an enrichment factor. As noted by Vologodskii et al.,[7] the body-centered cubic (bcc) lattice is particularly well suited in this respect. This will be shown first. Nearest neighbors on a bcc lattice differ by a vector $\vec{\delta} = (\delta_1, \delta_2, \delta_3)$ where $\vec{\delta}$ is one of eight different possibilities given by $\delta_i = \pm 1$, $i = 1, 3$. A random walk on this lattice is therefore a combination of three independent random walks. One of these one-dimensional random walks will be considered first. Suppose the walk is required to return to the origin after $2N$ steps and suppose position x_1 is reached after $2N - k$ steps have been completed. The total number of random walks that lead to the origin from x_1 in precisely the remaining k steps is given by[18] $\binom{k}{(k - x_1)/2}$. A subsequent step will go to either $x_1 + 1$ or $x_1 - 1$. The total number of random walks that reach the origin in $k - 1$ steps from $x_1 + 1$ and $x_1 - 1$ is given by $\binom{k-1}{(k-1-(x_1+1))/2}$ and $\binom{k-1}{(k-1-(x_1-1))/2}$, respectively. Therefore, the fraction of walks that reaches the origin in k steps from x_1 via $x_1 + 1$ and $x_1 - 1$ is $(k - x_1)/2k$ and $(k + x_1)/2k$, respectively. To create a closed one-dimensional random walk a probability $(k - x_1)/2k$ is given to continuation $\delta_1 = 1$ and a probability $(k + x_1)/2k$ to continuation $\delta_1 = -1$. For the three-dimensional random walk on a bcc lattice, this amounts to

$$P(k,\vec{r},\vec{\delta}) = \prod_{i=1}^{3} \frac{k - \delta_i x_i}{2k} \tag{2.1}$$

where $P(k,\vec{r},\vec{\delta})$ denotes the probability of continuing to $\vec{r} + \vec{\delta}$ if $\vec{r}$ is the position reached after $2N - k$ steps have been completed.[17] Strictly speaking, this procedure violates the independence of different steps.[31,32] But, the above discussion shows that the bias is such that accurate results should be obtained. Other methods have been introduced,[31-33] but this one has the advantage that it can easily be adapted to completely different problems, such as tight knots in the case of crystallization or knots in loops in the case of adsorption. In ref 17, backsteps were not allowed. To make a simple comparison with higher molecular weight polystyrene possible, backsteps were allowed in the present study. A backstep is, as pointed out before, also accompanied by a very small shift in an arbitrary direction of its end point.

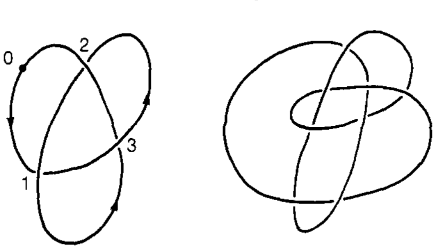

Figure 1. The simplest knot, 3_1, and the simplest knot not equal to 3_1, for which the Alexander polynomial evaluated at $t = -1$ is also 3.

Once closed, random walks are constructed, the next step is to investigate their knot structure. In this paper, three different subsets of rings will be considered separately: the unknotted (trivial) rings, rings containing an arbitrary knot, and rings containing the simplest type of knot, called a 3_1 knot. Figure 1 shows an example of the latter and also a more complicated knot. A convenient way to distinguish different types of knots is based on the Alexander polynomial.[19,20] Equivalent knots have the same Alexander polynomial and most, but not all, nonequivalent knots have different Alexander polynomials. This polynomial is calculated from a minor M of the Alexander matrix $\mathbf{A}$ of a ring in the following way.

First, a two-dimensional projection of the closed lattice walk must be made in such a way that the only multiple points are double points. In our case, this is accomplished by rotating the walk around the x axis over a suitable angle, followed by the xy projection. Next, the intersections in the xy projection are numbered in order of underpass by fixing a sense of direction along the contour (see Figure 1). Which part is underpass and which is overpass is determined by the value of the z coordinate before projection. Suppose a walk has K intersections in its projection. To every intersection belongs an underpass and an overpass. The overpass of a given underpass i is part of an arch which lies in between two subsequent underpasses, say j and $j + 1$, where, here and in the following, the indices are modulo K. The nonzero elements of the $\mathbf{K} \times \mathbf{K}$ Alexander matrix $\mathbf{A}$ are then given by the following:

1. If $j + 1$ equals i or $i + 1$

$$a_{i,i} = -1 \qquad a_{i,i+1} = 1$$

2. Otherwise, depending on the type of intersection

$$\text{type I:}\ a_{i,i} = 1,\ a_{i,i+1} = -t,\ \text{and}\ a_{i,j+1} = t - 1$$

$$\text{type II:}\ a_{i,i} = -t,\ a_{i,i+1} = 1,\ \text{and}\ a_{i,j+1} = t - 1$$

The definitions of types I and II are given in Figure 2. The arrows indicate the sense of direction fixed in the beginning.

Following this procedure for the 3_1 knot presented in Figure 1, the Alexander matrix is easily found to be

$$\mathbf{A} = \begin{pmatrix} 1 & -t & t-1 \\ t-1 & 1 & -t \\ -t & t-1 & 1 \end{pmatrix} \tag{2.2}$$

Table I
Results of Monte Carlo Calculations

				root mean square radius of gyration, Å			
no. of steps N	no. of rings	no. of knotted rings	no. of 3_1 knots	all rings	trivial rings	knotted rings	3_1 knots
10	45000	189 (0.4%)	182 (0.4%)	17.58	17.58	14.84	14.88
20	10000	234 (2.3%)	196 (2.0%)	24.24	24.31	20.74	20.96
40	3000	251 (8.4%)	196 (6.5%)	33.90	34.20	30.11	30.35
50	3000	290 (9.7%)	219 (7.3%)	37.92	38.35	33.65	34.79
60	2200	282 (12.8%)	184 (8.4%)	41.24	41.79	37.36	38.39
80	2000	382 (19.1%)	245 (12.2%)	47.57	48.37	43.90	44.83
100	2000	511 (25.6%)	306 (15.3%)	53.49	54.95	48.99	50.85
120	1500	422 (28.1%)	249 (16.6%)	58.25	59.93	53.79	55.69
140	1000	331 (33.1%)	174 (17.4%)	62.32	63.65	59.57	61.73
160	1000	374 (37.4%)	206 (20.6%)	67.33	69.22	64.04	65.87
				±0.47	±0.58	±0.88	±0.94

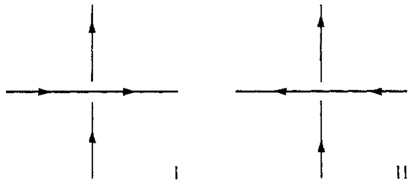

Figure 2. The two different types of intersection.

In general, it is a **K** × **K** matrix from which the Alexander polynomial $\Delta(t)$ is found by calculating any of its $(K-1)\times(K-1)$ minors. Then the result is multiplied by a factor $\pm t^{-m}$, where the sign and the integer m are chosen in such a way that the resulting polynomial contains a positive constant and only nonnegative powers of t. For the Alexander matrix of eq 2.2, this applies

$$\Delta(t) = \pm t^{m} \begin{vmatrix} 1 & -t \\ t-1 & 1 \end{vmatrix} = t^2 - t + 1 \qquad (2.3)$$

where the plus sign and $m = 0$ had to be used.

In the mathematical literature knots are classified according to the minimum number of intersections in their projections. References 19 and 20 contain a list of the Alexander polynomials of all the 84 different knots having less than or equal to nine intersections in this projection. For all these knots, $\Delta(t = -1) \neq 1$, whereas for a trivial ring $\Delta(t) \equiv 1$. Furthermore, only for the 3_1 knot and the 8_{19} knot, also presented in Figure 1, $\Delta(t = -1) = 3$. Moreover, for the walks considered in this paper, the number of 8_{19} knots will be very small if not zero.[17] Since the Alexander polynomial is found from the minor $M(t)$ of the Alexander matrix by multiplying with $\pm t^m$, the former can just as well be used to distinguish in a very good approximation between various subsets of rings. In this paper, rings will therefore be classified according to

$$M(-1) = \pm 1 \Rightarrow \text{unknotted rings}$$

$$M(-1) \neq \pm 1 \Rightarrow \text{knotted rings}$$

$$M(-1) = \pm 3 \Rightarrow 3_1 \text{ knots}$$

In fact, a far more detailed classification is possible, but the number of walks constructed with more complicated knot structures is too small to allow any reliable statistical average.

The comparison between numerical results and experimental results for ring polystyrene will be based on the equivalent chain concept.[15] A polystyrene chain of n C–C bonds under Θ-conditions will be represented by a random walk of n' steps of length l' on a bcc lattice by requiring

$$n'l' = r_{\max} n'l'^2 = \langle r^2 \rangle_0 \qquad (2.4)$$

where $r_{\max}$ is the length of a fully extended polystyrene chain, and $\langle r^2 \rangle_0$ the mean square end-to-end distance. Since $r_{\max} \simeq 0.83na$, $a = 1.53$ Å, and $\langle r^2 \rangle_0 = C_\infty na^2$ with the characteristic ratio $C_\infty \simeq 10.0$, a step on the bcc lattice corresponds to approximately 14.5 C–C bonds with $l' \simeq 12a$. This approach is necessarily of a semiquantitative nature. It describes correctly the spatial properties of long molecules but it is less accurate as far as the topological structure is concerned. Recently, Iwata et al.[34,35] discussed the topological interaction among ring polymers. On the basis of the experimental data of Roovers and Toporowski[30] for the second virial coefficient of PS in cyclohexane at 35 °C, Iwata[35] estimated that one step on a 6-choice simple cubic lattice model corresponds to approximately 7 C–C bonds of PS. Since, considered as an equivalent chain model, one step on a 6-choice simple cubic lattice corresponds to 14.5 C–C bonds, this indicates that flexibility is not the only parameter determining the topological structure.

3. Results and Discussion

Part of the results of the Monte Carlo calculations are summarized in Table I. As mentioned before, four different sets of rings were investigated. Columns 3 and 4 contain the number and percentage of knotted rings and rings with 3_1 knots. They are nearly identical with previously obtained results by Vologodskii et al.[17] and des Cloizeaux et al.[12] despite the differences in theoretical approaches. In ref 12, off-lattice Monte Carlo calculations were used, whereas, as discussed before, backsteps were not allowed in ref 17. It illustrates once more the limitations involved in using the equivalent chain concept. A step on a 7-choice body-centered cubic lattice, as adopted by Vologodskii et al.,[17] corresponds to an n' which is approximately 15% smaller than for the 8-choice model. If flexibility was the only determining factor, this should have led to a difference in the fraction of knotted walks larger than the statistical errors involved. Applied to polystyrene, our data indicate that for a molecular weight in the range of 10^5 approximately 30% of all rings can be knotted. This number is twice as large as predicted by Roovers,[1] using a scaling type argument. The root mean square radii of gyration for the different sets are given in columns 5–8, expressed in angstroms. The probable statistical errors involved are given for $N = 160$. For other values of N, they are of the small or smaller relative order of magnitude.

Figure 3 shows a log–log plot of the root mean square radius of gyration R_g of all rings (curve a) and all knotted rings (curve b) vs. the length N of the ring. A similar plot for the trivial rings (curve a) and rings with a 3_1 knot (curve b) is given in Figure 4. Generally,[14] the exponent ν is introduced to describe the dependence of R_g on N according to the scaling relation

$$R_g \sim N^{\nu} \qquad (3.1)$$

Table II lists the apparent values of ν for the different sets

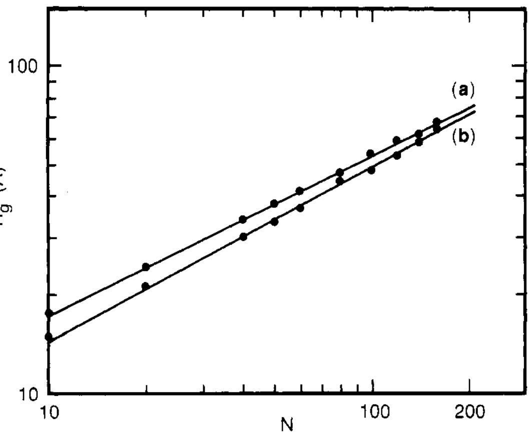

Figure 3. log–log plot of the root mean square radius of gyration R_g vs. length N: (a) all rings (knotted and unknotted); (b) all knotted rings.

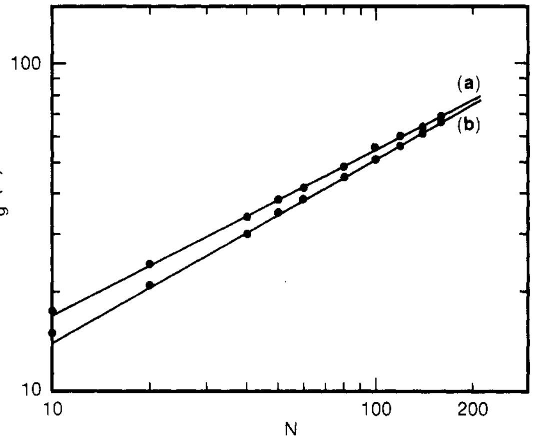

Figure 4. log–log plot of the root mean square radius of gyration R_g vs. length N: (a) unknotted rings; (b) 3_1 knots.

Table II
Exponent ν

(sub)set	ν
all rings	0.492 ± 0.01
trivial rings	0.503 ± 0.01
knotted rings	0.542 ± 0.02
3_1 knots	0.551 ± 0.02

of walks, apparent because we are still far away from the asymptotic region of large N where a relation like eq 3.1 is supposed to hold. Only the value for all rings is within the statistical error of the theoretically predicted random walk value $^1/_2$. As found previously by des Cloizeaux et al.,[12] the exponent of the trivial rings is also approximately $^1/_2$, notwithstanding the fact that the true value is believed to be identical with the excluded volume exponent ($\simeq$0.59) of closed self-avoiding walks[21] and linear self-avoiding walks,[14] but Table I also shows that the difference between the root mean square radius of gyration of all rings and of the unknotted rings, although small, steadily increases. The calculated difference of 0.01 for the corresponding values of ν (Table II) may well be real for the molecular weight range investigated. Assuming non-free-draining conditions, this translates into a difference of 0.03 ($a = 3\nu - 1$) for the Mark–Houwink exponent, a, of the intrinsic viscosity relation $[\eta] = KM^a$. As such, it could explain the value of $a = 0.53$ found by Lutz et al.[13] for ring polystyrene in cyclohexane at 35 °C. This tentative explanation implies that the samples used are nearly free of knots, an observation which, as will be shown further on, is not in conflict with our neutron scattering results.

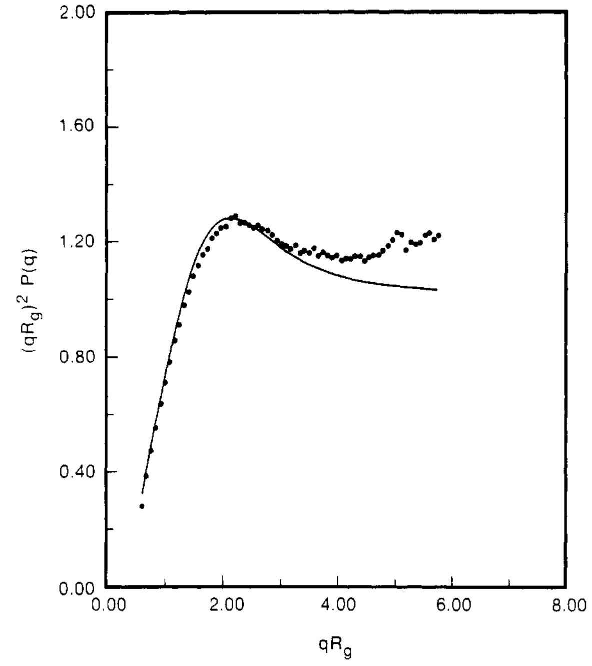

Figure 5. Kratky plot of SANS data of ring PS in deuteriated cyclohexane at 33 °C, together with the theoretically predicted scattering function (drawn curve).

The value of $\nu \simeq 0.55$ for rings with a 3_1 knot is at first somewhat unexpected. Although, also in this case, the true value may be due to the topological constraint turn out to be larger than 0.5, we certainly are not in the asymptotic region yet. This follows simply from the fact that the fraction of total rings with a 3_1 knot is still increasing at $N = 160$. The same argument holds for the set of all knotted rings. In both cases, the large value of ν is due to the fact that the constraint of having a knot becomes less severe as N increases. This also explains why the value of ν for rings with a 3_1 knot is larger than for rings with an arbitrary knot. In the latter case, larger values of N introduces new, more complicated knots, thereby suppressing the relaxation of the constraint.

Accurate measurements of the dimensions of ring polymers are one way of obtaining information about the average knot structure of the system, but the Monte Carlo results presented in Table I show that the differences will in general be small unless an unknotted sample is compared with a sample containing a more than average number of knots. A more complete picture is obtained by investigating the influence of the knot structure on the scattering function of ring polymers. Figure 5 presents the experimental data of neutron scattering measurements on a dilute solution of ring polystyrene in deuteriated cyclohexane at 33 °C.[6] The molecular weight of this particular sample is given by $M_w = 79\,500$ and the root mean square radius of gyration $R_{g,ring} = 56$ Å.[6] The experimental results are plotted in a Kratky plot, i.e., $(qR_{g,ring})^2P(q)$ as a function of $qR_{g,ring}$, where $P(q)$ is the particle scattering function and q the length of the scattering vector. Theoretically, $P(q)$ for a flexible ring was first derived by Casassa.[22] It is given by

$$P(q) = {}^2\!/_3 D(R_{g,lin}q/2) \qquad (3.2)$$

where $D(x)$ is the Dawson integral defined by

$$D(x) = e^{-t^2}\int_0^{x^2} e^{-t^2}\,dt \qquad (3.3)$$

$R_{g,lin}$ is the root mean square radius of gyration of the corresponding flexible linear chain, which theoretically is

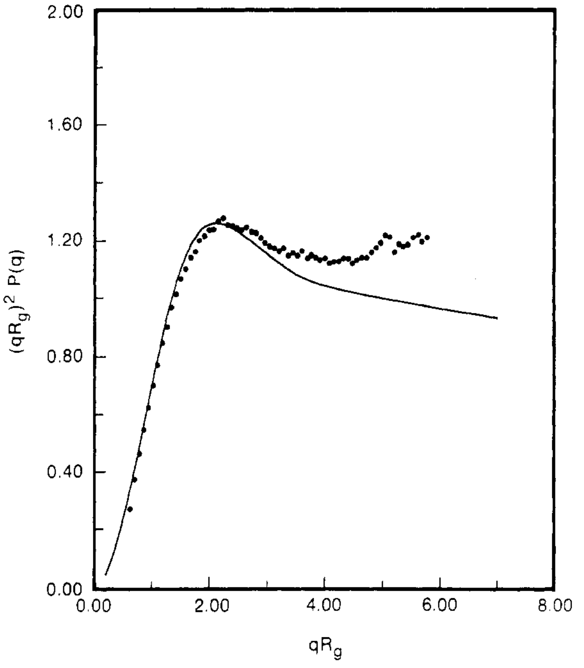

Figure 6. Kratky plot of SANS data of ring PS in deuteriated cyclohexane at 33 °C, together with the scattering function for unknotted rings as calculated by Monte Carlo simulations (drawn curve).

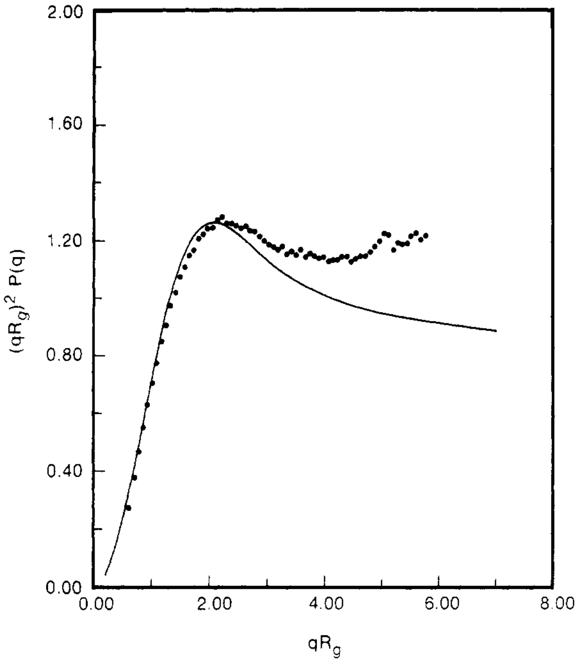

Figure 7. Kratky plot of SANS data of ring PS in deuteriated cyclohexane at 33 °C, together with the scattering function for all rings (knotted and unknotted) as calculated by Monte Carlo simulations (drawn curve).

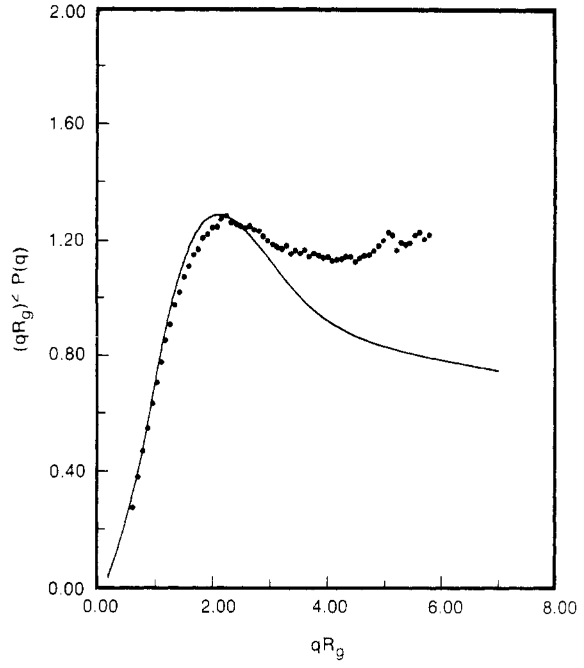

Figure 8. Kratky plot of SANS data of ring PS in deuteriated cyclohexane at 33 °C, together with the scattering function for all knotted rings as calculated by Monte Carlo simulation (drawn curve).

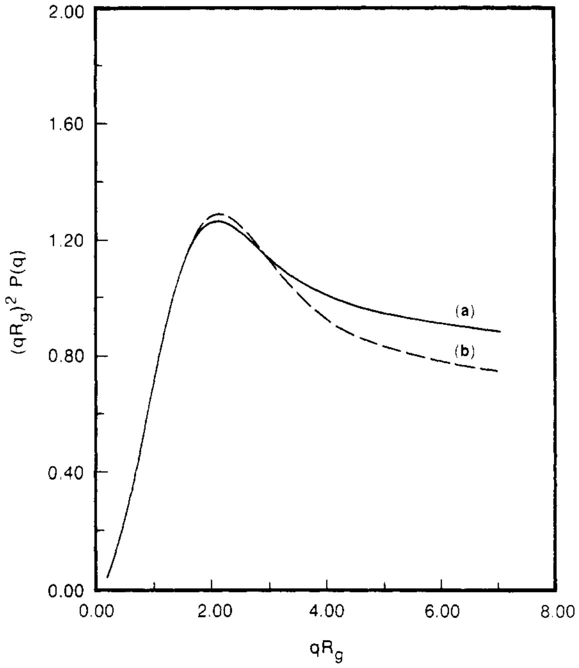

Figure 9. Comparison between the Monte Carlo calculations of the scattering function for all rings (knotted and unknotted) (curve a) and all knotted rings (curve b).

related to the root mean square radius of gyration of the flexible ring polymer $R_{\mathrm{g,ring}}$ by[11]

$$R_{\mathrm{g,lin}} = 2^{1/2}R_{\mathrm{g,ring}} \tag{3.4}$$

The theoretical curve is also presented in Figure 5, and is in reasonable agreement with the experimental data. Figures 6–8 show the same experimental data and the Monte Carlo calculations of the scattering function of trivial rings, knotted + unknotted rings, and knotted rings, respectively, for $N = 106$. This last figure corresponds to a molecular weight of approximately 79 500 on the basis of the equivalent chain model discussed before. The experimental data compare most favorably with the calculated scattering function of the trivial rings but a number of knots characteristic for cyclization under Θ-conditions cannot really be excluded. A more than average number of knots seems to be very unlikely.

Figure 9 presents a direct comparison between the scattering function of all rings (knotted and unknotted) and all knotted rings. It shows that a more knotted structure gives rise to a more pronounced maximum. This occurs because the constraints imposed by knots increase the segment density around the center of mass. A similar effect is observed in the case of star molecules where, for a given molecular weight, the maximum in the Kratky plot becomes more pronounced if the number of arms is in-

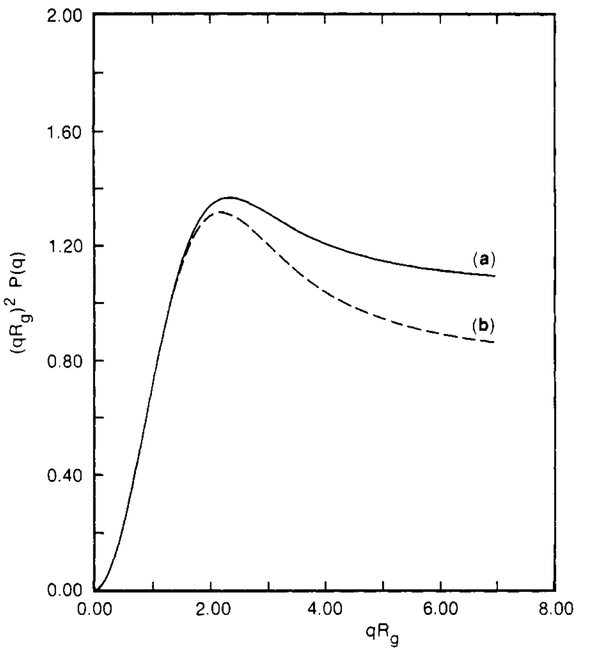

Figure 10. Comparison between the theoretically predicted scattering functions of star molecules of 5 arms (curve a) and 7 arms (curve b).

creased.[23,24] In fact, a more detailed comparison is possible. The scattering function for flexible star molecules is exactly known[25]

$$P(q) = \frac{2}{R_{\mathrm{g,lin}}^2 q^2}\left[\frac{f}{2}(f-1)e^{-2qR_{\mathrm{g,lin}}/f} - f(f-2)e^{-R_{\mathrm{g,lin}}q/f} + R_{\mathrm{g,lin}}q + \frac{f}{2}(f-3)\right] \quad (3.5)$$

where $R_{\mathrm{g,lin}}$ is the root mean square radius of gyration of the corresponding flexible linear chain of equal molecular weight and f is the number of arms. $R_{\mathrm{g,lin}}$ is related to the root mean square radius of gyration of the star molecules $R_{\mathrm{g,star}}$ by[11]

$$R_{\mathrm{g,star}}^2 = \frac{3f-2}{f^2}R_{\mathrm{g,lin}}^2 \quad (3.6)$$

It is well-known that the scattering functions of 5-arm star molecules and ring molecules are very similar.[22,24] Table I shows that in the range $N = 100$–120 removal of all trivial rings from the set containing all rings (knotted as well as unknotted) results in an approximately 10% smaller value for the root mean square radius of gyration. Equation 3.6 shows that about the same reduction may be obtained for star molecules by increasing the number of arms from 5 to 7. Figure 10 presents the theoretical predictions according to eq 3.5 for $f = 5$ (curve a) and $f = 7$ (curve b). The value used for $R_{\mathrm{g,lin}} = 77.44$ Å and corresponds to $N = 106$ of the equivalent chain. A comparison with Figure 9 confirms that the maximum becomes more pronounced in a similar fashion, but there is also a small difference. For rings polymers, the removal of unknotted rings slightly increases the height of the maximum, a fact invariably present in all the scattering functions calculated for different ring sizes. The introduction of more arms in the case of star polymers, on the other hand, decreases the value of the maximum.

4. Concluding Remarks

Methods of synthesizing ring polystyrenes have been discussed by various groups.[26-30] An important step in the whole process is the separation of ring molecules from the crude reaction product by either fractionated precipitation or preparative GPC. Knotted structures generally have smaller average dimensions. If knots are present, separation by GPC may therefore, in principle, be used to obtain fractions containing different amounts of knotted rings. In this way, we hope to confirm the main predictions of this work, which can be summarized as follows. If cyclization takes place under Θ-conditions, a large number of knots are present, even for moderate values of the molecular weight. Gradually removing the rings with the larger average dimensions should, in this case, lead to a more pronounced maximum in the Kratky plot of the neutron scattering in dilute solutions. And finally, in order to compare properties measured for different samples of this new class of macromolecules, special attention should be paid to the experimental preparative protocol, namely, cyclization temperature and fractionation procedure.

Acknowledgment. G.t.B acknowledges the financial support of IBM World Trade and IBM Netherlands and the hospitality of the staff of IBM Almaden Research Center, San Jose.

Registry No. PS, 9003-53-6.

References and Notes

(1) Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1117.
(2) Roovers, J. *Macromolecules* **1985**, *18*, 1359.
(3) Ragnetti, M.; Geiser, D.; Höcker, H.; Oberthür, R. C. *Makromol. Chem.* **1985**, *186*, 1701.
(4) Mills, P. J.; Mayer, J. W.; Kramer, E. J.; Hadziioannou, G.; Lutz, P.; Strazielle, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 513.
(5) McKenna, G. B.; Hadziioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 498.
(6) Hadziioannou, G.; Cotts, P.; ten Brinke, G.; Han, C.; Lutz, P.; Strazielle, C.; Rempp, P.; Kovacs, A. *Macromolecules* **1987**, *20*, 493.
(7) Vologodskii, A. V.; Lukashin, A. V.; Frank-Kamenetskii, M. D. *Sov. Phys.—JETP (Engl. Transl.)* **1975**, *40*, 932.
(8) Frank-Kamenetskii, M. D.; Lukashin, A. V.; Vologodskii, A. V. *Nature (London)* **1975**, *258*, 398.
(9) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(10) Candau, F.; Rempp, P.; Benoit, H. *Macromolecules* **1972**, *5*, 627.
(11) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(12) des Cloizeaux, J.; Mehta, M. L. *J. Phys. (Paris)* **1979**, *40*, 665.
(13) Lutz, P.; Strazielle, C.; Rempp, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*(1), 190.
(14) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca (NY) and London, 1979.
(15) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.
(16) Edwards, C. J. C.; Richards, R. W.; Stepto, R. F. T.; Dodgson, K.; Higgins, J. S.; Semlyen, J. A. *Polymer* **1984**, *25*, 365.
(17) Vologodskii, A. V.; Lukashin, A. V.; Frank-Kamenetskii, M. D.; Anshelevich, V. V. *Sov. Phys.—JETP (Engl. Transl.)* **1974**, *39*, 1059.
(18) Feller, W. *An Introduction to Probability Theory and Its Applications*; Wiley: New York, 1968; Vol. 1.
(19) Alexander, J. W. *Trans. Am. Math. Soc.* **1928**, *30*, 275.
(20) Reidemeister, K. *Ergeb. Math.* **1932**, *1*, No. 1.
(21) Baumgärtner, A. *J. Chem. Phys.* **1982**, *76*, 4275.
(22) Casassa, E. F. *J. Polym. Sci., Part A* **1965**, *3*, 605.
(23) Burchard, W. *Macromolecules* **1977**, *10*, 919.
(24) Kirste, R. G.; Oberthür, R. C. In *Small Angle X-ray Scattering*; Glatter, O., Kratky, O., Eds.; Academic: London, 1982.
(25) Benoit, H. *J. Polym. Sci.* **1953**, *11*, 561.
(26) Hild, G.; Kohler, A.; Rempp, P. *Eur. Polym. J.* **1980**, *16*, 525.
(27) Hild, G.; Strazielle, C.; Rempp, P. *Eur. Polym. J.* **1983**, *19*, 721.
(28) Geiser, D.; Höcker, H. *Macromolecules* **1980**, *13*, 653.
(29) Vollmert, B.; Huang, J.-X. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 333.
(30) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.
(31) Chen, Y. *J. Chem. Phys.* **1981**, *75*, 2447.
(32) Michels, J. P. J.; Wiegel, F. H. *Proc. Soc. London, Ser. A* **1986**, *403*, 269.
(33) Chen, Y. J. *J. Chem. Phys.* **1981**, *75*, 5160.
(34) Iwata, K.; Kimura, T. *J. Chem. Phys.* **1981**, *74*, 2039.
(35) Iwata, K. *Macromolecules* **1985**, *18*, 116.