$$c_{ij} = 6^{N+i-j}\Gamma_{j-i} \qquad (A4')$$

where we let Γ_n represent the number of unique closed paths of length n on the lattice. It follows that

$$C = 6^N[1 - w\sum_{i<j} 6^{i-j}\Gamma_{j-i}] + O(w^2) \qquad (A5)$$

and therefore, that the free energy is given by

$$\beta A = -N \ln 6 + w\sum_{i<j} 6^{i-j}\Gamma_{j-i} + O(w^2) \qquad (A6)$$

or

$$\beta A = -N \ln 6 + w\sum_{p=1}^{N} (N - p + 1)6^{-p}\Gamma_p + O(w^2) \qquad (A7)$$

Γ_n can be calculated combinatorally; the result is

$$\Gamma_n = \sum\nolimits_{\{n_1,n_2,n_3\}} \frac{n!}{(n_1!)^2(n_2!)^2(n_3!)^2} \qquad (A8)$$

where $\sum_{\{n_1,n_2,n_3\}}$ indicates a sum over all possible values of n_1, n_2, and n_3 such that n_1, n_2, and n_3 are nonnegative integers and $2(n_1 + n_2 + n_3) = n$. (Γ_n is zero for odd n.) The above calculations are almost trivial for today's tireless computers, and using eq A7 and A8 we were able to obtain accurate values for the quantity Q_N in the expansion

$$A = -N \ln 6 + Q_N w + O(w^2) \qquad (A9)$$

It has been established[8,9] that each coefficient such as Q_N in eq A9 can be written as a power series in $N^{-1/2}$; via a straightforward least-squares fit we have obtained:

$$Q_N = 0.51847N - 1.3087N^{1/2} + 1.3509 \qquad (A10)$$

Equation 10 is valid with a precision of better than 1% whenever $N \geq 20$. This leads directly to eq 13.

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Θ Temperature of Ring Polymers: Another Evidence of Topological Interaction

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ABSTRACT: Roovers and Toporowski (RT) have found that ring polystyrene (PS) in cyclohexane has a fairly large A_2 at the Θ temperature of the corresponding *linear* polymer, Θ; and the Θ temperature of the *ring*, Θ_r, is remarkably lower than that of the linear polymer. This abnormality is considered to come from the topological repulsion among the ring polymer molecules. The nonzero A_2 observed at Θ is called "topological second virial coefficient $A_2{}^{\Theta}$", which has been studied in the previous work. In the present paper, the excluded-volume potential is introduced into the previous theory, and the Θ temperature difference ΔΘ (=Θ_r − Θ) is computed for various ring polymers and solvents; for ring PS in cyclohexane, the computed results agree well with the experiments of RT. It is predicted that ΔΘ is inversely proportional to the temperature coefficient of the binary cluster integral among segments, and in some systems (say, PS in diethyl malonate and 1-chloro-*n*-undecane), ΔΘ is as large as 20°. It is argued that dilute solutions of ring polymer are the most fundamental system for studying polymer entanglement.

Introduction

Entanglement of polymers is usually discussed in terms of the tube model.[1] This model has succeeded in explaining the viscoelastic properties of entangled polymer systems very well,[1] but its application has been limited mainly to dynamic properties. It is recently considered that entanglement plays an important role in much broader properties of polymers, such as rubber elasticity[3,4] or solution properties of ring polymers.[2,5,6] It is, however, difficult to apply the tube model to these problems in a reasonable way, and a more fundamental approach must be taken to study them. Entanglement is more adequately described by introducing topological invariants such as the Gauss integral explicitly into the statistical mechanics of polymer molecules. From this consideration, we have been developing "topological theories of entanglement" to cover broader fields of entanglement, such as dynamics of linear polymers,[7] solution properties of ring polymers,[2,5] and elastic properties of network[3] and linear[8] polymers. These theories are constructed systematically so that entanglement of the all systems is characterized by single molecular parameter called the "topological interaction parameter $\bar{\gamma}$", which represents how strongly polymer molecules can entangle with each other. The present paper is a part of this series.

A dilute solution of a ring polymer is the simplest system in which the topological interaction exists. This system is particularly interesting in the study of entanglement, because its physical properties can be measured more accurately and their theoretical calculation is easier than in other entangled systems. Roovers and Toporowski (RT)[9,10] have found that ring polystyrene in cyclohexane

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has a fairly large A_2 at the Θ temperature of the *linear* polymer, Θ, and that the Θ temperature of the *ring* polymer, Θ_r, is remarkably lower than that of the *linear* polymer. We believe that these abnormalities come from the topological repulsion among the ring polymer molecules; the nonzero A_2 observed at Θ is therefore called the "topological second virial coefficient A_2^Θ". In ref 5, A_2^Θ was computed numerically and $\bar{\gamma}$ of polystyrene was estimated from A_2^Θ measured by RT.[5,9] In ref 8, $\bar{\gamma}$ for various polymers has been estimated from the plateau modulus of the melt polymer, G_N; $\bar{\gamma}$ of polystyrene thus estimated agrees well with that determined from A_2^Θ. In this work, an excluded-volume potential is introduced into the previous theories[2,5] and the Θ temperature is computed for various ring polymers and solvents by using these $\bar{\gamma}$.

The Θ temperature of ring polymers has been already studied by Tanaka from a similar point of view,[6] but the degree of approximation used for the topological and excluded-volume interaction in his work is not high enough. In this work, we study this problem in the same approximation as used in the usual excluded-volume theories so that we can get quantitative agreement with experiments. Although the present theory contains two empirical parameters, the topological interaction parameter $\bar{\gamma}$ and the binary cluster integral β, we can determine both of them using experimental data for linear polymers; hence we can predict A_2^Θ and Θ_r of ring polymers that have not yet been synthesized.

Theory

Let a and b be ring polymer molecules which are composed of n submolecules, $a_1, a_2, ..., a_n$ and $b_1, b_2, ..., b_n$. The Gauss integral (GI) for a and b is written as

$$T_{ab} = \sum_{i=1}^{n} \sum_{j=1}^{n} \Theta_{a_ib_j} \qquad (1)$$

where $\Theta_{a_ib_j}$ is the GI for submolecular pair (a_i, b_j). For a ring polymer, T_{ab} takes integer numbers alone. The probability density $P(\tau|\mathbf{w})$ for T_{ab} to take integer number τ under the condition that relative distance between their centers of mass is equal to $\mathbf{w}$ is given[2] by

$$P(\tau|\mathbf{w}) = \int_{\tau-0.5}^{\tau+0.5} \Phi(t|\mathbf{w})\, \mathrm{d}t \qquad (2)$$

$$\Phi(t|\mathbf{w}) = \langle \delta(t - \sum_i\sum_j \Theta_{a_ib_j}) \rangle_{\mathrm{w,ph}} \qquad (3)$$

where the symbol $\langle\ \rangle_{\mathrm{w,ph}}$ represents an average over the equilibrium distribution of "phantom" polymer molecules, keeping the relative distance between their centers of mass at $\mathbf{w}$. The function $\Phi(t|\mathbf{w})$ is written in terms of its Fourier transform

$$\hat{\Phi}(u|\mathbf{w}) = \langle \exp(iu\sum_i\sum_j \Theta_{a_ib_j}) \rangle_{\mathrm{w,ph}} \qquad (4)$$

as follows:

$$\Phi(t|\mathbf{w}) = \frac{1}{2\pi} \int e^{-iut} \hat{\Phi}(u|\mathbf{w})\, \mathrm{d}u \qquad (5)$$

When the right-hand side (rhs) of eq 4 is expanded into a power series in u, we find generally the following term:

$$\langle (\Theta_{a_ib_j})^m (\Theta_{a_{i'}b_{j'}})^{m'} (\Theta_{a_{i''}b_{j''}})^{m''} \ldots \rangle_{\mathrm{w,ph}}$$

where m, m', m'', ... are integers. When the submolecules are sufficiently long, this term disappears unless m, m', m'', ... are all even. We can therefore use the following "quadratic approximation"[2]

$$\langle (\sum_i\sum_j \Theta_{a_ib_j})^{2k} \rangle_{\mathrm{w,ph}} \approx (2k-1)!! \left\langle \left(\sum_i\sum_j {\Theta_{a_ib_j}}^2\right)^k \right\rangle_{\mathrm{w,ph}} \qquad (6)$$

on the rhs of eq 4. In this approximation, eq 4 is rewritten as follows:

$$\hat{\Phi}(u|\mathbf{w}) = \left\langle \exp\left(-\frac{u^2}{2} \sum_i\sum_j {\Theta_{a_ib_j}}^2 \right) \right\rangle_{\mathrm{w,ph}} \qquad (7)$$

Since ${\Theta_{a_ib_j}}^2$ is a short-range function of $\mathbf{r}_{a_ib_j}$, the relative distance between a_i and b_j, it is approximated by a δ function

$${\Theta_{a_ib_j}}^2 \approx \gamma' \delta(\mathbf{r}_{a_ib_j}) \qquad (8)$$

where γ' is "the topological interaction parameter for the submolecules", which is defined by[2,5]

$$\gamma' = \langle {\Theta_{a_ib_j}}^2 \rangle \qquad (9)$$

Now, the second virial coefficient, A_2, with or without the excluded-volume effect, is given in terms of the distribution function $P(\tau|\mathbf{w})$ of the ring polymer molecules in the nonentangled state $\tau = 0$ as follows:

$$A_2 = \frac{N_A}{2M^2} \int [1 - P(0|\mathbf{w})]\, \mathrm{d}\mathbf{w} \qquad (10)$$

where N_A is the Avogadro number and M the molecular weight of the polymer. Using eq 2–5 and 7, it is rewritten as

$$A_2 = (4\pi^{3/2}\langle S^2 \rangle)^{3/2} N_A M^{-2} \Psi_t \qquad (11)$$

where $\langle S^2 \rangle$ is the mean-square radius of gyration and Ψ_t is a "penetration function",[11] modified in the presence of the topological interaction; it is defined by

$$\Psi_t = \frac{2}{\pi} \int_0^\infty u^{-1} \sin(u/2) \Psi^*(u)\, \mathrm{d}u \qquad (12)$$

where

$$\begin{aligned} \Psi^*(u) &= (4\pi\langle S^2 \rangle)^{-3/2} \int \left\{ 1 - \left\langle \exp\left[-\frac{1}{2}\gamma' u^2 \sum_i\sum_j \delta(\mathbf{r}_{a_ib_j}) \right] \right\rangle_{\mathrm{w,ph}} \right\} \mathrm{d}\mathbf{w} \\ &= (4\pi\langle S^2 \rangle)^{-3/2} V^{-1} \int\int \left\{ P_{\mathrm{ph}}(\mathbf{r}_a) P_{\mathrm{ph}}(\mathbf{r}_b) - \exp\left[-\frac{1}{2}\gamma' u^2 \sum_i\sum_j \delta(\mathbf{r}_{a_ib_j}) \right] P_{\mathrm{ph}}(\mathbf{r}_a, \mathbf{r}_b) \right\} \mathrm{d}\mathbf{r}_a\, \mathrm{d}\mathbf{r}_b \end{aligned} \qquad (13)$$

Here V is the volume of the system, $\mathbf{r}_a$ and $\mathbf{r}_b$ are the coordinate set of the all submolecules in a and b, and $P_{\mathrm{ph}}(\mathbf{r}_a)$, $P_{\mathrm{ph}}(\mathbf{r}_b)$, and $P_{\mathrm{ph}}(\mathbf{r}_a,\mathbf{r}_b)$ are the distribution functions of $\mathbf{r}_a$ and $\mathbf{r}_b$ of the "phantom" polymer molecules. When the topological interaction is absent, $\Psi^*(u)$ reduces to the ordinary penetration function Ψ.

When there is no excluded-volume effect, $P_{\mathrm{ph}}(\mathbf{r}_a)$ etc. are reduced to those of the Gaussian model, $P_R(\mathbf{r}_a)$ etc.

$$P_R(\mathbf{r}_a) = \mathrm{const} \times \exp\left[-\frac{3}{2\nu b^2} \sum_{i=1}^{n} (\mathbf{r}_{a_i} - \mathbf{r}_{a_{i-1}})^2 \right] \quad \text{etc.} \qquad (14)$$

where $\mathbf{r}_{a_i}$ and $\mathbf{r}_{a_{i-1}}$ are the coordinates of the centers of submolecule a_i and a_{i-1}, ν is the number of main-chain atoms per submolecule, and b is the effective bond length. Excluded-volume potential between a_i and b_j is usually approximated by a δ function in regard to their relative distance $\mathbf{r}_{a_ib_j}$

$$k_B T \beta' \delta(\mathbf{r}_{a_ib_j}) \qquad (15)$$

where β' is the binary cluster integral for a pair of submolecules.[11] With this potential, $P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{a}})$, $P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{b}})$, and $P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{a}},\mathbf{r}_{\mathrm{b}})$ are written as

$$P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{a}}) = \exp[-\beta'\sum_i\sum_{i'}\delta(\mathbf{r}_{\mathrm{a}_i\mathrm{a}_{i'}})]P_{\mathrm{R}}(\mathbf{r}_{\mathrm{a}}) \qquad \text{etc.}$$

$$P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{a}},\mathbf{r}_{\mathrm{b}}) = \exp[-\beta'\sum_i\sum_j\delta(\mathbf{r}_{\mathrm{a}_i\mathrm{b}_j})]P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{a}})P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{b}}) \quad (16)$$

Function $\Psi^*(u)$ is now rewritten by

$$\Psi^*(u) = (4\pi\langle S^2\rangle)^{-3/2}V^{-1}\int\int P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{a}})P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{b}}) \times \{1 - \exp[-\beta^*(u)\sum_i\sum_j\delta(\mathbf{r}_{\mathrm{a}_i\mathrm{b}_j})]\}\, d\mathbf{r}_{\mathrm{a}}\, d\mathbf{r}_{\mathrm{b}} \quad (17)$$

with

$$\beta^*(u) = \beta' + \gamma' u^2/2 \quad (18)$$

The Θ temperature of the ring polymer is defined as the temperature at which A_2 disappears; i.e.

$$A_2 = 0 \qquad \text{or} \qquad \Psi_{\mathrm{t}} = 0 \quad (19)$$

Numerical Calculation

Since it is difficult to treat the intramolecular excluded-volume potential explicitly in the calculation of A_2, the following uniform expansion model has often been used:[11] namely, the distribution functions of polymer molecules a and b with an intramolecular excluded-volume effect, $P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{a}})$ and $P_{\mathrm{ph}}(\mathbf{r}_{\mathrm{b}})$, are approximated by those of a Gaussian model with modified effective bond length $\alpha_{\mathrm{s}}b$, where α_{s} is the expansion ratio. This model is particularly suitable for the present work in the vicinity of the Θ state. In this approximation, the expression for $\Psi^*(u)$, eq 17, is formally identical with that of the ordinary penetration function, Ψ, except that β' is replaced by $\beta^*(u)$. We can therefore use numerous expressions of penetration function Ψ so far presented. It is convenient to introduce here the binary cluster integral β and the topological interaction parameter γ per main-chain atom as follows:

$$\beta = \beta'/\nu^2 \qquad \gamma = \gamma'/\nu^2 \quad (20)$$

Usually Ψ is given as a function of the excluded-volume parameter[11]

$$z = (4\pi\langle S^2\rangle)^{-3/2}N^2\beta \quad (21)$$

where N ($=\nu n$) is the number of main-chain atoms per polymer molecules. In the present work, z should be replaced by

$$z^*(u) = z + u^2 z_{\mathrm{t}}/2 \quad (22)$$

where z_{t} is "a topological excluded-volume parameter" defined by

$$z_{\mathrm{t}} = (4\pi\langle S^2\rangle)^{-3/2}N^2\gamma \quad (23)$$

In the uniform expansion model, $z^*(u)$ should be further replaced by $\bar{z}^*(u) = z^*(\mathrm{u})/\alpha_{\mathrm{s}}^3$.

Perturbation expansions of $\Psi(z)$ and $\alpha_{\mathrm{s}}(z)$ for ring polymers have been derived by Casassa[12] as follows:

$$\Psi(z) = z(1 - 4.457z + ...) \quad (24)$$

$$\alpha_{\mathrm{s}}(z) = 1 + (\pi/2)z - ... \quad (25)$$

These equations hold only for very small z, say $|z| \leq 0.15$. For large z, a number of closed expressions have been presented and their validity has been tested in the scheme of the "two-parameter theory" by Yamakawa,[11] who has concluded that "modified Flory (mF)", "modified Flory–Krigbaum–Orofino (mFKO)", and "Kurata–Yamakawa (KY)" equations give reasonable agreement with experiments. The mF and mFKO equations are based on the mean-field approximation but their numerical coefficients are determined so that they agree with the perturbation equations (24) and (25) in the vicinity of $z = 0$. For ring polymers, mF and mFKO equations read[11]

$$\Psi(z) = [\ln(1 + 8.914z)]/8.914 \qquad \text{(mFKO)} \quad (26)$$

$$\alpha_{\mathrm{s}}^5 - \alpha_{\mathrm{s}}^3 = (\pi/2)z \qquad \text{(mF)} \quad (27)$$

To derive the corresponding KY equation, we need the first and second coefficient of the perturbation expansion,[11] but the second coefficient has not yet been computed for the ring polymer. In this work, therefore, we use mF and mFKO equations in the region $z \geq 0$, in which they agree fairly well with experiments. In region $z < 0$, however, eq 26 leads to a rapid decrease in Ψ and becomes inapplicable for $z \leq -0.1125$. Considering the way of deriving mF and mFKO equations, they are expected to be good for large positive z but not necessarily for negative z. In this work, we need $\Psi^*(z)$ and $\alpha_{\mathrm{s}}(z)$ for, say, $-0.15 \leq z < \infty$. For small negative z, the perturbation equations (24) and (25) or a superposition-type expression, say, the Fixman–Casassa–Markovitz (FCM) equation,[11] seems to be better than mF and mFKO equations. For the ring polymer, the FCM equation reads

$$\Psi(z) = [1 - \exp(-8.914z)]/8.914 \qquad \text{(FCM)} \quad (28)$$

It must be remembered that in deriving these equations summations over submolecules have been replaced by integrations. For this approximation to be possible, polymer molecules should contain a sufficiently large number of submolecules, but the ring polymer molecules considered here are rather small and some of them contain less than ten submolecules. In our previous work, therefore, we have performed the summations in regard to the submolecules explicitly, but in this paper we use eq 24–28, because we wish to consider this problem in the framework of the ordinary excluded-volume theory; the present theory is therefore expected to be inaccurate in the low molecular weight region where the excluded-volume theory fails. Because of this difference between the present and the previous method, A_2^{Θ} computed in the present work is slightly different from that in the previous one.[2,5]

Numerical calculations are performed as follows: (i) For the expansion ratio $\alpha_{\mathrm{s}}(z)$, mF equation (27) is used in the region $z \geq 0$ and the perturbation equation (25) in the region $z < 0$; (ii) for the penetration function $\Psi(z)$, the mFKO equation (26) is used in the region $z \geq 0$ and perturbation equation (24) or FCM equation (28) in the region $z < 0$; (iii) the modified penetration function $\Psi^*(u)$ is equated to $\Psi[\bar{z}^*(u)]$; (iv) the penetration function in the presence of the topological interaction, $\Psi_{\mathrm{t}}(z,z_{\mathrm{t}})$, is computed by numerical integration with respect to u on rhs of eq 12. Some of the results are given in Table I, and $\Psi_{\mathrm{t}}(z,z_{\mathrm{t}})$ is plotted against z for different values of z_{t} in Figure 1. In the figure, the curve for $z_{\mathrm{t}} = 0$ represents the ordinary penetration function, $\Psi(z)$, to which all curves approach as z increases; this means that the topological interaction cannot be observed in good solvents because it is hidden under the overwhelming excluded-volume effect. The penetration function $\Psi_{\mathrm{t}}(z,z_{\mathrm{t}})$ for $z = 0$ gives the topological second virial coefficient, A_2^{θ}. As stated in the above, numerical values of A_2^{Θ} are slightly different from the previous ones,[5,8] because the approximations used are different.

Θ Temperature of Ring Polymers

The Θ state of the ring polymer is defined by eq 19. To compute the Θ temperature of the ring polymer, Θ_{r}, we first determine the value of z at which $\Psi_{\mathrm{t}}(z,z_{\mathrm{t}})$ disappears, $z_{\Theta}(z_{\mathrm{t}})$, as a function of z_{t}. The ratio

$$\zeta(z_{\mathrm{t}}) = -z_{\Theta}(z_{\mathrm{t}})/z_{\mathrm{t}} \quad (29)$$

Table I
Penetration Function with the Topological Interaction, $\Psi(z,z_t)$

	z_t					
z	0.0	0.05	0.10	0.15	0.20	0.25
–0.15	–0.4490	–0.1987	–0.0999	–0.0428	–0.0029	–0.0028
–0.10	–0.2036	–0.0644	–0.0022	0.0367	0.0651	0.0875
–0.05	–0.0708	0.0063	0.0490	0.0778	0.0998	0.1177
0.0	0.0000	0.0444	0.0763	0.0994	0.1177	0.1328
0.1	0.0622	0.0083	0.1048	0.1219	0.1361	0.1482
0.2	0.0938	0.1065	0.1226	0.1362	0.1480	0.1583
0.4	0.1300	0.1360	0.1463	0.1560	0.1648	0.1728
0.6	0.1529	0.1555	0.1628	0.1702	0.1772	0.1837
1.0	0.1806	0.1817	0.1858	0.1906	0.1954	0.2001
1.5	0.2028	0.2031	0.2054	0.2085	0.2118	0.2152
2.0	0.2187	0.2186	0.2200	0.2221	0.2245	0.2271
3.0	0.2405	0.2402	0.2408	0.2419	0.2433	0.2449

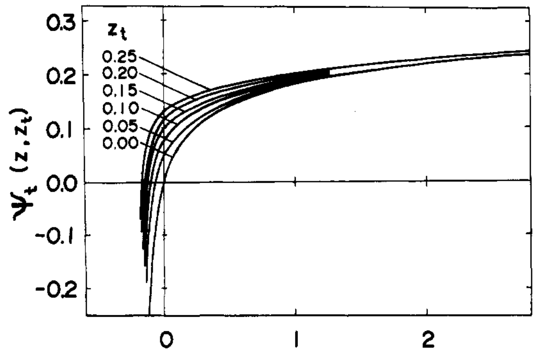

Figure 1. Penetration function with the topological interaction, $\Psi(z,z_t)$, plotted against z for various values of z_t.

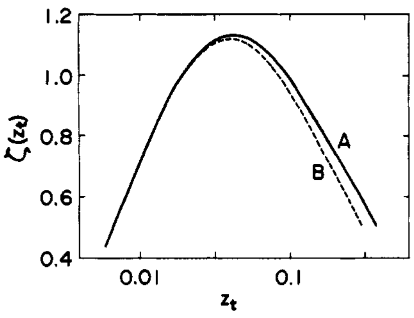

Figure 2. $\zeta(z_t)$ versus z.

Table II
Table of $\zeta(z_t)$

z_t	exp type[a]	FCM type[b]	z_t	exp type[a]	FCM type[b]
0.006	0.443	0.443	0.12	0.926	0.874
0.008	0.590	0.590	0.14	0.873	0.814
0.010	0.704	0.704	0.16	0.825	0.760
0.015	0.892	0.891	0.18	0.781	0.713
0.02	1.000	0.998	0.20	0.742	0.671
0.03	1.098	1.094	0.22	0.707	0.633
0.04	1.125	1.116	0.24	0.675	0.600
0.05	1.120	1.105	0.26	0.646	0.570
0.06	1.101	1.080	0.28	0.620	0.542
0.08	1.045	1.012	0.30	0.596	0.518
0.10	0.984	0.941			

[a] Computed with use of eq 24 in the region $z < 0$. [b] Computed with use of eq 28 in the region $z < 0$.

Table III
The Binary Cluster Integral and Θ Temperature

solvent	β_0, Å^3[a]	10^5M[b]	Θ, °C	$[\Delta\Theta]_{\min}$	ref
Polystyrene ($\bar\gamma$ = 0.0037,[c] b = 5.04 Å, $M_{\min} \approx$ 60 000[e])					
diethyl malonate	$7._6$	4.05	35.9	$-20._2$	*f*
cyclohexane	$25._5$	4.05	34.8	$-6._3$	*f*
	$21._5$	13.4–568.0	34.8	$-7._4$	*g*
1-chloro-*n*-undecane	$6._8$	4.05	32.8	$-22._1$	*f*
decalin	$24._4$	0.48–44.0	29.5	$-6._4$	*h*
Poly(α-methylstyrene) ($\bar\gamma$ = 0.0053,[d], b = 4.92 Å, $M_{\min} \approx$ 40 000[e])					
cyclohexane	$15._7$	31.0–300.0	35.0	$-13._3$	*i*
Poly(dimethylsiloxane) ($\bar\gamma$ = 0.0047,[c] b = 4.14 Å, $M_{\min} \approx$ 25 000[e])					
bromocyclohexane	$7._2$	10.6	29.	$-14._9$	*j*
bromobenzene	$10._2$	10.6	79.	$-12._4$	*j*
phenetole	$9._5$	10.6	89.	$-13._7$	*j*

[a] β_0 is given per main-chain atom. [b] Molecular weight range of β_0 measurement. [c] Given in ref 8. [d] Computed by the same method as in ref 8, using $G_N = 3.2 \times 10^6$ dyn/cm^2. [e] $M_{\min}$ is the molecular weight at which the minimum of ΔΘ occurs. [f] Orofino, T. A.; Mickey, J. W., Jr. *J. Chem. Phys.* **1963**, *38*, 2512. [g] Suzuki, H. *Br. Polym. J.* **1982**, *18*, 137. This has been determined by Suzuki using A_2 measured by Fujita's group of Osaka University (cf.: Miyaki, Y. Doctral Thesis, Osaka University, 1981). [h] Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550. [i] Kato, T.; Miyaso, K.; Nagasawa, M. *J. Phys. Chem.* **1968**, *72*, 2161. [j] Schultz, G. V.; Haug, A.; Kirste, R. *Z. Phys. Chem. Neue Folge* **1963**, *38*, 1. In this polymer, β_0 depends strongly on M; in the table, β_0 of the highest molecular weight sample measured is given. $[\Delta\Theta]_{\min}$'s estimated for this polymer are inaccurate.

is computed for various z_t and the results are shown in Table II and Figure 2. By eq 21 and 23, the ratio ζ is equal to $-\beta(\Theta_r)/\gamma$, where $\beta(\Theta_r)$ is the binary cluster integral at Θ_r. It is interesting that ζ is near unity; this means that at Θ_r, the negative excluded volume, $\beta(\Theta_r)$, is roughly canceled by the topological volume, γ, at the monomer level. In the vicinity of the Θ temperature of the linear polymer, Θ, the binary cluster integral is written as

$$\beta(T) = \beta_0(1 - \Theta/T) \qquad (30)$$

where β_0 is a parameter independent of T but dependent on the solvent. The Θ temperature difference between the ring and linear polymers, ΔΘ (=Θ_r – Θ), is given by

$$\Delta\Theta/\Theta = \frac{-\zeta(z_t)\gamma/\beta_0}{1 + \zeta(z_t)\gamma/\beta_0} \qquad (31)$$

To compute ΔΘ, we must know parameters γ and β_0 for each polymer.

Binary Cluster Integral $\beta(T)$. The parameter β_0 has been determined for many polymers from the temperature dependence of A_2 in the vicinity of Θ. By definition, β_0 should be independent of M, but in many polymers it increases as M decreases below several hundred thousand. Although this contradicts severely the fundamental assumption of the excluded-volume theory, there has so far been no explanation for it. In Table III, β_0 of several polymers in various solvents are given. Among them, β_0 of polystyrene (PS) in cyclohexane and decalin and of poly(α-methylstyrene) (PMS) in cyclohexane seem to be reliable, because their M-independence is confirmed in the molecular weight range indicated. Although β_0 of PDMS depends strongly on M (cf. footnote *j* the Table III), it is included in Table III because ring poly(dimethylsiloxane) (PDMS) has been already synthesized and we wish to know its Θ_r even crudely; in Table III, β_0's of the highest molecular weight PDMS measured ($M = 1.06 \times 10^6$) are given, but they may still depend on M even at this molecular weight.

Topological Interaction Parameter $\bar\gamma$. A dimensionless topological interaction parameter, $\bar\gamma$, is defined by[2]

$$\bar\gamma = \gamma/b^3 \qquad (32)$$

In previous works,[5,8] $\bar\gamma$ has been determined for many polymers by their plateau modulus G_N or topological second virial coefficient A_2^Θ. Parameter $\bar\gamma$ of PS and PDMS given in Table III has been determined previously;[8]

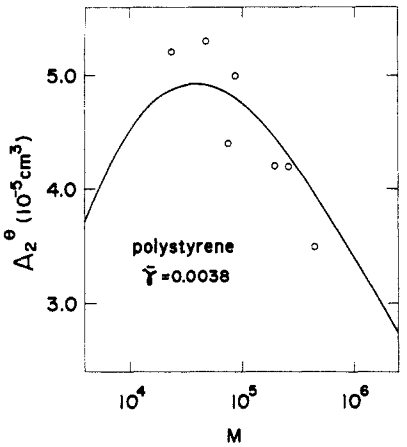

Figure 3. Topological second virial coefficient, A_2^Θ, of ring polystyrene plotted against M. The best agreement between the theory and the experiments of Roovers and Toporowski[9] is obtained for $\bar{\gamma}$ = 0.0038.

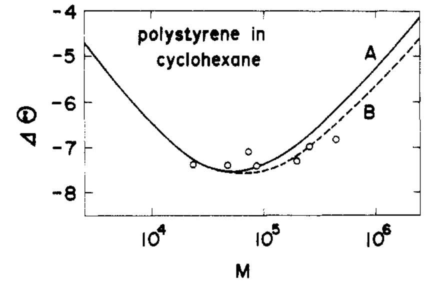

Figure 4. Difference between the Θ temperature of linear and ring polystyrene in cyclohaxane, $\Delta\Theta$, plotted against M. Curve A is computed by using the FCM equation, and curve B is the expansion equation for $\Psi(z)$ in the region $z < 0$. The points represent the experimental data of Roovers;[10] $\beta_0 = 21._5$ Å^3 and $\bar{\gamma}$ = 0.0037.

$\bar{\gamma}$ of PMS is determined for the first time in this work, using the same method as before. Since A_2^Θ computed by the present theory is slightly different from those of the previous ones, $\bar{\gamma}$ of PS is estimated again from the experimental data of A_2^Θ measured by Roovers and Toporowski (RT).[9] In Figure 3, A_2^Θ computed by the present theory is shown, together with their experimental data. Parameter $\bar{\gamma}$ is determined by the least-square fitting of the theory and the experiment; the result is $\bar{\gamma}$ = 0.038, which is slightly larger than the previous $\bar{\gamma}$ = 0.0032[5] but almost same as $\bar{\gamma}$ = 0.0037 determined from G_N.[8] Such a small discrepancy is inevitable in these approximate calculations. In this work, we use $\bar{\gamma}$ = 0.0037 for PS, because it is consistent with the present theory. For the other polymers, $\bar{\gamma}$ determined from G_N is used.

Θ Temperature of Ring Polymers, Θ_r. For PS in cyclohexane, $\Delta\Theta$ is computed from $\bar{\gamma}$ = 0.0037 and $\beta_0 = 21._5$ Å^3, and the results are plotted against M in Figure 4; the points in the figure represent experimental data of Roovers;[10] agreement between the theory and the experiment is good. It is important that $\Delta\Theta$ has a minimum at $M_{\min}$ and is roughly constant in a fairly broad molecular weight range around it. As noted by RT,[9,10] the observed Θ_r looks almost independent of M, but according to the present theory, this occurs simply because the M's of their samples happen to be in this stationary range. The present result is in contrast to that of Tanaka,[6] who predicted that $\Delta\Theta$ increases monotonically as M in contradiction to the observation of RT. This discrepancy seems to come from the difference in the degree of the approximations used. In Tanaka's theory, the topological distribution function contains only the second topological moment, while in our previous theories[2,5] it contains the second and fourth topological moments; in the present work, it is further improved so that the topological and the excluded-volume interactions are treated in the same degree of approximation as used in the excluded-volume theory. The accuracy of the present theory is expected to be the same as that of mFKO equation, which agrees fairly well with experiments.[11]

Although the magnitude of $\Delta\Theta/\Theta$ varies among polymers and solvents, its M-dependence is the same, except for the proportionality constants, as that of PS in cyclohexane shown in Figure 4. In other polymer–solvent systems, therefore, it is sufficient to know $[\Delta\Theta]_{\min}$, the minimum of $\Delta\Theta$, and $M_{\min}$, the molecular weight at which the minimum occurs. Since the maximum of ζ is equal to 1.12 (see Figure 2), we find

$$[\Delta\Theta]_{\min}/\Theta = \frac{-1.12\gamma/\beta_0}{1 + 1.12\gamma/\beta_0} \tag{33}$$

$[\Delta\Theta]_{\min}$ and $M_{\min}$ of various polymer–solvent systems are given on the fifth column of Table III. It must be remembered that in obtaining these results we have assumed that β_0 is independent of M; this assumption seems to be roughly satisfied in PS but not in PDMS; in the latter polymer, the present results represent only its qualitative behavior.

According to eq 31, $\Delta\Theta$ changes inversely proportional to β_0; this means that $\Delta\Theta$ depends strongly on the solvent. In fact, as seen from Table III, $[\Delta\Theta]_{\min}$ of PS changes from $-6._3$° in decalin to $-22._1$° in 1-chloro-*n*-undecane. Topological second virial coefficient A_2^Θ, on the other hand, must be almost independent of the solvent.[13] Therefore the simplest way to know the origin of the abnormality of ring polymers is to measure $\Delta\Theta$ and A_2^Θ for the same polymer in various solvents. Since the topological interaction among polymer molecules is the origin of entanglement, it is very important to observe it in its simplest form in the dilute solutions of ring polymer.

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