Intrachain Reaction of a Pair of Reactive Groups Attached to Polymer Ends. II. Monte Carlo Study on the Intrachain Reaction Proceeding on *trans/cis*-Polysarcosine Chain

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ABSTRACT: Monte Carlo calculation was performed to evaluate the ring-closure probability of short polysarcosine chains. Calculations were made for unperturbed *trans*-, non-self-intersecting *trans*-, and non-self-intersecting *trans/cis*-polysarcosine chains. In the latter case, the main chain amide bond was allowed to take cis as well as trans conformations. The ring-closure probability for unperturbed *trans*-polysarcosine chains was found to be substantially greater than for non-self-intersecting trans chains. Virtually no difference was observed between the ring-closure probabilities of non-self-intersecting trans chains and of non-self-intersecting trans/cis chains. The ring-closure probability was used to estimate the cyclization constant, i.e., the ratio of rate constant for the intramolecular reaction of the two terminal groups attached to the polymer ends to that of the intermolecular one. The results were compared with the experimental data for the intrachain reaction proceeding on polysarcosine chain reported in the first paper of this series. The Monte Carlo results roughly reproduced the experimental data and the calculated chain length dependence was consistent with the observed one for longer chains.

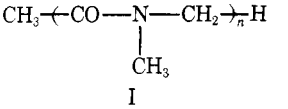
Intrachain reactions in X–Y-type polymers have been shown to depend on the conformation of the connecting polymer chain.[1-6] If the intrinsic rate of reaction between X and Y is sufficiently slow, the ensemble of the polymer chains is in an equilibrium state regardless of the reaction. In this case the rate of intrachain reaction is directly proportional to the ring-closure probability (RCP), which is defined as the probability for a polymer chain to have an end-to-end distance r being shorter than a critical value r_0.[2,3] There have been several works dealing with intrachain reactions proceeding on polymer chains.[1-6] Most of these intrachain reactions meet the above condition, except in a few cases in which an electron transfer reaction is concerned.[5,6] In the preceding paper we have presented the result of intramolecularly catalyzed hydrolysis of ester proceeding on a polysarcosine chain.[4] In the present investigation Monte Carlo calculation was done for polysarcosine chain and the RCP was evaluated for a comparison with the experimental one.

Evaluation of RCP for short polymethylene chains has been reported by some workers in connection with the intrachain reaction. Monte Carlo method was first applied by Fluendy[7] to the g-t rotational isomer model of polymethylene chain. Recently Winnik et al.[8] carried out a Monte Carlo calculation taking into account the detailed structure of terminal groups. One of the present authors (M.S.) applied the direct enumeration method to the g-t model of polymethylene chain to evaluate RCP and the rate of intrachain reaction of ω-hydroxycarboxylic acids.[3] DeLisi[9] calculated the RCP for short RNA chains by Monte Carlo method. He also obtained the higher even moments up to $\langle r^{60} \rangle$ and evaluated the RCP from the even moments. Recently Rubin and Kallenbach[10] also obtained the RCP of short RNA chains. RCP for various condensation polymers have been calculated in connection with the ring-chain equilibria in those polymers.[11] Very recently Guillard et al.[12] calculated the distribution function of end-to-end distance for several tetrapeptides. So far, however, no work has been reported on the RCP of longer poly-α-amino acid chains (or poly-α-imino acid chains). Monte Carlo calculations on poly-α-amino acid chains have been performed by many workers to evaluate various conformational characteristics such as the mean-square end-to-end distance $\langle r^2 \rangle$, the mean square radius of gyration $\langle s^2 \rangle$, and the distribution function of end-to-end distance.[13-15] However, the RCP has never been calculated. This is partly because the RCP has found only few applications to polymer physics, and partly because of the difficulty to evaluate a RCP value as small as 10^{-2} by a Monte Carlo method. In this study this difficulty was overcome by dealing with not-so-long chains and by separating the calculation of the RCP from the generation of non-self-intersecting chains.

Conformational properties of polysarcosine chain have been investigated by several workers.[16-19] In these studies, however, the existence of the cis amide bond was completely neglected[16,17] or taken into consideration as *all-cis*-polysarcosine.[18] The cis amide bond has been detected in polysarcosine by using NMR spectroscopy in a randomly scrambled form with trans.[20,21] Introduction of cis amide bond into a poly-α-amino acid chain makes the rotational states subjected to the influence of the neighboring units[16,19] and hence makes the calculation considerably difficult and time consuming. In the present calculation, the existence of cis amide bond was taken into consideration, but the time required for computation was much reduced by using the lists of allowed conformations for dimers and trimers.

Procedure for Computation

Outline of Monte Carlo Calculation. The essential part of the Monte Carlo calculation is summarized below. The detailed description will be made in a separate paper.[22] The structure of polysarcosine chain was taken as I.



I

The structure I represents *N*-acetylpolysarcosinedimethylamide. All atoms and the methyl groups were treated as hard spheres. The atomic radii and the structural parameters employed were the same as those used by Scott and coworkers.[17] Each amide bond was assumed to be planar. The rotational angles around the α carbon (ϕ, ψ) were changed from 5° to 355° with 10° increment. The end-to-end distance was measured from the center of *N*-acetyl methyl group to that of the terminal *N*-methyl group. Monte Carlo

calculation was made for three cases: unperturbed *trans*-polysarcosine, all amide bonds being trans; non-self-intersecting *trans*-polysarcosine; and non-self-intersecting *trans/cis*-polysarcosine, the amide bond being allowed to take cis as well as trans form with an equal probability at the beginning of the Monte Carlo calculation. As a result of chain attrition, however, the fraction of cis form in non-self-intersecting *trans/cis*-polysarcosine chain was about 0.19 over the whole range of the chain length studied.[22] The results for three cases were compared.

Evaluation of Ring-Closure Probability. RCP is evaluated from the fraction of allowed conformations where the end-to-end distance r is within a critical value r_0 (eq 1). In eq 1 $\Omega(r < r_0)$ is the number of chains with $r < r_0$, and Ω_t is the total number of chains.

$$W(r < r_0) = \Omega(r < r_0)/\Omega_t \quad (1)$$

Since RCP lies between 10^{-2} and 10^{-3}, a great many chains (at least 10^4–10^5) should be generated in the Monte Carlo calculations to obtain a reliable result by this method. This makes the computation very time consuming, especially for non-self-intersecting chains. In the iterative generation of non-self-intersecting chains, the check of atomic overlaps in the chain is most time consuming. Therefore it was hoped that the checking process is omitted in the generation of cyclic conformations. If we transform eq 1 into eq 2 using the number of total trials Ω_0, the numerator represents a fraction of non-self-intersecting cyclic chains in the total trial and the denominator represents a total fraction of non-self-intersecting chains.

$$W(r < r_0) = \frac{\Omega(r < r_0)/\Omega_0}{\Omega_t/\Omega_0} \quad (2)$$

Therefore to evaluate the RCP of non-self-intersecting chains, an unperturbed chain was generated at first. Then the check for the atomic overlaps was carried out only for the unperturbed chain with $r < r_0$. In this manner the numerator of eq 2 was evaluated. The denominator, the total fraction of non-self-intersecting chains, is usually not small enough for the evaluation to be made after small numbers of trials. Although the above method is applicable to any non-self-intersecting chains, it was not used for non-self-intersecting *trans/cis*-polysarcosine chains. In this case the chain attrition was extremely frequent and the evaluation of the numerator of eq 2 was difficult. For non-self-intersecting *trans/cis*-polysarcosine chains, RCP was evaluated by the direct Monte Carlo method (eq 1) with the Wall–Erpenbeck chain enrichment technique.[23]

Formally RCP can be obtained also from the distribution function of the end-to-end distance which was reconstructed from the even moments computed by the Monte Carlo method.[24] This method was first applied to the RNA chain by DeLisi.[9] In the present calculation the first 20 even moments (up to $\langle r^{40} \rangle$) were evaluated by the Monte Carlo method and the distribution function of the end-to-end distance was reconstructed. However, the convergence was insufficient for 5000 Monte Carlo chains. Little improvement was achieved by taking higher even moments and by generating many more chains (50 000 chains). Therefore this method was not used to evaluate RCP in the present study.

Results and Discussion

Distribution of End-to-End Distance. In the iterative Monte Carlo calculation, counts were made for the number of chains having particular end-to-end distance with 1 Å increment. The distributions normalized by the total number of chains are shown in Figures 1, 2, and 3, for unperturbed *trans*-, non-self-intersecting *trans*-, and non-self-intersecting *trans/cis*-polysarcosine chains, respectively. The end-to-end distributions for these chains are very similar to each other. Taking into account the excluded-volume effect, the peak position shifted slightly to a larger r. Introduction of cis amide bond, however, shifted the peak position to a little shorter r. With increasing the chain length, the peak position of the distribution shifted to a longer end-to-end distance and the distribution became more broadened and took a shape similar to the Gaussian

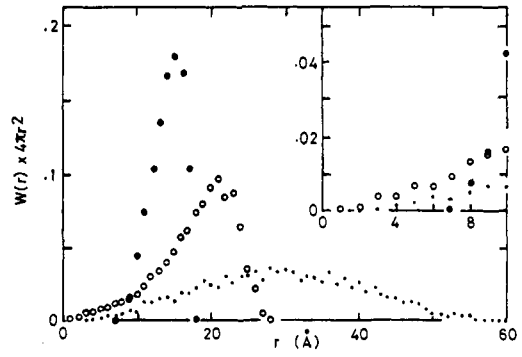


Figure 1. Distribution curves for the end-to-end distance of unperturbed *trans*-polysarcosine chains, having (●) $n = 5$, (○) $n = 8$, (·) $n = 20$. The insert facilitates the comparison for short end-to-end distances.

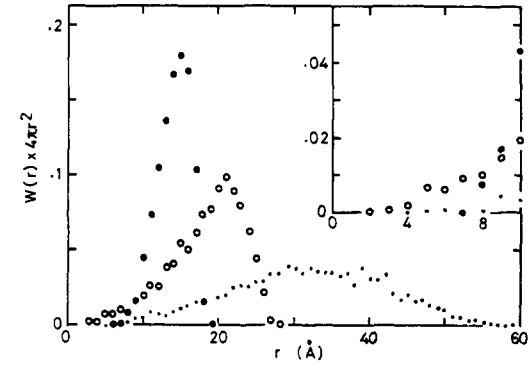


Figure 2. Distribution curves for the end-to-end distance of non-self-intersecting *trans*-polysarcosine chains, having (●) $n = 5$, (○) $n = 8$, (·) $n = 20$. The insert facilitates the comparison for short end-to-end distances.

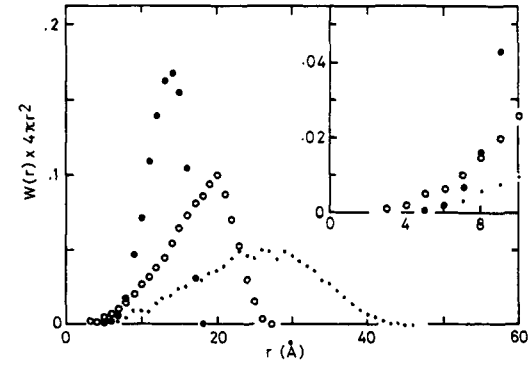


Figure 3. Distribution curves for the end-to-end distance of non-self-intersecting *trans/cis*-polysarcosine chains, having (●) $n = 5$, (○) $n = 8$, (·) $n = 15$. The insert facilitates the comparison for short end-to-end distances.

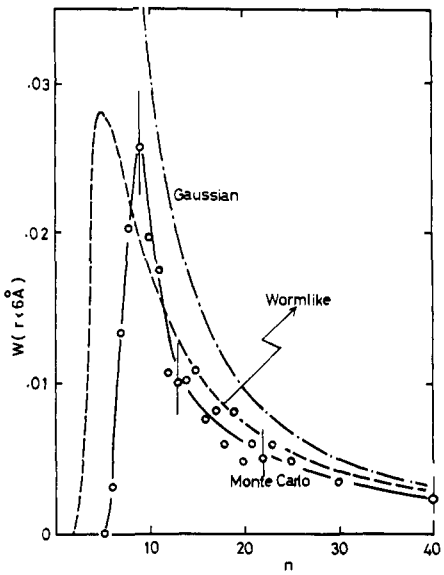


Figure 4. Ring-closure probability for unperturbed *trans*-polysarcosine chains with $r < 6$ Å, (O) Monte Carlo results; the vertical bars represent the 90% confidence range. (- - -) Wormlike chain model (eq 3 and 4); (---) Gaussian chain model (eq 8).

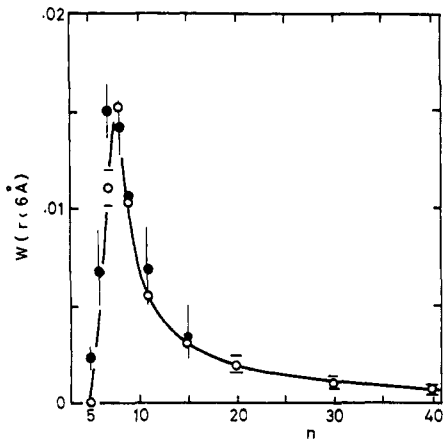


Figure 5. Ring-closure probability with $r < 6$ Å for (Q) non-self-intersecting *trans*-polysarcosine chain and (●) non-self-intersecting *trans/cis*-polysarcosine chain. The 90% confidence ranges were shown by pairs of horizontal lines for *trans*-polysarcosine chains and by vertical bars for *trans/cis*-polysarcosine chains.

distribution. For very short chains the fraction of chains having short end-to-end distance is very small. This implies that the short chains lack the flexibility for cyclization. In fact, the fraction for $r < 5$ Å is virtually zero for the pentamer. The fraction increases abruptly at about $n = 7$ at the expense of the sharpness of the distribution. These situations are more clearly seen in the plot of the RCP against n in Figures 4, 5, and 6.

Ring-Closure Probability. RCP's for unperturbed trans chains (Figure 4), non-self-intersecting trans chains (Figures 5 and 6), and non-self-intersecting trans/cis chains (Figures 5 and 6) are plotted against the chain length n. In calculating the RCP the critical end-to-end distance r_0 was selected to be 4 and 6 Å. These values may correspond to the radius of reaction sphere, in which two terminal groups can interact with each other. In Figures 4 and 5, RCP's with $r < 6$ Å are plotted, and in Figure 6, RCP's with $r < 4$

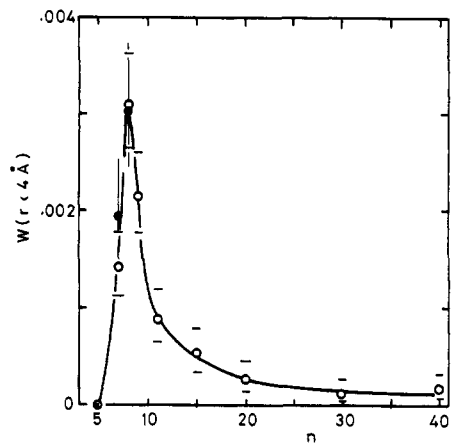


Figure 6. Ring-closure probability with $r < 4$ Å for (O) non-self-intersecting *trans*-polysarcosine chain and (●) non-self-intersecting *trans/cis*-polysarcosine chain. The 90% confidence ranges were shown by pairs of horizontal lines for *trans*-polysarcosine chains and by vertical bars for *trans/cis*-polysarcosine chains.

Å are plotted. The RCP's show sharp maxima at $n = 7$–9 in these figures, which correspond to the first return of the chain end to the origin. The small RCP for short chains indicates the lack of flexibility as mentioned above. The decrease of RCP for longer chains is ascribed to the increasing broadness of the end-to-end distribution. The effect of the excluded volume on the RCP is understandable if a comparison is made between Figures 4 and 5. The RCP was greatly diminished for non-self-intersecting chains. As will be described in a separate paper,[22] the atomic overlap is more important with the chains having a short end-to-end distance. This trend is also found by an inspection of the inserts of Figures 1 and 2, where one can compare the end-to-end distributions for 20-mers of unperturbed chain (Figure 1) and non-self-intersecting chain (Figure 2) for short end-to-end distances. This strongly indicates that the excluded-volume effect should not be ignored in the calculation of RCP. A large effect of excluded volume has also been noted in the calculation of RCP for short polymethylene chains.[3]

On the other hand, only a small change of RCP was observed with introducing cis amide units into the chain (see Figures 5 and 6). The maximum of RCP for $r < 6$ Å lies at $n = 8$ for non-self-intersecting trans chains and at $n = 7$ for trans/cis chains (Figure 5). The maximum of RCP for $r < 4$ Å lies at $n = 7$ in either trans or trans/cis chains (Figure 6). Except for the small difference observed with short chains, the RCP for $r < 6$ Å in trans chains is much the same as that in trans/cis chains. This finding allowed us to assume that the RCP for $r < 4$ Å in trans/cis chains is practically identical with that in trans chains, the former being considerably difficult to evaluate. In the following discussion the RCP of trans chains are used instead of that of trans/cis chains for longer chains.

Ring-Closure Probabilities for Gaussian and Wormlike Chains. Premilat and Hermans, Jr.,[15] reported Monte Carlo calculations on the short poly-L-alanine and polyglycine chains in an unperturbed state and found that the wormlike chain model described well these short poly-α-amino acid chains. The applicability of the wormlike chain model was also found for unperturbed *trans*-polysarcosine chains by us.[22] In this section the RCP was evaluated in terms of either a wormlike chain model or a Gaussian chain model. The RCP for a wormlike chain has been derived by Yamakawa and Stockmayer as[25]

$$W(r < r_0) = \frac{1}{(2a)^3}\left(\frac{3}{2\pi}\right)^{3/2} t^{-3/2}\left[1 - \frac{5}{8}t^{-1} - \frac{79}{640}t^{-2}\right] \times \tfrac{4}{3}\pi r_0^3 \qquad (t > 0.96) \quad (3)$$

$$W(r < r_0) = \frac{1}{(2a)^3}\left(\frac{3}{2\pi}\right)^{3/2} 1.0042t^{-1}\exp(-7.03/t) \times (1 - 0.81242t)\tfrac{4}{3}\pi r_0^3 \qquad (t < 0.96) \quad (4)$$

where t is the reduced chain length,

$$t = L/2a \quad (5)$$

L is the length of a fully extended chain[15,26] and for the *trans*-polysarcosine chain it can be written as

$$L = 3.61n \text{ Å} \quad (6)$$

The persistence length a is determined from the characteristic ratio $(\langle r^2\rangle_0/nl^2)_{n\to\infty}$.[15,26]

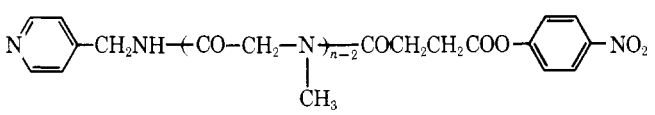
$$a = nl^2(\langle r^2\rangle_0/nl^2)_{n\to\infty}/2L \quad (7)$$

The characteristic ratio has been calculated for an unperturbed *trans*-polysarcosine chain to be 3.68,[22] giving a = 7.37. The RCP calculated by using those parameters is shown in Figure 4. In the same figure the RCP calculated for a Gaussian chain is also shown. The calculation was made using eq 8.[26]

$$W(r < r_0) = \left(\frac{3}{2\pi\langle r^2\rangle_0}\right)^{3/2}\frac{4}{3}r_0^3 \quad (8)$$

The RCP of unperturbed *trans*-polysarcosine determined by a wormlike chain model agreed fairly well with that calculated by Monte Carlo method. The peak position of the RCP for a wormlike chain model is somewhat unreliable because of approximations included in eq 3 and 4,[27,28] and does not deserve to be discussed in detail. The disagreement between the RCP of a Gaussian chain and that for a wormlike chain or the chains generated in the Monte Carlo calculations became less marked at longer chain lengths. For non-self-intersecting chains the results of Monte Carlo calculations cannot be compared with that for a wormlike chain model, because in the latter case the excluded-volume effect has not been taken into account. However, the results in Figure 4, together with other conformational properties studied by a wormlike chain model,[15,22] suggest the usefulness of the wormlike chain model for short polyamino acid chains.

Comparison with Experimental Data. The RCP calculated for polysarcosine chain was compared with the intrachain reaction between a *p*-nitrophenyl ester group and



II

a pyridyl group attached to the ends of polysarcosine chain II.[4] The cyclization constant, which is the ratio of the intrachain rate constant k_1 to the corresponding bimolecular rate constant k_2, is related to the RCP according to eq 9,[2,3]

$$k_1/k_2 = 3000W(r < r_0)/4\pi r_0^3 N_a \text{ mol/l.} \quad (9)$$

where N_a is Avogadro's number. The cyclization constant is equivalent to the effective concentration of one terminal group within the reaction sphere (radius r_0) of the other terminal group. According to eq 9 the cyclization constant was calculated for r_0 = 4 and 6 Å by using the results of Monte Carlo calculations shown in Figures 5 and 6. It should be noted here that the experimental data are the average values for polymers with Poisson-type molecular weight distribution (eq 10).[4]

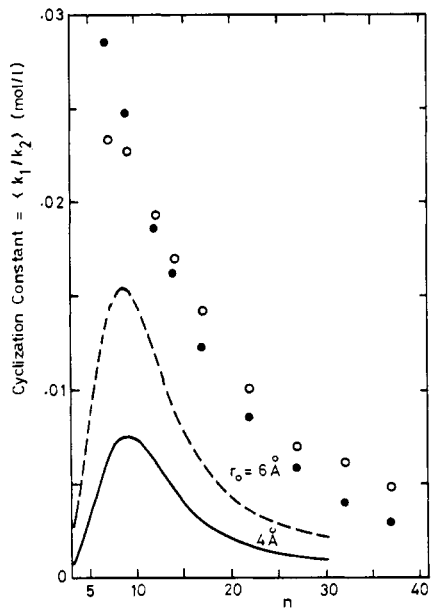


Figure 7. Cyclization constant calculated for polysarcosine chain having Poisson-type molecular weight distribution with (—) r_0 = 4 Å and (- - -) r_0 = 6 Å. Experimental values were shown for the intrachain ester hydrolysis proceeding on polysarcosine chain (II) at (○) 15 °C and (●) 35 °C.

$$f_i(\bar{n}) = \bar{n}^i\,[\exp(-\bar{n})/i!] \quad (10)$$

Therefore, before the comparison was made, the calculated cyclization constant was averaged for the Poisson-type distribution,

$$\langle k_1/k_2\rangle = \sum_i f_i(\bar{n})\,(k_1/k_2) \quad (11)$$

Values thus calculated are shown in Figure 7. As we should expect, the averaged curves showed less sharp maxima as compared with the original ones in Figures 5 and 6. In Figure 7 are also plotted the experimental data obtained at 15 and 35 °C.[4] It was assumed that the terminal aminomethyl and succinate groups in II are equivalent to two sarcosine units in counting n. This will be rationalized by the inspection of structures I and II.

In Figure 7 a rough agreement is seen between calculated and experimental values. However, the experimental values were found to be substantially greater than the calculated values. The neglect of the conformational energy in the Monte Carlo calculation could be a reason for the discrepancy. However, consideration of the conformational energy may lead to a smaller RCP or cyclization constant, because a cyclic conformation has in general a higher energy than a linear one. Indeed, the conformational activation enthalpy for the cyclization ($\Delta H_c^{\ddagger}$) has been found to be positive except for very short chains.[4] The assumption of random orientation of the two reacting groups could explain the discrepancy. However, the restriction of the solid angle for reaction usually reduces the RCP and cannot be a reason for the discrepancy. The arbitrariness of the parameter r_0 also cannot be a reason for the discrepancy because it is hard to take r_0 larger than 6 Å. For the intrachain esterification of ω-hydroxycarboxylic acid, r_0 was estimated to be about 3 Å.[3] The stabilization energy E_s operating between two reacting groups, if any does exist, should not affect the cyclization constant, since E_s affects k_1 as well as k_2 through

the same factor, $\exp(-E_s/RT)$. However, if the stabilization energy is different for intrachain reaction and for intermolecular reaction, its effect is not canceled and values of k_1/k_2 are considerably affected. An increase in the intrachain stabilization energy as small as 0.6 kcal/mol makes k_1/k_2 about 2.7 times larger than its original value. At present this is the most likely reason for the discrepancy, although the origin of the energy difference is not known.

The experimental value of the cyclization constant did not show a clear maximum in the short-chain-length region. To discuss this point in more detail, however, studies on the shorter chains having definite chain lengths are needed. It can be mentioned here that in the polymerization of DL-phenylalanine *N*-carboxyanhydride, initiated by poly(sarcosine)dimethylamide[29] and other poly(*N*-alkylglycine)dimethylamides,[30] the intrachain reaction rate constant showed a distinct maximum at n = 7–9. This is in agreement with the present calculation.

To conclude, the calculated dependence of the cyclization constant on the chain length was consistent with the experimental one, but the agreement of the absolute values between the calculation and the experiment was not perfect.

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Densities of Polymer Solutions to 1 kbar

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ABSTRACT: Volumetric measurements are reported for mixtures of polyisobutylene with benzene and with cyclohexane and for mixtures of polydimethylsiloxane with hexamethyldisiloxane and with cyclohexane. Measurements from 25 to 65 °C extend to 1 kbar. The experimental results show that the pure liquids, as well as their mixtures, are more compressible than predicted by Flory's equation of state.

During the last 10 years, the theory of polymer solutions, as developed by Flory, Patterson, and others, has given primary attention to "equation-of-state" effects, i.e., to that contribution to the solution's thermodynamic excess functions which can be ascribed to free-volume differences between polymer and solvent. At atmospheric pressure and at temperatures near the normal boiling point of the solvent, the free volume of the solvent is generally larger than that of the polymer. This difference in free volume produces significant contributions to both the excess entropy and the excess enthalpy. At higher temperatures, when the solvent is already well expanded, these free-volume differences become a dominant influence on the solution's properties, often leading to phase instability with a lower critical solution temperature.[1] To calculate the effect of free-volume differences, we require an equation of state and it has become common practice to use an equation of the van der Waals type, proposed by Flory.[2] In this work we study the applicability of Flory's equation to volumetric properties of some polymer solutions. Toward that end, we have obtained experimental data for the densities of four, binary polymer–solvent systems at pressures to 1 kbar.

Experimental Section

For high-pressure studies, the experimental equipment is the same as that used by Beret;[3] the central component is a high-pressure cell with a flexible bellows to contain the sample and to isolate it from the pressure-transmitting fluid.[4] The apparatus is calibrated with highly accurate PVT data for mercury and for heptane.[3]

Pressures are measured with a precision Heise gauge whose accuracy is 0.1% of full scale (±1 bar).

The high-pressure cell is located in a constant-temperature bath using silicone oil as heating fluid. The bath is controlled to ±0.01 °C by a Hallikainen proportional temperature controller. Calibrated thermometers, used for temperature measurements, are accurate to ±0.1 °C.

Taking into consideration errors in temperature and pressure measurements as well as errors in calibration, the overall uncertainty of our relative volume measurements is 0.04%.

For measuring specific volumes at atmospheric pressure, a conventional glass dilatometer was used. The dilatometer was cali-