A Monte Carlo Study of the Intrachain Reaction on a Poly(oxyethylene) Chain*

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Monte Carlo calculation was performed to estimate the ring-closure probability of a poly(oxyethylene) chain. The calculation was made for various chain lengths on the basis of a rotational isomeric state model in which the intrachain atomic overlaps were excluded in terms of the hard-sphere model. The chain-length dependence of the ring-closure probability thus obtained was compared with that of the rate-constant ratio of the intrachain reaction *vs.* the intermolecular reaction previously reported. For longer chains, the calculation agreed well with the experimental data. For shorter chains, the agreement was less satisfactory; this discrepancy was attributed to the effect of the bulky terminal groups of the poly(oxyethylene) chain. The thermodynamic parameters for the cyclization were determined, and it was found that the chain-length dependence of the ring-closure probability is mainly governed by the conformational enthalpy.

Intrachain reactions of X–Y-type polymers may provide information concerning the flexibility of a polymer chain, which is hard to determine quantitatively by other means. Provided that the reaction requires a moderately high activation energy, the rate of intrachain reaction on a polymer chain should be proportional to the ring-closure probability of the polymer chain.[1] The ring-closure probability of a polymer chain has been reported to be sensitive to the conformational property of the polymer chain.[2] In other words, the intrachain reaction on a polymer chain is strongly affected by the nature of the polymer chain. In this respect, a comparison of the experimental results of the intrachain reaction with the conformational calculation would seem to be interesting. This sort of comparison has been made for intrachain reactions on polymethylene chains,[1,3,4] polysarcosine chains,[5,6] and RNA chains.[7,8] The ring-closure probabilities of various condensation polymers have also been calculated in connection with the ring-chain equilibria in solution and in bulk.[9]

In our previous investigations,[7,8] a polysarcosine chain was used as a "spacer" for an intrachain aminolysis of a *p*-nitrophenyl ester group by a 4-pyridyl group in an aqueous solution. When the rate constants of the intrachain reaction were compared with those calculated by the Monte Carlo method, a fairly good agreement was found between them. This prompted us to carry out the Monte Carlo calculation for the poly(oxyethylene) chain, which has been used as a "spacer" for the same intrachain reaction.[10] Since the poly(oxyethylene) chain is different from other chains in its preference for the *gauche* conformational state for each bond, characteristic behavior in the ring-closure probability is expected. The ring-closure probability was calculated as a function of the chain length and was compared with experimental data on the rate-constant ratio of intrachain to intermolecular reactions. The agreement between them was compared with that previously obtained with polysarcosine.

Conformational calculations of poly(oxyethylene) chains have been conducted by Mark and Flory[11] and recently by Abe and Mark[12] on the basis of the *t-g* rotational isomer model. The most characteristic feature of the chain is the preference for the *gauche* rotational state, for reasons not yet completely clear. In the present calculation, therefore, the "*gauche* effect" was taken into consideration by adding a corrective energy for the *gauche* state, as was recently suggested by Abe and Mark.[12] By using these effective parameters, the conformational properties, such as the average dimensions and the dipole moment of poly(oxyethylene) chains, have been successfully reproduced.[12] Hence, the same parameters were used in the present Monte Carlo calculation.

Procedures for the Monte Carlo Calculation

Structure and Energy Parameters. As has been stated above, some ambiguity remains as to the conformational parameters for poly(oxyethylene) chains. In this study, the most recent values proposed by Abe and Mark[12] were used (Table 1). It should be noted that the rotational angles for the *gauche* states, $\phi_g\pm$, are taken as $\pm 110°$ instead of the usual value of $\pm 120°$. However, such small changes in the parameters did not cause any significant change in the ring-closure probability calculated. The bulkiness of the two terminal groups, a 4-pyridyl group and a *p*-nitrophenoxycarbonyl group, was not taken into considereation, and the computation was carried out for the skeletal structure I. It has been shown that the excluded volume effect is

$$\text{C-O-(-C-C-O-)}_m\text{-C},\ m=3\text{—}20 \qquad \text{(I)}$$

essential in the calculation of the ring-closure probability.[3] In this calculation, the skeletal overlaps were excluded in such a way that the conformations in which any pair of skeletal atoms fall within the sum of their atomic radii (Table 1) are rejected.

Table 1. Structure and energy parameters of poly(oxyethylene)

l(C-O) = 1.43 Å, l(C-C) = 1.53 Å,
$\angle$COC = $\angle$CCO = 111.5°
ϕ_g(C-O) = ϕ_g(C-C) = $\pm 110°$,
$E_{\sigma 2} = -0.5$ kcal/mol, $E_{\sigma 2'} = 0.9$ kcal/mol,
$E_{\omega 2} = 0.4$ kcal/mol.

For notations, see Ref. 12.

* Intrachain Reaction of a Pair of Reactive Groups Attached to Polymer Ends. Part VII.

Evaluation of the Ring-Closure Probability. The ring-closure probability is expressed as the ratio of the (conformational) partition function for ring conformations to that of the total ones. If a chain is regarded as cyclic when it takes an end-to-end distance, r, shorter than the critical distance, r_0, then the ring-closure probability is expressed as

$$W(r<r_0) = Z(r<r_0)/Z_t. \quad (1)$$

If the excluded volume effect is taken into account in the Monte Carlo calculation, the two partition functions should be estimated by generating the non-self-intersecting chains randomly. However, since the exclusion of the overlapping conformations requires a very long computation time, the exclusion process was performed after cyclic conformations were generated. For this purpose, Eq. 1 was rewritten as[6]

$$W(r<r_0) = \frac{Z(r<r_0)/Z_0}{Z_t/Z_0}, \quad (2)$$

where Z_0 is the total partition function for the conformations including any atomic overlaps. To calculate the numerator, a number of conformations were first generated without excluding the atomic overlaps, and then the check for the skeletal overlap was made only for the cyclic ($r<r_0$) conformations. The denominator represents the fraction of the non-self-intersecting conformations. This quantity can be calculated accurately from a relatively small number of Monte Carlo samples. The average value of the numerator was determined from 80000 Monte Carlo chains including skeletal overlaps. This procedure was repeated five times to obtain a total average of 400000 chains. The denominator was determined from $10000\times5=50000$ chains. In this case, the scattering among the five averages was not significant.

Results and Discussion

The ring-closure probabilities for poly(oxyethylene) chains whose chain lengths, m, range from 3 to 20 are shown in Fig. 1 for $r_0=6$ Å and in Fig. 2 for $r_0=4$ Å. The small open circles indicate the average value for 80000 chains, and the large open circles, the total average for 400000 chains. The probability shows a peak at $m=4$ or 5, indicating the presence of the optimum chain length for the intrachain reaction. In the two figures, the Monte Carlo data for polysarcosine chains[6] are also shown; they have been obtained by means of a hard-sphere model, without taking the conformational energy into account. The ring-closure probability for polysarcosine chains also shows a maximum, but the optimum chain length is considerably longer than that of poly(oxyethylene) chains. The ring-closure probability has been calculated for polymethylene chains[1] and found to reach a maximum at $j=20$, where j is the number of methylene units and corresponds approximately to 3 m. Therefore, the optimum chain length for the cyclization of poly(oxyethylene) chains is much shorter than for the other two chains. The conclusion from the calculation is undoubtedly related to the preference of a poly(oxyethylene) chain

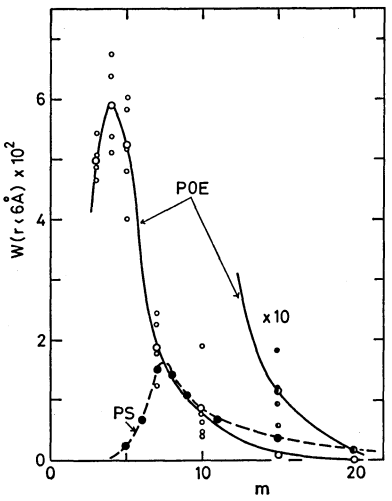


Fig. 1. Ring-closure probabilities for poly(oxyethylene) chain calculated for $r_0=6$Å. Small circles (○, ◐) indicate the local averages for 80000 chains and large circles (○, ◐) the total average for 400000 chains. (◐) and (◐) represent $W(r<6\text{Å})\times10^3$ for clarity for longer chains. Data for polysarcosine chain[6] are also shown with (●).

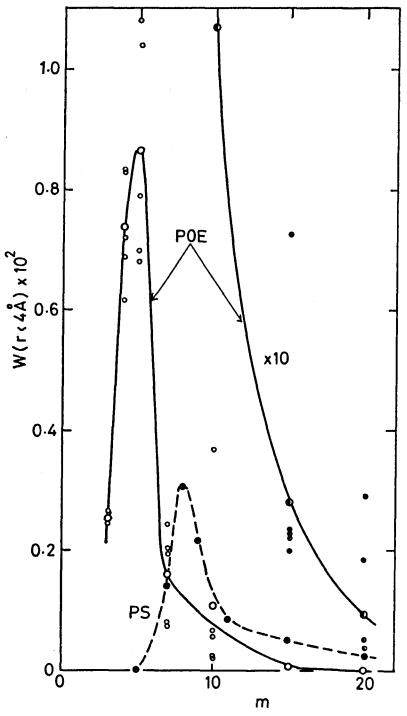


Fig. 2. Ring-closure probabilities for poly(oxyethylene) chain calculated for $r_0=4$Å. For the notations, see Fig. 1.

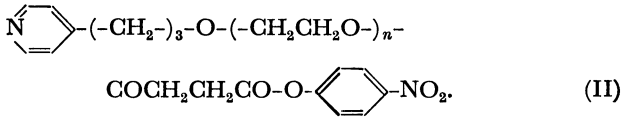
for *gauche* rotational states. Apart from the extraordinary high tendency to cyclize into a six-membered ring, which has been commonly found for various chains and is not included in the figures, the ring-closure probability at the optimum chain length is very large for poly(oxyethylene) chains. However, the probability decreases drastically with an increase in the chain length. For longer chains than $m=10$, the probability becomes smaller than that of polysarcosine chains, and

at $m=20$ it virtually vanishes.

The ratio of the rate constants for intra- and intermolecular reactions is related to the ring-closure probability, thus[1,3]

$$\frac{k_1}{k_2}=\frac{3000W(r<r_0)}{4\pi r_0^3 N_a}\ \text{mol/dm}^3, \tag{3}$$

where r_0 is the critical distance for the reaction and N_a is the Avogadro number. The ratios calculated for poly(oxyethylene) and polysarcosine chains by using the ring-closure probability for $r_0=4$ Å are shown in Fig. 3 (top), and there compared with the experimental results (bottom). The abscissa of Fig. 3 is taken as $n=m-2$ to match the actual structure (II) with the structure (I) of the poly(oxyethylene) model:



The agreement between the calculation and the experiment is fairly good for polysarcosine chain, except that the optimum chain length is not seen in the experimental data.[5] In contrast, with poly(oxyethylene) chains the optimum point is actually observed. However, the experimental rate-constant ratio at the optimum point is 10 times as small as the calculated one. For chains longer than $m=10$, the experimental rate-constant ratios for the poly(oxyethylene) chains are smaller than for the polysarcosine chains, as is to be expected from the calculation. The small ring-closure probabilities for long poly(oxyethylene) chains may be attributed to the high tendency to form small rings. In Fig. 3 the yield of cyclic n-mer in the oligomerization of ethylene oxide in dioxane initiated by BF_3 is also shown.[13] Because of the lack of detailed experimental data, however, the rate constant ratio cannot be obtained. In this case no bulky terminal group is present; hence, the yield can be compared with the k_1/k_2 calculated without considering the bulkiness of the two terminal groups. This permits a more direct comparison between the experimental and the calculated values than in the case of the intrachain reaction. In fact, a sharp maximum is seen in the yield of cyclic oligomers; this maximum is shorter by one oxyethylene unit than the calculated one. In summary, the results of the calculation on poly(oxyethylene) chains agreed with the observations of the intrachain reactions for longer chains. The deviation for shorter chains may be attributed to the steric repulsion between two terminal groups, which has not been taken into account in the calculation.

The ring-closure probabilities calculated at 15, 25, and 35 °C were used to determine thermodynamic parameters, ΔH_c and ΔS_c, for the conformational change accompanying the cyclization. The enthalpy change, ΔH_c, was determined from the temperature dependence of the ring-closure probabilities calculated for the same 80000 Monte Carlo samples. The total average for 400000 chains was calculated by using these locally averaged values. The entropy change, ΔS_c, was determined by using the total averages of the enthalpy and the ring-closure probability. The

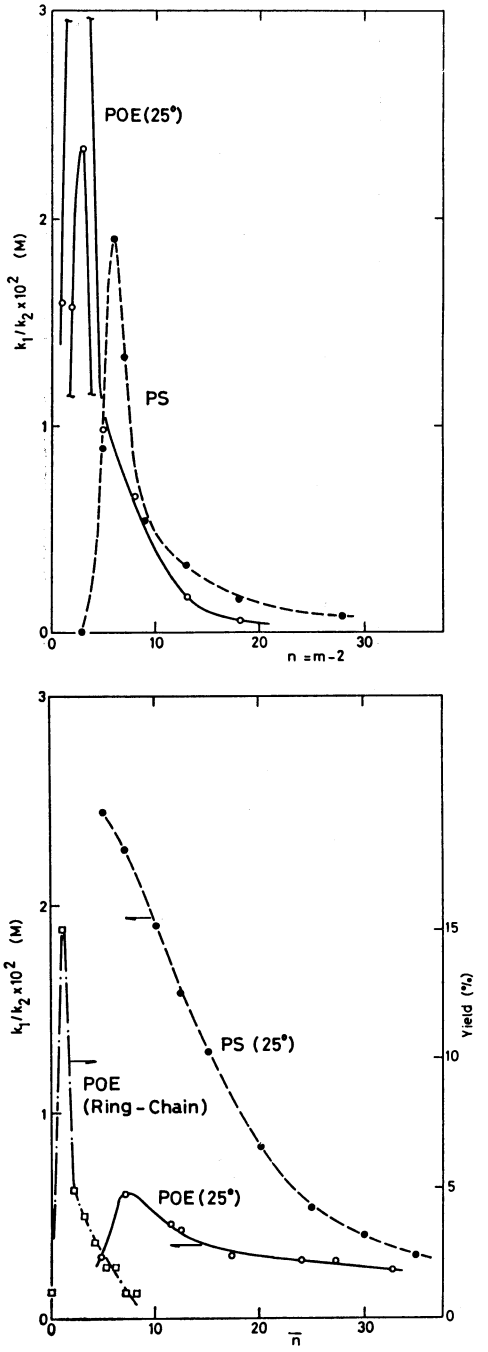


Fig. 3. Comparison of the observed (bottom) and the calculated (top) rate-constant ratio for intra- and intermolecular reactions. In the bottom, POE(Ring-Chain) represents the yield of cyclic oligomer in the ring-chain equilibrium attained in the oligomerization of ethylene oxide.[13] In the top, the data for poly(oxyethylene) chain having $n=4$ and 5 are subtracted by 3×10^{-2} for clarity. The abscissa is taken as $n=m-2$ to match the actual structure (II) with the model structure (I).

results are shown in Fig. 4, where the local average values of ΔH_c are indicated by small circles, and the total average, by a large circle. It is clear that the chain-length dependence of ΔH_c virtually determines the chain-length dependence of the ring-closure pro-

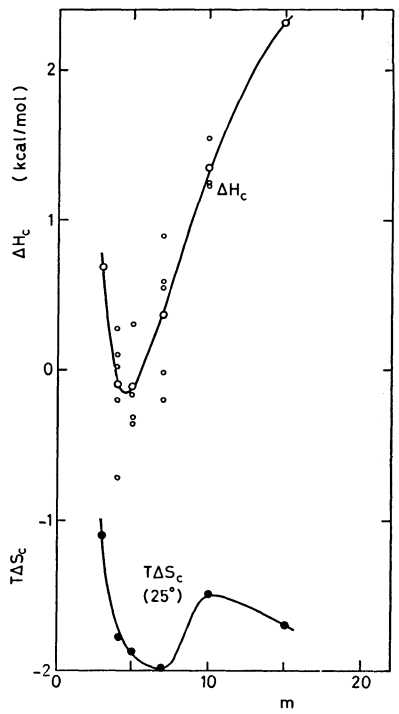


Fig. 4. Thermodynamic parameters for the cyclization and the chain length of poly(oxyethylene). Small and large open circles (○, ◯) indicate the local and the total averages of ΔH_c, respectively.

bability and, hence, the ease of the intrachain reaction. At the optimum chain length in the calculated k_1/k_2, ΔH_c is nearly zero, indicating that no excess energy is required for the optimum cyclization. The predominance of the enthalpy factor is somewhat unexpected, since it is natural to consider that the ease of the intrachain reaction is determined by the fraction of cyclic conformations and, hence, by the entropy factor. The predominance of the enthalpy factor has been found in the calculation for the ring-closure probability of polymethylene chains[3] and actually observed in some intrachain reactions on polysarcosine.[5] However, the entropy factor has been found experimentally to be important in the intrachain reaction on poly(oxyethylene) chains.[10] Since the chain-length dependence of the thermodynamic parameters has been reported to change drastically in different solvents,[14,15] the solvation of polymer chains may be another important factor in determining the thermodynamic parameters. The plot of the calculated values of ΔH_c against the calculated values of ΔS_c did not result in a straight line. This is in marked contrast with the same sort of plot between the experimental values of ΔH_c and ΔS_c, which gave a straight line.[10] This difference may also be attributed to the effect of solvation which operates in the real reaction, but which was ignored in the calculation. The solvation must compensate for the disadvantage due to the loss of entropy in a cyclic conformation and stabilize the latter, but the mechanism of solvation is not yet clear.

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