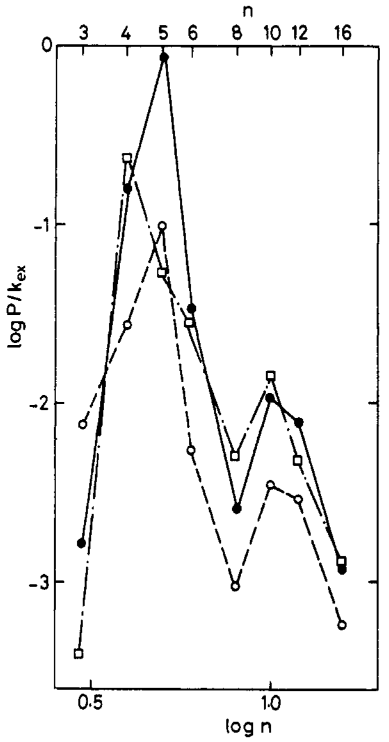

Figure 3. The ratios P/k_{ex} calculated for αN-(CH$_2$)$_n$-αN$^{-}\cdot$ using three types of reaction probabilites: (1) the core-type probability with r_0 = 6 Å (---□---), (2) the separation-dependent probability with a = 4.0 Å^{-1} (--○--), and (3) the separation- and orientation-dependent probability with a = 4.0 Å^{-1} (-●-).

sions of these calculations were the same as the present study, indicating that a small change in the structure of terminal groups or the connecting chain may not affect the orientational constraint for the terminal groups.

The results of the present calculation showed that the proximity and orientation constraints are not serious in the intramolecular reaction on a poly(methylene) chain and the reaction can be adequately treated with the core-type reaction probability. These findings are compatible with the fact that calculations based on the core-probability model show good agreement with the experimental data.[11-16] In other words, the experimental data of the intramolecular reaction may not afford any information as to the orientation dependence of the reaction probability.

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Computer Simulation of the Intramolecular Electron Transfer in PI(CH$_2$)$_n$PI$^-$• and PI(CH$_2$CH$_2$O)$_m$CH$_2$CH$_2$PI$^-$• Systems

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The end-to-end intrachain reaction of a chain molecule may provide information on the dynamics and the statics of the chain conformation depending upon the activation energy of the reaction.[1] If the activation energy of the reaction is intrinsically low, the intrachain reaction will be controlled by the diffusion process of two terminal reactive groups approaching each other.[2-6] In the previous paper, we reported a study on the frequency of intramolecular electron transfer in αN-(CH$_2$)$_n$-αN$^{-}\cdot$, where αN denotes an α-naphthyl group.[7-9] The frequency was considered as that of the exchange between the favorable conformation for the electron transfer and the unfavorable ones and was calculated as the ratio of the static probability of finding the chain molecule in favorable conformations to the mean lifetime of the favorable conformations. Good agreement between calculated and experimentally obtained results was observed when the favorable conformations for electron transfer were assumed to have end-to-end distances, r, shorter than a critical distance r_0 (r_0 was 8 Å). The good applicability of the dynamic model to the real system prompted us to simulate the frequency of intramolecular electron transfer in PI-(CH$_2$)$_n$PI$^{-}\cdot$ and PI(CH$_2$CH$_2$O)$_m$PI$^{-}\cdot$ systems, where PI denotes an N-phthalimide group.[10] As the chain length dependences of the electron transfer frequency in these three systems are substantially different, the simulation is expected to give an insight into the static and dynamic behaviors of chain conformations.

Hence, conformational calculations of poly(methylene) and poly(oxyethylene) chains were carried out, the structure of the PI group being explicitly taken into consideration. The probability $W(r \leq r_0)$ of finding conformations favorable for the electron transfer having

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their end-to-end distance r shorter than r_0 was calculated.

The probability was calculated by the direct enumeration of non-self-intersecting conformations of PI(CH$_2$)$_n$PI and PI(CH$_2$CH$_2$O)$_m$PI molecules, where the bulkiness of the terminal N-phthalimide groups was taken into consideration.[1,3,9] For those groups having $n \geq 12$, the Monte-Carlo method was used instead of direct enumeration.[9] Calculations were also made for *trans*-1,4-bis(N-phthalimidoylmethyl)cyclohexane and *cis*-1,3-bis(N-phthalimidoylmethyl)cyclohexane.[11]

Conformational energy for 1-(N-phthalimidoyl)propane was calculated using semiempirical potential functions. Structural parameters are shown in Figure 1. The N-phthalimide group was assumed to be planar, and the bond lengths and bond angles were taken from succinimide[12] and benzene.[13] Semiempirical potential functions were the same as those used by Brant and Flory.[14] The rotational potential around ϕ_2 was neglected.[9] Positions of energy minima and the contour lines 500 cal/mol higher than each minimum were calculated in (ϕ_2, ϕ_3) coordinates. Each region surrounded by the contour line was very large, and it seemed inadequate to represent each by a single point positioned at the minimum. Hence, two or three points were taken from each region as the stable rotational isomeric states for the two terminal C–C bonds. The points, their energies, and their weights are collected in Table I. The weight for each point (ϕ_2, ϕ_3) was calculated as the area surrounded by the contour line divided by the number of points contained in the region. Calculation of conformational energy was also carried out for (N-phthalimidoylmethyl)cyclohexane where an N-phthalimidoylmethyl group is attached to an equatorial position of the cyclohexane ring. Structural and energy parameters were the same as those used above, although tetrahedral bond angles were used for the cyclohexane ring. In this case, each allowed region surrounded by the contour line of 500 cal/mol is small enough to be approximated by a single point located at each minimum. The rotational angles, energy, and weight are listed in Table II.

Conformations of the two polymeric molecules were generated on the basis of the trans-gauche rotational isomeric state model.[15] Geometrical and energy parameters for the poly(methylene) chain were the same as those used by Abe et al.[16] except for the penultimate and the ultimate bonds. Parameters for the latter two bonds were taken from Table I. Parameters for the poly(oxyethylene) chain were taken from the recent paper of Abe and Mark,[17] where the rotational angles for gauche states are assumed to be ±110°. A direct enumeration method was applied for poly(methylene) chains with $n \leq 10$ for poly(oxyethylene) chains with m = 1-4. Intrachain atomic overlap was excluded by means of assigning an atomic radius of 1.5 Å to a carbon atom and 1.3 Å to oxygen and nitrogen atoms.[18] Conformations having any skeletal atom pairs closer than the sum of their atomic radii were discarded. For each non-self-intersecting conformation, the energy (E), the statistical weight for the rotational states of terminal C–C bonds ($w = w_{\text{right}}w_{\text{left}}$), and the end-to-end distance (r) were obtained. The end-to-end distance was measured between the centers of C$_2^{\text{P}}$–C$_7^{\text{P}}$ bonds (Figure 1) of the two phthalimide groups.

For poly(methylene) chains with $n \geq 12$, the direct enumeration was impractically time consuming, and the Monte-Carlo method was applied instead. In the latter case, 4000 non-self-intersecting chains were generated and average quantities were obtained. This step was repeated four times and the total average was calculated from the 16 000 samples. At n = 10, calculations were carried out by the two methods, and the two results agreed within the statistical error of the Monte-Carlo method.

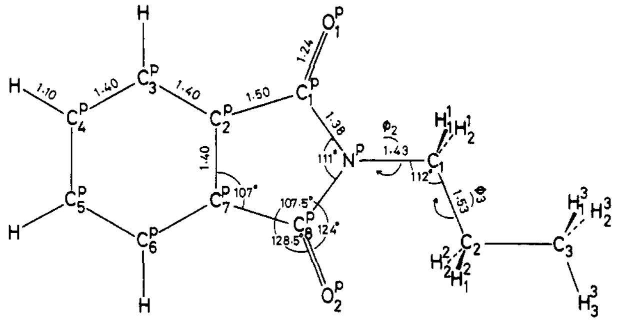

Figure 1. Structural parameters of 1-(N-phthalimidoyl)propane. The conformation at $\phi_2 = \phi_3 = 0$ is shown.

Table I
Stable Rotational States for the N-C$_1$ Bond (ϕ_2) and the C$_1$-C$_2$ Bond (ϕ_3) in PICH$_2$CH$_2$CH$_3$

ϕ_2, deg	ϕ_3, deg	E, kcal/mol[a]	w[b]
95	120	0	1.125
110	120	0	1.125
70	0	1056	1.597
90	0	1056	1.597
110	0	1056	1.597
70	−120	0	1.125
85	−120	0	1.125

[a] Conformational energy at the potential minimum. [b] Statistical weight (arbitrary scale).

Table II
Stable Rotational States for the N-C$_1$ Bond (ϕ_2) and the C$_1$-C$_2$ Bond (ϕ_3) in PIC$_1$C$_6$H$_{11}$[c]

ϕ_2, deg	ϕ_3, deg	E, kcal/mol[a]	w[b]
80	0	534	2.05
90	240	0	0.61
100	120	534	2.05

[a] Conformational energy at the potential minimum. [b] Statistical weight (arbitrary scale). [c] The origin of ϕ_3 is taken in such a manner that the two C–C bonds attached to C$_2$ are located at t (ϕ_3 = 0) and g^+ (120°).

Calculations for *trans*-1,4-bis(N-phthalimidoylmethyl)cyclohexane and *cis*-1,3-bis(N-phthalimidoylmethyl)cyclohexane were also made by the direct enumeration technique. The former is analogous to a linear chain with n = 6 in the x-x-t-g^--t-x-x conformation (x = t, g^+, or g^-), and hence it will be referred to as n = 6c. Similarly, the latter molecule is analogous to a linear one with n = 5 in the x-x-t-t-x-x conformation and will be referred to as n = 5c.

The principle of microscopic balance can be applied to the dynamic equilibrium between conformations favorable for electron transfer and unfavorable for electron transfer.[9] Thus the frequency P of intramolecular electron transfer is related to the equilibrium probability $W(r \leq r_0)$ of finding the molecule in a cyclic conformation with $r \leq r_0$, as

$$P = W(r \leq r_0)/2\langle\tau\rangle_1 \qquad (1)$$

where $\langle\tau\rangle_1$ is the mean lifetime of the cyclic conformation.[9] Here, we assume that $\langle\tau\rangle_1$ is approximately independent of chain length and nearly equal to the mean lifetime $\langle\tau\rangle_2$ of the intermolecular encounter.[9] This assumption yields the following simple relation for the ratio of the transfer frequency to the corresponding bimolecular rate constant k_{ex}:[9]

$$P/k_{\text{ex}} = 3000W(r \leq r_0)/4\pi r_0^3 N_{\text{a}} \qquad (2)$$

where N_a is Avogadro's number. In the following part of this paper, the probability $W(r \leq r_0)$ will be calculated for various values of r_0 and will be used to evaluate P/k_{ex}.

The results for the $PI(CH_2)_nPI$ system are shown in Figure 2. When we assume $r_0 = 7$ Å, the calculated chain length dependence and the absolute values of P/k_{ex} are in good agreement with the observed data in HMPA (hexamethylphosphoric triamide)[10] except for the molecule with $n = 3$, where the calculated value vanishes. It should be noted that the minimum of P/k_{ex} is also seen in the calculated data with $r_0 = 7$ Å, although the minimum point is shifted from $n = 6$ (observed) to $n = 9$ (calculated). When $r_0 = 9$ Å, the calculated value decreases monotonically with increase of the chain length. When $r_0 = 6$ Å is adopted, the calculated probability vanishes at $n = 3$, 4, 5, and 6, and therefore the value is not acceptable. In Figure 2, the data for n = 5c are also shown. Results calculated for n = 5c with r_0 = 6, 7, and 9 Å exceed considerably the observed value. A calculation for n = 6c revealed that there is no possibility for this molecule to make the two phthalimide groups closer than 8.5 Å. This finding is in accordance with the unmeasurably low frequency of electron transfer observed for this molecule.[11] These considerations lead us to conclude that the best value of r_0 is 7 Å for the electron transfer between two phthalimide groups in HMPA solution.

The dependence of P/k_{ex} for the poly(oxyethylene) series with $m = 1$ to 4 is shown in Figure 3. The results calculated with $r_0 = 7$ Å are again in good agreement with the observed results, except for the shortest chain ($m = 1$). The value calculated with $r_0 = 9$ Å decreases monotonically with the increase of m, and this contradicts the observed data. If we assume $r_0 = 6$ Å, the calculated values are substantially smaller than the observed ones, except for $m = 1$.

As was seen in Figures 2 and 3, good agreements were obtained only for long chains. The disagreements at short chains were not improved by a small change of the structural parameters, e.g., by taking only minima as the stable rotational states of ϕ_2 and ϕ_3 or by changing the rotational angles for the gauche state of oxyethylene chain from 110 to 120°. Three possible reasons for the disagreement may be considered. (1) In short chains the mean lifetime $\langle\tau\rangle_1$ of favorable conformations may be somewhat larger than that for longer chains, because of a reduced degree of conformational freedom. According to eq 1, a larger mean lifetime leads to a lower frequency of electron transfer. However, in the previous calculation on the $\alpha N\text{-}(CH_2)_n\text{-}\alpha N^{-}\cdot$ system, no substantial discrepancy was seen even at $n = 4$.[9] Therefore, this is an unlikely reason. (2) The second possible reason is an orientation effect which has not been considered in this calculation. If face-to-face conformations, which may be favorable for the electron transfer, are very few in short chains, the observed frequency may be much lower than that estimated without considering the orientation. However, a more detailed calculation where the orientation effect was included indicated that the effect is not so large as to alter the chain length dependence of P/k_{ex}, except for the case of $n = 3$.[19] Hence this effect also cannot be a reason for the discrepancy. (3) The third reason is the effect of dipole–monopole interaction between a phthalimide group and a phthalimide anion radical. The interaction may stabilize or destabilize the cyclic conformations depending on the mutual orientation of the two groups and affect $W(r \leq r_0)$ and $\langle\tau\rangle_1$, especially for short chains.

The substitution of a phthalimide group for an α-naphthyl group may affect the intramolecular electron transfer in two ways: (1) it may change the critical distance r_0 and (2) the conformations of the poly(methylene) chain. These may result in the different chain length dependence of the transfer frequency. In the present study, the best value of r_0 for the *N*-phthalimide group was found to be 7 Å, which is a little shorter than that for the α-naphthyl group (8 Å).[9] The shorter r_0 value for the phthalimide group has been strongly suggested from the comparison of the frequencies of electron transfer in *trans*-1,4-bis(α-naphthylmethyl)cyclohexane ($P = 0.9 \times 10^7$ s^{-1}, at 15 °C) and its phthalimidoyl analogue (P is unmeasurably small)[11] in HMPA solution. It is interesting to note that the chain length dependence of the probability $W(r \leq r_0)$

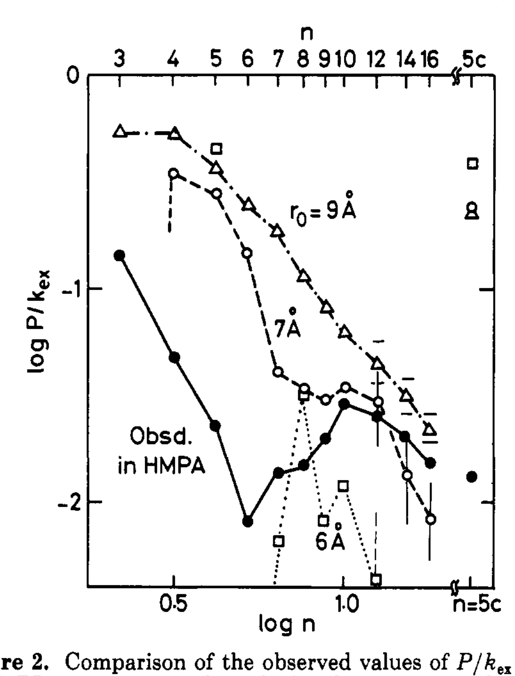

Figure 2. Comparison of the observed values of P/k_{ex} in $PI(CH_2)_nPI$ systems with the calculated ones at 15 °C: (-●-) observed value in HMPA; (---△---) calculated value with r_0 = 9 Å, (- -○- -) r_0 = 7 Å, and (···□···) r_0 = 6 Å. The pair of horizontal bars and the vertical bars for the calculated values at n = 12, 14, and 16 indicate the range of the scattering of the Monte-Carlo data with 4000 samples.

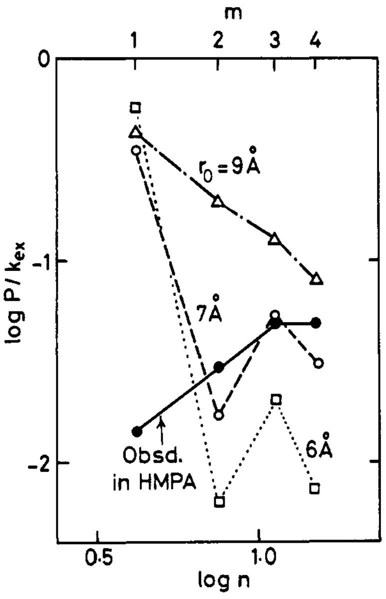

Figure 3. Comparison of the observed values of P/k_{ex} in $PI(CH_2CH_2O)_mCH_2CH_2PI$ systems with the calculated ones at 15 °C: (-●-) observed value in HMPA; (---△---) calculated value with r_0 = 9 Å, (- -○- -) r_0 = 7 Å, and (···□···) r_0 = 6 Å.

changes remarkably with different r_0 values (see Figures 2 and 3). For small r_0 values, a minimum at $n = 6$–8 appears. With increasing r_0, the minimum disappears and the probability decreases monotonically with n. The same trend has been obtained in the αN-$(CH_2)_n$-αN system.[9] It should be pointed out that the intramolecular ring-closure reaction in the $X(CH_2)_nY$-type molecule is highly difficult at $n = 8$–13, and it becomes easy at longer chain lengths.[3] This is in accordance with the present study as the critical distance for ordinary ring closure reaction may be very small, being about 3 Å. Here, care must be taken when the results of the diffusion-controlled reactions and those of the ordinary reactions with a moderately high activation energy are discussed on the same ground. The chain length dependences of the two types of reactions can be compared only when the mean lifetime of the favorable conformations $\langle\tau\rangle_1$ is independent of the chain length (see eq 1).

The effect of different steric restrictions caused by the phthalimide and the α-naphthyl groups on the conformations of the methylene chain is apparent when the probability $W(r \le r_0)$ obtained for $PI(CH_2)_nPI$ is compared with that for αN-$(CH_2)_n$-αN.[9] When $r_0 = 9$ Å, they reveal approximately the same values in both systems. On the other hand, when $r_0 = 7$ Å, a substitution of the phthalimide group by the naphthyl reduced the probability at $n = 6$ by a factor of 0.2 and shifted the minimum point from $n = 9$ to 6. If we adopt $r_0 = 6$ Å, the same substitution causes an even larger change in the chain length dependence of the probability for chains of $n \le 8$. These findings indicate the importance of the steric structure of terminal groups in the conformational calculation of $X(CH_2)Y$-type molecules, especially when r_0 is small.

To conclude, the calculation of the chain length dependence of the frequency of intramolecular electron transfer in $PI(CH_2)_nPI$ with $n = 7$–14 or PI-$(CH_2CH_2O)_mCH_2CH_2PI$ with $m = 2$–4 reproduced the relevant experimental findings. The disagreement between calculated and observed results is found in short chains.

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Random-Coil Configurations of the Polyformals $[CH_2O(CH_2)_yO-]$. 3. The Temperature Coefficient of the Unperturbed Dimensions of Poly(1,3-dioxolane) $[CH_2O(CH_2)_2O-]$

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The two properties which have been most extensively used to characterize the spatial configurations of polymer chains are the unperturbed dimension $\langle r^2\rangle_0$[1,2] and dipole moments $\langle\mu^2\rangle_0$.[3] The information obtained from these two properties is frequently supplementary since different properties generally have a different sensitivity to temperature, to chain length, and to the statistical weights used to characterize the various permitted conformations of the chain. The temperature coefficients of $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$ are frequently also very different. For example, in the case of poly(oxymethylene) (POM) $[CH_2\text{–}O\text{–}]$, $d \ln \langle r^2\rangle_0/dT$ is large and negative whereas $d \ln \langle\mu^2\rangle_0/dT$ is large and positive.[3-5] This results from the fact that the low-energy conformation of the chain is the all-gauche 9_5 helix; it is of high spatial extension but of almost zero dipole moment so disruption of these helical sequences by increase in temperature decreases $\langle r^2\rangle_0$ but increases $\langle\mu^2\rangle_0$.[3-5]

Poly(1,3-dioxolane) (PXL) $[CH_2\text{–}O\text{–}CH_2\text{–}CH_2\text{–}O\text{–}]$ represents a very similar situation in some respects.[6] The coefficient $d \ln \langle\mu^2\rangle_0/dT$ is large and positive, primarily because of the temperature-induced disruptions of the POM-type helical sequences; the experimental value of $6.0 \times 10^{-3}\ K^{-1}$ is in fact well reproduced by rotational isomeric state calculations.[6] The unperturbed dimensions of PXL depend more strongly on all of the conformational transitions than do the dipole moments (nonpolar as well as polar skeletal bonds contribute to $\langle r^2\rangle_0$, and the fact that two of the five skeletal bonds in the repeat unit prefer trans states becomes more important).[7] As a result, calculations based on a rotational isomeric state model[6-8] of PXL predict that $d \ln \langle r^2\rangle_0/dT$ should be positive and about an order of magnitude smaller than $d \ln \langle\mu^2\rangle_0/dT$. Specifically, preliminary calculations predict $10^3\ d \ln \langle r^2\rangle_0/dT \simeq 0.2\ K^{-1}$.[7] This is puzzling since the only published experimental values[9] of this coefficient are $-1.7\ K^{-1}$ (in benzene) and $-3.9\ K^{-1}$ (in chloroform). These experimental results are highly suspect, however, since they were obtained by viscosity–molecular weight extrapolation methods which are of questionable reliability,[10] particularly when used to determine a relatively small quantity such as $d \ln \langle r^2\rangle_0/dT$.[11] The present study was therefore undertaken in order to provide a more reliable estimate of this important quantity, using viscosity–temperature measurements in an athermal solvent.

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