Journal of the Korean Chemical Society
2007, *Vol. 51, No. 3*
Printed in the Republic of Korea

First Passage Time between Ends of a Polymer Chain

성 재 영*
중앙대학교 화학과
(2007. 4. 12 접수)

First Passage Time between Ends of a Polymer Chain

Jaeyoung Sung*
Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea
(Received April 12, 2007)

요 약. 윌렘스키-픽스만(Wilehemski-Fixmann)의 사슬고분자 내 화학반응동력학 이론을 반응 그룹들 간의 배제효과를 고려하여 개선하였다. 가우스 체인 양극단 반응 모델의 반응 동력학에 대한 해석적인 표현을 얻어 이를 브라운 동력학 모의 실험결과와 비교하였다. 비교결과 본 이론의 예측이 기존 이론들의 예측 보다 모의실험 결과와 더 잘 일치하였다.

주제어: 사슬고분자, 반응동력학, 브라운운동, 최초만남시간

Abstract. We improve Wilehemski-Fixmann theory for intrachain reaction dynamics of a polymer chain by taking into account excluded volume effects between reactive groups in the polymerchain. An approximate analytic expression for the intra-chain reaction dynamics is obtained for Gaussian chain model and compared to Brownian dynamics simulation results. The results of the present theory are in a better agreement to Brownian dynamics simulation results than those calculated by previously reported theories.

Keywords: Chain Polymer, Reaction dynamics, Brownian motion, First Passage Time

INTRODUCTION

A number of complex dynamical processes in nature are stochastic processes, and it is often of our concern to know the time when a particular event occurs for the first time in a sequence of a stochastic process. In the present paper we investigate the first reaction time between highly reactive units in a chain polymer undergoing Brownian motion, which has been investigated for long times, but the exact analytic solution for this problem has not been yet found even for the simplest case where the chain polymer is a Gaussian chain such as Rouse chain and the reactive units complete the reaction on their first encounter at a predefined contact distance, σ.

Recenlty, solokov reported a numerical approach that can providethe first passage time (FPT) distribution between two ends of Rouse chain with a given initial separation by solving the integral equation satisfied by the FPT distribution. However, it is notfeasible to make a straightforward application of the latter method to the frequently encountered situation where the initial end-to-end (ETE) distance of a chain polymer is distributedaccording to the Boltzmann distribution. Up to now, analytic theories that can handle the latter situation are the Wilemski and Fixman theory (WF theory) and the Szabo, Schulten, and Schulten theory (SSS theory). Pastor, Zwanzig and Szabo (PZS) made a comparison between predictions of these theories and results of Brownian dynamics simulations for the ETE mean first passage time (MFPT) of Rouse chain. Theyfound that the WF theory gives a better agreement to the BD simulation results than the SSS theory in general. This is because the non-Markov ETE dynamics of Rouse chain is better approximated in the WF theory.

However, in the extreme case where the number of beads comprising Rouse chain is only two or three, the ETE dynamics of the Rouse chain becomes a Markov process and results of the SSS theory are exact whereas those of the WF theory is not. What is missing in the WF theory but taken into account in the SSS theory is the excluded volume effects between the ends of the Rouse chain. In the presence of the reaction at a predefined ETE distance, σ, the chain polymer with the ETE distance smaller than σ does not exist for the whole reaction time, which should be taken into account both in the initial distribution and in the evolution dynamics of the Rouse chain.

In the present contribution, we enhance the WF theory for an intrachain reaction in taking into account the absorbing boundary between reactive beads. For the short Rouse chain composed of two or three beads, the result of the present theory is exact as that of the SSS theory. For other cases, results of the present theory are in a better agreement with the accurate Brownian dynamics simulation results than those of the previous WF or the SSS theories.

MODEL

In the present paper we will consider the first passage time between the ends in the Rouse chain composed of N+1 beads sequentially connected by N harmonic springs. If $\mathbf{r}_j$(j = 0,1,2,...,N) denotes the position vector of the j-th bead, the potential of mean force U of the Rouse chain is given by

$$U = \frac{3\beta^{-1}}{2b^2}\sum_{i=1}^{N}(\mathbf{r}_i - \mathbf{r}_{i-1})^2 \tag{1}$$

where β^{-1} and b^2 denote the thermal energy and the equilibrium mean squared length of a single bond of the Rouse chain, respectively. Note that, in the Rouse chain model, neither the excluded volume interactions between beads nor the chain stiffness existsso that the beads composing Rouse chain can pass through each other and relative angles between bonds can change freeof any change in the potential of mean force. For Rouse Chain model the hydrodynamic interactions between beads are absent either, so that the stochastic force exerted on a bead in the Rouse chain responsible for the Brownian motion of the bead is not correlated to that exerted on another bead in the chain. For the Rouse chain model, it is established that the probability density $\psi(\mathbf{r}^{N+1}, t)$ that the N+1 beads are located at $\mathbf{r}^{N+1} \equiv (\mathbf{r}_0, \mathbf{r}_1, ..., \mathbf{r}_N)$ at time t satisfies the following Fokker-Planck equation,

$$\frac{\partial\psi}{\partial t} = D_1\left\{\sum_{j=0}^{N}\frac{\partial}{\partial\mathbf{r}_j}\cdot\exp(-\beta U)\frac{\partial}{\partial\mathbf{r}_j}[\exp(\beta U)\psi]\right\} \tag{2}$$

where D_1 is the diffusion constant of a single bead.

For the purpose of comparison, we adopt the reaction model considered by PZS in their Brownian dynamics simulation, in which the Rouse chain with its end-to-end separation R greater than a predefined distance σ is initially distributed according to the Boltzmann distribution and afterwards a fast irreversible reaction occurs when distance R between the ends of the Rouse chain becomes σ for the first time.

Although the above-mentioned model is very simple, the mathematical method developed in the present theory is straightforwardly applicable to investigation of the first passage time between an arbitrary pair of beads in a more complex Gaussian chain model with the excluded volume interactions between non-reactive beads, the chain stiffness, and the hydrodynamic interactions taken into account.

THEORY

The FPT probability $F_N(\sigma, t|R_0, 0)dt$ that the Rouse chain composed of N+1 beads with the initial end-to-end separation being R_0 has its ETE separation at σ for the first time in time interval $(t, t+dt)$ satisfies the following integral equation:[4)]

$$G(\sigma, t|R_0, 0) = \int_0^t F(\sigma, t'|R_0, 0)G(\sigma, t|\sigma, t'; R_0, 0)dt' \tag{3}$$

Here $G(\sigma, t|R_0, 0)$ is the conditional probability that the value of the ETE distance, R, of Rouse chain is σ at time t in the absence of any reaction, provided that the initial value of R is R_0 and $G(\sigma,t|\sigma,t';R_0,0)$ is the multi-time conditional probability that the value of R is σ at time t in the absence of any reaction, provided that the value of R was at σ at an earlier time t' and was initially R_0. For a Gaussian chain such as Rouse chain, the analytic expressions for $G(R,t|R_0,0)$ and $G(R,t|R,t';R_0,0)$ are available in case of free boundary, which will be denoted by $G^0(R,t|R_0,0)$ and $G^0(R,t|R,t';R_0,0)$. 4 By solving Eq. (3) numerically with the latter conditional probabilities, one can calculate $F(\sigma,t|R_0)$ of the Rouse chain with a given initial end-to-end separation R_0.4 However, it is not easy to apply this method to calculate the FPT distribution $F(\sigma,t|eq)$ between the ends of the Rouse chain initially prepared in thermal equilibrium state, which is often of interest in intrachain fluorescence quenching or energy transfer experiments of an ensemble of chain polymers. To calculate $F(\sigma,t|eq)$ by this method, one has to solve Eq. (3) numerically for every value of R_0 to obtain the average of $F(\sigma,t|R_0)$ over the initial equilibrium distribution $P^0_{eq}(R_0)$ of R_0, which is not feasible.

One of the simple approximate methods to obtain the analytic expression for $F(r,t|eq)$ is to assume the encounter dynamics of the ends of Rouse chain is a Markov process, i.e.

$$G^0(\sigma,t|\sigma,t';r_0,0)\cong G^0(\sigma,t|\sigma,t') = G^0(\sigma,t-t'|\sigma,0) \tag{4}$$

With this approximation, Eq. (3) yields the result of the WF theory, which reads as

$$\hat{F}^{WF}(\sigma,u|R_0) = \frac{\hat{G}^0(\sigma,u|R_0)}{\hat{G}^0(\sigma,u|\sigma)} \tag{5}$$

in Laplace domain,[5)] where u denotes the Laplace variable. From Eq. (5) and the following property of the conditional probability, $\int G^0(r,t|r_0)P^0_{eq}(r_0)d\mathbf{r}_0 = P^0_{eq}(r)$, one can obtain the expression for $\hat{F}(r,u|eq)$ as follows:

$$\hat{F}^{WF}(\sigma,u|eq)\cong\frac{R^0_{eq}(\sigma)}{u\hat{G}^0(\sigma,u|\sigma)} \tag{6}$$

In addition, the expression for the mean first passage time, $t_{\mathrm{MFPT}}(\sigma)$, defined by $t_{\mathrm{MFPT}}(\sigma|eq) = \int_0^\infty dtF(\sigma,t|eq)t = -\partial\hat{F}(r,u|eq)/\partial u|_{u=0}$, can be obtained from small u expansion of the R.H.S. of Eq. (6), $\hat{F}(r,u|eq) = \sum_{n=0}^{\infty}\{1-[u\hat{G}^0(r,u|r)/P^0_{eq}(r)]\}^n$ as follows:

$$t^{WF}_{MFPT}(\sigma|eq) = \int_0^\infty dt\left[\frac{G^0(\sigma,t|\sigma)}{G^0(\sigma,\infty|\sigma)}-1\right] \tag{7}$$

Note here that $G^0(\sigma,\infty|\sigma)$ is the same as $P^0_{eq}(\sigma)$. Comparison between $t^{WF}_{MFPT}(\sigma|eq)$ given in Eq. (7) and Brownian dynamics simulation results was made in Ref. 3, which shows Eq. (7) works better for the case with smaller σ but the accuracy of Eq. (7) decreases with the value of σ. This is because Eq. (7) does not take into account the sizeeffects between the reactive beads or the ends of the Rouse chain. In the Brownian dynamics simulation reported in Ref. 3, only those Rouse chain with its initial ETE distance R_0 greater than σ can contribute to the simulation results, whereas, to Eq. (7), Rouse chain with R_0 smaller than σ contribute as well. For the latter reason, even for the Rouse chain composed of only two or three beads for which the approximation given in Eq. (4) happens to be correct, Eq. (7) does not yield the correct result.

To take into account the excluded volume effects neglected in Eq. (7), one can replace the propagator G^0 for the case with free boundary by the propagator $\underline{G}^r$ in the presence of reflecting boundary at $R = \sigma$.

$$t_{MFPT}(\sigma|eq) = \int_0^\infty dt\left[\frac{G^r(\sigma,t|\sigma)}{r(\sigma,\infty|\sigma)}-1\right] \tag{8}$$

Although the exact expression of G^r for Rouse chain is not yet available in general case, we manage to obtain an approximate expression for G^r as follows:

$$G(X,t|X_0) = \frac{1}{4\pi XX_0}e^{-\frac{X^2}{2}}\sum_{n=0}^{\infty}\frac{U\left(-\frac{\lambda_n+1}{2},\frac{1}{2},\frac{X^2}{2}\right)U\left(-\frac{\lambda_n+1}{2},\frac{1}{2},\frac{X_0^2}{2}\right)}{\int_{\sigma_X}^{\infty}dXe^{-\frac{X^2}{2}}U^2\left(-\frac{\lambda_n+1}{2},\frac{1}{2},\frac{X^2}{2}\right)}(\phi(t))^{\lambda_n} \tag{9}$$

where $X = |\mathbf{X}| = \left|\frac{1}{b}\sqrt{\frac{3}{N}}\mathbf{R}\right|$ and $\sigma_X = \left|\frac{1}{b}\sqrt{\frac{3}{N}}\sigma\right|$. U is the Kummer's function of the second kind and the eigenvalues.[7] λ_n is determined by the following equation:

$$\lambda_n U\left(-\frac{\lambda_n+1}{2}, \frac{1}{2}, \frac{\sigma^2}{2}\right) = 0 \tag{10}$$

Here, $\lambda_0 = 0$ and λ_1 is the smallest positive root and λ_2 is the next smallest positive root and so on. In Eq. (9), $\phi(t)$ is given by

$$\phi(t) = \frac{8}{N(N+1)}\sum_{odd\,k}\left(\frac{1}{\chi_k^R} - \frac{1}{4}\right)\exp(-3\chi_k^R t\, D_1/b^2) \tag{11}$$

with χ_k^R being the k-th Rouse eigenvalue, i.e.

$$\chi_k^R = 4\sin^2\left(\frac{k\pi}{2(N+1)}\right) \tag{12}$$

Substituting Eq. (9) into Eq. (8), we obtain the mean first passage time as

$$\langle t\rangle = \frac{1}{P_{eq}(\sigma_X)4\pi\sigma_X^2}\sum_{n=0}^{\infty}\frac{e^{-\frac{X^2}{2}}U^2\left(-\frac{\lambda_n+1}{2}, \frac{1}{2}, \frac{\sigma_X^2}{2}\right)}{\int_{\sigma_X}^{\infty} dX e^{-\frac{X^2}{2}}U^2\left(-\frac{\lambda_n+1}{2}, \frac{1}{2}, \frac{X^2}{2}\right)}$$

$$\int_{\sigma_X}^{\infty} dt(\phi(t))^{\lambda_n} \tag{13}$$

DISCUSSION AND CONCLUSION

In the present section, we compare the values calculated by our method with those by the computer simulation. For this, we use the parameter set used in Ref. 3. The detailed simulation method and simulation parameters also follow the paper. Thus, in *Table* 1 we cite the values in the data table of the paper without modifications. We also present our results in *Table* 1. For the calculations, we use the program Mathematica 4.0 and Compaq Visual Fortran Compiler Version 6.6 with IMSL Library and the Zhang and Zin's Parabolic Cylinder Function Routine To enumerate the sum of the infinite series in Eq. (13), we directly calculate the sum of the first 5000 summands. The residual sum can be efficiently estimated as the magnitude of the k-th term in the series decreases with k following a power-law at large k. If S_k denotes the k-th summand in the series, i.e.

$$S_k = \frac{H_{\lambda_k+1}(\sigma_x/2^{1/2})^2}{\int_{\sigma_X}^{\infty} dX e^{-x^2/2} H_{\lambda_k+1}(x/2^{1/2})^{\sigma_X}}\int_{\sigma_X}^{\infty} dt\phi(t)^{\lambda_k}$$

In S_k can be fitted excellently to $-a\ln k+c$ for k greater than 5000. Given the fitted values of a and c, one can estimate $\sum_{k=5001}^{\infty} S_k$ by $\exp(c)\sum_{k=5001}^{\infty} k^{-a}$, which is approximately given by $\exp(c)5001^{-a+1}/(a-1)$.

Table 1 shows that the predictions of the present theory is in a better agreement with the computer simulation results than those of the previous WF theory. This is because the effects of excluded volume between reactive units is taken into account in the present theory.

CONCLUSION

In the present work, we improve the Wilemski-Fixman theory for intrachain reaciton dynamics of Rouse chain by taking into account the excluded volume effects between reactive units in the Rouse chain.

Table 1. Comparison of the MFPT predicted by the WF theory, our theory, and simulation

N	σ	$\sigma_X (= \sqrt{\frac{3}{N}}\sigma)$	Simulation (95% confidence)	WF	Present Theory
50	0.5	0.1225	174(±10)	205	194.21
	1.0	0.2450	110(±5)	141	126.33
75	0.5	0.1	410(±20)	446	424.60
	1.0	0.2	250(±10)	326	294.82
100	0.5	0.08660	680(±30)	778	741.95
	1.0	0.1732	450(±20)	590	537.15

Acknowledgment. This work is supported by Chung-Ang University Research Grant in 2006.

REFERFNCES

1. G. Wilemski and M. Fixman, *J. Chem. Phys*. **1974**, *60*, 866; **1974**, *60*, 878.
2. A. Szabo, K. Schulten, and Z. Schulten, *J. Chem. Phys*. **1980**, *72*, 4350.
3. R. W. Pastor, R. Zwanzig, and A. Szabo, *J. Chem. Phys.* **1996**, *105*, 3878.
4. I. M. Sokolov, *Phys. Rev. Lett*. **2003**, *90*, 080601.
5. S. Redner, *A Guide to First-Passage Processes,* Cambridege University Press, United Kingdom, 2001.
6. C. Eun, et al., J. Phys. Chem. (submitted for publication).
7. Abramowitz, M.; Stegun, I.A. *Handbook of Mathematical Functions; Dover: New York, 1970.*
8. S. Zhang and J. Jin, *Computation of Special Functions*, John Wiley & Sons, 1996.