

Cyclization of a polymer with charged reactive end groups

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We calculate the cyclization rate $k(t)$ of a single polymer chain with charged end groups, where cyclization takes place with probability of one when the ends approach each other at a distance smaller than the reaction radius R . Using Monte Carlo simulations in a kink-jump model we show that the long-time asymptotic value of k for longer chains and attractive Coulomb interaction does not depend on R , but depends strongly on the Onsager radius, which characterizes the strength of electrostatic interaction. This result relies only on the large-scale behavior of the chain and is reproduced within a simple harmonic-spring approximation. The harmonic-spring model leads to a diffusion equation which is solved numerically. The solution for long chains is confirmed with analytical approximations. © 2001 American Institute of Physics. [DOI: 10.1063/1.1348273]

I. INTRODUCTION

Polymer reactions have been of considerable interest in chemical physics for many years. Termination reactions in radical polymerization, excimer formation and quenching of fluorescent dyes on polymers,^{1–10} reactive blending of two immiscible polymer phases¹¹ and polymer reactions under shear flow¹² have been investigated both experimentally and theoretically to understand both the reaction dynamics and the polymer dynamics itself. Conceptually, polymer cyclization is especially important, since it allows the study of the reaction process without approximations for the mutual influence of different chains. The cyclization reaction of uncharged chains has been extensively explored. Depending on the physical situation, different models for polymer dynamics have been applied, for example, Rouse-like models with and without excluded volume or hydrodynamic interactions^{2,4,6,9,10} and the reptation model.⁷ On the other hand, little attention has been paid to the fact that in many cases these reactions take place between units which are strongly charged. Here we consider the simplest situation, the purely diffusion-controlled ring closure reaction of a single flexible polymer chain bearing electrically charged reactive end groups, which moves in a concentrated solution or melt of uncharged chains (so that no electrostatic screening takes place).

We assume that the cyclization reaction takes place with probability one when the end groups approach each other at a distance smaller than the reaction radius R .^{5,13,14} The quantity of interest is the fraction $\psi(t) = N(t)/N(0)$ of the chains still unclosed up to the time t , whose decay is described by the cyclization rate $k(t)$:

$$\frac{d\psi(t)}{dt} = -k(t)\psi(t). \quad (1)$$

In a typical case, after a short transient, the value of $k(t)$ stagnates: $k(t) \rightarrow k^\infty$, and this value determines the overall reaction kinetics. This value will be of most interest in our

present article. To have a microscopic basis for our investigation, we first simulate the cyclization of a polymer with oppositely charged reactive ends in the off-lattice kink-jump model,^{15,16} whose dynamics are Rouse like. The long-time reaction rate in Rouse systems k_R^∞ is in the uncharged case known to be asymptotically independent of the reaction radius R for long chains and not too small R 's.^{2,4} This fact is connected to the compact exploration of the reaction volume by reacting ends, a fact due to the small-scale modes of Rouse motion. In our simulations we find that for chains with moderate and large root mean square (rms) end-to-end distance L (say, $L = \sqrt{\langle r^2 \rangle} \geq \sqrt{30}R$) and relatively small bond length b (in our simulations we took $b = R/2$) the R dependence of the cyclization rate of the uncharged chain is really rather weak. On the other hand, under attractive Coulomb interaction of moderate strength the reaction rate k_R^∞ becomes fully independent of the reaction radius R , but depends strongly on the Onsager radius r_c characterizing the strength of Coulomb interaction. This leads us to the conclusion that sufficiently strong Coulomb attraction makes the small-scale modes of the chain unimportant for the reaction kinetics, which are thus determined only by large-scale motion. In Sec. III we show that the behavior found for strong enough interaction can be explained by the harmonic-spring model,^{2,3,8,9} where only the longest Rouse mode is taken into account. We perform a numerical calculation of the resulting diffusion equation for a broad range of parameters and present a simple analytical solution for the charged harmonic-spring model in the limit of long chains $R/L \rightarrow 0$.

II. MONTE CARLO SIMULATION OF ROUSE DYNAMICS

The Rouse model is the widely used basic model for the dynamics of polymers in concentrated solutions or melts.¹⁷ Its dynamical properties are reproduced well by the off-lattice kink-jump algorithm.^{15,16} Using this algorithm we performed a Monte Carlo simulation of a chain with oppositely charged reactive ends while the environment of the chain was assumed to be uncharged. Hydrodynamic and excluded

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volume interactions were neglected. A bead rod chain consisting of $N+1$ beads, which are connected by rigid bonds of length b , moves by rotating a randomly chosen inner bead by a randomly chosen angle around the connection line between the two neighboring beads or by randomly choosing a new direction for one or the other end bond. In the motion of the end beads we additionally included a Metropolis prescription taking into account the difference in the Coulomb potential $U_C(r)$ before and after a possible move as the difference of the energy.¹⁸ That means that moving of the end is always accepted, if it leads to a decrease in the potential energy, and is accepted with probability $\exp(-\Delta U_C/k_B T)$ (here k_B denotes the Boltzmann constant), if the potential energy of interaction is increased by an amount ΔU_C . The Coulomb interaction between the chain's ends is

$$U_C(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0\epsilon r} = \frac{r_c}{r} k_B T, \quad (2)$$

where Q_1 and Q_2 are the electrical charges of the chain ends, and ϵ is the permittivity of the solution or melt. The strength of the Coulomb interaction is characterized by the Onsager radius $r_c = Q_1 Q_2 / (4\pi\epsilon_0\epsilon k_B T)$. For end-to-end distances smaller than $|r_c|$ the absolute value of the Coulomb interaction exceeds the thermal energy $k_B T$ (and thus the chain dynamics are more influenced by the electrical charges than by diffusive motion) while at $r \gg |r_c|$ the influence of electrostatic interaction becomes negligible. The Onsager radius is positive for repulsive Coulomb interaction and negative for attractive Coulomb interaction.

Since the initial condition influences only the transient and does not affect the value of k_R^∞ , in our simulations it was chosen for the sake of simplicity to follow an equilibrium configuration of a chargeless chain, i.e., a random walk. Then the chain was left to evolve according to its kink-jump/Metropolis dynamics until its ends came closer together than the reaction radius R . The fraction of uncyclized chains as a function of time was determined from typically 2000 (up to 12 000) realizations for each set of parameters. The Monte Carlo time step (MCS) corresponds to the time after which each monomer has attempted one move on average.¹⁶ The long-time reaction constant was found by linear regression of $\log[\psi(t)]$. In Refs. 9 and 10 the mean reaction time of the two ends of an uncharged Rouse chain $\bar{t} = \int_0^\infty \psi(t) dt \approx 1/k_R^\infty$ (Ref. 8) (for long chains) was already investigated by molecular dynamics and Monte Carlo simulations. To compare these results with the ones of the present simulations we need to know the Rouse time t_R , which can be obtained from an independent simulation of the diffusion of the center of mass of the chain, $\mathbf{R}_G(t)$. The diffusion constant D_0 of one bead of the Rouse chain is then given by

$$D_0 = (N+1) \left(\lim_{t \rightarrow \infty} \frac{\langle (\mathbf{R}_G(t) - \mathbf{R}_G(0))^2 \rangle}{6t} \right).$$

On the other hand $D_0 = \omega_0 b^2$, where ω_0 is a model-specific, b -independent microscopic jump frequency,⁵ which in our case is $\omega_0 = 0.1686 \text{MCS}^{-1}$. The Rouse time t_R is then

TABLE I. Quotient $Q_R = K_R^\infty(R=0.5)/K_R^\infty(R=1.0)$ (kink-jump model) for $L^2=30$ for different values of Coulomb interaction.

$r_c=0$	$r_c=-1$	$r_c=-2$	$r_c=-3$
0.82 ± 0.04	0.89 ± 0.04	1.00 ± 0.02	0.98 ± 0.03

$$t_R = \frac{(N+1)^2}{3\pi^2\omega_0} = \text{const} \frac{1}{k_{R,\text{WF}}^\infty}, \quad (3)$$

where $k_{R,\text{WF}}^\infty$ is the Rouse cyclization rate in the approach of Wilemski and Fixman.^{2,4}

For $b \geq R$ cyclization rates in our model (for $r_c=0$) are R dependent (a fact already reported in Refs. 9 and 10). To include the effect of the small-scale fluctuations we choose in the following $b=R/2$. For $R=1$ our rates are then 18% ($L^2=30$) and 7% ($L^2=100$), respectively, higher than those from the Brownian dynamics simulation with $b=R$ in Ref. 9 ($L^2=Nb^2$ for the Rouse chain), so our model yields quite accurate results despite the rigid bonds.

We consider now the reduced long-time cyclization rate,

$$K_R^\infty = t_R k_{R,\text{WF}}^\infty. \quad (4)$$

We made simulations for $L^2=30$ with $R=0.5$ ($b=0.25$) and $R=1$ ($b=0.5$) to reveal the R dependence of K_R^∞ ; furthermore we chose $L^2=60$ and 100 with $R=1$ ($b=0.5$) to find the r_c dependence of the rate. Since the computation time increases with N faster than N^3 , we refrained from simulation of longer chains; the results show a clear tendency for even longer chains to behave similarly.

Our simulations reveal the practical independence of K_R^∞ on the reaction radius R of the chain. In Table I the values of the quotient of the rates at different reaction radii $Q_R = K_R^\infty(R=0.5)/K_R^\infty(R=1.0)$ with $L^2=30$ are presented. Even though these chains are not too long and b is still not orders of magnitude lower than R , all Q_R 's are of the order of unity. For the uncharged chains, this fact has been known in theory for a long time: for the Rouse chain the long-time cyclization rate k_R^∞ becomes independent of the reaction radius R , since, due to fast small-scale motion, the end of a Rouse chain explores compactly a volume around the chain's other end.^{4,5} This leads to the fact that for $r_c=0$ the dimensionless rate K_R^∞ becomes an L -independent constant [see Eq. (3)], i.e., the problem is essentially parameterless.

The mechanism of compact exploration due to the small-scale fluctuations, which makes K_R^∞ independent of R for $r_c=0$, does not govern the reaction dynamics for $r_c < 0$. One could assume that for strong enough attractive Coulomb interaction the value of $|r_c|$ (playing the role of an effective capture radius) appears in the reaction rate instead of R , as is typically the case in reactions between discrete charged particles. In this case one would anticipate that K_R^∞ is independent of r_c as it was independent of R in the interaction-free case. The simulations show that such an assumption does not hold. This can be seen from Fig. 1, where K_R^∞ as function of r_c is plotted for different chain lengths ($b=0.5, R=1$). Without charges the reduced rates from the simulations are in fact nearly equal. On the other hand, in the case of attractive Coulomb interaction, K_R^∞ is a linear function of r_c . The

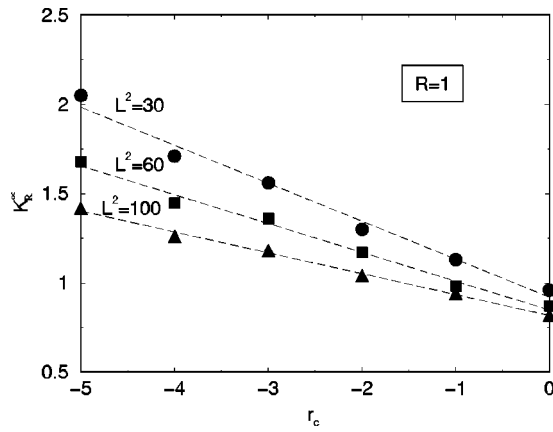


FIG. 1. Reduced long-time reaction rate $K_R^\infty = t_R k_R^\infty$ (kink-jump model, with $R=1$) as a function of the strength of the Coulomb interaction r_c for different chain lengths.

slopes of the regression lines (-0.213 , -0.161 and -0.117 for $L^2 = 30, 60$ and 100) are compatible with the assumption that the slope goes as L^{-1} , so that the dependence of K_R^∞ on the effective radius does not vanish.

Thus the behavior of the oppositely charged reacting polymer is determined primarily by r_c and L and not by the local scales R or b (as long as $b \ll R$), i.e., it is characterized by dominance of large-scale behavior. As we proceed to show, the harmonic-spring model, which takes into account only the large-scale behavior of the chain, may be sufficient to explain these results.

III. HARMONIC-SPRING MODEL APPROACH

The Rouse chain consists of $N+1$ beads connected by N springs and describes the dynamics of a polymer chain on all scales from the bond length to the end to end distance. The harmonic-spring model consists of two beads connected by one spring and though contains only the longest Rouse mode. Consequently the reaction behavior (where the reaction radius $R < L$ comes into play) of the uncharged harmonic-spring chain is vastly different from that of the long Rouse chain (where the long-time reaction constant is independent of R , as described in Sec. II). Thus, in Ref. 3 it was found that the long-time asymptotic of the cyclization rate in the harmonic-spring model goes as $k^\infty \sim R/L$ in the limit of $R/L \rightarrow 0$, in contrast to the Rouse case. On the other hand, as we proceed to show, this model is quite adequate for the case in which the Coulomb attraction between the chain is strong enough.

Let us fix the origin of coordinates on one end of the chain and consider the probability of the other end (termed a particle) is found at distance r from the origin. In the simplest model this motion can be considered as diffusion of a particle in an external potential $U(r)$, consisting of the free energy $F(r)$ of an uncharged chain (as a function of its end-to-end distance r) and of the Coulomb interaction, Eq. (2). For a Gaussian chain $F(r)$ corresponds to a harmonic potential $F(r) = \kappa r^2/2$ with the ‘‘spring constant’’ $\kappa = 3k_B T/L^2$. Thus the potential $U(r)$ can be put into the form,

$$U(r) = F(r) + U_c(r) = \frac{3k_B T}{2L^2} r^2 + \frac{r_c k_B T}{r}. \quad (5)$$

The single-chain cyclization is a two-particle reaction problem, for which the Smoluchowski approach to a reaction holds.¹³ Thus, the relative number of uncyclized chains $\psi(t)$ is equal to the probability that the reacting end stays outside of the reaction sphere all the time, and that the reaction rate $k(t)$ equals the flux of reacting particles on the reaction sphere. The overall number of uncyclized chains is thus given by

$$\psi(t) = \frac{1}{4\pi} \int d^3 r \rho(\mathbf{r}, t), \quad (6)$$

where $\rho(\mathbf{r}, t)$ is the probability density that the end to end vector at time t is equal to \mathbf{r} . This probability density satisfies the Smoluchowski equation in the potential U :¹⁷

$$\frac{\partial \rho}{\partial t} = D \nabla \cdot \left(\nabla \rho + \frac{1}{k_B T} (\nabla U) \rho \right), \quad (7)$$

under the absorbing boundary condition $\rho(\mathbf{r}, t)|_{|\mathbf{r}|=R} = 0$. Here $D = k_B T/\zeta = 2D_0$ is the mutual diffusion constant of the chain ends and ζ the friction coefficient. Using the spherical symmetry of the problem one can rewrite Eq. (7) in the form,

$$\frac{1}{D} \frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial r^2} + \left(\frac{2}{r} - \frac{r_c}{r^2} + \frac{3r}{L^2} \right) \frac{\partial \rho}{\partial r} + \frac{9}{L^2} \rho, \quad (8)$$

with the boundary condition

$$\rho(R, t) = 0. \quad (9)$$

We take the system at the beginning to be in thermal equilibrium, so that the initial condition for ρ corresponds to a Boltzmann distribution:

$$\rho(r, 0) = A \exp(-U(r)/k_B T),$$

with

$$A = \frac{1}{4\pi \int_R^\infty dr r^2 \exp(-U(r)/k_B T)}. \quad (10)$$

For the numerical solution the diffusion problem can be reduced to a finite interval by noticing that the particles’ density in a harmonic potential at larger distances decays so fast [essentially as $\rho \sim \exp(-3r^2/2L^2)$] that a reflecting outer boundary condition can be posed at a distance r_{\max} sufficiently larger than L . This condition would read

$$\frac{\partial \rho}{\partial r} + \left(\frac{-r_c}{r^2} + \frac{3r}{L^2} \right) \rho \Big|_{r=r_{\max}} = \frac{1}{D} j \Big|_{r=r_{\max}} = 0. \quad (11)$$

Values of r_{\max} in the range of $3-4L$ are typically sufficient. The diffusion problem, Eqs. (8)–(11), is solved numerically for fixed $k_B T = 1$ and $\zeta = 1$ using the Crank–Nicholson algorithm, which is well suited for parabolic equations. This is a semi-implicit scheme, in which the derivatives of ρ with respect to r in Eq. (8) are evaluated as the mean of the derivatives with respect to r at two succeeding time steps $n\Delta t$, $(n+1)\Delta t$.¹⁹ The concentration at the reflecting outer boundary was evaluated only at time $(n+1)\Delta t$. In our calculations

we investigated the influence of the Onsager length r_c on the behavior of the cyclization rate. The chain length L (entering through the spring constant κ) was also varied. All calculations were made for two different values of the reaction radius, $R=1$ and 0.3 . To compare our results for different chain lengths we introduce the reduced time,

$$\tau = \frac{t}{t_L}, \quad (12)$$

where $t_L = L^2/(6D)$ is a characteristic diffusion time. The time t_L in Eq. (12) has a similar meaning as t_R in Eq. (3). Note, however, that for our choice of parameters t_L and t_R are very different, so the absolute values of the rates K_R^∞ and K^∞ in the Figures cannot be compared. The dimensionless cyclization rate $K(\tau) = (t/\tau)k(t) = t_L k(t)$ can then be found according to Eq. (1) as a logarithmic derivative of $\psi(t)$ in Eq. (6):

$$K(\tau) = -t_L \frac{d\psi/dt}{\psi} \approx -t_L \frac{\psi(t+\Delta t) - \psi(t)}{\psi \Delta t}.$$

This method is more accurate for the Coulomb case than determining the reaction rate by calculating the flux through the surface of the reaction sphere (where the potential changes are huge); this second method was still used for control.

In Figs. 2(a) and 2(b) the cyclization rate $K(\tau)$ is plotted as a function of the reduced time τ for different cases (with and without attractive Coulomb interaction, for two different values of R and for different chain lengths). All curves show qualitatively the same behavior: after a steeply decreasing transient in the beginning the cyclization rate tends towards a constant K^∞ . Thus, for longer times an exponential decay of ψ sets in.

Let us now focus on the behavior of K^∞ as a function of R , r_c and L . In Fig. 3 K^∞ is plotted as function of r_c for $r_c < 0$ and for different chain lengths. For longer chains and stronger Coulomb attraction the behavior of $K^\infty \propto r_c$ is evident, similar to our findings for the Rouse model, Fig. 1. To reveal the L dependence of K^∞ , we plot in Fig. 4 K^∞ as a function of $1/L$. For uncharged chains we have the behavior $K^\infty \propto L^{-1}$, exactly like the findings in Ref. 3. For attractive Coulomb interaction $K^\infty \propto L^{-1}$ might still be valid for long chains.

We now turn to the results for the R dependence of K^∞ . In Table II we compare the results for the two different values of R by presenting the values of the quotient $Q = K^\infty(R=0.3)/K^\infty(R=1.0)$ for different values of L and Onsager radius r_c . In the noninteracting case ($r_c=0$) the value of Q approaches $0.3/1.0=0.3$ for L large. This confirms the results of Ref. 3, where K^∞ was shown to be proportional to R/L for R/L small. For $R=0.5$ and 1.0 , respectively (the values of the Q_R calculation in Table I), Q would be still smaller than 0.5 for $r_c=0$. For $r_c=-3$ the value of Q tends towards a number close to 1 for increasing chain lengths L : as we already saw in the kink-jump simulation, if the Coulomb interaction is attractive and not too weak ($r_c/R \ll -1$), the Onsager length r_c acts as an effective capture radius; if the distance between the two reactive groups is smaller than $|r_c|$, they become attracted and thus react nearly independent of

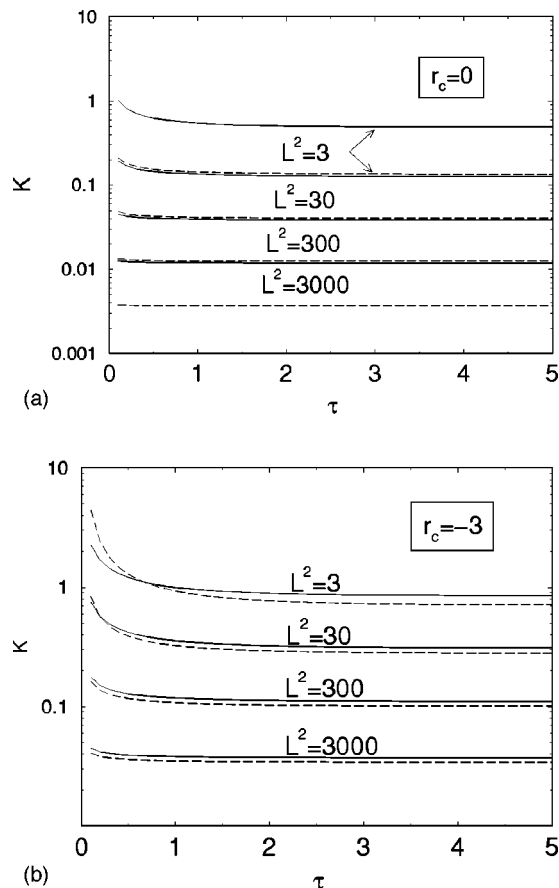


FIG. 2. (a) Time dependence ($\tau=t/t_L$) of the reduced reaction rate $K = t_L k$ (harmonic-spring model) without Coulomb interaction ($r_c=0$) for different chain lengths. The two reaction radii are $R=1$ (solid lines) and 0.3 (dashed lines). (b) Same as (a), but with attractive Coulomb interaction ($r_c=-3$).

R . Let us mention that for *repulsive* Coulomb interaction ($r_c=3$) the opposite is the case: The cyclization rate is extremely R dependent, since the particles have to overcome a potential barrier which is higher and thicker, the larger the Onsager radius is compared to the reaction radius R . Thus, for attractive Coulomb interaction that is strong enough the reaction rates in the Rouse and in the harmonic-spring mod-

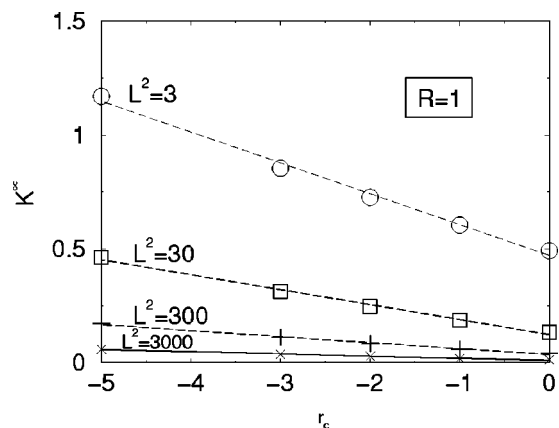


FIG. 3. Reduced long time reaction rate $K^\infty = t_L k^\infty$ (with $R=1$) in the harmonic-spring model as a function of the strength of the Coulomb interaction r_c for different chain lengths.

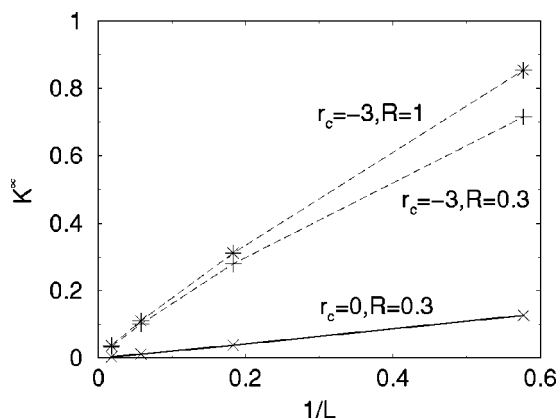


FIG. 4. L dependence of the reduced long-time reaction rate $K^\infty = t_L k^\infty$ in the harmonic-spring model. The solid line corresponds to the case without Coulomb interaction ($r_c=0$), and the dashed lines represent the results with attractive Coulomb interaction ($r_c=-3$).

els behave in a similar way; the reaction rate can then be viewed to good approximation as determined only by the longest Rouse mode.

The behavior of the cyclization rate found numerically can be qualitatively explained for long chains within a simple analytical picture similar to one employed in Ref. 3 for the uncharged case. Thus, the role of an entropic force reduces to confining a particle at a distance $r \leq L$ from the origin. Then, according to a result in Ref. 20, the long-time first-order cyclization rate within the limit of long chains is connected to the steady state second-order reaction rate K_2^∞ of a reaction center A fixed at the origin with particles B spread within a confining sphere with the constant density $n_B \approx L^{-3}$. As an approximation one can take $n_B \approx 1/[(4\pi/3)L^3]$. The fraction ψ of unclosed chains is proportional to the density of reaction centers of particles of type A , which is governed by¹⁴

$$dn_A/dt = -K_2^\infty n_A(t) n_B.$$

A comparison with Eq. (1) yields

$$K^\infty = K_2^\infty n_B \approx K_2^\infty \frac{3}{4\pi L^3}, \quad \frac{R}{L} \rightarrow 0. \quad (13)$$

The values for the second-order reaction rate K_2^∞ are known: for the uncharged chains the Smoluchowski result $K_2^\infty = 4\pi DR$ holds,¹³ and for charged particles one has the Debye solution $K_2^\infty = 4\pi r_c D / [\exp(r_c/R) - 1]$.²¹ Thus, for charged chains, Eq. (13) reads

TABLE II. Quotient $Q = K^\infty(R=0.3)/K^\infty(R=1.0)$ in the harmonic-spring model as a function of the mean squared end-to-end distance L^2 for different values of Coulomb interaction. The values for infinite long chains are calculated with Eq. (14).

	$L^2=3$	$L^2=30$	$L^2=300$	$L^2=3000$	$L^2 \rightarrow \infty$
$r_c = -3$	0.862	0.929	0.945	0.949	0.950
$r_c = -1$	0.532	0.617	0.644	0.652	0.656
$r_c = 0$	0.257	0.285	0.295	0.298	0.3
$r_c = 3$	0.001 448	0.000 940	0.000 876	0.000 869	0.000 867

$$K^\infty \approx \frac{r_c}{2L} \frac{1}{\exp(r_c/R) - 1}, \quad \frac{R}{L} \rightarrow 0, \quad (14)$$

from which the limiting values of Q in the right column of Table II follow. Note that the values of Q are independent of n_B , which cancels out in the final expression, and thus can be considered as asymptotically exact. The asymptotic r_c and R dependences of K^∞ are

$$K^\infty \approx \begin{cases} -r_c/2L, & r_c/R \ll -1, \\ \frac{r_c}{2L} \exp\left(-\frac{r_c}{R}\right), & r_c/R \gg 1, \end{cases} \quad \frac{R}{L} \rightarrow 0. \quad (15)$$

Hence the cyclization rate constant is proportional to r_c and independent of the reaction radius for large negative r_c , and shows an exponential dependence on r_c/R for strong repulsive Coulomb interactions. The $\partial K_R^\infty / \partial r_c \approx 1/L$ behavior ($r_c < 0$) for Rouse chains is also confirmed.

IV. SUMMARY

We considered the cyclization rate for a polymer with charged end groups in the simplest case of diffusion-controlled kinetics. After a short transient, the cyclization rate stagnates and its value becomes independent of the initial condition; this long-time asymptotic reaction rate k_R^∞ is the quantity of major interest for reaction kinetics. Monte Carlo simulations in the kink-jump model (giving rise to Rouse dynamics) show that even for not too long chains with bond lengths that are reasonably small compared to the microscopic reaction radius R , k_R^∞ is independent of the reaction radius. On the other hand, for attractive Coulomb interaction k_R^∞ is a linear function of the Onsager radius r_c which characterizes the interaction strength. This leads us to the conclusion that (contrary to the uncharged case) the behavior of k_R^∞ is dominated by large-scale motion. Indeed, similar behavior is found in the harmonic-spring model, taking into account only the longest mode of Rouse motion. The findings for the harmonic-spring model can be explained within a simple theoretical framework, which gives the behavior of the cyclization rates in the limiting case of very long chains ($L \rightarrow \infty$).

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