Theory of Intramolecular Reactions in Polymeric Liquids

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ABSTRACT: We calculate irreversible intramolecular reaction rates $k(t)$ between two reactive groups attached to a flexible polymer chain. Results are derived using scaling arguments; in addition, a detailed renormalization-group treatment is developed which justifies and extends the scaling results. Asymptotically, reaction kinetics are either "diffusion-controlled" (DC) or "law of mass action" (LMA) as determined by a characteristic exponent, θ, depending only on the class of polymer–solvent system. For unentangled melts (Rouse dynamics) of sufficiently long chains $k(t)$ is of DC form for cyclization (case 1), and for one end and one deeply internal group (case 2): the long time rate $k_\infty \propto 1/\tau_s$ (τ_s is the relaxation time of the chain segment of length s connecting the groups), while at short times $k(t) \propto t^{-1/4}$. When both groups are deeply internal (case 3), k_∞ suffers logarithmic corrections. For dilute solutions in good solvents $k(t)$ is so weakened by excluded-volume repulsions that laws of mass action apply (LMA) even for very reactive groups; a diffusion-controlled limit does not exist. Case i is governed by the ith correlation hole exponent of des Cloizeaux ($i = 1, 2, 3$) and $k(t)$ has only weak time dependence. Θ solvents are marginal (on the DC/LMA boundary), and $k(t)$ collects logarithmic corrections in time, group location, and chain length.

I. Introduction

Much theoretical and experimental effort has been invested in the study of intramolecular reactions in polymeric liquids in which active groups attached at various points along the polymer chain backbone may react with one another if the chain motion happens to bring them into close proximity of one another (see Figure 1). Depending on the system, the event may produce a permanent or temporary loop, or the result may simply be a chemical or physical change of the groups involved without bond formation.

These systems are interesting in part on account of their technological relevance through polymerization reactions.[1] The competition between ring and chain formation in linear polymerizations, for example, plays an important role in determining final molecular weight distributions[1-4] while the evolution of multifunctional polymerizations is strongly influenced by intramolecular reactions which create loops modifying the gel point and the structure of the final network.[5]

Intrapolymeric reactions have also found extensive use as probes to test the fundamental theories of polymer statics and dynamics; comparison of experimentally monitored reaction rates with theoretical predictions tests the basic polymer models employed. Much of this work has involved fluorescent probes such as pyrene. For example, in studies exploiting pyrene excimer formation the "reacting" groups are pyrene molecules which are excited by irradiation. When two such pyrenes encounter, they form a tightly bound dimer or "excimer" which fluoresces differently from the monomer; the encounter rate can thus be followed. The excimer lifetime is somewhat smaller than but close to typical high polymer relaxation times in dilute solution and thus allows the probing of internal polymer dynamics. Cuniberti and Perico[6] were the first to exploit this system, measuring cyclization rates with pyrene end-capped polymer chains and subsequently reactions between internally positioned pyrene groups.[7,8] Winnik and collaborators have used the pyrene probe in a large number of experiments to measure both cyclization rates[9-13] and reactions between internally positioned groups along the chain backbone.[14,15] Other experiments of this type include the use of anthracene triplet–triplet annihilation[16,17] as well as nonphotophysical methods such as hydrolysis of attached ester groups.[18]

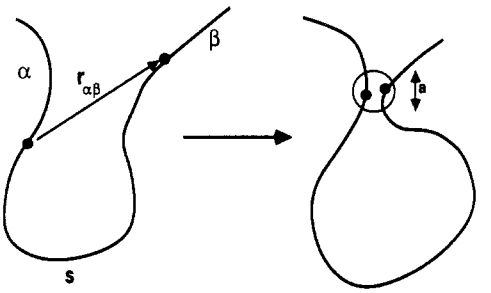

Figure 1. Chains react irreversibly, with a probability Q per unit time, if the two reactive groups diffuse to within a distance a of one another.

In this paper we develop a first principles theory describing irreversible intrapolymeric reactions between two arbitrarily positioned groups (see Figure 1), generalizing the present authors' calculations for the particular case where the groups are at the chain ends (cyclization).[19-21] We present a unified treatment of reaction rates for short and long times as a function of group position and identify a number of experimentally accessible quantities whose values we predict to be independent of the particular reacting polymer system used.

The first theoretical studies of intrapolymeric reaction rates to account for the many-body nature of the problem were those of Wilemski and Fixman,[22] whose framework was used by Doi[23] to obtain analytical forms for cyclization in dilute solution and by Cuniberti and Perico[24,25] to treat finite molecular weight effects. However, in order to cope with the technical complexity involved, these and other theoretical studies[26,27] treated hydrodynamical and excluded-volume interactions in an approximate way and used Wilemski and Fixman's "closure approximation". The latter is a self-consistent treatment of the chain distribution function which allows the extraction of the reaction rate. Ideally, one would like to attack the problem in a more systematic way.

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The first study to treat the cyclization problem without such ad hoc assumptions was the renormalization group theory of the present authors[19-21] in which reaction rates were calculated from "first principles". An interesting conclusion was that for very long polymers the molecular weight dependence of cyclization rates was entirely determined by the polymer dynamics, regardless of the properties of the reacting end groups. For example, in dilute solutions of sufficiently high molecular weight polymers, reaction rates are proportional to the equilibrium chain-end contact probability in good solvents. This is true no matter how strongly reactive the end groups may be; i.e., no diffusion-controlled behavior is realizable; rather, a "law of mass action" is generic. The more reactive the end groups, the longer the chains must be to reach the final regime; however, the chemistry of the reacting groups has no influence on the nature of this asymptotic behavior.

The theoretical framework in the present study does not attempt to deal with entanglements. When entanglements dominate, a first principles theory is at present intractable; studies of intramolecular reactions in these cases have employed the reptation model framework[28,29] both for the cyclization case[30,31] and for the case of internal groups.[32,33]

In this paper the general theory will be applied to a number of cases, beginning with reactions in polymer melts for which we use a Rouse dynamics framework. Thus our results describe situations where entanglements are unimportant[34] of which there are two types. When chains are short enough that entanglements *never* matter, Rouse dynamics are well testified experimentally[34] and our results should apply for all times. However, even for entangled melts Rouse behavior is observed on time scales short compared to the "entanglement time";[34] in such cases only our predictions on short time reaction rates are experimentally relevant.

Following this, we will investigate what happens when excluded-volume interactions are present by treating the case which we call "Rouse plus excluded volume" dynamics. This model does not describe any real polymer system (due to the neglect of hydrodynamics) but is interesting theoretically and clearly demonstrates the crucial role played by excluded-volume correlations. Moreover, it provides an interesting system to investigate numerically and would presumably be computationally far easier to handle than (more realistic) simulations incorporating long-ranged hydrodynamical interactions.

Finally, we will treat dilute solutions where hydrodynamical effects play a crucial role ("non-free-draining" cases). These are our most important experimental predictions. We treat both good solvents and Θ solvents where statics are roughly ideal.[34]

In the following section the basic model is presented and in section III scaling arguments are employed to understand the basic forms of reaction kinetics. The emphasis in this paper is on this relatively straightforward scaling approach, and we limit ourselves in section IV to an outline of the more formal approach which involves renormalizing a bare perturbation theory for reaction rates. A specific example is worked through in some detail, and then experimentally relevant results for all other cases are presented. The reader wishing to avoid details of the renormalization group calculations may omit section IVA without loss of continuity. We conclude with a discussion in section V.

II. The Problem

Consider a solution or melt of polymer chains, each comprising N units, in which some or all of the chains carry two reactive groups, positioned at distances α and β respectively from the chain ends as illustrated in Figure 1. We define $s \equiv N - (\alpha + \beta)$ to be the distance between the active groups. By "distance" here we mean "number of chain units" as measured along the polymer backbone. One unit may be identified with one monomer, but this is unnecessary; the important feature is that the quantities α, β, s, and N are each proportional to the molecular weights of the sections of chain which they label.

As the chain diffuses from one configuration to another, it may happen that the reactive groups are brought close together, let us say to within a distance of order a of one another, in which case they may react with a probability per unit time Q (see Figure 1). Thus a and Q are respectively the reaction range and local reactivity. If reaction ensues, the event is irreversible. We deal with situations in which reacting chains are sufficiently dilute that only *intra*molecular reactions need be considered; in the typical time scale in which an intramolecular reaction occurs, the chances of two reactive chains encountering one another and reacting *inter*molecularly are negligible. The corresponding physical systems to which the present analysis is applicable are therefore either very dilute solutions in which a large fraction of chains may be reactive or melts in which this fraction is small; i.e., one has a few reactive chains in a background sea of unreactive but otherwise identical polymers.

Imagine that we "switch on" reactions at time $t = 0$ (physically this might correspond, for example, to the instant at which a pyrene-labeled sample is irradiated) when the polymers are taken to be in equilibrium (note that as reaction proceeds the configurational distribution will become shifted away from the equilibrium one). The aim is to calculate the reaction rate $k(t)$, which we define in terms of $\mathcal{N}(t)$, the fraction of those chains bearing reactive groups which have not reacted after time t:

$$k(t) \equiv -\mathrm{d} \ln \mathcal{N}/\mathrm{d}t \tag{1}$$

At long times we anticipate exponential decay, $\mathcal{N}(t) \sim \mathrm{e}^{-k_\infty t}$ where, from eq 1, the decay rate is the long time limit of $k(t)$,

$$k_\infty \equiv \lim_{t\to\infty} k(t) \tag{2}$$

At short times one expects, in general, time-dependent behavior. If $\mathcal{N}(t)$ is very close to $\mathcal{N}(0) = 1$, then from eq 1 to leading order the short time reaction rate $k_0(t)$ is

$$k(t) \approx -\mathrm{d}\mathcal{N}/\mathrm{d}t \equiv k_0(t), \quad \text{small times} \tag{3}$$

It is clear from eqs 2 and 3 that the definition of k (eq 1) is the natural one to span all time scales.

We will follow the dynamics of the chain depicted in Figure 1; a chain configuration is defined by $\{r(n, t)\}_{n=0}^{n=N}$ where $r(n, t)$ is the location in space of the nth chain segment at time t. Our model[19-21] for the evolution of the configurational probability distribution $P(\{r(n)\}, t)$ is the Fokker–Planck equation

$$\frac{\partial P}{\partial t} = FP + u_0\delta(r_{\alpha\beta})P \tag{4}$$

where $r_{\alpha\beta}$ denotes the position of one reactive group relative to the other (see Figure 1)

$$r_{\alpha\beta} \equiv r(N - \beta) - r(\alpha) \tag{5}$$

The operator F is the usual operator for the dynamics of a chain without reactive groups and is presented explicitly

in Appendix A. The particular form of F depends of course on the experimental situation we wish to model (dilute solution in good or poor solvents, melts). In its simplest form (in which the hydrodynamical and excluded-volume interactions are deleted) it describes Rouse dynamics.[35,36] The sink term in eq 4 selects configurations whose reactive groups are in contact and "reacts them" with probability Q per unit time where the sink strength u_0 is identified with Qa^d in d-dimensional space.

A few comments on our model (eq 4) are desirable at this point. This kind of model, the usual evolution equation for P plus a sink term, was first proposed and studied by Wilemski and Fixman[22] and has been the standard framework for subsequent theoretical work. However, our choice of the sink function is particular. The δ function models a sink of reactivity Q and width a (volume of order a^d in d-dimensional space) in the case that a is much smaller than other scales in the problem; it is the "natural" model of a localized sink. Our conjecture is that observable physical quantities (i.e., associated with long time scales compared to typical sink time scales) are correctly captured by the δ function *no matter what form the "real" sink may have*. In other words, if one chose a different form of the sink function, the long time properties would be the same as for the δ function case; in all cases only the single parameter $u_0 \equiv Qa^d$ would survive as a characteristic of the particular chosen form of sink. This type of conjecture is by now wholly accepted in many fields. For example, the δ-function interaction potential is believed to yield the same exponent for a self-avoiding polymer as would be obtained from a more "realistic" potential; under the coarse-graining of the renormalization group any interaction potential would ultimately be transformed into a δ function. Precisely the same logic is conjectured to apply here; under coarse-graining any sink potential would become a δ function. Making this assumption, our theory predicts considerable *universality* in experimental observables, that is, insensitivity to details of the polymer–reactive group system. Though as yet by no means systematically tested, there already exist some indications of universality both from numerical[37] and real[10] experiments. The natural theoretical framework to explain and extract this universality is the renormalization group which we will use in section IV to calculate $k(t)$. However, our emphasis in this paper will be on simple scaling derivations which we now proceed to develop in section III.

III. Scaling Arguments

A. General Framework. Without detailed calculation, we can understand much of the physics of the problem via simple scaling arguments.[21] It is conceptually helpful to phrase our arguments in terms of a general spatial dimension d; ultimately we set $d = 3$ of course to compare to experiment. Now in the *cyclization* problem[21] the form of the reaction rates turned out to be determined by the exponent θ:

$$\theta \equiv \frac{d+g}{z} \tag{6}$$

Here z is the dynamical exponent ($\tau \sim R^z$ where τ and R are respectively the longest relaxation time and root-mean-square end-to-end distance of a single polymer chain) and g is the "correlation hole exponent" which quantifies the diminished probability that the chain ends meet one another.[38] When excluded-volume interactions are not screened, then the relevant end-to-end equilibrium probability distribution, $p(r)$, is that describing self-avoiding walks,[34,38]

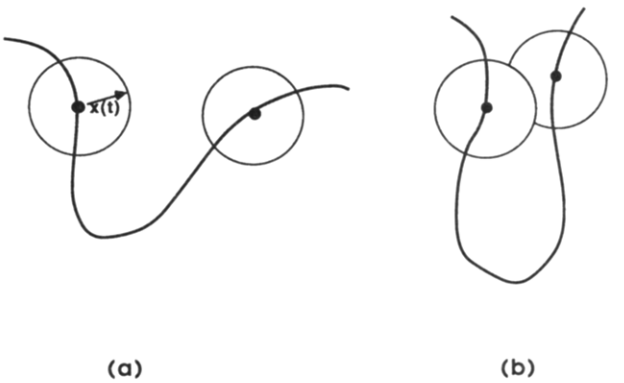

Figure 2. In the text, O_t is defined to be the fraction of chains whose exploration volumes overlap. Shown in the figure are typical chain configurations at $t = 0$. Chains such as (a), whose reactive groups were initially separated by more than $x(t)$, do not belong to this fraction; chains such as (b) do.

$$p(r) = R^{-d} f(r/R) \tag{7}$$

where $R = aN^\nu$ and ν is the Flory exponent relating chain size to the number of segments N each of size a. The function f has a universal form for long chains, exhibiting algebraic behavior for small r/R: $f(x) \sim x^g$ for $x \ll 1$. This is the correlation hole; the distribution decays to zero as the end separation goes to zero. In melts and Θ solvents excluded volume effects are screened and Gaussian statistics are recovered; $p(0)$ then equals a nonzero constant, g vanishes, and the reaction exponent (eq 6) reduces to $\theta = d/z$.

We now review the arguments of ref 21 and generalize them to internal groups. Reactions are switched on at time $t = 0$, and we seek the reacted fraction after time t, R_t. If the active chain units (the αth and $(N-\beta)$th) overlap, reaction may occur with probability Q per unit time (this corresponds to a "sink" of size a and strength Q). The relevant distribution function is now $p_{\alpha\beta}(r_{\alpha\beta})$ where $r_{\alpha\beta}$ is the vector joining the two reactive groups. Let $x(t)$ denote the root-mean-square displacement after time t of one of the two groups. Then for small times the "overlap fraction" O_t, namely, the fraction of chains for which the exploration volumes of the two reactive groups overlap after time t (see Figure 2), scales as the probability that the groups were initially within a distance $x(t)$ of one another:

$$O_t \approx \int_{|r_{\alpha\beta}|<x(t)} \mathrm{d}^d r_{\alpha\beta}\, p_{\alpha\beta}(r_{\alpha\beta}) \tag{8}$$

Evidently this estimate employs the *equilibrium* probability distribution function $p_{\alpha\beta}$; the implicit assumption has been made that when reactions occur the distribution will not be seriously distorted relative to equilibrium. Now for self-avoiding polymers this equilibrium distribution was calculated by des Cloizeaux,[39] who found that $p_{\alpha\beta}$ assumed relatively simple scaling forms in three extreme cases which are depicted in Figure 3: end groups ("extreme case 1"), one end group plus one internal group very far from the other end ("extreme case 2") and two internal groups both very far from the chain ends ("extreme case 3"). Throughout this study cases 1–3 will refer respectively to end groups, one end and one internal, and both internal. For extreme cases $p_{\alpha\beta}$ is a scaling function featuring only the one length scale $R_{\alpha\beta} \approx as^\nu$ which is the root-mean-square value of $r_{\alpha\beta}$ (s is the number of units in the chain segment connecting the groups) so one can relabel $r_{\alpha\beta}$, $R_{\alpha\beta} \to r_s$, R_s since these quantities are parametrized by s alone. Now subsequently Oono and Ohta[40] studied $p_{\alpha\beta}$

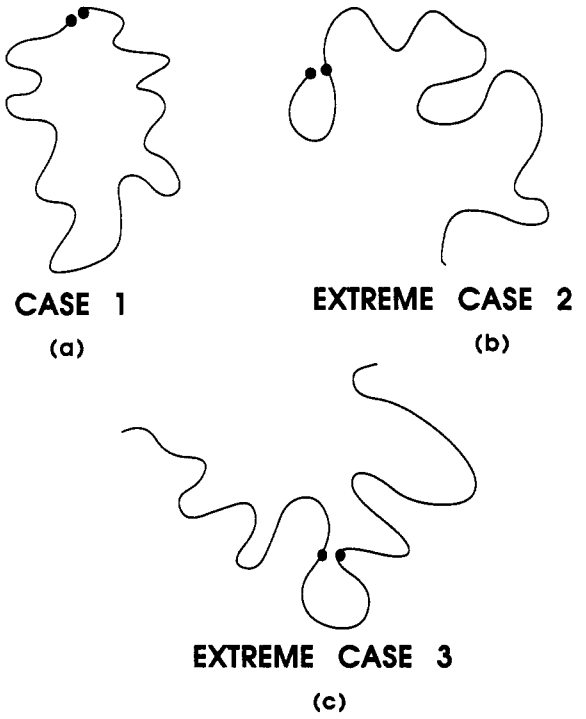

Figure 3. "Extreme" instances of cases 1–3. (a) Case 1 (cyclization). In "extreme case 2" one group is deeply internal, $s/\alpha \ll 1$. (c) In "extreme case 3" both groups are very far from chain ends, $s/\alpha \ll 1, s/\beta \ll 1$. For good solvents these three cases correspond respectively to the three correlation hole exponents g_1, g_2, and g_3 calculated by des Cloizeaux.

for quite general ("nonextreme") cases, deducing the following general form:

$$p(r_s) = \frac{1}{R_s^d} f\left(\frac{r_s}{R_s}, \frac{\alpha}{s}, \frac{\beta}{s}\right) \tag{9}$$

where f depends algebraically on its first argument for small values of that argument: $f(x,u,v) \to x^g H(u,v)$ for $x \ll 1$. This is a generalization of eq 7 for chain ends, with the form of the function f, and in particular the value of the exponent g and the form of the function H, now being case dependent. When u and v become very large (i.e., we approach the "extreme" situations), the functions H approach constant values; then $p(r_s)$ involves only simple powers of s at small r_s. The values of g in three-dimensional space[39] are given by

$$\begin{aligned} g &\approx 0.27 \quad \text{case 1} \\ g &\approx 0.46 \quad \text{case 2} \\ g &\approx 0.71 \quad \text{case 3} \end{aligned} \tag{10}$$

We have quoted des Cloizeaux's renormalization group (RG) results to second order in the parameter $\epsilon \equiv 4 - d$. Since our RG calculations of section IV will be to order ϵ, we will have frequent occasion to refer to des Cloizeaux's results to first order in ϵ: $g = \epsilon/4$, $\epsilon/2$, and ϵ for cases 1–3, respectively.

Let us now derive reaction rates for each of the three cases. Our arguments encompass both self-avoidance (Rouse plus excluded volume and good solutions) and the instances of Gaussian statistics (poor solvents and melts) when g vanishes. Let $\tau_s \equiv t_a s^{\nu z}$ be the relaxation time of the segment of polymer connecting the groups, where t_a is the relaxation time of a single chain unit and z is the dynamical exponent.[34] For times much smaller than τ_s the relevant scales r_s in the distribution of eq 9 are much smaller than R_s and we can use the small argument form of f in p_s which determines the overlap fraction O_t via eq 8. Noting that $x(t)/R_s \approx (t/\tau_s)^{1/z}$, this leads to

$$O_t = \int_{|r_s|<x(t)} d^d r_s \frac{1}{R_s^d} f\left(\frac{r_s}{R_s}, \frac{\alpha}{s}, \frac{\beta}{s}\right) \approx H\left(\frac{\alpha}{s}, \frac{\beta}{s}\right)\left(\frac{t}{\tau_s}\right)^\theta, \quad t \ll \tau_s \tag{11}$$

Now we must consider whether members of the overlapping fraction are likely to have reacted or not. To estimate the probability of reaction, consider the average total number of "collisions", $Z(t)$, experienced by a pair whose exploration volumes overlapped in the time t. A collision means an encounter closer than the "sink size" a such that reaction may have occurred. Now the total number of "steps" made equals t/t_a; however, the fraction of these steps for which the groups were in contact is given by the equilibrium conditional probability that the two groups are within a of one another *given* that they are within $x(t)$ of one another (this is the ergodic property of the dynamics). Thus

$$Z(t) \approx \left(\frac{t}{t_a}\right) \frac{\int_{|r_s|<a} p_s}{\int_{|r_s|<x(t)} p_s} = \left(\frac{t}{t_a}\right)^{1-\theta} \tag{12}$$

We have used the expression of eq 11. The above expression defines two cases[21] characterized by radically different reaction kinetics. The first case is when $\theta > 1$; then the average number of collisions is very small for large t/t_a. Now for a sink of strength Q the reaction probability per encounter is of order Qt_a; thus, the total reaction probability is of order ZQt_a and is much less than unity. Hence, using eq 12, the overall fraction of chains which have reacted, R_t, is given by

$$R_t \approx O_t(Z(t)Qt_a) = Qt\rho_{eq} \tag{13}$$

where ρ_{eq} is the equilibrium probability that the reactive groups are in "contact" with one another (i.e., within a of each other),

$$\rho_{eq} = \frac{1}{s^{\nu(d+g)}} H\left(\frac{\alpha}{s}, \frac{\beta}{s}\right) \tag{14}$$

Thus the reaction rate for small times is given by (see eq 3)

$$k_0(t) = \frac{dR_t}{dt} \approx Q\rho_{eq}, \quad \left(\frac{t}{\tau_s}\right) \ll 1, \quad \theta > 1 \tag{15}$$

The reaction rate is simply proportional to the equilibrium contact probability, i.e., obeys a law of mass action (LMA). A nonuniversal sink-dependent prefactor Q multiplies a universal power of s times a universal function of α/s and β/s. In extreme cases this last function drops out.

The second case is $\theta < 1$; then Z (eq 12) is very large for large t/t_a. Even when Qt_a is small (weakly reactive groups) the reacted fraction estimate ZQt_a becomes very large for large enough times. When ZQt_a exceeds unity, this signifies that reaction almost definitely occurred; thus the reacted fraction in these cases is simply the overlap fraction itself, $R_t \approx O_t$ and the reaction rate is

$$k_0(t) \approx H\left(\frac{\alpha}{s}, \frac{\beta}{s}\right) \frac{1}{\tau_s} \left(\frac{t}{\tau_s}\right)^{\theta-1}, \quad \left(\frac{t}{\tau_s}\right) \ll 1, \quad \theta < 1 \tag{16}$$

Any pair which encounters will have reacted and we may refer to this as the diffusion-controlled case (DC). Note that the form of $k(t)$ is universal, being independent of any characteristics of the sink.

Let us estimate k_∞ now. Now the system is able to relax from the perturbing effect of the reactive groups in a time scale τ_s. Each "cycle" of period τ_s a fraction R_{τ_s} reacts; as

time proceeds this process repeats itself multiplicatively. Thus the change $\Delta\mathcal{N}$ in the number of unreacted chains during one relaxation time has the form

$$\frac{\Delta\mathcal{N}}{\Delta t} \approx \frac{-\mathcal{N}(t)\, R_{\tau_s}}{\tau_s} \tag{17}$$

When $\theta > 1$, the reacted fraction after time τ_s is of order $Q\tau_s\rho_{eq}$ (using eq 13). Thus we have (coarse-graining eq 17 over a time scale τ_s) $d\mathcal{N}/dt = -k_\infty\mathcal{N}$ where k_∞ is of LMA form,

$$k_\infty = k_\infty^{LMA} \approx Q\rho_{eq}, \quad \theta > 1 \tag{18}$$

The long and short time rates are essentially the same (cf. eq 15). Consider now $\theta < 1$, beginning with the extreme cases; then since $R_{\tau_s} \approx O_{\tau_s} \approx 1$, we have from eq 17 $\Delta\mathcal{N}/\Delta t \approx -\mathcal{N}(t)/\tau_s$, so

$$k_\infty = k_\infty^{DC} \approx \frac{1}{\tau_s}, \quad \theta < 1 \tag{19}$$

This is of DC form, $k_\infty = k_\infty^{DC}$ being characterized by one time only, τ_s, which is the time scale in which diffusion brings the two groups together. For nonextreme cases k_∞ is as in eq 19 but multiplied by a function of α/s and β/s. As for small times, in the DC case, $\theta < 1$, one sees that the rate depends on quantities characterizing the dynamics of the chain *without* reactive groups; no features of the reactive sink appear. The determinant of the type of behavior, the exponent θ, is similarly universal. One may view the exhibition of one type of behavior or the other (LMA or DC) as the result of a competition between the two types of processes from which the slowest (rate-limiting) process emerges as the victor. From eqs 18 and 19 the ratio of rates is given by (taking extreme cases for simplicity)

$$\frac{k_\infty^{LMA}}{k_\infty^{DC}} = \frac{Qt_a}{s^{\nu z(\theta-1)}} = Qt_a\left(\frac{\tau_s}{t_a}\right)^{1-\theta} \tag{20}$$

Thus for large enough s the rate-limiting step is k_∞^{LMA} if $\theta > 1$ or k_∞^{DC} if $\theta < 1$. A guess at the behavior for "finite" values of s is $1/k_\infty = 1/k_\infty^{LMA} + 1/k_\infty^{DC}$; if, say, $\theta > 1$, this equation interpolates between DC behavior at small s and LMA behavior at large s. The crossover is in the reverse direction when $\theta < 1$. In both cases the exponent governing this crossover is θ, as is clear from eq 20. Indeed, in the renormalization group analysis[41] the exponent θ governs the approach to the asymptotic $N \to \infty$ behavior.

In summary, we have seen that reaction kinetics can belong to one of two classes, according as to whether $\theta > 1$ or $\theta < 1$. This classification generalizes the scheme of de Gennes,[42] who showed that reaction rates have quite different forms depending on whether the exploration of the reactive species is "compact" ($x^d(t) < t$) or "noncompact" ($x^d(t) > t$) which translates to a comparison of d/z with unity. This is the same as our criterion on θ (eq 6), in the case $g = 0$ as is appropriate to melts and Θ solvents. Thus our results generalize to cases when there are *correlations* between the spatial distributions of the reacting groups. This is necessary to treat the case of dilute solutions where two groups dislike straying close to one another since the polymer segments to which they are attached are mutually repellent.

In the remainder of this section the general expressions above will be specialized in turn to the two free-draining cases and the two dilute solution cases.

B. Melts. In melts Rouse dynamics apply for short times.[34,36,43] This translates to $g = 0$, H = constant (Gaussian statistics), and $z = 4$ which via eq 6 implies $\theta = d/4$. In three dimensions $\theta = {}^3/_4$ is less than unity and we predict DC behavior according to eqs 16 and 19:

$$k_0(t) \approx \frac{1}{\tau_s}\left(\frac{t}{\tau_s}\right)^{-1/4}, \quad \tau_s = s^2t_a, \quad \text{melts}, \quad t \ll \tau_{ent} \tag{21}$$

where τ_{ent} is the entanglement time. For unentangled melts the long time DC ($\theta < 1$) Rouse result (eq 19) is also applicable:

$$k_\infty \approx 1/\tau_s \text{ (unentangled melts)} \tag{22}$$

Notice that $d = 4$ is marginal; above 4 dimensions this DC behavior gives way to LMA forms for reaction rates, $k(t) \approx \rho_{eq} \sim 1/s^{d/2}$ since $\nu = {}^1/_2$. In the renormalization analysis of later sections one exploits this special role of $d = 4$ by expanding away from the (relatively "trivial") LMA regime ($d > 4$) in powers of $\epsilon \equiv 4 - d$.

C. Rouse Plus Excluded Volume. This second case does not correspond to any physical system but as we will see exhibits particularly interesting behavior in which excluded-volume effects predominate. Consider the value of θ to order ϵ. Now since[44] $z = 2 + 1/\nu$ and $\nu = (1 + \epsilon/8)/2 + O(\epsilon^2)$, one finds

$$\begin{aligned} &\theta = 1 - \epsilon/8 \quad && \text{case 1} \\ &\theta = 1 - \epsilon/16 && \text{case 2} \\ &\theta = 1 + \epsilon/16 && \text{case 3} \end{aligned}$$

(Rouse plus excluded volume) (23)

using des Cloizeaux's $O(\epsilon)$ results for g. The conclusion is that cases 1 and 2 are DC ($\theta < 1$) while case 3 is LMA ($\theta > 1$)! Remarkably, the reaction processes for different positionings of the reactive groups in the same polymer system belong to different "universality classes". When both groups are internal to the polymer chain, the correlation hole effect is so strong as to shift the behavior away from DC to LMA. In the extreme cases the DC forms for short and long times respectively are $k(t) \approx (t/\tau_s)^{\theta-1}/\tau_s$ and $k_\infty \approx 1/\tau_s$, whence

$$k(t \ll \tau_s) \approx \frac{1}{\tau_s}\left(\frac{t}{\tau_s}\right)^{-\epsilon/8} \to \frac{1}{\tau_s}\left(\frac{t}{\tau_s}\right)^{-1/8}, \quad d = 3, \quad \text{case 1}$$

$$k(t \ll \tau_s) \approx \frac{1}{\tau_s}\left(\frac{t}{\tau_s}\right)^{-\epsilon/16} \to \frac{1}{\tau_s}\left(\frac{t}{\tau_s}\right)^{-1/16}, \quad d = 3, \quad \text{case 2}$$

$$k_\infty \approx 1/\tau_s \text{ cases 1 and 2}, \quad \tau = t_a s^{2\nu+1}$$

(Rouse plus excluded volume) (24)

The case 3 behavior is of LMA form, $k(t) \approx Q\rho_{eq} \approx Qs^{-\nu(d+g)}$ for all times, i.e.

$$k(t) \approx \frac{Q}{s^{\nu(d+g)}} \approx \frac{Q}{s^{2+\epsilon/4}} \to \frac{Q}{s^{9/4}}, \quad d = 3, \quad \text{case 3}$$

(Rouse plus excluded volume) (25)

Note that the DC result for case 3 (were it applicable) would predict $k \sim 1/\tau_s \sim s^{-17/8}$ to order ϵ; to this order, then, the magnitude of this exponent exceeds that of the LMA prediction above by ${}^1/_8$.

The above results in eqs 24 and 25 were for extreme cases. For general instances of cases 2 and 3 these results are all multiplied by functions of α/s and β/s.

D. Good Solvents. For hydrodynamical cases the long time relaxation dynamics are similar to those of a hard sphere; i.e., the relaxation time scales[34,36] as the volume of the polymer R^d. This implies $z = d$, and $\theta \to 1 + g/d$. In good solvents excluded-volume interactions are strong and so $g > 0$, implying $\theta > 1$; one expects LMA behavior, i.e., $k(t)$ should scale as ρ_{eq}, the equilibrium probability

the active groups are in contact:

$$k(t) \approx Q\rho_{eq} \tag{26}$$

The prefactor Q represents the local reactivity, and the form of ρ_{eq} is given in eq 14. Now since for good solvents[45] $\nu(d+g) = 2(1-\epsilon/8+g/4)$ to leading order in ϵ, one finds

$$k(t) \approx \frac{Q}{s^{2-\epsilon/8}} \to \frac{Q}{s^{15/8}}, \quad d=3, \quad \text{case 1}$$

$$k(t) \approx H\left(\frac{\alpha}{s},\frac{\beta}{s}\right)\frac{Q}{s^2}, \quad \text{all } d, \quad \text{case 2}$$

$$k(t) \approx H\left(\frac{\alpha}{s},\frac{\beta}{s}\right)\frac{Q}{s^{9\epsilon/4}} \to H\left(\frac{\alpha}{s},\frac{\beta}{s}\right)\frac{Q}{s^{9/4}}, \quad d=3, \quad \text{case 3,}$$

good solvents (27)

In the extreme cases the H functions above become constants. The predicted power of s is different for the three cases, with this power increasing, and hence the rate decreasing, as the groups become more internal (cases 1 → 2 → 3) and thus more mutually repulsive. Note, as always in LMA forms, the presence of the nonuniversal prefactor Q in all cases. The excluded-volume interactions play a crucial role, in all cases the correlation hole diminishing the reaction probability to such a degree that $k \sim 1/\tau_s$ (the DC result) is never true, even when Q is very large. For the case of very *small* Q, the importance of excluded-volume interactions in the case of *inter*molecular reactions was noted by Khokhlov and coworkers;[46,47] in this limit they found that k was determined by these same des Cloizeaux exponents.

Now away from the extreme cases the dependence of k on group positioning is in general quite complex. However, at fixed relative group positions α/s and β/s, as one increases molecular weight $N \equiv \alpha + \beta + s$, one expects k to scale with N according to the same des Cloizeaux exponents as in eq 27 consistent with the scaling behavior[40] of ρ_{eq}. Thus at *fixed* relative group locations in good solvents, the prediction is $k \sim N^{-15/8}$, N^{-2}, and $N^{-9/4}$ for cases 1–3, respectively.

E. Θ Solvents. Clearly, the correlation hole plays a central role for good solvents. On the other hand, in Θ solvents, where ideality is approximately recovered, $g = 0$ and one has $\theta = 1$; this is *marginal* behavior. We have established time-dependent behavior for short times in DC cases, and no time dependence in LMA cases. For short times, therefore, "marginal" signifies the boundary separating time-dependent from time-independent (or at most weakly time-dependent) behavior. Consistently with this fact, we will see later that $k(t)$ for short times exhibits logarithmic time dependencies. In this marginal case the long time DC and LMA results coincide: $k_\infty^{DC} \sim k_\infty^{LMA} \sim 1/s^{\nu d} \to 1/s^{3/2}$ in $d = 3$ ($\nu = 1/2$). Indeed, in the following sections we will find such s-dependence multiplying logarithmic corrections. Generally, such logarithmic corrections are typical of marginal phenomena in statistical mechanics.[48] Thus we anticipate

$$k(t) \approx \left(\frac{1}{s}\right)^{3/2} \times [\text{logs of } s \text{ and } t] \quad (\Theta \text{ solvents}) \tag{28}$$

IV. Renormalization Group Calculations of Reaction Rates

Beyond the scaling analyses employed in the previous section, we have performed systematic calculations, starting from the Fokker–Planck equation of section II and using renormalization group (RG) methods, which quantify and justify these physically motivated arguments. Moreover, the RG calculations identify certain universal measurable quantities, allow prediction of "crossover behavior" (i.e., chains of finite molecular weight or equivalently functional groups of finite reactivity), and enable us to calculate k for Θ solvents. Here our aim is to outline and discuss the formal procedure, rather than present all of its technical details which will appear elsewhere.[41] As a relatively simple concrete example, we will treat Rouse dynamics, case 3 in some detail. Other experimentally observable RG results will merely by presented at the end of this section.

The general procedure is as follows. The Fokker–Planck equation (eq 4) is solved in powers of the sink coupling constant u_0, and via eq 1 one obtains a corresponding series for $k(t)$. Now since our aim is to understand $k(t)$ for very large molecular weight, it turns out that this series (the "unrenormalized" or "bare" series) is not useful to us in its original form. For example, in case 1 (cyclization) for $d = 3$, we will see below that it is actually a series in powers of the dimensionless parameter $u_0\zeta_0 N_0^{1/2}$ (where ζ_0 is the time scale associated with a single chain unit and subscript 0 is used to denote the unrenormalized, or bare, counterparts to the unsubscripted quantities). For large N_0 this parameter becomes large no matter how small u_0 may be, thus rendering the perturbative result meaningless.

The methods of RG theory furnish a cure for this problem.[45,48] We normalize the perturbation theory in such a way as to extract the correct long time and high molecular weight properties. In the process this provides us with a small expansion parameter in the shape of $\epsilon \equiv 4-d$ in powers of which one reformulates the expansion.[45] Thus, we end up by expanding away from 4 dimensions whose special role has already been exposed by the scaling arguments of the previous section.

The following results generalize those of the present authors in their study of cyclization.[20,21] We shall refer to these works as FO1 and FO2, respectively.

A. Example: Rouse Dynamics, Case 3. We begin by expressing $k(t)$ in terms of equilibrium quantities. The solution to eq 4 may be written self-consistently as

$$P(\{r\},t) = P_{eq}(\{r\}) + \int_0^t dt' \int d\{r'\}\, G(\{r\},\{r'\},t-t')\, u_0\delta(r'_{\alpha\beta})\, P(\{r'\},t') \tag{29}$$

where initially the distribution P equals $P_{eq}(\{r\})$, the equilibrium distribution. $G(\{r\},\{r'\},t-t')$ is Green's function, namely, the conditional probability at time t of a chain configuration $\{r\}$ given that the configuration was $\{r'\}$ at time t'. Integrating both sides of eq 29 over all possible configurations $\{r\}$ yields the following equation for the unreacted fraction $\mathcal{N}(t) \equiv \int d\{r\}\, P(\{r\},t)$:

$$\mathcal{N}(t) = 1 + u_0\int_0^t dt' \int d\{r'\}\, \delta(r'_{\alpha\beta})\, P(\{r'\},t') \tag{30}$$

Solving eq 29 iteratively gives $P = P_{eq} + u_0\int\int dt' \int d\{r'\}\, G\, \delta(r'_{\alpha\beta})\, P_{eq}$ to first order in u_0. Substituting this series for P into eq 30, one obtains

$$-k(t) \equiv \frac{d\mathcal{N}(t)/dt}{\mathcal{N}(t)} = u_0\langle\delta(r_{\alpha\beta})\rangle + u_0^2\int_0^t dt'\, \langle\delta(r_{\alpha\beta}(t'))\delta(r_{\alpha\beta}(0))\rangle_c + O(u_0^3) \tag{31}$$

Here $\langle\cdots\rangle$ denotes the equilibrium average (i.e., for the dynamics *in the absence of reactive groups*) and $\langle\cdots\rangle_c$ denotes the second cumulant. Thus to second order in all coupling constants

$$-k_\infty = u_0\rho_{eq} + (u_0\rho_{eq}^\circ)^2\int_0^\infty dt\, [S(t)-1] + \ldots$$

$$-k_0(t) = u_0\rho_{eq} + (u_0\rho_{eq}^{\circ})^2\int_0^t dt'\, S(t') + \ldots$$

$$\rho_{eq} \equiv \langle\delta(r_{\alpha\beta})\rangle, \quad \rho_{eq}^{\circ} \equiv \langle\delta(r_{\alpha\beta})\rangle_0 = \frac{1}{(2\pi s)^{d/2}}$$

$$S(t) \equiv \frac{\langle\delta(r_{\alpha\beta}(t))\,\delta(r_{\alpha\beta}(0))\rangle_0}{(\rho_{eq}^{\circ})^2} \tag{32}$$

The average taken in eq 32, $\langle\cdots\rangle_0$, denotes the "noninteracting" average under Rouse statics and dynamics. The equilibrium loop probability is ρ_{eq} (cf. eq 14), and ρ_{eq}° is the same for a Gaussian chain. The key function $S(t)$ is the dimensionless return probability under Rouse dynamics. Since $S(\infty) = 1$, it follows that the second-order term in the expression for k_∞ above is proportional to the finite part of the integral of the return probability. The crucial feature is the short time behavior $S(t) \sim t^{-d/4}$ which follows since $S(t)$ scales as the inverse volume explored and at short times $x(t) \sim t^{1/4}$ for Rouse chains.[36] The time integrals in eq 32 thus diverge as d approaches 4 from below, and we find[41] the following $1/\epsilon$ divergences:

$$\int_0^t dt'\, S(t') = \left[\tau_s^0\frac{\pi^3}{4}\right]\left\{\frac{1}{\epsilon}\left(\frac{t}{\tau_s^0}\right)^{\epsilon/4} + O_c(\epsilon^0)\right\} + O\left(\frac{t}{\tau_s^0}\right)^{(1/2+\epsilon/4)}$$

$$\int_0^\infty dt\,[S(t) - 1] = \left[\tau_s^0\frac{\pi^3}{4}\right]\left\{\frac{1}{\epsilon} + g(\alpha_0,\beta_0,s_0) + O_c(\epsilon^0)\right\}, \quad \text{case 3} \tag{33}$$

The symbol $O_c(\epsilon^0)$ denotes order ϵ^0 terms which are pure constants, i.e., are independent of α_0, β_0, s_0, and t. The function g contains[41] all the dependence on α_0, β_0, and s_0 which is of order ϵ^0 and $\tau_s^0 \equiv \zeta_0 s_0^2/\pi^2$ is the Rouse time for the chain length s_0 where ζ_0 is the Rouse bead coefficient (see Appendix A). We define τ_α^0 and τ_β^0 analogously. Note that the definition of short time, namely, the domain of validity of $k_0(t)$, is $t \ll \tau_\alpha^0, \tau_\beta^0, \tau_s^0$.

The form of the bare series (eq 32) is reminiscent in some respects of the Wilemski–Fixman expressions for k in the "closure approximation"[22-24,42] in the case of a δ function sink. In both cases the return probability is involved. The closure approximation is that the polymer configurations are as in equilibrium when the reactive groups are in contact. This amounts to factorizing the multiple return probabilities which would appear in higher order terms in the series eq 32.

For the rest of this subsection the results of eqs 32 and 33, which are generally true, will be developed for the specific instance of Rouse case 3. Using the divergences in eq 32, one obtains to second order for Rouse dynamics case 3

$$-k_0(t)\,\zeta_0 s_0^2 = w_0\left(\frac{s_0}{L}\right)^{\epsilon/2} + w_0^2\left(\frac{s_0}{L}\right)^{\epsilon}\left\{\frac{\pi}{4\epsilon}\left(\frac{t}{\tau_s^0}\right)^{\epsilon/4} + O_c(\epsilon^0)\right\}$$

$$-k_\infty\zeta_0 s_0^2 = w_0\left(\frac{s_0}{L}\right)^{\epsilon/2} + w_0^2\left(\frac{s_0}{L}\right)^{\epsilon}\frac{\pi}{4}\left\{\frac{1}{\epsilon} + g(\alpha_0,\beta_0,s_0) + O_c(\epsilon^0)\right\} \tag{34}$$

where we have defined a dimensionless reaction (w_0) coupling constant: $(2\pi)^2 w_0 \equiv u_0\zeta_0(2\pi L)^{\epsilon/2}$ (in Appendix A we show that w_0 is indeed dimensionless). Here L is a phenomenological polymer contour length scale of arbitrary magnitude[45] which roughly speaking may be thought of as the number of original chain units per "blob" in a new coarse-grained polymer of blobs.

Equation 34 will be renormalized to yield nondivergent expressions for $k(t)$ using the renormalization scheme of Oono.[45] Notice that the above series is a sum of powers of $w_0 s_0^{\epsilon/2}$; this parameter becomes large for large molecular weight and renders the perturbative expression useless in its bare form, as discussed previously.

We assume, as in FO1 and FO2, that neither ζ_0 nor chain contour lengths are renormalized, i.e., $\zeta = \zeta_0$, $s = s_0$, etc. (renormalized quantities are unsubscripted). The RG equation (RGE) is $L(\partial k/\partial L) = 0$ (the derivative being taken at fixed unrenormalized quantities); i.e., $\beta_w(\partial k/\partial w) + L(\partial k/\partial L) = 0$ where $\beta_w = (\epsilon w_0/2)\, dw/dw_0$. Its general solution is ($\tau_s = \tau_s^0$)

$$k(t) = \frac{1}{\tau_s}G\left(\frac{\alpha}{s},\frac{\beta}{s},\frac{s}{L}e^{\int dw/\beta_w},\frac{t}{\tau_s}\right), \quad \text{Rouse} \tag{35}$$

where G is an arbitrary function and the dimensional analysis of k and ζ was used (see Appendix A). The actual form of G must be inferred from the renormalized series itself. Choosing the relationship between w_0 and w such as to absorb the divergences in the standard way,[45] we obtain the following renormalized series for short times

$$-k_0(t)\,\zeta s^2 = w\left\{1 + \left[1 - \frac{w}{w^*}\right]\frac{\epsilon}{2}\ln\frac{s}{L} - \frac{w}{w^*}\frac{\epsilon}{4}\ln\frac{t}{\tau_s} + O_c(\epsilon) + O(\epsilon^2)\right\}, \quad \text{Rouse} \tag{36}$$

where $w^* = -\epsilon/\pi$ (for case 3) is the stable zero of $\beta_w = \epsilon w(w^* - w)/2w$. All α,β,s,t-dependent terms up to order ϵ^2 have been accounted for. The infinite N behavior is determined by substituting $w = w^*$ in the renormalized series eq 36. In this large N limit the solution of the RGE eq 35 becomes $k(t) = \tau_s^{-1}F(\alpha/s,\beta/s,t/\tau_s)$ for another function F. Note that this solution applies for all times, while eq 36 refers to the smallest times; this suggests that for small times $\alpha/s,\beta/s$ dependence drops out which makes physical sense since for such times the reactive groups are causally isolated from chain ends and so do not "know" about α, β, and s. Motivated by the scaling arguments, we exponentiate[49] the logarithm (i.e., we interpret the $\epsilon\ln(t/\tau_s)$ term as the first-order term in the expansion of a power law), leading to ($\epsilon = 1$)

$$k_0(t) = \frac{4}{\pi^3\tau_s}\left(\frac{t}{\tau_s}\right)^{-1/4}, \quad \text{Rouse, case 3, } N \to \infty \tag{37}$$

If we accept that $\alpha/s,\beta/s$ dependencies drop out at these short times, then the RG solution tells us that $k_0(t) =$ constant $\times\, \tau_s^{-1}(t/\tau_s)^{-1/4}$ where the constant is an asymptote of G and so is *universal*. The renormalized series tells us that to order ϵ this universal constant equals $4\epsilon/\pi^3$. The result we have derived in eq 37 is of precisely the DC form anticipated by the scaling arguments of section III (eq 21).

The renormalization procedure for the long time rate k_∞ is very similar. One obtains for the renormalized series

$$-k_\infty\zeta s^2 = w\left\{1 + \left[1 - \frac{w}{w^*}\right]\frac{\epsilon}{2}\ln\frac{s}{L} + w\frac{\pi}{4}g(\alpha,\beta,s) + O_c(\epsilon) + O(\epsilon^2)\right\}, \quad \text{Rouse, case 3} \tag{38}$$

Here we consider k_∞ for extreme case 3, when one finds[41] $g \approx (4/\pi^2)\ln(\alpha/s)$ for the symmetric case $\alpha = \beta$ which for

$d = 3$ and $N \to \infty$ ($w = w^*$) gives from eq 38

$$k_\infty \tau_s = \frac{4}{\pi^3} \frac{1}{(4/\pi^2)\ln(\alpha/s) + c}, \quad \text{extreme case 3, Rouse, } N \to \infty \tag{39}$$

where c is a constant and we have exponentiated the $\ln(\alpha/s)$ which leads to a rather interesting result. One is forced into some kind of exponentiation since otherwise ($k_\infty \propto 1 - (4/\pi^2)\ln(\alpha/s)$) the logarithm would give a nonsensically negative reaction rate as α increases at fixed s. Our choice renders k_∞ finite and positive and is also motivated by scaling arguments which[50] yield this same form. This means that for large enough α

$$k_\infty \tau_s \approx \frac{1}{\pi \ln(\alpha/s)}, \quad \text{extreme case 3 } (\alpha \approx \beta \gg s) \tag{40}$$

The rather surprising prediction is that k_∞ does not quite scale with the inverse relaxation time of the portion of polymer connecting the groups (namely, $1/\tau_s$).

Up to this point the results in this subsection have concerned the $N \to \infty$ limit when $w = w^*$ governs the renormalized series. Let us consider now *finitely* long chains, taking long times as an example. In this case we must consider the full solution to the RG equation for nonvanishing β_w in eq 35. We find $k(t) = \tau_s^{-1} G(\alpha/s, \beta/s, X, t/\tau_s)$ where

$$X \equiv \left(\frac{s}{L}\right)^{\epsilon/2} \frac{w}{w^* - w} \tag{41}$$

The "crossover" parameter X is revealed as the natural parameter in terms of which to phrase the renormalized series rather than w itself. Solving for w and substituting into the renormalized series for long times (eq 38), one obtains

$$-k_\infty \zeta s^2 = \frac{X}{X+1} w^* \left\{1 - \frac{X}{X+1}\epsilon g(\alpha,\beta,s) + O_c(\epsilon) + O(\epsilon^2)\right\}, \quad \text{finite } N, \text{ Rouse} \tag{42}$$

Motivated by the $s/L \to \infty (X \to \infty)$ result of eq 39, this gives

$$k_\infty \tau_s = Y \frac{4}{\pi^3} \frac{1}{Y(4/\pi^2)\ln(\alpha/s) + c + \ldots}, \quad Y \equiv \frac{X}{X+1}, \quad \text{Rouse, extreme case 3} \tag{43}$$

Note the important distinction between a high ratio α/s (i.e., very extreme) and large molecular weight as represented by X which grows as s/L grows. X (or Y) parametrizes a "proximity" to infinite N behavior at fixed ratios α/s and β/s. At small values of Y, eq 43 yields a LMA form $k_\infty \sim s^{-3/2}$; increasing Y describes the "trajectory" from this limit to the DC form at very large s ($Y \to 1$). Note also another interesting result when α becomes large at fixed s, i.e., at fixed Y; k_∞ approaches the result of eq 40 which is an infinite N DC form with logarithmic corrections.

B. Assembled Results. Tables I and II list respectively the chief free-draining and non-free-draining experimental predictions arising from our RG calculations. For simplicity's sake we have quoted only results for infinitely long chains (i.e., long enough that crossover effects have died out) and for extreme cases (however, we remark that the exhibited *short* time results are still valid in nonextreme situations since chain ends and groups cannot communicate on sufficiently small time scales). The numerical values of exponents have been estimated using the second-order des Cloizeaux results for g (eq 10) and setting[34] $\nu = {}^3/_5$ (recall that exponents in section III were all derived to first order in ϵ). In all cases the time scale τ_s is defined such as to equal the longest relaxation time of the polymer τ_N when s is set equal to the chain length N, i.e., $\tau_s \equiv (s/N)^{\nu z}\tau_N$.

Table I. Experimentally Observable RG Results for "Free Draining" Cases (Numerically Observable for Rouse plus Excluded Volume)[a]

	short time $k_0(t)$	long time k_∞	case
Rouse, τ_s = constant × s^2	$A_1/\tau_s(t/\tau_s)^{-1/4}$	A_1/τ_s	1
	$A_2/\tau_s(t/\tau_s)^{-1/4}$	A_2/τ_s	2
	$A_3/\tau_s(t/\tau_s)^{-1/4}$	$A_4/[\tau_s \ln(\alpha/s)]$	3
Rouse + excluded volume, τ_s = constant × $s^{2.2}$	$B_1/\tau_s(t/\tau_s)^{-0.11}$	B_1/τ_s	1
	$B_2/\tau_s(t/\tau_s)^{-0.06}$	B_2/τ_s	2
	constant × $s^{-2.23}$	as for $k_0(t)$	3

[a] All results are for "infinitely" long chains and "extreme" cases (see Figure 3). Exponents are estimated using $\nu = {}^3/_5$ and the second-order des Cloizeaux results for g. The universal constants to $O(\epsilon)$ are $A_1 = 16/\pi^3$, $A_2 = 9/\pi^3$, $A_3 = 4/\pi^3$, $A_4 = 1/\pi$, $B_1 = 8/\pi^3$, and $B_2 = 9/4\pi^3$.

Table II. Experimentally Observable RG Results for Dilute Solutions[a]

	short time $k_0(t)$	long time k_∞	case
Θ solvents, τ_s = constant × $s^{3/2}$	$2C_1/[\tau_s \ln(t/t_0)]$	$C_1/[\tau_s \ln(s/s_0)]$	1
	$2C_2/[\tau_s \ln(t/t_0)]$	$C_2/[\tau_s \ln(s/s_0)]$	2
	$2C_3/[\tau_s \ln(t/t_0)]$	$C_4/[\tau_s \ln(\alpha/s)]$	3
good solvents	constant × $s^{-1.96}$	as for $k_0(t)$	1
	constant × $s^{-2.08}$	as for $k_0(t)$	2
	constant × $s^{-2.23}$	as for $k_0(t)$	3

[a] Results are for "infinitely" long chains and "extreme" cases, and "constant" denotes a nonuniversal constant prefactor. The case 3 result for Θ solvents is for $\alpha = \beta$. The universal constants to $O(\epsilon)$ are $C_1 \approx 1.08$, $C_2 \approx 0.61$, $C_3 \approx 0.27$, and $C_4 \approx 2.67$. The small scales t_0 and s_0 are nonuniversal and case-dependent constants.

A few technical comments are worthwhile. At the level of the bare perturbation theory, excluded-volume interactions enter through ρ_{eq} in eq 32 and dependence on group position arises through ρ_{eq}, through the case dependence of the small time return probability divergences, and through the function g of eq 33. The general technical feature which emerges is a relationship between the fixed point reaction coupling and the nature of reaction kinetics: $w^* < 0$ corresponds to DC kinetics (e.g., Rouse) while $w^* = 0$ to LMA kinetics (dilute solutions).

The results in Table I confirm the scaling conclusions of section III, including the Rouse plus excluded volume DC → LMA crossover as groups are moved deep into the chain interior; cases 1 and 2 are DC, and case 3 is LMA. Other than for this case, all free-draining results are characterized by universal prefactors (the constants A_i and B_i), with our $O(\epsilon)$ calculations of these constants quoted in the table caption.

For good solvents (Table II), one finds $w^* = 0$ in all cases, implying that the long chain behavior is determined entirely by crossover. This leads to the anticipated scaling form $k(t) \sim \rho_{eq} \sim s^{-\nu(d+g)}$. For example, for case 3 we find for long chains (η is the solvent viscosity).

$$k(t) \approx \frac{-2w}{\eta(2\pi L)^{3/2}} \left(\frac{s}{L}\right)^{-\nu(3+g)} \left\{1 + \frac{1}{8}\left[h\left(\frac{\alpha}{s}\right) + h\left(\frac{\beta}{s}\right) - \ln\left(1 + \frac{s}{\alpha+\beta}\right)\right]\right\} \tag{44}$$

with corrections of order $s^{-\nu g}$ (including small time-dependent corrections) and h a function with asymptotics

$h(x \ll 1) \approx -2 \ln x$ and $h(x \gg 1) \approx 1/x$. The above expression appears to be proportional to ρ_{eq} as inferred from Oono and Ohta's calculation of intrachain correlations[40] in the limit of small separations. Notice the nonuniversality of the prefactor in eq 44, depending on w which is a nonuniversal sink coupling. This is the RG's way of telling us that k, though scaling in a universal manner, depends on the details of the functional groups (reactivity, shape, etc.) even for large N. Reflecting this, the good solvent results in Table II all have nonuniversal prefactors (for which we use the symbol "constant").

Also listed in Table II are Θ solvent results involving the anticipated logarithms and, in contrast to good solvents, universal prefactors. The time and chain contour scales, t_0 and s_0, respectively, are nonuniversal local scales which contain all the dependence on the reactivity and other qualities of the functional groups. Roughly, t_0 is the relaxation time associated with s_0. Thus functional group dependence appears only *logarithmically*. For groups of vanishing reactivity t_0, s_0 vanish, thereby causing k to vanish. The essential feature of the RG which corresponds to the marginality identified by the scaling arguments and which leads to these logarithms, is a double zero in the function[48] β_w.

V. Discussion

In this work we have developed a systematic calculation scheme for intramolecular reaction rates in high molecular weight polymer systems. Our calculations have investigated how reaction rates vary as the reactive groups are positioned at different points along the polymer backbone and the main results for very long chains and extreme cases (Figure 3) are presented in Tables I and II. The results of calculations for finite chains will be presented in detail elsewhere;[41] however, a representative example of crossover effects was presented in section IV.

Generally, the form of reaction kinetics is determined by the exponent θ of eq 6. For instance, the picture for unentangled melts ($\theta < 1$) is that long chain reaction rates are of intrinsically diffusion-controlled (DC) form; i.e., long time rates, for example, scale (Table I) as the inverse relaxation time of the segment of chain connecting the reactive groups (with important logarithmic corrections for extreme case 3). Shorter chains, or chains with relatively weakly reactive groups, obey law of mass action (LMA) reaction kinetics; i.e., rates scale as the equilibrium probability the reactive groups are in contact with one another. However, if one maintains the same weakly reactive groups but increases the molecular weight of such a LMA system, the behavior inevitably *crosses over* from LMA to DC.

DC behavior is characterized by universal forms of k_∞ and $k_0(t)$, involving independently observable quantities and universal prefactors. Thus for Rouse dynamics (Table I) k_∞ equals a system-independent constant times $\tau_s \equiv \tau_N(s/N)^2$ where τ_N is the measurable longest polymer relaxation time. Similar remarks apply to the short time rate. Correspondingly, certain ratios of reaction rates are predicted to be universal; e.g., the ratio of a case 1 to an extreme case 2 is $k_\infty^1/k_\infty^2 = A_1/A_2 \approx 16/9$ where the case 2 polymer is obtained by adding a very long segment to the end of the case 1 polymer.

In stark contrast to melts, intrapolymeric reactions in dilute solutions with good solvents (Table II) are of intrinsically LMA form ($\theta > 1$) for very long chains. Thus for good solvents k is *not* proportional to the inverse time scale asociated with the polymer connecting the groups, which would be the DC result as predicted by previous theoretical works. For the case of cyclization, the present experimental data[10] are not quite able to distinguish between the two forms, LMA and DC. The power laws are quite close since[34] $\tau_s \propto s^{3\nu}$ for good solvents, so $k_\infty \propto 1/\tau_s$ would lead to $k_\infty \propto s^{-1.8}$ to be compared to the exponent of about 1.96 predicted by our theory. However, recent numerical simulations of cyclization[51,52] though not entirely conclusive tend to support the LMA law. It is interesting to notice that the difference between LMA and DC predictions increases as the groups become more internal. Experiments and simulations for extreme case 3 are attractive in this respect: the difference in exponents is about 0.43 which should be far easier to detect than the 0.16 difference for cyclization.

This good solvent behavior derives from the fact that the excluded-volume repulsion between the segments bearing the reactive groups becomes very strong for high molecular weight (the correlation hole effect). In consequence of this effect, plus the rapid relaxation time due to hydrodynamics, the effective reactivity becomes so small as to provide only a weak perturbation to the equilibrium coil configuration. Thus the reaction rate $k(t)$ is proportional to the *equilibrium* probability that the reactive segments occupy the same position in space (LMA); this probability depends on the correlation hole exponent g whose value is a maximum when both groups are internal. Experimental measurements of $k(t)$ for internal groups thus provide a direct probe of des Cloizeaux's trio of correlation hole exponents. It is important to note, however, that although we deal with finite molecular weight as far as the effective reactivity is concerned, in our calculations we have always taken the excluded-volume interactions to be asymptotic; i.e., we assume that all relevant lengths of polymer are long enough to have statistics characterized by the standard excluded-volume exponents.

Intrinsic to LMA kinetics are *nonuniversal* prefactors, depending on the detailed structure of the polymer and the reactivity of the functional groups, etc. Thus, for example, it may be tempting to assume that $k(t) \propto 1/\eta$ at fixed molecular weight since the nonuniversal prefactors in k for a dilute solution are inversely proportional to η (see eq 44). This is quite wrong, however, since changing the solvent will modify the strength of the excluded-volume interactions and the effective reactivity of the active groups (in addition to the viscosity effect) in their complex environment attached to the polymer. In theoretical terms, changing the solvent or polymer in any way changes the entire system; molecular weights will get renormalized at a different "rate" and the dimensionless reactivity $w(L)$ will be modified in a nonuniversal way. The most one can say is that in order of magnitude terms the prefactors may be associated with the reactivity of the isolated active groups and the solvent viscosity (it is of course physically reasonable that more weakly reactive groups and more viscous solvents should tend to reduce k). The point is that once in the polymer environment their effective reactivity is highly system-dependent.

The two other regimes we have studied here are Rouse plus excluded volume and Θ solvents. The former system provides interesting numerical possibilities, exhibiting a rather novel switch in universality class when both reactive groups are internally positioned. This directly reflects the large magnitude of the correlation hole exponent in that case (very strong excluded-volume repulsions). Θ solvents ($\theta = 1$) are marginal, and since the nonuniversal details of the reactive groups appear only logarithmically,

experiments testing universal ratios are in principle available.

Finally, let us briefly list some general principles which have emerged from this study:

1. The asymptotic (i.e., very long polymers) *form of* $k(t)$ (i.e., LMA or DC) is universal, i.e., is entirely independent of the particular polymer, solvent, and reactive group species. It is determined only by the value of the exponent $\theta \equiv (d + g)/z$, which depends only on the class of the system (melts, dilute solution in good solvents, etc.).

2. For DC systems $k(t)$ is universal both qualitatively and quantitatively speaking. For example, $k_\infty \tau_s$ is a universal constant depending only on reactive group location; the value of k_∞ is completely independent of the chemistry of the reactive groups. Correspondingly, in a calculation or computer simulation the particular form of the sink function is irrelevant. This of course is only asymptotically so; for small chains the sink form is felt, but this is a transient. During the transient k is a universal function of a crossover parameter (X). One should distinguish between the prediction that $k_\infty \tau_s$ is a universal constant (which we claim to be an exact statement for DC systems) and the prediction of the numerical value of that constant (which we have calculated approximately here, to first order in ϵ).

3. For LMA systems the molecular weight dependence is universal, but the prefactor is nonuniversal. Thus the magnitude of k is highly system-dependent, but not the general form. For example, k_∞ in good solvents equals $\tilde{Q}\rho_{eq}$, where $\tilde{Q}$ is a local rate constant. The power law dependence of ρ_{eq} is the same for all polymers in good solvents, but $\tilde{Q}$ and the length scale involved in ρ_{eq} are quite different for different polymers and reactive groups. Correspondingly, the choice of sink function in calculation or simulation will have a significant and unpredictable effect on the numerical value of k but will not affect the dependencies on the polymer lengths. Again, this is only so asymptotically; in particular, for chains too short to obey self-avoiding-walk statistics, transient effects will influence k. The nonuniversal nature of the prefactor makes it an extremely difficult quantity to predict experimentally, since it involves the small scale details of the reactive groups and their manner of attachment to the polymer, etc.

4. Rouse dynamics (unentangled melts) belong to the DC class for cases 1 and 2. In extreme case 3 k_∞ suffers a logarithmic correction.

5. Rouse plus excluded volume dynamics belong to the DC class for cases 1 and 2 but to the LMA class for case 3.

6. Good solvents belong to the LMA class for all 3 cases.

7. Θ solvents are marginal; correspondingly k collects logarithmic corrections. The dependence on reactive group properties is logarithmic and prefactors are universal.

In summary, we have calculated a number of quantities which should be directly measurable using, for example, pyrene excimer formation. In fact, a number of such experiments, measuring reactions involving internally positioned groups, have been performed.[7,8,14,15] We hope that the results here will motivate a range of systematic experimental measurements of reaction rates, in melts and dilute solution, between groups carefully positioned along the polymer backbone. Both short time and long time intramolecular reaction kinetics provide illuminating probes of single-chain polymer dynamics.

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Appendix A. The Diffusion Operator F

The operator F describing the chain dynamics in the absence of reactive groups, which appears in $\dot{P} = FP + u_0\delta(r_{\alpha\beta})P$, is given by

$$F = \int_0^{N_0} dn \int_0^{N_0} dn' \sum_{i,j} \frac{\delta}{\delta r_i(n)} \left[\frac{\delta_{i,j}}{\zeta_0} \delta(n-n') + T_{ij}(r(n)-r(n')) \right] \left[\frac{\delta}{\delta r_j(n')} + \frac{\delta H}{\delta r_j(n')} \right]$$

where

$$T_{ij}(x) = \frac{1}{2\pi^d} \int \frac{d^d k}{\eta k^2} \left[\delta_{ij} - \frac{k_i k_j}{k^2} \right] e^{ikx}, \quad H = H_0 + H_I$$

$$H_0 = \frac{1}{2} \int_0^{N_0} dn \left(\frac{dr}{dn} \right)^2, \quad H_I = \frac{v_0}{2} \int_0^{N_0} dn \int_0^{N_0} dn' \, \delta(r(n)-r(n')) \tag{A1}$$

Here ζ_0 and v_0 are the bare friction and excluded-volume coupling constants, respectively, and η is the solvent viscosity. The "Edwards Hamiltonian" H represents excluded-volume interactions, and the connectivity of the polymer and the Oseen tensor $\mathbf{T}$ generates hydrodynamical interactions. The Hamiltonian is H_0 when excluded volume is screened (melts); H_0 describes Gaussian statistics where each of the N_0 steps of the chain has a root-mean-square size equal to the dimension of space d. The "core" of F, when v_0 is deleted, describes Rouse dynamics. In this case the remaining coupling constant ζ_0 is just the chain unit friction coefficient.

Let us now dimensionally analyze F and its coupling constants using the symbols t, r, and n to denote the dimensions $[t]$, $[r]$, and $[n]$, respectively. First, $-k \equiv d(\ln \mathcal{N}/dt)$ immediately tells us that $[k] = 1/t$. Now L, introduced in eq 34, has dimensions of polymer contour length; i.e., $[L] = [n]$. Thus from eq 4 one has $[u_0] = r^d/t$ and $[F] = 1/t$. Moreover the first term in eq A1 above tells us that $1/t = n(1/rn)(1/\zeta_0)(1/rn)$ where we have used $[\delta/\delta r(n)] = (1/rn)$. Hence, $[\zeta_0] = t/(r^2 n)$. But since H is dimensionless (since $[\delta/\delta r] = [\delta H/\delta r]$ from eq A1), we have $r^2 = n$ from H_0. Thus it follows that $[\zeta_0] = t/n^2$ and hence that the only dimensionless combination of the parameters u_0, ζ_0, and L is $w_0 = u_0 \zeta_0 L^{\epsilon/2}$ (since $[u_0\zeta_0] = n^{d/2-2}$).

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