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Short time behavior and universal relations in polymer cyclization

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Abstract. — This paper is a renormalization group study of the short time irreversible reaction rate for a single polymer with reactive groups attached to its ends (cyclization). In melts we predict that for times less than the entanglement time the reaction rate $k(t)$ scales as $t^{-a}$ where $a$ is a nonuniversal power which depends on the molecular weight. This power tends to 1/4 as the chains become very long, the asymptotic behavior is «diffusion controlled» independently of the reactivity of the end groups. In dilute theta solvents we find marginal behavior in which $k(t)$ depends logarithmically on $t$. For cyclization in good solvents the correlation hole plays a crucial role, causing asymptotic mean-field or «law of mass action» behavior, again independently of the chemistry of the reactive groups. $k(t)$ scales as the equilibrium probability of chain end contact with weak time dependent corrections. Eliminating the nonuniversal elements between these results for $k(t)$ and previously calculated long time reaction rates $k_\infty$ allows the derivation of universal relations between the experimentally observable quantities $k(t)$, $k_\infty$ and the unperturbed longest polymer relaxation time $\tau$.

1. Introduction.

Polymer cyclization, in which polymer chains bearing reactive end groups react to form rings (see Fig 1), is an important process in many polymerizing systems [1-4]. Much experimental effort has been invested in the photophysical measurement of irreversible cyclization rates in carefully prepared dilute polymer solutions [5-7], such experiments not only tell us about cyclization kinetics themselves but also test the current fundamental theories of polymer dynamics. The quantity usually measured is the long-time irreversible cyclization rate $k_\infty$ which is defined as the asymptotic decay rate of $A(t)$, the fraction of the polymers which are uncyclized after time $t$.

$$A(t) \sim \exp (-k_\infty t), \hspace{1cm} t \gg \tau$$  (1)

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Fig 1 — Each polymer has reactive groups at the chain ends. Reactions are «switched on» at \( t = 0 \), when the chains are in equilibrium, and the groups can react with one another (with a certain probability per unit time) if they come into contact. After time \( t \), each group has diffused a distance of order \( r(t) \) and explored a volume in d-dimensional space of order \( r(t)^d \) (shaded regions). The figure depicts 2 different polymers at the same time \( t \) (a) Configuration such as these cannot possibly have cyclized since the exploration volumes do not overlap (b) Since the exploration volumes of such configurations overlap they may have reacted, depending on the value of the exponent \( \theta \) (see Eq. (5) in text). If \( \theta < 1 \), reaction occurs with probability of order unity («diffusion-controlled» behavior). If \( \theta > 1 \), reaction probability is much less than unity («law of mass action»).

This long-time regime is anticipated for times large compared to \( \tau \), the longest relaxation time of the «unperturbed» polymer (i.e., without reactive end groups).

This paper addresses the short-time cyclization rate \( k(t) \) and the relationships, which in our renormalization group framework are predicted to be universal, between the experimental observables \( k(t) \) and \( k_\infty \). We define \( k(t) \) as the rate of decrease of \( A(t) \) for short times

\[
k(t) = - \frac{dA(t)}{dt}, \quad t \ll \tau
\]

For these times the system has yet to reach steady state and one expects time-dependent behavior. Though we consider both dilute and concentrated polymer solutions (or melts), the polymers bearing reactive groups are always assumed dilute (e.g., a few reactive polymers in a background of dense unreactive chains). Thus intermolecular reactions are negligibly infrequent and ours is essentially a single chain cyclization problem.

While short time cyclization kinetics have been studied theoretically in the case of entangled melts [8-10], studies of dilute solutions have emphasized long time rates \( k_\infty \) [11-14]. Recently the present authors calculated \( k_\infty \) for dilute solutions and nonentangled melts using renormalization group techniques [13-14]; we refer to reference [14] as «FO» throughout this paper. In contrast to previous work FO was a «first principles» calculation in the sense that excluded volume and hydrodynamical interactions were systematically incorporated (without preaveraging) and no use was made of Wilemski and Fixman’s «closure approximation» [11] (an approximate method for including the effect of the reaction sink term in the Fokker-Planck equation). The main conclusion from FO is that the asymptotic (high molecular weight) form of \( k_\infty \) is independent of the strength and other details of the reacting end groups, being determined only by the universality class to which the
polymer dynamics belongs (see below). For example, in the case of dilute polymers in a good solvent, the asymptotic behavior is of «law of mass action» form with \( k_\infty \) scaling as the equilibrium probability that the chain ends are together \( k_\infty \sim N^{-\nu(d+g)} \) where \( N \) is the number of segments in a polymer Here \( \nu \) and \( d \) are respectively the Flory exponent and dimension of space, and \( g \) is the «correlation hole» exponent [15-17] The existence of the «correlation hole», the reduced probability of chain end contact, is the underlying reason that \( k_\infty \) does not scale as the inverse polymer relaxation time as has been widely assumed in the past If we refer to the asymptotic (\( N \) very large) behavior in good solvents then, we may say that there are no such things as «diffusion-controlled» reaction kinetics: no matter how strongly reactive the end groups the system gets «driven» to law of mass action behavior for large enough \( N \) (corresponding to the vanishing fixed point value of the sink coupling constant) Similarly, cyclization of unentangled polymers in a melt (which are believed to obey «Rouse» dynamics [16, 18, 19]) is intrinsically diffusion-controlled no matter how weakly reactive the end groups, provided the chains are long enough (Although entanglements may modify the dynamics before realization of the asymptotic form for \( k_\infty \), the asymptotic diffusion-controlled form for \( k(t) \) is expected to be robust, even when entanglements are present—see below.) In the present study we will consider cyclization in melts («Rouse» dynamics), in theta solvents («Zimm» dynamics [16-18]) and in good solvents («Zimm» plus excluded volume interactions) Fortunately our results for melts are expected to apply even when the chains are long enough to be entangled, provided one considers time scales less than the «entanglement time» [16-18], for such times Rouse dynamics apply [16, 18, 19] One further, unphysical case we will consider is that of Rouse dynamics plus excluded volume (no hydrodynamics) This is an academic interest and, moreover, is testable by numerical simulation In the following section simple scaling arguments are invoked to motivate the small time behavior \( k(t) \) for each of the dynamical classes to be treated here As for long times, the correlation hole plays an important role when excluded volume is present In section 3 the renormalization group calculations of \( k(t) \) are presented, and in section 4 we summarise our predicted universal relations between \( k(t) \) and \( k_\infty \) which should be experimentally measurable Section 4 concludes with a brief discussion of the experimental outlook.
initially separated by, say, $r$ will have reacted after time $t$ provided $r(t) > r$ (see Fig 1). In section 3 we will show that very long Rouse chains always exhibit diffusion controlled behavior. Then for small times the fraction of unreacted chains should scale like

$$A(t) \approx 1 - \int_{|r| < r(t)} \text{d}^d r \ p(r) \approx 1 - (r(t)/R)^d \quad \text{(Rouse)}.$$  \hspace{1cm} (3)

We have used the small $r$ behavior of the equilibrium end-to-end distribution function, $p(r) = R^{-d} f(r/R)$. $R$ is the rms end-to-end distance. An essential component of this argument is the good behavior of $p(r)$ at the origin, for Rouse chains the function $f$ is proportional to a Gaussian, which asymptotes a constant (unity) at $r = 0$. Then since $[16] r(t) \sim t^{1/2}; \ R \sim t^{1/2}$, with $z = 4$ for Rouse dynamics, we have

$$k(t) = -\frac{\text{d} A(t)}{\text{d} t} = 1/\tau \ (t/\tau)^{d z - 1}$$

$$= 1/\tau \ (t/\tau)^{-\varepsilon/z} \quad \text{(Rouse)}$$ \hspace{1cm} (4)

where $\varepsilon = 4 - d$. Our prediction for real experiments ($d = 3, \; \varepsilon = 1$) on very long chains in a melt is thus $k(t) \sim t^{-1/4}$. In section 3 we will derive this result more systematically, as well as its generalization to finite chains.

Now consider the effects of excluded volume (as is relevant to dilute solutions). We will see that the scaling form of equation (4) is incorrect and that the criterion determining the reaction behavior is not simply a comparison of $d/z$ with unity. As is well-known, $p(r)$ now vanishes algebraically at the origin $[15-17]$, $f(r/R) \sim (r/R)^g$. This leads to

$$k(t) = \frac{\text{d}}{\text{d} t} \int_{|r| < r(t)} \text{d}^d r \ p(r) \approx 1/\tau \ (t/\tau)^{g - 1}, \; \theta < 1,$$

where

$$\theta = (d + g)/z$$ \hspace{1cm} (5)

Unlike the Rouse case the distribution $p(r)$ is not evenly spread over the coil volume $R^d$, there being a special penalty for the meeting of chain ends. Hence the relevant exponent involves the correlation hole exponent $g$. When $\theta < 1$, $k(t) \sim t^{\theta - 1}$ represents «diffusion-controlled» behavior since the number ($\sim t^\theta$) of accessible reactive groups (in the ensemble), i.e. within the exploration volume (see Fig 1), is less than the number ($\sim t$) of accessible «steps» (one could imagine discretizing time into small units of size $\Delta t$, so in a time $t$ each group makes $(t/\Delta t)$ «steps» of size $\Delta r$ where $\Delta r$ is the rms displacement in the time $\Delta t$ [20]). If it happens that $\theta > 1$, there are more accessible reactive groups than could possibly have been visited in the time $t$, a small fraction will have reacted, the system will always remain close to equilibrium and $k(t)$ should scale as the equilibrium probability that the chain ends are within the «sink radius» $a$ of one another ($Q$ is a local reaction rate):

$$k(t) \approx Q (a/R)^d (a/R)^g \sim N^{-\nu(d+g)}, \; \theta > 1.$$ \hspace{1cm} (6)

Let us apply equations (5) and (6) to some specific cases. An interesting (albeit unphysical) case is that of Rouse dynamics plus excluded volume interactions for which $[21] z = 2 + 1/\nu$ whence $\theta = \nu(d + g)/(2 \nu + 1) = 1 - \varepsilon/8 + O(\varepsilon^2)$ using the first order expressions $[15-17] \nu = (1 + \varepsilon/8)/2, \; g = \varepsilon/4$. Thus $\theta < 1$ and we identify a «diffusion-controlled» case

$$k(t) \sim t^{-\varepsilon/8} \quad \text{(Rouse + excl vol)}$$ \hspace{1cm} (7)
When hydrodynamics are included the situation is more subtle. In theta solvents the correlation hole effect vanishes \( (g = 0) \) and since \( z = d \) we have \( \theta = 1 \). This is a marginal case and simple scaling cannot tell us more. A natural expectation, by analogy with other marginal phenomena in statistical mechanics [22] is logarithmic time dependence. A similar situation arises in «ordinary» brownian particle diffusion which is marginal in 2 dimensions \( (\theta = d/z = 1) \), for small times [23] the reaction rate can be expressed as \((C \) and \( C' \) are constants):

\[
    k(t) = \frac{(C/\tau)}{\ln (t/t_L) + C'} \quad \text{Brownian particles, } d = 2 \quad (8)
\]

In this expression \( \tau \) is the longest relaxation time of the system and \( t_L \) proportional to \( L^2 \) is the diffusion time for the sink of size \( L \). The result is for the limit of an infinitely reactive sink. In section 3 we will arrive at a result for theta solvents of precisely this form.

Finally, in good solvents both excluded volume and hydrodynamical interactions feature, with \( z = d \) and \( \theta = 1 + g/d \) from equation (5) Since \( g > 0 \), thus \( \theta > 1 \) and one identifies a «law of mass action» case. From equation (6) we anticipate

\[
    k(t) \sim N^{-\nu(d + g)} \quad \text{good solvents}. \quad (9)
\]

We expect at most a weak time dependence in \( k(t) \), certainly no algebraic behavior \( k(t) \) has the same form, in fact, as \( k_\infty \) as derived in FO and does not scale like \( \tau^{-1} \). (The significance of the exponent \( \theta \) of equation (5) in determining \( k_\infty \) is discussed in FO in terms of the parameter \( Z \sim N^{z(\theta - 1)} \) which measures the number of chain end «collisions» in one polymer relaxation time \( \tau \).) For good solvents, then, the correlation hole «tips the balance» in favor of mean-field law of mass action behavior away from the apparently marginal situation suggested by \( z = d \).

3. Renormalization group calculations of \( k(t) \).

The scaling arguments of the previous section have already suggested a special role for \( d = 4 \), for example equations (4) and (7) describe behavior which changes from diffusion-controlled to mean-field as \( d \) passes through 4. In this section we exploit this fact by deriving \( k(t) \) for the various cases in an epsilon expansion about four dimensions.

3.1 Bare series for \( k(t) \). — We describe the cyclization process by the following Fokker-Planck equation for \( P(\{c\}, t) \), the probability of a polymer configuration \( \{c(\tau)\} \)

\[
    \frac{dP}{dt} = FP + u_0 \delta (c(0) - c(N_0)) P. \quad (10)
\]

\( F \), whose explicit form is given in appendix A, is the diffusion operator [17] including the effect of hydrodynamics through the Oseen tensor and excluded volume through the Edwards Hamiltonian. The various dynamical classes considered here are defined by switching on and off various of these interactions in \( F \). i.e. setting the corresponding coupling constants to zero \( u_0 \) is the bare reaction rate and \( N_0 \) the bare polymer contour length. The reader is referred to FO for a fuller discussion of the model.

The solution of equation (10) can be expressed in terms of the Green’s function (without sink) \( G(\{c'\}, \{c\}, t - t') \) as

\[
    P(\{c\}, t) = P_{eq}(\{c\}) + \int_0^t dt' \int d\{c'\} \ G(\{c'\}, \{c\}, t - t') u_0 \delta (c'(0) - c'(N_0)) P(\{c'\}, t') \quad (11)
\]
where the chains are assumed to be in equilibrium, \( P_{eq} \{ \cdot \} \), at \( t = 0 \) By integrating equation (10) one obtains the dynamics of the normalization \( A(t) \)

\[
\frac{dA}{dt} = u_0 \int d \{ c \} \delta (c(0) - c(N_0)) P(\{ c \}, t)
\]

(12)

Solving iteratively for \( P \) in powers of \( u_0 \) from equation (11) and substituting in (12) we find to second order in \( u_0 \)

\[
\frac{dA}{dt} = u_0 \langle \delta (R) \rangle + u_0^2 \int_0^t \langle \delta (R_0) \delta (R_t) \rangle
\]

(13)

where \( \langle . \rangle \) denotes an average over the equilibrium distribution \( P_{eq} (\text{no sink}) \), \( R = c(0) - c(N_0) \) and \( R_t = c(0, t) - c(N_0, t) \) is the end-to-end vector at time \( t \). The second order term is the time integral of the « return probability » that an initially looped chain is again looped at time \( t \) in the absence of reactions (see FO). In Appendix B we outline the evaluation of the terms in equation (13) for small times \( (t \ll \tau_R \text{ where } \tau_R = \xi_0 N_0^2/\pi^2 \) is the longest relaxation time in the Rouse model).

In terms of the dimensionless coupling constants \( w_0 = u_0 L^{\varepsilon/2} \xi_0 \) and \( e_0 = f_0 L^{\varepsilon/2} \) \( (f_0 \) and \( \xi_0 \) being respectively the bare excluded volume and hydrodynamic coupling constants and \( L \) a phenomenological length scale [17]) the final result for the small time bare series reads

\[
-k(t) N_0^2 = A(w_0/\xi_0)(N_0/L)^{\varepsilon/2} + w_0^2/\xi_0(N_0/L)^{\varepsilon} B/\varepsilon (t/\tau_R)^{\varepsilon/4}
\]

\[
+ w_0 e_0/\xi_0 [N_0/L]^{\varepsilon} [D/\varepsilon + E],
\]

where

\[
A = (2/\pi)^{(\varepsilon/2)-2}, \quad B = 4^{(5/4)-1} \pi^{(\varepsilon/4)-3}, \quad D = 6(2/\pi)^{\varepsilon-4}
\]

(14)

and \( E \) is dimensionless and depends nonsingularly on spatial dimension. Since the singularities in the bare series for \( k_\infty \) (see FO) derive from the integral of the small time behavior of the return probability and excluded volume effects in \( \langle \delta (R) \rangle \), one can see from equation (13) that \( k(t) \) has the same singularities to second order. Thus the beta functions and the fixed point values of the renormalised coupling constants \( w, e, \xi \) are as for \( k_\infty \) and we can use the results from FO. Of course this must be true if the theory is renormalizable.

3.2 MELTS — We now specialise to the various types of dynamics, beginning with the Rouse model for which \( e_0 = 0 \) in equation (14). We emphasize that Rouse behavior is believed to apply even to entangled melts for the short times which we will consider in the following, enabling us to employ renormalization group methods. Renormalising the bare series (see Appendix C) leads to the following expressions for the fixed point coupling constant \( w^* \) (to first order in \( \varepsilon \) ) and for the renormalised series for \( k(t) \) (to order \( w^3 \))

\[
w^* = -64 \pi \varepsilon + O(\varepsilon^2)
\]

\[
-k(t) \xi N_0^2 = Aw(N/L)^{\varepsilon/2} + \left( B/\varepsilon [(t/\tau_R)^{\varepsilon/4} - 1] (N/L)^{\varepsilon} + H \right) w^2 + O(w^3)
\]

where \( H = O(\varepsilon^0) \) (Rouse)

(15)
and $A$ and $B$ have been defined in equation (14). $H$ depends on $N$ and $L$ but the important property here is simply that $H$ is independent of time. Note that $\xi_0 = \xi$ and $N_0 = N$ are unrenormalised in the Rouse case and that the $1/\epsilon$ singularity has been renormalised away. From (15) one has $k(t) = - Aw^* / (\xi N^2)$ to first order in $\epsilon$ at the fixed point; we seem to have a time independent result at odds with our scaling expectations, equation (4)! The following observation, however, resolves the apparent contradiction. While we do not know $k(t)$ to second order in $\epsilon$ (for which purpose we would require $w^*$ to $O(\epsilon^2)$), the time-dependent part can be inferred to its leading order of $\epsilon^2$, as may be seen by expanding the expression in equation (15)

$$-k(t) \xi N^2 = Aw (N/L)^{\epsilon/2} + \{ B/4 \ln (t/\tau_R) + G \} \epsilon^2,$$

(16)

where all time dependent terms in $G$ are $O(\epsilon)$. Since $B = O(\epsilon^0)$ and the $Aw$ term cannot generate time dependence, equation (16) yields the leading $O(\epsilon^2)$ time dependent term when $w^*$ is known to $O(\epsilon)$. At the fixed point equation (16) can be written

$$k(t) = 16 \epsilon \pi N^2 \xi / \{1 - \epsilon/4 \ln (t/\tau_R)\} + \ldots$$

(17)

Motivated by the scaling arguments we exponentiate this form to obtain the large $N$ behavior to first order in $\epsilon$ for chains in a melt

$$k(t) = 16 \epsilon \pi N^2 \xi / \{ (t/\tau_R)^{-\epsilon/4}\} \quad \text{melts, } N \text{ very large} .$$

(18)

The result agrees with the scaling prediction of equation (4). The subtlety involved in this type of exponentiation is discussed in reference [26].

For finite chains we must consider crossover effects. The renormalization group equation dictates (see Appendix D) that $k(t)$ has the following form ($f$ is an arbitrary function)

$$k(t) = 1/\tau_R f (t/\tau_R, X)$$

where

$$X = (N/L)^{\epsilon/2} w/(w^* - w) .$$

(19)

Therefore we rewrite the renormalized series equation (16) in terms of the good variable $X$, the time independent part to $O(\epsilon)$ and the time dependent part to $O(\epsilon^2)$. The result is

$$k(t) = 16 \epsilon \pi N^2 \xi / \{ 1 + \frac{X}{1 + X}\} \left[1 - \frac{X}{1 + X}\right] \epsilon/4 \ln (t/\tau_R) .$$

(20)

Since the fixed point result must be recovered when $X$ becomes large, exponentiation is again suggested

$$k(t) = k_\infty (t/\tau_R)^{-\epsilon/4 (X/(1 + X))}$$

$$k_\infty = 16 \epsilon / \pi^3 \frac{X}{\tau_R (1 + X)}$$

$$\tau_R = \xi N^2 \pi^2 \quad \text{melts} .$$

(21)

The result is expressed in terms of $k_\infty$ from FO. Very long chains correspond to $X$ becoming large when the fixed point result equation (18) is recovered. The experimental prediction may be stated thus for melts, entangled or unentangled, we predict $k(t)$ decays as a nonuniversal power law for sufficiently short times (less than the entanglement time), with
that power law tending to $-1/4$ as the chains become longer. Of course if the chains are entangled then the observed $k_\infty$ is not given by the expression in (21).

3.3 ROUSE PLUS EXCLUDED VOLUME. — Before proceeding to dilute solution, let us investigate the effects of the correlation hole by treating the unphysical but interesting case of Rouse dynamics plus excluded volume interactions, the bare series is then obtained by the full expression, equation (14). Having the same singularities as for the series for $k_\infty$ which was analysed in detail in FO, it follows that $\xi_0, N_0, w_0$ and $e_0$ are renormalised in the same way and $e$ and $w$ have the same fixed point values, with $w^* = -32\pi e$ being the stable sink fixed point value to order $e$ (see FO). The crucial point is that the first order term and the leading time dependent term of the renormalised series have the same form as for the Rouse case, equation (15). This is true because these two terms derive respectively from the $w_0$ and $w_0^2$ terms in equation (14) whose leading contributions to the renormalised series derive from the leading dependence of $w_0$ on $w$ and $e$, namely $w_0 = w$. The $w_0 e_0$ term does not enter the picture, being second order and time independent. Furthermore, one can set $\xi_0 N_0^2 = \xi N^2$ to this order since higher order renormalization of $\xi_0 N_0^2$ produces only second order time independent and third order time dependent terms. Finally, the choice of renormalization constants is so as to subtract off the $1/e$ divergence in the $w_0^2$ term, just as for the Rouse case. The renormalised series must therefore be of the same form as in equation (16), other than the presence of higher order terms involving $e$.

$$-k(t)\xi N^2 = A w \left[1 + \frac{B w}{4 A} \ln \left(t/\tau_R\right)\right] + O(w^2) + O(\epsilon w).$$  

(22)

The time dependence in the higher order terms is of $O(\epsilon^3)$ when $w$ and $e$ are of order $\epsilon$. If we were to set $w$ equal to the Rouse fixed point value ($w^* = -64\pi e$) in the above expression, the Rouse result would be recovered (Eq. (18)). The only difference lies in the new fixed point value, $w^* = -32\pi e$; being half of the Rouse value, the final exponent is halved from $-\epsilon/4$ to $-\epsilon/8$. Explicitly, with $B/A = 1/(64\pi)$ when $\epsilon = 0$, we have $Bw^*/(4 A) = -\epsilon/8$. Noting that $A = 1/(4\pi^2)$ when $\epsilon = 0$, and exponentiating as before, we have for very long chains

$$k(t) = \frac{8\epsilon}{\pi\xi N^2} (t/\tau_R)^{-\epsilon/8} \quad \text{(Rouse + ex. vol.)}$$  

(23)

Now in FO the renormalization group equation for $k_\infty$ was solved, at the fixed point the solution was of the form $k_\infty$ proportional to $1/\tau_{RX}$ where $\tau_{RX} \sim N^{(2r+1)}$ is the longest relaxation time in this model. A similar calculation shows that $k(t) = f(t/\tau_{RX})/\tau_{RX}$ for some function $f$. Since, to zeroth order in $\epsilon$, $\tau_{R} = \tau_{RX}$ [24, 25] the form of $k(t)$ in equations (23) is consistent with this result and one can simply replace $\tau_{R}$ with $\tau_{RX}$ since the prefactor and the exponent are both valid only to order $\epsilon$. Using the expression for $k_\infty$ from FO our final result is of precisely the form in equations (7) suggested by scaling arguments, exhibiting the importance of the correlation hole:

$$k(t) = k_\infty (t/\tau_{RX})^{-\epsilon/8}$$

$$k_\infty = 8\epsilon/(\pi^3 \tau_{RX}) \quad \text{(Rouse + ex. vol, large N)}$$  

(24)

3.4 DILUTE SOLUTION — We will treat the cases of «strong» hydrodynamic interaction (i.e. all expressions will be evaluated at the fixed point of the friction constant $\xi$). Once again, the renormalised series is unchanged from the Rouse case (to the orders of interest to us) by
virtue of similar arguments to those expounded in the Rouse plus excluded volume case. Thus equation (22) is still valid. An important new feature, however, is that now $\xi$ plays the role of a coupling constant. More precisely, there is an additional coupling constant $\xi_0 = (\xi_0/\eta) L^{d/2}$ [17] and our strong hydrodynamic results are at the fixed point value of $\xi$, namely $\xi^*$. Therefore the renormalised series reads

$$-k(t) \eta_\xi^* L^{-\varepsilon/2} N^2 = A w \left[ 1 + \frac{B w}{4 A} \ln \left( t/\tau_R \right) \right] + ... \quad \text{(hydrodynamics).} \quad (25)$$

Consider firstly theta solvents for which excluded volume interactions vanish, i.e. $w = 0$. Renormalization is as for $k_\infty$ in FO, where it was shown that at the fixed point, $\xi^* = 8 \pi^2 \varepsilon/3$, the beta function $\beta_w = w^2/(128 \pi)$ to order $\varepsilon$, i.e. to this order it has no nontrivial fixed point. Thus to understand the large $N$ behavior of $k(t)$ one must study crossover behavior describing the approach of $w$ to zero.

Now $k(t)$ obeys the same renormalization group equation as $k_\infty$. In appendix B of FO this was solved at the nondondraining fixed point to order $\varepsilon$: $k = H(L \exp[128 \pi/w])$ where $H$ is a well behaved function. Thus to this order

$$k(t) = G (L \exp[128 \pi/w], t) \quad (26)$$

for some $G$

When hydrodynamics is present the relevant dimensions are $[t] = [k(t)]^{-1} = [L]^{d/2}$ (this may be seen from the form of the diffusion operator $F$, (Eq (A1)), and the Fokker-Planck equation, (Eq. (10)). Thus

$$k(t) / C^{d/2} = G (C L \exp[128 \pi/w], C^{d/2} t) \quad (27)$$

Choosing $C = 1/N$ dictates, for some function $I$, the form $k(t) = (1/N^{d/2}) I((L/N) \exp[128 \pi/w], t/N^{d/2})$ Recognising that $N^{d/2}$ equals the longest relaxation time $\tau_z$ (the « Zimm » time) to within a dimension independent constant [26] we have for some function $f$

$$k(t) = 1/\tau_z f(X, t/\tau_z)$$

$$X = 128 \pi/w + \ln (L/N) \quad \text{(theta solvents).} \quad (28)$$

We now express equation (25) in a form compatible with equation (28) [17] Substituting $w = 128 \pi/[X – \ln (L/N)]$ into the leading order time independent and dependent terms (in powers of $\varepsilon$) of equation (25) we have

$$-k(t) \eta N^2 8 \pi^2 \varepsilon/3 = \frac{32}{\pi (X - \ln (L/N))} \left[ 1 + \frac{\ln \left( t/\tau_R \right)}{2(X - \ln (L/N))} \right], \quad (29)$$

where $\xi^* = 8 \pi^2 \varepsilon/3$, $B/A = 1/64 \pi + O (\varepsilon)$, $A = 1/4 \pi^2 + O (\varepsilon)$ and the fact that $w = O (\varepsilon)$ have been used. Now the correspondence of the above expression to that in equation (25) to leading order is not affected by adding and subtracting higher order terms in (29) Thus we replace $N^2$ with $N^{d/2}$, and $X – \ln (L/N)$ with $X$, thereby rendering the expression compatible with the requirement of equation (28) :

$$k(t) = -\frac{12}{\varepsilon \pi^3 \eta N^{d/2} X} \left[ 1 + 1/(2 X) \ln \left( t/\tau_z \right) \right] \quad \text{(theta solvents).} \quad (30)$$

Note that $w$ and therefore $X$ are negative, ensuring the correct sign of $k(t)$. Note also that the argument of the logarithm is undetermined to within a multiplicative constant by our
derivation (such a factor induces higher order time-independent terms). In equation (30) we have made the simplest choice, with the ambiguity understood.

At this point we are guided by the arguments of section 2 to exponentiate to a logarithmic form (cf. Eq. (8)) rather than a power law. Using the result for \( k_\infty \) (Eq. (40) of FO) the final result is

\[
k(t) = \frac{-12}{\varepsilon \pi^3 \eta N^{d/2} X (1 - 1/(2\ X) \ln (t/\tau_z))} \cdot \frac{1}{1 - 1/(2\ X) \ln (t/\tau_z)}
\]

where

\[
k_\infty = - C_1/(X \tau_z), \quad C_1 = 1.08 \quad \text{and} \quad X = 128 \ \pi /w + \ln (L/N) \quad \text{(theta solvents)}.
\]

The result [26] \( \tau_z = (\pi^{5-d/2} C_1/12) \eta \varepsilon N^{d/2} \) has been used. It is remarkable that the above expression is consistent (to the orders to which we work) with a result which is of precisely the same form as the Brownian particle result, equation (8). Specifically, by explicitly substituting for \( X \) and interpreting \( 2 \ln (N/L) \) as the zeroth order truncation of \( (d/2) \ln (N/L) \) one obtains

\[
k(t) = \frac{2 C_1}{\tau [\ln (t/\tau_z) - 256 \ \pi /w]} \quad \text{(theta solvents)},
\]

where \( t_L \) proportional to \( L^{d/2} \) may loosely be thought of as the relaxation time of the renormalised «sink», namely the end «blobs» of the coarse grained polymer each containing \( L \) segments.

The last case to consider is that of good solvents (full bare series, Eq (14)). Again, renormalization proceeds as for \( k_\infty \) for which (see Eq. (39A) of FO) to leading order \( \beta_w = -w (w^* - w)/128 \ \pi \) at the self avoiding non-free draining fixed point \( (\varepsilon^* = \pi^2 \varepsilon/2, \ \xi^* = 2 \pi^2 \varepsilon) \) where \( w^* = 16 \ \pi \varepsilon \) is the unphysical positive fixed point. The physical fixed point again vanishes, necessitating crossover analysis. Since \( k(t) \) obeys the same renormalization group equation as \( k_\infty \) \( (t \) is not renormalised), the solution has a similar form to that for \( k_\infty \) (cf. Eq. (C3) of FO)

\[
k(t) = G (LN^{-1/\gamma}, L [(w - w^*)/w]^{-8/\varepsilon}, t)
\]

where \( \gamma = \gamma_N(e^*), \ \gamma_N(e) = L(\delta \ln Z_N/\delta L)_{e^*} \) and \( N_0 = Z_N N \) [17]. The relevant dimensions are \([t] = [k]^{-1} = [L]^{d/2}. \) Thus under the rescaling \( L, \ N \) go to \( CL, \ CN \) we have

\[
G(C^{1-1/\gamma} LN^{-1/\gamma}, CL [(w - w^*)/w]^{-8/\varepsilon}, C^{d/2} t) = C^{-d/2} k(t).
\]

Choosing \( C \) such that \( C^{1-1/\gamma} LN^{-1/\gamma} = 1, \ \text{i.e.} \ C = (N/L)^{1/(\gamma - 1)} L^{-1} = (L/N)^{2\nu} L^{-1} \) (since [17] \( 2 \nu = 1/(1 - \gamma) \)) and using [17] the fact that \( \tau_g \) is proportional to \( (N/L)^{\nu} L^{d/2} \) we have

\[
k(t) = 1/\tau_g f(X, t/\tau_g)
\]

where

\[
X = (N/L)^{\nu/4} (w - w^*)/w \quad \text{(good solvents)}.
\]

Substituting \( w = (N/L)^{\nu/4} w^* /[(N/L)^{\nu/4} - X], \) which to order \( \varepsilon \) becomes
\[ w = - \frac{w^*}{(X - 1)} \]

into the renormalised series equation (25) and insisting on the form in equation (35) we obtain

\[ k(t) = \frac{2}{\pi^2 \eta} \frac{(L/N)^{d/2}}{L^{d/2}(X - 1)} \left[ 1 - \frac{\varepsilon}{16(X - 1)} \ln \left( t/\tau_g \right) \right] \quad \text{(good solvents).} \quad (36) \]

Our scaling arguments have led us to expect no algebraic time dependence in this case, so we leave equation (36) unexponentiated and interpret the logarithm as a weak time dependent modification of a result which essentially scales as the equilibrium loop probability. This follows if we assume weak \( N \)-dependence of \( w \) such that \( X \sim N^{-\nu/4} \) for large \( N \), then \( k(t) \sim N^{-\nu(d + \varepsilon/4)} \) to within logarithmic time dependence. Since \( \varepsilon = \varepsilon/4 \) to first order we recognise this exponent as \( -\nu(d + g) \) to this order, i.e. this is the scaling result of equation (9).

Finally, we summarise our good solvent result in terms of \( k_\infty \) (Eq. (41) of FO) and [17]

\[ \tau_g = \varepsilon \eta (N/L)^{d/2} 2(2\pi)^{d/2} 16 \exp \{\varepsilon I/4 - \varepsilon 3 J/8\} , \]

where \( I \) and \( J \) are constants given in equations (340), (341) of [17]

\[ \frac{k(t)}{k_\infty} = \frac{C_2}{(X - 1) \tau_g} \quad C_2 = 64 \pi \varepsilon \]

and

\[ X = (N/L)^{\nu/4} (w - 16 \pi \varepsilon)/w \quad \text{(good solvents).} \quad (37) \]

The simple relation between \( k(t) \) and \( k_\infty \) in equation (37) suggests there should be a simple formula which interpolates between the short time reaction rate \( k(t) \) and the long time reaction rate \( k_\infty \). We derive such an approximate interpolation formula in appendix E.

4. Universal relations and experiment.

In this study we have derived universal relationships between 3 quantities which are (in principle) experimentally measurable: the short cyclization reaction rate \( k(t) \), the long time cyclization rate \( k_\infty \) and the longest relaxation time \( \tau \) of the unperturbed polymer (i.e. no reactive groups). These relations apply to the crossover regime i.e. they are not limited to «infinitely» long polymer chains, and are independent of the strength and chemistry of the reacting end groups.

For theta solvents this relationship may be stated as (see Eq. (31))

\[ k(t) = \frac{k_\infty}{1 + (k_\infty \tau_g/2 C_1) \ln \left( t/\tau_z \right)} \quad \text{(theta solvents)} \quad (38) \]

where \( C_1 \) is a constant defined in equation (31). The relationship has no free parameters other than a possible constant multiplying the \( t/\tau_z \) argument of the logarithm (see discussion following Eq. (30)). For good solvents, equation (37) implies the no-free-parameter relation

\[ k(t) = k_\infty \left( 1 - \frac{k_\infty \tau_g}{1024 \pi} \ln \left( t/\tau_g \right) \right) \quad \text{(good solvents),} \quad (39) \]

which in practice may be indistinguishable from \( k(t) = k_\infty \).
Turning now to polymer melts below the entanglement threshold, equation (21) predicts that
\[ k(t) = k_\infty (t/\tau_R)^{-k_\infty \tau_R \pi^{1/6}} \] (untangled melts) \hfill (40)

The presence of entanglements invalidates this relationship of course; in that case our results are confined to the short time regime (less than the entanglement time). We restate the result for 3 dimensions for completeness (Eq. (21))
\[ k(t) = \frac{16}{\pi^3 \tau_R} X/(1 + X) (t/\tau_R)^{-1/4(X(1 + X))} \]
which tends to
\[ \frac{16}{\pi^3 \tau_R} (t/\tau_R)^{-1/4} \] as \( N \) becomes large \hfill (41)

Winnik [5] has reviewed many of the existing experimental measurements of long time cyclization rates in dilute polymer solutions. Fluorescence measurements of \( k_\infty \) on pyrene end-capped polystyrene in a theta solvent [5] are consistent with the theoretical \( k_\infty \) (as calculated in FO) with a value of the crossover parameter \( X = -12 \). The predicted logarithmic time dependence of \( k(t) \) (Eq. (31)) may then be observable for this system, though the prefactor is rather small. Similar measurements in good solvents [5] suggest a value \( X = 5 \), from equation (36) this logarithm in \( k(t) \) may be unmeasurable. At least for this system, then, it is perhaps more realistic to predict that \( k(t) \) and \( k_\infty \) are very close to one another.

Evidently, then, short time cyclization in melts and solutions exhibits much rich behavior. We are unaware of any existent systematic measurements probing this regime and we hope, for such experiments in the future.

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Appendix A: the diffusion operator \( F \).
The operator \( F \) appearing in equation (10), describing hydrodynamics through the Oseen tensor \( T_{\alpha \beta} \) and excluded volume interactions through the Edwards Hamiltonian \( H \), is given by
\[
\dot{F} = \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \sum_{\alpha \beta} \delta/\delta c_\alpha(\tau) \left[ \delta_{\alpha \beta}/\xi_0 \delta(\tau - \tau') + T_{\alpha \beta}(c(\tau) - c(\tau')) \right] \times \\
\times \left[ \delta/\delta c_\beta(\tau') + \delta H/\delta c_\beta(\tau') \right],
\]
\[
T_{\alpha \beta}(\chi) = (2\pi)^{-d} \int d^d k \ 1/(\eta k^2) \left[ \delta_{\alpha \beta} - k_\alpha k_\beta/k^2 \right] e^{i k \cdot \chi}, \quad H = H_0 + H_1
\]
\[
H_0 = 1/2 \int_0^{N_0} d\tau [\dot{c}(\tau)]^2,
\]
\[
H_1 = f_0/2 \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \delta (c(\tau) - c(\tau')).
\] \hfill (A1)
Here \( \zeta_0 \) and \( f_0 \) are the bare friction and excluded volume coupling constants, respectively, and \( \eta \) is the fluid viscosity.

Appendix B : derivation of bare series equation (14) from equation (13).

The \( u_0 \langle \delta (R) \rangle \) term in equation (13) is relatively straightforward to calculate, being a static quantity which needs to be evaluated only to first order in \( e_0 \) (since we require the series for \( k(t) \) to second order). In fact, no new calculation is necessary, since by comparing equation (13) to the expression for \( k_\infty \) in equation (10) of FO, one sees that both expressions contain \( u_0 \langle \delta (R) \rangle \). This term generated the \( w_0 \) and \( w_0 e_0 \) terms in the final bare series for \( k_\infty \) (Eq. (21) of FO); consequently the same 2 terms must appear in the analogous expression for \( k(t) \), equation (14). The reader is referred to FO for details.

The \( u_0^2 \) term in equation (13) is different, however, to that in equation (10) of FO: the upper limit of the time integral is \( t \) (not \( \infty \)), and the integrand does not have \( \langle \delta (R) \rangle^2 \) subtracted off. It follows that the analogous equation to equation (18) of FO is (refer to FO for a full explanation)

\[
\int_0^t dt' \langle \delta (R_0) \delta (R_{t'}) \rangle = (2 \pi N_0)^{-d} \xi_0 N_0^2 / \pi^2 \int_0^{t/\tau_R} ds (1 - f^2(s))^{-d/2}
\]

where \( f(s) = \langle R_0 R_s \rangle / \langle R^2 \rangle = (8/\pi^2) \sum_{odd \, p} \exp(-p^2 s)/p^2 \) is the end to end correlation for Rouse dynamics in terms of the dimensionless time \( s \). The averages do not involve excluded volume or hydrodynamics since these would generate higher order terms. Substituting the small time behavior \( f(s) \sim 1 - 4 s^{3/2} / \pi^{3/2} \) into (B1), the second order term in (13) has the following form for \( t/\tau_R \ll 1 \)

\[
u_0^2 \int_0^t dt' \langle \delta (R_0) \delta (R_{t'}) \rangle \sim \frac{\mu_0^2 \xi_0 N_0^2}{(2 \pi N_0)^d \pi^2} \left( \frac{\pi^{3/2}}{8} \right)^{d/2} \int_0^{t/\tau_R} ds \, s^{-d/4} = \frac{\dot{w}_0^2}{(2 \pi)^d \pi^2 N_0^2 \xi_0} (N_0/L)^e \frac{\pi^{3/2} \dot{A}}{8^{d/2} \varepsilon} (t/\tau_R)^{e/4}
\]

where \( w_0 = u_0 L^{e/2} \xi_0 \). This gives the \( w_0^2 \) term for \( -k(t) N_0^2 \) in equation (14).

Appendix C : derivation of renormalised Rouse series, equation (15).

Since the singularities in the bare series, equation (14), are identical to those in \( k_\infty \) (see Eq. (21) of FO) thus the renormalization is unchanged For Rouse plus sink \( \xi_0 \) and \( N_0 \) are unrenormalised and the stable fixed point for the renormalised sink coupling constant \( w \) is \( w^* = -64 \pi \varepsilon \) (see FO). Now since \( w_0 = w^* \) to first order, from equation (14) the first order term in the renormalised series for \( k(t) \xi N^2 \) equals \( \dot{A} w (N/L)^{e/2} \), while the leading order time dependence is simply \( w^2 (N/L)^e (B/\varepsilon) (t/\tau_R)^{e/4} \) minus the singularity, namely \( w^2 B/\varepsilon \) (with \( B \) evaluated at \( \varepsilon = 0 \)). The constant \( A_1 \) in the relation \( w_0 = w + \dot{A}_1 \) to second order is indeed chosen so as to eliminate this singularity (via the first order term in the bare series). Thus the renormalised series to second order may be expressed as in equation (15) with time independent \( H \).
Appendix D: solution of renormalization group equation for Rouse case.

The renormalization group equation in this case is

\[ (L \partial / \partial L + \beta_w \partial / \partial w) k(L, w, N, \xi, t) = 0 \]  \hspace{1cm} (D1)

where the dependence of \( k(t) \) on all parameters has been made explicit. Now from \( w_0 = w - w^2 / (64 \pi \varepsilon) \) (determined by removing the second order singularity from the bare series), and recalling that \( w_0 = u_0 \xi_0 L^{1/2} \), one finds \( \beta_w = L \partial w / \partial L \). It is \( w = (w - w^*) / (128 \pi) \) where \( w^* = -64 \pi \varepsilon \). This of course is exactly the same as in FO for \( k_\infty \). The general solution of (D1) is

\[ k(t) = g \left( L \exp \left( - \int dw / \beta_w \right), N, \xi, t \right) \]  \hspace{1cm} (D2)

for any function \( g \). Choosing a convenient lower limit we find

\[ \int_{w^*/2}^{w} dw' / \beta_w = - (2/\varepsilon) \ln \left( (w^* - w) / w \right) \]. Thus

\[ k(t) = g \left( (w^* - w) / w \right)^{2/\varepsilon}, N, \xi, t \right). \]  \hspace{1cm} (D3)

The dimensional analysis of \( k(t) \) and its arguments is the same as for \( k_\infty \) in FO. Defining \( [N] = L \) and \( [t] = t \), then equations (10) and (A1) imply \( [\xi] = t / L^2 \), \( [k(t)] = 1 / t \). Thus under rescalings \( L, N \) go to \( C_1 L, C_1 N \) and \( t \) goes to \( C_2 t \) one must have that \( k(t) \) is rescaled to \( (1 / C_2) k(t) \) and \( \xi \) to \( (C_2 / C_1^2) \xi \). Thus equation (D3) implies that

\[ g \left( C_1 L \left( (w^* - w) / w \right)^{2/\varepsilon}, C_1 N, (C_2^2 / C_1^2) \xi, C_2 t \right) = 1 / C_2 k(t) \]  \hspace{1cm} (D4)

must be obeyed by \( g \). Choosing \( C_1 = 1 / N \) and \( C_2 = 1 / (\xi N^2) \) one arrives at

\[ k(t) = 1 / \tau_R f \left( (N / L)^{1/2} w / (w^* - w), t / \tau_R \right) \]  \hspace{1cm} (D5)

where \( f \) is some function and \( \tau_R = \xi N^2 / \pi^2 \) is the Rouse time. This is the form of equation (19).

At the fixed point \( \beta_w = 0 \) and (D1) constrains \( k(t) \) to be independent of \( L \), \( k(t) = g \left( N, \xi, t \right) \). Dimensional analysis then yields \( k(t) = f \left( t / \tau_R \right) / \tau_R \), with which form equation (18) is indeed consistent.

Appendix E: interpolation between long and short times.

In this appendix we sketch the derivation of an approximate interpolation formula, for the good solvent case, between \( k_\infty \) and \( k(t) \). For this purpose it is convenient to define a quantity \( r(t) \) namely

\[ r(t) = - \frac{d \ln A}{dt} \]  \hspace{1cm} (E1)

At short times \( r(t) \) is the same as \( k(t) \) defined previously (Eq. (2)) ; as \( t \) approaches infinity \( r(t) \) goes to \( k_\infty \) A straightforward calculation gives to second order in \( u_0 \)

\[ - r(t) = u_0 \langle \delta (R) \rangle + u_0^2 \int_0^t dt' \langle \delta (R_0) \delta (R_{t'}) \rangle - \langle \delta (R) \rangle^2 \]  \hspace{1cm} (E2)
We are thus faced with evaluating the expression
\[
\int_0^t dt' \left( \langle \delta(R_0) \delta(R_t) \rangle - \langle \delta(R) \rangle^2 \right) =
(2 \pi N_0)^{-d} \xi_0 N_0^2/\pi^2 \int_0^{t/\tau_g} ds \left\{ (1 - f^2(s))^{-d/2} - 1 \right\}
\] (E3)

where \( f(s) = (8/\pi^2) \sum_{\text{odd } p} \exp(-p^2 s)/p^2 \), at arbitrary time \( t \). Unfortunately this is not completely straightforward due to the complicated form of \( f^2(s) \). We therefore approximate \( f^2(s) \) with a simpler function having the same behavior at small and large times. Our approximation for \( f^2(s) \) is
\[
g(s) = \theta(a - s) f_1 + \theta(s - a) f_2
\]
where \( \theta(t) \) is a step function and
\[
\begin{align*}
f_1 &= 1 - 8 s^{1/2}/\pi^{3/2} \\
f_2 &= (8/\pi^2)^2 e^{-2s}.
\end{align*}
\] (E4)

Here \( a \) is the unique value of \( s \) so that our approximate \( f^2(s) \) is continuous (i.e. where \( f_1 \) and \( f_2 \) cross). A simple numerical calculation gives \( a \approx 0.1067 \). Straightforward manipulations then lead to the following approximate expression for \( r(t) \) valid for all times
\[
r(t) = \frac{2}{\pi^3} \left( L/N \right)^d \frac{1}{L^{d/2}(X - 1)} c(t)
\]
where for \( t/\tau_g < a \)
\[
c(t) = 1 - \frac{\varepsilon}{16(X - 1)} \ln(t/\tau_g) + \frac{4 \varepsilon}{\pi^3(X - 1)} \frac{t/\tau_g}{L^{d/2}(X - 1)}
\] (E5)
and for \( t/\tau_g > a \)
\[
c(t) = 1 - \frac{\varepsilon}{16(X - 1)} \ln(a) + \frac{2 \varepsilon}{\pi^3(X - 1)} \left\{ \frac{\exp(2 t/\tau_g)}{\exp(2 t/\tau_g) - C} - \ln \left[ \frac{\exp(2 t/\tau_g) - C}{\exp(2 a) - C} \right] \right. - \frac{\exp(2 a) - C}{\exp(2 a) - C} + 2 t/\tau_g \}
\]
where \( C = (8/\pi^2)^2 \).

We note that the expression is continuous and has a continuous derivative for all \( t \). At short times it agrees with our result equation (36) and at long times it goes to a time independent result which agrees to lowest order with the result in FO for \( k_\infty \) (Note that (E5) does not reproduce the correct leading order correction to \( k(t) \) at short times. To obtain this correction, proportional to \( t^{1/2} \), one needs to include the next leading order correction, proportional to \( s \) for \( f_1 \). We have included the term proportional to \( t \) for \( c(t) \), \( t/\tau_g < a \), so the expression for \( r(t) \) is continuous.) Using the value \( X = 5 \) to plot \( c(t) \), we note only small corrections to \( k_\infty \) other than for very short times.
References