From Mean Field to Diffusion-Controlled Kinetics:
Concentration-Induced Transition in Reacting Polymer Solutions

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We study irreversible interpolymeric reaction rates k in polymer solutions as a function of concentration ϕ. At high dilution, kinetics obey mean field theory, and screening of excluded-volume repulsions as ϕ increases results in a growth, $k \sim \phi^{3g/4}$, where g is the monomer contact exponent. Screening effects cause a transition to diffusion-controlled kinetics at a value ϕ^{**}, beyond which (for entangled solutions) k decreases as $k \sim \phi^{-(5/8+\gamma)}$, γ being the entanglement exponent. Thus k is peaked at ϕ^{**} which, in agreement with experiment, is distinct from the overlap threshold.

The key to understanding linear polymerizations is establishing the dependence of polymer-polymer reaction rates on chain length, polymer concentration, and reactivity of the functional groups (see Fig. 1). This has been one of the principal motivations for the substantial research effort directed towards the development of fundamental theories of high polymer reactions [1–7] and the precise measurement of reaction rates k using photophysical and other methods [8–10]. At present, however, no fundamental theory for k exists across the concentration range of relevance, in consequence of which "first principles" theories of various types of polymerization are unavailable in spite of the vast body of experimental and theoretical work on the subject [11,12]. In this Letter we present a basic theory of irreversible reaction kinetics as a function of polymer concentration from dilute solution through the semidilute regime into the melt. Beyond polymerization, our motivation is both the interpretation of photophysical measurements (which furnish a fundamental probe of polymer behavior) plus the understanding of a variety of other "reacting" systems such as surfactant solutions in which molecules aggregate into long flexible chains [13] ("living polymers").

In the various types of linear polymerization processes which exist [11] the basic interpolymeric reaction event, usually irreversible, is as follows. Should the functional groups of two reactive chains, each comprising N units of

(a)   (b)

FIG. 1. (a) A pair of reacting polymers (with reactive end groups) in a semidilute environment of "mesh spacing" ξ is analogous to a reacting pair in the *melt*, depicted in (b), where the "monomers" are blobs of size ξ and the "reactive blobs" are of effective reaction range ξ and reactivity Q_{eff}.

size h, happen to overlap (i.e., diffuse to within a distance h of one another where h is the reaction range) then reaction occurs with probability Q per unit time [see Fig. 1(a)]. Now for very small values of the functional group reactivity Q, since equilibrium is presumably only slightly disturbed one anticipates that mean field theory should be applicable, i.e., $k \propto P_{\text{eq}}^{\text{cont}}$, where $P_{\text{eq}}^{\text{cont}}$ is the equilibrium reactive group-group contact probability [3]. Less clear is what should happen for "large" or "intermediate" Q when the possibility of a nonequilibrium polymer state [14,15] arises.

The classic example of a "large Q" reaction is termination in free radical polymerization [11]. Studies of molecular weight evolution and propagation rates in free radical systems thus constitute an important source of data on k. The general picture [11] is that after an initial increase as polymer concentration increases from diluteness [16,17], k drops dramatically at higher concentrations, ultimately leading to the celebrated Tromsdorff or "gel" effect [11,12] in which polymerization rates exhibit enormous increases. The reduced k allows chains to grow longer which enhances the rate at which the concentration of the environment increases, thus further reducing k, and so on: The polymerization "autoaccelerates" into an entangled melt. However, the most unambiguous available experimental data are that of Mita, Horie, and Takeda who measured phosphorescence quenching rates (large Q) in end-labeled polystyrene solutions [8, 10], reporting a rather novel behavior. In good solvents, after an initial increase as polymer volume fraction ϕ increased into the semidilute regime ($\phi > \phi^*$ where [18] $\phi^* \approx N^{-4/5}$ is the polymer overlap threshold), k was observed to *peak* at a certain value of ϕ and then decay monotonically for greater values [see Fig. 2(a)]. For the longest chains the peak did *not* appear to coincide with ϕ^*.

The long time reaction rate constant k determines the evolution of the number density, n, of reactive chains (each bearing one functional group) via $\dot{n} = -kn^2/2$, after making the standard assumption that density correlations on scales much greater than the polymer size can
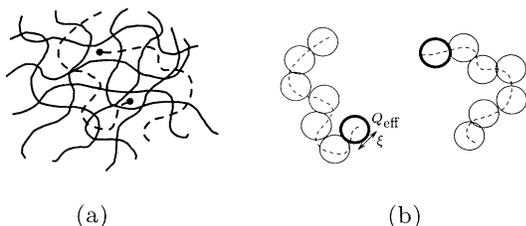
be ignored. There is considerable evidence that for spatial dimensions $d > 2$ this is justified [4,19,20]. The polymer scale fluctuations, however, are crucial and determine the structure of k as will be shown below. As depicted in Fig. 1(a), we will consider reactive chains dilute in an inert background at volume fraction ϕ, this being precisely the type of situation realized in both free radical polymerizations and the photophysical experiments mentioned above. For simplicity, we consider chains of equal length. A straightforward generalization of de Gennes' procedure [4] to the case of finite Q leads to

$$k = \frac{QVP_{eq}^{cont}}{1+Q\int_0^\infty dt\, S(t)}, \tag{1}$$

where V is the system volume and the "return probability" [4] in the *absence of reactions*, $S(t) \equiv \int_{r<h} G(r,0,t)$, is defined in terms of the Green's function $G(r,r',t)$, namely, the probability density that the reactive groups of a pair of chains would be separated by r after time t

(a)

(b)
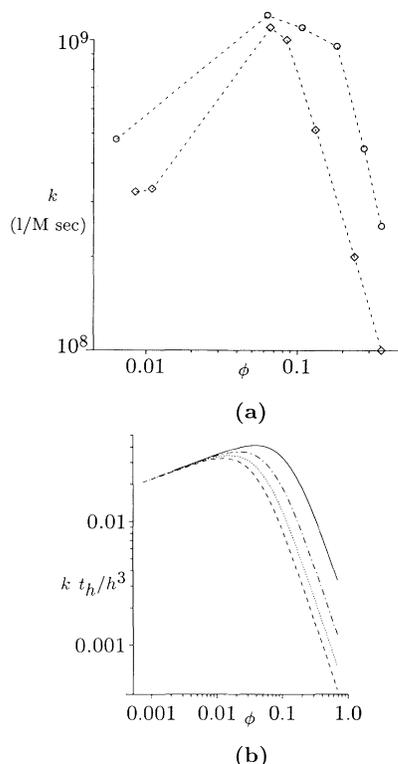
FIG. 2. (a) Phosphorescence quenching rates taken from Ref. [8] for polystyrene, end capped with benzil and anthryl groups, in benzene solvent at 30 °C. O: reacting chains, 800 and 640 units; inert chains, 1000 units. ◇: background, 3800 units; reacting, 3900 and 2900 units (four smallest ϕ values) and 3300 and 1200 units (three largest ϕ values). Estimates of ϕ^* are 0.006 (O) and 0.002 (◇). All ϕ values were calculated taking estimate $h = 5.5$ Å. (b) Theoretical dimensionless k versus ϕ for four "weak" systems. Parameters are $\tilde{Q}t_h = 0.1$, $N_e = 200$, $\gamma = 1$, with $N = 4000$ (solid line), $N = 8000$ (dash-dotted line), $N = 12000$ (dotted line), and $N = 16000$ (dashed line).

given an initial value r', if their reactivity were "switched off." The importance of Eq. (1) is that it relates the nonequilibrium observable k to static and dynamical quantities characteristic of the equilibrium state; more rigorous renormalization group studies [5] provide convincing evidence of its validity (at least in terms of its ability to reproduce exponents correctly). In metals ($P_{eq}^{cont} \to h^d/V$) and for $Q \to \infty$, Eq. (1) matches the expression obtained by de Gennes [4] who established radically differing reaction kinetics depending on whether $S(t)$ described "compact" exploration of space (in which the volume explored by a reactive species grows less rapidly than linearly in time) or "noncompact" exploration [4]. Our aim is to extend these ideas to situations where spatial correlations exist between the functional groups, unlike melts where screening effects dominate [18].

What is the general structure of $S(t)$ when correlations may be present? To answer this we invoke the principle of detailed balance which dictates that

$$P_{eq}(r')G(r,r',t) = P_{eq}(r)G(r',r,t), \tag{2}$$

where $P_{eq}(r)$ is the equilibrium distribution. Second, we assert that $G(r,r',t)$ is approximately independent of r' for values of r' much less than the rms chain unit displacement after time t, namely, $x_t \approx h(t/t_h)^{1/z}$ where t_h and z are, respectively, the relaxation time of a single chain unit and the dynamical exponent. This is simply the principle of finite memory: The initial condition r' will be forgotten after a time scale much greater than the diffusion time corresponding to r'; i.e., when the width of G as a function of r greatly exceeds r' one may simply replace r' with zero. Thus, specializing Eq. (2) to small values of r and r', we have

$$\frac{G(r,0,t)}{P_{eq}(r)} = \frac{G(r',0,t)}{P_{eq}(r')}, \quad r,r' \ll x_t, \tag{3}$$

implying that $G(r,0,t)/P_{eq}(r)$ is *independent* of r for $r \ll x_t$; i.e., the asymptotic behavior must match that of the equilibrium distribution, $P_{eq}(r) \sim r^g$, where [18,21,22] g is the correlation hole exponent quantifying the reduced contact probability between chain units due to excluded-volume repulsions (g vanishes for melts). Finally, let us assume that the only scales in G are r and x_t. Then the dimensions of G force the following structure:

$$G(r,0,t) \approx \frac{1}{x_t^d} \left[\frac{r}{x_t}\right]^g \quad (r \ll x_t). \tag{4}$$

This result is physically reasonable; $G(r,0,t)$ is essentially equal to the conditional equilibrium probability that the groups are separated by r, given that they lie within x_t of each other. That is, the dynamics are ergodic in a region of volume x_t^d only, so within that portion of r space relative probabilities are *as in equilibrium*. From the definition of $S(t)$, Eq. (4) then leads to the following scaling form:

$$S(t) \sim t^{-\theta}, \quad \theta \equiv (d+g)/z, \tag{5}$$

where θ is the characteristic "reaction exponent" [23]. Switching off correlations ($g \to 0$), one recovers the result of de Gennes [4].

On scales much larger than the rms polymer coil size $R = hN^v$ and longest relaxation time $\tau \equiv t_h(R/h)^z$ (v being the Flory exponent [18]), center of gravity diffusion takes over ($z \to 2$) and statics are ideal ($g = 0$), whence $\theta = d/2$; i.e., $S(t)$ is integrable in three dimensions [4]. Then k depends on the short time behavior of $S(t)$, $t \ll \tau$, which for unentangled melts and dilute solutions (good solvents are assumed throughout) involves only a single value of θ. Integrating Eq. (5), Eq. (1) then gives

$$k = \frac{\tilde{Q} V P_{eq}^{cont}}{1 + \tilde{Q} t_h \mathcal{N}^{coll}}, \quad \mathcal{N}^{coll} \approx \left(\frac{\tau}{t_h} \right)^{1 - \theta}, \tag{6}$$

where $\mathcal{N}^{coll}$ is identified as the mean number of "collisions" between the reactive groups of two overlapping chains during the overlap period of order τ. Thus $\tilde{Q} t_h \mathcal{N}^{coll}$ measures the total reaction probability when two coils collide due to center of gravity diffusion. Note that Q is replaced by an "effective" local reactivity $\tilde{Q} \approx Q/(1 + Q t_h)$ which saturates at the local relaxation rate t_h^{-1}. Now since unentangled melts are known to exhibit Rouse-like [18] dynamics ($z = 4$ and $g = 0$), it follows that for $d = 3$ this reaction probability approaches unity for $N \gg 1$ since $\theta = d/4 < 1$. That is, the kinetics are driven to diffusion-controlled (DC) form by increasing N, and Eq. (6) leads to Doi's result [2] $k \approx R^3/\tau$. In contrast, dilute solution kinetics are intrinsically of mean field (MF) form since $\theta > 1$ ($z = d$, $g > 0$) and reaction is very improbable when two coils collide; increasing N drives kinetics to the MF result [24] $k \approx \tilde{Q} V P_{eq}^{cont}$. The essential point is that the mean numbers of functional group collisions are, respectively, increasing ($\mathcal{N}^{coll} \approx N^{1/2}$) and decreasing ($\mathcal{N}^{coll} \approx N^{-vg}$) functions of chain length in melts and dilute solutions.

Let us now address general polymer concentrations between these two extremes. It is well known [18,25] that semidilute polymer solutions in which the chains overlap strongly are characterized by a screening length ξ. One may think of these screening effects in terms of a "melt of blobs" picture [18] in which the blob size is identified with the screening length; properties within a blob are dilutelike, while on large scales screening results in meltlike behavior. Note that in relating dynamical properties in the melt to those in the semidilute state it is essential to allow for concentration dependence [18,26] of the chain length at which entanglements onset, N_e. This dependence will feature prominently in our results for entangled systems (see below). Thus (see Fig. 1), our problem translates into a melt containing reactive polymers, each viewed as a string of N/s blobs where [18] $s \approx \phi^{-5/4}$ is the number of monomers per blob. One blob per reactive chain has effective reactivity Q_{eff}, determined by the small scale MF dilute solution kinetics: $Q_{eff} = \tilde{Q}(h/\xi)^{d+g}$. This is reduced from $\tilde{Q}$ by a factor equal to the conditional functional group contact probability given

that a pair of reactive blobs overlap one another. Formally, beginning with unentangled solutions, one finds two short time reaction exponents: $\theta_1 = 1 + g/d$ (dilutelike) and $\theta_2 = d/4$ (meltlike) for scales, respectively, less than and greater than the blob scale. Equation (1) then leads to the same structure as that in Eq. (6), but now with a concentration-dependent $\mathcal{N}^{coll}$ ($d = 3$):

$$\mathcal{N}^{coll} \approx (N/s)^{1/2} s^{-vg}. \tag{7}$$

This expression is simply the melts result for chains of N/s units multiplied by the dilute result for chains of length s; i.e., $\mathcal{N}^{coll}$ is the product of the number of reactive blob collisions with the number of reactive group collisions per reactive blob collision. Since s is a strongly decreasing function of ϕ, Eq. (7) tells us that the total reaction probability grows with increasing polymer concentration, ultimately driving the kinetics to DC form. Explicitly, expressing $\mathcal{N}^{coll}$ in terms of ϕ, one finds

$$k = \frac{k^{dil}(\phi/\phi^*)^{3g/4}}{1 + (\phi/\phi_{un}^{**})^{3g/4 + 5/8}} \quad (\phi > \phi^*),$$

$$\phi_{un}^{**} \equiv [(\tilde{Q} t_h)^2 N]^{-4/(5 + 6g)}, \tag{8}$$

where $k^{dil} \approx \tilde{Q} h^3 N^{-vg}$ is the dilute ($\phi < \phi^*$) result [24].

Thus far we have ignored entanglements [4] which will dominate the dynamics of chains longer than a certain concentration-dependent threshold $N_e(\phi)$. We assume a power law $N_e(\phi) = N_e^{melts} \phi^{-\gamma}$, where experimental values [26] of the exponent lie in the range $1 \lesssim \gamma \lesssim 1.3$. Calculating $S(t)$ in the framework of the reptation model [4] one finds $\mathcal{N}^{coll} \approx (N/s)^{3/2}(s/N_e)s^{-vg}$, which is again a strongly increasing function of ϕ. The same logic dictates, therefore, that increasing polymer concentration drives the kinetics from MF to DC form:

$$k = \frac{k^{dil}(\phi/\phi^*)^{3g/4}}{1 + (\phi/\phi_{ent}^{**})^{3g/4 + 5/8 + \gamma}} \quad (\phi > \phi^*),$$

$$\phi_{ent}^{**} \equiv \left[\left(\frac{\tilde{Q} t_h}{N_e^{melts}} \right)^{2/3} N \right]^{-12/(5 + 6g + 8\gamma)}. \tag{9}$$

At fixed N, Eq. (9) reproduces the experimental behavior, at least qualitatively (see Fig. 2). In the MF regime ($\phi^* < \phi < \phi_{ent}^{**}$), the key property is a purely static one, P_{eq}^{cont}, which increases with concentration as excluded-volume repulsions become increasingly screened out. Thus k itself increases, $k \sim \phi^{3g/4} \approx \phi^{0.2}$ for end groups (since [21] $g \approx 0.27$). We note that this is close to, but different from, the conclusion of Kent et al. [17] who ascribed the increase of k in this regime to both reduced intercoil repulsions and increased relaxation time. However, this screening has a second effect: The reaction probability ($\tilde{Q} t_h \mathcal{N}^{coll}$) grows, reaching unity by $\phi \approx \phi_{ent}^{**} \sim N^{-0.82}$ (taking $\gamma = 1$) where DC kinetics onset. Beyond this concentration, therefore, $k \sim R^3/\tau$ is rapidly decreasing since both coil size R and relaxation rate τ^{-1} diminish, leading to $k \sim \phi^{-(5/8 + \gamma)}$. That is, k exhibits a

peak at about $\phi = \phi_{ent}^{**}$. (Note the strong dependence on reactive group location via g; shifting the groups from chain ends to internal locations, for instance, the MF regime is a considerably stronger growth, $k \sim \phi^{0.53}$, since [21] $g \approx 0.71$ is much larger.) The sequence for the unentangled case [Eq. (8)] is similar, but with a peak around $\phi_{un}^{**} \sim N^{-0.6}$ followed by a milder decay, $k \sim \phi^{-5/8}$. Though quantitative comparison with the experimental data of Mita, Horie, and Takeda [Fig. 2(a)] is rather difficult, since the two reacting species and the inert chains are of three unequal molecular weights, its important feature for the longest chain sample is the peak in k at a concentration well above the overlap threshold ϕ^*, beyond which the slope of slightly less than -1.6 suggests in our picture $\gamma \approx 1$.

The question remains as to which of the two evolutions in reaction kinetics, entangled or unentangled, is actually realized for a given system. This depends on the value of ϕ_e, namely, the concentration, at fixed N, at which entanglements first become important: $N_e(\phi_e) \equiv N$, i.e., $\phi_e = (N/N_e^{melts})^{-1/\gamma}$. In fact, from the expressions for ϕ_{un}^{**} and ϕ_{ent}^{**}, an important relationship follows:

$$\phi_{un}^{**}(\phi_e)^{\alpha} = (\phi_{ent}^{**})^{1+\alpha}, \quad \alpha \equiv 8\gamma/(5+6g), \tag{10}$$

implying that ϕ_{ent}^{**} *always lies between* ϕ_{un}^{**} and ϕ_e. Thus a given reacting polymer system may be classified as either "weakly reactive" ($\phi_e < \phi_{ent}^{**} < \phi_{un}^{**}$) or "strongly reactive" ($\phi_{un}^{**} < \phi_{ent}^{**} < \phi_e$). In "weak" systems the observed behavior is that of Eq. (9); i.e., the entire "trajectory" of k as ϕ increases is that described within the entanglements picture. Meanwhile in a "strong" system the unentangled DC regime ($k \sim \phi^{-5/8}$) onsets *before* entanglements become important; k is then governed by Eq. (8) for $\phi < \phi_e$, switching directly to the entangled DC regime for $\phi > \phi_e$, i.e., $k \sim \phi^{-(5/8+\gamma)}$. Returning to the data of Fig. 2(a), if one takes [27] $\gamma = 1$ and $N_e^{melts} \approx 200$, then $\phi_e \approx 0.05$ and the system would appear to be a weak one (ϕ_e being less than the ϕ value at which k is peaked).

In conclusion, we have found that reaction kinetics in semidilute solution are closely related to those in melts and dilute solutions; these latter determine, respectively, the large and the small scale features of the kinetics. In a "melt of blobs" picture, since melt kinetics are *intrinsically* DC, the dilute MF kinetics inevitably cross over to DC as concentration is increased. The essential point is that the total probability of reaction, P, when two live coils encounter one another is an increasing function of polymer concentration ϕ due to the enhancement of screening. At low ϕ, P is small and mean field kinetics pertain which dictate that k increases with ϕ, due also to screening. However, P eventually reaches unity at a certain concentration ϕ^{**} and reaction is then inevitable whenever two coils collide: These are DC kinetics, under which k is a decreasing function of ϕ. It follows that k is peaked at ϕ^{**}. Thus a coherent theoretical picture of reaction kinetics now exists across the entire concentration

range; we have demonstrated qualitative agreement with experiment which exhibits power law decay in the DC regime suggestive of a value of the entanglement exponent, γ, close to unity. Systematic experimental explorations of the semidilute regime are motivated by the present work, and a number of new possibilities are now available, among the most interesting being the development of a "first principles" theory of free radical polymerization.

[1] G. Wilemski and M. Fixman, J. Chem. Phys. **60**, 878 (1974).

[2] M. Doi, Chem. Phys. **11**, 115 (1975).

[3] A. R. Khokhlov, Makromol. Chem. **2**, 633 (1981).

[4] P. G. de Gennes, J. Chem. Phys. **76**, 3316 (1982); **76**, 3322 (1982).

[5] B. Friedman and B. O'Shaughnessy, Phys. Rev. Lett. **60**, 64 (1988).

[6] A. Rey and J. J. Freire, Macromolecules **24**, 4673 (1991).

[7] J.-M. Debierre and L. Turban, J. Phys. A **20**, 4457 (1987).

[8] I. Mita, K. Horie, and M. Takeda, Macromolecules **14**, 1428 (1981).

[9] M. S. Gebert and J. M. Torkelson, Polymer **31**, 2402 (1990).

[10] I. Mita and K. Horie, J. Macromol. Sci., Rev. Macromol. Chem. Phys. C **27**, 91 (1987).

[11] P. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, New York, 1971).

[12] T. J. Tulig and M. Tirrell, Macromolecules **14**, 1501 (1981).

[13] M. E. Cates and S. F. Candau, J. Phys. Condens. Matter **2**, 6869 (1990).

[14] T. L. Madden and J. M. Deutsch, J. Chem. Phys. **94**, 1584 (1991).

[15] Y. Rabin and H. C. Ottinger, Europhys. Lett. **13**, 423 (1990).

[16] A. M. North and G. A. Reed, Trans. Faraday Soc. **57**, 859 (1961).

[17] M. S. Kent, A. Faldi, M. Tirrell, and T. P. Lodge, Macromolecules **25**, 4501 (1992).

[18] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, New York, 1985).

[19] M. Doi, J. Phys. A **9**, 1479 (1976).

[20] B. Friedman, G. Levine, and B. O'Shaughnessy, Phys. Rev. A **46**, R7343 (1992).

[21] J. des Cloizeaux, J. Phys. (Paris) **41**, 223 (1980).

[22] T. A. Witten and J. J. Prentis, J. Chem. Phys. **77**, 4247 (1982).

[23] B. Friedman and B. O'Shaughnessy, Europhys. Lett. **21**, 779 (1993).

[24] B. Friedman and B. O'Shaughnessy, Macromolecules (to be published).

[25] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).

[26] W. W. Graessley and S. F. Edwards, Polymer **22**, 1329 (1981).

[27] J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley and Sons, New York, 1980), 3rd ed.