Kinetic Isolation of Macroradicals

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Kinetics of irreversible reactions between polymer chains bearing reactive groups[1−4] are interesting for many reasons. Every reaction event between a pair of functional groups relies on the motion and configurations of the host macromolecules to enable the groups to meet. Consequently, rate constants reflect not only the local chemistry of the reactive groups but also static and dynamical properties of polymer chains in the liquid state. Measurements of polymer−polymer reaction rate constants, k_{PP}, thus probe fundamental aspects of polymer science. Interpolymeric reactions are also central to a great number of applications such as free radical polymerization (FRP).[5] Many phenomena in FRP are driven by the dependence of k_{PP} on chain length and concentration.[6,7]

A rather complete theoretical picture for k_{PP} by now exists.[2] Theory predicts universal scaling laws for sufficiently high degrees of polymerization, N. For example, for highly reactive functional groups

$$k_{\rm PP} \sim 1/{\rm N}^{\alpha} \qquad (1)$$

is predicted, where α depends on the concentration regime of the environment. For entangled melts, de Gennes[3] obtained $\alpha = 3/2$ while Doi found $\alpha = 1/2$ for the unentangled case.[4] For end-functionalized chains in dilute solutions a much weaker power, $\alpha \approx 0.16$, is predicted.[8] Various other universal scaling dependencies on polymer concentration have also been derived theoretically.[9]

Unfortunately, these and many other predictions have not been accessible to experiment. For instance, the $1/N^{1/2}$ and $1/N^{3/2}$ melt predictions have never been tested, to the best of our knowledge. The most useful technique to date, phosphorescence quenching, is limited by typical phosphorescence lifetimes[1] of the order of 10^{-4} s. This excludes measurement of k_{PP} in polymer solutions of high concentration and in melts, where polymer relaxation times become very large. In dilute and semidilute solutions, a few studies exist[1] though power laws predicted by theory[8,9] are difficult to infer from these data. No direct measurements whatsoever exist, to our knowledge, on chain length dependencies at very high concentrations or in melts.

In this communication we present a theoretical analysis of a reacting radical−macroradical system. Our findings suggest that experimental implementation of this system would allow measurement of the exponent α in concentrated solutions or melts for the first time. The essential prediction is that a finite fraction of the macroradicals (polymer chains bearing radical end groups) are *kinetically isolated* after an initial transient; this allows the pure polymer−polymer reaction kinetics to be measured in the late stages. The great advantage is that radical lifetimes can be made extremely long provided the environment is carefully chosen.[10−12] Hence monitoring of macroradical recombination rates by direct spectroscopy is possible over time scales ranging from nanoseconds to seconds or even longer.[10,11] We emphasize that the systems considered here always involve *inert* backgrounds: there are no polymerization processes occurring.

In the proposed experiment, a mixture of small molecule radicals (M) and macroradicals (P) of length N is created by flash photolysis[10] of appropriately end-labeled precursors in a series of well-characterized inert concentrated polymer solution or melt backgrounds (Scheme 1). We show that, after an initial transient the small radicals will virtually disappear, leaving behind macroradicals only. The time scale for the disappearance of the macroradicals thereafter is determined by simple bimolecular reaction kinetics governed by k_{PP}. Experimental measurement of this time scale for different N thus constitutes a direct measurement of the fundamental exponent α of eq 1. The origin of the macroradicals' kinetic isolation is their extremely low self-reactivity. In the terminology of Ingold and Fischer[13,14] they are "persistent radicals." These authors and many others[15] have used this label for radicals with very small self-reactivities, which, nonetheless, may react at near diffusion-controlled rates with other types of radicals.

Why are these macroradicals "persistent"? Let us take an entangled[16] melt background as an example. Due to their much lower mobility, the bulky macroradicals react at a much lower rate with one another than the small molecules. Specifically, theory predicts[3] $k_{PP} \approx k_0\, N_e/N^{3/2}$, where the entanglement threshold[16] N_e has a typical value of $N_e \approx 200$. Now typically k_0 and the small radical self-reactivity, k_{MM}, are of the same order of magnitude. Thus $k_{PP}/k_{MM} \approx N_e/N^{3/2}$. For $N = 10^4$, as an example, k_{PP} is nearly 10^4 times smaller than k_{MM}. On the other hand, theory predicts[17] (with some experimental support[18,19]) that the cross-reactivity k_{MP} is dominated by the more mobile M species, and is of order k_0. This is a perfect example of a persistent radical.

Persistent radicals are encountered widely in chemistry and in biology.[11,15,20,21] Some of the best known persistent radicals are nitroxides,[21] Co(II),[22] and NO radicals.[23] In addition, *any* ordinary, nonpersistent radical can in principle be rendered persistent by electrostatic or steric substitution, as suggested by Ingold and Fischer,[13] or by lowering its mobility by some means, as in the example of macroradicals dealt with here.

Before detailed calculation, we remark that the analysis presented below is general, regardless of any

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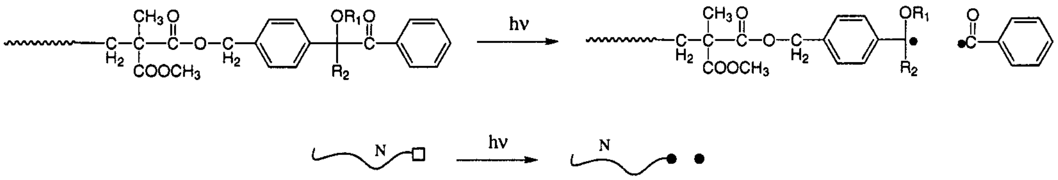
Scheme 1



specific radical types. We consider a general initial ratio r of M and P concentrations, even though the proposed experiment involves $r = 1$. Our calculations extend Fischer's theoretical analysis[13] of steady state situations to the case of transient persistent radical kinetics. Fischer[13,14] considered the case where persistent and nonpersistent radicals are generated continuously at time-independent rates and showed theoretically[13] that very high product selectivities could be obtained from such mixtures under certain circumstances, a very unusual feature for reactions involving free radical intermediates. In the case of transient kinetics analyzed here, an equally surprising finding is that in certain cases the persistent radicals are kinetically isolated *regardless of their initial concentration*.

We consider a system where at $t = 0$ there are P_0 persistent and M_0 nonpersistent radicals per unit volume, created, for example, by a laser flash from appropriate precursors as in Scheme 1. There is no radical production thereafter, and the radical concentrations M and P decay according to

$$\dot{M} = -k_{\mathrm{MP}}MP - k_{\mathrm{MM}}M^2, \qquad \dot{P} = -k_{\mathrm{MP}}MP - k_{\mathrm{PP}}P^2 \tag{2}$$

where the self-reactivity of the persistent radical, k_{PP}, is much smaller than the other rate constants. That is, the quantity $\epsilon \equiv k_{PP}/k_{MP}$ is small: $\epsilon \ll 1$.

We consider the *trajectory* in the $M-P$ plane followed by the reactants as time progresses. In fact, it is more convenient to use scaled concentration variables, $m \equiv M/M_0$ and $p \equiv P/P_0$. Eliminating the time variable in eqs 2 one obtains

$$\frac{\dot{m}}{\dot{p}} = \frac{\mathrm{d}m}{\mathrm{d}p} = \frac{(1-\omega)(m/p)^2 + r(m/p)}{\epsilon r + (m/p)} \tag{3}$$

where $r \equiv P_0/M_0$ is the initial ratio of reactant concentrations, and $\omega \equiv 1 - k_{MM}/k_{MP}$ is a dimensionless measure of the difference between the larger rate constants.

A given experimental system is characterized by r and ω. Each (r, ω) pair defines a trajectory in the $m-p$ plane. Trajectories start at (1, 1) and the reactant concentrations decrease monotonically thereafter, as shown in Figure 1. Differentiating eq 3 with respect to p shows that there exist two classes of trajectory, one with negative and the other with positive curvature, depending on the initial concentration ratio r. Along the critical line separating these two classes one has $\mathrm{d}m/\mathrm{d}p = m/p = 1$, whence $r = r_c \equiv \omega/(1 - \epsilon)$, after using eq 3.

The trajectories that lie above the critical line in Figure 1, $r < r_c$, have negative curvature. Using the change of variables $v \equiv m/p$ in eq 3, it can be shown that $\mathrm{d}v/\mathrm{d}p < 0$ for this class of trajectory. This has the following important consequence: the term ϵr in eq 3, which is much smaller than m/p at the start of the trajectory, remains so throughout the rest of the trajectory as p decreases. Therefore, with small errors, we solve eq 3 by setting $\epsilon = 0$, with the help of the variable $v \equiv m/p$. The solution is

$$m \approx \frac{r}{r_{\mathrm{c}}}p + \left(\frac{r_{\mathrm{c}} - r}{r_{\mathrm{c}}}\right)p^{1-r_{\mathrm{c}}} \qquad \omega \neq 0 \qquad (r < r_{\mathrm{c}}) \tag{4}$$

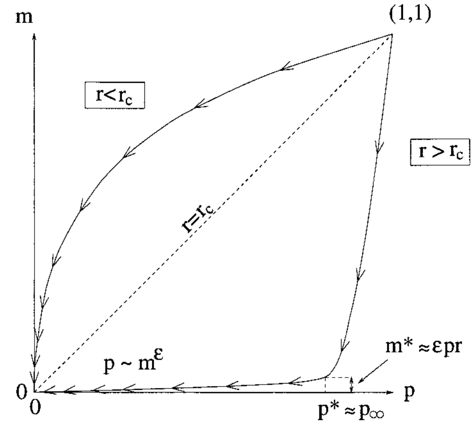


Figure 1. For sufficiently high initial P concentration ($r > r_c$) a fraction $p^* \approx p_\infty$ of the persistent P radicals are essentially isolated from the initial mixture. This isolation process occurs on a time scale $\tau_{\mathrm{early}} \equiv 1/(k_{\mathrm{MP}}P_0)$, during which the cross coupling and M self-reactions are dominant. The surviving P species react with one another following their isolation and disappear on a much longer time scale, $\tau_{\mathrm{late}} \equiv 1/(k_{\mathrm{PP}}P_0p_\infty)$. During this late period reactions are primarily of P−P type.

Consider now the trajectories, $r > r_c$, lying below the critical line in Figure 1. These trajectories possessing positive curvature exhibit two distinct regimes. Let us describe a trajectory in this class as p decreases, starting from (1, 1). In the "early" stages one has $m/p \gg \epsilon r$; hence the ϵr term in eq 3 is negligible and this part of the trajectory is described approximately by eq 4. However, now the ratio m/p decreases as p decreases. This follows from the inequality $\mathrm{d}v/\mathrm{d}p > 0$, which can be obtained by the change of variables $v \equiv m/p$ in eq 3, as before. Hence, eventually there comes a point where m/p becomes comparable to ϵr and the behavior is changed. That is, a second, "late" stage commences at (m^*, p^*) where

$$m^* \approx \epsilon r p_\infty, \qquad p^* \approx p_\infty \equiv \left[\frac{r - r_{\mathrm{c}}^{\mathrm{o}}}{r}\right]^{1/\omega} \tag{5}$$

Here p_∞ is the asymptotic value p would have if the persistent radical self-reactivity actually vanished, $\epsilon = 0$, for $r > r_c^o \equiv \omega$. This is obtained by setting $m = 0$ in eq 4, correct to leading order in ϵ. Note that this crossover occurs when the P−P reaction rate, negligible in the early stages, first becomes comparable to the M−P reaction rate: $k_{PP}P^2 \approx k_{MP}MP$. Now as p decreases past p^*, the ratio m/p continues to decrease.

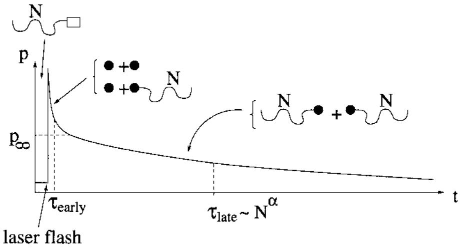


Figure 2. A solution or melt of polymer chains (degree of polymerization *N*), a fraction of which carrying photolabile chemical groups, is photolyzed by a laser flash at $t = 0$, creating a mixture of small radicals and "macroradicals". During an initial transient (time scale τ_{early}) the much more mobile small radicals are consumed through self-reactions and cross coupling reactions, leaving behind a finite fraction p_∞ of the macroradicals. The subsequent kinetics involve essentially only macroradical–macroradical reactions and are much slower, occurring on a time scale $\tau_{\text{late}} \sim 1/k_{\text{PP}} \sim 1/N^\alpha$. Measurement of τ_{late} for different *N* thus amounts to measuring the fundamental exponent α.

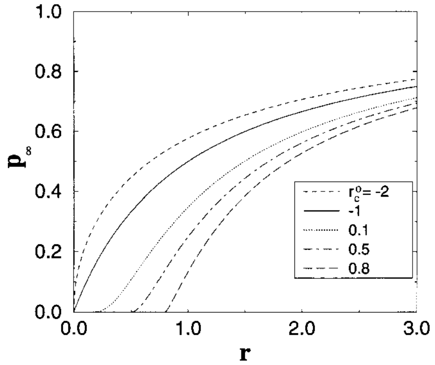


Figure 3. The surviving fraction, p_∞ (see Figures 1 and 2), of the persistent P radicals in the case of zero self-reactivity ($\epsilon = 0$) is plotted for various (fixed) values of the critical initial concentration ratio, $r_c^o \equiv \omega$, as a function of the initial concentration ratio, *r*. The surviving fraction p_∞ is finite for $r > r_c^o$ and zero for $r < r_c^o$. When the cross coupling reactivity is weaker than the M self-reactivity, $k_{MP} < k_{MM}$, r_c^o is negative and p_∞ is finite for *any* $r > 0$.

Solving eq 3 with $m/p \ll \epsilon r$ gives a weak power law, $p \sim m^\epsilon$. In this phase there are virtually no M radicals left, and hence the P–P reactions dominate.

The remarks above are summarized in Figure 3, where the isolated fraction p_∞ of P_0 is shown as a function of *r* for several values of r_c^o. Note that p_∞ is finite only if $r > r_c^o$ (see the curves for $r_c^o > 0$ in Figure 3). Surprisingly, there exist cases where p_∞ is *always* finite regardless of the initial concentration ratio *r*. This will occur if the cross coupling reactivity is weaker than the M self-reactivity (which seems to be usually the case[24]): if $k_{MP} < k_{MM}$, one has $\omega \equiv 1 - k_{MM}/k_{MP} < 0$ and it follows that $r > r_c^o$ is always true (curves for $r_c^o = -1$, -2 in Figure 3). This is perhaps the most interesting conclusion reported in this communication.

Let us now consider the kinetics. For $r < r_c$ trajectories the decay of the P radicals occurs on a characteristic time scale $\tau \equiv 1/(k_{MP}P_0)$. For the other type of trajectory, $r > r_c$, the same time scale holds true ($\tau_{\text{early}} = \tau$) only for the "early" phase where the M–P reactions dominate over the P–P reactions. During the "late" stages however, essentially the only reactive species present is the P radicals, and hence simple bimolecular kinetics apply:

$$p(t) \approx \frac{p_\infty}{t/\tau_{\text{late}} + 1}, \ \tau_{\text{late}} \equiv 1/(k_{\text{PP}}\, P_0\, p_\infty), \qquad \left(t \gg \tau_{\text{early}} \equiv \frac{1}{k_{\text{MP}}P_0}\right) \tag{6}$$

Note that in the experiment proposed to measure polymer–polymer reaction kinetics the macroradicals and small radicals are generated in equal amounts (Scheme 1); that is, the ratio of initial densities, $r \equiv P_0/M_0$, is unity. This guarantees that after an initial transient the small radicals will virtually disappear, leaving behind macroradicals only (see eq 5). The time scale for the disappearance of these macroradicals is τ_{late} of eq 6. The expected two-stage decay is depicted in Figure 2. Experimental measurement of $\tau_{\text{late}} \sim 1/k_{\text{PP}} \sim N^\alpha$ for different *N* thus constitutes a direct measurement of the fundamental exponent α.

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