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A Model for Defect–Diffusion-Controlled Polymerization at a Surface as Typified by the Alkali-Metal Mediated Synthesis of Polysilanes

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ABSTRACT: We describe a model for polymerization at a surface, in which local kinks within the chain, excited at the free end, may diffuse to the surface, causing termination by disengagement. A model in which kinks do not interact gives a monomodal but broad distribution when kink diffusion is slow. In a more realistic model that permits kink–antikink annihilation, some of the chains escape the kink-controlled population and produce a “living”, high molecular weight fraction. A reaction for which this has been characterized is the Wurtz-type reductive coupling of organosilanes, though the phenomenon may be more general.

1. Introduction

Silicon chemistry does not allow the ready synthesis of stable precursors to polysilanes that provide the means for easy and controllable polymerization reactions such as those found in carbon chemistry. Thus, despite a continuing search for alternative synthetic procedures, most polysilanes are synthesized by the condensation of the corresponding dichlorodiorganosilane using dispersed alkali metal, usually sodium, i.e., using the Wurtz-type reductive dehalogenation reaction shown in Figure 1.¹ To this day it remains the most general and common procedure for the synthesis of polysilane homopolymers and copolymers. It is a commonplace feature of all such syntheses that the molecular weight distributions of the immediate reaction products are broad and polymodal. One such distribution, that of a poly(methylphenylsilane), (SiMePh)_n, is shown in Figure 2 and is seen to consist of low ($M_{r,w} < 1000$), intermediate ($M_{r,w} = 1000$ to 5×10^4), and high ($M_{r,w} = 5 \times 10^4$ to several million) molecular weight fractions. The formation of the low molecular weight fraction is well understood. It consists of cyclic oligomers, predominantly of cyclopentasilanes and cyclohexasilanes, respectively formed either by end-biting in the early stages of chain growth or by a back-biting reaction at any subsequent stage. However, the underlying reasons for the bimodal polymeric fraction are not easily understood. The molecular weights at peak of the polymeric fractions tabulated by Miller and Michl in their review of polysilanes² reveal the generality of this phenomenon over a wide range of polysilane polymers and copolymers prepared using the Wurtz reaction but until recently, nothing approaching a reasonable explanation has been forthcoming.

Polysilanes are not simple random coil polymers but should be viewed as consisting of a random coil of semirigid segments (a form of persistent chain). Each particular polymer is considered to have a characteristic structure that facilitates the semirigidity of the segments. Typically, in the case of (SiMePh)_n, the polymer chains have long been considered to consist of sequences

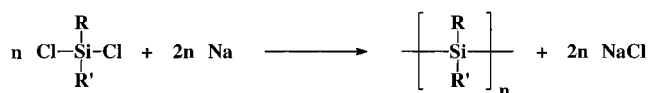


Figure 1. Scheme for sodium-surface polymerization of polysilanes.

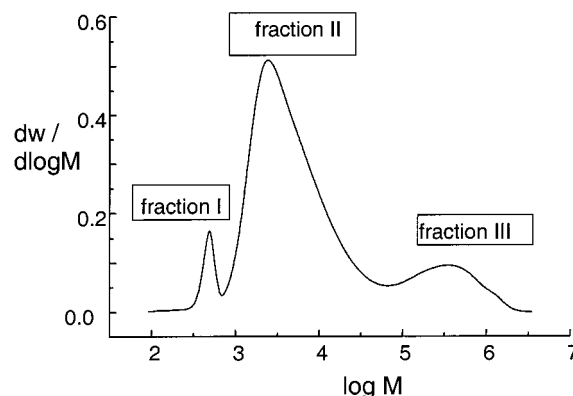


Figure 2. Representative molecular weight distribution of a poly(methylphenylsilane) prepared by Wurtz-type reductive-coupling in refluxing toluene. Reprinted from ref 8. Copyright 1998 American Chemical Society.

of silicon atoms in all-trans conformation, over which the σ -electrons of the backbone are delocalized.² These sequences are separated by strong gauche-like turns in the chain. However, this is now known to be an oversimplification, and the chain, in both the solid and solution, is best described as a random-coil consisting of a mixture of irregular P and M helical segments.³ These segments are again separated by chain defects, though in this case they consist of atoms at which reversals occur. For either description, the segments have a specific average length,^{4,5,6,7} which for (SiMePh)_n corresponds to 35 silicon atoms, a value that is in excellent agreement with the degree of polymerization at peak for the intermediate molecular weight fraction identified as the product of the Wurtz synthetic method.⁸ Illustrated by reference to (SiMePh)_n, the following descriptive model of the polymerization reaction has been developed from the above structural considerations.^{8,9} There may be other polymerization reactions

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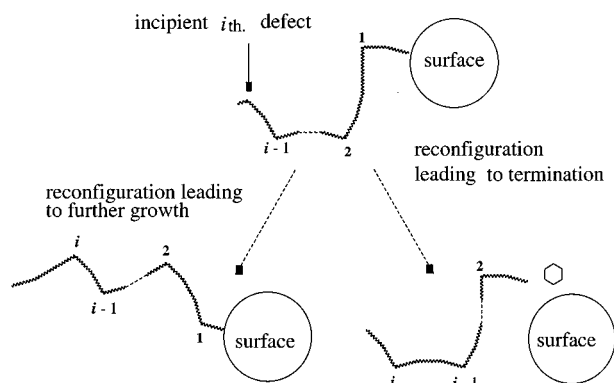


Figure 3. Schematic of the progress of a defect-diffusion-controlled, catalyzed polymerization.

in which similar influences determine the molecular weight distribution, but to the best of our knowledge, this is the first for which it has been characterized since the model requires the notion of an increasing stability with chain length up to a limiting value. That notion applies to the Wurtz-type synthesis of polysilanes.

A polymer molecule in the early stages of growth extends away from the metal surface as a semirigid sequence of increasing length. As the number of atoms in the chain increases, its stability increases as a consequence of the increasing delocalization of the σ -electrons of the backbone that is facilitated by the adoption of this structure. When the chain is on average a given number of units long (in the case of $(\text{SiMePh})_n$, 30–40 units) there is no further energetic advantage to be gained in maintaining the conformation, and it is inevitable that a defect will eventually appear, most probably at the free chain end. The chain then undergoes a conformational reorganization to minimize the energy of what are now two sequences, so the defect is translated along the chain. If it travels as far as the metal surface, the molecule is then conformationally well disposed for a backbiting reaction. If that occurs, a cyclic oligomer is clipped out, the chain disengages from the metal surface, and its growth is terminated. If it does not occur, the polymer molecule continues to grow at the metal surface, the two sequences attain the maximum stability associated with them each being on average the same defined number of units long, another defect introduces itself, and another conformational reorganization ensues. The first defect is again propelled toward the metal surface, but the probability of its getting there is reduced because of the greater overall stability associated with average sequence lengths that are determined by the distribution of two defects over double the number of units (about 70 in the case of $(\text{SiMePh})_n$). If it does reach the metal surface, then the same backbiting considerations will apply. It follows that the probability of disengagement of polymer chains from the metal surface leading to termination of growth, as represented in Figure 3, decreases with increasing chain length. Eventually, those chains that remain associated with the metal surface reach such a length that the probability of disengagement is effectively zero.

The weakness of this descriptive model is that it assumes that the chains that remain attached to the metal surface will continue to grow to a very high degree of polymerization in a termination free process. It also ignores the residual mobility of defects along the growing chain that may cause them either to terminate the polymerization or interact with each other. It does

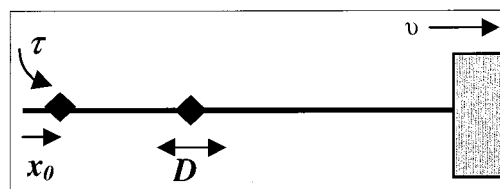


Figure 4. Illustration of the model of kink (filled diamonds) diffusion simultaneously with growing chain at a metal surface (gray rectangle).

suggest that the polymerization will have assumed living characteristics and that it is in this mode that the high molecular weight fraction is formed. However, there is nothing in the arguments presented to indicate that the polymeric fraction should be bimodal. This paper presents a mathematical analysis that demonstrates that the model is essentially valid but overlooks one vital point which, when taken into account, results in a bimodal distribution.

2. A Model for Kink Propagation and Termination

The chain itself is taken to grow by monomer addition at one end, attached to a solid surface, leaving the other end (where the chain was initiated) free in the solution. We assume that monomer is added at a rate of ν monomers per second. This may be thought of as a velocity of propagation of the surface site in the frame of reference fixed with respect to the initiation site; in what follows, we measure all distances along the chain in units of monomers. The chain continues to grow with time t with degree of polymerization $N = \nu t$ until either all monomer is exhausted or until a structural defect, which we may think of as a "kink", arrives at the metal surface.

We treat a simplified model for these general chain defects that may propagate along a polymerizing chain, though we may think of them as local gauche states in an otherwise trans-dominated chain, or as the defects separating sequences of P and M helical segments as discussed in the Introduction. In this model, they may be formed only very near the free end (this is motivated by the prohibitive requirement for cooperative motion of large pieces of chain if they are to be nucleated anywhere else) randomly at rate τ_k^{-1} . The defect-nucleation rate will depend on the details of the chain dynamics, and on the energetics of the σ -bond stabilization. These details will not affect the conclusions of the model. We take the distance of the kink nucleation site from the free end to be the (small) distance x_0 . Once nucleated, the kinks undergo one-dimensional diffusion along the polymerizing chains until they disappear at the free end (which has no effect on the chain) or at the surface (which causes the polymerization to terminate). The model is illustrated in Figure 4.

Note that the model already contains several length scales (or, equivalently, characteristic molecular weights). As well as x_0 (which is necessarily nonzero because of the absorbing boundary condition for chain defects at the free end), there is the typical distance grown by the chain in the interval between introduction of defects, $\tau_k \nu$. A third important distance scale is set by the kink diffusion. It is the distance N_c over which a kink will typically diffuse in the same time that the chain takes to convect it. This distance is therefore set by the approximate equality

$$N_c = \sqrt{Dt} = vt \quad (1)$$

Here D is the effective one-dimensional diffusion constant for the motion of defects along the polymerizing chain, v the rate of polymerization and t the time after initiation of a defect. So the critical distance is given by

$$N_c = \frac{D}{v} \quad (2)$$

Since the kinks propagate diffusively as $t^{1/2}$, while the chain grows "ballistically" as t , we might expect two regimes of behavior in molecular weight: $vt < N_c$, in which diffusing kinks rapidly kill growing chains, and $vt > N_c$, in which most chains "escape" the kinks by polymerization before they typically reach the critical length. We will find in the following that this picture holds qualitatively but not quantitatively.

A second consideration examines the interaction between the kinks themselves. In the first model we treat, they are assumed not to interact with each other, but this is not necessarily realistic. For example, gauche conformations may be of either sign; if diffusion brings two opposite defects into contact, they may annihilate. This would have an important effect on the molecular weight distribution, for if kinks self-annihilate, they will be less effective in terminating the chain. A key question to ask of both noninteracting and interacting models is whether and under what conditions the kink-termination alone is sufficient to control the entire distribution, including the high molecular weight tail. The alternative is that the long chains outstrip all effective termination by kinks nucleated at the free end, themselves only terminating in a living polymerization when the supply of monomer or growth-enabling surface is exhausted.

In this way, the model we have outlined contains both the ingredients of defect mobility and the possibility of interaction that have been left out of descriptive accounts to date. In the following part, we shall first treat the noninteracting case and then introduce kink-kink annihilation, deducing the possible forms of molecular weight distribution produced in each case.

3. Molecular Weight Distribution from Noninteracting Defects

To treat this case quantitatively, we first derive an expression for the rate at which kink defects arrive at the surface and then apply this to the calculation of a molecular weight distribution function.

3.1. Expression for the Kink Diffusion Current.

We are interested in the rate (probability) with which diffusing kinks introduced at a distance x_0 at one end of a chain of length N arrive at the other end (surface) at a time t , since it is this process that controls the MWD. (At a later point we will allow the position of this other absorbing end to propagate with time as $N = vt$.) If we know the probability distribution $p(x, t)$ for the density of kinks, then the probability current j arriving at the surface is just

$$j(N, t) = -D \frac{\partial p}{\partial x} \Big|_{x=N} \quad (3)$$

and where $p(x, t)$ satisfies the following diffusion equation and boundary conditions:

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2}, \quad p(0, t) = p(N, t) = 0; \quad p(x, 0) = \delta(x - x_0) \quad (4)$$

The probability distribution function p is readily solved by eigenfunction expansion to give

$$p(x, t) = \frac{2}{N} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi x_0}{N}\right) \sin\left(\frac{n\pi x}{N}\right) e^{-Dn^2\pi^2 t/N^2} \quad (5)$$

Substituting in eq 3 gives the expression for j :

$$j(N, t) = \frac{2\pi D}{N^2} \sum_n n \sin\left(\frac{n\pi x_0}{N}\right) e^{-Dn^2\pi^2 t/N^2} \quad (6)$$

Because for all cases of interest $x_0/N \ll 1$, we may usually take just the first term of the series expansion of the sin so that

$$j(N, t) \approx \frac{2\pi^2 D x_0}{N^3} \sum_n n^2 e^{-Dn^2\pi^2 t/N^2} \quad (7)$$

This expression may be further approximated in the two cases in which N is greater than or less than the typical diffusion distance \sqrt{Dt} . When $N \ll \sqrt{Dt}$, only the first term in the sum for j is significant and

$$j(N, t) \approx \frac{2\pi^2 D x_0^2}{N^3} e^{-D\pi^2 t/N^2} \quad (8)$$

The current of diffusers reaching the surface at N falls very rapidly in the diffusion-dominated domain as most have diffused off the chain at a fixed time t . On the other hand, for $N > \sqrt{Dt}$, the sum may be replaced by an integral and

$$j(N, t) \approx \frac{2\pi^2 D x_0^2}{N^3} \int_0^{\infty} dn n^2 e^{-Dn^2\pi^2 t/N^2} \approx \sqrt{\frac{x_0^2}{4\pi Dt^3}} \quad (9)$$

which is independent of N . So some diffusers escape far beyond the typical length and contribute to a steady termination of chains by arriving at the surface. This will be important in the following calculation of the resulting molecular weight distribution.

3.2. Molecular Weight Distribution. We will find it convenient in the first instance to calculate the complementary cumulative number distribution function, that is the probability that a randomly chosen chain has a degree of polymerization greater than N , $P_>(N)$. For chains growing at a polymerization rate v , this is equivalent to the statement that the chain has not been terminated by a time $t = N/v$. We expand this probability in a sum over the number of kinks nucleated in the chain (this approach will be useful in the case of interacting kinks in the next section). So, conceptually

$$\begin{aligned}
P_>(N) = & \text{prob}(0 \text{ kinks}) \\
& + \text{prob}(1 \text{ kink, nucleated at } t_1) \times \text{prob} \\
& \quad (\text{kink did not reach } N) \\
& + \text{prob}(2 \text{ kinks, nucleated at } t_1, t_2) \times \text{prob} \\
& \quad (\text{kinks did not reach } N) \\
& + \dots
\end{aligned} \quad (10)$$

Each term of this series has simple mathematical form. The probability that no kinks have nucleated in time t is just $e^{-t/\tau_k} = e^{-N/\nu\tau_k}$. The probability that just one kink nucleated at time t_1 is the product

$$e^{-t_1/\tau_k}(dt_1/\tau_k)e^{-(t-t_1)/\tau_k} = e^{-t/\tau_k}(dt_1/\tau_k)$$

Finally the probability that the kink did not reach the surface site at N is just $J(N, t - t_1)$, the integrated probability flux for all times later than t :

$$J(N, t) = \int_t^\infty j(N, t') dt' = \frac{2}{\pi} \sum_n \frac{1}{n} \sin\left(\frac{n\pi x_0}{N}\right) e^{-Dn^2\pi^2 t/N^2} \quad (11)$$

The general n th term in eq 10 is therefore found by integration over all the intermediate times at which the kinks may be nucleated, so the expression for $P_>$ becomes

$$\begin{aligned}
P_>(N) = & e^{-t/\tau_k} \\
& + e^{-t/\tau_k} \int_0^t \frac{dt_1}{\tau_k} J(N, t - t_1) \\
& + e^{-t/\tau_k} \int_0^t \frac{dt_1}{\tau_k} \int_{t_1}^t \frac{dt_2}{\tau_k} J(N, t - t_1) J(N, t - t_2) \\
& + \dots \\
& + e^{-t/\tau_k} \int_0^t \frac{dt_1}{\tau_k} \int_{t_1}^t \frac{dt_2}{\tau_k} \dots \int_{t_{n-1}}^t \frac{dt_n}{\tau_k} J(N, t - t_1) J \\
& \quad (N, t - t_2) \dots J(N, t - t_n) \\
& + \dots
\end{aligned} \quad (12)$$

The n integrals in the time-ordered product may be simply factorized by losing the time-ordering at the expense of dividing by the $n!$ ordering permutations. The series then becomes that of an exponential expansion, and may be exactly summed to give at $t = N/\nu$:

$$\begin{aligned}
P_>(N) = & \exp\left\{-\frac{t}{\tau_k} + \frac{1}{\tau_k} \int_0^t J(N, t - t') dt'\right\} \quad (13) \\
= & \exp\left\{-\frac{N}{\nu\tau_k} + \frac{2N^2}{\pi^3 D\tau_k} \sum_n \frac{1}{n^3} \sin\left(\frac{n\pi x_0}{N}\right) (1 - e^{-Dn^2\pi^2/N\nu})\right\} \quad (14)
\end{aligned}$$

If we are interested in the high molecular weight tail of the distribution, $N > N_c$, then the sum in the full expression for $P_>(N)$ can be replaced by an integral, arriving at the compact approximation

$$P_>(N) \simeq \exp\left\{-\frac{N}{\nu\tau_k} + \sqrt{\frac{4Nx_0^2}{\pi^2 D\nu\tau_k^2}}\right\} \quad (15)$$

Finally the weight-distribution function $f(N)$ may be calculated by $f(N) \sim -N(dP_>/dN)$, giving

$$f(N) = \Omega \left(\frac{N}{\bar{N}} - \frac{\beta}{2}\sqrt{\bar{N}}\right) e^{-(N/\bar{N} - \beta\sqrt{\bar{N}})} \quad (16)$$

where \bar{N} is the chain length set by the mean distance between successively introduced kinks $\nu\tau_k$, and $\beta = 4x_0^2/\pi^2 D\nu\tau_k^2$ which will generally be a small number. Ω is the necessary normalization. The distribution function becomes comparable to the simple exponential term when $\beta\sqrt{\bar{N}}$ is of order one, setting the condition for strong departure from simple exponential form to

$$\tau_k < \frac{x_0^2}{D} \quad (17)$$

which means that kinks are introduced at a rate that matches or exceeds their reabsorption by diffusion at the free end. If this is the case, then the single-exponential distribution, arising from the typical elimination by a kink after the waiting time τ_k , is strongly modified in favor of higher molecular weights. Alternatively, in the limit of high kink diffusion constant, the molecular weight distribution tends toward the single exponential that corresponds to waiting for only one kink to appear, (when the chain has grown to a mean degree of polymerization of $\nu\tau_k$) then rapidly to propagate to the surface, there to terminate the chain. In Figure 5, we show the single-exponential distribution function ($\beta = 0$) and the modified distribution (bold) with $\beta = 0.4$ in the approximation of eq 16. Although the extreme high molecular weight tail tends to the same exponential form as the $\beta = 0$ distribution, the peak is already considerably broader.

However, it is already clear that the noninteracting model is always controlled by kink diffusion. The distribution $P_>(N)$ always tends to 0 near-exponentially as $N \rightarrow \infty$, so the distribution $f(N)$ is automatically normalizable. This model is not an explanation of the high molecular peak observed in some experiments, where some chains seem to have escaped the kink-controlled distribution altogether.

4. Distribution from Interacting Defects

We now turn to some simple models for interacting kinks, which have a radically different behavior from the noninteracting model studied above.

4.1. Single Kink Model. In reality, kinks may self-annihilate when of opposite sign and when they come into close proximity. If this occurs, then the supply of defects able to terminate the chain will be reduced, and the average molecular weight will increase. We need to examine this case for the possibility that a dynamic phase transition occurs, permitting some fraction of the chain population to grow without bound (so that its molecular weight is governed by supply of monomer). A simple way of seeing how the mathematical structure of the problem may be modified by such a process is to consider that the efficiency of kinks in destroying a growing chain decreases with chain length, say by $e^{-\gamma'N}$. Then the leading behavior of the cumulative distribution function is just $P_>(N) \sim e^{-N/\nu\tau + \gamma'N} = e^{-(1/\nu\tau - \gamma')N}$. When $\gamma' = 1/\nu\tau$, there is a critical transition, and the limit of $P_>(N)$ as $N \rightarrow \infty$ become finite. This limit then represents that part of the distribution (which in this "toy" case is the whole distribution) that consists of growing,

living chains that have escaped from termination by kink diffusion.

First, we treat a very simple model of kink self-annihilation. We assume that only chains on which there is just one defect may be terminated by diffusion of the defect onto the surface. As soon as there are two or more defects, we assume that they self-annihilate and are no longer able to terminate the chain growth. Now our expression for $P_>(N)$ becomes (thinking at first in terms of the polymerization time t as before)

$$P_>(N) = e^{-t/\tau_k} + e^{-t/\tau_k} \int_0^t \frac{dt_1}{\tau_k} J(N, t - t_1) \quad (18)$$

$$+ \int_0^t \frac{dt_1}{\tau_k} e^{-t_1/\tau_k} \int_{t_1}^t \frac{dt_2}{\tau_k} e^{-(t_2-t_1)/\tau_k} J(N, t_2 - t_1) \quad (19)$$

The first two terms represent the survival probability of the chain in the presence of no defects, and just one defect as before. The new second term now just requires the chain to survive diffusion of the kink in the interval between the first and second defects appearing. This term now terminates the series as all higher numbers of kinks are now counted implicitly in the second term. Evaluating the terms in the series as before now gives

$$\begin{aligned} P_>(N) = & e^{-N/v_k} + 2e^{-N/v_k} \sqrt{\frac{Nx_0}{\pi D v_k^2}} \quad (20) \\ & + \frac{2}{\pi} \sum_n \frac{1}{n} \frac{N^2}{D n^2 \pi^2 \tau_k + N^2} \sin\left(\frac{n\pi x_0}{N}\right) e^{-N/v_k} \\ & - \frac{2}{\pi} \frac{N^2}{D \tau_k} \sum_n \frac{1}{n} \frac{N^2}{D n^2 \pi^2 \tau_k + N^2} \sin\left(\frac{n\pi x_0}{N}\right) e^{-N/v_k} \\ & + \frac{2}{\pi} \frac{N^2}{\tau_k^2} \sum_n \frac{1}{n} \frac{N^2}{D n^2 \pi^2 \tau_k + N^2} \times \\ & \quad \sin\left(\frac{n\pi x_0}{N}\right) e^{-N/v(1/\tau_k + D n^2 \pi^2 / N^2)} \\ & + \frac{2}{\pi} \sum_n \frac{1}{n} \frac{N^2}{D n^2 \pi^2 \tau_k + N^2} \sin\left(\frac{n\pi x_0}{N}\right) \end{aligned}$$

In this rather formidable expression (which notwithstanding has some more pleasant asymptotics), only the last term concerns the high molecular weight tail as the exponential term is missing. Expanding the sine as usual in the limit of small x_0 , the sum then becomes a standard result expressible in terms of the derivative of the γ -function. The final asymptotic result for large N is

$$\lim_{N \rightarrow \infty} P_>(N) = \frac{x_0}{\pi \sqrt{D \tau_k}} \quad (21)$$

This number is just the finite fraction of chains that escapes the kink diffusion. In this exact, if simple model, the fraction is of course not unity: the rest is contained in a rather polydisperse peaked fraction described by all the other terms in eq 20.

4.2. Multiple Kink Model. A slightly more physical model of kink interaction takes an idea from our “toy”

model but calculates with it exactly. Each kink is endowed with a decay lifetime as well as its diffusional motion. The decay rate is taken to be proportional to the rate at which new kinks are introduced to the chain. In this case we replace $J(N, t)$ with a new probability that no termination has occurred in time t :

$$J(N, t) \rightarrow J_\gamma(N, t) = 1 - e^{-\gamma t/\tau_k} + e^{-\gamma t/\tau_k} J(N, t) \quad (22)$$

The annihilation rate for kinks is taken to be γ/τ_k , so the chain is only required to survive the diffusion of the kink if the kink survives in the first place. The dimensionless number γ describes the efficiency with which kinks mutually annihilate. In this case the evaluation of $P_>(N)$ is straightforward and yields a similar (but exponentiated) behavior to the one-kink model above.

$$P_>(N) = \exp\left\{\frac{1}{\gamma}(e^{-\gamma N/v_k} - 1) + \frac{x_0}{\pi \sqrt{D \tau_k \gamma}}(1 - e^{-\gamma N/v_k})\right\} \quad (23)$$

The normalized derivative of this distribution gives the analogy of eq 16 for the weight distribution function in the multiple kink model. This distribution recovers the exponential in the case that the kink-annihilation rate $\gamma \rightarrow 0$ but in other cases picks up a finite fraction of living chain material, whose fraction of all chains is

$$P_1 = \exp\left\{-\frac{1}{\gamma} + \frac{\beta}{2\sqrt{N\gamma}}\right\} \quad (24)$$

with β defined as before. We note that the limiting asymptotic form of the distribution function taken here is the appropriate one when P_1 is finite, even though it does not recover (eq 15). For when this is so the physical limit $P_1 < 1$ sets $\zeta \equiv -1/\gamma + \beta/2\sqrt{N\gamma} < 0$. This in turn sets an upper bound on γ , while strong departure from a simple exponential distribution sets a lower bound of order unity. For values of interaction parameter γ smaller than this, the noninteracting distribution of eq 15 becomes valid. The living fraction can be increased either by increasing the kink interaction γ , or by increasing β by reducing the kink diffusion rate D or birth rate τ_k . Figure 6 shows the type of behavior predicted for one value of γ and three values of β . The molecular weight at which the “living” peak appears is entirely a matter of choice here—it depends on parameters not affecting the low molecular weight peak such as the ratio of surface sites to monomer in the reaction vessel. However, the decrease in the position of the high molecular weight peak will occur as the number of chains in the living part of the ensemble increases.

Of particular interest with regard to experimental comparison is the polydispersity of the middle mode of the distribution, as parametrized by the ratio of M_w/M_n calculated for this peak alone. The polydispersity ratio is plotted as a function of ζ in Figure 7 in the approximation of eq 23. From a near-exponential distribution coming from very strong kink-annihilation at $\zeta = 0$, the ratio grows as the kink annihilation probability drops. In the approximation, we have used in this section, values of γ less than unity are not accurate (a full enumeration of the sums generated by the multiple kink theory is possible for a more accurate crossover to the noninteracting case). But significantly, within this

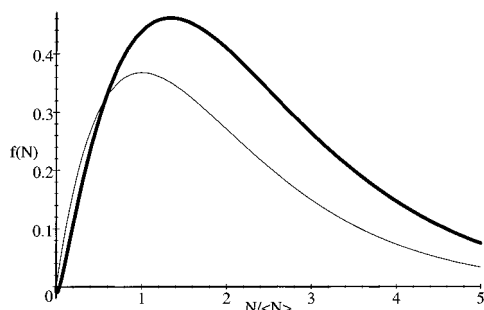


Figure 5. Predictions of the noninteracting kink model for the distribution function in the cases of fast (narrow) and slow (bold) kink diffusion (see text).

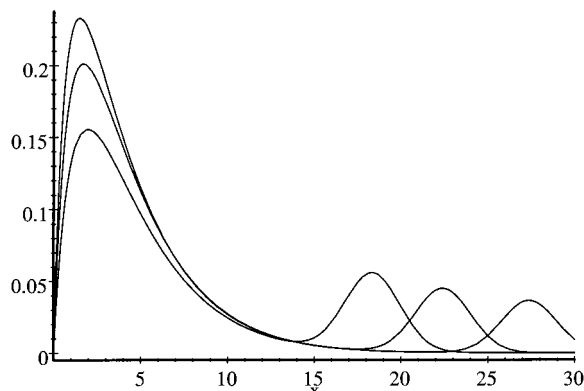


Figure 6. Predictions for the normalized molecular weight distribution of the interacting defect model for $\gamma = 0.4$ and $\beta = 0.4, 0.5$, and 0.6 (in decreasing order of high molecular weight peak). Values of the parameter ζ are 2.2, 2.1, and 2.0.

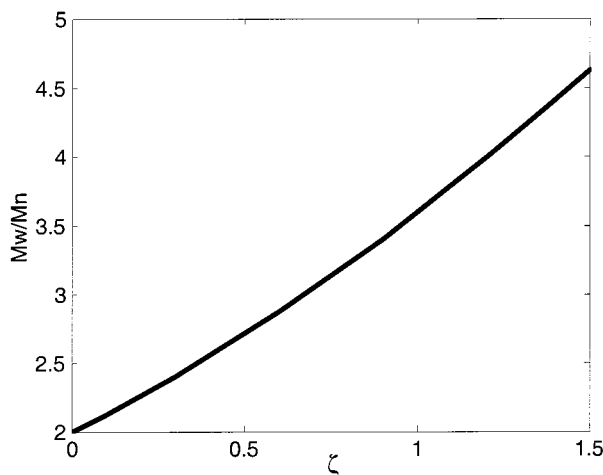


Figure 7. Predicted form of the polydispersity of the middle peak in the MWD as a function of its reduced control parameter $\zeta = (1/\gamma - \beta/2\sqrt{N\gamma})$.

physically reasonable range of values for γ , the values of the polydispersity are within the range found experimentally.⁸

One remarkable prediction of the model is that both the polydispersity of the middle mode and the amount of material in the high, living, mode are set by the one parameter ζ . The most polydisperse middle fractions should occur in those reactions with the smallest amount of material in the high molecular weight living peak. This observation suggests a simple set of experiments that would provide an immediate qualitative test.

5. Conclusions

We have a simple model for the defect–diffusion-controlled polymerization of single-site growing chains such as $(\text{SiMePh})_n$. The dominant molecular weight of the ensemble is set by the rate of polymerization and the waiting time for nucleation of the defect at the chain free end. The kink diffusion constant then affects the functional form of the distribution. Noninteracting defects, or kinks, may strongly perturb the ensemble from the Flory distribution but do not account for an observed high molecular weight “living” ensemble seen in some cases. However, two simple models of interacting defects do produce a fraction of the growing chains whose termination is not controlled by defects but by the eventual exhaustion of monomer. The model suggests quantitative and qualitative experiments.

Appendix A. Details of Noninteracting Calculations

From the expression

$$P_>(N) = \exp \left\{ -\frac{N}{v\tau_k} + \frac{2N^2}{\pi^3 D\tau_k} \sum_n \frac{1}{n^3} \sin \left(\frac{n\pi x_0}{N} \right) \left(1 - e^{-Dn^2\pi^2/Nv} \right) \right\}$$

we first take just the first term of the sin, since x_0 is small ($\ll N$), then write the second term of the sum as

$$I(\alpha) = \int_1^\infty \frac{1}{n^2} e^{-\alpha n^2} dn$$

where $I(0) = 6/\pi^2$. The parametrized integral $I(\alpha)$ satisfies

$$\frac{dI}{d\alpha} \sim -\frac{1}{2} \sqrt{\frac{\pi}{\alpha}}, \quad \alpha \lesssim 1$$

so an approximation for the sum when $\alpha = D\pi^2/Nv$ is small is

$$I(\alpha) = \frac{6}{\pi^2} - \sqrt{\pi\alpha}$$

from which the result of eq 15 follows.

Appendix B. Details of Interacting Calculations

The full expression for $P_>(N)$ in this case, using $J_\gamma(N, t)$ for J in eq 13 reads:

$$P_>(N) = \exp \left\{ \frac{1}{\gamma} (e^{-Nv\tau_k} - 1) + \frac{2N^2}{\pi\tau_k} \sum_n \frac{1}{n} \times \sin \left(\frac{n\pi x_0}{N} \right) \frac{1}{D\pi^2 n^2 + \gamma \frac{N^2}{\tau_k}} (1 - e^{-(Dn^2\pi^2/Nv + \gamma N/\tau_k)}) \right\}$$

We use the approximation for the sum

$$\sum_n \frac{1}{n^2 + a^2} \approx \frac{\pi}{2a}$$

for $a \gg 1$, where $a^2 = \gamma N^2 / D\pi^2 \tau_k = \gamma / \pi^2 (N/N_c)(N/\bar{N})$ thus is larger than unity by two factors of normalized degrees of polymerization. The result of eq 23 follows.

References and Notes

- (1) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall Inc.: Upper Saddle River, NJ, 1992; pp 186–236.
- (2) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359 and references therein
- (3) Fujiki, M.; Koe J. R. In *Silicon-based Polymers: The Science and Technology of their Synthesis and Applications*; Jones, R. G., Ando, W., Chojnowski, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000; pp 643–665; Michl, J. *J. Mol. Struct.* **2000**, *556*, 105; Michl, J.; West, R. *Acc. Chem. Res.* **2000**, *33*, 821.
- (4) Shukla, P.; Cotts, P. M.; Miller, R. D.; Russell, T. P.; Smith, B. A.; Walraff, G. M.; Baier, M.; Thiyagarajn, P. *Macromolecules* **1991**, *24*, 5606.
- (5) Welsh, W. J.; Damewood, J. R., Jr.; West, R. C. *Macromolecules* **1989**, *22*, 2947.
- (6) Strazielle, C.; de Mahieu, A. F.; Daoust, D.; Devaux, J. *Polymer* **1992**, *33*, 4174.
- (7) Sanji, T.; Sakamoto, K.; Sakurai, H. *Chem. Lett.* **1995**, 291.
- (8) Jones, R. G.; Wong, W. K. C.; Holder, S. J. *Organometallics* **1998**, *17*, 59.
- (9) Jones, R. G.; Holder, S. J. In *Silicon-based Polymers: The Science and Technology of their Synthesis and Applications*; Jones, R. G., Ando, W., Chojnowski, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000; pp 353–373.

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