Competing irreversible cooperative reactions on polymer chains

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Abstract
We analyze model processes involving competition between several irreversible reactions at the sites of a 1D, infinite, uniform polymer chain. These reactions can be cooperative, i.e., the corresponding rates depend on the state of the surrounding sites. An infinite hierarchy of rate equations is readily derived for the probabilities of various subconfigurations. By exploiting a shielding property of suitable blocks of unreacted sites, we show how exact hierarchy truncation and solution is sometimes possible. The behavior of solutions is illustrated in several cases by plotting families of “reaction trajectories” for varying ratios of reactant concentrations. As a specific application, we consider competition between coordination of ZnCl2 to pairs of oxygen atoms and to single oxygen atoms in poly(propylene oxide). The observed glass transition temperature behavior is elucidated.

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Competing irreversible cooperative reactions on polymer chains

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We analyze model processes involving competition between several irreversible reactions at the sites of a 1D, infinite, uniform polymer chain. These reactions can be cooperative, i.e., the corresponding rates depend on the state of the surrounding sites. An infinite hierarchy of rate equations is readily derived for the probabilities of various subconfigurations. By exploiting a shielding property of suitable blocks of unreacted sites, we show how exact hierarchy truncation and solution is sometimes possible. The behavior of solutions is illustrated in several cases by plotting families of "reaction trajectories" for varying ratios of reactant concentrations. As a specific application, we consider competition between coordination of ZnCl$_2$ to pairs of oxygen atoms and to single oxygen atoms in poly(propylene oxide). The observed glass transition temperature behavior is elucidated.

I. INTRODUCTION

The kinetics of chemical transformations on polymer chains has been the subject of extensive investigation over the last two decades. An important class of processes can be modeled by assuming reactions occur irreversibly at the individual sites (monomer units or pendant groups) along a polymer chain. If reaction at any site is independent of the state of the others, then the distribution of reacted sites is obviously random. However, typically, the probability of reaction at a site depends on the state of both its neighbors and sometimes as well on the second nearest neighbor, etc. The kinetics of such processes can always be described by a hierarchy of rate equations for the probabilities of various subconfigurations of sites. Although these hierarchies are finite for long (but finite) polymers, they involve many equations and so are effectively infinite. Furthermore, polymers are often modeled by infinite chains so the hierarchy becomes strictly infinite. Extension to the description of processes where reactions involve more than one site (e.g., cyclization or large ligand binding) is straightforward.

For an infinite, uniform polymer chain, it is easy to see that reaction at single sites with range $r$ blocking and further range $r'$ general cooperative effects is isomorphic to the binding of $(r+1)$-mers (to $r+1$ consecutive sites) with corresponding range $r'$ general cooperative effects. Several workers have given exact closed form solutions for $r'=1$ [nearest neighbor (nn) cooperative effects] and general $r$. More general, exactly solvable problems are discussed by Wolf. Extensions have been made to finite and semi-infinite polymers and to nonuniform polymers, e.g., binary periodic and stochastic copolymers. The common basis of the method of solution is the unreacted site shielding property: Consider a block of unreacted sites sufficiently wide that reactions are not simultaneously affected by the state of sites on both sides. Then this block shields sites on one side from the influence of those on the others. This property together with the fact that one has an exact closed hierarchy for the probabilities of "unreacted subconfigurations," and in the above cases, for unreacted $n$-tuples of sites, leads to exact hierarchy truncation.

To date, processes involving several competing irreversible reactions have received little attention. In general here one can not write a closed hierarchy for the probabilities of unreacted subconfigurations. The only exception is where the rates of reaction depend only on whether sites in the influencing environment have reacted and not on the type of reaction that they have undergone. Solution for unreacted subconfiguration probabilities is then similar to the single type reaction case (Epstein has discussed the special case of binding of n-mers of various lengths to a polymer chain). Here we analyze more general irreversible processes involving competing reactions. The only such previous analysis involved formal "density" (conversion) expansions for which convergence problems can arise.

In this work we show that the unreacted site shielding property, as stated above, is still valid and in some cases leads to exact hierarchy truncation and solution in closed form. In Sec. II, we consider processes involving several competing irreversible reactions at single sites, with nn cooperative effects, on an infinite, uniform polymer chain. An explicit proof of shielding is given together with the exact solution. Generic cases considered in detail include poisoning of an autoinhibitory by a random reaction, and competition between two autoinhibitory reactions. In Sec. III, we discuss the extension of this analysis to more general reactions and cooperative effects. We consider in detail competition between a single site reaction and a cyclization reaction (involving $n$ pairs of sites), both with $n$ cooperative effects. In Sec. IV this particular model is applied to the analysis of competition between coordination of ZnCl$_2$ to pairs of oxygen atoms and to single oxygen atoms in poly(propylene oxide). Experimentally observed glass transition temperature behavior associated with varying degrees of coordination is elucidated. Some brief concluding remarks are made in Sec. V together with indication of the applicability of these analyses.
The following notation is used. The probability of finding a subconfiguration \( \sigma \) is denoted \( f_\sigma \). We sometimes refer to the conditional probabilities \( q_{\sigma,\sigma'} / f_\sigma \) of \( \sigma \) given \( \sigma' \). For typographic reasons, empty conditioning sites \( \bar{0} \) are sometimes denoted by \( \phi \). Translational invariance is always assumed.

II. COMPETING IRRERVERSIBLE REACTIONS AT SINGLE SITES ON A POLYMER CHAIN: NN COOPERATIVE EFFECTS

A. Exact solution for \( N \) competing reactions

We consider here a process on an infinite, uniform polymer chain where each site can undergo any one of \( N \) types of competing irreversible reactions denoted \( 0 \rightarrow 1,0 \rightarrow 2, \ldots, 0 \rightarrow N \). Furthermore, we suppose that the probability of reaction at a site depends on the state of both its neighbors (only). The corresponding rates for \( 0 \rightarrow \bar{i} \) \( (i = 1, 2, \ldots, N) \) are denoted by \( r_{ik} \) where \( j(k) = 0, 1, \ldots, N \) is the state of the left-(right)-hand neighbor. Thus, in general, there are \( N(N+1)^2 \) such independent rates [or \( 1/N(N+1)(N+2) \) with reflection symmetry]. It is also convenient to define

\[
\tau_{ik} = \sum_{j=0}^{N} r_{ij} f_{kj},
\tag{2.1}
\]

the total reaction rate for a site given its left-(right)-hand neighbor is in state \( j(k) \).

Hierarchical rate equations for the probabilities of various subconfigurations (which are translationally invariant) can be written down intuitively. For example,

\[
\begin{align*}
\frac{d}{dt} f_{00} & = - \sum_{k=0}^{N} \tau_{k0} f_{k0} + \sum_{l=0}^{N} \tau_{l0} f_{0l} , \\
\frac{d}{dt} f_{0i} & = - \sum_{k=0}^{N} \tau_{ik} f_{k0} + \sum_{l=0}^{N} \tau_{il} f_{0l}, \\
\frac{d}{dt} f_{i0} & = - \sum_{k=0}^{N} \tau_{ki} f_{0k} + \sum_{l=0}^{N} \tau_{il} f_{0l}, \\
\frac{d}{dt} f_{ij} & = + \sum_{k=0}^{N} \tau_{ki} f_{k0} - \sum_{l=0}^{N} \tau_{il} f_{0l} + \sum_{k=0}^{N} \tau_{ik} f_{0k} - \sum_{l=0}^{N} \tau_{il} f_{0l} + \sum_{k=0}^{N} \tau_{ik} f_{k0},
\end{align*}
\tag{2.2}
\]

where \( 1 \leq i,j \leq N \).

Note that we have not assumed reflection invariance of the rates. The basis of the truncation method of solution for this hierarchy is the "shielding property" of an adjacent pair of unreacted sites (i.e., these shield sites on one side from the effect of those on the other). The proof of this property is discussed in a very general context in Ref. 3 and is based on consistency with respect to the hierarchy equations. For completeness, a more explicit proof for the quantities of interest here is given in Appendix A.

The key shielding results used here are that

\[
q_{00k} (== f_{00k} / f_{00}) = q_{00i} (== f_{00i} / f_{00}),
\tag{2.3}
\]

where \( k,l = 0, 1, \ldots, N \), together with an analogous identity for the corresponding reflected quantities. The closed equations for this set of \( q \)'s follow from the \( q \)-hierarchy equations given in Appendix A and are

\[
\begin{align*}
\frac{d}{dt} q_{00} & = - \tau_{00} f_{00} \quad \text{(note that } q_{00} = q_{000}), \\
\frac{d}{dt} q_{0i} & = - \tau_{0i} f_{0i} + \tau_{i0} q_{i0} + \sum_{k=0}^{N} \tau_{ik} q_{0k}, \\
& \quad \text{where } 1 \leq i \leq N,
\end{align*}
\tag{2.4}
\]

and analogous "reflected" set of equations for \( q_{i0} \). Note first that Eq. (2.4a) has precisely the same form as for the case of a single type of reaction.\(^{10,11}\) Second, we mention that the above \( q \)'s are not all independent, since by conservation of probability

\[
\sum_{i=0}^{N} q_{i0} = 1.
\tag{2.5}
\]

This is consistent with Eq. (2.4) which, when summed, gives

\[
\frac{d}{dt} \left( \sum_{i=0}^{N} q_{i0} \right) = \left( \sum_{i=0}^{N} \tau_{i0} q_{i0} \right) \left( \sum_{i=0}^{N} q_{i0} - 1 \right).
\tag{2.6}
\]

Using Eq. (2.5), one of the equations in Eq. (2.4) can, of course, be eliminated.

It is clear from Eq. (2.5) that at least one of \( q_{i0} \), \( i = 1, 2, \ldots, N \), must be nonzero at \( t = \infty \). However, typically only a subset of these \( q \)'s, characterized below, is nonzero. Suppose first that \( \tau_{ik} < \tau_{j0} \) for \( k = 1, 2, \ldots, N \) (except \( i^* \)). Then we have shown in Appendix B that \( q_{i^*00} = 1 \) and \( q_{i0} = 0, k = i^* \) at \( t = \infty \). More generally, if several \( \tau_{i0}, i \in E \) \( (C \subseteq \{1, 2, \ldots, N\}) \) are equal and less than the rest, then \( q_{i0} \) (or \( q_{j0} \)) > 0 only for these \( i \in E \) and their values depend on the other rates.

To solve Eq. (2.2) for \( f_{00}, f_{0i}, f_{ij}, \) and \( f_{ij} \) as functions of time, we must simply substitute into the right-hand side the identities

\[
\begin{align*}
f_{00} & = q_{00} f_{00}, \\
f_{0i} & = q_{0i} f_{00}, \\
f_{i0} & = q_{i0} f_{00}, \\
f_{ij} & = q_{ij} f_{00}.
\end{align*}
\tag{2.7}
\]

and integrate the resulting set of equations together with Eq. (2.4) (which close the set). Just as for the \( q \) equations, some of the \( f \) equations can be eliminated using conservation of probability, e.g.,

\[
\begin{align*}
s_{00} & = f_{00} - \sum_{j=0}^{N} f_{0j}, \\
s_{m0} & = f_{m0} - \sum_{j=0}^{N} f_{0j} - \sum_{j=0}^{N} f_{0j} + \sum_{j=0}^{N} f_{0j},
\end{align*}
\tag{2.8}
\]

From the above quantities, it is possible to also determine exactly

\[
f_{00} = q_{00} (q_{00})^{n-2} f_{00}, \quad n > 2
\tag{2.9}
\]

for any \( i,j \).

Note that since \( f_{i0}, f_{ij} \), \( i,j \neq 1 \), can not be determined from the above \( f \)'s, it may be convenient to add the equations

\[
\begin{align*}
\frac{d}{dt} f_{i0} & = \sum_{k=0}^{N} \tau_{ik} f_{k0}, \\
\frac{d}{dt} f_{ij} & = \sum_{k=0}^{N} \tau_{ik} f_{k0} + \sum_{l=0}^{N} \tau_{ik} f_{l0},
\end{align*}
\tag{2.10}
\]
which close together with the above set. Obviously we still cannot determine all subconfiguration probabilities from the above quantities. For example, one cannot determine \( f_{a_i} \) \((i,j,k \neq 0,0,0)\), probabilities for larger clusters of reacted sites. Analogous difficulty for the case of single type of reaction has been noted by several authors and this problem was first solved exactly by Plate et al.\textsuperscript{11} The essential feature (as discussed in Ref. 3 in a general context) is that larger hierarchies for probabilities of disconnected configurations must be exactly truncated (using shielding) and integrated with the minimal set of closed equations. The same approach is required for this more general problem and is quite straightforward so details are not given. The two-site and other correlations will exhibit the same sort of large separation “fast” asymptotic decay as discussed in Ref. 12.

B. An example: Two competing reactions

Here we restrict our attention to the special case of two competing irreversible reactions, denoted \( 0 \rightarrow a \), \( 0 \rightarrow b \) (replacing \( i = 1, 2 \)). We also assume that the polymer is initially completely unreacted and that the rates have reflection symmetry (so 12 generally independent rates are required as input to our equations). These assumptions guarantee that subconfiguration probabilities are invariant under reflection (of the subconfiguration).

From the preceding analysis, it should be clear that a minimal closed set of equations can be obtained for

\[ q_{0a0}, q_{0b0}, f_{0a}, f_{0b}, f_{a0}, f_{b0} \]

(or the corresponding quantities with “a” replaced by “b”). Solution of these equations also allows one to evaluate

\[ p_{0a0}, p_{0b0}, f_{0a}, f_{0b}, f_{a0}, f_{b0}, p_{n0} \]

for \( n > 1 \) \((0_n\) represents an \(n\)-tuple of unreacted sites) and corresponding (equal) reflected quantities. It is convenient to add the equation for \( f_s \) which closes with the above set and allows one to calculate in addition \( f_a, f_b \). Adding the equation for \( f_{bo} \) also yields \( f_{bo}, f_a, f_b \).

In the specific cases discussed below, we assume that the rates are proportional to the \( a \)- \((b)\) reactant concentrations \( c_a/c_b \) and the rates prescribed are for unit concentrations. We shall typically plot the “reaction trajectories” in the \((f_a, f_b)\) plane for various \( c_b/c_a \). To elucidate the behavior of solutions in various cooperativity regimes, it will often prove useful to examine their behavior in the corresponding limiting cases.

First we consider competition between a random reaction \( 0 \rightarrow b \) [all rates equal \( \tau \)] and a highly autoinhibitory reaction \( 0 \rightarrow a \) with rates \( \tau, \epsilon \tau, \epsilon^2 \tau \) for \( 0, 1, 2 \) \( a \)-reacted \( nn \), where \( \epsilon < 1 \), irrespective of the number of \( b \)-reacted \( nn \). When \( c_b = 0 \), the \( 0 \rightarrow a \) reaction occurs in three stages: reaction of sites with 0, 1, 2 reacted \( nn \) and final conversions \( \frac{1}{2}(1 - e^{-2}) \), \( \frac{1}{2}(1 - e^{-2}) \), 1 consecutively.\textsuperscript{2,3,13} This is reflected in the reaction trajectories for infinitesimal \( \epsilon \), varying \( c_b/c_a \) (Fig. 1). Corresponding behavior away from the limit is shown in Fig. 2 where \( \tau_{00}, \tau_{01}, \tau_{a0}, \tau_{ab}, \tau_{ba} \) correspond to reaction of CH\(_3\) SOCH\(_2\)Na onto atactic PMMA.\textsuperscript{14}

Second we consider competition between two highly autoinhibitory reactions \( 0 \rightarrow a \) with rates \( \tau, \epsilon \tau, \epsilon^2 \tau \) for \( 0, 1, 2 \)

\( a \)-reacted \( nn \) where \( \epsilon < 1 \) and \( 0 \rightarrow b \) (with rates \( \tau, \epsilon \tau, \epsilon^2 \tau \) for \( 0, 1, 2 \) \( b \)-reacted \( nn \)). Thus \( b \)-reacted \( nn \) do not affect \( 0 \rightarrow a \) and vice versa. Here we have the symmetry property that if \( (f_a, f_b) \) \((\theta_1, \theta_2)\) is on the \( c_a/c_b = \alpha \) trajectory, then \( (f_a, f_b) \) \((\theta_2, \theta_1)\) is on the \( c_a/c_b = \alpha \) trajectory. We have plotted the reaction trajectories, for infinitesimal \( \epsilon \), in Fig. 3.

As the trajectory behavior is complicated here, some features deserve further comment. When \( c_a/c_b = 0(1) \), the first stage of the process corresponds to \( 0 \rightarrow a \) and \( 0 \rightarrow b \) reaction with no \( a \)- \((b)\) reacted \( nn \) and at the end of which \( f_s = f_0 \) \((s = s, \) say). The minimum \( s \approx 0.408 \) occurs when \( c_a/c_b = 1 \) and the maximum \( s \approx 0.432 \) when \( c_b/c_a \rightarrow 0 \) \( \infty \). At the end of this stage, “0” appears only in \( ab0 \) or \( b0a \) subconfigurations so clearly these then react such that \( \partial f_{ab}/f_{00} = c_a/c_b \) (i.e., the trajectories are linear). The zig-zag trajectory of the case where \( 1 > c_b/c_a > \epsilon \) is particularly interesting. Here reactions \( 0 \rightarrow a \) dominates up to conversion \( \theta \approx f_a \approx \frac{1}{2}(1 - e^{-2}) \) where there are no remaining triples 000.\textsuperscript{2} Here \( f_{aa0} \approx f_{00} \approx e^{-2}, f_{aa0} \approx e^{-1} \) \( 1 - e^{-2} \). Since further \( 0 \rightarrow a \) reactions would have at least one \( a \)-reacted \( nn \), instead \( 0 \rightarrow b \) now dominates creating \( aba, ab0a, \) and \( ab0a \) subconfigurations \( \text{so } f_j \) increases to \( \frac{1}{2}(1 - e^{-2}) \). Finally \( 0 \rightarrow a \) occurs at remaining \( b0a, ab0b, \) subconfigurations.
The above discussion and Fig. 3 shows that reaction trajectories can intersect. This has important ramifications for formal density expansions. Similar crossing behavior for a specific (nonlimiting) choice of rates is shown in Fig. 4.

An example of competition between autoinhibitory reactions for physically reasonable rates is shown in Fig. 5. Notice the similar features to the above limiting case. The unusual behavior of $q_{a|a}$ vs $q_{b|b}$, for various $c_a/c_b$, described previously in a general context, is shown in Fig. 6. Various probabilities are plotted as a function of total conversion $\theta = f_a + f_b$ for $c_a/c_b = 0.25$ in Fig. 7.

III. OTHER COMPETING IRREVERSIBLE REACTIONS

The method of proof of the unreacted site shielding condition and corresponding exact hierarchy truncation procedure described for the special process of Sec. II have more general applicability. It is not difficult to see that if one can exactly solve the hierarchy equations separately for each of several types of competing irreversible events, then one can also solve them for a process involving competition between these. Here we consider only competition between irrevers-
ible cyclization of (or binding to pairs of) $nn$ sites $00\rightarrow bb$ and a single site reaction $0\rightarrow a$, both with $nn$ cooperative effects. The rates for $00\rightarrow bb$ ($0\rightarrow a$) are denoted $\tau^0_{\sigma\sigma'}(\tau^a_{\sigma\sigma'})$ where $\sigma$, $\sigma' = 0, a, b$.

The hierarchial rate equations for the (translationally invariant) probabilities are

$$\frac{d}{dt} f_0 = -2\sum_{\sigma,\sigma'} \tau^0_{\sigma\sigma'} f_{0\sigma\sigma'} - \sum_{\sigma'} \tau^0_{0\sigma'} f_{0\sigma0}$$

$$\frac{d}{dt} f_a = \sum_{\sigma,\sigma'} \tau^a_{\sigma\sigma'} f_{a\sigma\sigma'}$$

$$\frac{d}{dt} f_{0\sigma0} = -\sum_{\sigma'} \tau^0_{0\sigma0} f_{0\sigma0\sigma'} + \tau^0_{0\sigma0} f_{0\sigma0\sigma}$$

where $\Sigma_\sigma$ denotes summation of $\sigma$ over $0, a, b$.

For this process a triple of unreacted sites shield completely, as may be shown by an analysis similar to Appendix A. Specifically, such an analysis shows that, e.g.,

$$q_{0,0,0} = f_{0,0,0} = q_{0,0,0}$$

and

$$q_{a,0,0} = f_{a,0,0}/f_{a,0} = q_{a,0,0}$$

for $n \geq 3$ and $\sigma = 0, a, b$.

(3.2)

together with analogous identities for corresponding reflected quantities (note that $q_{0,0,0} = q_{0,0,0}$). Furthermore one has that

$$\frac{d}{dt} \ln q_{0000} = (\frac{d}{dt} f_{0000})/f_{0000} - (\frac{d}{dt} f_{0000})/f_{0000}$$

$$= - (\tau^0_{000} + \tau^0_{00})$$

$$\frac{d}{dt} \ln q_{a000} = (\frac{d}{dt} f_{a000})/f_{a000} - (\frac{d}{dt} f_{a000})/f_{a000}$$

$$= - (\tau^a_{a0} + \tau^a_{a0}) + (q_{0000} + 1)\sum_{\sigma} \tau^0_{a0} q_{0000}$$

$$+ (\frac{q_{a000}}{q_{0000}} + 1)\sum_{\sigma} \tau^a_{a0} q_{a000}$$

and a similar equation holds for $q_{a000}$. Note that

$$q_{0000} + q_{a000} + q_{a000} = 1$$

which closes Eq. (3.3) for $q_{0000}, q_{a000}$. Using Eqs. (3.1), (3.2), and (3.3) and conservation of a probability [e.g., Eq. (3.4)], an exact closed set of equations may be obtained for $f_0 f_{0000}, f_{a0} f_{a000}, f_{a0} f_{a000}, q_{0000}, q_{a000}, q_{a000}$, and the corresponding reflected quantities. (Alternatively a closed set of equations could be obtained for a corresponding subset of $f$'s and $q$'s involving only sites specified 0 and/or $b$.) Equations for other $f$'s can be added, e.g., that for $f_a$ closes with the above set. Below we analyze several special cases for reaction on an initially completely unreacted polymer chain and for reflection invariant rates (and thus $f$'s). In the specific cases discussed below, we assume that the $0\rightarrow a$ rates are proportional to the $a$-reactant concentration $c_a$. The $00\rightarrow bb$ rates are assumed proportional to $c_{bb}$ which represents a reactant concentration or is set to unity as, e.g., with cyclization where no external reactant is involved. Rates prescribed below are for unit concentrations. Again "reaction trajectories" are plotted varying $c_a/c_{bb}$ for several cooperatively regimes (usually in the appropriate limits).

First we consider the case where both $0\rightarrow a$ and $00\rightarrow bb$ occur randomly (with equal rates when $c_a/c_{bb} = 1$, say) (see Fig. 8). The low $c_a/c_{bb}$ regime might correspond to poisoning of the Flory dimer filling problem [i.e., of poly(methyl-vinyl ketone condensation)] and the high $c_a/c_{bb}$ regime to poisoning of random single site reaction by cyclization. Second we consider the competition between a random reaction $0\rightarrow a$ (all rates equal $\tau$) and a highly autoinhibitory reaction $00\rightarrow bb$ (with rates $\tau, \tau, \tau, \tau$ for 0, 1, 2 $b$-reacted $nn$ where $c < 1$). When $c_a = 0$, $00\rightarrow bb$ reaction occurs in three stages: reaction of pairs of sites with 0, 1, 2 reacted $nn$ and final conversions $0.549$ (0...), $0.648$ (6...), $0.802$ (2...), respectively. (These values were obtained from the analysis in Ref. 16 of the isomorphic process of monomer filling with $nn$ blocking and highly autoinhibitory second $nn$ rates.) This staged filling behavior is reflected in the reaction trajectories varying $c_a/c_{bb}$. These are plotted, for infinitesimal $\epsilon$, in Fig. 9.
Finally we consider the competition between a highly autoinhibitory reaction 0→a (with rates $r_{ca}$, $r_{ca'}$, $r_{ca''}$ for 0, 1, 2 a-reacted nn where $c<1$) and a random reaction 0→bb (all rates equal $r$). Reaction trajectories, for infinitesimal $\epsilon$, plotted in Fig. 10. When $c_a/c_{bb} = 0.1$, the first stage of the process corresponds to random 0→a reaction at sites with no a-reacted nn competing with random 0→bb reaction. Note that when $c_a = c_{bb} = 2f_a$ throughout this stage. This obvious from an “event lattice” picture of the process [see Fig. 11] where 0→bb is represented by 0→b* on sites between the physical polymer sites. The process is “symmetric” in 0→a and 0→b*.

At the end of this stage the only remaining sites have nn either $a$ or $b$ reacted so the process proceeds via 0→a reaction to completion. The case where $\epsilon^{-1}c_a/c_{bb} > 1$ is particularly interesting. Here reaction 0→a dominates up to a conversion $\theta \approx f_a \approx (1 - \epsilon^{-2})$ where there are no remaining triples 000 and $f_{000} \approx \epsilon^{-2}$. Since further 0→a reactions would have at least one $a$-reacted nn, instead 0→bb dominates (specifically, $a00a\rightarrow abba$) so $f_a$ increases to $\approx 2\epsilon^{-2}$. Finally 0→a occurs at the remaining $a0a$ subconfigurations. Other features of Fig. 10 can be similarly explained.

IV. COORDINATION OF ZINC HALIDES WITH POLY(PROPYLENE OXIDE): ANALYSIS OF GLASS TRANSITION TEMPERATURE DATA

Here we apply the model of the preceding section to analyze in detail a specific process involving ZnCl$_2$ coordination to poly(propylene oxide). Observed behavior of the glass transition temperature (see below) is adequately reproduced (admittedly by appropriate choice of several parameters).

The temperature $T_g$ at which a polymer undergoes a transition from a glassy/brittle state to a rubbery state is called the glass transition temperature. Considerable unrestrained localized segmental (micro-Brownian) motion can occur above $T_g$. It has been shown that addition of metal salts to amorphous poly(propylene oxide) PPO(L) often creates a single phase complex with elevated $T_g$. In Fig. 12, we have displayed the experimental $T_g$ data of James et al. for PPO(L)-ZnCl$_2$ complexes prepared with various mole fractions $m$ of the salt [with respect to moles of the monomer repeat unit in PPO(L)].

The observation that $T_g$ levels out at $m \approx 0.35$ motivated the working hypothesis that most ZnCl$_2$ molecules are coordinated to two oxygen atoms (see Fig. 13), i.e., a single cyclization reaction 00→bb, say, occurs. Elevation of $T_g$ caused by the consequent stiffening of the polymer chain can be modeled by the Gordon–Taylor–Wood equation\textsuperscript{16,19}

$$kW_{bb}(T_g - T_g^0) + W_0(T_g - T_g^0) = 0,$$

(4.1)

where $W_{bb}, W_0 = 1 - W_{bb}$ are weight fractions of coordinated (uncoordinated) units, respectively, so here $W_{bb}: W_0 = 126 f_a : 58 f_a$. Also

$$f_a + f_b = 1, \quad m = f_a/2,$$

(4.2)

and $k = 0.3, T_g^0 = 208$ K, $T_g^b = 400$ K (the latter chosen to fit experimental data). Equations (4.1) and (4.2) reproduce $T_g$ accurately up to $m \approx 0.25$ (see Fig. 13).

The limitation of the above analysis should be obvious. First we remark that above the value of $m$ for which no further coordination occurs, ZnCl$_2$ forms a second phase and $T_g$ should remain constant. Now if ZnCl$_2$ coordination occurs only to pairs of oxygen atoms and is not autocatalytic, an upper bound on $f_a$ of $1 - \epsilon^{-2} - 0.846 (m - 0.432)$ follows from Flory’s work.\textsuperscript{15} Since $T_g$ still increases slightly above this value, James et al.\textsuperscript{16} conclude that ZnCl$_2$ must also be able to coordinate to single units causing a further slight increase in $T_g$. Thus the process is actually of the type described in Sec. III involving competition between coordination to pairs 00→bb and to single units 0→a, the former having a much greater effect on $T_g$ and dominating the process for low $m$. Consequently, we expect $T_g$ to be described more accurately by a relationship of the form

$$kW_{bb}(T_g - T_g^b) + k'W_b(T_g - T_g^0) + W_0(T_g - T_g^0) = 0,$$

(4.3)

where $W_{bb}, W_a, W_0$ are the weight fractions of $b$-coordinated, $a$-coordinated, and uncoordinated units, respectively so $W_{bb} : W_a : W_0 = 126 f_a : 194 f_a : 58 f_a$. Equation (4.3) reproduces...
the correct low m behavior irrespective of the as yet unchosen values of $k'$ and $T_g^*$ since $W_a \equiv 0$ there. Here Eq. (4.3) is supplemented by the relationships

$$f_0 + f_a + f_b = 1, \quad m = f_s/2 + f_a$$

(4.4)

(the latter assumes all ZnCl$_2$ are coordinated).

Finally we consider the cooperativity required to reproduce $T_g$. If 00→bb coordination was random (and initially dominated 0→a), one would expect Eqs. (4.1) and (4.2) to be accurate up to $f_0 \approx 0.864$ ($m \approx 0.432$). Instead, marked deviation at $f_0 \approx 0.54$ ($m \approx 0.27$) suggests that 00→bb occurs with highly autoinhibitory nn cooperative effects (no doubt, at least in part due to steric hindrance) whence 00→bb first occurs on sites with no coordinated nn up to conversion $f_0 \approx 0.549$ (see Sec. IIII). To achieve deviation for higher m, we assume that next the processes b 000b→bbbb 0b or b 0bbb and b 000b→b 0a0b dominate and are competitive. After completion of this stage, we suppose that b 000b→bbbb and b 000b→baob are competitive and finally 0→a occurs on remaining isolated reacted sites. The details of the latter two stages are obviously speculative. The point we wish to emphasize, however, is that analysis of the model of Sec. III is clearly required for a quantitative understanding of this process and can explain the observed behavior.

To obtain explicit results from the model of Sec. III, the following somewhat arbitrary assignments are made. For $T_g$

$$[\text{CH}_2-\text{CH}=0]_n$$

ZnCl$_2$ to a pair of oxygen atoms in poly(propylene oxide).

FIG. 13. Coordination of ZnCl$_2$ to a pair of oxygen atoms in poly(propylene oxide).

V. DISCUSSION

Although the processes considered here have much more structure than those analyzed previously with a single type of reaction, in certain fundamental cases we have still been able to obtain exact solutions. The use of an unreacted site shielding property was central to achieving the required exact hierarchy truncation. Although all previous detailed analyses of irreversible cooperative processes on polymer chains deal with single reactions, there are doubtless many cases where this is an oversimplification. Also competitive reaction offers the possibility of creating copolymers of various compositions and hopefully the results presented here would facilitate such preparations. Given the generality of the applicability of these models, most of the specific results presented were for several generic types of competitive reaction. However, the analysis provided of ZnCl$_2$ coordination on PPO(L) illustrates their utility in treating specific processes. We also remark that results obtained here should provide insight to the behavior of corresponding processes on higher dimensional lattices, e.g., competitive irreversible coadsorption on a 2D (substrate) lattice. Approximate hierarchy truncation techniques could be developed from those of Ref. 3.

APPENDIX A

Let $q_0$ denote an n tuple of unreacted sites. Then using

$$d/dt \ln q_{\alpha \alpha'} = S(\sigma + \alpha') - S(\alpha'),$$

(A1)

where $S(\alpha') = (d/d\tau_{\alpha'})/(f_{\alpha'})$, and suitably rewriting terms on the right-hand side where appropriate, one obtains, for $n \geq 2$,

$$d/dt \ln q_{0 \alpha} = - \sum_{i=0}^{\alpha-1} \tau_{i \alpha} (q_{i+1 \alpha} - q_{i \alpha}) - \sum_{i=0}^{\alpha} \tau_{0 i} (q_{\alpha+1 \alpha} - q_{\alpha \alpha})$$

$$- \tau_{00}$$

(A2a)

and note that $q_{0 \alpha} = q_{\alpha 0}$.
\[ \frac{d}{dt} \ln q_i \delta^k_i = -\sum_{k=0}^{N} \tau_{0k} (q^k_{\delta^k_k} - q^k_{\delta^k_k}) \\
\quad - \tau_{0i} + \sum_{k=0}^{N} \tau_{ik} q_k \delta^k_i \\
+ \sum_{k=0}^{N} \tau_{ik} q_k \delta^k_i q^k_0 \delta^k_i / q^k_i \delta^k_i, \quad i \neq 0, \]

\[ (A2b) \]

\[ \frac{d}{dt} \ln q_i \delta^k_{ij} = \sum_{k=0}^{N} \tau_{0k} (q^k_{\delta^k_k} - q^k_{\delta^k_k}) \\
- \tau_{0i} + \sum_{k=0}^{N} \tau_{ik} q_k \delta^k_{ij} \\
+ \sum_{k=0}^{N} \tau_{ik} q_k \delta^k_{ij} q^k_0 \delta^k_{ij} / q^k_i \delta^k_{ij}, \quad i, j \neq 0. \]

\[ (A2c) \]

Analogous reflected sets of equations hold for \( q^k_{\delta^k_i} \) and \( q^k_{\delta^k_i} \), \( i, j \neq 0. \)

By inspection, it is clear that a set of solutions to these equations satisfies:

\[ q_0 \delta^k_i = q_{00} \delta^k_i, \quad q_i \delta^k_i = q_i \delta^k_i, \quad i \neq 0 \text{ for } n > 2. \]

We assume this is the unique solution.

**APPENDIX B**

Using Eq. (2.5), it is convenient to rewrite Eq. (2.4b) as

\[ \frac{d}{dt} q_{l+\delta} = \sum_{k=0}^{N} \tau_{k0} (q^k_{\delta^k_k} - q^k_{\delta^k_k}) \\
+ \sum_{k=0}^{N} \tau_{ik} q_k \delta^k_{ij} q^k_0 \delta^k_{ij} + \text{positive terms}. \]

\[ (B1) \]

Suppose \( \tau_{i+0} < \tau_{k0} \) for \( k = 1, 2, \ldots, N \) (except for \( l * \)). Then from Eq. (B1),

\[ \frac{d}{dt} q_{l+\delta} = \{\tau_{00} - \tau_{l+0}\} q_{00} q_{l+\delta} + \sum_{k=0}^{N} \tau_{00} (q^k_{\delta^k_k} - q^k_{\delta^k_k}) + \text{positive terms} \]

\[ (B2) \]

where the second term is also strictly positive (for finite time). If also \( \tau_{00} < \tau_{l+0} \), then \( \frac{d}{dt} q_{l+\delta} > 0 \) for \( l < \infty \) so \( q_{l+\delta} \) is strictly positive for \( t < \infty \). Suppose next that \( \tau_{00} < \tau_{l+0} \), and that \( q_{l+\delta} \) goes to zero as \( t \to \infty \). Then clearly the first (negative) term in Eq. (B1) must dominate the others for large \( t \). However since \( q_{l+\delta} \) is strictly positive for some \( k * \) and

\[ (B3) \]

for large times, this is not possible. Thus we conclude, in this case also, that \( q_{l+\delta} \) is also positive. From this we conclude that \( q_{l+\delta} \) is strictly positive for some \( l \leq L \) as \( l \to \infty \).

It should be clear that when several \( \tau_{l+0} \) are less than the rest, then \( q_{l+\delta} \) is strictly positive for only these \( l \leq L \) as \( l \to \infty \).