1983

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Irreversible reaction on a polymer chain with range two cooperative effects

Abstract
We consider the kinetics of an irreversible reaction at the sites of an infinite, uniform, 1D polymer chain with first and second nearest neighbor (nn) cooperative effects. The special cases with just nn cooperative effects, and with nn blocking and general second nn cooperative effects have previously been solved exactly. For the latter case, we present several new results for highly autoinhibitory and autocatalytic rates. The general problem cannot be solved exactly but we apply the techniques of the preceding paper, which for this process exploit a shielding property of quadruples of unreacted sites, to obtain approximate solutions. Various cooperativity regimes are considered.

Keywords
Polymers, Polymerization, Solution processes

Disciplines
Biological and Chemical Physics | Physics

Comments
Irreversible reaction on a polymer chain with range two cooperative effects

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(Received 14 December 1982; accepted 2 August 1983)

We consider the kinetics of an irreversible reaction at the sites of an infinite, uniform, 1D polymer chain. Except for a general discussion by Wolf, previous treatments based on exact hierarchical rate equations for probabilities of various subconfigurations of sites have assumed either just nearest neighbor (nn) cooperative effects, or range r blocking and (r + 1)th nn cooperative effects. These problems are exactly solvable. The process considered here, with general range 2 cooperative effects, is of particular interest being the simplest such irreversible process not amenable to exact solution. It is also of practical interest, e.g., in the determination of the perturbative influence of second nn cooperative effects on the kinetics, final yields etc.

In Sec. II, we briefly review the exact solution of the special case with nn blocking and second nn cooperative effects. The following interesting new results are also given. An analysis of highly autoinhibitory second nn rates (filling in stages) is included. This, incidentally, leads to an elegant expression for the saturation coverage for random trimer filling. Autocatalytic rates which result in a sequential (clustering) reaction are also considered. Expressions for final "island" sizes are analyzed. Some new identities for probabilities of certain disconnected unreacted configurations are included.

A detailed analysis of the process with general range 2 cooperative effects is given in Sec. III. Approximate solutions are obtained by applying the techniques developed in the preceding paper. These are based on observations of the structure of the infinite hierarchy of rate equations describing the process, and of an exact shielding property of quadruples of unreacted sites. The latter, which implies exact relationships between certain probabilities, is incorporated into the approximate solution so that these relationships are preserved. This could not be accomplished if one "borrowed" equilibrium style, e.g., Kirkwood factorization approximations to truncate the hierarchy. The approximate solutions obtained are examined for several cooperativity regimes.

Before proceeding with these detailed analyses, we introduce some notation and give an explicit example of the rate equations for this process. These have been described in Ref. 3 in a general context. The reaction is denoted by \( \sigma \rightarrow a \). Let \( f_\sigma \) denote the probability of finding a subconfiguration \( \sigma \) (probabilities considered here will have translational invariance). Let \( \tau_{0000}, \tau_{00000}, \ldots \) denote the rates for reaction with no reacted first and second nn, only one reacted left nn, \ldots. The rate equation for the probability \( f_\sigma \), that some site is unreacted, is given by

\[
-\frac{d}{dt} f_\sigma = \frac{d}{dt} f_\emptyset = \tau_{0000} f_{0000} + \tau_{00000} f_{00000} + \cdots + \tau_{0a0a} f_{0a0a0a0a} + \cdots \\
= \tau_{0000} f_{0000} + \tau_{00000} f_{00000} + \cdots \\
+ \tau_{0a0a} (f_\sigma - 2f_{0\sigma} - 2f_{0a0} + 3f_{000} + f_{0a0} + f_{00a} + f_{a00} + f_{a0a} \\
- f_{000} - f_{0a0} - 2f_{00a} + f_{0000})
\]

(1.1)

using an obvious notation for the \( f_\sigma \)'s. Conservation of probability has been used on the right-hand side of Eq. (1.1) producing empty configurations which are not connected but are "effectively connected," i.e., there are no unspecified gaps of more than one site. Rate equations can be obtained similarly for other \( f_\sigma \)'s.

The conditional probabilities \( q_{\phi|\sigma} = f_\sigma / f_\phi \) of \( \sigma \) given \( \phi \) also play an important role in our analysis. The hierarchical rate equations for these are most conveniently written in the form

\[
\frac{d}{dt} \ln q_{\phi|\sigma} = S(\sigma + \sigma') - S(\sigma),
\]

(1.2)

where \( S(\sigma') = [d/dt f(\sigma')]/f(\sigma') \) can be expressed in terms of \( q_\sigma \)'s. For typographic convenience, unreacted conditioning sites \( \delta \) will often be denoted by \( \phi \) here. An important example of Eq. (1.2) is
Since quadruples of unreacted sites shield for this process (assuming this holds for the initial conditions, as, e.g., with an initially completely unreacted polymer) (see Ref. 3 and the Appendix),
\[
-\frac{d}{dt} \ln q_{0000} = \sum_{\sigma_1,\sigma_2,\sigma_3} \left[ \tau_{0000} (q_{0000} - q_{0000}) + \tau_{0000} (q_{0000} - q_{0000}) \right] + \sum_{\sigma_1,\sigma_2,\sigma_3} \left[ \tau_{0000} (q_{0000} - q_{0000}) + \tau_{0000} (q_{0000} - q_{0000}) \right] + \tau_{0000} \text{ for } m \geq 4. \tag{1.3}
\]

This result has only been recognized previously for the abovementioned exactly solvable subcases, but is true for general range 2 cooperative effects. In later work, we show that an analogous relation holds for general range \( R \) cooperative effects (see the Appendix).

\section*{II. EXACT SOLUTION FOR REACTION WITH NN BLOCKING AND SECOND NN COOPERATIVE EFFECTS}

Here rates with one or two reacted nn, i.e., \( \tau_{0000} \), \( \tau_{0000} \), \( \tau_{0000} \), \( \tau_{0000} \), are zero. This problem has been solved exactly previously\(^{1,4}\) but here we emphasize how the shielding condition, and specifically Eq. (1.5), lead immediately to exact hierarchy truncation and solution. If \( q_0 \) denotes an \( m \)-tuple of empty sites, then the key point is that the minimal, closed hierarchy for probabilities of unreacted configurations involves only \( f_0 \) and \( f_4 \), \( m \geq 5 \). Thus, one can use \( f_0 = q_0 q_0 \), \( m \geq 4 \) [which follows from Eq. (1.5)] to exactly truncate this hierarchy obtaining a closed set of \( d/dt \) equations for \( f_0, f_4, f_0, f_4 \), and \( q_4 \) (see Refs. 1 and 4 for these). Note that if the polymer is initially completely unreacted, then \( f_0 = 1 - 2\theta \) where the conversion \( \theta = f_0 \), since each reaction destroys two unreacted pairs \( oo \). These \( d/dt \) equations can be transformed to \( d/dt (f_0) \), \( d/dt (q_4) \) equations if convenient by simply dividing by the \( d/dt (q_4) dt \) equation. From the solution of any of these, we also obtain exact expressions for \( f_0 = f_0 q_4, m \geq 4 \), \( f_0 = f_0 \) and \( f_0 \), for \( n = 0 \). Finally note that, due to blocking, the minimal hierarchy does not involve all effectively connected unreacted configurations\(^5\) (e.g., \( o-o \), \( oo-o \), ... are missing). Henceforth, we consider only the case of an initial completely unreacted polymer chain.

One quantity of particular interest is the final conversion \( \theta^* \) where \( \theta^* < 1/2 \) (see Fig. 1). An expression for \( \theta^* \) is most easily obtained from the \( d/dt q_4 \) equations. The \( d/dt f_0 q_4 \) equation may be immediately integrated to yield\(^6\)

\[
\theta^* = \frac{D(2) - e^{-3} D(1) \approx 0.27455}{f_{0000} |_{\theta^*} = e^{-3},} \tag{2.3}
\]

where \( D(x) = e^{-3} [\frac{1}{2} \ln 2] dt \) is Dawson’s integral.\(^8\) Simple isomorphism arguments show that \( \theta^* \) is 1/3 of the satu-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The yield \( \theta^* \) for the single site reaction on an infinite, uniform polymer chain with blocking by m reacted sites and second nn cooperative effects with rates \( \tau_{0000} \), \( \tau_{0000} \), \( \tau_{0000} \), and \( \tau_{0000} \).}
\end{figure}
ration coverage for 1D random trimer filling. In the second stage, reaction occurs only at sites with one reacted second nn so \( d/d\theta f_{\theta=0} = -2 \), \( d/d\theta f_{\theta=0} = -1 \) and \( f_{\theta=0} = 0 \) at the end of this stage \((\theta = \theta^* = \text{say})\). Thus,

\[
\theta^* = \theta^0 + f_{\theta=0} \theta^0 = D(2) + e^2(1 - D(2)) \approx 0.32434. \tag{2.4}
\]

It is also useful to calculate

\[
f_{\theta=0} | \theta^* = f_{\theta=0} \theta^* - 2(\theta^* - \theta^0) = 1 - 3D(2) + e^2(2 - 3D(2)). \tag{2.5}
\]

In the third stage, reaction occurs at sites with two reacted second nn, \( d/d\theta f_{\theta=0} = -1 \) and \( f_{\theta=0} = 0 \) at the end of the stage \((\theta = \theta^* = \text{say})\) so

\[
\theta^* = \theta^0 + f_{\theta=0} \theta^0 \theta^0 - 0.401 11. \tag{2.6}
\]

B. Random reaction with nn blocking

Here

\[ T_{\theta=0} = T_{\theta=0} = T_{\theta=0} = T_{\theta=0} \]

and \( \theta^* = (1 - e^{-S})/2 \) (half the saturation coverage for random dimer filling).

C. Highly autocatalytic reactions (island formation)

For \( T_{\theta=0} = T_{\theta=0} \gg T_{\theta=0} \), \( \theta^* \gg 1 \), the process involves competition between reaction of (relatively few) sites with unreacted second nn (island birth) and growth of islands of the type \( \ldots \text{o...o...o...o...o...o...o...} \ldots \) around these. One can show here that the average number of reacted sites per island is \( \theta/f_{\theta=0} \). Large \( \rho \) asymptotic behavior of the final conversion \( \theta^* \) follows from a steepest descent analysis of the right-hand side of Eq. (2.2). The dominant contribution of \( 1/2 - 7/8(\pi/\rho)^{1/2} + O(\rho^0) \) comes from the second term (reaction of sites with exactly one reacted second nn, i.e., island growth). The last term (reaction of sites with no reacted second nn, i.e., island birth) gives a contribution \( 1/2(\pi/\rho)^{1/2} + O(\rho^0) \). We conclude that, in the special case where \( \rho = 0 \),

\[
1/2 - \theta^*(\rho, \theta = 0) = 3/8(\pi/\rho)^{1/2} + O(\rho^0), \quad \rho \to -\infty. \tag{2.7}
\]

The value of \( \theta^* \) for \( \rho \neq 0 \) can be obtained from Eq. (2.7) through the following reasoning. At the end of the \( \theta = 0 \) process, the islands are separated by either pairs \( \ldots \text{o...o...o...o...o...o...} \ldots \) of empty sites or triples \( \ldots \text{o...o...o...o...o...o...o...o...} \ldots \) of empty sites. Since each pair (triple) results in one (two) additional unreacted sites, compared with \( \rho = -\infty \) perfect ordering, it then follows that \( 1/3(2/3) \) of the right-hand side of Eq. (2.7), in this large \( \rho \) limit, is associated with pairs (triples). For a process with the same \( \rho \) but \( \theta \neq 0 \), the center sites of these triples will have also reacted at some stage during the process. Consequently, \( 1/2 - \theta^*(\rho, \theta = 0) = 1/6(\pi/\rho)^{1/2} + O(\rho^0) \), as \( \rho \to -\infty \) \( (2.8) \) and since here \( f_{\theta=0} + f_{\theta=0} = 1 - 2\theta^0 \) at the end of the process, the average number of reacted sites per island approaches

\[
\theta^*(1 - 2\theta^0)^{-1} - 2(\rho/\rho)^{1/2} + (1 + O(\rho^0)). \tag{2.9}
\]

(cf. similar behavior discovered in Ref. 3).

As mentioned previously, the minimal hierarchy here does not include probabilities for all effectively connected configurations. For example, \( f_{\theta=0} \) is excluded but can be calculated from the quantities determined above observing that

\[
f_{\theta=0} = f_{\theta=0} + f_{\theta=0} = f_{\theta=0} - 1 - f_{\theta=0} + f_{\theta=0};
\]

similarly \( f_{\theta=0} \) can be determined recursively using

\[
f_{\theta=0} = f_{\theta=0} + f_{\theta=0} - 2f_{\theta=0} + f_{\theta=0} \quad \text{and} \quad f_{\theta=0} \text{ from } f_{\theta=0} = 1 - 2f_{\theta=0} + 2f_{\theta=0} - f_{\theta=0} + f_{\theta=0} + f_{\theta=0} \text{ (Ref. 9).} \]

Not all effectively connected probabilities can be directly determined from the \( f_{\theta=0} \) (the simplest such example being \( f_{\theta=0} \)). However, expressions for all these can be obtained from the hierarchy using shielding to achieve truncation. For example, all \( f_{\theta=0} \), can be written in terms of those with \( m, n < 4 \) and a closed set of equations (incorporating \( f_{\theta=0} \)) can be obtained for this subset.

III. APPROXIMATE SOLUTION FOR REACTION WITH GENERAL FIRST AND SECOND NN COOPERATIVE EFFECTS

The approximate truncation scheme used here is based on the hierarchy equations (1.2) for conditional probabilities. We have described in Ref. 3 how to obtain an infinite, closed set of equations for \( q's \) where \( q \) is a single unreacted site and \( \theta' \) involves only unreacted sites. Here, these equations for \( q = f_{\theta}, q_{\theta} = f_{\theta}/f_{\theta} \ldots \) become

\[
-d/dt \ln q_o = -S(o) = \tau_{\theta=0} q_{\theta=0} + \tau_{\theta=0} q_{\theta=0} + \cdots + \tau_{\theta=0} q_{\theta=0} + \tau_{\theta=0} (q_{\theta=0} - q_{\theta=0}) + \cdots
\]

\[
+ \tau_{\theta=0} (1 - q_{\theta=0} - q_{\theta=0} - q_{\theta=0} + q_{\theta=0} + q_{\theta=0} + q_{\theta=0} + q_{\theta=0}) - q_{\theta=0} - q_{\theta=0} - q_{\theta=0} - q_{\theta=0} - q_{\theta=0} - q_{\theta=0} - q_{\theta=0} - q_{\theta=0}.
\tag{3.1a}
\]

\[
d/dt q_{\theta} = S(o) - S(o),
\]

where

\[
S(o) = \tau_{\theta=0} (q_{\theta=0} + q_{\theta=0}) + \cdots \ldots
\tag{3.1b}
\]

The \( q's \) appearing on the right-hand side can be factored, usually nonuniquely, in terms of those with a single o-site, e.g.,

\[
q_{\theta=0} = q_{\theta=0} + q_{\theta=0} = \begin{cases} q_{\theta=0} & q_{\theta=0} \\ q_{\theta=0} & q_{\theta=0} \end{cases}
\]

\[
= q_{\theta=0} + q_{\theta=0} = \begin{cases} q_{\theta=0} & q_{\theta=0} \\ q_{\theta=0} & q_{\theta=0} \end{cases}
\]

\[
= q_{\theta=0} + q_{\theta=0} = \begin{cases} q_{\theta=0} & q_{\theta=0} \\ q_{\theta=0} & q_{\theta=0} \end{cases}.
\tag{3.2}
\]
Equation (3.2) also illustrates product relationships which must be satisfied by these \( q \)'s. All choices in Eq. (3.2) after substitution into Eq. (3.1) yield equivalent closed hierarchies for \( q \)'s with a single \( o \) site. Note that configurations appearing are not connected, but "effectively connected."

Here we implement an \( n \)th order \( \Phi \)-Markovian truncation approximation on the above equations after factorization [i.e., we keep only conditioning \( \phi \) sites \( \leq n \) sites from the single \( o \) site]. Several important features of this truncation scheme are discussed in Ref. 3. Choosing \( n > 4 \) avoids explicit truncation of the \( f_{n} = q_{o} \) equation and preserves Eqs. (1.5). It remains only to prescribe unambiguously the factorization procedure. The rule implemented is to always take the outside conditioned \( o \) site first, e.g.,

\[
q_{o}o_{o}o_{o}o_{o} = q_{o}o_{o}o_{o}o_{o} o_{o}o_{o}o_{o}o_{o}
\]

rather than \( q_{o}o_{o}o_{o}o_{o} o_{o}o_{o}o_{o}o_{o} \),

which is replaced by \( q_{o}o_{o}o_{o}o_{o} o_{o}o_{o}o_{o}o_{o} \) in the fifth order and \( q_{o}o_{o}o_{o}o_{o} o_{o}o_{o}o_{o}o_{o} \) in the fourth order \( \Phi \)-Markovian approximations. This prescription is still ambiguous for the \( q \)'s

\[
q_{o}o_{o}o_{o} \equiv q_{o}o_{o}o_{o} \text{ or } q_{o}o_{o}o_{o}.
\]

\[
q_{o}o_{o}o_{o} \equiv q_{o}o_{o}o_{o} \text{ or } q_{o}o_{o}o_{o}.
\]

\[
q_{o}o_{o}o_{o} \equiv q_{o}o_{o}o_{o} \text{ or } q_{o}o_{o}o_{o}.
\]

However, since no resulting \( q \)'s are truncated and all are in the retained set, these choices are equivalent by virtue of "product consistency" proved in Ref. 3.

In Table I, we list the \( q \)'s retained and \( S ( \phi \)'s to be calculated in the fourth order as well as the additional ones for the fifth order \( \Phi \)-Markovian approximations. (Reflection invariance of rates and \( f \)'s is assumed.) The corresponding equations are rather complex and thus not given here.

Let us first consider the truncated equations in the limit of \( n \) cooperative effects. Consider the exact \( q \)

hierarchy for the \( q_{o}o_{o}o_{o} \), \( m = 0, 1, 2, \ldots \). The coefficients of \( q \)'s appearing with unspecified gaps on the right-hand side approach zero in the \( n \) cooperative limit. The same is true for the factorized and truncated equations. It is thus clear that exact results are obtained for these \( q \)'s in the \( n \) cooperative limit (and thus for \( f_{o} = \frac{1}{\alpha} \) and \( f_{o} = \frac{1}{\alpha} \)). Second, consider the truncated equations in the limit of \( n \) blocking. A similar analysis to that above shows that explicit results are recovered for \( q_{o}o_{o}o_{o} \) as well as \( q_{o}o_{o} \) (and thus for \( f_{o} = \frac{1}{\alpha} \) and \( f_{o} = \frac{1}{\alpha} \)). Below we examine the behavior of the solutions of the truncated equations in several different and important cooperative regimes for an initially completely unreacted polymer chain.

A. Perturbation of \( n \) (by second \( n \)) cooperative effects

Suppose that the \( n \) rates are autoinhibitory, that each reacted \( n \) changes \( \tau_{o}o_{o}o_{o} \) by a factor of \( \alpha < 1 (\beta = 1) \). Thus, e.g., \( \tau_{o}o_{o}o_{o} \equiv \beta \tau_{o}o_{o}o_{o} \). In Fig. 2, we plot \( f_{o} \) as a function of \( \theta \) for \( \alpha = 1/5 \) and a variety of \( \beta \). There is no significant difference between results from the fourth and fifth order truncations; however, variation of \( \beta \) does cause significant changes in the values of \( f_{o} \). The results presented here indicate that the approximate solutions are accurate in this regime and, furthermore, that relatively mild second \( n \) cooperative effects will change significantly the values of such probabilities as \( f_{o} \).

Next we consider a choice of rates where one reacted \( n \) changes \( \tau_{o}o_{o}o_{o} \) by a factor of \( \alpha \), two reacted \( n \) block reaction and each reacted \( n \) changes \( \tau_{o}o_{o}o_{o} \) by a factor of \( \beta \). The final conversion \( \theta^{*} \) is less than one for this process (the case \( \beta = 1 \) has been discussed previously; see Ref. 3). In Fig. 3, we examine the dependence of \( \theta^{*} \) on \( \beta \) for two specific systems. Only slight differences between fourth and fifth order truncations are observed. In the high \( \beta \) limit, the solutions of the truncated equations produce the correct result \( \theta^{*} = 0.5 \).
B. Approach to the nn blocking limit

Here and in all later examples, we choose rates where each reacted nn changes $\tau_{0\rightarrow0}$ by a factor of $\alpha$ and each second nn by a factor of $\beta$ (equal to 2, here). In Fig. 4, we have plotted $f_{aa}$ and $f_{a-\alpha}$ as functions of $\theta$ for a range of $\alpha$ from 1 to 1/100. The limiting behavior as $\alpha \to 0$ is correctly recovered (the process occurs in three stages: reaction of sites with 0, 1, and 2 reacted nn consecutively). There are no significant discrepancies between fourth and fifth order truncations.

C. Highly autocatalytic rates for reacted second nn (island formation)

The viability of the hierarchy truncation method in treated processes involving clustering is of general interest. Although truncation occurs on a short distance scale (of a few lattice vectors) compared with island sizes, the 2D examples of Ref. 3 suggest that this causes no intrinsic problem. Here, however, there is also a great difference in the size of various rates, e.g., $\beta^5 \gg \beta \gg 1$. For $\theta < 1/2$, islands of the form \ldots $00000000000\ldots$ tend to build up so terms in the $q$ hierarchy with a factor $\beta$ should dominate. Thus, the coefficient of $\beta^5$ should be small. Apparently overestimate due to truncation leads to spurious behavior in $f_{aa}$ (which does not achieve its high $\beta$ limiting form $f_{aa} = 0$ for $0 < \theta < 1/2$, $= 2\theta - 1$ for $1/2 < \theta < 1$), but not in $f_{a-\alpha} - \theta$ as $\beta \to \infty$ (see Fig. 5).

D. Reaction in (effective) stages

If $\alpha \ll \beta^2 \ll \beta \ll 1$, the process effectively occurs in stages, namely, reaction of sites with 0, 1, and 2 reacted second nn (and no reacted nn) and then with 1 and 2 reacted nn. From the analysis of Sec. II, one can show that these stages end at $\theta = 0.274, 0.324, 0.401, 0.599, 1.00$, respectively.

IV. CONCLUSIONS

The approximate hierarchy truncation scheme adopted here has been quite successful in a variety of cooperativity regimes (no doubt in part due to the incorporation of the exact shielding property of quadruples of unreacted sites). This has allowed, e.g., estimation of the perturbative influence of second nn cooperative effects. Finally, we emphasize that the basic technique adopted from Ref. 3 is quite general and can be applied to study the kinetics of various other polymer reactions for which exact solutions are not available.

APPENDIX

Here we sketch the proof of the unreacted site shielding property which basically just involves observing self-consistency with the $q$ hierarchy equations. Consider first $q_{0000000\ldots}$, where $\sigma$, $\sigma'$, $\sigma''$ involve only unreacted sites and, as the notation implies, $\sigma$ is to the left, and $\sigma'$, $\sigma''$ to the right of 0000. These $q$'s together
with the corresponding reflected quantities satisfy a closed set of hierarchy equations (after using conservation of probability to convert any reacted to unreacted sites). If $r_{ij}$ denotes the rate of reaction at site $j$ given first and second $nn$ in state $\sigma^j$ and if $\sigma^j_\downarrow$ denotes the part of $\sigma^j$ not overlapping other conditioning sites, then

$$\frac{d}{dt} \ln q_{\sigma^j \sigma^j_\uparrow \sigma^j_\downarrow} = \sum_{j \in \text{sites}} \sum_{\sigma^j_\uparrow \neq \emptyset} r_{ij} \left( q_{\sigma^j \sigma^j_\uparrow \sigma^j_\downarrow} - q_{\sigma^j \sigma^j_\uparrow \sigma^j_\downarrow} \right)$$

$$+ \sum_{j \in \text{sites}} \sum_{\sigma^j_\downarrow \neq \emptyset} \sum_{\sigma^j_\uparrow \neq \emptyset} r_{ij} q_{\sigma^j \sigma^j_\uparrow \sigma^j_\downarrow} - \sum_{j \in \text{sites}} \sum_{\sigma^j_\uparrow \neq \emptyset} r_{ij} q_{\sigma^j \sigma^j_\uparrow \sigma^j_\downarrow}^\prime.$$  \hspace{1cm} (A1)

The analogous reflected quantities satisfy a similar set of equations. If the initial conditions satisfy the condition that an unreacted quadruple shields, then it is easy to see that the above equations are consistent with this condition for all time. For example, in Eq. (A1), the first term cancels and the last two are independent of $\sigma$ consistent with $q_{\sigma^j \sigma^j_\uparrow \sigma^j_\downarrow}^\prime$ being independent of $\sigma$.

We can relax the restriction that $\sigma$, $\sigma'$, and $\sigma''$ be empty which will give more complicated $q$ equations, but the proof goes through unchanged in spirit. If a quadruple of unreacted sites does not shield initially, but an $n$-tuple, $n > 4$ does, then the proof can be easily modified to show that this $n$-tuple will shield for all times. Finally, we remark that this proof easily extends to the case of range $R$ cooperative effects to show that a $2R$-tuple of unreacted sites shield (if this holds for the initial conditions).

5. P. Krishnaswami and D. P. Yadav, J. Appl. Polym. Sci. 20, 1175 (1976), have previously attempted an analysis of this problem. However, the kinetic equations used were incorrect, for example, in that for $f(aaa\alpha\alpha)$, they take account of the destruction of $aaaa\alpha\alpha$ configurations due to reaction $\alpha\alpha$ at the center site and the creation from $aaaa\alpha\alpha$ or $aaa\alpha\alpha$, but neglect the creation of $aaaa\alpha\alpha$ or $aaa\alpha\alpha$, due to reaction at the noncentral "$\alpha$" site.